



Élaboration de membranes échangeuses d'anions à architecture réseaux interpénétrés de polymères pour des batteries lithium-air

Bruno Bertolotti

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Doctoral School “Sciences and Engineering”

University of Cergy-Pontoise

THESIS

To obtain the degree of doctor of the University of Cergy-Pontoise

Specialty: Polymer Chemistry

**Development of anion exchange membranes based on
interpenetrating polymer networks architecture for
lithium-air batteries**

Presented by

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Defended the 9th December 2013 in front of the jury:

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List of Abbreviations

AEM	Anion Exchange Membrane
AFC	Alkaline Fuel Cell
AIBN	2,2'-Azobis(2-methylpropionitrile)
DABCO	1,4-diazabicyclo-[2.2.2]-octane
DMA	Dynamic Thermomechanical Analysis
DMF	N,N-dimethylformamide
EGDMA	Ethylene glycol dimethacrylate
IEC	Ion Exchange Capacity
IPN	Interpenetrating Polymer Network
MEA	Membrane Electrode Assembly
OCV	Open Circuit Voltage
PECH	Poly(epichlorohydrin)
PHEMA	Poly(2-hydroxyethyl methacrylate)
SF	Soluble Fraction
SPE	Solid Polymer Electrolytes
t^-	Anion Transport Number
TGA	Thermogravimetric Analysis
T_a	Mechanical Relaxation Temperature
WU	Water Uptake

General Introduction

Electric vehicles show great promise in terms of petroleum dependence reduction and of greenhouse-gas emission decrease. Today, the commercialization of such vehicles is limited, essentially due to its low driving-distance range and to insufficient recharge infrastructures. The autonomy of electric vehicles is limited by the specific energy (or power to weight ratio) of batteries. The current batteries have a low energy density, their cost is high, and their lifetime is uncertain. Recently, concerns about their safety, depending on the chemistry and specific energy, have also arisen. The battery currently developed for electric vehicles is the lithium-ion battery. Recently, the Tesla Model S surpassed the 400 km driving range with an 85 kWh Li-ion battery. However, this battery contributes at least for US\$ 25000 to the vehicle price.¹ Although this cost is likely to decrease, through continued advances in technology and reductions in manufacturing costs via increased production volume, it still represents the most expensive part of the vehicle.² However, the relatively low energy density of this kind of battery forces a limited driving range of electric vehicles.

On the opposite of lithium-ion battery, metal-air batteries have the advantage of having a positive electrode (the air electrode) with infinite capacity since the active material, the oxygen, is taken from the surrounding air. These batteries are of special interest due to their high theoretical specific energy (Figure 1). Among metal-air batteries, the lithium-air battery has the highest theoretical specific energy (more than 10000 Wh/kg).⁴ This high specific energy can lead to a significantly increase in the driving range of electric vehicles at a lower cost, and enable electric vehicles to exceed 500 km of autonomy.³

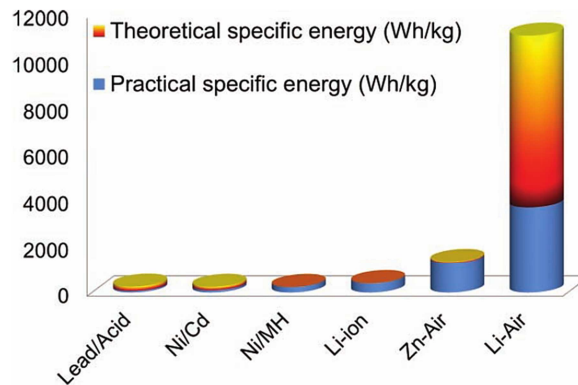


Figure 1: Theoretical and practical energy densities of various types of rechargeable batteries⁴

The aqueous lithium-air battery consists of a lithium metal anode protected from the electrolyte by a water stable and lithium ion conducting ceramic. The cathode, where the oxygen reduction takes place, is a carbon air electrode fed with ambient air. The electrolyte is aqueous saturated LiOH solution (Figure 2).

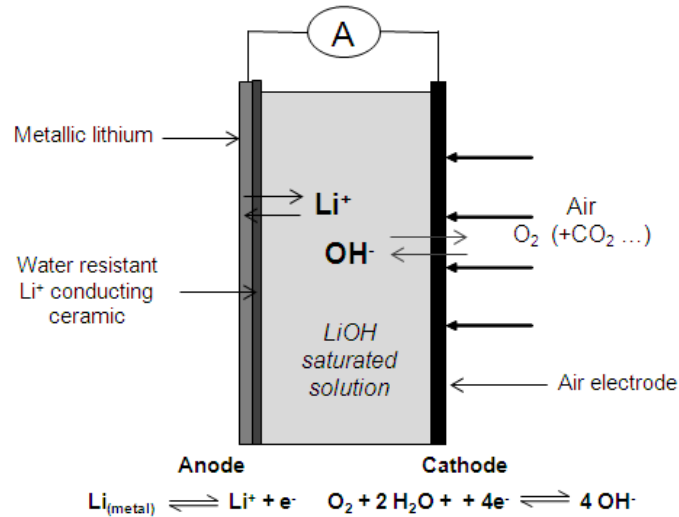


Figure 2: Scheme of the aqueous lithium-air battery

However, technical barriers persist for the development of such a battery operating in ambient air. For example, air electrodes show a limited lifetime in the alkaline electrolyte that is necessary for its operation. This is mainly caused by the reaction between carbon dioxide from atmospheric air and the liquid alkaline electrolyte (saturated LiOH) leading to lithium carbonate formation. The precipitation of this carbonate inside the air electrode porosity impedes oxygen diffusion, necessary for the electrochemical reaction. As a result, the resistance of the system increases during operation, and a loss of stability is observed after a few hours of operation.

The most common way to avoid the negative effect of carbon dioxide is simply to remove it by using commercial CO₂ air scrubbers, or by feeding the battery with pure oxygen. But this strategy reduces the interest of metal-air battery systems due to the increment in total weight. Under atmospheric air, a potential solution to ensure a better electrochemical stability of the air electrode in alkaline environment is to protect it with a polymer membrane placed in the electrolyte side. This polyelectrolyte membrane must ensure the hydroxide conduction from the electrolyte to at the air electrode for the electrochemical reactions and it must also prevent the transport of cationic species from the electrolyte towards the electrode to avoid the carbonate formation.

This work carried out in the *Laboratoire de Physicochimie des Polymères et des Interfaces* (LPPI – EA2528) of *Université de Cergy-Pontoise*, is part of the LiO2 project, financed by the ANR STOCK-E program. This project is directed by EDF R&D, and combines, in addition to the LPPI, different partners with complementary competences:

- Renault (France) assesses of the technical compatibility of the project developments with the electric vehicle application.
- LRCS (Amiens), ICMCB-ENSCBP (Bordeaux), CTI and CIRIMAT (Toulouse) study the cyclability of the metallic lithium anode, the interphase between metallic lithium and protective ceramic membrane, and synthesize Li^+ conductive-water resistant ceramic membrane.
- Solvay (Bollate, Italy) synthesizes fluorinated anionic polymer membranes for air electrode protection and supplies fluorinated monomers for the synthesis of semi-IPNs and IPNs in collaboration with the LPPI.

The objective of the LiO2 project, after a successful 2 year project (LiO), is to improve the performance of the lithium-air system, towards a new battery for an electric vehicle with very high autonomy. To achieve this, the LiO2 project aims to increase the current density of 50 mA/cm^2 and the number of cycles to over a hundred. At the end of the project, the progress will be shown on a module consisting of 5 cells using ambient air with the following characteristics:

- Electrolyte: saturated (5 M) LiOH
- 2 Ah, 15 V, 30 Wh
- 200 mAh/cm^2 , 10 cm^2
- 100 cycles

The objective of this thesis, as part of the LiO2 project, is to develop a polymer membrane to be placed in the electrolyte side of the air electrode. As required for the LiO2 project, the air electrode must operate in cycling of discharge and rest. As a reference, an unprotected air electrode is stable under these conditions only few hours. This membrane must prevent the precipitation of insoluble salts in the electrode during its operation.⁵ For this purpose, interpenetrating polymer networks (IPN) combining an anion conductive polymer network, and a neutral polymer network, will be developed.

The ionic (positively charged) network allows the conduction of anions while preventing the passage of cations. The neutral network will limit the swelling of the membrane and will increase its mechanical and chemical resistances. The air-electrode modified by the different polymer membranes will be characterized in half-cell.

In the first chapter, we will discuss the metal-air battery technology and its technical limitations. We will continue by identifying the limitations of the air electrode, and the solutions to increase its stability, or life-time in alkaline medium. Particular attention will be given to the identification of polymer membranes stable in alkaline medium.

The second chapter will describe the electrochemical properties of the air electrode chosen in this work. Then the synthesis and optimization of an anion conductive polymer network based on poly(epichlorohydrin) (PECH) will be presented. Finally, the protection of the air electrode by this membrane will be analyzed.

In the third chapter, the former hydrogenated polyelectrolyte single network will be associated with a neutral hydrogenated network in interpenetrating polymer network architecture in different proportions. The physicochemical properties of these IPNs, and the electrochemical properties of the electrode modified with them will be quantified.

The fourth chapter will describe the association of the PECH polyelectrolyte network with a fluorinated network again in IPN architecture. As previously, the physicochemical properties of these original IPNs, as well as the properties of the air electrode modified with them will be evaluated.

-
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Chapter I: Literature Review

Batteries are devices that convert chemical energy (the Gibbs free energy of electrochemical redox reactions at the electrodes) into electrical energy and vice versa. They are composed of two electrodes with different chemical potentials separated by the electrolyte. When these electrodes are connected, electrons spontaneously flow from the more negative to the more positive potential. Electrical energy can be extracted by the external circuit by connecting an electrical device represented by the cross in Figure I - 1. Simultaneously, ions are transported through the electrolyte to maintain the charge balance.

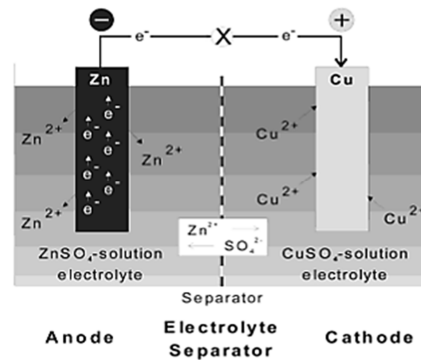


Figure I - 1: Scheme of a battery (Daniell cell)¹

Batteries have a limited amount of chemical reactants contained within a closed space. In non-rechargeable batteries (primary batteries), the cell reaction is irreversible. On the other side, in rechargeable batteries (secondary batteries), the cell reaction can be reversed using electric energy, because the electrode reactions are generally reversible.² The Ni-metal hybrid batteries are the most common secondary systems.³

Rechargeable batteries are of interest as a power source for electric and hybrid electric vehicles. They can be used as:³

- a. Energy storage devices that deliver additional energy on demand to a prime energy source (as by a fuel cell or by a combustion engine in hybrid systems). They are charged by the primary source when not used.
- b. Discharged system (similar in use to a primary battery) which is then recharged, either directly in the equipment in which it is included or separately. Most consumer electronics, electric-vehicle, and some stationary battery applications are in this category.

Typical characteristics and applications of secondary batteries are summarized in Table I - 1.

Table I - 1: Battery chemistries, adapted from Armand and Tarascon⁴

Battery type	Features	Applications	Environmental impact
Lead-acid	Poor energy density, moderate power, low cost	Large-scale, start-up power, stationary	Limited: cyclability, Lead toxicity Efficiently recycled
Ni-Cd Ni-Metal Hybrid	Low voltage, moderate energy density, high power density	Portable, large-scale	High. Nickel not “green”, toxic Recyclable
Lithium ion	High density, high power and cyclability	Portable, large scale Electric vehicles	Use of cobalt (low availability), but begins to be replaced by manganese and iron Recycling possible but highly energy-demanding

The lead-acid battery was developed in 1859 by Planté⁵. It is still the most widely used battery for the functioning of combustion engine. The pocket-plate nickel-cadmium battery has been manufactured since 1909⁶ and was used primarily for heavy-duty industrial applications. The sintered-plate design, which allowed increasing the power capacity and energy density of this system, opened the market for aircraft engine starting and communications applications during the 1950s. Finally, the development of the sealed nickel-cadmium battery led to its widespread use in portable and other applications⁷. As with the primary battery systems, significant performance improvements have been made with the secondary battery systems, and newer types, such as the silver-zinc and nickel-zinc⁸, nickel-hydrogen⁹, and lithium ion¹⁰ batteries have been introduced into commercial use. Thus, the dominance of the nickel-cadmium technology in the portable rechargeable market has been supplanted by nickel-metal hydride in 1990 and more recently by lithium-ion battery, which provides higher specific energy and energy density. This last, invented by Sony at the end of the years 1980^{11,12}, exchanges the Li^+ ion between the graphite (Li_xC_6) anode and a layered-oxide ($\text{Li}_{1-x}\text{T}^{\text{M}}\text{O}_2$) cathode ($\text{T}^{\text{M}} = \text{Co}, \text{Ni}, \text{Mn}$). Although its high cost, it is now the most widely used battery system in portable applications and in electric vehicles.¹³

General battery performance can be described by:

- the electrochemical equivalent of the metal which is the weight, in grams, produced or consumed by one coulomb of electric charge (or 1 A·s), and can also be expressed in Ah/g (1 Ah = 3600 C),
- the cell voltage which is the electrical potential difference (in volts) between the two electrodes of an electrochemical cell,
- the specific energy of a cell which is the amount of electrical energy stored per weight unit, typically expressed as Wh/kg.

In summary, Figure I - 2 illustrates the performance trends of rechargeable batteries for portable applications.

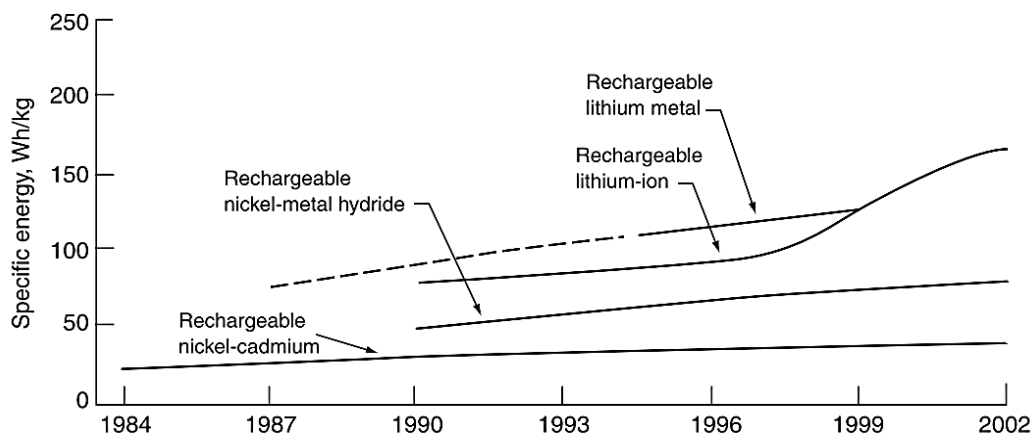


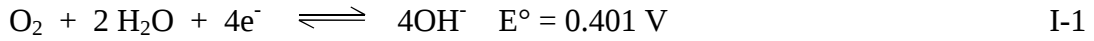
Figure I - 2: Specific energy (Wh/kg) of portable rechargeable batteries³

The specific energy of portable rechargeable nickel-cadmium batteries has not improved significantly in the past decade. Through the use of new hydrogen-storage alloys, improved performance in nickel-metal hydride batteries has been achieved and that system now provides 80 Wh/kg. Lithium ion systems now provide a specific energy of 180 Wh/kg.¹⁴

For higher specific energies, metal-air batteries have been developed. Metal-air cells are composed of an electrolyte separating an anode made from pure metal and an external cathode supplied with ambient air. Thus, the metal-air cell specific energies are higher than that of cell of common batteries because the cathode active material (oxygen) is not stored in the battery, but can be accessed from the environment. The theoretical specific energy of metal/air batteries is based only on the negative electrode (anode or fuel electrode during discharge) as this is the only reactant in the battery.

1. Metal-air Batteries

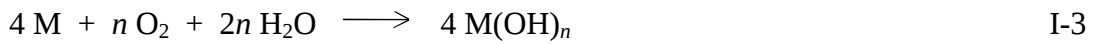
Different electrolytes can be used in metal/air batteries: solid, organic, aqueous, or the last two separated by a conducting membrane (hybrid). In aqueous metal/air batteries using neutral or alkaline electrolytes, the oxygen reduction during discharge may be written:



Simultaneously, the reaction at the negative electrode can be generalized as:



and the overall discharge reaction



where M is the metal and the value of n depends on the valence change for the metal oxidation. However, most metals are thermodynamically unstable in an aqueous electrolyte: they are oxidized by the electrolyte and hydrogen is generated. This reaction must be therefore avoided or minimized.

The main common advantages and disadvantages of the metal/air battery system are summarized in Table I - 2.

Table I - 2: Main advantages and disadvantages of the metal/air batteries (aqueous electrolyte)³

Advantages	Disadvantages
• High energy density • Long shelf life (dry storage) • Few ecological problems • Low cost • Capacity independent of load and temperature (within operating range)	• Depend on environmental conditions (drying-out limits shelf life once opened to air, flooding limits power output) • Limited power output • Limited operating temperature range • H₂ from anode corrosion • Carbonation of alkali electrolyte

Table I - 3 lists the metals that have been considered in metal/air batteries with several of their electrical characteristics.

Table I - 3: Characteristics of metal/air cells³

Anode metal	Electrochemical equivalent of metal (Ah/g)	Theoretical cell voltage* (V)	Theoretical specific energy of metal (kWh/kg)	Practical operating voltage (V)
Li	3.86	3.4	13.0	2.4
Ca	1.34	3.4	4.6	2.0
Mg	2.20	3.1	6.8	1.2 – 1.4
Al	2.98	2.7	8.1	1.1 – 1.4
Zn	0.82	1.6	1.3	1.0 – 1.2
Fe	0.96	1.3	1.2	1.0

*Cell voltage with oxygen cathode

Among the potential candidates, zinc has received the most attention because it is the most electropositive metal relatively stable in aqueous and alkaline media. Problems of dendrite formation, non-uniform zinc dissolution and deposition, limited solubility of the reaction products, and unsatisfactory air electrode performance have slowed progress. However, there is a continued search for a practical system.^{8,15,16,17,18}

As a result of the high specific capacity of the metal (3.86 Ah/g for lithium vs. 0.82 Ah/g for zinc), a significant effort has gone into lithium/air battery development. Considering the high operational voltages (2.4 V), the theoretical maximum energy density based on Li metal electrode can be over 13 kWh/kg, which is not only much higher than that of any advanced batteries but is also higher than that of fuel cells. The Li-air battery however, has a maximum theoretical cell energy density of 1.3 kWh/kg.¹⁹ The significant reduction of cell capacity from the specific capacity of Li metal is due to the weight of the electrolyte and air electrode materials.

Lithium-based batteries are thus the most promising together with their zinc counterpart. Nevertheless, recent studies have shown that the availability of lithium could be a limitation as there are not yet practical technologies to extract lithium from seawater, and intensive recycling of used batteries is not achieved.^{20,21}

2. Lithium-air Battery

Researchers at Lockheed proposed the use of an aqueous alkaline electrolyte for the Li-air battery. The overall reaction for Li-air cell is:^{22,23}



However, problems relating to low efficiency and major safety problems related to the side reactions of Li with water and H₂ formation:



In addition, the presence of alkaline electrolyte results in air electrode failure due to the formation of insoluble Li₂CO₃ from the reaction of lithium hydroxide and CO₂:²⁴



These difficulties led to the abandonment of this concept in the 1980s until 1997 when new electrolytes began to be studied.²⁵

2.1. Lithium-air Battery Electrolyte

2.1.1. Anhydrous Electrolyte

In order to eliminate or minimize water presence in the cell (ambient humidity can still enter across the air electrode), one approach is to use as electrolyte an organic solvent in which water solubility is minimized. By using an organic-based²⁶ or ionic liquid-based electrolyte solution, Li₂O and Li₂O₂ are produced during the global cell reactions:²⁷



Because both Li₂O and Li₂O₂ are not soluble in organic electrolyte solutions, both oxides precipitate in pores of the porous carbon-based cathode. The air electrode is gradually covered by discharge products, which prevent oxygen from diffusing to the reaction sites of carbon. Impedance of the air electrode is progressively increased and the cell life is limited.

The aprotic electrolyte solution has advantage to have a high dielectric constant to minimize ion pairing, a low viscosity to maximize specific conductivity and to minimize water solubility while maximizing oxygen solubility. In 1996, Abraham and Jiang²⁸ proposed a mixture of polyacrylonitrile, ethylene carbonate, propylene carbonate and LiPF₆ as

electrolyte. With an operating voltage of 2.9 - 3.1 V, a specific energy between 250 and 350 Wh/kg and a maximum capacity of 1.41 Ah/g were obtained. Read²⁹ employed liquid aprotic organic solvents as electrolyte solution and obtained 1.91 Ah/g. Kuboki et al.³⁰ obtained a maximum of 5.36 Ah/g with ionic liquid electrolyte.

Zhang et al.³¹ assembled Li-air batteries based on non-aqueous electrolytes (1 M LiTFSI in propylene carbonate/ethylene carbonate and 1,2-dimethoxyethane). However, a porous PTFE membrane was placed airside of the air-electrode both as an oxygen-diffusion membrane and as a moisture barrier. This membrane can also minimize the evaporation of the electrolyte. These Li/air batteries were operated more than one month with a specific energy of 362 Wh/kg under ambient conditions. The authors found that only 20 % of the pore volume of the air electrode was occupied by reaction products after discharge.

Crowther et al.³² proposed an organic-based Li-air cell in which O₂ selective membranes based on hydrophobic silicone rubbers (polysiloxane-methacrylate copolymer and a commercial silicone, Semicosil 964), associated air-side of the air-electrode (Figure I - 3). The membranes exhibit high oxygen permeability and impede water transport from the atmosphere into the cell and solvent loss from the cell into the atmosphere.

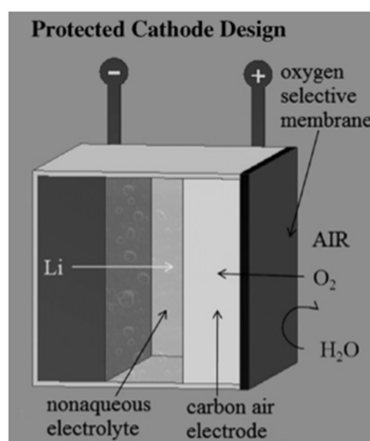


Figure I - 3: Protected air electrode in Li-air cell³²

These cells show lower specific capacity in air at relative humidity between 15 and 43 % compared to cells discharged in pure oxygen. That is due to the lower partial pressure of oxygen, which results in higher overpotentials at the cathode, and to the precipitation of Li₂O and Li₂O₂ into the cathode.

While literature on organic Li-air batteries suggests that it will be able to provide rechargeable batteries with higher gravimetric energy densities than those currently available, the above mentioned challenges still have to be overcome.

2.1.2. Aqueous Electrolyte

Despite the fact that the theoretical specific energy for the Li-air cell in aqueous electrolyte solutions is lower than in organic solutions,²⁵ aqueous-based systems represent an interesting alternative approach for long operational life. Indeed, the reaction products of oxygen reduction are generally very soluble in aqueous solutions. Moreover, the operational life times of these aqueous systems are “anode-limited” depending upon the amount of metallic Li used. In addition, the aqueous Li-air cells have “nominal” potentials (i.e., practical operating voltage) of around 3.0 to 3.3 V instead of 2.6 to 2.7 V for the non-aqueous analog.

In accordance with the conclusions drawn from the former experiments on aqueous-based Li-air cell, the key problem to be addressed in developing an aqueous-based Li-air cell is the complete elimination of the reaction between metallic lithium and water. To protect the lithium anode from reacting with water, a water-stable Li^+ -conducting solid-state plate or “membrane” must be placed on the lithium anode, as shown schematically in Figure I - 4.

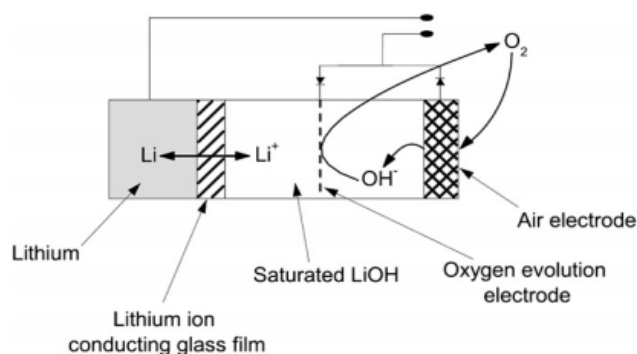


Figure I - 4: Schema of the aqueous Li-air cell³³

Wang and Zhou³⁴ presented a non-rechargeable aqueous Li-air battery, in which the metallic lithium is separated from the alkaline aqueous electrolyte by a super-ionic conductor glass membrane (LiSICON). The authors reported a maximum of 500 h continuous discharge at 0.5 mA/cm² current density.

This result shows that aqueous Li-air batteries are chemical power sources potentially viable with high energy density. However, they are currently in the initial stages of development. The lithium anode is still the limiting part of the battery. On the other hand, technological barriers coming from carbonate precipitation in the air electrode must also be solved.

2.2. The Air Electrode

Standard air electrodes, such as those developed for alkaline fuel cells or zinc-air batteries, are designed to work as oxygen reduction electrodes only. Indeed, the catalyst and carbon materials would be subjected to corrosion at high potential during charging process, which causes mechanical breakdown of the fragile porous structure and subsequent electrode failure. Typical air electrodes are composed of a mixture of carbon black, catalyst and Teflon[®] (PTFE) binder, supported on a porous hydrophobic film. The current is collected by a metal mesh embedded in the catalyst/Teflon[®] matrix. Under operating conditions, the catalyst particles form porous (and electronically conducting) agglomerates that are filled with electrolyte. The binder which holds together the catalyst layer creates hydrophobic channels for gas diffusion,^{35,36} as shown in Figure I - 5.

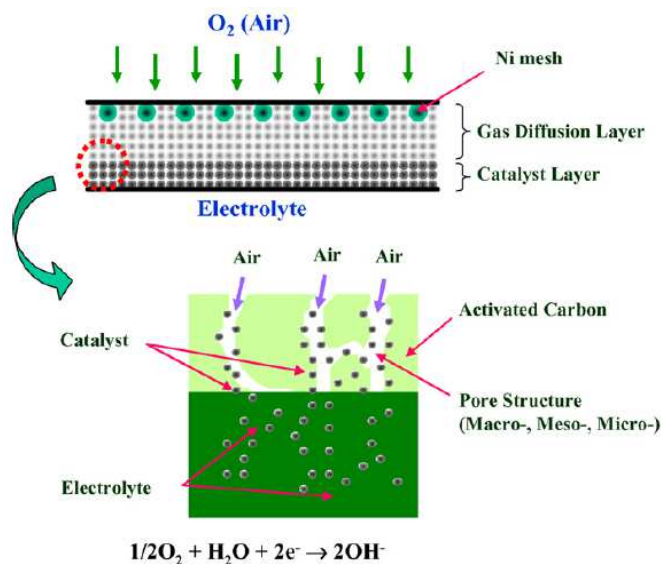


Figure I - 5: Scheme of the cathode in metal-air batteries, adapted from Eom et al.³⁷

The electrocatalytic oxygen reaction occurs at a three-phase contact zone between air, liquid electrolyte and solid catalyst (even though oxygen may also dissolve in the electrolyte), as schematically shown in Figure I - 6. This three-phase interface must not be flooded by the

electrolyte, which would exclude the gas. Thus, the balance between hydrophobic and hydrophilic properties is significantly important for air electrodes used in aqueous metal–air batteries.^{37,38}

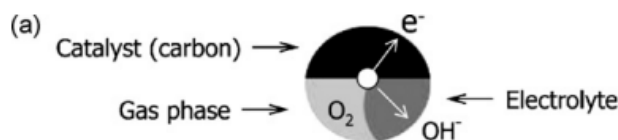
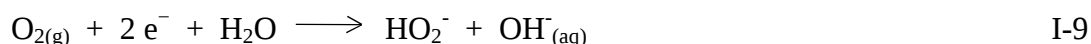


Figure I - 6: Scheme of the three-phase zone in an air electrode³⁹

The reduction of O_2 at carbon based solid electrodes has been a major topic of research.^{40,41,42,43} Research in electrode modifications and new electrocatalysts is continuous and has permitted to decrease the electrode polarization and to increase its efficiency.⁴⁴

The mechanism of O_2 reduction to HO_2^- on carbon in alkaline solution has been examined several times, but clear agreement on the steps involved has not emerged.^{41,45,46,47} However, it is accepted that a first reduction step (to peroxide) occurs:^{43,46,48,49}



Followed by the disproportionation of HO_2^- to H_2O by the catalyst:^{40,42,50,51,52,53}



To obtain the overall reaction:



2.3. Polarization Curves

The voltage of a metal/air battery drops with increasing current. Figure I - 7 shows a typical voltage-current (E vs. I) discharge curve for a cell, and the different causes of the polarization.

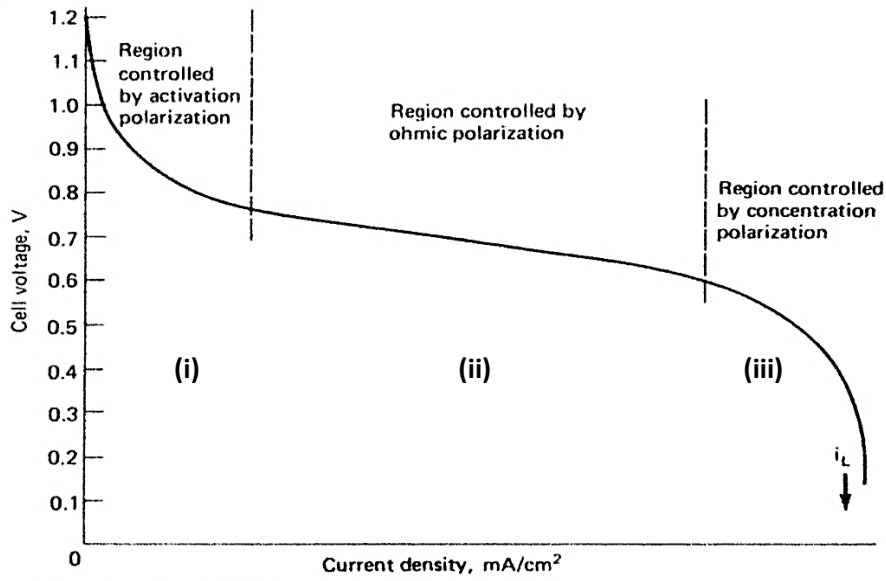


Figure I - 7: Typical polarization curve for a fuel cell: voltage drops due to (i) surface reaction kinetics, (ii) electrolyte resistance, (iii) reactant/product diffusion rates³

At low currents, the performance of a fuel cell is dominated by energy losses associated with the electrode reactions. This corresponds to the activation energy of the electrochemical reaction, and takes the form:

$$\eta_{\text{act}} = a + b \ln i \quad \text{I-12}$$

where η_{act} (mV) is activation polarization, a and b are constants, and i (mA/cm²) the current density. Activation polarization is associated with each electrode independently and

$$\eta_{\text{act}} = \eta_{\text{act}(\text{anode})} + \eta_{\text{act}(\text{cathode})} \quad \text{I-13}$$

At intermediate currents, ohmic polarization (η_{ohm}) represents the addition of all ohmic losses, including electronic impedances through electrodes, contacts, current collectors and ionic impedance through the electrolyte. These losses follow Ohm's law:

$$\eta_{\text{ohm}} = iR \quad \text{I-14}$$

where R is the overall resistance of the cell.

Polarization observed at higher currents represents the energy losses associated with mass transport effects (limiting diffusion processes). These losses are due to reactants not being able to reach the electrocatalytic sites. Typically, oxygen cannot reach the electrocatalytic sites when the cathode is flooded by liquid water, but ions can also cause mass-transfer limitations.⁴⁷

2.4. Limitations of Lithium-air Batteries

The capacity of the lithium-air battery is currently limited by the anode and the method for storage of reaction products. However, the performance is also affected by electrolyte leaking, electrode flooding and electrolyte carbonation.

2.4.1. Electrolyte Leaking

As the cell is open to air, water vapor can be transferred outside due to the difference in partial vapor pressure between the electrolyte and the surrounding environment. Water loss increases the electrolyte concentration and leads to drying out and premature failure. Leaking can cause flooding of the air electrode pores due to the inability of the air to reach the reaction sites.⁵⁴

In aqueous KOH electrolyte, the leaking of the electrolyte through the electrodes was described as the result of physical damage to the electrode. Rolla et al.⁵⁵ suggested that this was caused by the precipitation of potassium bicarbonates ($\delta = 2.17 \text{ g/cm}^3$) in the electrode pores, followed by the decrease of the precipitate volume caused by recrystallization into potassium carbonate ($\delta = 2.42 \text{ g/cm}^3$).

2.4.2. Electrode Flooding

Gouérec et al.⁵⁶ demonstrated that for an air electrode, over a 1500 - 2000 h working period (KOH electrolyte), the degradation of the performance is due to a slow and constant physical flooding (Figure I - 8).

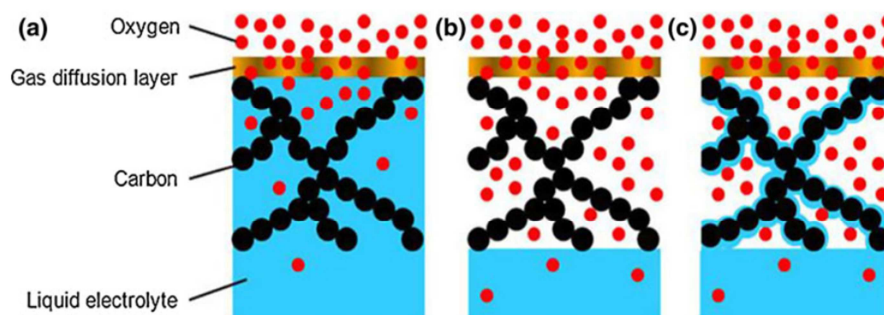


Figure I - 8: Schematic view of electrolyte filling in (a) flooded cathode, (b) dry cathode, and (c) wetted cathode⁵⁷

The flooding of the electrode restricts the O_2 diffusion because O_2 mobility is lower in a liquid. Therefore, the kinetics of the system is slow and limits the electrode capacity. The flooding could be due to imperfections in the wet proofing coating. Several strategies have been evaluated to stop, or to reduce, the rate of flooding. One of these strategies is the modification of the operating procedure of the battery to minimise the time during which a module is inoperative but in contact with the electrolyte. Alternative is to use a more hydrophobic carbons, to optimize of the PTFE quantity and the heat treatments of the intermediates or the finished electrodes.

2.4.3. Electrolyte Carbonation

The CO_2 contained naturally in air (300 - 350 ppm) was identified⁵⁵ as the principal factor determining the ageing of air electrodes if the cell is fed with untreated air. An increase in air humidity as well as electrode porosity was found to retard this phenomenon. This electrolyte carbonation and carbonate precipitation were responsible for the loss of performance⁵⁸. Indeed, on contact with CO_2 , the alkaline electrolyte reacts to form the corresponding carbonate, reducing the OH^- concentration (eq. I-6). If a significant reduction in the concentration of OH^- ions occurs, one observes a reduction in the ionic-conductivity of the electrolyte (carbonates are less conductive than the corresponding hydroxides), as well as an increase of the electrolyte viscosity. This also results in interference with electrode kinetics and diffusion properties.

The carbonate precipitation may block gases pores and thus limit the gas diffusion inside the catalytic layer to the active sites, and can also cause mechanical damage and decrease electrode performance.⁵⁵ Lithium hydroxide and lithium carbonate have a much lower solubility than the corresponding potassium salts (125 g/L and 13 g/L vs. 1210 g/L and 1110 g/L, respectively).⁵⁹ Thus the carbonate precipitation is a critical problem in the case of LiOH electrolyte.

2.5. Conclusion

In summary, the main cause for the decreasing performance of the air electrode in the aqueous lithium-air battery is the precipitation of lithium carbonate in the porous structure. This carbonation is observed when untreated air feeds the electrode. The use of pure oxygen, or air scrubbers as feed to eliminate the presence of CO_2 , limits the application of the cell for

vehicle propulsion, due to the increase of the system total weight. As we will see next, in an aqueous electrolyte cell the use of a polymer membrane to separate the air-electrode from the electrolyte can reduce the negative effects of CO_2 .

3. Air-Electrode Protection by Anion Exchange Membranes (AEM)

The protecting membrane must be a solid polymer electrolyte (SPE) that ensures the required hydroxide conduction for the electrochemical reactions performed at the air electrode and also prevents the transport of cationic species (K^+ , Li^+ , etc.) from the electrolyte towards the electrode to avoid the carbonate formation (Figure I - 9). The cationic charge of the SPE will prevent or limit the passage of these cations. As the cations in the liquid electrolyte will not reach the pores of the electrode, the carbonates formed by the reaction of OH^- with CO_2 will be no more observed inside. In addition, leakage of electrolyte can be reduced. Thus, employing an anion exchange membrane (AEM) should slow down performance degradation with time.

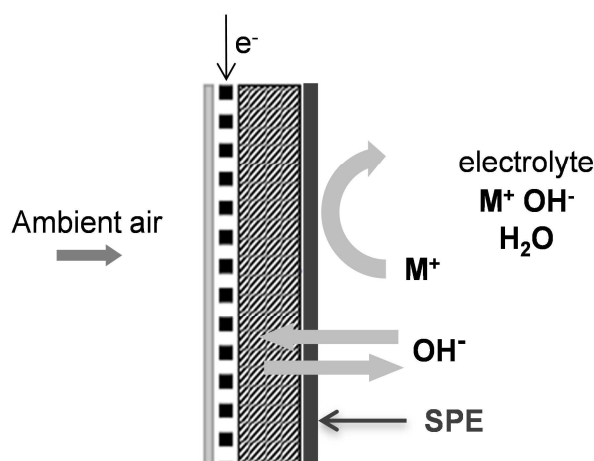


Figure I - 9: Structure of an air electrode protected from the electrolyte with a SPE

Few studies have been carried out on the air electrode protection by an anionic polymer membrane. However, due to the similarity between the operating principles of alkaline fuel cells (AFC) and metal/air batteries, most of examples reported below concern the developments in AFC. Indeed, development of an AFC based on anion-conducting polymer electrolytes to replace the hydroxide solution has been particularly studied.^{54,60,61,62}

In addition to its ion selectivity, the air electrode modified by a polymer membrane has to attain performances close to those obtained with unmodified electrode. On one hand, anion

exchange membranes (AEM) require adequate electrochemical properties such as ionic conductivity which must be high enough (≥ 1 mS/cm) to support a large current with minimal resistive losses. It can be improved by increasing the amount of charges groups in the membrane. However, an increase in ionic charge usually causes a loss of the mechanical resistance due to an excessive water uptake. On the other hand, the selection of the cationic group is crucial since it will influence the chemical stability of the membrane. Indeed, AEM can suffer of a poor chemical stability in alkaline media due to the hydroxide attack on the cationic group. This degradation generally induces an important loss in the number of anionic exchange groups, and leads to a decrease of the ionic conductivity. Therefore, the different properties required for the AEMs are now described in detail and then the different cationic groups and their properties are listed.

3.1. Hydroxide Transport for Conductivity

The first role of the protecting membrane is to conduct hydroxide ions. Due to its early stage of development, the fundamental studies on the hydroxide transport through membranes are not abundant in the literature and debates on the exact transport mechanism are always in progress⁵⁴. Available data on proton transport in proton exchange membranes (PEM) are usually employed to describe the different types of hydroxide transport.⁶³

Proton transport mechanisms include combinations of the Grotthuss mechanism, mass diffusion, migration, surface site hopping, and convective processes.^{64,65,66} It has been also experimentally observed that the proton conductivity depends on environmental conditions, such as temperature, relative humidity and pressure.⁶⁷ Although anion conductivity is several times smaller than proton conductivity in Nafion[®], similar dependency on relative humidity and temperature has been observed. Based on these similarities, it was assumed that hydroxide transport mechanisms in the AEM could be analogous to that of the transport of protons in proton exchange membranes⁶⁸ and they are schematized in Figure I - 10.

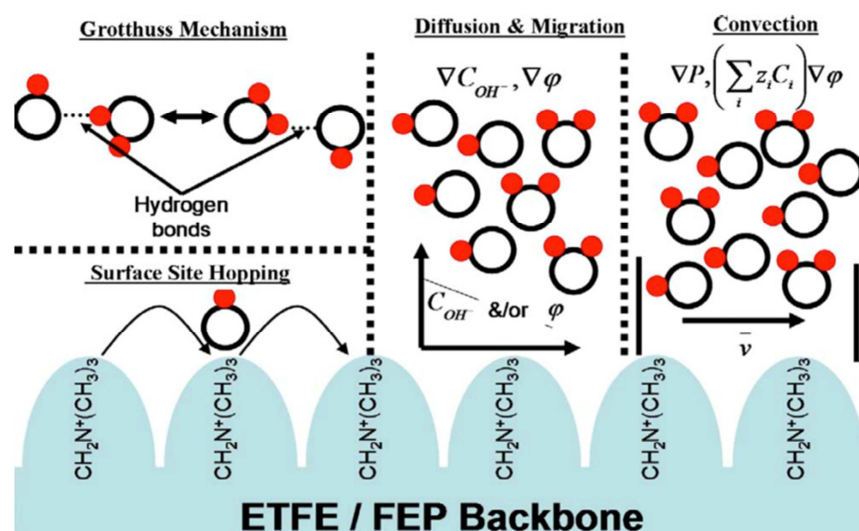


Figure I - 10: Scheme of different hydroxide transport mechanisms in an AEM, from Grew and Chiu⁶⁸

The Grotthuss mechanism, diffusion, migration, and convection are considered to be the dominant transport mechanisms.^{69,70} According to the Grotthuss mechanism, hydroxide diffuses through the hydrogen-bonded network of water molecules through the formation/cleavage of covalent bonds⁷¹. Diffusive and migration transports occur in the presence of a concentration and/or electrical potential gradient. Convective transport appears because hydroxides moving through the membrane drag water molecules with them, thus generating a convective flow of water molecules. Surface site hopping of hydroxide anions is considered as secondary because the water interacts strongly with the fixed charges of the membrane, and limits interaction of hydroxide with those groups.⁵⁴

Hibbs et al.⁶⁷ explored the transport properties of different AEMs based on polysulfone with different degree of functionalization. The effects of the ionic exchange capacity (IEC - the number of moles of cationic groups per gram of dry polymer) on water uptake, ion conductivity, effective water self-diffusion coefficient, and pressure-driven water permeability have been studied. Although the self-diffusion coefficient of free-water is greater in AEMs than in PEMs, the ion conductivity and pressure-driven water permeability were lower in AEM than in PEMs. The authors suggest that this is an effect of the different morphologies. The ionic groups in the PEMs form phase-separated domains, which can promote high transport rates. The weak basicity of the quaternary ammonium groups ($pK_b = 3 - 4$)⁷² associated with the lower OH^- mobility ($20.5 \cdot 10^{-8} \text{ m}^2/\text{s}\cdot\text{V}$) compared to that of H^+ ($36.30 \cdot 10^{-8} \text{ m}^2/\text{s}\cdot\text{V}$)⁷³ can also explain the low conductivity of AEMs.

Grew and Chiu⁶⁸ proposed that in the Grotthuss mechanism, hydroxide anion tends to have stable solvation shells that reorganize the solvent molecules and perturb the hydrogen bond network, whereas protons are naturally integrated into the hydrogen-bonding network of water. As the mobility of hydroxide ions is only 40 % lower than that of protons, the authors proposed that other factors, as insufficient OH⁻ dissociation and solvation, and membrane structure can be responsible for the lower conductivity.

In summary, no unanimous agreement or consensus on the exact mechanism and the relative importance of the different transport mechanisms for hydroxide transport occurring in AEMs exists, and transport through the membrane must be the product of a combination of the mechanisms described above.⁵⁴

3.2. Ion Transport Number for Selectivity

The selectivity of a polymer membrane with respect to anions and cations can be evaluated from the measurement of the number of transport. The anion transport number quantifies the amount of anion that is transported through the membrane. As the sum of the transport numbers of cations and anions is equal to 1, the more the anion transport number approaches 1, less cations cross through the membrane and the latter is selective towards cations.

A static method derived from Henderson's equation determines the transport numbers under diffusion.^{74,75,76} In this method, a membrane separates a two-compartment cell and each of the compartments is filled with KOH solutions at different concentrations. The resulting potential over the membrane is measured ($E_M = \Delta U - E_{NERST}$) and allows calculating the anion transport number (t^-) using Henderson's equation:

$$t^- = \frac{1}{2} \times \left(1 - E_M \times \frac{1}{\ln \frac{a_1}{a_2}} \right) \quad \text{I-14}$$

where a_1 and a_2 are the activities of the two KOH solutions.

The transport number can be affected by the ion exchange capacity (IEC) of the polymer. IEC is determined as hydroxide counterions, fixed in the polymer matrix and it is measured by titration of the hydroxide with HCl. If the fixed charges are monovalent, the IEC is usually expressed in millimoles per gram or in milliequivalents per gram. In general, the conductivity increases linearly with the ion exchange capacity, and is also dependent on the nature of the polymer.^{77,78}

3.3. Swelling

The swelling (or uptake according to the measurements carried out) capacity of a membrane determines its dimensional stability and also affects its selectivity and electrical resistance. The swelling depends on several parameters such as the nature of the polymer and the ion exchange groups, the counter ions (swelling of the membrane increases after the replacement of the haloid counter-ions by the hydroxide ions), the charge density and the cross-linking density of the membrane.

The presence of water is necessary to obtain an efficient conductivity by enhancing the mobility of the ions. However, extensive water uptake reduces the mechanical stability and has an opposite effect on the ionic conductivity, as it reduces the charge density or ion concentration in the membrane by dilution.⁷⁹ The water content of the AEM generally increases with the increase of the temperature which brings about the opening of the micropores and the formation of the hydrated ion clusters.

A final important property required for the polymer membranes is stability in alkaline media. This will be discussed in more detail for the different types of membrane in the following section.

4. Different Types of Anion Exchange Membranes

Solid polymer electrolytes used as anion exchange membrane can be of two types: either non-ionic ion solvating polymers (ISP) swelled in an electrolyte, or ionic polymers (i.e. polyelectrolytes) with the mobile adequate counter ion.

4.1. Ion Solvating Polymers (ISP)

An ion solvating polymer (ISP) is a polymer-salt complex, in which the salt acts as ion-exchanger. They consist of a water-soluble polymer, a hydroxide salt (i.e. KOH) and sometimes one or more plasticizers. These combinations have the mechanical properties of the polymer and the electrochemical and conductive properties of the alkaline salt. The majority of them have been developed for Ni–Zn, Ni–MH or Zn–air battery application.

The polymer contains electronegative heteroatoms such as oxygen, nitrogen, or sulfur, which interact with the cations of the salt by a dipole-ion interaction.

Studies of ion transport mechanisms in ISP have demonstrated that the ionic conductivity is enabled by segmental motion of the polymer hosts and the binding energy between cations and anions. Indeed, the best conductivity should then occur for the most liquid-like (lowest T_g) solid polymeric electrolyte.⁸⁰

4.1.1. Poly(ethylene oxide) (PEO)

The most developed system is based on PEO⁸¹ because it solvates cations by interaction with polar ether groups in the main chain⁸² and forms homogeneous polymer films (Figure I - 11).

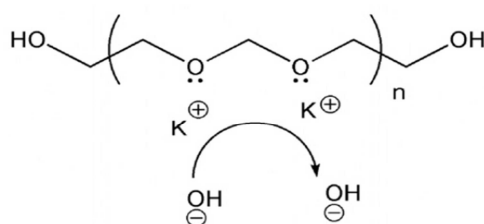


Figure I - 11: Mechanism of ionic transport in a PEO matrix

The ionic conductivity strongly depends on the proportion of KOH and water in the films. Fauvarque et al.^{83,84} developed ISPs, based on PEO, KOH and water with a maximum ionic conductivity of 1 mS/cm at room temperature. Nevertheless, its conductivity cannot be improved because the PEO matrix crystallizes with increasing salt concentration, decreasing the ionic conductivity. The required ionic conductivity could only be obtained above their melting temperature, which limits the operating temperature range.

Different approaches have been attempted to reduce the crystallinity of PEO-based electrolytes such as the addition of an amorphous polymer host with a similar solvating behavior. For instance, Vassal et al.⁸⁵ developed an ISP based on copolymers of poly(epichlorohydrin) (PECH) and PEO (Figure I - 12), with KOH as a conducting salt.

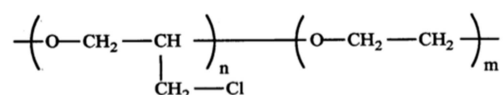


Figure I - 12: Chemical formula of poly(epichlorohydrin-co-ethylene oxide)

The ionic conductivity reached 1 mS/cm at room temperature. Although this value was comparable to that of the PEO/KOH system, an increase of the hydroxide transport number was observed. The authors suggest that a nucleophilic substitution reaction occurs on the chloride atoms leading to the formation of $-\text{CH}_2\text{O}^- \text{K}^+$, which decreases in the potassium ion mobility. This demonstrates the interest of copolymer use, and the possible implication of alkoxide groups in OH^- transport.

4.1.2. Poly(vinyl alcohol) (PVA)

Other works on ISP focused on poly(vinyl alcohol) (PVA) (Figure I - 13) which is chemically stable.^{86,87} This semi-crystalline polymer has a glass transition temperature at about 85 °C, a melting temperature at 180 - 200 °C, and a storage modulus of about 8 GPa^{88,89} (values depending on the PVA's molar weight).

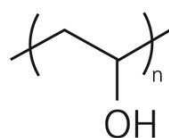


Figure I - 13: Chemical formula of poly(vinyl alcohol) (PVA)

Lewandowski et al.⁹⁰ found that the ionic conductivity of the PVA/KOH/H₂O polymer electrolyte was around 1 mS/cm at room temperature. This conductivity highly depends on the weight proportions of KOH and water. By increasing the KOH and water proportions in the PVA matrix, an ionic conductivity of 47 mS/cm is obtained at room temperature.⁸⁸ However, the mechanical resistance diminishes when greater amounts of KOH (up to 4 M) are introduced. The use of a support (such as glass fiber cloth) can enhance the mechanical strength, but may lead to a decrease of conductivity.⁵⁴

In order to increase their conductivity, PVA based blends have been carried out to decrease its crystalline phase amount. For example, blends of PVA and poly(epichlorohydrin) (PECH) containing KOH shows a conductivity between 1 and 10 mS/cm at room temperature because the crystallinity ratio was decreased.⁹¹

Since the first studies on ion solvating polymer for AEM, new types of polymer electrolytes have been developed. Today, the ionic conductivity generally reaches 10 mS/cm. Nevertheless, its selectivity is relatively low compared to ionic polymers.

4.2. Ionic Polymers

The different ionic polymers described in the literature will be now discussed, according to their stability at high pH. In fact, a major challenge in the development of alkaline AEMs is their stability in highly alkaline solutions, which requires stability of the polymer backbone as well of the cationic groups.

Degradation of the polymer backbone is generally the result of oxygen⁹² or hydroxide attack⁹³. Some polymers show good chemical stability, such as polysulfones and fluorocarbons.^{94,62} However, while poly(tetrafluoroethylene) (PTFE) is stable in alkaline environment (pH 10 - 14), polyvinylidene fluoride (PVDF) and vinylidene fluoride (VDF) copolymers are degraded almost immediately (Figure I - 14) generating a darkening and a loss of the mechanical properties of the membrane.^{95,96}

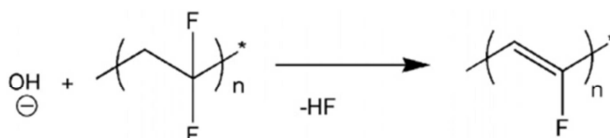


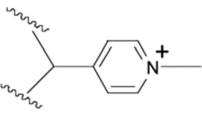
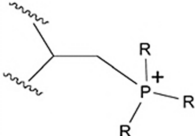
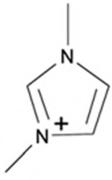
Figure I - 14: Degradation of PVDF in alkaline environment

More important, degradation of the cationic groups causes a dramatic loss of ionic conductivity and functionality of the membrane. These groups have to be stable at high pH to be resistant against attack by the hydroxide ions.

Thus, to identify the chemical nature of the polymer that would be best suited to withstand the conditions imposed by the lithium-air battery, while performing the functions assigned, a comprehensive review, but certainly not exhaustive, of the various exchange polymer membranes ion was performed. Different polymers have been grouped according to the nature of their skeleton and that of cationic group (Table I - 4). IEC values, conductivity, water uptake, and chemical stability were reported when available and will be discussed in the following paragraphs.

Main cationic groups used in AEM, with some AEM examples that we consider of interest, are presented in Table I - 4. In the presented membranes, the chemical nature of the cation appears to be the determinant factor affecting the AEM stability. For this reason, we will focus on the cationic groups in the next part of this chapter.

Table I - 4: Properties and nature of anion exchange membranes described

Polymer backbone	IEC (meq/g)	Conductivity (mS/cm)	Water uptake (wt. %)	Stability at pH > 10	Ref.
 Pyridinium					
Poly(vinyl alcohol) (PVA)	0.6 - 2	4 - 10	60 - 70	Not reported	97
 Phosphonium					
Polystyrene (PS)	Not reported	0.1 – 0.5 (HCO ₃ ⁻ counterion)	10 - 50	Unstable in 0.1 M KOH	98
Tris(2,4,6-trimethoxyphenyl) polysulfonemethylene	1.2 – 1.6	17-38	15	10 M KOH for 48 h	99,100
Polyethylene	0.6	2.2	50	Stable in 15 M KOH for 138 h at room temperature	101
 Imidazolium					
Poly(methyl methacrylate) (PMMA) Poly(butyl methacrylate) (PBMA)	1.5 - 1.6	33	27 - 28	Stable in 6 M NaOH, 80 °C for 120 h	102
Poly(methacryloyloxy)	Not reported	10	Not reported	Only in mild conditions, [KOH] < 1 M	103
Poly(phenylene oxide)	1 - 2	10 - 37	10 – 50	Degradation after 7 days in 2 M KOH at room temperature	104

4.2.1. Polymers Containing Pyridinium Groups

Some work has been done on poly(vinyl pyridinium) based membranes,¹⁰⁵ known for their application in electrodialysis or desalination. For instance, Choi et al.⁹⁷ prepared membranes based on PVA on which 4-formyl-1-methylpyridinium benzene sulfonate (FP) was grafted (Figure I - 15). The resulting membrane exhibited a low electrical resistance (4-10 mS/cm) and a swelling in water between 60 and 70 %.

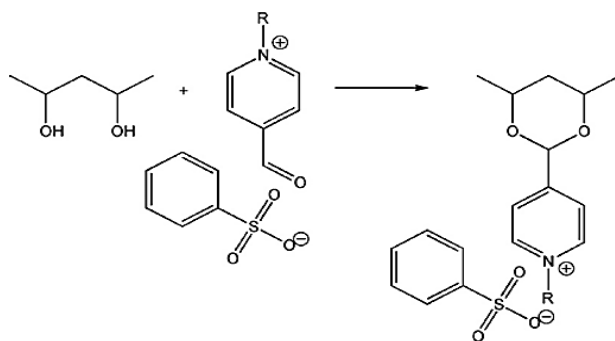


Figure I - 15: Synthesis of pyridinium PVA

However, even though these membranes show the required electrochemical properties, they are not commonly used because at pH higher than 12, the pyridinium group is chemically degraded by the hydroxide ions^{54,92} according to the mechanism shown in Figure I - 16, which decreases the numbers of ionic sites.

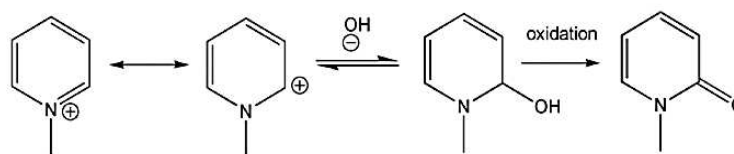


Figure I - 16: Degradation of the pyridinium groups in alkaline media

4.2.2. Polymers Containing Phosphonium Groups

Polymers containing quaternary phosphonium are studied as AEM materials because the strong basicity of the tertiary phosphine suggests that they are good anionic groups for AEM. However, as the pyridinium group, the phosphonium group is rapidly degraded at pH higher than 12, and consequently it has limited interest in AEM.^{54,61} Nevertheless, some research groups are studying new approaches to increase its chemical stability and its use in

applications at moderate pH values. This cationic group has been grafted on polystyrene, polyethylene or polysulfone polymer.

Ye et al.⁹⁸ have prepared and characterized phosphonium-based bicarbonate anion exchange random copolymers, poly(styrene-trimethylvinylbenzyl phosphonium bicarbonate) (Figure I - 17).

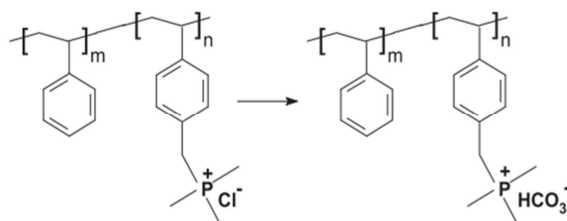


Figure I - 17: Phosphonium based bicarbonate AEM.⁹⁸

The swelling is between 10 and 50 wt.% depending on the copolymer composition and the HCO_3^- conductivity is between 0.1 and 0.5 mS/cm. These AEM are thermally stable (up to 110 °C) and are chemically stable at pH lower than 12 (they are stable in 0.1 M K_2CO_3 but not in 0.1 M KOH). The degradation mechanism proposed by the authors is presented in Figure I - 18.

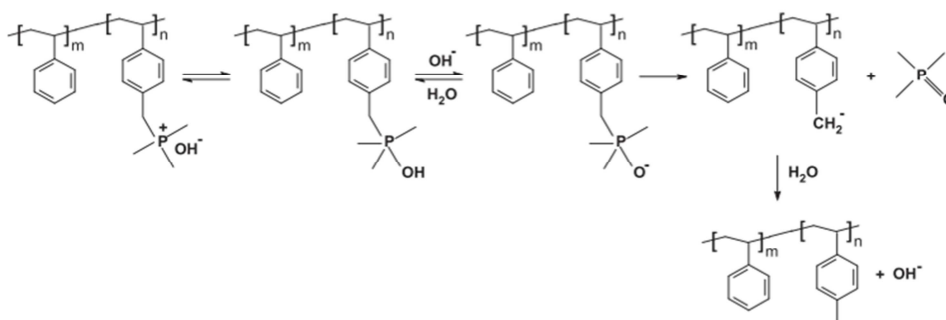
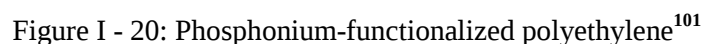


Figure I - 18: Chemical degradation in KOH of phosphonium-based AEM⁹⁸

Gu et al.^{99,100} synthesized a membrane based on tris(2,4,6-trimethoxyphenyl) polysulfonemethylene quaternary phosphonium hydroxide (TPQPOH) (Figure I - 19).



Noonan et al.¹⁰¹ showed that a higher chemical stability was obtained when tetrakis(dialkylamino)phosphonium was grafted on polyethylene (Figure I - 20).



While improvements have been made to the stability of phosphonium-based AEM, this type of membrane has not yet attained an industrial interest. Additionally, these two last examples show that, for an equivalent ionic group, stability of the polymer depends additionally on backbone

4.2.3. Polymers Containing Imidazolium Groups

There is a growing interest in imidazolium functionalized AEMs, partially due to its relatively high conductivities. Much work is being done on such polymers to improve their low stability in alkaline media.¹⁰⁶ Guo et al.¹⁰² reported the synthesis of copolymers of 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid with methyl methacrylate (MMA) and butyl methacrylate (BMA) (Figure I - 21 A). No difference was found between the MMA and the BMA-based copolymers. The AEM showed a hydroxide ionic conductivity of 33 mS/cm at 30 °C. The membranes retained good conductivity after treated with 6 M NaOH solution at 80 °C for 120 h.

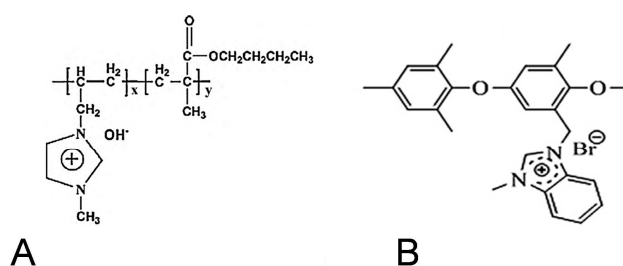


Figure I - 21: Structure of poly(AmimCl-BMA) (A) and BIm-PPO AEM (B)

It should be noted that it would have been interesting if the authors had crosslinked the membrane by introducing a few percent of crosslinking during synthesis of the copolymer for long term mechanical stability.

Ye et al.¹⁰³ characterized the chemical stability of poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium hydroxide) (Figure I - 22) by ionic conductivity measurements. This AEM presented a maximum conductivity of 9.6 mS/cm. High chemical stability was observed in mild alkaline conditions ([KOH] < 1 M) at 25 °C but the membrane is not stable under dry conditions (10 % RH) at 80 °C or at higher alkaline concentrations ([KOH] > 1 M). Figure I - 22 shows the degradation conditions and products identified by NMR spectroscopy.

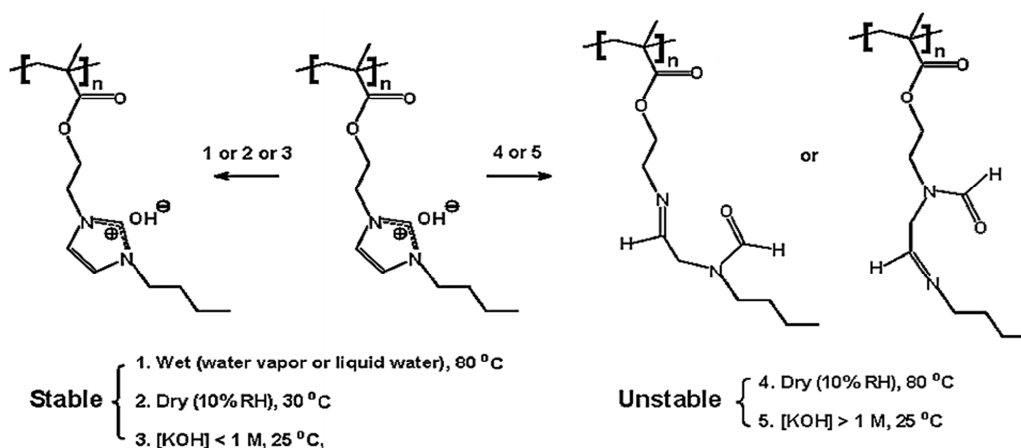


Figure I - 22: Chemical structure of poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium hydroxide) and degradation products¹⁰³

Lin et al.¹⁰⁴ studied benzimidazolium (BIm) functionalized AEMs (Figure I - 21 B). These AEMs show good mechanical and thermal stabilities, an IEC between 1 and 2 meq/g, water uptake between 10 and 50 wt.% and an anionic conductivity between 10 and 37 mS/cm. However, the authors found that the conductivity, the IEC and the water uptake of the AEM decreased after 7 days in 2 M KOH at room temperature.

These recent published studies suggest that further research should be made to find a suitable BIm-based AEM.

This initial analysis shows that among the studied cationic groups, sterically hindered phosphonium salts appear to have the best chemical stability in concentrated alkali. However, the behaviour of quaternary ammonium groups is still to be examined. They are the most studied anionic group in the literature and will be presented in the following paragraph.

4.2.4. Polymers Containing Ammonium Groups

Ammonium degradation in alkaline conditions can occur through different mechanisms. The cleavage of the quaternary ammonium by OH⁻ followed by elimination is called Hofmann degradation or E2 elimination. The hydroxyl ions attack a β-hydrogen of the ammonium, leading to the formation of an alkene, an amine and a water molecule (Figure I - 23).

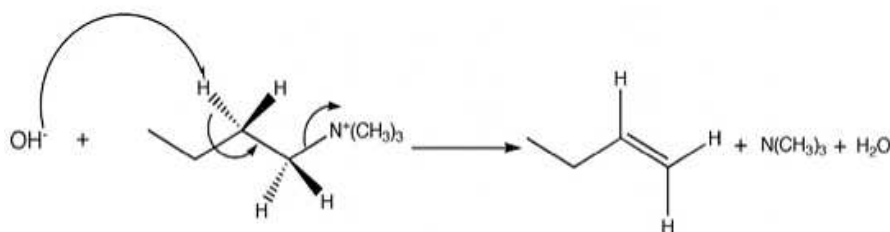


Figure I - 23: Degradation of the ammonium group in alkali by E2 elimination (Hofmann degradation)

When the atom carrying the charges is bulky, an E1 elimination can occur on the carbon located in the α or β position of the ammonium. The hydroxide ions attack the hydrogen of the methyl group belonging to the ammonium, and then a rearrangement occurs, leading to the formation of an alkene and an amine, like in Hofmann degradation (Figure I - 24).

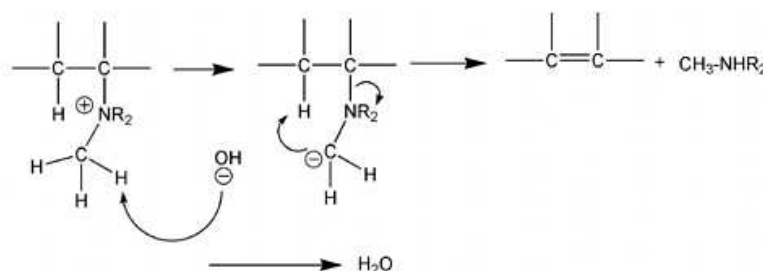


Figure I - 24: Degradation of ammonium groups by E1 elimination

A last mechanism consists in the degradation by nucleophilic substitution S_N2 at the α -carbon on the ammonium. This results in the formation of an alcohol and an amine (Figure I - 25).

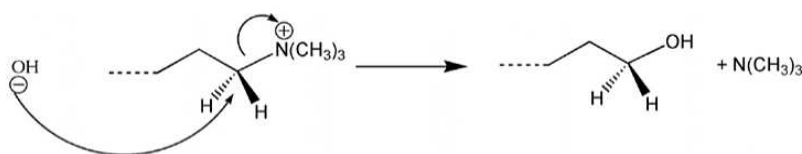
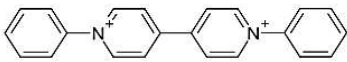
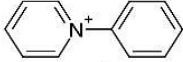
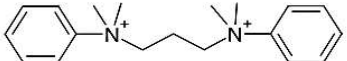
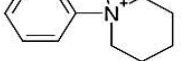
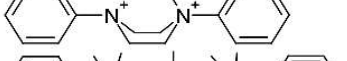
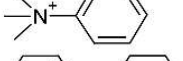
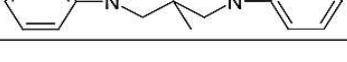
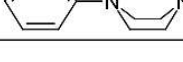


Figure I - 25: Degradation of ammonium groups by nucleophilic substitution

All the reviewed degradation mechanisms lead to the loss of the ionic group, and thus, a decrease in ionic conductivity. Thus, current research to find stable anion exchange membrane at high pH focuses on polymers that do not contain α -hydrogens to the cationic groups to prevent S_N2 substitution¹⁰⁷ (Figure I - 25) or β -hydrogens to prevent Hofmann degradation.^{72,92}

Bauer et al.¹⁰⁸ compared the stability of different benzyl ammonium groups in relatively severe conditions (Table I - 5).

Table I - 5: Half-time (in min) of different quaternary ammonium ions (2 M KOH, 160 °C, N₂ atmosphere) from Bauer et al.¹⁰⁸

Bis-(quaternary ammonium) compounds	$t_{1/2}$ (min)	Mono-(quaternary ammonium) compounds	$t_{1/2}$ (min)
	<0.2		<0.2
	2.1		18.4
	2.3		29.1
	4.7		42.0

They found for these model compounds that a molecule with two neighboring ammoniums is less stable than its mono-ammonium homologue. In the literature, particular attention has been given to 1,4-diazabicyclo-[2.2.2]-octane (DABCO) (Figure I - 26) as reagent for the formation of cationic groups.

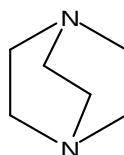


Figure I - 26: 1,4-diazabicyclo-[2.2.2]-octane (DABCO)

The mono-quaternary DABCO was indeed the most stable of the tested ammonium groups (Table I - 5, $t_{1/2}$ = 42 min). This stability would be due to the molecular conformation that makes ionic groups less sensible to elimination reactions (see below). Nonetheless the authors found that the bis-quaternary DABCO structure can be degraded into a piperazine system (Figure I - 27).

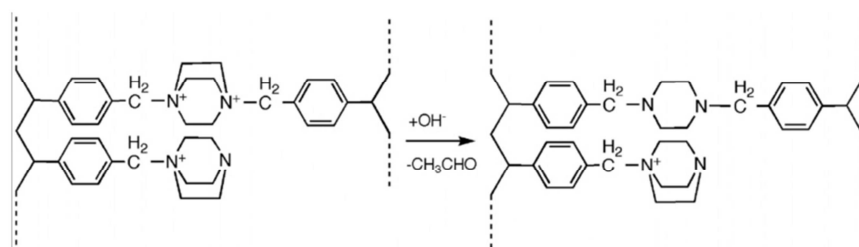


Figure I - 27: Degradation of the bis-quaternary DABCO structure¹⁰⁸

Similar results were obtained with poly(vinylbenzyl chloride)-grafted poly(ethylene-alt-tetrafluoroethylene) (ETFE-g-PVBC) films subsequently treated with different amines (Figure I - 28).¹⁰⁹

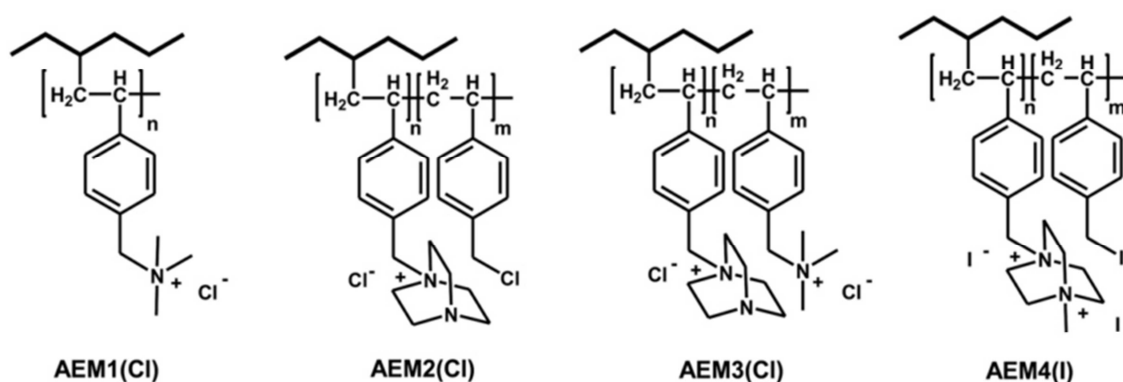


Figure I - 28: Anion exchange membranes studied by Ko et al. (shown before counterion exchange)¹⁰⁹

These membranes were immersed in 10 M NaOH solution at 60 °C for 3 days. AEM1(OH) having quaternized trimethylamine was found to be stable while AEM4(OH) having bisquaternized DABCO was found to be unstable in this condition (Figure I - 29). The low chemical stability of AEM4(OH) is considered to be an effect of the bis-quaternary ammonium group which is known to be prone to nucleophilic substitution by hydroxyl ions. The initial decrease in chemical stability of AEM2(OH) and AEM3(OH) can be also attributed to bis-quaternized DABCO linkage that can form via the reaction of two adjacent chloromethyl groups during the quaternarization with DABCO. After 3 day test, AEM2(OH) and AEM4(OH) with lower water uptakes maintained their shapes but AEM1(OH) and AEM3(OH) with higher water uptakes did not.

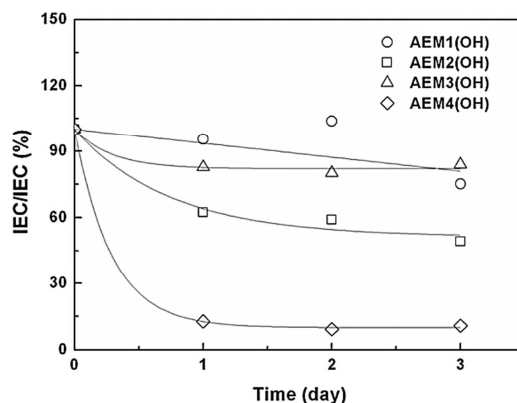


Figure I - 29: Evolution of IEC vs. time for AEM1(OH), AEM2(OH), AEM3(OH), and AEM4(OH) tested in alkaline condition (10 M NaOH at 60 °C for 3 days)¹⁰⁹

We must note that the authors used for this study benzylic quaternary ammonium compounds. However, it is known that benzylic quaternary ammoniums are subject to the Sommelet–Hauser rearrangement when exposed to strong bases (Figure I - 30):^{72,110}

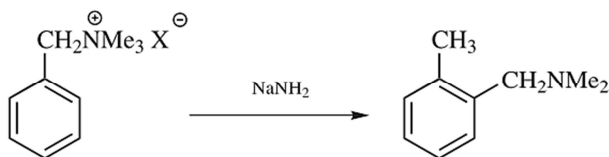


Figure I - 30: Sommelet-Hauser rearrangement of a benzylic quaternary ammonium

and to the Stevens rearrangement at high temperatures (Figure I - 31):^{72,111}

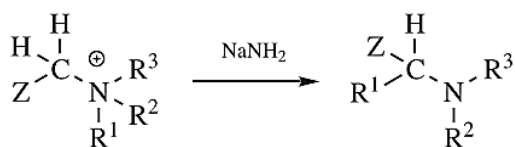


Figure I - 31: Stevens rearrangement of a benzylic quaternary ammonium

Thus, the use of quaternized benzylic groups should be avoided in highly alkaline conditions. To avoid any degradation favored by a neighboring benzyl group, DABCO has been used to form quaternary groups with different polymers, for example with poly(epichlorohydrin) (PECH) (Figure I - 32).

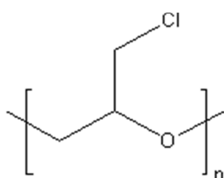


Figure I - 32: Poly(epichlorohydrin) (PECH)

PECH is similar in structure to PEO. In contrast, PECH is hydrophobic and does not crystallize. PECH homopolymer is an elastomer widely used in fuel hoses, air ducts, and engine compartments due to its oil and ozone resistance. PECH can be used as anionic exchange membrane if quaternary ammoniums are grafted on its skeleton.

PECH substituted by DABCO shows higher chemical stability in alkaline medium than the examples previously described. Indeed, DABCO moiety does not undergo Hofmann degradation, because the hydrogen atom and the nitrogen group involved in the process cannot adopt a *trans* or *cis* configuration to one another with a dihedral angle of 180° (anti-periplanar) or 0° (syn-periplanar).¹⁰⁸ Though the reaction may occur at the polymer backbone (Figure I - 33) it is assumed to be negligible due to the lower reactivity of the secondary carbon and the hindering of the C–O bond.

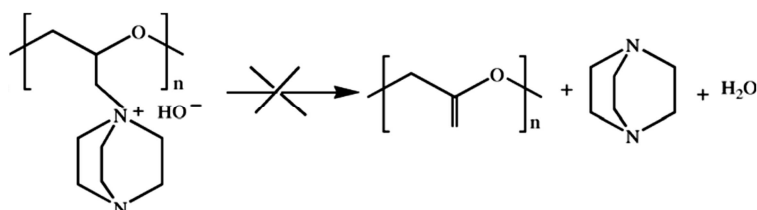


Figure I - 33: Schema of possible degradation of DABCO-modified PECH

PECH based membranes have been largely studied by Fauvarque et al. for alkaline fuel cell application (AFC).^{75,76,112} First, PECH in DMF was quaternized with 20 mol % DABCO and then the membrane was prepared by solvent evaporation.^{75,113} An IEC in the range of 0.5 - 0.6 meq./g after 2 days of immersion in a KOH solution was measured. The authors found this value to be lower than the theoretical, and explained that this could be due to an incomplete counterion exchange. However, longer exchange times did not increase the IEC values. Water uptake (WU) of 13 - 18 wt.% for the PECH-DABCO membrane in the Cl^- form was found to be smaller than in the OH^- form, with a maximum of 31 - 45 wt. %. This membrane was selective as its hydroxide transport number was between 0.95 and 1. The intrinsic

conductivity (in water) of the quaternized PECH membranes was low (between 0.05 and 0.10 mS/cm). Swollen with KOH, the ionic conductivity at 25 °C depends on the KOH solution concentration with a maximum of 40 mS/cm for 3.5 M KOH. The authors successfully assembled AFCs with the developed anion-exchange membranes. When the mechanical resistance of the membrane was not sufficient, the authors used a polyamide support, but this was suspected to reduce the conductivity of the membrane.

4.2.5. Fluorinated Polymers Containing Ammonium Groups

Fluorinated polymers can be used as anion exchange materials. Indeed, it is well known that fluorinated polymers exhibit high chemical stability imparted by the strong C-F and C-C bonds and shielding of the polymer backbone by the sheath of nonbonding electrons from the fluorine atoms¹¹⁴. For example, Valade et al. synthesized fluorinated copolymers with pendant ammonium groups via radical polymerization of fluorinated olefins with vinyl ethers, quaternized poly(chlorotrifluoroethylene-*alt*-vinyl ether) (Figure I - 34).^{115,116}

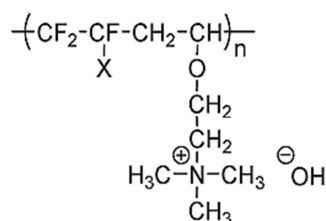


Figure I - 34: Quaternized poly(chlorotrifluoroethylene-*alt*-vinyl ether)

Resulting membranes showed hydroxide conductivity of around 0.1 mS/cm at room temperature. However, no information on the stability of the cationic group is given by the authors, but a low stability at pH higher than 12 can be expected.

The same authors prepared AEMs of chlorotrifluoroethylene (CTFE) and diallyldimethylammonium chloride (DADMAC) (Figure I - 35).¹¹⁷ The membranes soluble in DMSO but insoluble in water presented an IEC of 0.7 and a maximum conductivity of 0.9 mS/cm.

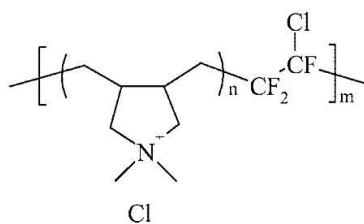


Figure I - 35: Copolymer of chlorotrifluoroethylene (CTFE) and diallyldimethylammonium chloride (DADMAC), poly(CTFE-co-DADMAC)

Similarly, Couture et al.¹¹⁸ report the synthesis of the copolymers poly(CTFE-*alt*-VE)-co-poly(CTFE-*alt*-FAVE8) for use in solid alkaline fuel cells (Figure I - 36). The synthesized AEM are reported as hydrophobic, but no further characterizations are described.

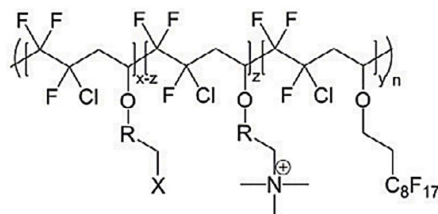


Figure I - 36. Poly(CTFE-*alt*-VE)-co-poly(CTFE-*alt*-FAVE8) (R can be aromatic or aliphatic)

Recently, anionic exchange membranes have been also developed from fluorinated commercial proton exchange polymers, such as Nafion[®]. Recently, Salerno et al. have reported the modification of Nafion[®] with different cations (Figure I - 37).^{119,120}

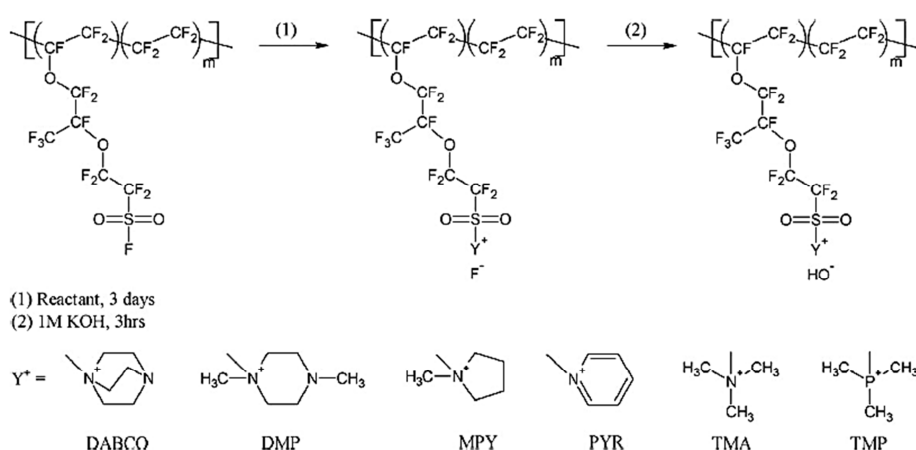


Figure I - 37: Synthesis of Nafion-based AEM with different cations: DABCO, piperazinium (DMP), pyrrolidinium (MPY), pyridinium (PYR), trimethylammonium (TMA) and trimethylphosphonium (TMP).

The hydroxide conductivities with the different cations are all in the same range: 1.4 - 4.1 mS/cm at 30 °C. The chemical stability of these polymers was also tested. Polymers with DABCO, DMP, MPY, or TMA cation were not significantly affected when they are exposed for 24 h at 80°C either under water saturated or 1 M KOH solution. However, significantly lower conductivities were observed for the polymer bearing the TMP cation. The most extreme case was at 1 M KOH at 80 °C, where the membrane with the TMP cation lost mechanical strength and broke apart into fragments that were too small to measure conductivity.

Though fluorinated polymers containing cationic groups are of great interest, its use as AEM materials is still in its early stages of development.

Chemical ageing studies of polymers with different ammonium groups are generally done by immersion in solutions of sodium or potassium hydroxide, in concentrations ranging from 1 to 15 M, but also at temperatures ranging from room temperature to 80 °C. Given the diversity of possible experimental conditions, it has proved difficult to clearly conclude on the stability of these different ammonium groups.

Another approach to improve the resistance of AEM by limiting their swelling is to crosslink the cationic polymers, as will be subsequently discussed.

4.3. Cross-linked Anionic Membranes

To restrict the membrane swelling and improve its mechanical strength and eventually its chemical resistance while increasing the IEC, one method is to crosslink the polyelectrolyte.

4.3.1. Cross-linked Quaternary Ammonium Polymers

In this section, we have considered only the crosslinked polymers containing ammonium groups whose stability has been tested in alkaline medium. All identified materials and some of their properties are summarized in Table I - 6. It should be noted that most of these studies are very recent, showing the interest of developing such materials.

Table I - 6: Representative cross-linked quaternary ammonium polymers

Polymer backbone	Cation	IEC (meq./g)	Conductivity (mS/cm)	Water uptake (wt. %)	Stability			Ref.
					Solution	Temp.	Time	
Polystyrene network in porous PE	DABCO	1.1 - 1.3	5 - 38	44 - 47	1 M NaOH	60 °C	75 h	121
poly(vinyltrimethoxysilane-co-2-(dimethylamino)ethylmethacrylate)	TMA	2.1 - 2.9	3.8 - 6.6	55.5	From 1 to 8 M NaOH	25 °C	24h	122
poly 1,5-dimethylpolyphenylene oxide	DABCO and TMA	0,6-1,1	0,9-5,4	--	1 M KOH	90°C	10 days	123
quaternized poly(vinylbenzyl) ammonium	TMA	1,3-1,7	26-43	35-69	5 M NaOH	50°C	1500h	124
poly(ether ether ketone)	TMA	0,9-1,4	12-17	25-32	1 M NaOH	60°C	12 days	125
poly(ETFE) grafted vinyl benzyl chloride	DABCO and TMA	1,7-2,1	22-34	54-89	From 1 to 10 M KOH	60°C	120h	126
copolymer of styrene, acrylonitrile, divinylbenzene and N,N,N-trimethyl-1-(4-vinylphenyl) methanaminium chloride	TMA	1,6	10	86-92	1 M KOH	60 °C	100 h	127
Hexyl methyl styrene divinylbenzene	TMA	3 - 4	n.a.	n.a.	dry	100 °C	1 month	128

TMA = trimethyl ammonium, DABCO = 1,4-diazabicyclo-[2.2.2]-octane, DMA: dimethyldialkyl ammonium

Hybrid anion exchange membranes have been synthesized from poly(vinyltrimethoxysilane-co-2-(dimethylamino)ethylmethacrylate) copolymer (VTMS-co-DMAEMA) which is crosslinked by sol-gel reaction in the presence of PVA (Figure I - 38).¹²²

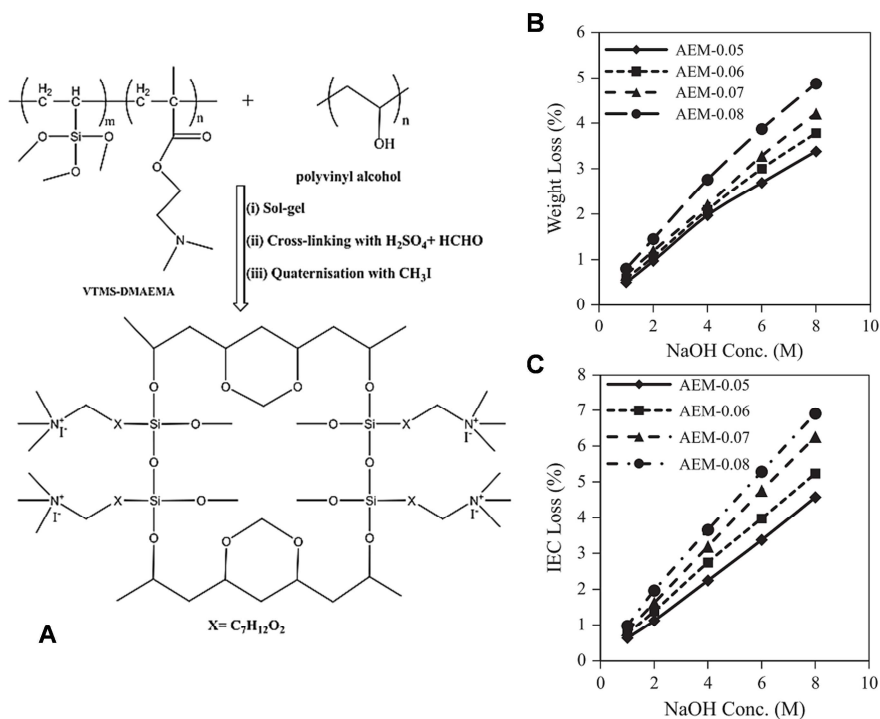


Figure I - 38: Crosslinked poly (vinyltrimethoxysilane-co-2-(dimethylamino)ethylmethacrylate) (VTMS-co-DMAEMA) (A) and weight (B) and IEC (C) loss under alkaline environment for different membranes

Stability of this hybrid AEM in NaOH solutions at different concentrations has been characterized by IEC and weight measurements. Losses in weight and IEC were increased with DMAEMA content (density of functional groups) (Figure I - 38 B and C). Further, deterioration in weight and IEC was less than 20%, because of cross-linked silica network. Moreover, AEMs were less stable in alkaline medium in comparison with neutral or acidic media. The hybrid materials do not seem thus to be an appropriate pathway to obtain stable membranes in alkaline medium.

In a similar way, Tomoi et al.¹²⁸ used DVB to cross-link quaternized polymers based on bromoalkoxy styrenes and bromoalkoxy methyl styrenes followed by quaternization with trimethylamine (Figure I - 39). The ion exchange capacity is a function of the bromoalkoxy used, and was in the order of 3 - 4 meq./g. This membrane exhibited no change in the IEC after heating for 1 month at 100 °C. No information is given on the conductivity or water uptake of the membrane.

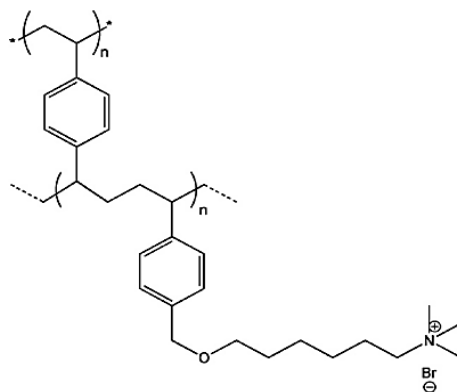


Figure I - 39: AEM based on DVB and quaternized bromohexyl methyl styrene

Anion exchange membranes have been also synthesized from cross-linked poly(ether ether ketone)s containing pendant quaternary ammonium groups with different IEC values.¹²⁹ One of the cross-linked membranes with an IEC of 1.18 meq./g showed a conductivity of 36 mS/cm and a swelling ratio of 6.6 % at 80 °C, in addition to a good chemical stability in 1 M NaOH at 60°C. Indeed, the conductivity remained at about 25 mS/cm after 30 days. It proved that the aromatic-side-chain type could keep the quaternary ammonium groups with a reasonable stability.

Komkova et al.¹³⁰ studied the stability in 2 M NaOH solution at 40 °C of polyether sulfone membranes crosslinked with various aliphatic diamines leading to quaternization (Figure I - 40).

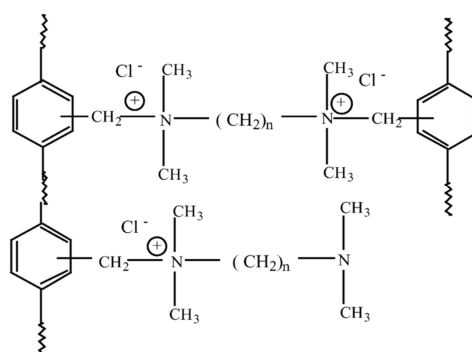


Figure I - 40: Quaternization with aliphatic diamines of various lengths of the aliphatic chain¹³⁰

The loss of the quaternary ammonium is observed in the first hours of immersion and the longer the aliphatic chain of the diamine, the slower the degradation rate. Contrary to the behavior observed previously by Bauer et al.¹⁰⁸ on model molecules (cf. § 4.2.4), the membranes based on the bis-quaternization were more stable than the membranes based on

the mono-quaternization. In this case, the increase in steric hindrance seemed to decrease the stability. Therefore, non-sterically hindered diamines seem the most promising quaternization and crosslinking agents.

Two cross-linked anion exchange membranes with the same IEC, were synthesized via in situ copolymerization of DVB, styrene, acrylonitrile and 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (MVBIm), or N,N,N-trimethyl-1-(4-vinylphenyl) methanaminium chloride (TMVPMA), respectively (Figure I - 41).¹²⁷

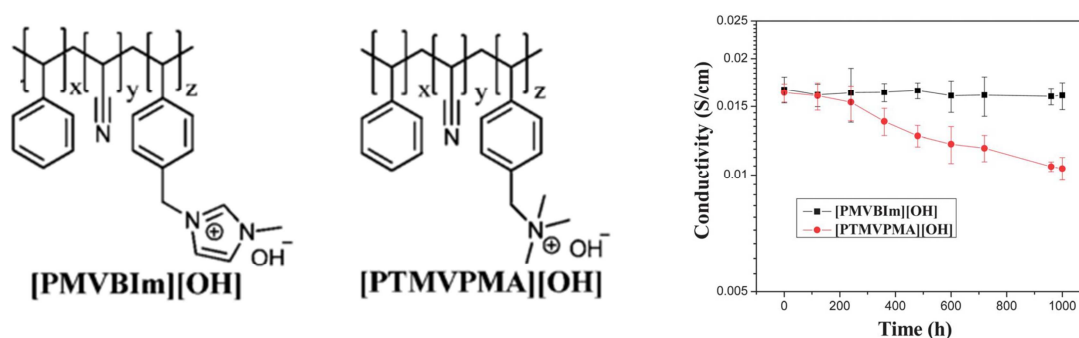
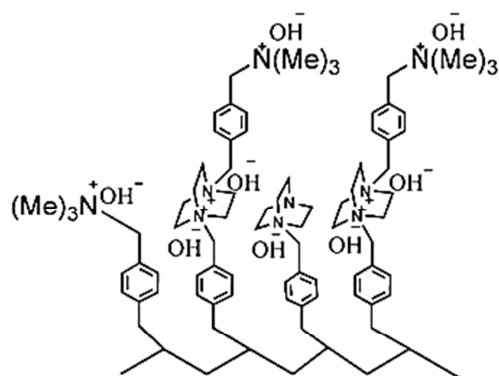


Figure I - 41: [PMVBIm][OH] and [PTMVPMA][OH] anion exchange membranes and change in hydroxide conductivity after immersion in 1 MKOH solution at 60 °C.¹²⁷

Both types of copolymer membranes exhibit hydroxide conductivity above 10 mS/cm. Alkaline imidazolium showed an excellent chemical stability of up to 1000 h without obvious loss of ion conductivity after immersion in 1 M KOH solution at 60 °C, whereas the membranes based on quaternary ammonium salts degraded in high pH. The results of this study suggest that the imidazolium cation is more stable in alkaline medium than trimethyl ammonium (not hindered ammonium group) one in a cross-linked polymer.

Diamines can also be used to cross-link polymers based on styrene leading to a very high ratio of ammonium groups. AEMs based on poly(ethylene-co-tetrafluoroethylene) (ETFE) films on which vinyl benzyl chloride (VBC) was grafted by radiation followed by quaternization and crosslinking with 1,4-diazabicyclo-[2.2.2]-octane (DABCO) (Figure I - 42).¹²⁶



AAEM

Figure I - 42: ETFE-based radiation-grafted AAEM.¹²⁶

The conductivity of these membranes was stable for 120 h at 60°C in KOH solution, the concentration of which varying from 1 to 10 M. The same polymer has been also cross-linked with divinylbenzene and included into porous PE as a composite pore filled AEM.¹²¹ Then, their alkaline stability was evaluated by immersing in 1 M NaOH at 60 °C for 75 h. The ionic conductivity did not significantly changed, suggesting that the functional groups were not significantly degraded in the composite pore-filled AEMs. The alkaline stability of these AEMs has been explained by the physical reinforcement by the PE substrate in which the membrane is synthesized. The pore-filled structure is described as advantageous for maintaining functional groups at extreme pH values. This result is confirmed by study on a cross-linked polymer between N,N-bis(acryloyl)piperazine and poly(vinylbenzyl) trimethylammonium chloride in a porous polyolefin substrate.¹²⁴ The resulting membrane has hydroxide conductivity in excess of 40 mS/cm and does not exhibit significant changes in ion conductivity and IEC in 5 M NaOH at 50 °C for 1500 h.

DABCO has been also used to cross-link brominated 1,5-dimethylpolyphenylenoxide (BrPPO) (Figure I - 43).¹²³ To investigate the influence of the size of the network, additional diiodobutane (DIB) was used.

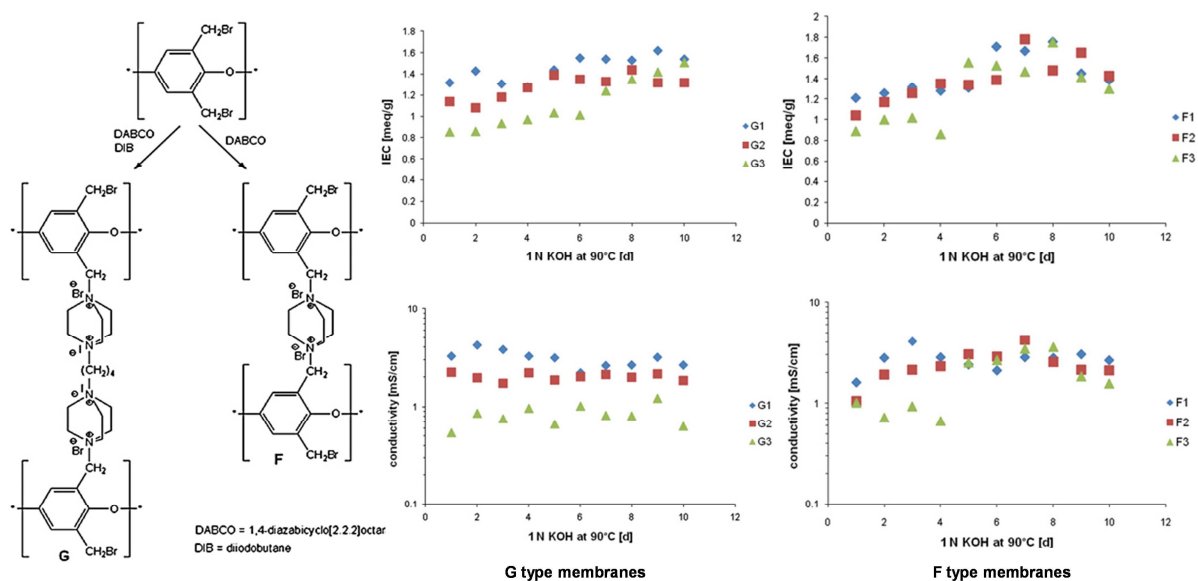


Figure I - 43: Cross-linking of BrPPO with DABCO and diiodobutane, Cl^- conductivity and IEC evolution vs. immersion time in 1 M KOH at 90 °C for the two membranes types

With additional DIB, the ion conductivity rises from 2.3 to 5.4 mS/cm and an IEC around 1 meq./g was reached. The alkaline stability was investigated at 90°C in 1M KOH for 10 days. The different membranes show a stable conductivity and IEC values under these conditions showing that DABCO cross-linking is stable.

From these aging studies, it appears that DABCO leads to the formation of the most stable ammonium groups in concentrated alkaline media. It has the added advantage of being simultaneously the ionic group and a crosslinking agent. We will describe this in more detail in the next section.

4.3.2. Poly(epichlorohydrin) Networks

As DABCO is considered as one of the most stable amines, it was widely used for PECH membrane preparation according to a procedure described in detail by Yassir.¹¹³ In a first step, 8 wt. % of non-modified PECH was dissolved in DMF at 90 °C. 20 mol % DABCO with respect to PECH moieties were added. The membrane was obtained by solvent-casting process at ambient temperature, and after evaporation of the solvent the membranes are heated at 120 °C for 30 min.

The obtained membrane presented a high swelling in water and was very fragile. It is not possible to conclude on the membrane crosslinking as the author does not report solubility

tests of the material. To reduce the swelling and improve the mechanical resistance the author used a second cross-linker, 0.1 % of trithiocyanuric acid was added to the modified PECH solution. The membrane IEC was 1.2 meq./g. A 30 wt. % uptake was measured in 0.1 M KOH solution. Ionic conductivity in 1 M KCl solution was 15 mS/cm, and chloride transport number was 0.97. The author reports a polarization test on a laboratory built AFC modified with this membrane, but no further information is given.

To increase the mechanical resistance of the membrane, Stoica et al.¹³¹ synthesized a poly(epichlorohydrin-allyl glycidyl ether) copolymer membrane quaternized by the incorporation of DABCO and 1-azabicyclo-[2.2.2]-octane (quinuclidine), in DMF at 80-90 °C for approximately 10 h (Figure I - 44). To crosslink the polymer, hexanedithiol (30 mol % versus allylic functions) and a photoinitiator (Irgacure[®] 2959, 3 wt. %) were added to the solution. The membrane was obtained by solution casting followed by UV curing. The authors do not mention the possibility of DABCO acting as a crosslinking agent, but the modified PECH is not post-cured in this study.

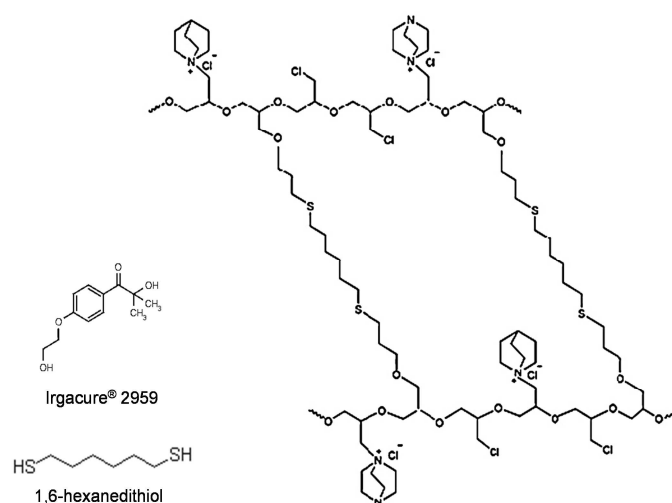


Figure I - 44: Cross-linked quaternized poly(epichlorohydrin-co-allyl glycidyl ether).

An IEC of 1.3 meq./g was measured for the membranes. The cross-linked membranes exhibited an elastomeric behaviour with a T_g at -4 °C. The mechanical properties of the membrane swollen in water cannot be measured due to its fragility. So it was further reinforced by a polyamide support. A swelling ration (SR) of 35 and 50 wt.% was obtained for polyamide-supported and non-supported membranes respectively. The intrinsic ionic conductivity of the non-supported membrane was 2.5 mS/cm at 20 °C and increased to 13 mS/cm at 60 °C, comparable to the conductivity of AEMs based in linear polymers. The

use of the non-conducting polyamide support only slightly decreased the conductivity of the membrane. Therefore the mechanical properties were improved by the polyamide support without compromising the ionic conductivity.

Another possibility to limit swelling and improve the properties of AEM is to combine the crosslinked polyelectrolyte with another polymer network, to obtain an interpenetrating polymer networks (IPN) architecture which is presented now.

5. Interpenetrating Polymer Networks (IPNs)

Sperling¹³² defines IPNs as the combination of two polymer networks that are synthesized in juxtaposition. According to the IUPAC, *“an IPN is a polymer comprising two or more polymer networks which are at least partially interlaced on a molecular scale, but not covalently bonded to each other and cannot be separated unless chemical bonds are broken”*.¹³³ Analogously, *“a semi-IPN is a polymer comprising one or more polymer networks and one or more linear or branched polymers characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched chains”*.

The purpose of this type of polymer associations is generally to combine each partner's properties inside a homogenous material while their flaws can be cancelled. These materials have been used in many applications due to their improved solvent resistance and mechanical properties.^{79,134,135,136,137,138} The synthesis of fuel cell membranes based on this type of architecture has been initiated with success in our laboratory.^{139,140}

5.1. Synthesis

IPNs can be synthesized from two synthetic pathways: sequential synthesis or *in-situ* synthesis.

5.1.1. Sequential Synthesis

In the sequential synthesis method, a first network is formed and subsequently swollen with the reagents of the second network, which is then synthesized inside the first network (Figure I - 45). By this method, the morphology is generally imposed by the first network, and the IPN composition range is limited by the maximum swelling of first network by the second network reagents.

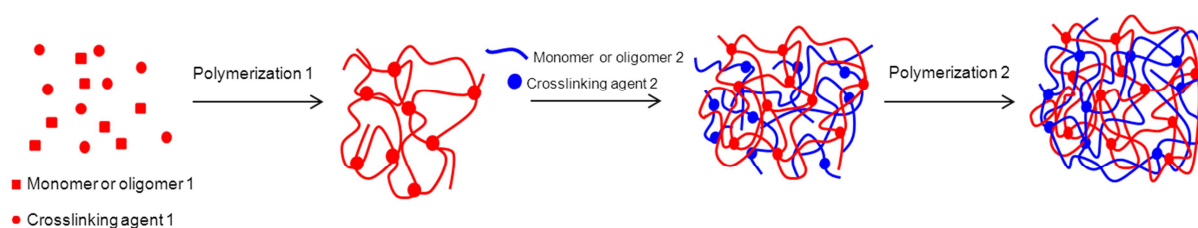


Figure I - 45: Sequential synthesis of IPN

5.1.2. *In-situ* Synthesis

In the *in-situ* method, all reagents are mixed at the beginning of the synthesis. The two network formations can be, or not, started simultaneously (Figure I - 46). It is necessary for the two network formation mechanisms to be different and independent. Otherwise a single polymer, or copolymer network, is obtained. By this method the ratio of the two networks can be almost freely modified by adjusting the reagent proportions.

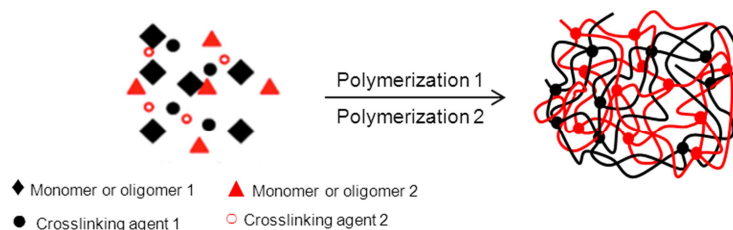


Figure I - 46: *In-situ* IPN synthesis

These two synthetic methods allow the association of crosslinked polymer networks of different chemical nature. The properties and the morphology of the obtained materials can be adjusted by modifying the partner proportions, the formation rates of each network compared

with the other, the thermodynamical phenomena driven the phase separation (before crosslinking) of most polymers. Thus, IPNs undergo phase separation, but at a smaller scale than linear polymer blends. During polymerization and network formation, the polymer molar weights increases, the mixture deviates from equilibrium, and demixing appears. Network formation opposes to phase separation, and thus the faster the network formation and the smaller the obtained domains.

Phase separation in the polymer blend can occur according to two mechanisms, depending on the temperature and composition of the mixture. First, in a nucleation/growth mechanism, nodules of one of the two components are formed. These nodules increase with time and eventually percolate during phase separation (Figure I - 47).

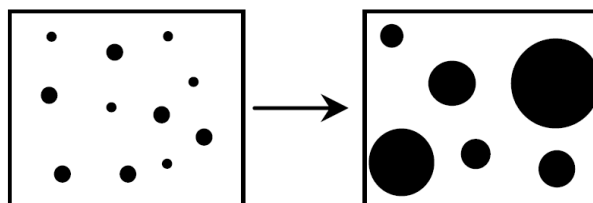


Figure I - 47: Nucleation and growth mechanism

The spinodal decomposition mechanism is also possible. This mechanism produces materials in which domains with a high concentration of one polymer are dispersed in a matrix with a high concentration of the second polymer. It corresponds to a meta-stable system in which domains with complex shapes appear. Chemical composition of these domains evolves with time; each species becomes predominant in one of the domains with time. This mechanism creates a co-continuity of the two phases that is also named as gyroïdal structure (Figure I - 48).¹³²

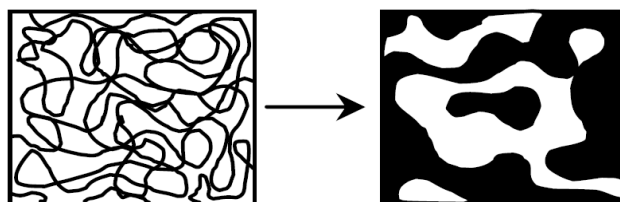


Figure I - 48: Gyroïdal structure

The phase separation mechanism depends on the proportion of the two polymers. Nucleation/growth mechanism is favored if one of the precursors is in low concentration. As

the concentration of this component increases a mixture of discrete nodules and complex domains formed by spinodal decomposition are observed. If the two components are present in equal amounts, phase separation often occurs by a spinodal decomposition mechanism and two co-continuous phases are obtained.^{141,142}

Few studies have reported the synthesis of PECH-based IPNs.^{143,144,145} In these cases, the PECH network was synthesized starting from a hydroxide-terminated polyepichlorohydrin and a pluri-isocyanate cross-linker via an alcohol-isocyanate addition leading to a urethane group formation. This PECH network has been associated with a poly(methyl methacrylate) (PMMA) or poly(ethyl methacrylate) (PEMA) networks in order to obtain a reinforced elastomer. All the IPNs with various compositions have a single T_g , which corresponds to only one mechanical relaxation detected by DMA measurements. However these relaxation range from -30 °C to 150 °C, which is typical of distribution of relaxation temperature corresponding to various degree of polymer interaction. Indeed, both partner networks are partially phase separated as confirmed by TEM microscopy (Figure I - 49).

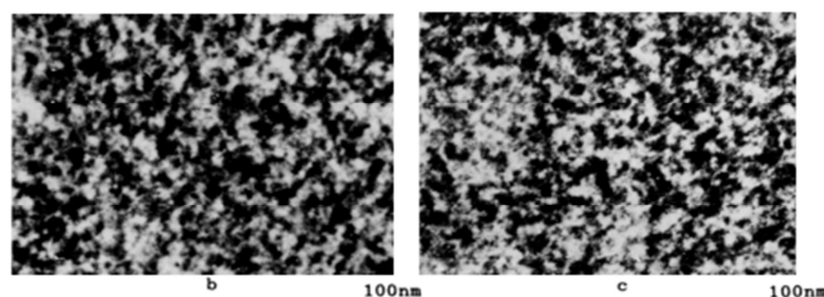


Figure I - 49: TEM photograph of (b) PECH/PMMA, (c) PECH/PEMA¹⁴⁵

The black area on the photos is the PECH network (stained by RuO_4), and the white area is the partner network. The phase separation in the IPNs was dependent on the miscibility of two networks and polymerization conditions. PECH and PMMA have almost the same solubility parameters δ (10.14 vs. 9.5 kcal/mol·K) so the miscibility is good between the two networks. The solubility parameters of PECH network and PEMA are more different (10.14 vs. 8.9 kcal/mol·K) and phase separation is more important but all samples have two-phase structures: the domain size of PECH network has a range of 40 - 120 nm.¹⁴⁵

However, PECH is neutral in all the presented IPNs and cannot be used as anion exchange membrane. On the contrary, a few AEM has been synthesized in a semi-IPN architecture (one of the polymer is not cross-linked) and they are now presented.

5.2. Semi-Interpenetrating Polymer Network (semi-IPN) as AEM

The combination of a polyelectrolyte with a neutral polymer in a semi-interpenetrating polymer network (semi-IPN) allows combining the properties of both polymers in the resulting material. Thus, the ionic conductivity of the polyelectrolyte has to be maintained while an improvement in the mechanical properties from the neutral polymer, which limits also the water swelling, is expected. For example, Luo et al.¹⁴⁶ reported the synthesis of a quaternized poly(methylmethacrylate-co-vinylbenzyl chloride) (QPMV) / poly(divinylbenzene) (PDVB) semi-IPN for use as AEM in alkaline fuel cells (Figure I - 50). The addition of 10 wt.% of the PDVB network was found to reduce the water uptake from 200 to 60 wt.%, but also the conductivity of the network was also reduced. A conductivity of 10 mS/cm was obtained above 50 °C.

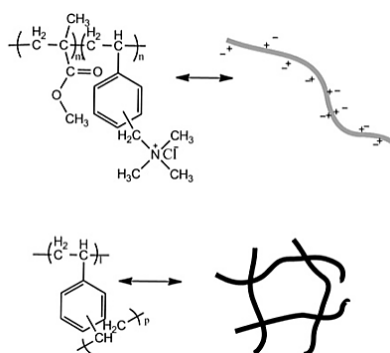


Figure I - 50: Synthesis of QPMV/PDVB semi-IPN¹⁴⁶

Less than 20 references related to semi-IPNs combining a polycation and a neutral network have been described in the literature. Among these, only the stability of some of them has been tested and they are summarized in Table I - 7.

Table I - 7: Properties of semi-IPN anion exchange membranes described in this work

Linear polymer	Crosslinked polymer	IEC (meq./g)	Conductivity (mS/cm)	Water uptake (wt.%)	Stability	Ref.
Quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)	vinylbenzyl chloride (VBC) - divinylbenzene (DVB) copolymer	1.55	22	20	Unstable in 2 M NaOH at 25°C and KOH 2M ≥ 50°C	147
Polystyrene (PS)	quaternized chitosan	0.85	28 (80 °C)	21	Unstable KOH 1M 60°C	148
poly(diallyldimethylammonium chloride) (PDDA)	PVA	0.77-0.89	15-25 (80 °C)	80-220	Stable in 8 M KOH	149
trimethyl amine quaternized cardopolyetherketone	PDVD - PS copolymer	1.43-1.72	19-22	15-165	Not stable in 2 M KOH, 25 °C	150
quaternized hydroxyethylcellulose ethoxylate	PVA		0.27-1.3 (19 °C)		Stable in 6M KOH at 60°C for one week	151

Wu et al.¹⁴⁷ synthesized an ammonium quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) / crosslinked poly(vinylbenzyl chloride) (VBC) - divinylbenzene (DVB) semi-IPN (Figure I - 51). This semi-IPN shows a conductivity of 22 mS/cm, 20 % water uptake and an IEC of 1.55 meq./g. However, this membrane is not stable in NaOH 2 M at room temperature, probably an effect of the unstable trimethylammonium cationic group.

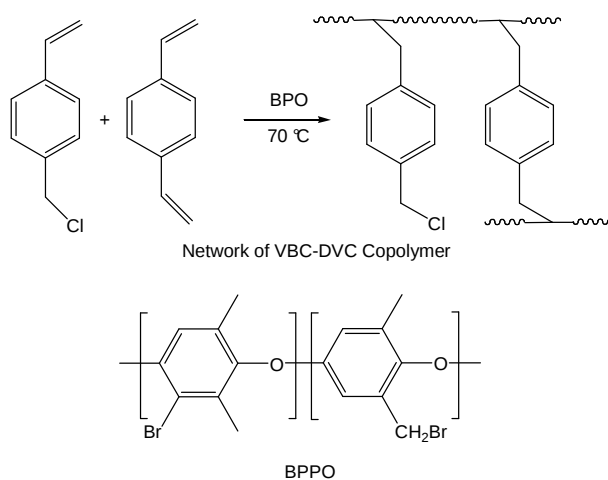


Figure I - 51: poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) / crosslinked vinylbenzyl chloride (VBC) – divinylbenzene (DVB) semi-IPN, later quaternized with trimethylamine¹⁴⁷

Wang et al.¹⁴⁸ reported the synthesis of trimethylammonium quaternized chitosan network in which polystyrene is entrapped (Figure I - 52).

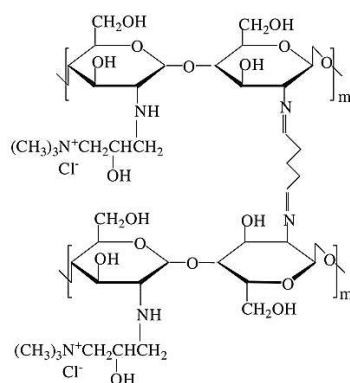


Figure I - 52: Crosslinked quaternized chitosan¹⁴⁸

A conductivity of 28 mS/cm at 80 °C, and 21 wt.% of water uptake were reported. The membrane conductivity remained stable in 1 M NaOH at room temperature for 72 h and at 60 °C for 50 h. However lost mechanical resistance and the conductivity could not be measured after immersion in 1 M KOH at 60 °C. This example shows the importance of the electrolyte nature in which the ageing test is carried out.

Qiao et al.^{149, 152, 153} synthesized semi-IPNs from crosslinked poly(vinyl alcohol) (PVA) and poly(diallyldimethylammonium chloride) (PDMA) (Figure I - 53). The AEM presented a conductivity between 15 and 25 mS/cm at 80 °C, and a water uptake between 80 and 200 wt.%. The authors conclude that the semi-IPN architecture reduces the swelling and improves the chemical and mechanical resistance of the polyelectrolyte.

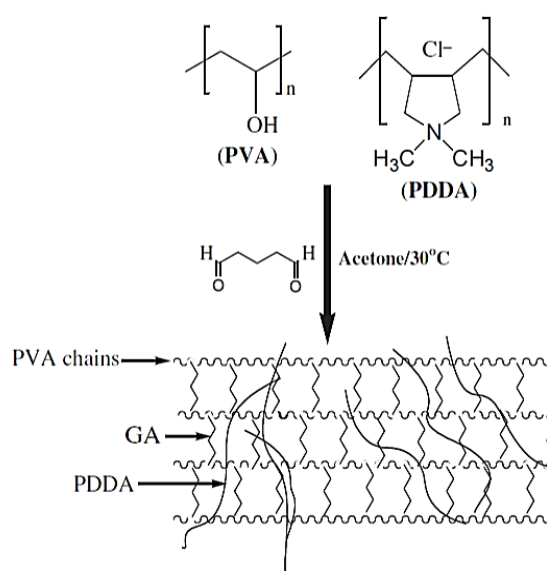


Figure I - 53: PVA/PDPA semi-IPN

PVA network has been also used as partner network of quaternized hydroxyethylcellulose ethoxylate (QHECE) (Figure I - 54).¹⁵¹

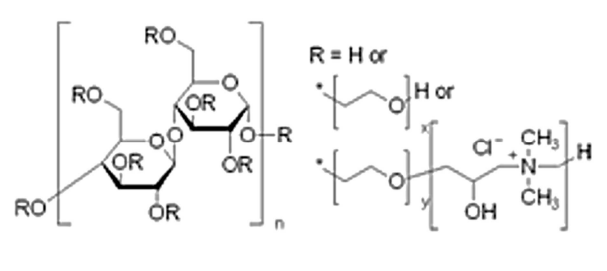


Figure I - 54: Quaternized hydroxyethylcellulose ethoxylate (QHECE)

The chemical stability was tracked by immersing the semi-IPNs in 6M KOH solution at 60°C and no decrease in conductivity was observed.

Recently Lin et al.¹⁵⁰ synthesized a semi-IPN of vinylbenzylchloride-divinylbenzene and cardopolyetherketone quaternized with trimethylamine. An IEC between 1.43 and 1.72, a conductivity between 19 and 22 mS/cm and a water uptake between 15 and 165 wt.% was reported. Nevertheless, the synthesized semi-IPNs were not stable in 2 M KOH at room temperature.

5.3. Conclusions

Use of a semi-IPN architecture for AEM is a very recent topic of research, and the development of semi-IPNs for AEM are still in the laboratory stage. Indeed, it was not possible to find in the literature IPNs for use as anion exchange membranes. AEMs reviewed by Merle et al.⁵⁴ and presented as IPNs do not have a true IPN architecture, but are instead polymer mixtures, co-polymers or semi-IPNs presented previously. Similarly, AEM reviewed by Couture et al.⁶¹ and Wang et al.⁶² only present membranes of semi-IPN architecture. On the contrary, a few proton-conducting membranes of IPN architecture are found in the literature for use in fuel cells.¹⁵⁴ Particularly, IPNs of hydrogenated and fluorinated polymers are developed in our laboratory.^{139,155}

6. Commercial Membranes

In parallel with these fundamental studies, anionic membranes have been or are currently sold. Their commercialization suggests that they show the required stability of the polymer backbone and of the fixed charges. Table I - 8 summarizes some of the few commercially available AEM.

Table I - 8: Properties and nature of commercial anion exchange membranes^{54,156}

Membrane and manufacturer	Chemical nature	IEC (meq/g)	Ionic conductivity (mS/cm)	Comment:	Ref.
Neosepta AMX Tokuyama Corp. and ASTOM Corp. Japan	PS/DVB backbone Quaternary ammonium cation	1 - 2	6	Attacked by KOH and ammonia Semi-RIP PS/DVB + PVC	http://www.astom-corp.jp
AMI-7001 Membranes International Inc. USA	PS/DVB Quaternary ammonium cation	1.3	1 (in 0.5 M NaCl)	Stable at pH 1-10	http://www.membranesinternational.com/tech-ami.htm
FAA-3-PK-130 Fumatech GmbH, Germany	Not specified Polyketone reinforced membrane	1.4	8 (Cl ⁻ form in 0.5 M NaCl, 25 °C)	Stable at pH 1-14 (25 °C)	http://www.fumatech.com
AM(H), AMH5E-HD MEGA a.s., Czech Republic	Backbone not specified Quaternary ammonium cation	1.8	5	Stability not specified	http://www.mega.cz
Morgane Solvay S.A., Belgium	Fluorinated Quaternary ammonium cation	1 - 3	1 - 3	Production discontinued	http://www.solvay.com
MA-41 Shchekinoazot United Chemical Company, Russia	Heterogeneous: polyethylene + anion exchange polymer not specified	--	3	Stability not specified	http://n-azot.ru
Shanghai Nanda Chemical Plant, China	Not specified	1.8 - 2.0	3	Stability not specified	http://www.nanda-chem.com
Tianwei Membrane Co. Ltd., China	Not specified	1.2 - 1.4	3	Stability not specified	http://en.sdtianwei.com

Some AEMs, as Solvay Morgane[®] membrane are no longer available. The Morgane[®] membrane was developed for use in alkaline methanol fuel cells. It could be used up to 60 °C. Its methanol diffusion coefficient was between 2 and 3 times lower than for Nafion[®]. However, this membrane was not stable in strong alkaline media since it discolors in 1 M NaOH.^{157,158}

The most interesting membrane for use in alkaline electrolyte seems to be the FAA-3-PK-130 produced by Fumatech which is claimed to resist a pH 14 in ambient temperature. The apparent lack of commercial membranes confirms the interest of continuing fundamental research in this area.

In 1996, Sata et al.¹⁵⁹ studied the stability of commercially available anion exchange membranes in concentrated (4 – 6 M) sodium hydroxide at high temperature (up to 75 °C). The different membranes were obtained from Tokuyama Corporation, Asahi Chemical Industries Co., Pall-RAI, ... and were reinforced (with poly(vinyl chloride) generally). The authors show that the membranes deteriorated by three processes: deterioration of backing fabric, decomposition of the polymer matrix to which anion exchange groups are bonded, and decomposition of anion exchange groups. At higher stability was obtained with benzyl trimethylammonium cationic groups than with N-methylpyridinium groups. This result is in agreement with the stability reported for each individual cation in the literature.

7. Anion Exchange Membranes for Metal-air Batteries

Very few publications, to our knowledge, report experimental results on the assembly of an air cathode protected by an AEM in a configuration comparable to that of an aqueous metal-air battery.

Tsuchida et al.^{160,161} demonstrate the assembly of an aqueous zinc-air cell, in which the air cathode was protected with a pressure assembled poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate) membrane (Figure I - 55).

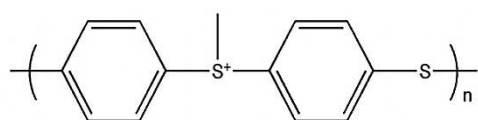


Figure I - 55: Structure of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate)

The polysulfonium was effective in preventing cation permeation and that the cell capacity was increased (0.6 V, 124.8 h, 86.4 mAh/g) compared to the use of a polypropylene separator (1.32 V, 70.5 h, 14.5 mAh/g). However, the capacity was not increased at KOH concentrations higher than 1 M, and no information is given on the chemical stability of the cation, which we can expect to be very low.

More recently, an air electrode was modified with a hydrogenated AEM with quaternary ammonium groups (1.4 meq./g, thickness 27 µm, AEM non-specified, supplied by Tokuyama Corp.) by hot-pressing over the home-made air electrode¹⁶². The modified electrode was tested in half-cell, in a configuration equivalent to that used in rechargeable metal-air

batteries, with aqueous KOH electrolyte from 0.5 to 8 M. It showed excellent activity and durability. The AEM-type air electrode was less affected by CO₂ (even in an accelerated experiment with pure CO₂) compared to conventional air electrodes without an AEM. As expected, the AEM prevented the entry of CO₂ into the alkaline electrolyte and inhibited the permeation of cations from the alkaline electrolyte to the air electrode, while suppressing the precipitation of carbonate in the pores of the air electrode. No other information of the capacity of the intended battery is detailed.

8. Conclusions

In view of this bibliographic chapter, the protection of the air electrode by a polymer membrane, as proposed in the LiO₂ project, seems certainly possible. The present problem is the choice of the membrane that will be permeable to hydroxyl ions but impermeable to lithium ions, and at the same time stable for the longest possible time in contact with concentrated lithium hydroxide, an electrolyte that to our knowledge has not been reported in stability studies.

Among the different cationic groups studied, quaternary ammonium is the most stable in alkaline electrolyte, and is thus the preferred cation in AEM. The chemical resistance of an ammonium ion is strongly dependent on its structure. A particular molecule, 1,4-diazabicyclo-[2.2.2]-octane (DABCO), is reported to produce ammonium ion highly stable at high pH. This compound, a diamine, can react onto a polymer chain and form a quaternary ammonium ion. Being bifunctional, it can also be a crosslink point in a polymer network. Indeed, the crosslinking of the polyelectrolyte is an interesting approach to improve its physicochemical properties, i.e. prevent polyelectrolyte dissolution, reduce the water uptake and increase the mechanical resistance. Poly(epichlorohydrin) (PECH) can be modified by DABCO and this modification has been studied in the last decade. The obtained crosslinked polyelectrolyte shows interesting characteristics for use as an AEM in fuel cell application.

To improve the properties of an AEM polyelectrolyte, this can be associated with a second polymer, to obtain a combination of their properties. When one of these polymers is crosslinked, a semi-interpenetrating polymer network (semi-IPN) is obtained. AEMs with semi-IPN architecture are only very recently reported in the literature, and, to our knowledge, consist of two hydrogenated polymers. However, properties of an AEM consisting of two polymers can be further improved if both are crosslinked. In this last case, an interpenetrating

polymer network (IPN) architecture is obtained. The synthesis of anion exchange membrane based on IPN has not been reported in the literature.

In this work we propose the use of IPN architecture for the synthesis of AEM. The polyelectrolyte network will be poly(epichlorohydrin) cross-linked with DABCO. This last will be associated to, on the one hand, a hydrogenated network and, on another hand, a fluorinated network. These original materials will be used to modify a commercial air-electrode which will be tested in working conditions of the air cathode of the lithium-air battery.

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Chapter II:

Synthesis and Characterization of PECH Networks

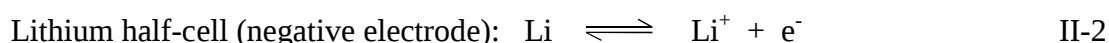
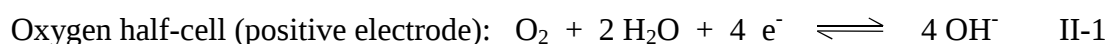
To ensure a better electrochemical stability of the air electrode in alkaline electrolyte and under atmospheric air (close to standard conditions for temperature and pressure), it was chosen to protect the air electrode with a polymer membrane set on the electrolyte side. Poly(epichlorohydrin) (PECH) quaternized by 1,4-diazabicyclo[2.2.2]octane (DABCO) will be used as polyelectrolyte network because of its stability in alkali, as described in the previous chapter.

In a first time, to demonstrate the concept of the protection of the air electrode under the conditions imposed by the aqueous lithium air battery, we will identify and characterize a commercial air electrode. In a second time, the PECH networks will be developed by different synthetic routes and will be characterized. We will focus particularly on the effect of the proportion of DABCO introduced during synthesis, resulting more or less important charge and crosslinking densities. In a third time, we will discuss the assembly of these membranes on the air electrode. A particular attention will be given to the interface between the electrode and the membrane to obtain the membrane electrode assembly (MEA) with a polarization as close as possible to that of the bare electrode, so that it does not have an impact in the battery performance. Once the best method of assembly is identified, the effects of the membrane thickness and of the DABCO amount on the air electrode stability will be studied. The stability tests will be performed by cycling the newly developed MEA, to verify the efficiency of the electrode protection by the polymer membrane.

1. Unmodified Air Electrode

First we studied the electrochemical properties of the commercial air electrodes and we estimated their lifetime under the lithium-air battery conditions.

As previously mentioned (Chapter I § 3), the aqueous lithium-air battery can be divided for practical purposes in the oxygen half-cell and the lithium half-cell, as shown in Figure II - 1. The electrode reactions correspond to the following equations:



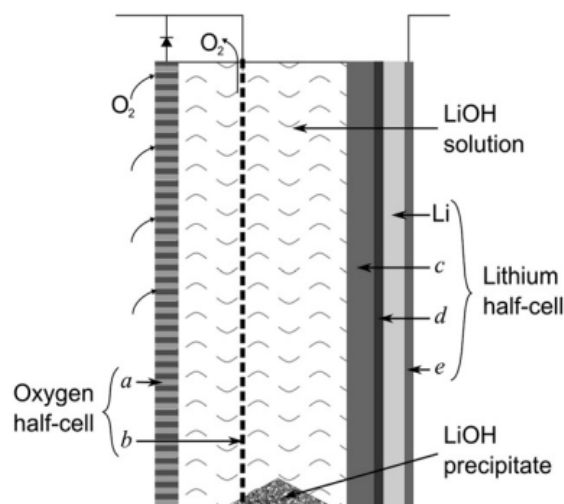


Figure II - 1: Aqueous lithium-air battery¹. *a*: O₂ reduction electrode with anion-exchange membrane. *b*: O₂ evolution electrode. *c*: LiSICON membrane, *d*: protective LiPON film, *e*: stainless steel current collector, Li film: electrochemically deposited after cell assembling.

In the lithium half-cell, a ceramic membrane protects the metallic lithium from the aqueous electrolyte. In the oxygen half-cell, the anion exchange membrane will separate the electrode from the electrolyte. This electrolyte is a 5 mol/L LiOH aqueous solution (LiOH solubility at 25 °C is 5.2 mol/L)² in order to assure an excess of Li⁺ during the battery charge. Rest / discharge cycling was chosen because of another technological limitation for the metal-air batteries to be rechargeable. Typical air-electrodes are designed to work as oxygen reduction electrodes only. Indeed, the catalyst and carbon materials would corrode at high potential during charging process, and oxygen evolution could cause mechanical breakdown of the fragile porous structure. This problem was solved by EDF with the development of a bi-electrode consisting of an air electrode (used during the discharge for oxygen reduction) coupled with an oxygen gas evolution electrode (used during charge), without being a penalty for the energy density of the battery.^{3,4} During the battery charge, the air-electrode is at rest. At present, performance of the battery is limited by the lithium half-cell in which the maximum current density is between 2 and 6 mA/cm².⁵ We have thus decided to characterize the stability of the air electrode by cycling 10 h at rest followed by 10 h of discharge at -10 mA/cm².

1.1. Characteristics of Air-Electrode

Two commercial air electrodes produced by Electric Fuel[®] Ltd., denoted E-4 and E-5 have been used. As schematized in Figure II - 2, both electrodes are composed of an active layer of porous carbon black that contains the catalyst, a metallic nickel mesh that serves as current collector and a blocking layer of laminated porous poly(tetrafluoroethylene) (PTFE) film.

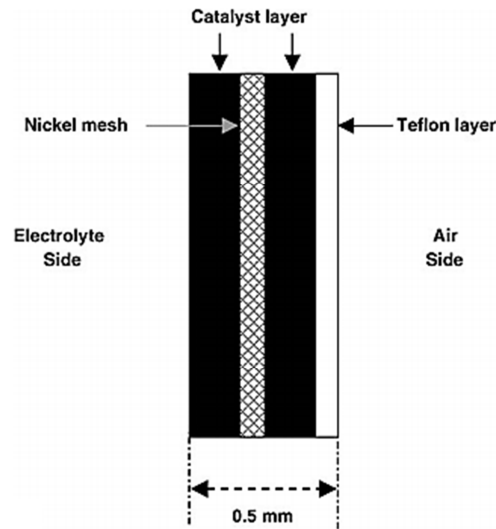


Figure II - 2: Cross-section of a commercial air electrode⁶

The E-4 electrode contains manganese based catalyzed carbon. It was designed for low and high power applications, in metal-air batteries and alkaline fuel cells. It is currently used in commercial alkaline primary batteries.

The E-5 electrode contains cobalt based catalyzed carbon and was designed for oxygen reduction in high power applications. It is currently used in prototype applications. Its porous structure has been observed by scanning electron microscopy (Figure II - 3).

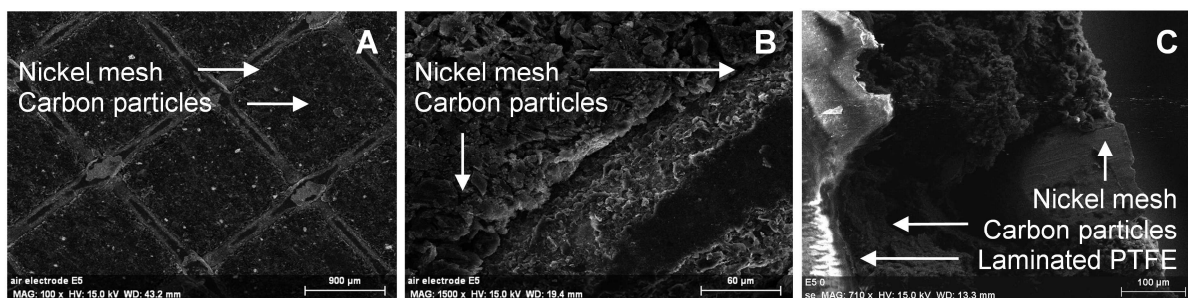


Figure II - 3: SEM image of E-5 air electrode (Electric Fuel) on electrolyte side (A and B) and cross-section (C)

SEM micrographs show carbon black particles blended with PTFE binder in a 400 μm thick active layer. The nickel mesh (current collector), composed of 150 μm thick filaments is visible on the catalyst side (Figure II - 3 A). The EDX analysis is shown in Figure II - 4.

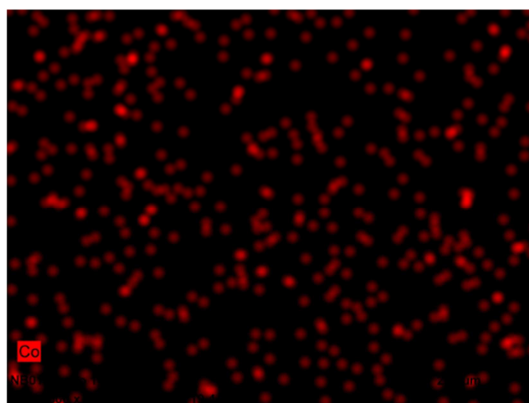


Figure II - 4: Distribution of cobalt on E-5 air electrode surface analyzed by EDX. Magnification: 500x, HV: 15 kV

The EDX cartography shows that the cobalt, the catalyst used in the E-5 electrode, is uniformly distributes in the the air electrode.

1.2. Experimental Conditions

All the electrochemical characterizations will refer to the oxygen reduction reaction (ORR) at the air electrode which was characterized in homemade conventional three electrodes glass half-cell (Figure II - 5).

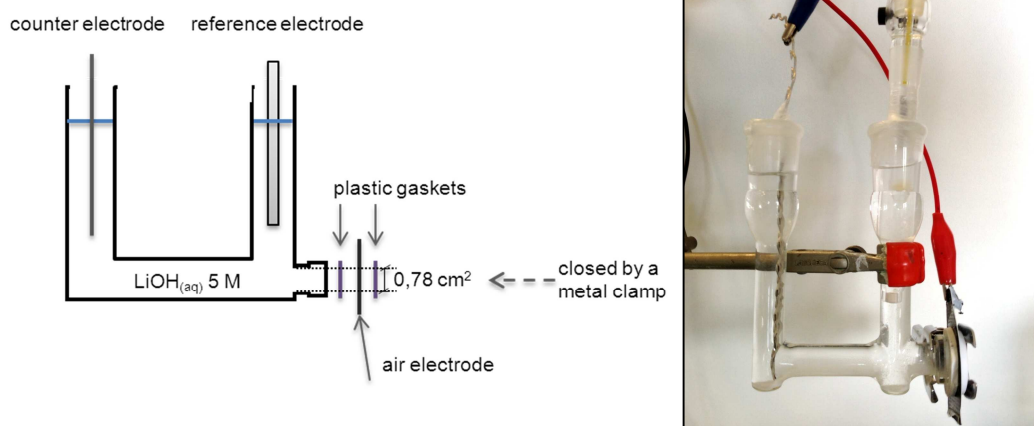


Figure II - 5: Scheme and photograph of homemade test half-cell for electrochemical characterization of air electrodes.

The working electrode was consisted of an air electrode with circular geometric area of 0.78 cm^2 . An Hg/HgO/1 M KOH electrode was used as reference and a platinized titanium grid as counter electrode. The air electrode positioned between two plastic gaskets was tightly fastened to the half-cell with a metallic clamp.

A 5 mol/L LiOH aqueous solution was used as alkaline electrolyte. All measurements were made at ambient temperature and pressure with untreated air, unless otherwise stated. The air-electrodes were equilibrated in the electrolyte solution for at least 1 h before starting the measurements to obtain the potential versus current (polarization) or potential versus time (stability) curves. Measurements were made with a multi-channel potentiostat-galvanostat (VMP Biologic[®]).

1.3. Electrochemical characterizations

1.3.1. Cyclic Voltammetry

The electrochemical stability domain of air electrode was determined by cyclic voltammetry.

The voltamperogram was recorded on the E-5 air electrode in 5 mol/L LiOH at 2.5 mV/s.

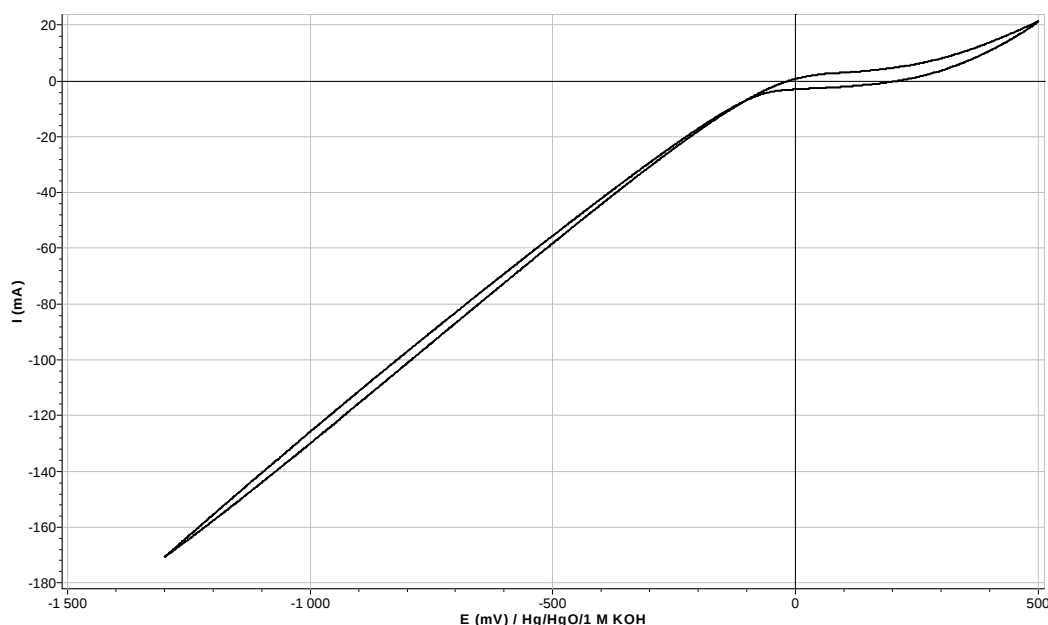


Figure II - 6: Cyclic voltammogram of E-5 air electrode - Electrolyte: 5 mol/L LiOH. Room temperature and atmospheric pressure. Reference electrode: Hg/HgO/1 mol/L KOH. Counter electrode: platinized titanium grid

Neither oxidation nor reduction of the electrolyte was detected between 0.2 and -1.3 V/(Hg/HgO) (Figure II - 6). The O_2 reduction reaction (ORR) is observed from -40 mV/(Hg/HgO), witnessing the cobalt based catalyst activity.

1.3.2. Polarization Curves

For the polarization curves, the current density applied was increased step-wise from -1 to -30 mA/cm². Each current density was maintained until a stable value of potential is obtained, usually after 5 min (Figure II - 7 A). The electrode potential is measured at the end of the stabilization period. Figure II - 7 B shows the potential vs. current polarization curves for the E-4 and E-5 electrodes.

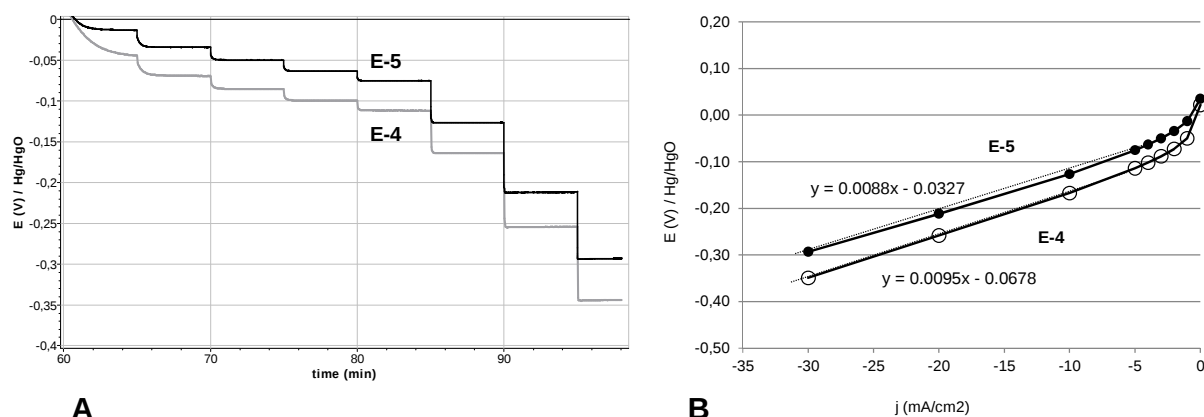


Figure II - 7: Potential vs. time (A) and potential vs. current density (B) polarization curves of E-4 (○) and E-5 (●) air electrodes and linear regressions in the region controlled by ohmic polarization in 5 mol/L LiOH

In Figure II - 7 A, the E-4 potential is about -50 mV/(Hg/HgO) at -1 mA/cm² current density and attains a value of -160 mV at -10 mA/cm² and -350 mV at -30 mA/cm². The E-5 potential is about -30 mV/(Hg/HgO) at -1 mA/cm² current density and attains -130 mV at -10 mA/cm² and -290 mV at -30 mA/cm². Thus, polarization of the E-5 electrode is lower than for the E-4 one.

As discussed in chapter I (cf. § 3.1), the polarization curve can be divided in three areas (Figure II - 7 B). The linear part corresponds to the ohmic polarization (η_{ohm}) which represents the addition of all ohmic losses, including electronic impedances through electrodes, contacts, current collectors and ion diffusion impedance through the electrolyte. These losses follow Ohm's law $\eta_{ohm} = iR$. Thus, the total cell resistance can be calculated from the linear region of the polarization curve. Cell resistances with E-5 and E-4 air electrodes are 9 and 10 $\Omega \cdot \text{cm}^2$ respectively. Consequently, we decided to use the E-5 electrode to obtain the best electrochemical performance at the current densities required in this project. The polarization curve obtained for the non-modified E-5 will be used as reference curve for the characterization of the modified electrodes.

1.3.3. Electrode Stability

As previously justified the electrode was cycled for 10h at rest followed by 10h of discharge at -10 mA/cm² to evaluate its stability. The 10 h at open circuit voltage (OCV) represent the time the battery is in charge. For all stability tests, we consider that the electrode is

irreversibly damaged after reaching a potential of $-400 \text{ mV}/(\text{Hg}/\text{HgO})$. This time is recorded as the life-time of the electrode. The stability of the air electrode is thus equal to $50 \text{ h} (\pm 20 \text{ h})$.

To confirm the role of carbon dioxide in the loss of performance of the air electrode in aqueous alkaline electrolyte (cf. Chapter I - § 3.4.3), the E-5 stability was evaluated, on the one hand, with ambient air, and, on the other hand, with CO_2 free air for comparison (Figure II - 8). To obtain the CO_2 -free air, a low-pressure air flow was bubbled through a 6.4 mol/L KOH solution,² and then through a saturated KCl solution to adjust its relative humidity to 84 % to match that measured in the laboratory. After feeding the half-cell, the air flow was bubbled through a saturated $\text{Ca}(\text{OH})_2$ solution. No CaCO_3 precipitate was observed in this solution confirming thus the absence of CO_2 .

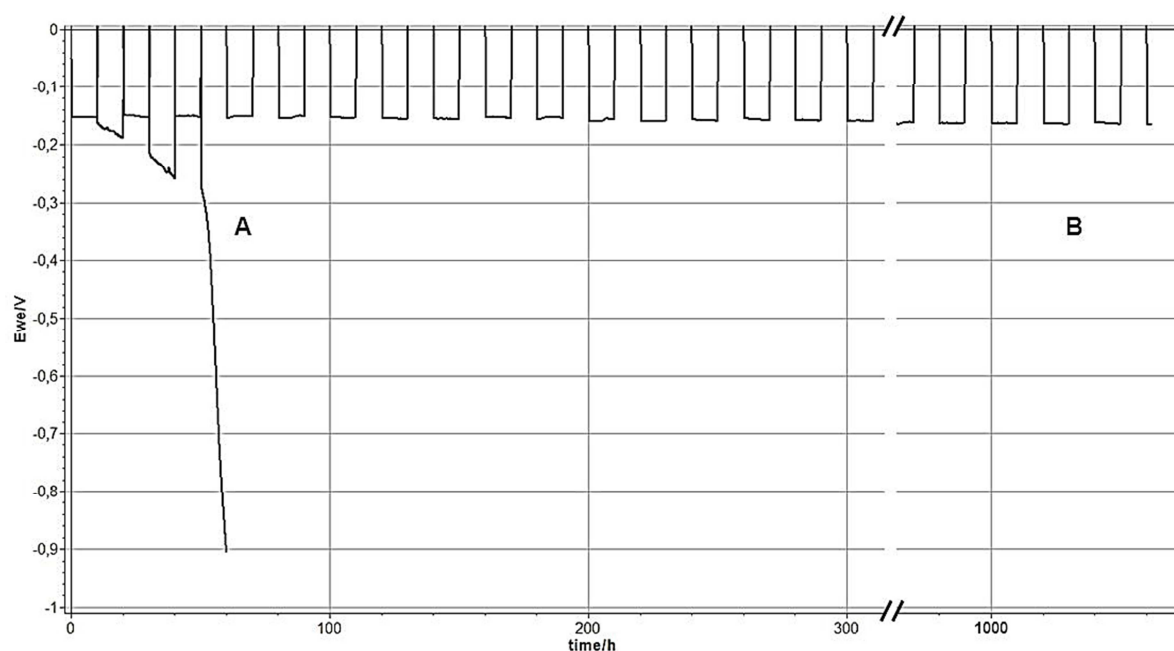


Figure II - 8: Potential-time curves of an E-5 bare electrode supplied with untreated (A) and treated (B) air. Cycle: $-10 \text{ mA}/\text{cm}^2$ for 10 h and OCV for 10 h. Electrolyte: 5 M LiOH . Room temperature and atmospheric pressure. Reference electrode: Hg/HgO .

When the half-cell is fed with untreated (ambient) air, the electrode polarization is $-130 \text{ mV}/(\text{Hg}/\text{HgO})$ at the beginning of the first cycle. Then it begins to increase and attains $-300 \text{ mV}/(\text{Hg}/\text{HgO})$ at the end of the third cycle. During the fourth discharge, the potential reaches $-400 \text{ mV}/(\text{Hg}/\text{HgO})$ and then drops abruptly. Under CO_2 -free air, the air electrode potential remains stable (between -130 and $-160 \text{ mV}/(\text{Hg}/\text{HgO})$) without significant polarization increase during cycling in 5 M LiOH for more than 1000 h (the experiment was stopped at that time). The comparison of results of both experiments clearly confirms that the loss of the

air electrode performance is essentially due to the presence of CO₂ in air, as described in the literature.^{7,8}

This initial study shows that the commercial air electrode cannot be used in the lithium–air cell fed with untreated air without the quick loss of its performance due to the precipitation of lithium carbonate. To protect the air electrode from the precipitation of lithium carbonate, a polymer membrane can be placed at the interface between the air electrode and the aqueous alkaline electrolyte. This membrane must be sufficiently selective, allowing the passage of hydroxyl ions while preventing the passage of lithium ions, as presented before (Chapter I, Figure I - 9). To block or limit the passage of Li⁺, the membrane must contain cationic groups that will repel the cations by electrostatic repulsion. At the same time, these cationic groups will conduct the hydroxyl ions produced by the electrochemical reaction in the air electrode.

The effects of the anionic exchange membrane and of the interface that is created with the electrode will be particularly studied thereafter.

2. Poly(epichlorohydrin) (PECH) Based Polyelectrolyte Network

Poly(epichlorohydrin) (PECH) substituted by 1,4-diazabicyclo[2.2.2]octane (DABCO) was chosen as polyelectrolyte because of its chemical stability in alkaline condition (Chapter 1 § 4.2.4). Indeed, in alkaline medium, as previously discussed, the degradation of polymers bearing quaternary ammonium groups generally occurs by the Hofmann mechanism: this reaction is reported as negligible in the case of DABCO modified PECH.⁹ Moreover, DABCO containing two tertiary amines, their reaction leads to the PECH cross-linking.¹⁰

2.1. PECH modification by 1,4-diazabicyclo[2.2.2]octane (DABCO)

PECH can be modified according to a nucleophilic substitution reaction (S_N2) between one tertiary amine and a secondary carbon α- to a chloride atom of PECH. This reaction, carried out at 80-95 °C, leads to quaternary ammonium groups in the polymer chain (Figure II - 9 A).

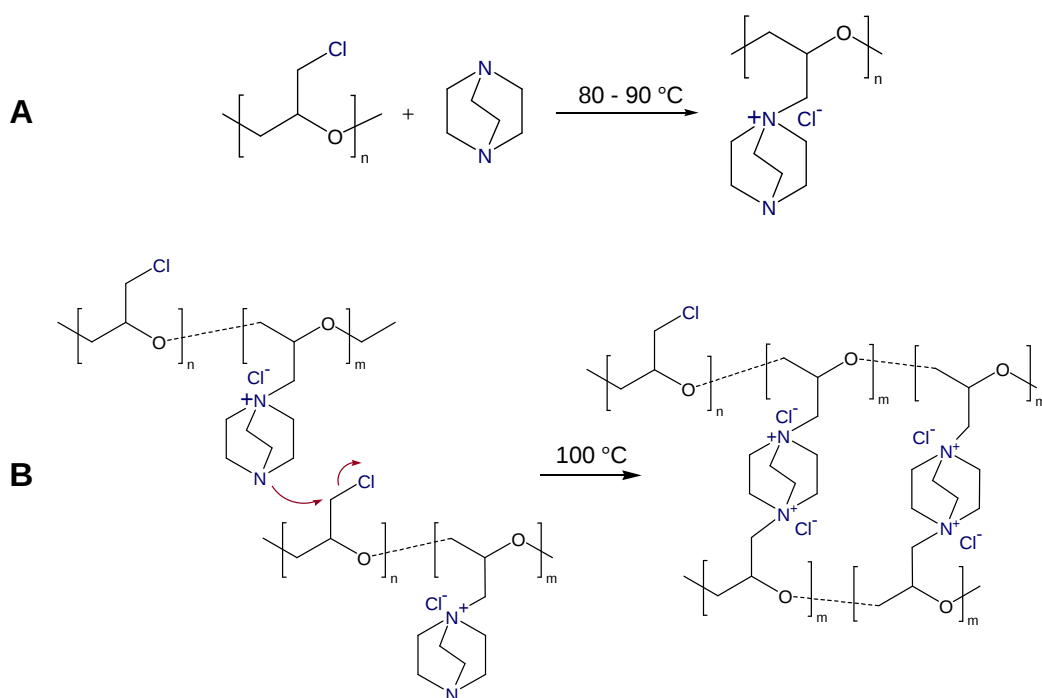


Figure II - 9: Reaction scheme of PECH and DABCO (A) and crosslinking of modified PECH (B)

The first amine group of DABCO is more reactive than the second one. In addition, the DABCO diffusion is limited once grafted into the PECH chain, and because of steric hindrance of the polymer chain.¹¹ In consequence, the network synthesis is obtained after two consecutive steps at different temperatures: DABCO grafting (quaternization) below 95 °C and the cross-linking reaction (network formation) over 95 °C (Figure II - 9 B).

In a first time, we tried to modify the PECH with DABCO just before the network synthesis in a *one-pot* process. However, the quaternization and the cross-linking of PECH under these conditions proved to require very long synthesis times (at least 8 h at 100 °C) after which the cross-linking was not necessarily complete. For this reason we choose to synthesize the PECH network directly from a PECH pre-modified with 10 mol % DABCO, available in 10 wt.% DMF solution (ERAS Labo, France). In this work, the materials obtained from this solution will be designated as PECH₁₀, where the subscript 10 refers to the DABCO proportion, 10 mol % / PECH repeat unit.

2.2. PECH Network Synthesis

Solution casting and reaction molding methods were used in this work for membrane synthesis. Indeed, solution casting is currently used for the fuel cell membranes synthesis.

However, this method cannot be applied when the reactions require an inert atmosphere or when it is preferable that solvent cannot evaporate during the synthesis. That is why the membrane synthesis by reaction molding has been also studied.

2.2.1. Solution Casting

The PECH network can be synthesized by casting of the commercial 10 mol % DABCO modified PECH solution in DMF according to a procedure previously described.¹⁰ Routinely, the PECH network was prepared by pouring an appropriated amount of the commercial solution in an open mold (Petri dish). It was then heated in a ventilated oven at 100 °C for 4 h. The synthesized material (noted PECH₁₀ network) is homogeneous, transparent and slightly yellow colored.

To confirm the correct crosslinking of the materials solid-liquid (Soxhlet) extraction of materials with DMF has been carried out by quantifying the amount of soluble material, which can be unreacted monomers or linear polymer (cf. Experimental part). Thus, a low soluble fraction confirms the correct cross-linking of the network precursors.

First, the extraction time needed has been determined by measuring the soluble fraction of the PECH₁₀ network at different extraction times with DMF (Figure II - 10).

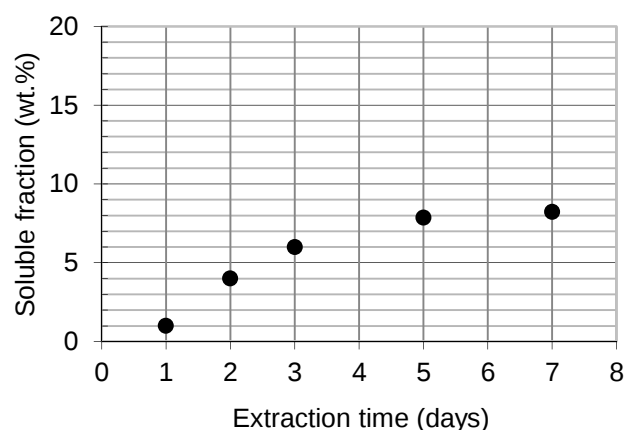


Figure II - 10: Soluble fraction vs. extraction time with DMF of a PECH₁₀ network synthesized from solution casting – Synthesis: 4h at 100°C.

The soluble fractions increased from 1 to 6 wt.% between 1 and 3 days of extraction. As the soluble fraction increases only marginally thereafter, the extraction time has been set at 3 days for all samples. This represents a good compromise between a complete extraction and adequate essay duration.

These measurements show that the commercial 10 mol % DABCO grafted PECH can be efficiently cross-linked by solvent casting. However, by this technique, volatile components such as light molar weight monomers cannot be used, and maintaining an inert atmosphere is complex.

2.2.2. Reaction Molding

The synthesis of the PECH₁₀ network has been also studied in closed mold. For that, the reaction solution was injected into a mold made from two glass plates clamped together and sealed with a Teflon[®] gasket (Figure II - 11). Then the mold was set in an oven and the suitable thermal program was applied.

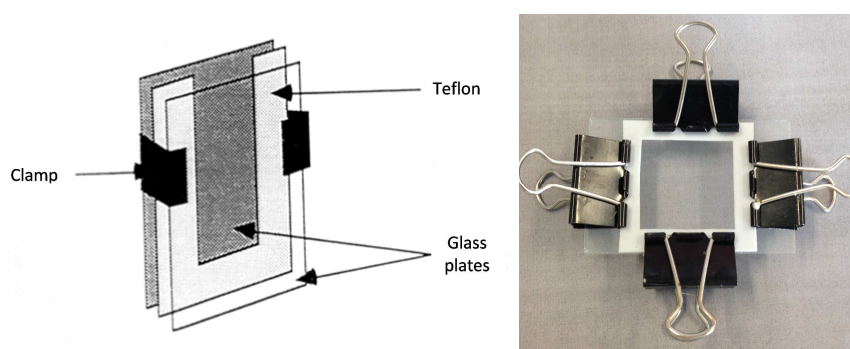


Figure II - 11: Scheme and photography of the mold for the reaction molding of polymer membranes

It is not possible to obtain a PECH₁₀ network by reaction molding from the commercial PECH solution at 10 wt. % in DMF. Indeed, even after 8 h at 100 °C, the solution remains liquid thus the gel point is not reached. In contrast, if the same PECH solution is left at room temperature for 1 month in a closed mold, a gel is obtained indicating an effect of reaction rate. Reactant concentration is an important factor that influences the reaction rate.¹¹ In a closed mold, the DABCO concentration is low (≈ 1 wt.%) and constant during synthesis because solvent does not evaporate, as it does in an open mold. We have calculated by the Carothers method for a solution at 10 wt.% PECH modified with 10 mol % DABCO that gel point is reached when 0.1 mol % of the DABCO second amine have reacted (50.1 % of total amines). This value is very low and it should be reached. However, in a dilute medium, the polymer should be in the form of statistics spheres with the DABCO mainly inside. Thus, when the amines react, in a first time microgels should be obtained. Indeed, Kumar et al. have observed on polymerization of phenol with formaldehyde that the gel point is preceded by the

formation of microgel particles, which are too small to be visible to the naked eye.^{12,13} Hence, no gel is observed even if enough functions have reacted to reach the theoretical gel point. However, in our case this point cannot be verified. Indeed, all analyses carried out by infrared spectroscopy to follow the reaction in real time were unsuccessful because no characteristic absorption band could be identified.

To obtain a PECH network in closed mold in an industrially acceptable time, the concentration of reactive functional groups should be increased. By increasing the concentration, we should increase the reaction rate and the material should be obtained.

PECH commercial solution in DMF was concentrated under vacuum at ambient temperature to around 18 wt.% prior to use. This is the highest concentration that can be obtained without causing a spontaneous gelification of the solution. This concentrated solution was poured inside a mold and heated at 100 °C for 4 h. A homogeneous, transparent, slightly yellow colored material was obtained, with a soluble fraction of 9 wt.% (DMF, 72 h), which proves the correct cross-linking of PECH. Under those experimental conditions, the PECH₁₀ network can thus be synthesized by reaction molding.

Properties of the membranes synthesized via solution casting and reaction molding were then characterized and compared.

2.3. Physicochemical Characterization of Different PECH₁₀ Networks

In order for the membrane to protect the air electrode, it must satisfy some contradictory features. For example, it must not show an important swelling in water or in an aqueous electrolyte to preserve a high selectivity towards lithium ions. But, for the same purpose, its ionic exchange capacity must be high to ensure a sufficient ionic conductivity and a transport number as close as possible to 1. Finally, it must be stable in concentrated lithium hydroxide, electrolyte in which it will be immersed during its operation. These different properties have been thus analyzed.

The PECH₁₀ network (synthesized by solution casting) was dried after synthesis under vacuum (< 5 mmHg) at 70 °C until constant weight.

All the networks were tested in their hydroxyl form. For counterion exchange (from Cl⁻ to OH⁻), the samples were immersed in a 1 M KOH solution for 24 h, rinsed with water until neutral pH and then equilibrated in water for 24 h.

2.3.1. Water Uptake

The water uptake (WU) of PECH₁₀ network synthesized by solution casting was determined by swelling of the material in water up to equilibrium (i.e. at least 24 h). The WU value is calculated from the difference between the dry weight (w_d) and the swollen weight (w_s) of the sample according to the following equation:

$$WU \text{ (wt. \%)} = 100 \times (w_s - w_d) / w_d \quad \text{II-3}$$

The PECH₁₀ network synthesized by solution casting has a mean water uptake of 110 wt.%. The PECH₁₀ network synthesized by reaction molding is swollen with DMF after synthesis. The water uptake was thus measured by an adapted method. After synthesis, the membrane was unmolded and immediately immersed in a 1 M KOH_(aq) solution, in which the synthesis solvent and Cl⁻ ions were exchanged with the alkaline solution and OH⁻ ions, respectively. Then the membrane was rinsed with water until neutral pH and stored in water to equilibrium, weighted (w_s) and finally dried and weighted (w_d). The WU of the PECH₁₀ network synthesized by reaction molding is 1200 wt.%; i.e. 10 times higher than that of PECH₁₀ network synthesized by solution casting.

To explain this difference, the effect of drying has to be taken into account. As the solvent evaporates during solution casting, the PECH₁₀ network synthesized by this method is dry at the end of the synthesis. The network synthesized by reaction molding previously described was not dried after synthesis. Instead, it was immersed in 1 M KOH for counterion exchange, and then rinsed and equilibrated in water to measure its swelling. When this PECH₁₀ network is dried before WU measurements, its water uptake is 200 wt.% (5 times lower).

The difference in water uptake can be explained by, an irreversible collapse of some domains of the polyelectrolyte during drying. Another possible explanation is the post-crosslinking of the network during drying at 70 °C.

To evaluate the charge density and the crosslinking density, the ionic exchange capacity and the mechanical properties of the material were evaluated. The charge density can be estimated from the ion exchange capacity (IEC) of the material whereas the cross-linking density affects the mechanical relaxation temperature (T_α) of the material. These different parameters have been thus measured and compared.

2.3.2. Ionic Exchange Capacity (IEC)

Ionic exchange capacity allows determining the number of functional ionic sites in a gram of dry material, expressed as meq./g (cf. Experimental part).

The IEC of a PECH₁₀ network synthesized by solution casting is 1.6 meq./g. However, when this network was synthesized by reaction molding an IEC of 0.8 meq./g was measured. The charge density is lower in the PECH₁₀ network synthesized by reaction molding than that by solution casting. We must note that both results are below the theoretic value 1.9 meq./g, calculated assuming all nitrogen atoms have reacted. In the case of the reaction molded membrane, the measured IEC of 0.8 meq./g is even lower than the theoretical IEC of linear PECH₁₀ (1.0 meq./g). This observation is not in agreement with the fact that an insoluble material is obtained. An underestimation in the IEC has already been observed and could also be associated with an incomplete exchange of the Cl⁻ ions in the network. Stoica et al.¹⁴ report an IEC value of 1.3 meq./g for a comparable PECH network (cf. Chapter I § 4.2.4). The authors found that the exchange reaction with 1 M KOH was incomplete even after 7 days, with 0.6 meq./g of Cl⁻ ions still present in the material. Therefore, the incomplete exchange of Cl⁻ for OH⁻ ions can explain the lower measured IEC, as our experimental procedure relies on the titration of OH⁻ ions in the material.

However, the IEC values suggest that the reaction between PECH and DABCO is more exhaustive by solution casting than in reaction molding. If that was the case, the crosslinking density should be higher, which was verified by DMA measurements.

2.3.3. Thermomechanical Analysis

To determine if there is a difference of cross-linking density, the thermomechanical properties (cf. Experimental part) of solution casted and reaction molded PECH₁₀ networks were compared. Their storage modulus (E') and $\tan\delta$ were reported as a function of temperature in Figure II - 12. Indeed, the more the network is crosslinked, the more the mechanical relaxation ($\tan\delta$) peak is shifted to higher temperatures and the more the rubbery plateau modulus is high.¹⁵

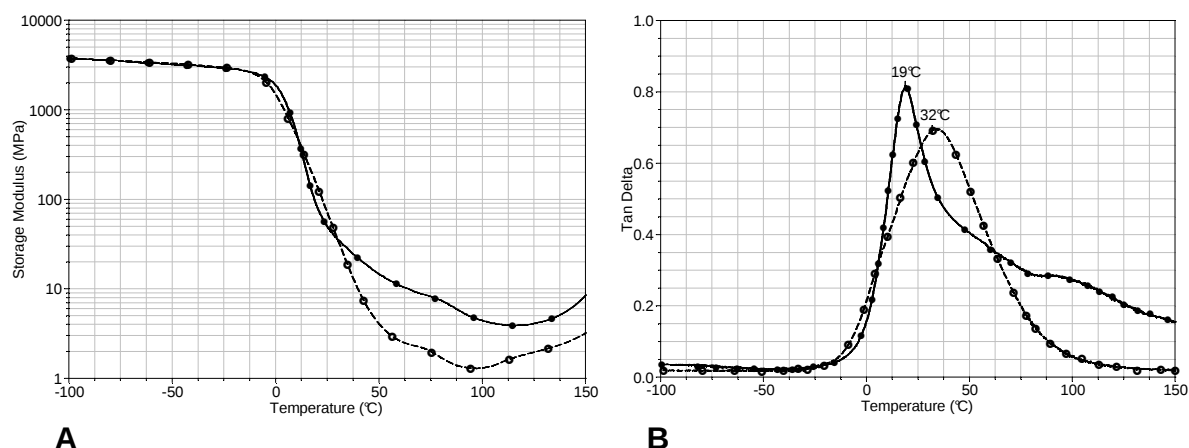


Figure II - 12: (A) Storage modulus E' and (B) $\tan\delta$ versus temperature of PECH₁₀ networks synthesized by solution casting (○) and reaction molding (●)

The storage modulus at the rubbery plateau (above 50 °C) is about twice lower when the membrane is synthesized by solution casting (Figure II - 12 A). However a shift in the $\tan\delta$ peak from 19 to 32 °C is observed for this sample. These two observations are contradictory but one have to take into account the shape of the $\tan\delta$ peak. The peak of PECH₁₀ by solution casting is Gaussian-like, which indicates a homogeneous crosslinking density. Contrarily, that of the reaction molded network is not symmetric. Even if a main peak is observed at 19 °C, the mechanical relaxation continues up to 150 °C. The reactive molded network has an inhomogeneous cross-linking density, which is also evidenced by a weak $\tan\delta$ peak at 90 °C. This is consistent with the assumption of formation of microgel particles at the first stage of the network synthesis. The inhomogeneity of the crosslinking for the reaction molded network can also explain its high water uptake. Actually, the loosely crosslinked domains should absorb more water.

It is important to note the slight increase in storage modulus observed for the two networks above 100 °C. This corresponds to a post-crosslinking of the PECH₁₀ networks. This was confirmed by a second scan in DMA, in which a higher modulus was obtained together with a wider $\tan\delta$ peak.

In conclusion, the solution casted membrane appears to have a higher crosslink density, at the same time and the crosslinking is more homogeneous. In contrast, the ionic charge cannot be directly compared by IEC measurements because of the underestimation of this value probably due to an incomplete counterion exchange.

2.3.4. Ionic Conductivity

Measurements of ionic conductivity were made at ambient temperature on the fully swollen materials. After synthesis each membrane was exchanged OH⁻ form and stored in water at ambient temperature. A sample of network with thickness t and surface S was placed between two stainless steel electrodes connected to an electrochemical impedance spectroscopy apparatus in order to measure the sample resistance (R). Conductivity (σ) is calculated from the following equation:

$$\sigma = t / (S \cdot R) \quad \text{II-4}$$

The intrinsic conductivity is 1.0 ± 0.1 mS/cm for the PECH₁₀ network synthesized by solution casting, whereas that of the PECH₁₀ network synthesized by reaction molding has a conductivity of 0.4 ± 0.1 mS/cm. This last network is 2 times less ionic conductor than the PECH₁₀ network synthesized by solution casting. This difference is in agreement with its IEC value which is 2 times lower. In addition, it swells than 10 more times in water. This excessive water uptake could explain the conductivity difference because it can lead to a dilution of the ionic sites and thus to a decrease in conductivity¹⁶. Indeed, if the PECH₁₀ network synthesized by reaction molding is dried after synthesis and then swollen with water, the water uptake is reduced to 200 wt.% and the conductivity increases to 1.7 ± 0.3 mS/cm. However, we cannot exclude the effect of a post-crosslinking during drying of the membrane, and a difference in the crosslinking density of the two membranes.

2.3.5. Transport Number

The anion transport number (t^-) (cf. Experimental part) informs about the ionic selectivity of the sample.

The PECH₁₀ network synthesized by solution casting has a hydroxide transport number of 0.92 which is in agreement with the transport number values generally reported for similar PECH-based network¹⁰. When the PECH₁₀ network is synthesized by reaction molding (not dried after synthesis), the hydroxide transport number is 0.78. The difference between the selectivity of the two networks can be also in agreement with the higher charge density of the solution casted material (IEC value of 1.6 vs. 0.8 meq./g for the reaction molded network). The difference can be also explained by the different water uptake of the materials: 110 and 1200 % WU for the solution casted and the reaction molded networks respectively. Due to the higher water uptake of the reaction molded network, the grafted positive charges are more

diluted than they are in the casted material. A higher distance between the grafted quaternary ammonium should make the membrane less selective by allowing the passage of cations together with anions. However, both reaction molded membranes, dried (WU = 200 %) and not dried (WU = 1200 %) after synthesis have a similar $\bar{t}$ (0.80 and 0.78, respectively). Therefore the different WU cannot be the only reason for the lower selectivity. We can also propose that the lower $\bar{t}$ is caused by the inhomogeneous crosslinking: the weakly charged domains will have a low selectivity and the total selectivity of the membrane could be reduced.

In conclusion, the S_N2 reaction is more effective in open mold than in closed mold due to the increase of reactive function concentration during reaction. The further completion of the reaction should lead to a higher number of ionic sites, and possibly to a higher crosslinking density. Indeed, a PECH₁₀ network synthesized by solution casting shows a swelling of 110 wt.%, while the same network synthesized by reaction molding, has a swelling of 200 wt.% if dried after synthesis and of 1200 wt.% when non-dried after synthesis. The IEC values indicate that the casted membrane has a higher number of ionic sites. However, this measurement appears to underestimate the number of anionic sites in the material and no clear conclusions can be made.

DMA measurements show that the solution casted membrane has a higher crosslinking density, and that the crosslinking density is homogeneous. Inversely, the reaction molded network, with a lower crosslinking density, presents an inhomogeneous crosslinking. This is revealed by a wide mechanical transition from 0 °C to 100 °C, a main $\tan\delta$ peak at 19 °C and a second at 90 °C. WU difference could also be explained by the difference in crosslinking homogeneity. It is also important to note a post-crosslinking of both networks beginning at 100 °C, revealed by an increase in E' .

Both networks have an ionic conductivity around 1 mS/cm. In the case of the reaction molded network, the conductivity is higher when the membrane is dried after synthesis. This could be due to the difference in WU between the dried and the non-dried network. Also, $\bar{t}$ is higher for the casted membrane, possibly due to the lower WU. Both differences can be explained by the different crosslinking. The more homogeneous crosslinking of the solution casted network can explain its higher conductivity and higher selectivity.

The properties of both networks are appropriate for our application; nevertheless, the best characteristics are obtained when the membrane is casted. Thus, the optimization of the reaction molded membrane has been carried out to improve its properties.

3. DABCO Concentration Effect

The effect of the DABCO content in the network synthesized by reaction molding was studied. The DABCO content in the PECH network is responsible of antagonist features. Indeed, the cationic sites formed in the PECH - DABCO reaction are responsible for ionic conduction: the higher the DABCO concentration, the higher ionic conduction and the higher water swelling. However, DABCO is also the crosslinker of the PECH network: the higher the crosslink density, the lower the water swelling. Therefore the DABCO content can significantly affect the properties of the resulting properties of the material that has to be experimentally assessed.

In consequence, PECH networks with different DABCO concentrations have been synthesized by reaction molding. These networks will be designated as PECH_x, where the subscript X refers to the DABCO proportion in mol % per PECH repeat unit.

For the network synthesis, a suitable DABCO proportion has been dissolved in the concentrated 18 wt.% PECH solution in DMF to attain 15, 20, 30, 40 and 50 mol % with respect to chloromethyl function. The reaction molding was carried out at 100 °C for 4 h. After synthesis, the membranes were unmolded and immediately immersed in a 1 M KOH_(aq) solution, for Cl⁻ exchange with OH⁻. Then the membranes were rinsed with water until neutral pH and finally dried and weighted. Soluble fractions contained in these networks were quantified (Figure II - 13).

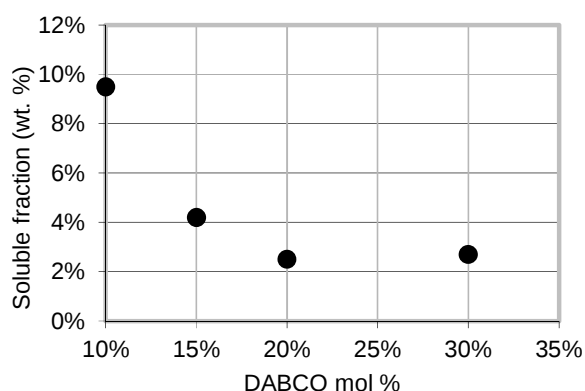


Figure II - 13: Soluble fraction of PECH networks with different DABCO content synthesized by reaction molding. Soxhlet extraction with DMF for 72 h.

The soluble fraction decreases when the DABCO content increases. The increase in crosslinker concentration reduces the probability of having free linear PECH in the material, thus decreasing the soluble fraction. This decrease also confirms that additional DABCO has

reacted with PECH. Indeed, if this was not the case for the PECH₃₀ for example, all added DABCO would have been extracted, and a soluble fraction of 18 wt.%, corresponding to the weight proportion added in the reactive medium, would have been obtained (corresponding to 20 mol % DABCO). Additionally, ¹H and ¹³C NMR analysis of the extracted material did not revealed the presence of unreacted DABCO. Consequently, we can conclude that added DABCO reacts with the PECH.

The DABCO addition must lead to a higher cross-linking density of the PECH network, which will be verified by different analyses.

3.1. Cross-linking density

First, to evaluate the crosslinking density of the PECH networks, their thermomechanical properties were measured (Figure II - 14).

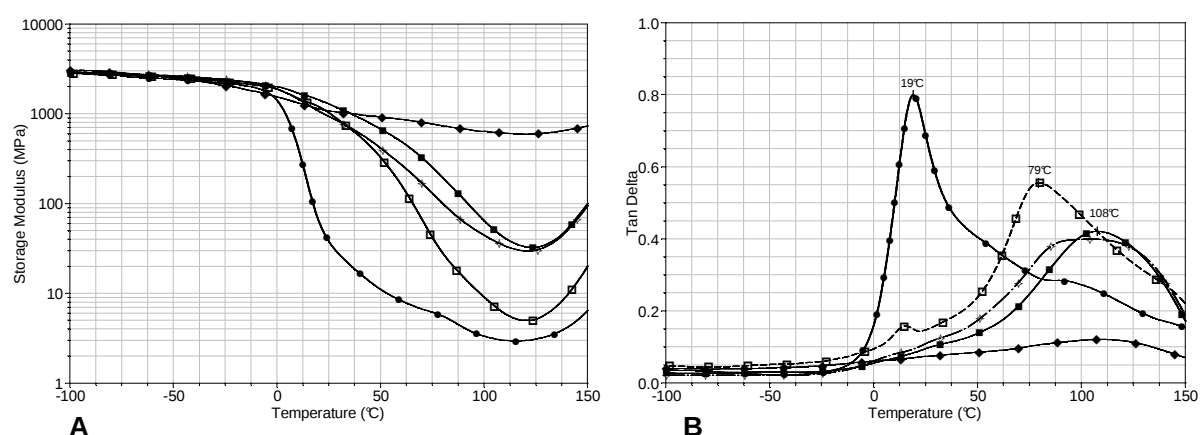


Figure II - 14: (A) Storage modulus E' and (B) $\tan \delta$ versus temperature of PECH₁₀ (●), PECH₁₅ (□), PECH₂₀ (◇), PECH₃₀ (■) and PECH₅₀ (◆) networks synthesized by reaction molding

The storage modulus at the rubbery plateau (at around 120 °C) increases regularly with the increase in DABCO content in the network. The PECH₁₀ network storage modulus is about 3 MPa while that of PECH₅₀ it is of 500 MPa. This behavior is characteristic of an increase in the crosslinking density with increasing DABCO content. Consistently, a shift in the $\tan \delta$ peak is observed from $T_\alpha=19$ °C for PECH₁₀ to 79 °C for the PECH₁₅ one, and to about 110 °C for PECH₂₀, PECH₃₀ and PECH₅₀ networks. Simultaneously, the $\tan \delta$ peak intensity decreases. The simultaneous increase of T_α and the decrease of intensity of $\tan \delta$ peak are characteristic of an increase in the crosslinking density with an increase in the DABCO content. Addition of 5 % and more of DABCO (PECH₁₅ and above) leads to an increase in

crosslinking homogeneity. At the same time, an increase in DABCO should increase the IEC value.

3.2. Ionic Exchange Capacity

The IEC values for PECH networks with 10 to 50 mol % DABCO are reported in Figure II - 15.

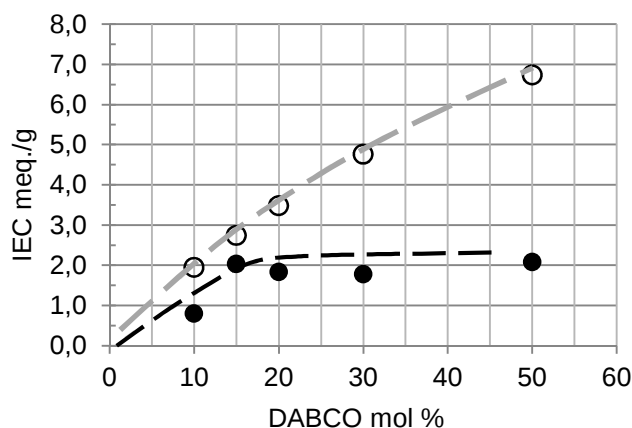


Figure II - 15: Experimental (●) and theoretical (○) IEC values for PECH single networks of different DABCO content

The measured IEC value increases from 0.8 to 2.0 meq./g when the DABCO molar proportion increases from the 10 to 15 mol %. At DABCO concentrations higher than 15 mol %, the IEC does not further increase, remaining at around 2.0 meq./g. As in the case of the PECH₁₀ networks (cf. § 2.3.2), the theoretical IEC are higher than the experimental values for all the composition tested. The difference is even more important when the amount of DABCO introduced is high. The measurements of soluble fractions and DMA analysis show that the additional DABCO leads to a higher crosslinking density, thus a higher charge density. As previously assumed, the incomplete exchange of Cl⁻ counterions could lead to the underestimation of the IEC value. However, another reason for this underestimation could be the counterion condensation, resulting in a neutralization of the ionic sites. This phenomenon, the Manning condensation^{17,18,19} consists in the condensation of counterions onto the polyelectrolyte until the charged density between neighboring charges along the chain is reduced below a critical value. To calculate this critical value, the polyelectrolyte chain is represented by an ideal line of zero radius and finite charge density. The condensed counterion layer is assumed to be in equilibrium with the ionic surrounding of the

polyelectrolyte. The counterion condensation occurs when the dimensionless Coulomb coupling strength $\Gamma = \lambda_B/l_{charge}$ (λ_B represents the Bjerrum length and l_{charge} the distance between neighboring charged units) is superior to 1. In this case the Coulomb interactions dominate over the thermal interactions and the counterion condensation is favored. For many polyelectrolytes, this condensation is relevant, since the distance between neighboring units is close to λ_B (which is $\approx 7 \text{ \AA}$ in pure water, and decreases with the increase in ionic strength). In PECH networks at DABCO proportions superior to 20 mol %, the distance between ionic charges would approach λ_B . Thus the effect of increase in the ionic sites would be masked by the partial neutralization of ionic sites due to Manning condensation. To confirm this assumption the water uptake of the materials was measured. Indeed, if the ionic sites are partially neutralized, the water uptake will be not increased by the DABCO proportion increase.

3.3. Water Uptake

The water uptake of the different networks have been measured and calculated using equation II-3 and shown in Figure II - 16.

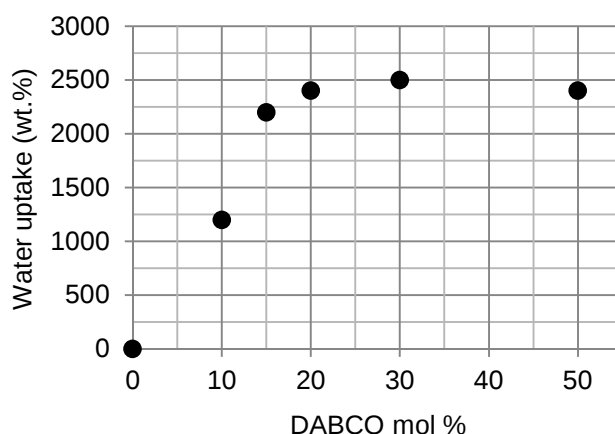


Figure II - 16: Water uptake of PECH networks with different DABCO contents. Networks synthesized by reaction molding immersed after synthesis in the hydroxide exchange solution, rinsed and equilibrated in water.

The water uptake of the networks increases with increasing DABCO content to attain a maximum of 2400 wt.% at 20 mol % DABCO (Figure II - 16). The WU does not increase any further with an increase in DABCO content. Up to 20 mol % DABCO the cationic sites

formed in the PECH - DABCO reaction do not lead to a water uptake increase. This result is in agreement with the assumption of the Manning condensation when the DABCO proportion is higher than 20 mol %.

The effects of the DABCO content on the other properties of the PECH networks have been then studied.

3.4. Ionic Conductivity

The cationic sites formed by the grafting of DABCO molecules into PECH must be responsible for anion conduction; the conductivity of the network should thus depend on DABCO concentration (Figure II - 17).

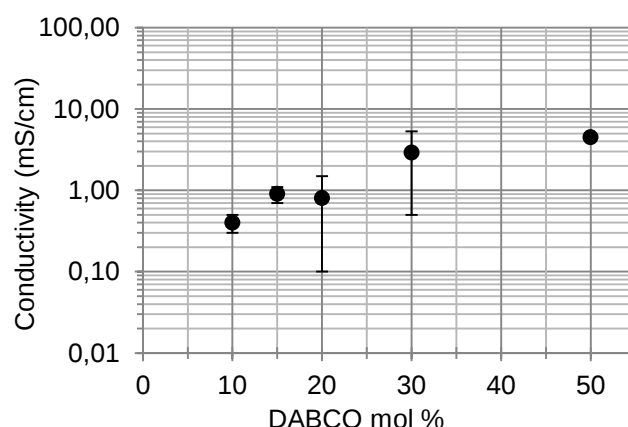


Figure II - 17: Ionic conductivity of PECH networks with variable DABCO content. Network synthesized by reaction molding, non-dried after synthesis.

In the studied range of DABCO proportions, all the PECH networks are ion conducting. They have a conductivity increasing from 0.4 mS/cm for PECH₁₀ network to 4 mS/cm for PECH₅₀ network. Thus, although the ions partially condensed, due to Manning condensation when the DABCO proportion exceeds 20 mol %, the latter, under the action of an electric field, contribute to the ionic conduction of the material. Nevertheless 15 mol % DABCO content is enough to obtain a PECH network with an ionic conductivity in the mS/cm range, sufficient for our application.

3.5. Transport Number

Finally, transport numbers (t^-) were measured on a series of the PECH networks directly immersed in 1 M KOH after synthesis and then rinsed and equilibrated in water (Figure II - 18).

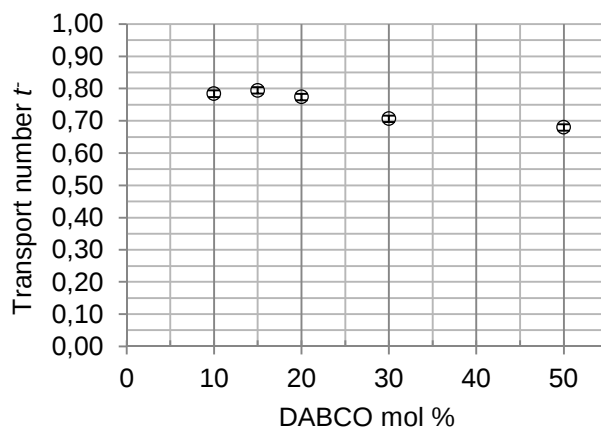


Figure II - 18: Transport number for PECH networks by reaction molding ($\odot$) vs. DABCO content.

As previously reported, the PECH₁₀ network has a t^- of 0.78. An increase in the DABCO diminishes the t^- value of the networks until 0.68 for the PECH₅₀ network. The slight decrease in selectivity with the DABCO content increase can be due to the increase in the water uptake of the network compared with that of PECH₁₀ and PECH₁₅ networks. Indeed, the WU between 10 and 20 mol % DABCO, reaching a maximum value for PECH₂₀ and then remains stable. Nevertheless, all the networks have a t^- between 0.68 and 0.79, and they can be considered as selective.

In conclusion, when the synthesis of PECH network is carried out in a closed mold, it is preferable to set the molar ratio of DABCO to 15 mol % per repeat unit of the PECH. Indeed, under these conditions, crosslinking of the PECH network is more homogeneous, the ionic conductivity is sufficient and the membrane is selective.

Before the electrochemical characterization of these networks assembled on air electrode, their chemical stability was studied *ex-situ* in concentrated lithium hydroxide, the environment in which they will be immersed later.

3.6. Chemical Stability

The chemical stability of the PECH₁₀ network synthesized by solution casting was characterized after immersion at room temperature in a 5 M LiOH_(aq) solution from 1 up to 7 days. The LiOH saturated solution was chosen because it will be the electrolyte in contact with the membrane in the alkaline aqueous Li-air battery. The possible degradation of the ionic sites (cf. Chapter I § 4.2.4) would cause a decrease in PECH₁₀ network conductivity. The conductivity values of the material, previously rinsed and equilibrated in water, are reported as function of the immersion time in LiOH in Figure II - 19.

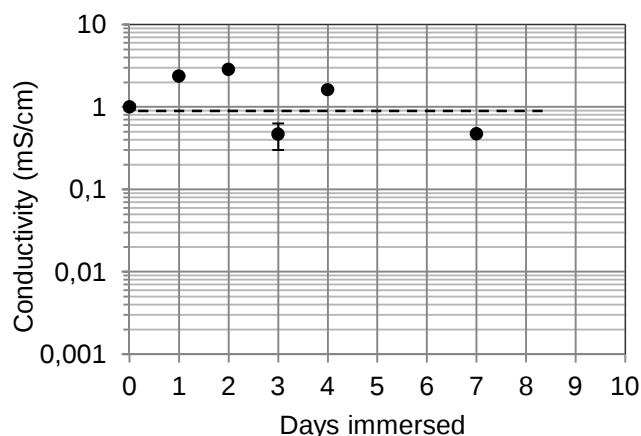


Figure II - 19: Ionic conductivity of solution casted PECH₁₀ network after different immersion time in 5 M LiOH at room temperature

The conductivity of the PECH₁₀ network remains unchanged after 7 days at room temperature in saturated LiOH, confirming the stability of this material.

The degradation can be accelerated by increasing the temperature. Additionally, the stability of the PECH₁₅ synthesized by reaction molding was determined in 5 M LiOH solution, at 50 °C (Figure II - 20).

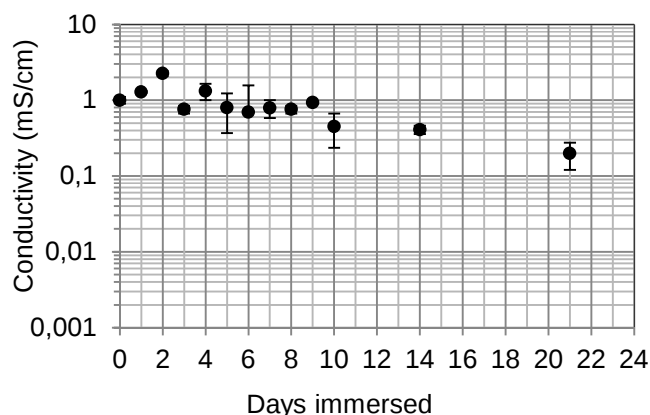


Figure II - 20: Ionic conductivity of reaction molded PECH₁₅ network after different immersion time in 5 M LiOH at 50 °C.

The PECH₁₅ network conductivity begins decreasing noticeably after 10 days of immersion in 5 M LiOH at 50 °C. After 14 days the conductivity is 0.4 mS/cm and after 21 days the conductivity is 0.2 mS/cm, 5 times less than at the beginning of the ageing test. Thus, the accelerated aging shows that, although the ammonium sites of PECH-DABCO are described as the most stable in relation to the Hofmann degradation (cf. Chapter I § 4.2.4), they can however be degraded during their prolonged immersion in concentrated lithium hydroxide.

In conclusion, the increase of DABCO molar proportion in the PECH network synthesized by reaction molding increases the water uptake and the conductivity of the network, while decreasing its selectivity. In fact, it appears that a maximum of water uptake and conductivity is reached at 20 mol % of DABCO, further increase in the DABCO content has no effect on these network properties. The selectivity of the network, evaluated by $\bar{\tau}$, diminishes from 0.78 to 0.68 when DABCO is increased from 10 to 50 mol %; this effect is probably due to both Manning condensation and an increase in WU. Indeed, the network properties appear to evolve with the DABCO content between 10 and 20 mol %. After 20 mol %, stabilization in its properties is observed. A PECH₁₅ membrane appears to have the most appropriate physicochemical characteristics for its use as anion exchange membrane.

In the next part, the membrane-air electrode assembly with these membranes will be studied.

4. Electrochemical Characterization of PECH Network / Electrode Assembly

In the first part of this chapter (cf. § 1.3) we have characterized electrochemically the air electrode. We will next present a method for assembling a PECH network over the air electrode to form the membrane/electrode assembly (MEA). The membrane should allow the passage of hydroxide ions while preventing the passage of lithium ions. It should also block the permeation or leakage of the alkaline electrolyte into the gas-diffusion layer. However, this structure should yield a low additional resistance in order to not decrease the air electrode performance. First, we investigated the importance of assembling the membrane dried or wet, exchanged or not, with or without a membrane solution in order to decrease the interface resistance.

4.1. Membrane / Electrode Assembly (MEA) Optimization

The optimization of the MEA was made using PECH₁₀ networks as described in § 2.2. Before assembly, the chloride anions were exchanged into hydroxide ions after synthesis by immersion in 1 M KOH for 24 h, rinsed until neutral pH and equilibrated in water.

4.1.1. Membrane Synthesized Ex-Situ

In a first time, a PECH₁₀ network synthesized by solution casting (≈ 100 μm thickness) was placed over the electrode but it does not adhere to the air electrode. Nevertheless, after a prolonged contact with the electrolyte, we can expect to obtain an ionic contact between the two. However, after assembly and 5 h of rest in the half-cell, the polarization of the MEA is always very high (< -1 V/ Hg/HgO) and no further tests can be performed. We can conclude that the PECH₁₀ network synthesized by solution casting cause an important ohmic drop, because of the no ionic contact with the electrode.

Subsequently, the MEA was prepared by lightly pressing a PECH₁₀ network, previously swollen in water, on the electrolyte side of the electrode (Figure II - 21). The swollen membrane adheres slightly to the electrode.

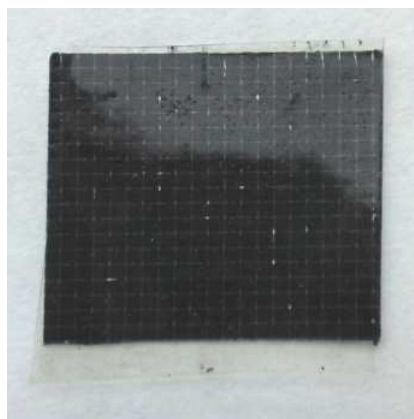


Figure II - 21: Photograph of an air electrode/ PECH₁₀ network assembly

First, the electrochemical stability domain of this air electrode/PECH₁₀ assembly was determined by voltamperometry. The voltamperograms were recorded in 5 M LiOH at 2.5 mV/s (vs. Hg/HgO), with a platinized titanium counter electrode. (Figure II - 22).

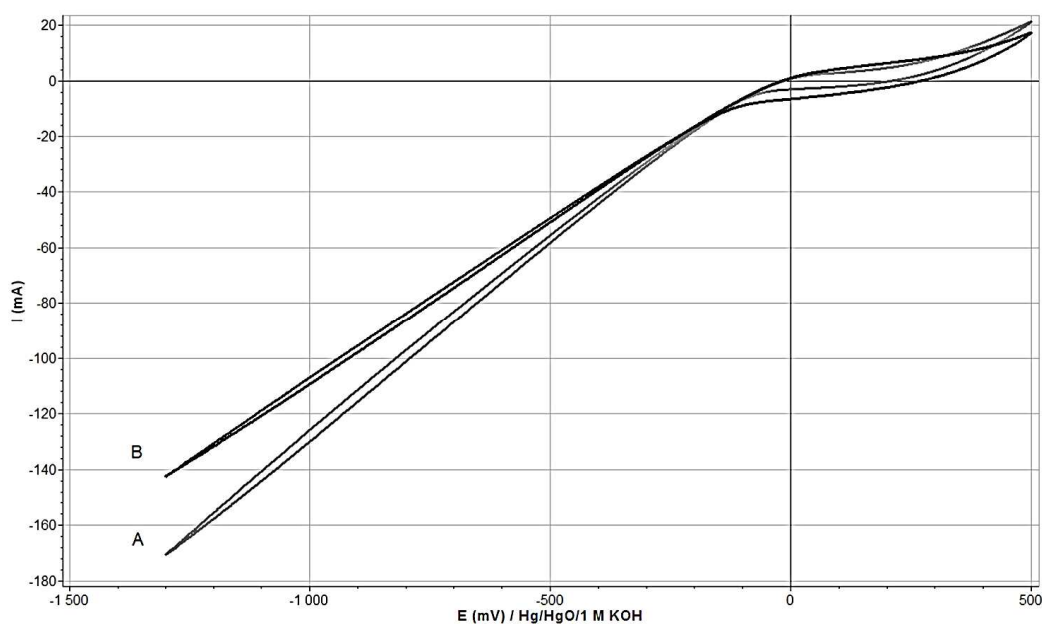


Figure II - 22: Cyclic voltammograms of non-modified air electrode (A) and modified with a PECH₁₀ network (B) - Electrolyte: 5 M LiOH. Room temperature and atmospheric pressure. Reference electrode: Hg/HgO

As for the air electrode, neither oxidation nor reduction peak of the electrolyte were detected between 200 and -1300 mV/(Hg/HgO). Thus, the PECH₁₀ network does not reduce the electrochemical stability domain of the air-electrode. Nevertheless, the electroactivity of the electrode is slightly reduced by the presence of the network. Indeed, at -1 V the current is

reduced from -130 mA to -110 mA. This reduction in the activity can be due to the slower diffusion of the active species through the membrane. However, this reduction can be considered as sufficiently small to not affect the performance of the air electrode.

Agel²⁰ and Akrou²¹ demonstrated that a “membrane solution” is necessary between the electrode and the membrane to assure the ionic contact. They obtained the best performance with a polyacrylic acid/KOH gel. During a previous study in our laboratory, it was found that a concentrated PECH solution in DMF could be used as a more efficient membrane solution. Consequently we used concentrated PECH solution as “membrane solution”. This highly viscous solution was applied over the electrolyte side of the electrode as an adhesive and then a dry, on the one hand, and a water-swollen, on the other hand, PECH₁₀ networks were lightly pressed against the electrode and assembled in a half-cell. Polarization curves were recorded on the both MEAs by applying current densities varying from -1 to -30 mA/cm² (Figure II - 23).

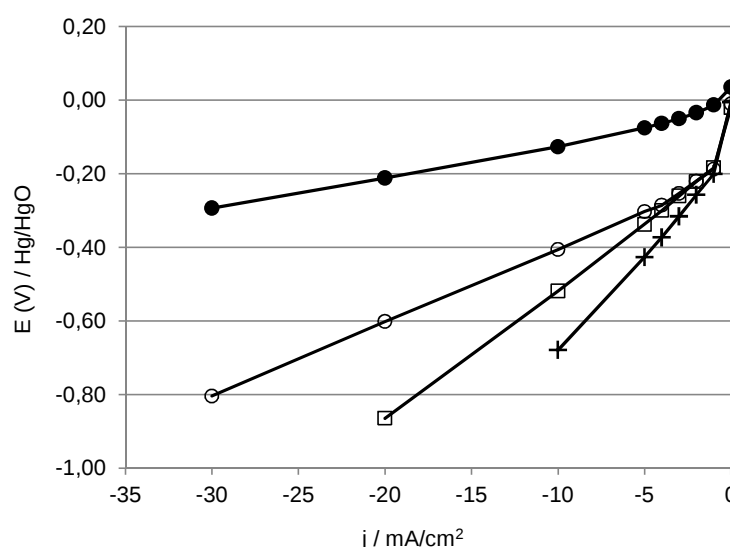


Figure II - 23: Potential-current density curves recorded on air-electrode (●) unmodified and modified with PECH₁₀ network water swollen without (+) and with (○) membrane solution, and with dry PECH₁₀ network associated with membrane solution (□). Electrolyte: 5 M LiOH. Room temperature, atmospheric pressure. Reference electrode: Hg/HgO

As previously reported (cf. § 1.3), the bare electrode potential is about -30 mV/(Hg/HgO) at -1 mA/cm² current density and attains a value of -130 mV at -10 mA/cm². When a wet PECH₁₀ network is placed over the electrode without membrane solution, the potential is significantly increased from -130 to -700 mV at -10 mA/cm². The polarization of the MEA is 570 mV higher than that of the bare electrode at the same current density. This sharp increase indicates

an important resistance due to an insufficient ionic contact between the electrode and the membrane. Indeed, when the same water-swollen PECH₁₀ network is assembled over the electrode with the membrane solution, the potential is decreased from -700 to -400 mV at -10 mA/cm². To confirm, when a dry PECH₁₀ network is placed over the electrode with the membrane solution, the electrode potential is -500 mV at -10 mA/cm² while it is not possible to measure it without the membrane solution. The polarization of the MEA is 370 mV higher than that of the bare electrode at -10 mA/cm².

The polarization of MEA is smaller when the membrane solution is used but it is still high for the operation of a half-cell.

Finally, observation of the MEA was carried out after the polarization test and 24 h in contact of the electrolyte in the half cell (Figure II - 24).

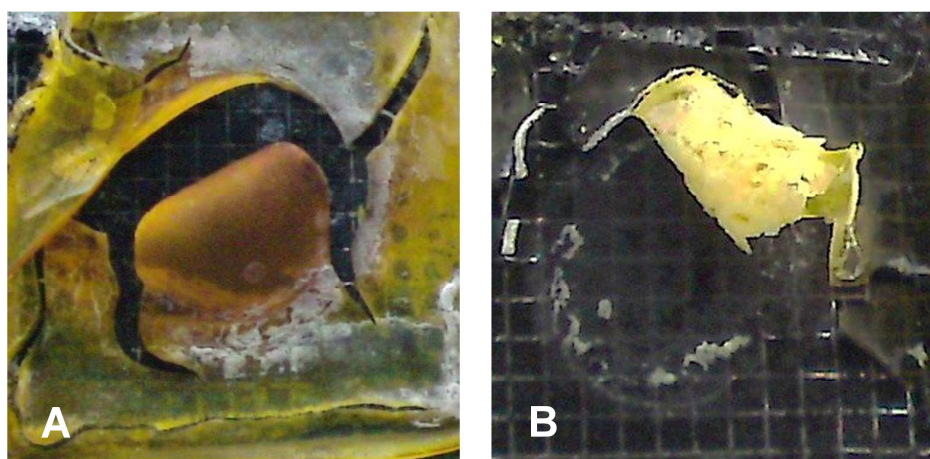


Figure II - 24: Photography of MEA after 24 h in half-cell. Electrode modified with (A) dry and (B) water swollen PECH₁₀ network and assembled with membrane solution.

The networks are torn, they are detached from the electrode, and the interface between the electrode and the membrane is not preserved. The PECH₁₀ networks being damaged, the air electrode was then exposed to the electrolyte. The rupture of the membrane can be explained by the volume variation the PECH₁₀ network in contact with the membrane solution on the one side and with the cell electrolyte on the other side. To confirm this assumption, the volume swelling ratios of dry PECH₁₀ network were measured in different liquids (Table II - 1).

Table II - 1: Swelling ratios of a PECH₁₀ network synthesized by casting method, dried and immersed in different liquids at room temperature for 24 h.

Liquid	Swelling ratio (vol. %)
Water	27
1 M KOH	85
5 M LiOH	90
DMF	170

Dry PECH₁₀ network swells of 27 vol.% when it is immersed in water (this corresponds to the 110 wt.% water uptake previously reported). The same dry network swells of 170 vol.% when it is immersed in DMF, while its swelling in 5 M LiOH is only 90 vol.%. Thus a dry network in contact with the membrane solution containing DMF swells and when the network is then exposed to the electrolyte in the half-cell, the swelling is lower. The strain caused by the different swelling ratio on the both sides of the PECH₁₀ network after assembly can be responsible for its mechanical failure.

The high polarization of the MEA along with the physical damage of the membrane caused by the volume variations in the half-cell test make this assembly method inadequate for the application. Consequently another approach has been studied to assemble the polymer membrane and the electrode.

4.1.2. Membranes Synthesized Directly over the Electrode

To obtain a better interface between the electrode and the polymer membrane, the later was synthesized directly over the electrode. Initially, we verified that the air electrode was not damaged and its electrochemical performance was not altered by the synthesis process (temperature and solvent presence). Two tests were made: first the electrode was heated for 4 h at 100 °C in air and second, the electrode was heated similarly, while immersed in DMF. Both electrodes were tested afterwards and their electrochemical characteristics were found to be unaltered.

In a first test, the PECH₁₀ network was solution casted over the electrode (§ 2.2.1). A 50 µm thick membrane was obtained. When this MEA was immersed in a 1 M KOH solution for counterion exchange, the membrane increased in volume and detached from the electrode.

Thus this membrane could not be exchanged, and was tested directly in half cell. After 24 h at rest in the half cell (for counterion exchange) a polarization test was run. A polarization curve equivalent to that of the non-modified electrode was obtained. Immediately after, a stability test was run, and stability equal to that of the non-modified electrode was obtained. Thus a solution casted membrane has no effect in the performance of the air electrode.

Therefore, the PECH₁₀ network was directly synthesized over the electrode by reaction molding. The PECH₁₀ network synthesis was made by pouring the reaction solution (cf. § 2.2.2) over the catalyst side of the air electrode, placed between two silylated glass plates (Figure II - 25 A). The membrane thickness was fixed by the Teflon[®] gasket (500 μ m), which acts also as a hermetic seal during the reaction. After synthesis, once removed from the mold, the PECH₁₀ network in the MEA is swollen in DMF and in Cl⁻ form. It has the same thickness than that of the gasket of the mold used for the synthesis (Figure II - 25 B).

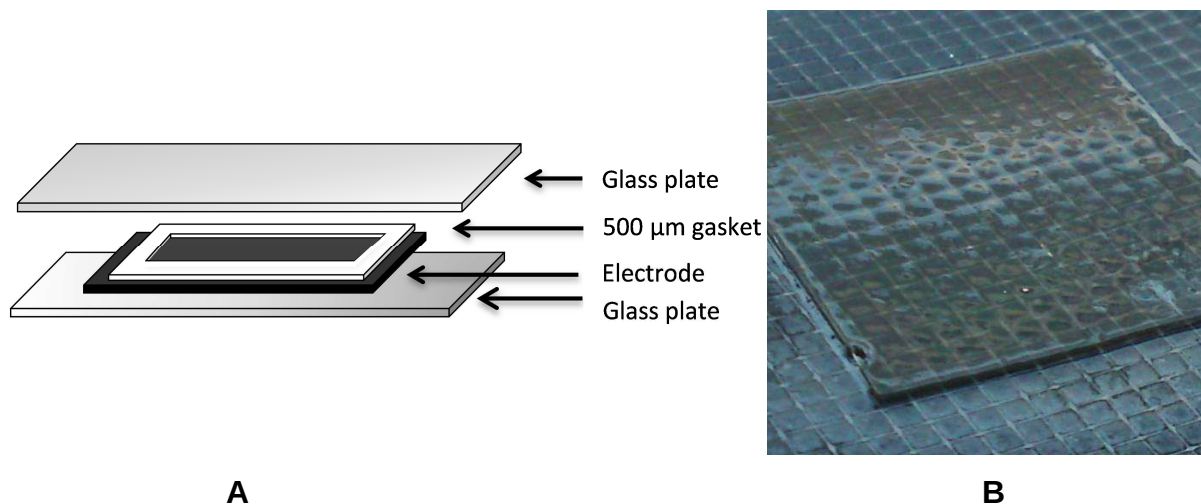


Figure II - 25: (A) Schema of the mold for the membrane synthesis over an air-electrode and (B) 500 μ m thick PECH₁₀ network synthesized by reaction molded over an air electrode

To remove the DMF and exchange the counterion, three procedures were tested. First, the assembly was dried and then placed in half-cell to perform the exchange in the electrolyte (5 M LiOH). Once dried, the PECH₁₀ network has a final thickness of about 100 μ m. This assembly presents an important polarization (< -1 V) even at low currents. To allow its swelling by electrolyte and the ionic exchange the assembly was left at rest in the cell and the polarization was recorded every 24 h. The potential reached a minimum of -500 mV/(Hg/HgO) at -10 mA/cm² after 7 days and this value did not reduced further. This high polarization reveals insufficient membrane conductivity and this MEA cannot be further characterized.

Second, the assembly was dried and then immersed in 1M KOH for 24 h for counterion exchange, dried and mounted in half-cell for testing. The dried PECH₁₀ network on the electrode has also a thickness of about 100 μm . Similarly to the previous MEA, the polarization was lower than -1 V immediately after the assembly, attained a minimum - 500 mV at - 10 mA/cm² after 4 days at rest in the cell and did not further evolved.

From the both precedent results, we can conclude that drying of the membrane should be avoided.

Finally, the assembly was immersed immediately after the synthesis in 1M KOH for 24 h for counterion and DMF exchange with the aqueous electrolyte, and the assembly was then mounted in half-cell for testing. The polarization of this assembly was measured and compared with that of bare electrode (Figure II - 26).

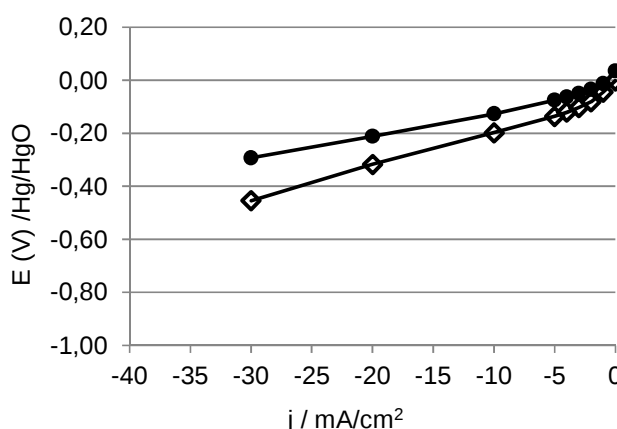


Figure II - 26: Potential-current density curves recorded on bare air electrode (●) and modified with PECH₁₀ network (◇) directly synthesized over the electrode. Electrolyte: 5 M LiOH. Ambient temperature, atmospheric pressure. Reference electrode: Hg/HgO

The modified electrode potential was -190 mV at -10 mA/cm², i.e. only a 60 mV polarization higher than that of the bare electrode. This additional polarization is the smallest when the PECH₁₀ network is synthesized over the electrode. The cell resistance calculated from polarization curve is only 12 $\Omega\cdot\text{cm}^2$, and thus the membrane imposes only an additional resistance of 3 $\Omega\cdot\text{cm}^2$ (the resistance of the bare electrode is 9 $\Omega\cdot\text{cm}^2$ cf. § 1.3.2).

As previously detailed, a PECH membrane synthesized by solution casting has a conductivity of 1.0 ± 0.1 mS/cm and the same membrane synthesized by reactive molding has a conductivity of 0.4 ± 0.1 mS/cm (cf. § 2.3.4). Consequently, the lower polarization of the MEA cannot be explained by the membrane intrinsic conductivity. The reduction of the polarization could then be due to a better interface between the polymer membrane and the

electrode. The reaction solution can impregnate the electrode and effectively cover the catalyzed carbon black particles, reducing the resistance of the MEA. This behavior was described by Fujiwara et al.²² for an air electrode modified with an anion exchange membrane to be used in rechargeable metal-air batteries with aqueous KOH as electrolyte (Figure II - 27).

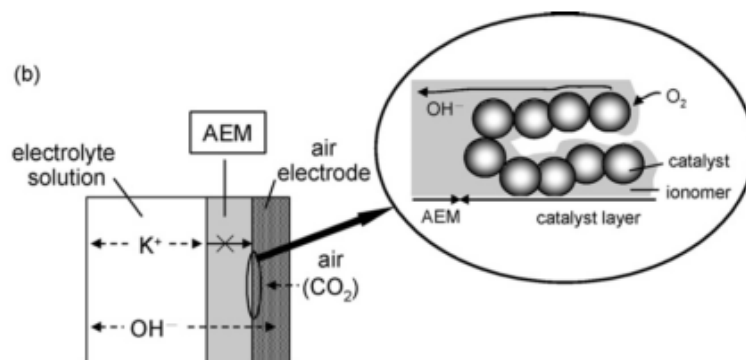


Figure II - 27: Schematic illustration of AEM modified air electrode, adapted from Fujiwara et al.²²

To confirm the migration of the polymer into the catalyst layer, a transversal cut of a PECH₁₀ MEA was observed by scanning electron microscopy (Figure II - 28).

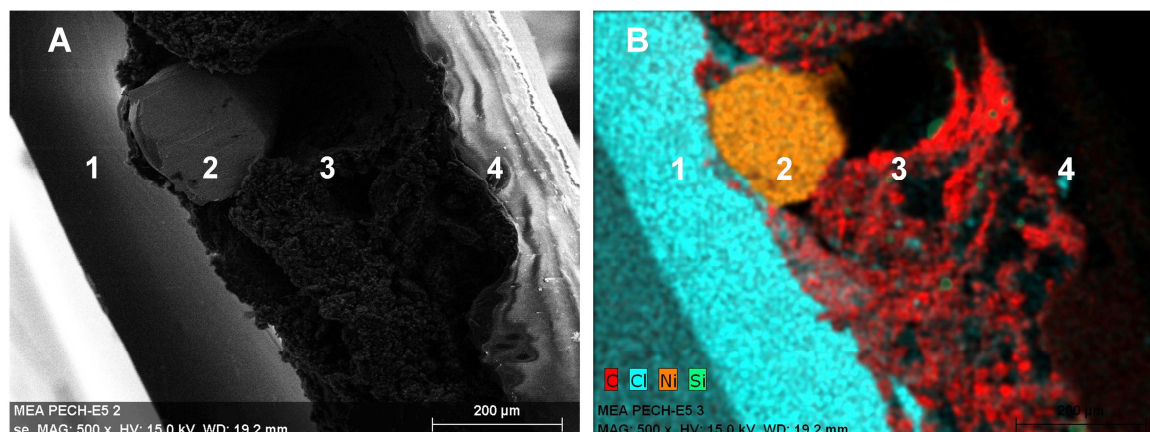


Figure II - 28: (A) SEM image of a PECH₁₀ MEA. 1: PECH₁₀ network. 2: Current collector (Ni). 3: Catalyst layer. 4: Teflon film separating electrode from air. (B) EDX analysis.

SEM micrograph (Figure II - 28 A) show the polymer membrane (1) covering the catalyst layer (3) in which the current collector is (2). The PTFE film that serves as a separate from the air is also observed (4). The EDX analysis (Figure II - 28 B) shows the chloride atoms from the PECH₁₀ network inside the catalyst layer. This demonstrates that the polymer network has impregnated the catalyst layer, covering the carbon black particles and forming a good interphase. This confirms the interest of the choice of our method to assemble the

membrane over the air electrode. As a result, PECH₁₀ network can be directly assembled with an air electrode by molding without important performance losses compared with the bare electrode.

4.1.3. Ion Exchange Time

To define the immersion time in 1 M KOH of the MEA for an optimal exchange of the Cl⁻ ions and the synthesis solvent, several PECH₁₀ network-modified electrodes were prepared and immersed in 1 M KOH for different durations. After the fixed immersion time, the MEA stability was measured in half cell in 5 M LiOH. For that, each modified electrode was cycled for 10h at rest followed by 10h of discharge at -10 mA/cm². We consider that the electrode is irreversibly damaged after reaching a potential of -400 mV/(Hg/HgO). This time is considered as the life-time of the MEA (Figure II - 29).

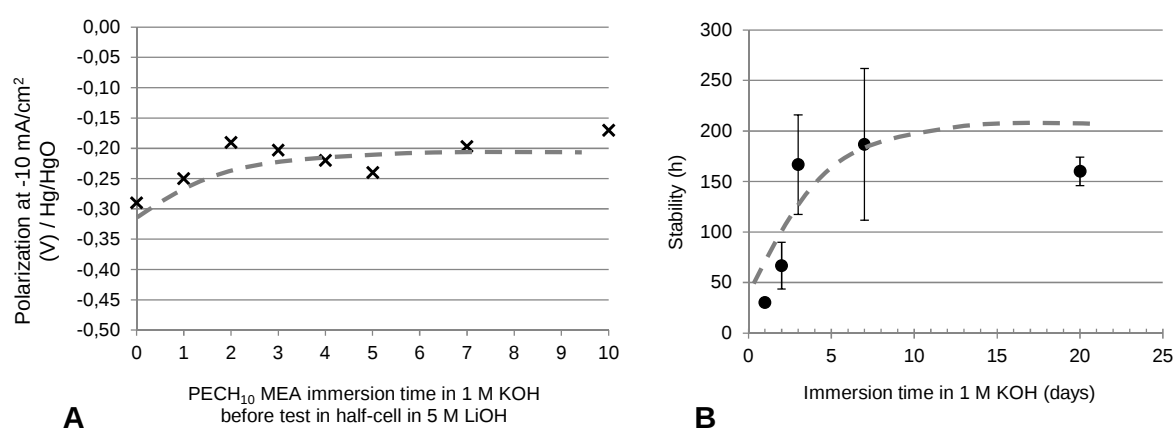


Figure II - 29: (A) Polarization at the beginning of the first discharge and (B) Stability of PECH₁₀ network MEA (time at which polarization attains -400 mV) vs. immersion time in 1 M KOH before measurements. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature and atmospheric pressure. Reference electrode: Hg/HgO

The polarization at discharge is nearly -300 mV when the electrode has not been immersed in 1 M KOH before the test. This can be due to the DMF present in the membrane, and the Cl⁻ ions that have not been exchanged into hydroxide. In this case, the MEA stability is of 30 h, i.e. lower than the bare electrode (50 h – cf. § 1.3.3). After 48 h of immersion in 1 M KOH the polarization attains -190 mV, and does not changes noticeably with increasing immersion time (Figure II - 29 - A). However, the stability increases when the MEA is previously immersed for 3 days in 1 M KOH to attain 150 h. Thus we decided to immerse systematically all the MEA for at least 3 days before the different measurements in half-cell.

4.1.4. Stability of PECH₁₀ Network / Electrode Assembly

Figure II - 30 shows the evolution of the potential as function of time of the air electrode modified with a PECH₁₀ network synthesized over the electrode and immersed for 3 days in 1M KOH. The same measurement carried out on non-modified electrode is reported for comparison.

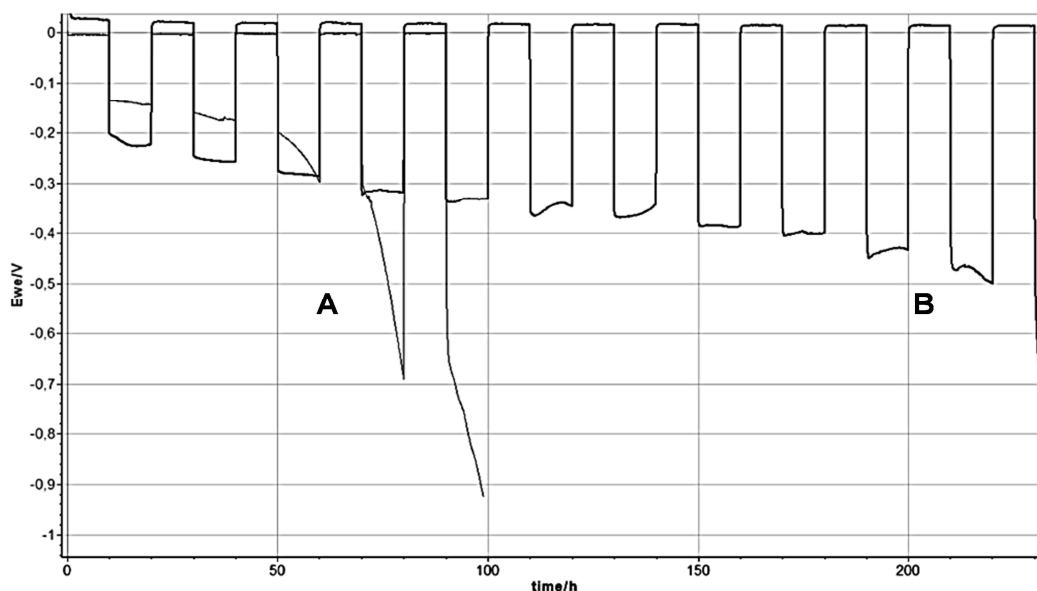


Figure II - 30: Potential-time curves of a bare electrode (A) and a PECH₁₀ modified electrode (B). Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO.

At the beginning of the first discharge the MEA potential is -200 mV/(Hg/HgO), and corresponds to the value measured during the polarization test (Figure II - 26). The MEA potential decreases slowly during the stability test, and it has reached -400 mV after 160 h. To verify the validity of this result, the synthesis and the electrochemical measurements were repeated more times and a mean stability of 160 h with a standard deviation of 50 h was obtained. Thus the PECH₁₀ MEA is considered as stable for 160 ± 50 h.

The MEA stability is about 3 times higher than that of a bare electrode (50 h). These results confirm that an air electrode functioning in 5 M LiOH aqueous solution, with ambient air, can be protected from the lithium carbonate formation by applying an anion conducting/selective membrane on the electrolyte side.

4.1.5. MEA After Functioning in Half-Cell

After the half-cell test end (polarization higher than $-400 \text{ mV}/(\text{Hg}/\text{HgO})$), the PECH_{10} network modified electrode shows no apparent damage, as shown in Figure II - 31. A decrease of the polarization has been obtained and physical damage is prevented.

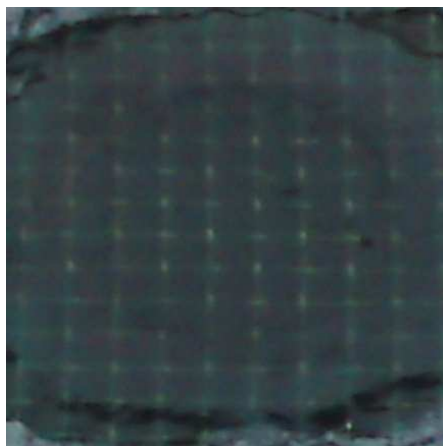


Figure II - 31: Tested area of PECH_{10} network reactive molded over the air electrode after 150 h of stability test

Inversely to PECH_{10} network synthesized by casting method (Table II - 1), when the PECH_{10} network was synthesized by molding and was immersed in 1 M KOH directly after synthesis, its volume was reduced by 45 %. When it was then immersed in 5 M LiOH, its volume was reduced by 50 %. The contraction of the polymer membrane molded over the electrode, opposed to the expansion of a casted network, and can explain that in the first case no delamination is observed. At the same time, there is a better adhesion between electrode and membrane in the case of the direct synthesis on the electrode.

We will thereafter study the improvement of the MEA performance, focusing on the membrane characteristics such as its thickness and DABCO content.

4.1.6. Effect of the Membrane Thickness

First, the effect of the membrane thickness was studied. MEAs with different PECH_{10} network thickness were prepared and their stability was evaluated (Figure II - 32).

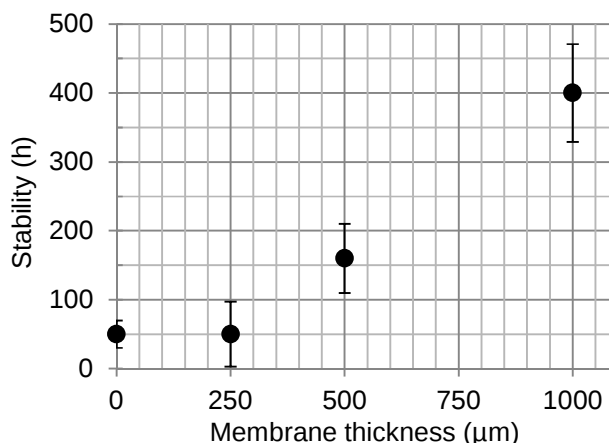


Figure II - 32: Stability of MEA as the function of PECH₁₀ network thickness. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO.

A 500 μm thickness at least is necessary to increase significantly the air electrode stability. Above this values, the stability increases with increasing thickness of the polymer membrane. Thus, a MEA with a 1000 μm thick PECH₁₀ network shows a stability of 400 h. However, a 1000 μm thickness is not suitable for application in the Li-air battery. For practical application the thickness must be kept as low as possible. Thus, a thickness of 500 μm was preferred in our work.

4.2. Effect of the DABCO content

As previously shown (c.f. § 3.4), it is possible to increase 10 times the conductivity of the PECH₁₀ network by increasing the DABCO content. This conductivity increase implies a resistance decrease that should lead to a reduced polarization of the corresponding MEA. Thus, PECH networks with different DABCO amounts were prepared over an air electrode (cf. §. 3 and § 4.1.2). The polarization curves of the different MEAs recorded in 5 M LiOH electrolyte are shown in Figure II - 33.

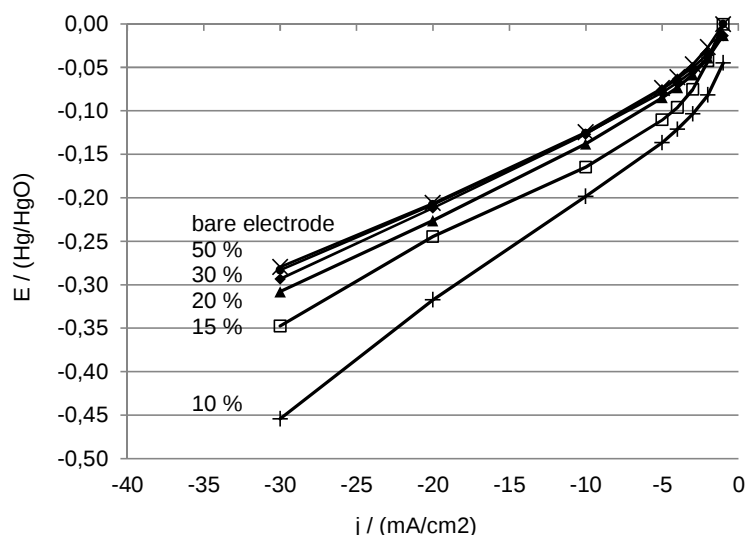


Figure II - 33: Potential-current density curves recorded on bare electrode (x) and PECH₁₀ (+), PECH₁₅ (□), PECH₂₀ (▲), PECH₃₀ (◆) and PECH₅₀ (●) network modified electrodes. Electrolyte: 5 M LiOH. Room temperature, atmospheric pressure. Reference electrode: Hg/HgO.

Regardless the current density, the polarization of the MEA decreases as the DABCO content increases. For PECH₃₀ and PECH₅₀ networks, the polarizations of the modified and the bare electrode are equivalent. When the DABCO content is lower than 20 mol %, the potential of the MEA is only 35 mV higher than that of the bare electrode at -10 mA/cm². The total cell resistances and those of the MEAs were calculated from these polarization curves and they are presented in Table II - 2.

Table II - 2: Resistance of in-situ PECH network-modified electrodes vs. DABCO mol %

Tested MEA <i>In-situ</i> molded PECH network	Assembly Resistance ($\Omega \cdot \text{cm}^2$)	Additional resistance ($\Omega \cdot \text{cm}^2$)
Non modified electrode	9	---
PECH ₁₀ MEA	12	3
PECH ₁₅ MEA	10	1
PECH ₂₀ MEA	9	0
PECH ₃₀ MEA	9	0
PECH ₅₀ MEA	9	0

When the DABCO molar proportion in the networks exceeds 15 %, the additional resistance imposed by the membrane becomes negligible. This result is in agreement with the conductivity values of the PECH network which become higher than 1 mS/cm (cf. § 2.3.4) for DABCO contents superior to 15 mol %.

Stability tests were then run on the electrodes with the usual rest/discharge cycles: OCV for 10 h and -10 mA/cm² for 10 h (Figure II - 34).

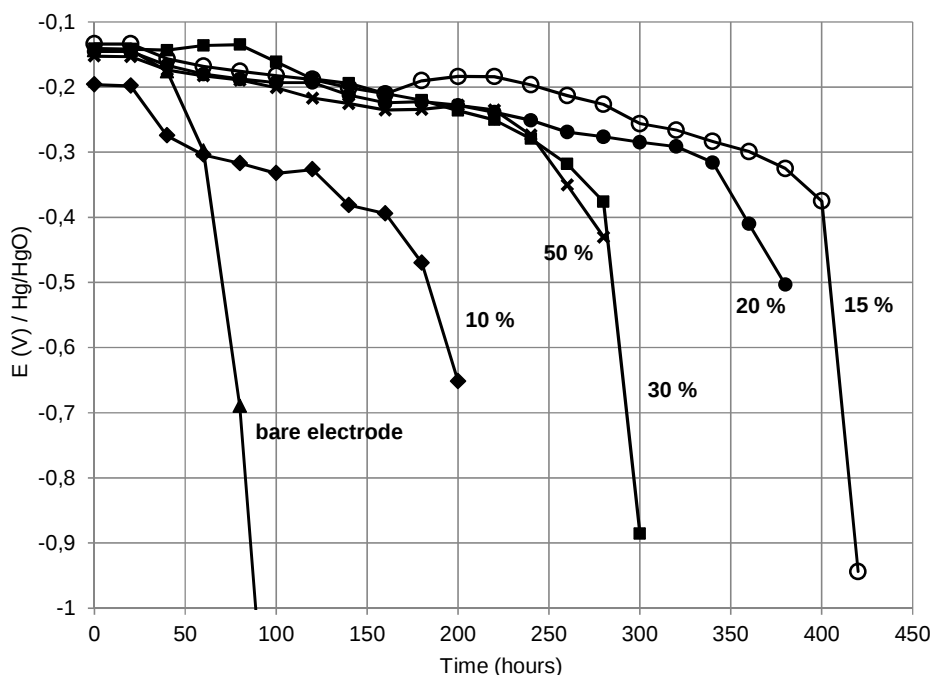


Figure II - 34: Potential at discharge vs. time curves for the bare electrode (▲) and PECH₁₀ (◆), PECH₁₅ (○), PECH₂₀ (●), PECH₃₀ (■) PECH₅₀ (×) network modified electrodes. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO.

The reduction of the MEA polarization observed in the potential-current curves (Figure II - 33) according to the DABCO proportion in the networks is also observed at the beginning of the potential vs. time curves. The potentials during the first discharge for MEAs with DABCO proportions superior to 15 mol % are equivalent to the potential of the non-modified electrode. The tests were repeated several times, and the mean stability was calculated for different membrane compositions (Figure II - 35).

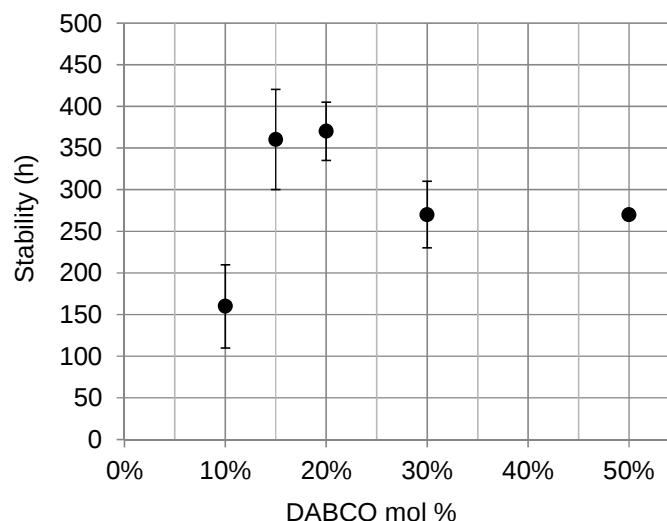


Figure II - 35: Mean stability and standard deviation for electrodes modified with PECH networks synthesized with different DABCO contents. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO.

Stability of PECH₁₅ and PECH₂₀ networks can be considered to be equivalent: 360 ± 60 h. With a further increase in the DABCO concentration the stability diminishes. This result is in agreement with the *ex-situ* physicochemical characterization since these networks show also the best selectivity. Thus, after the physicochemical and the electrochemical characterization of the membranes, we decided that the PECH₁₅ network was the best polyelectrolyte network for the protection of the electrode.

5. Conclusion

In a first time, we have identified and characterized air electrodes under the operating conditions of the lithium air battery. These electrodes when supplied with untreated air show a significant increase in polarization after 50 h of operation.

In the literature review conducted previously, we had identified the DABCO modified / crosslinked poly(epichlorohydrin) as a polyelectrolyte membrane that may protect the electrode. Thus, the PECH network synthesis was optimized. It can be synthesized at 100 °C for 4 h from the commercial solution of modified PECH in DMF either by solution casting or reaction molding from concentrated commercial solution of modified PECH in DMF (18 wt.%). The correct crosslinking of the materials, verified by Soxhlet extraction, as well as a high conductivity and high ionic selectivity are the most important characteristics of the ion

exchange membranes. For the reactive molding, we found that the most interesting network is the PECH₁₅ network. At this DABCO concentration, the highest ionic conductivity and selectivity are obtained. Then, we have successfully achieved a suitable interface between the electrode and the membrane that give the same polarization as bare air electrode. The best compromise was obtained with PECH membrane synthesized directly over the electrode, not dried, ion exchanged in 1 M KOH for 3 days before stability test.

In particular, the stability of the bare electrode has been increased from 160 h to 360 h by increasing the DABCO content in the PECH network from 10 to 15 mol %. This increase corresponds to an increase in conductivity from 0.4 to 1.0 mS/cm for the PECH₁₀ and PECH₁₅ networks, respectively. The best performance obtained with the PECH₁₅ network is in agreement with the physicochemical characteristics of this network.

With the purpose of reinforcing the mechanical properties and limiting the electrolyte swollen of the anion exchange membrane, in the next chapter we will discuss the use of interpenetrating polymer networks (IPN) architecture for the MEA. We will describe the synthesis and characterization of hydrogenated IPNs, based on PECH network and poly(2-hydroxyethyl methacrylate) (PHEMA) cross-linked with ethylene glycol dimethacrylate(EGDMA).

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Chapter III:

Hydrogenated IPN Membranes

As we have seen in the previous chapter, the selectivity of the polymer membrane protecting the air electrode is an important parameter for the subsequent stability of the membrane electrode assembly under the conditions imposed by the lithium-air battery. This selectivity is dependent on the swelling of the membrane in aqueous solutions increases. To reduce the swelling of PECH network used as polyelectrolyte, one possible approach is to increase its crosslinking density. However, we have previously shown that increasing the proportion of DABCO as the PECH crosslinker beyond 20 % did not permit to significantly improve the stability of the assembly. Different methods are proposed in the literature to crosslink the PECH network. For example, the use of crosslinking agents that do not lead to cationic groups formation.¹ Nonetheless, the single PECH network exhibits a high water uptake which causes a loss in its dimensional stability. The PECH based membrane can be also synthesized inside a polyamide support.² However, the intrinsic conductivity of the polyamide supported PECH membrane was found to be low: 10^{-1} - 10^{-2} mS/cm against 1 mS/cm for the pure PECH material. The polyamide support was suspected to decrease the membrane water affinity as well as ionic mobility.³

Another strategy that could limit the water swelling of such PECH network consists in including it into an interpenetrating polymer networks (IPN) architecture with an neutral polymer network. The purpose of this type of polymer association is generally to combine each partner's properties inside a homogenous material. In this case, PECH network would continue to ensure the ionic conductivity of the material, while the neutral network limit its swelling in the electrolyte. The synthesis of fuel cell membranes based on this type of architecture has been initiated with success in our laboratory.^{4,5,6}

In this chapter PECH polyelectrolyte network will be associated with an adequate partner network that should not interfere with the electrochemical reaction at the air electrode. Therefore, it should be permeable to oxygen. Ideally, it should also increase the mechanical resistance of the PECH network so that the material, in the form of thin film, can be easily handled and applied on the electrode when the material is not synthesized on the electrode. A polymer with a glass transition temperature above room temperature (working conditions of the battery) is preferable.

Therefore, we decided to associate the PECH network to a poly(2-hydroxyethyl methacrylate) (PHEMA) network. Indeed, this polymer is used in the manufacture of contact lenses and thus it is permeable to oxygen.^{7,8} Crosslinked PHEMA has a glass transition temperature of around 100 °C.⁹ The network can be synthesized by a radical polymerization reaction which should

not normally interfere with the nucleophilic substitution reaction leading to PECH network during the IPN synthesis. As a result, PHEMA was considered as a suitable partner.

1. Synthesis of PECH₁₀/PHEMA IPNs

Ex-situ PECH₁₀/PHEMA IPNs presented in the first part of this chapter, were synthesized and characterized without air electrode. These syntheses and characterizations were made in parallel to the optimization of the PECH network synthesis and of the membrane/electrode assembly (MEA) discussed in Chapter II. For this reason, DABCO content was set at 10 mol % for the optimization of the PECH/PHEMA IPNs synthesis. For the same reasons, the assembly on the electrode of these new membranes has been done, at first, with the membranes synthesized in a mold and then placed on the electrode. An optimized procedure is presented in the next part of this chapter.

1.1. Experimental

The PECH₁₀ network used in this part as reference corresponds to PECH₁₀ network synthesized by molding in the previous chapter (cf. Chapter II § 2.2.2).

In a typical synthesis, PHEMA network was synthesized by free radical polymerization by mixing 0.9 g 2-hydroxyethyl methacrylate (HEMA), 0.1 g ethylene glycol dimethacrylate (EGDMA - EGDMA:HEMA = 1:9 wt:wt) as cross-linker and 40 mg 2,2'-Azobis(2-methylpropionitrile) (AIBN - 4 wt.% with respect to monomers) as thermal initiator. The mixture was degassed under argon for 15 min and poured into a mold made from two silylated glass plates clamped together and sealed with a 500 µm thick Teflon[®] gasket (Figure II - 11). The mold was heated at 60 °C for 16 h and a homogeneous, rigid and transparent PHEMA network was obtained. The material was dried under vacuum at 60 °C for 24 h.

The PECH₁₀/PHEMA IPNs were synthesized by a *one-pot* process: in which all reactants are initially mixed. The PHEMA network is formed by free radical polymerization initiated with AIBN at 60 °C, and as seen in the previous chapter, the PECH is crosslinked at 100 °C by nucleophile substitution (Figure III - 1).

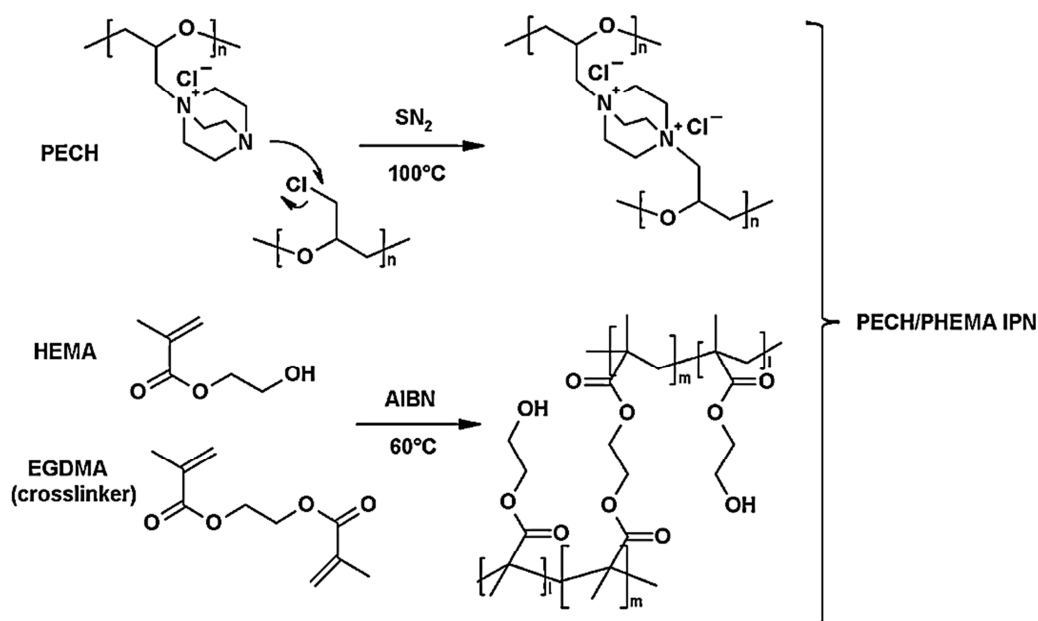


Figure III - 1: Scheme of PECH/PHEMA IPN synthesis

For this, HEMA and EGDMA (EGDMA:HEMA = 1:9 wt.) were added to the PECH solution (18 wt.% in DMF, $[\text{DABCO}]/[\text{C-Cl}] = 0.10$) at the appropriate ratios for the desired composition of the IPN. For example, to synthesize a PECH₁₀/PHEMA 68/32 IPN, 0.085 g EGDMA and 0.762 g HEMA (0.847 g of methacrylate monomers) were added to 10 g PECH solution (1.8 g PECH). The mixture was stirred under argon for 10 min and then 0.034 g AIBN were added (4 wt.% of methacrylate monomers). The solution was stirred under argon for 15 min more. The solution was then injected in the mold previously described, which was then heated, according to a non-optimized curing, at 60°C for 16 h and at 100°C for 2 h.

IPNs with different PECH contents ranging from 37 to 90 wt.% were synthesized by keeping the same proportions between monomer, cross-linker and initiator for PHEMA network. All the materials were synthesized from 10 g PECH solution (18 wt.% in DMF) to which different HEMA and EGDMA amounts were added. All investigated PECH/PHEMA compositions are reported in weight ratio. The IPNs are noted PECH_X/PHEMA y/z IPN where y and z are the weight proportions in the dry final material of PECH and PHEMA, respectively. The index X of PECH corresponds to the DABCO molar proportion in the PECH network.

The PECH/PHEMA IPN films were unmolded at room temperature. The materials were dried under vacuum at 60 °C until constant weight. All the IPNs are homogeneous, rigid and transparent.

To verify that the cross-linking is complete, the amount of soluble fraction contained in the different materials was determined by Soxhlet extraction for 72 h with DMF, which is a good solvent of the different precursors (Table III - 1).

Table III - 1: Soluble fraction in DMF of PECH₁₀ / PHEMA IPNs and corresponding single networks

PECH₁₀/PHEMA IPN (w/w)	Soluble fraction (wt.%)
PHEMA network	8
37/63	7
43/57	9
50/50	7
68/32	5
PECH ₁₀ network	9

All the soluble fractions are lower than 9 wt.%. For example, the PECH₁₀/PHEMA 68/32 IPN contains 5 wt.% of soluble fraction, which confirms the correct cross-linking of these polymers. This fraction was identified by ¹H NMR as being linear PECH and PHEMA.

1.2. Evidence of True IPN Architecture

The nucleophilic substitution and the radical polymerization reactions were chosen in order to synthesize these IPNs, assuming that they are non-interfering processes, without chain transfer reactions of radicals at the C-Cl bond of PECH, for instance. To confirm that no grafting reaction occurs between both networks during the IPN synthesis, three different PECH₁₀/PHEMA 68/32 semi-IPNs were synthesized. If no grafting reaction occurs, the linear polymer can be extracted quantitatively with DMF from each semi-IPN.

These semi-IPNs were synthesized according to the same synthetic method as the IPNs. First, to obtain semi-IPNs in which PHEMA is linear, EGDMA was not added to the reaction mixture. The soluble fraction of the obtain material is equal to 32 wt.%, i.e. the weight proportion of HEMA included in the IPN synthesis. The soluble fraction has been identified by ¹³C NMR as linear PHEMA. This result shows that no grafting reaction occurred between the PHEMA and the PECH network. Second, a semi-IPN in which PECH is not crosslinked,

was synthesized. For that the cure at 100 °C was not carried out to avoid the cross-linking reaction of the PECH. The soluble fraction of this material is equal to 47 wt.% instead of the expected 62 wt.%. The soluble fraction was identified by ^{13}C NMR as linear PECH. This result suggests that the PECH modified with DABCO can partially cross-link at 60 °C. To verify this assumption, a similar semi-IPN has been synthesized with linear PECH non-modified with DABCO and the post-cure at 100 °C being maintained. In this case, the soluble fraction in DMF is equal to 72 wt.% confirming that linear PECH can be extracted from the PHEMA network.

As the linear polymers can be quantitatively extracted from semi-IPNs, we can conclude that both networks are formed independently without any side reaction. The PECH does not play the role of chain transfer agent in the free radical polymerization of HEMA. As a result the synthesized materials can be considered as IPNs.

1.3. Physicochemical characterizations of PECH₁₀/PHEMA IPNs

Before the characterizations, all samples were dried after synthesis under vacuum until constant weight. It is important to verify that the PECH based IPNs show suitable mechanical properties, i.e. they are easy to handle and show a significant resistance such that they can be placed over the electrode by pressing on the surface of air electrode without breaking or perforating. Indeed, this was the protocol used with these membranes before the optimization described in Chapter II § 4.1. Thus the IPNs have been characterized, in a first time, in dry state and in a second time, in water swollen state.

1.3.1. Thermomechanical properties

Storage modulus (E') and loss factor ($\tan\delta$) of the single networks and IPNs were measured by dynamic mechanical analysis (DMA) (Figure III - 2).

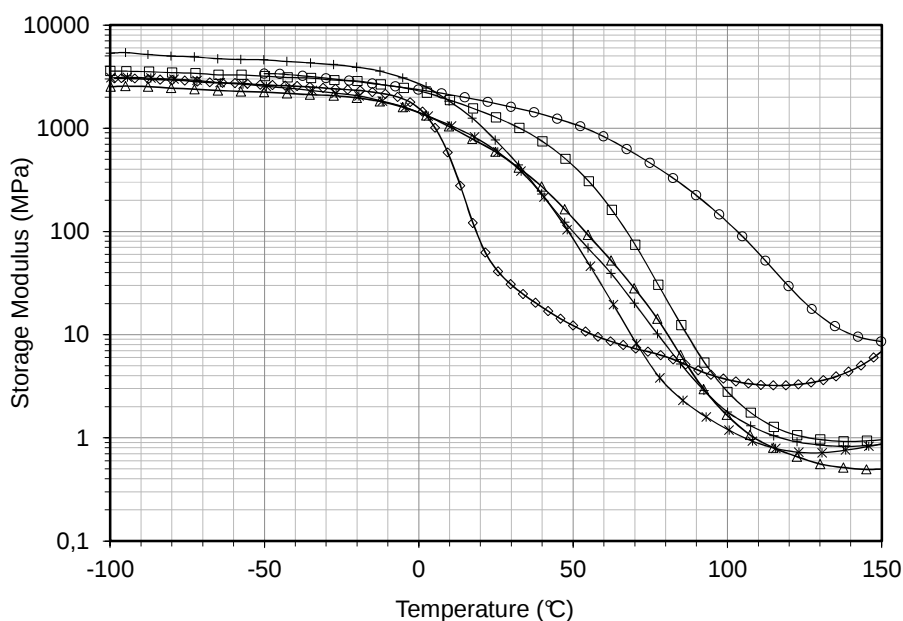


Figure III - 2: Storage modulus (E') versus temperature of single PECH ($\diamond$) and PHEMA ($\circ$) networks and PECH/PHEMA 37/63 ($\square$), 43/57 (Δ), 50/50 (+) and 68/32 (*) IPNs

As previously described (cf. Chapter II), single PECH₁₀ network displays a glassy plateau ($E' \approx 3$ GPa) at temperatures lower than 0 °C. Above this temperature, the storage modulus value decreases sharply and a rubbery plateau is reached at 50 °C ($E' = 2$ MPa). PHEMA network shows also a single mechanical relaxation. The glassy plateau extends up to 50 °C and the rubbery plateau is reached at 130 °C ($E' = 10$ MPa). At room temperature, PECH/PHEMA IPNs show a higher storage modulus than single PECH₁₀ network whatever their composition. Thus PECH network association with a PHEMA network as inside an IPN architecture leads to an improvement of the storage modulus (i.e. stiffness). In addition, the IPN storage modulus is higher than 1000 MPa up to 40 °C. This storage modulus value is comparable with that of PECH network supported by a polyamide support.³ Thus, IPN materials can be used from 0 to 40 °C without any change in its mechanical properties.

The $\tan\delta$ vs. temperature curves recorded on PECH₁₀/PHEMA IPNs and corresponding homopolymer networks are shown in Figure III - 3.

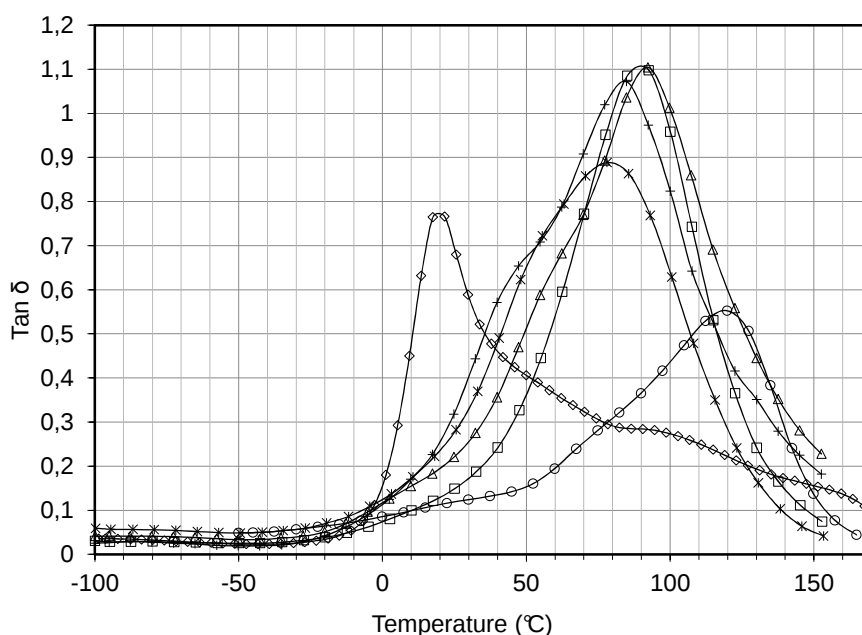


Figure III - 3: $\tan \delta$ versus temperature of single PECH_{10} ($\diamond$) and PHEMA ($\circ$) networks and PECH_{10} /PHEMA 37/63 ($\square$), 43/57 (Δ), 50/50 (+) and 68/32 (*) IPNs

The mechanical relaxation temperatures, located at the maximum of $\tan \delta$ peak (T_α), of single PECH_{10} and PHEMA networks are detected at 19 and 120 °C, respectively. All the IPNs show a main mechanical α -relaxation characterized by one $\tan \delta$ peak detected at intermediate temperature in between those of the two single networks. This T_α depends on the IPN composition. For example, PECH_{10} /PHEMA (68/32) IPN shows a mechanical relaxation at 77 °C, while the α -relaxation of PECH_{10} /PHEMA 50/50, 37/63, 43/57 IPNs occur at 84, 88, and 93 °C, respectively. Thus, when the PHEMA proportion is above 50 wt.% in the IPN, the relaxation temperature T_α approaches that of the PHEMA single network. The presence of a main mechanical relaxation temperature confirms a correct interpenetration of both networks inside the IPN architecture. In fact, if that was not the case, two mechanical relaxations would be detected at temperatures near those of the single networks.

1.3.2. Thermogravimetric Analysis (TGA)

The thermal stabilities of the IPN membranes were evaluated by TGA measurements. This property is of interest for the battery operation, as its temperature in an operating vehicle can reach 50 °C, or even 60 °C in hot climates. Figure III - 4 shows the thermograms recorded on single PECH_{10} and PHEMA networks and on IPNs containing different PECH_{10} weight compositions.

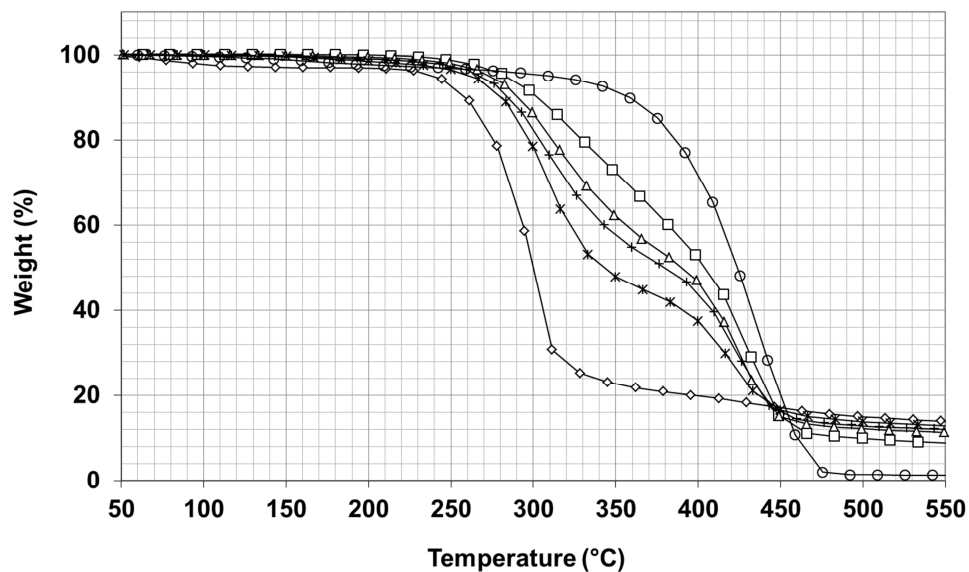


Figure III - 4: TGA thermograms recorded on single PECH₁₀($\diamond$), and PHEMA($\circ$) networks and PECH₁₀/PHEMA 37/63 ($\square$), 43/57 (Δ), 50/50(+), and 68/32 (x) IPNs under argon atmosphere. Heating rate: 20 °C/min.

The main weight loss of the PECH₁₀ network starts at 270 °C up to 320 °C. This thermal degradation in a single step has been associated with the loss of chlorine radicals and production of HCl.¹⁰ This result is similar to that obtained by Stoica et al.³ The single PHEMA network presents a one-step degradation starting at 330 °C indicating a higher thermal stability compared with that of single PECH₁₀ network. The different IPNs show an intermediate behavior between those of the PECH₁₀ and PHEMA networks. IPNs exhibit a first thermal degradation at 250 °C which can be assigned to the PECH₁₀ network degradation. The second thermal degradation is detected at 350 °C and can be assigned to that of the PHEMA network. Therefore, the degradation temperature (5 wt.% weight loss) increases from 270 to 300 °C when PHEMA proportion increases from 32 to 63 wt.%. The higher the PHEMA proportion, the higher the degradation temperature. Thus, the incorporation of the PHEMA network inside a PECH network increases also its thermal stability. In addition, the measurements carried out on the different IPNs deviate from the thermogravimetric curve calculated as the weighted average of those of the single PECH₁₀ and PHEMA networks. Thus, PECH₁₀/PHEMA IPNs cannot be considered as a polymer blend in which the networks would be independent: interactions exist between both associated networks.

These different materials have been then characterized in wet state because of their use in aqueous electrolyte environment.

1.3.3. Water Uptake

The maximum water uptake (WU) at 20 °C of the different PECH₁₀ based IPNs as a function of the PECH proportion is shown in Figure III - 5. This WU is measured after 24 h of immersion in deionized water.

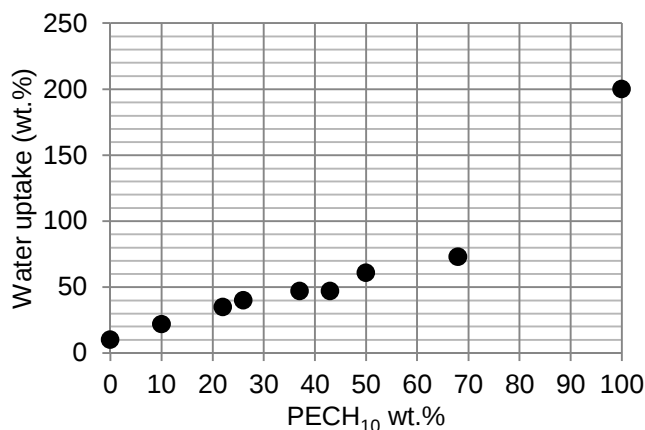


Figure III - 5: Water uptake of the PECH₁₀ /PHEMA IPNs as a function of the PECH₁₀ weight proportion at 20 °C

Single PHEMA and PECH₁₀ networks show water uptake of 10 and 200 %, respectively. Water uptake of IPNs varies linearly from 26 to 73 % when the PECH weight proportion increases from 10 to 68 wt.%. The total amount of water in a swollen IPN is lower than the weight average of water that can be absorbed by each network separately. This behavior highlights that, as expected, the PHEMA neutral network limits the water swelling of the PECH₁₀ network in the IPN architecture. That is possible only if both phases, each rich in one of the polymers, are co-continuous on the whole material.

1.3.4. Storage and Loss Shear Moduli of Water Swollen IPNs

In order to quantify the mechanical resistance of the materials in the swollen state, as close as possible to the conditions of the networks in the electrolyte, the mechanical strength of the wet materials, storage (G') and loss (G'') shear moduli were measured at 25 °C. The single networks and PECH₁₀/PHEMA IPNs are in Cl⁻ form in the maximum swollen state. All the signals are stable on the studied frequency range (0.1 – 100 Hz) and storage and loss moduli measured at 1 Hz are reported in Figure III - 6.

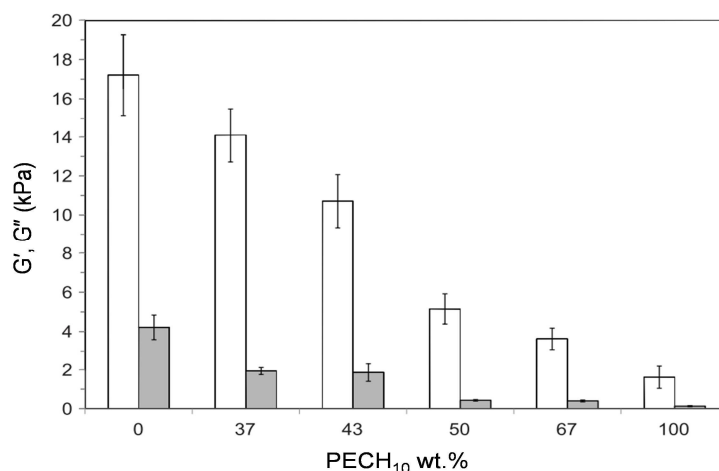


Figure III - 6: Storage (G' , white bar) and loss (G'' , grey bar) shear moduli of water swollen single PECH₁₀ and PHEMA networks and PECH₁₀/PHEMA 37/63, 43/57, 50/50, and 67/33 IPNs.

The loss moduli of the swollen PHEMA and PECH₁₀ networks are equal to 4.2 and 0.1 kPa, respectively. The IPN loss moduli are in between those values and decrease with the PECH weight proportion. Whatever the membrane composition, the storage modulus is higher than the respective loss modulus that is characteristic of a solid viscoelastic mechanical behavior. The G' values vary from 17.2 to 1.6 kPa with the PECH proportion ranging from 0 to 100 wt.%. The mechanical stiffness is consistent with their water amount absorbed, which is an important parameter related to intrinsic conductivity performance, as well. If the amount of water is too high, mechanical performance is notably impaired. On the other hand, an insufficient water amount would produce a weak ionic conductivity, since water is essential for anion mobility. The ionic conductivity of the different materials has been thus measured then.

1.3.5. Ion Conductivity

The ion conductivity values of water swollen IPNs with various PECH weight proportions were measured (Figure III - 7). The materials were tested in their Cl^- and OH^- form. For the ionic exchange the materials were immersed in 1 M KOH for 24 h, then rinsed in water until neutral pH, and equilibrated in water for 24 hours before the test.

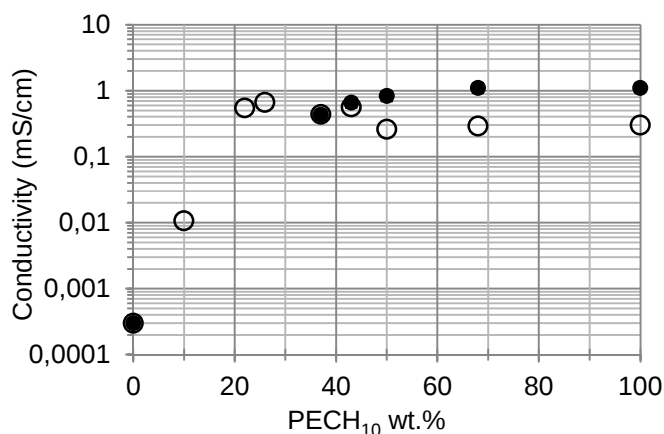


Figure III - 7: Ionic conductivity of the water swollen PECH₁₀ based IPNs as a function of the weight proportion of PECH in Cl⁻ (○) and OH⁻ (●) forms. T=20 °C.

As expected, the PHEMA network is not an ion conducting material ($\sigma = 3 \cdot 10^{-4}$ mS/cm). The anionic conductivity of the single PECH₁₀ network in the fully hydrated state and OH⁻ form is 1 mS/cm (WU = 200 wt.%). Conductivities of the PECH₁₀/PHEMA IPNs depend on the PECH weight proportion. The conductivity is lower than 0.5 mS/cm when the PECH proportion is lower than 20 wt.%, which corresponds to a threshold percolation value. This is confirmed by the conductivity values of the networks in Cl⁻ form. For higher PECH proportions, all the IPNs have conductivity values close to 1 mS/cm, not depending on the IPN composition. Accordingly, for these compositions, the PECH₁₀ network forms a continuous phase in the entire material. For the intended application the membranes must show the highest possible conductivity, and thus, for attaining a conductivity of 1 mS/cm the IPNs must contain at least 50 wt.% in PECH.

However, these anionic conductivity values are ten times lower than the highest values generally reported for quaternized polymer membranes. Indeed, Slade et Varcoe¹¹ reported a conductivity of 10 mS/cm for quaternized poly(vinylbenzyl chloride) membrane. Anionic conductivities of 7 mS/cm were also reported for cross-linked quaternized poly(vinyl alcohol)¹² and nearly 10 mS/cm for quaternized chitosan membranes.¹³ The difference between the conductivity values of PECH-based IPN and other cross-linked quaternized polymer membranes can be explained by a lower water uptake of the IPNs. For example, the cross-linked quaternized poly(vinyl alcohol) shows a water uptake of 240 % instead of less than 100 % for the PECH-based IPNs, explaining the better ionic mobility.

Additionally, the measured IEC of the PECH₁₀/PHEMA 68/32 IPN was 0.5 meq./g which is consistent with the measured IEC of the PECH₁₀ network 0.8 meq./g (cf. Chapter II § 2.3.2). Furthermore, the IEC of this PECH₁₀/PHEMA 68/32 IPN is lower than the 1.2 meq./g IEC reported for quaternized poly(vinylbenzyl chloride) membranes.¹²

1.3.6. Transport Number

The anionic transport number (t^-) delivers information on the ionic selectivity of a membrane under an electric field. The t^- values of PECH₁₀/PHEMA IPNs in OH⁻ form are reported in Table III - 2. For these measurements, all the samples have been synthesized by molding reaction, have been dried and then water swollen.

Table III - 2: Anionic transport number of PECH₁₀/PHEMA IPNs

PECH₁₀ / PHEMA IPN (w/w)	t^- (OH⁻ transport number)
PHEMA network	0.64
37/63	0.84
43/57	0.86
50/50	0.87
68/32	0.90
PECH network	0.80

The single PECH₁₀ network shows a hydroxide transport number of 0.80 (cf. Chapter II § 2.3.5). Whereas the PECH network can be considered as selective towards cations, the PHEMA network is less selective ($t^- = 0.64$). This value is higher than the expected for a non-selective network (0.50) probably due to the effect of OH groups in PHEMA that can have a slight complexing effect on cations. When the PHEMA network is included into the IPN architecture, it induces a significant increase in the IPN selectivity compared with that of single PECH₁₀ network synthesized under the same conditions. Indeed, the PECH₁₀/PHEMA IPNs are characterized by a transport number value ranging from 0.84 to 0.90 indicating that the ionic transport inside the IPN is mainly anionic. This improvement can be explained by the lower water uptake of the IPNs compared with that of the single PECH network. Thus, the alkaline ions (K⁺, Li⁺, Na⁺, etc.) of an electrolyte will be blocked, or at least their diffusion would be considerably retarded by the IPN placed over the air electrode surface.

For the application pursued, it is important for the ionic conductivity to be as high as possible, but with a limited water uptake to preserve the selectivity of the membrane. Therefore, from the ex-situ characterizations, the PECH₁₀/PHEMA 68/32 IPN which has a t^- value of 0.90, a water uptake of less than 80 % and a conductivity of 1.1 mS/cm appears as an appropriate candidate.

1.4. Electrochemical Characterization of PECH₁₀/PHEMA IPNs MEA

For the first electrochemical characterization of these IPNs, the membranes were synthesized between two glass plates (cf. chapter II § 2.2.2), dried after synthesis, were assembled over the air electrode without membrane solution, as follows. The water swollen membranes in OH⁻ form (100-150 µm) were pressed at 3 bar for 30 s on the catalyst side of the air electrode. Then, the MEA was placed between two Teflon[®] plates which were pressed at 3 bars at 60 °C for 30 min. This procedure was developed prior to the optimization of the PECH₁₀ network MEA (Chapter II § 5.1). The optimized procedure will be presented in the next part of this chapter.

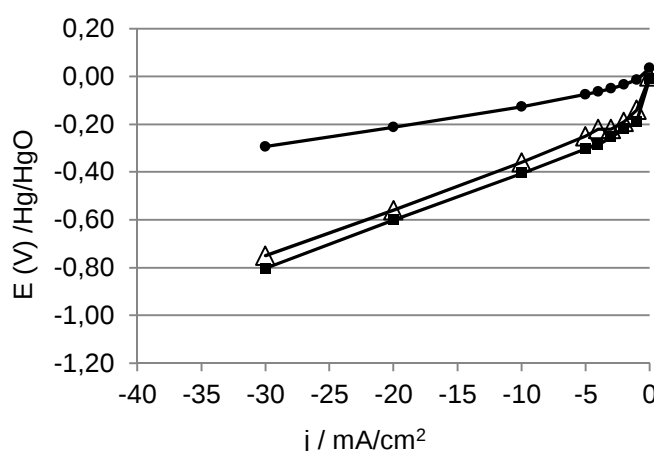


Figure III - 8: Polarization curves recorded on a bare electrode (●) and MEA with a PECH₁₀ network (Δ) and PECH₁₀/PHEMA 68/32 IPN (■). Electrolyte: 5 M LiOH, room temperature, untreated air, atmospheric pressure, reference electrode Hg/HgO.

Figure III - 8 shows the polarization curves of the air-electrode modified or not with a PECH₁₀ network and a PECH₁₀/PHEMA 68/32 IPN (polarization curves are identical whatever the IPN composition). The modified electrode potentials are about -100 mV/(Hg/HgO) at current densities of -1 mA/cm² and reach a value of about -800 mV at -30 mA/cm² indicating a similar ohmic loss when the electrode is modified with PECH₁₀ network or IPN.

Finally, the polarization vs. time (stability) curves of the MEAs were recorded in cycling, 10 h at OCV and 10 h discharge at -10 mA/cm^2 (Figure III - 9). We must note that the polarization of the MEA is further reduced after 10 h at rest in the half cell (the first part of the stability test). For this reason, during the first discharge in the stability test a polarization between -130 and -190 mV is measured, instead of about -400 mV on the polarization curves.

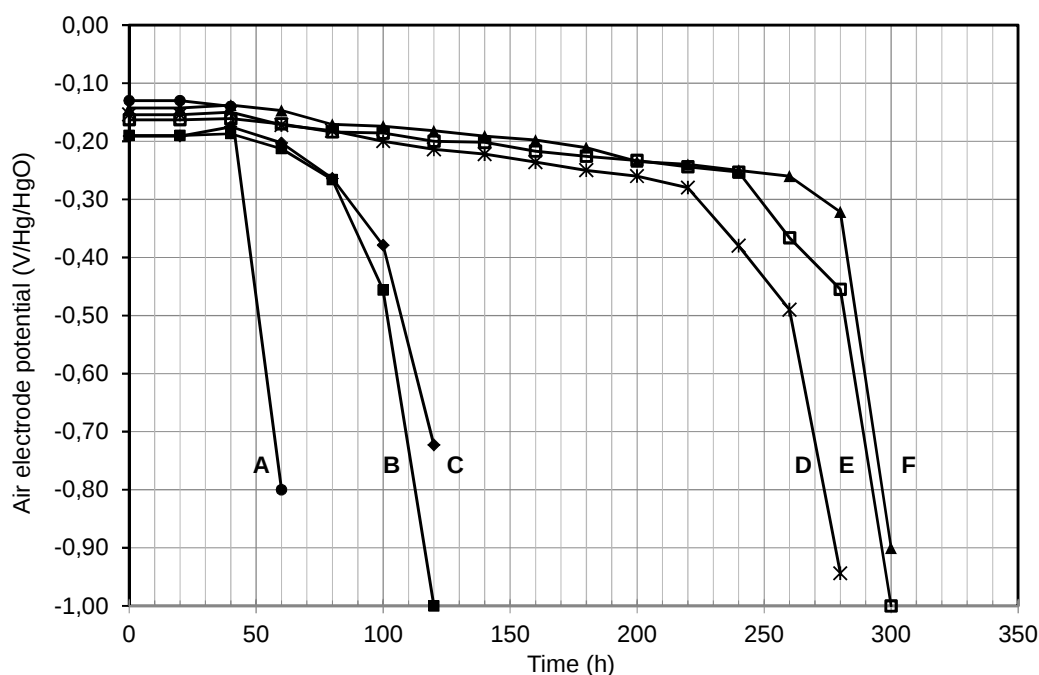


Figure III - 9: Potential at discharge - time curves recorded on (● - A) bare electrode, (◆ - B) air electrode/PECH₁₀ network assembly, air electrode/PECH₁₀/PHEMA 37/63 (■ - C), 43/57 (X - D) and 68/32 (▲ - F) and 90/10 (□ - E) IPNs assemblies

The stability curve recorded on PECH₁₀ network MEA shows that, as seen in Chapter II, the presence of the single PECH₁₀ network increases the air electrode stability under untreated air to about 100 h, which is lower than that obtained when PECH network is directly synthesized over the electrode (160 h – cf. Chapter II § 4.1.4). The PECH₁₀/PHEMA IPNs however, causes a much important increase in the stability of the MEA stability. The results for PECH₁₀/PHEMA IPNs of different compositions are summarized in Figure III - 10.

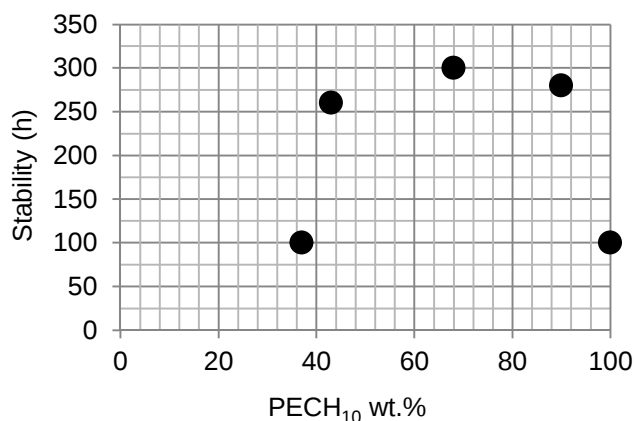


Figure III - 10: Time at which the assembly potential is higher than -400 mV/(Hg/HgO) vs. PECH weight proportion in the IPN. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, untreated air, atmospheric pressure. Reference electrode: Hg/HgO.

Accordingly, even if the polarization curves are similar, the stabilities of the MEAs depend strongly on the IPN composition. Thus, PECH₁₀/PHEMA 68/32 IPN increases the stability of the air electrode from 50 to approximately 300 h. One can note that this IPN shows the highest conductivity of 1 mS/cm, and the highest transport number of 0.90.

At the end of the polarization test, the half-cell was disassembled and it was found that the membrane was mechanically damaged and detached from the electrode (Figure III - 11).



Figure III - 11: PECH₁₀/PHEMA 68/32 IPN MEA after 300 h stability test in half-cell

These results have been published in the Journal of Power Sources.¹⁴

As for the PECH₁₀ network MEA described in chapter II, to obtain a better interface between the electrode and the polymer membrane, the later has been directly synthesized over the electrode by reaction molding to form the MEA to create a better interface. The MEA is then

immersed in KOH 1M solution to exchange synthesis solvent and counter-ions. This method should reduce volume variations that cause physical damage to the membrane or its detachment from the electrode. We decided to optimize the assembly of PECH₁₀/PHEMA 68/32 IPN which showed the highest stability and an adequate balance of properties among the different composition tested.

2. Optimization of PECH₁₅/PHEMA 68/32 IPN Synthesis

As for the single PECH network, we have modified the DABCO content to increase the number of ionic sites and the PECH network cross-linking, and the method for assembling the membrane over the air electrode according to the optimized procedure (cf. Chapter II § 4.1.2).

2.1. Experimental

The IPNs in which the DABCO content is increased have been synthesized according to the same protocol as the previous IPNs but additional DABCO was added to attain 15 mol %, which was found to be an appropriate concentration in previous chapter.

10 g of PECH solution (1.8 g PECH = 17.3 mmol DABCO already grafted) were mixed with 0.097 g DABCO (8.67 mmol) and stirred until complete dissolution. 0.089 g EGDMA and 0.804 g HEMA were added. The mixture was stirred under argon for 10 min and then 0.036 g AIBN was added (4 wt.% of methacrylate monomers). The solution was stirred under argon for 10 min and the solution was injected in a mold made of silylated glass plates separated by a 500 μ m thick Teflon[®] gasket.

In these new syntheses, we chose to carry out the first step of the IPN synthesis at 70 °C rather than 60 °C to accelerate the rate of the PHEMA network formation and decrease the synthesis time (6 h instead of 18 h). This is possible because the AIBN half-life ($t_{1/2}$) is 6 h at 70 °C and 23 h at 60 °C (in benzene).¹⁵ The assembly was then heated at 70 °C for 2 h and at 100 °C for 4 h. Under these new conditions, the soluble content in PECH₁₅/PHEMA 68/32 IPN was found to be 3 wt.%, equivalent to the 5 wt.% for the previous conditions, and the membranes can be also considered as correctly crosslinked.

The storage moduli vs. temperature for PECH₁₀/PHEMA 68/32 IPNs synthesized according both cure programs and for PECH₁₅/PHEMA 68/32 IPN are compared in Figure III - 12.

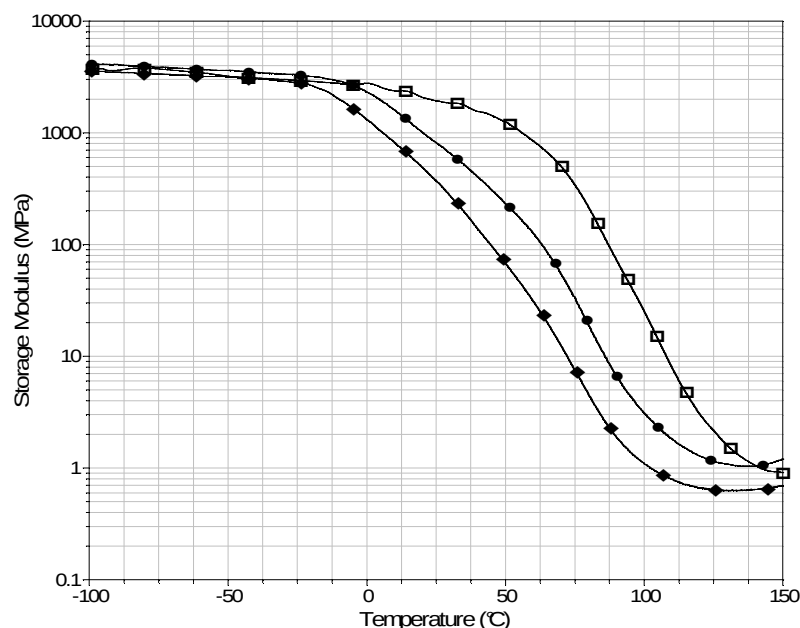


Figure III - 12: Storage modulus (E') versus temperature of PECH₁₀/PHEMA 68/32 IPN synthesized at 70 °C for 2 h and 100°C for 4 h (●) and at 60 °C for 16 h and 100°C for 4 h (◆), and PECH₁₅/PHEMA 68/32 IPN synthesized at 70 °C for 2 h and 100°C for 4 h (□).

With the former protocol, PECH₁₀/PHEMA 68/32 IPN is glassy below -25°C before a single relaxation occurs with storage modulus decrease until 0.6 MPa at 125°C. With the new protocol, PECH₁₀/PHEMA 68/32 IPN is in glassy state ($E' \approx 3$ GPa) at temperatures lower than 0 °C. Above this temperature, the storage modulus values decrease sharply and a rubbery plateau is reached at 125 °C ($E' \approx 1$ MPa). The change in the thermal program causes a 2-fold increase in the conservation modulus at temperatures between the glassy and the rubbery plateau. PECH₁₅/PHEMA 68/32 IPN shows also a single mechanical relaxation, the glassy plateau extends up to 10 °C and the rubbery plateau is reached at 140 °C ($E' = 1$ MPa). The PECH₁₅/PHEMA 68/32 IPN shows a higher storage modulus than the PECH₁₀/PHEMA 68/32 IPN.

The corresponding $\tan\delta$ vs. temperature curves recorded for different IPNs are shown in Figure III - 13.

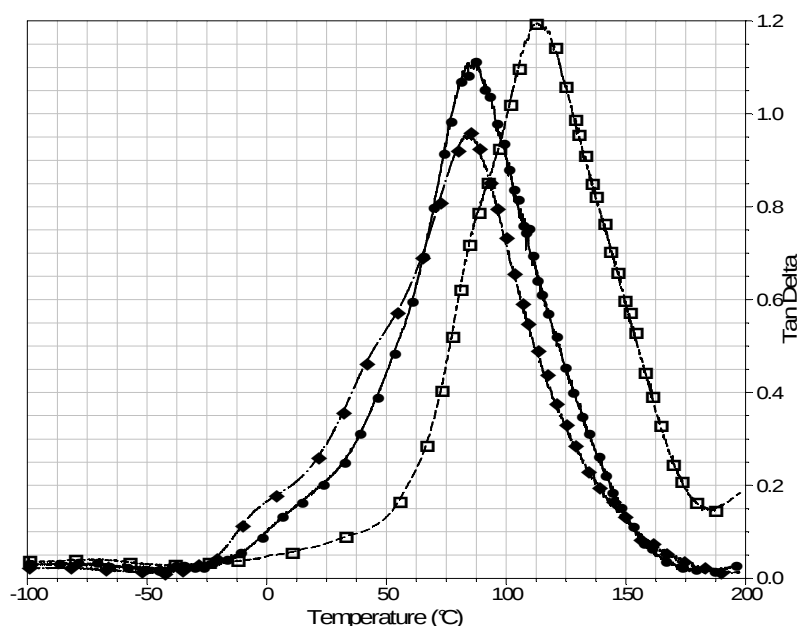


Figure III - 13: $\tan\delta$ versus temperature of PECH₁₀/PHEMA 68/32 IPN synthesized at 70 °C for 2 h and 100°C for 4 h (●), and at 60 °C for 16 h and 100°C for 2 h (◆), and PECH₁₅/PHEMA 68/32 IPN synthesized at 70 °C for 2 h and 100°C for 4 h (□).

The presence of a main mechanical relaxation temperature confirms a correct interpenetration of both networks inside the IPN architecture whatever the protocol. With the former protocol, the single mechanical relaxation of the PECH₁₀/PHEMA 68/32 IPN, displayed by the modulus decrease, is associated with a single large $\tan\delta$ peak centered on 85°C. With the new protocol (synthesis at 70 °C), the mechanical relaxation temperatures (T_α) of PECH₁₀/PHEMA 68/32 IPN was unchanged but the $\tan\delta$ peak is spreading on smaller temperature range witnessing of a more homogeneous cross-linking density. Simultaneously, the $\tan\delta$ peak intensity is increased from 0.95 to 1.10. These slight modifications witness of a slight change in the IPN morphology according the synthesis protocol. When the DABCO proportion is increased from 10 to 15 mol % in the PECH₁₅/PHEMA 68/32 IPN, the mechanical relaxation temperatures (T_α) is shifted from 85 to 110 °C. The shift to higher temperature points out a higher crosslinking degree. This analysis confirms the importance of the development of the new protocol. In addition, the increase in the DABCO content appears, as expected, to increase the crosslink density of the network.

For the next characterizations, the PECH₁₅/PHEMA 68/32 IPN was immersed in a 1 M KOH solution just after synthesis to exchange the counterion and synthesis solvent, and then rinsed and equilibrated in water. If necessary, it is then dried for the physicochemical characterizations.

2.2. Physicochemical Characterization of PECH₁₅/PHEMA 68/32 IPN

The PECH₁₅/PHEMA (68/32) IPN presents a water uptake of 1000 wt.%, while the WU of the single PECH₁₅ network is 2200 wt.% (cf. Chapter II. § 4.3). Thus, as previously, the introduction of only 32 wt.% PHEMA in an IPN architecture still reduces the WU by 2. However, the present PECH₁₅/PHEMA 68/32 IPN swells more in water than the corresponding PECH₁₀/PHEMA 68/32 IPN (800 wt.%). The same effect of the process synthesis has been observed on the water uptake of the PECH network (cf Chapter II).

IEC was found to be 1.3 meq./g, as expected for an IPN with 68 wt.% PECH₁₅ (IEC PECH₁₅ = 2.0 meq./g). Next, the $\bar{t}$ was measured for the water swollen PECH₁₅/PHEMA 68/32 IPN. A $\bar{t}$ of 0.74 was found, while it is 0.79 for the PECH₁₅ network synthesized under the same conditions. Thus, contrarily to the previous synthesis process, the association of the PHEMA network to the PECH network leads to a slight decrease of membrane selectivity.

The ionic conductivity of the PECH₁₅/PHEMA IPN is 2 mS/cm, twice the conductivity of the PECH₁₅ network. This conductivity increase while the polyelectrolyte in the material is lower can also be explained by the limited swelling. The charges are thus twice lower diluted.

Finally, the chemical stability of a PECH₁₅/PHEMA 68/32 IPN was tested by immersion in 5 M LiOH at 50 °C to accelerate the chemical degradation process and was compared with a that of a PECH₁₅ network in Figure III - 14 (cf. Chapter II - § 3.6).

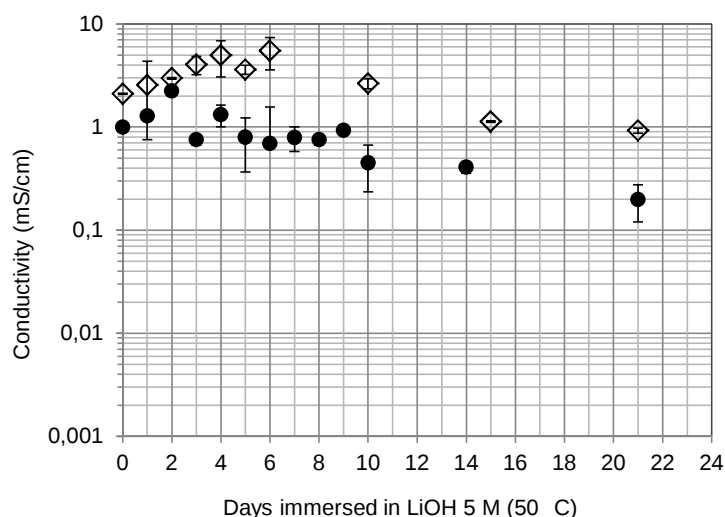


Figure III - 14: Conductivity versus immersion time in 5 M LiOH at 50 °C for a single PECH₁₅ network (●) and a PECH₁₅/PHEMA 68/32 IPN (◇)

The non-aged IPN has a conductivity of 2 mS/cm. The conductivity increases slightly for the first 6 days. This increase could be due to a more efficient counterion exchange in the material. In the starting material the counterion exchange would be incomplete, and only after 6 days a complete exchange and a maximum conductivity is attained. The conductivity is about of the same order of magnitude for 10 days. After 15 days of immersion, a conductivity of 1 mS/cm is still obtained. Consequently, there has not been significant degradation of the ionic sites in the IPN under those conditions. Inversely, the single PECH₁₅ network shows a drop in conductivity after 10 days of immersion, and we can conclude that, as expected, the IPN architecture is protecting the PECH network from degradation. Visual observation of the membranes after 10 days of ageing test (Figure III - 15) shows a color change but the physical integrity of the two membranes is maintained.

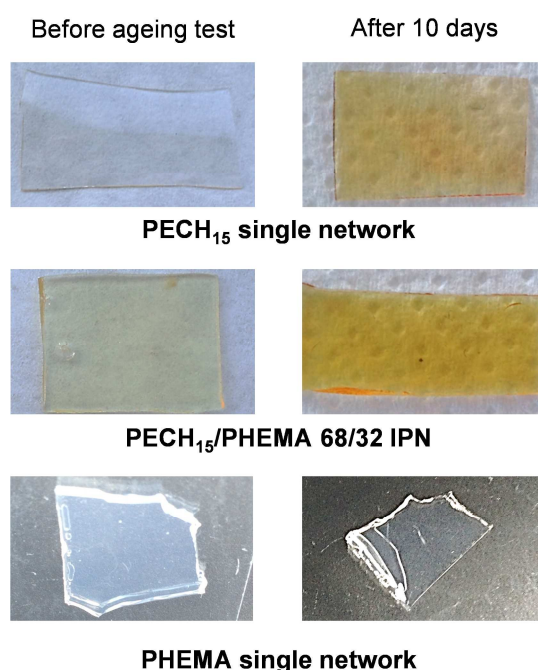


Figure III - 15: Single PECH₁₅ and PHEMA networks and PECH₁₅/PHEMA 68/32 IPNs before and after 10 days of ageing in 5 M LiOH at 50 °C

Additionally, the PHEMA single network was not visually altered during the test. At the end of the 21 days in 5 M LiOH, the PHEMA network maintained its integrity and did not showed any color change. The yellow color observed on the aged IPN is thus due to the PECH network.

3. Optimization of the PECH/PHEMA IPN Electrode Assembly

In the end of chapter II, we concluded that the best electrochemical properties were obtained for the PECH₁₅ network membrane directly synthesized over the electrode, and that drying of the membrane should be avoided. To obtain the best performances, the MEA was immersed immediately in 1 M KOH to counterion exchange before the test in half cell. This procedure was used for the following characterizations.

3.1. Experimental

All syntheses were made by pouring the PECH_x/PHEMA 68/32 IPN reaction solution over the catalyst side of the air electrode and placed between two silylated glass plates as previously described (cf. Chapter II § 4.1.2). The thickness of the membrane was fixed at 500 μm by a Teflon[®] gasket. After synthesis, the MEA was unmolded and immersed in 1 M KOH for at least 3 days before the half-cell test.

3.2. PECH/PHEMA IPNs MEA Characterization

The polarization curves of PECH₁₀/PHEMA 68/32 and PECH₁₅/PHEMA 68/32 IPN are shown in Figure III - 16, and were compared with a single PECH₁₀/PHEMA 68/32 IPN synthesized *ex-situ* and assembled after drying over the air electrode (cf. § 1.4).

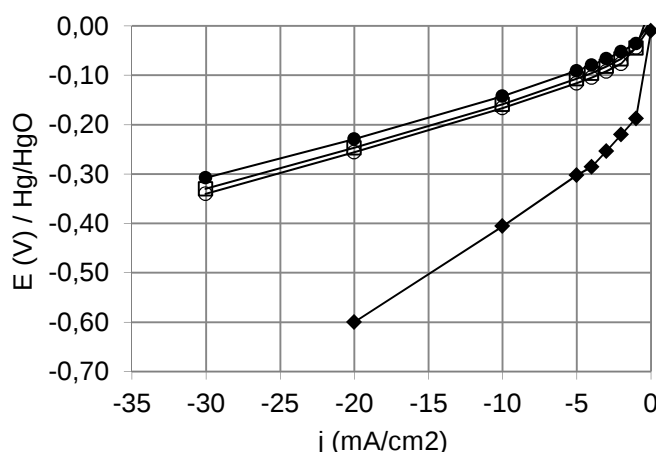


Figure III - 16: Potential-current density curves recorded on bare electrode (●), *in-situ* PECH₁₀/PHEMA 68/32 IPN (□), and PECH₁₅/PHEMA 68/32 IPN (○) and *ex-situ* PECH₁₀/PHEMA 68/32 IPN (◆) modified electrodes. Electrolyte: 5 M LiOH. Room temperature, atmospheric pressure. Reference electrode: Hg/HgO

When the polymer membranes are synthesized directly over the electrode (*in-situ*), the polarization of the MEA is lower than for the *ex-situ* synthesis. At -10 mA/cm^2 the polarization diminished from $-400 \text{ mV}/(\text{Hg}/\text{HgO})$ for the *ex-situ* $\text{PECH}_{10}/\text{PHEMA}$ 68/32 IPN to -160 mV for the $\text{PECH}_{10}/\text{PHEMA}$ 68/32 IPNs, which is closer to the value of the bare electrode (-140 mV). This reduction in polarization can be explained by the better ionic contact obtained when the network is synthesized directly over the electrode, as demonstrated for the PECH_{10} network (Chapter II § 4.1 and Figure II-29). These results confirm the choice of the *in-situ* assembly method. Furthermore, a polarization close to that of the bare electrode is also obtained. Thus the interest of the $\text{PECH}_{15}/\text{PHEMA}$ 68/32 IPN is shown. All networks further presented were directly synthesized over the electrode by reaction molding.

Afterward, the stability of these MEAs was tested and the stability curves are compared in Figure III - 17.

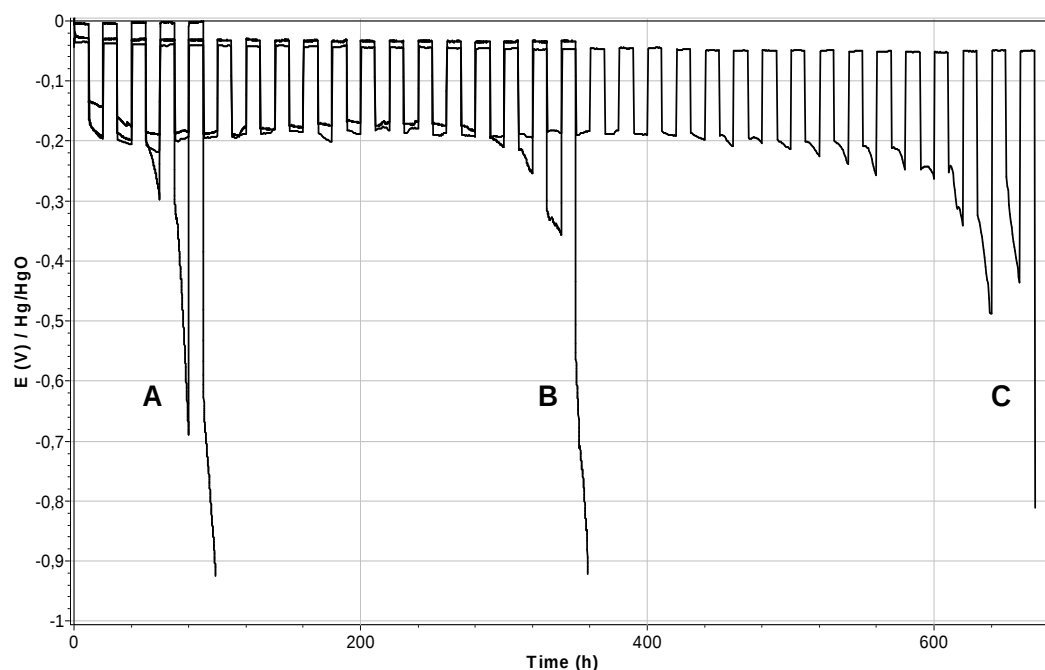


Figure III - 17: Potential vs. time curves for the non-modified electrode (A), $\text{PECH}_{10}/\text{PHEMA}$ 68/32 (B) and $\text{PECH}_{15}/\text{PHEMA}$ 68/32 (C) IPN modified electrodes. Cycle: OCV for 10 h and -10 mA/cm^2 for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure, reference electrode: Hg/HgO

The electrode modified with a $\text{PECH}_{10}/\text{PHEMA}$ 68/32 IPN shows a polarization during cycling lower than -200 mV and a stability of 350 h, compared to 50 h for the non-modified electrode and to 160 h for the PECH_{10} modified electrode. By the use of the IPN, the air-electrode stability has been increased to 350 h when the polymer membrane is directly

synthesized over the electrode. This 350 h stability represents a slight increase in the stability obtained when the IPN membrane is synthesized *ex-situ* and later assembled over the air electrode (300 h).

In addition, when the DABCO concentration was increased to 15 mol %, the stability of the air electrode modified with the PECH₁₅/PHEMA 68/32 IPN was increased to 650 h. This stability is twice that of the electrode modified with the single PECH₁₅ network, and also twice that of the polymer membrane is PECH₁₀/PHEMA 68/32 IPN. This improvement in the stability of the modified electrode can be explained by the optimization of the DABCO content, and also of the interface electrode-membrane. Indeed, after the stability test, no visible damage or delamination of the membrane is observed (Figure III - 18). We must also note that the membrane has become yellow at the end of the test. This is an indication of the membrane ageing in LiOH, as observed in the accelerated ageing test in 5 M LiOH at 50 °C (§ 2.2).

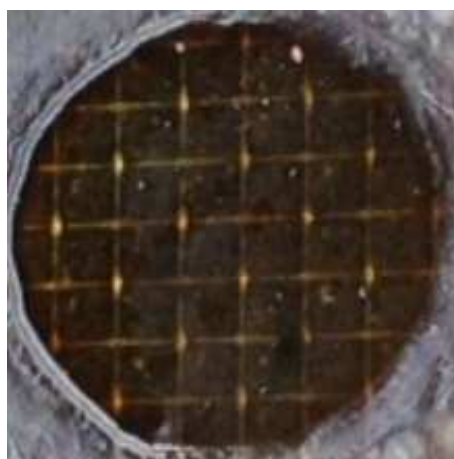


Figure III - 18: Photography of PECH₁₅/PHEMA 68/32 IPN MEA after 650 h stability test in half-cell

To confirm the role of carbonate precipitation in the loss of stability of the air electrode, we removed any possible precipitate from the tested MEA. For that, the MEA was rinsed in a large excess of deionized water by immersing it overnight and changing the water daily during two weeks. The same procedure was followed for a non-modified aged electrode as a reference. No visible change in the electrodes was observed after rinsing. The rinsed electrodes were assembled in half cell and their stability was tested again (Figure III - 19).

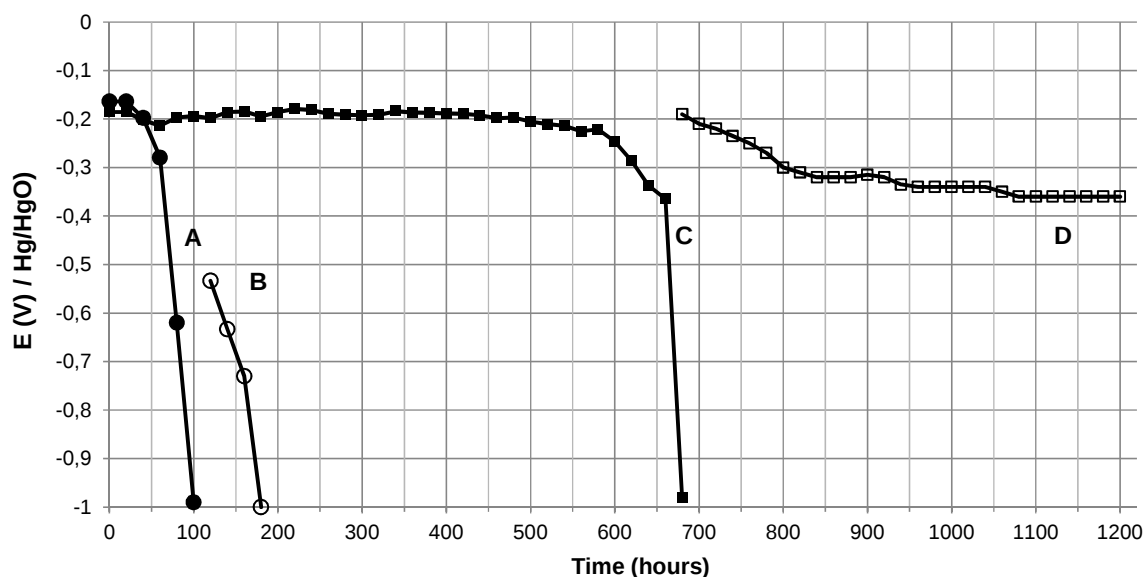


Figure III - 19: First stability curves for the non-modified electrode (A) and PECH₁₅/PHEMA 68/32 IPN MEA(C) and stability curves after the rinsing for the non-modified electrode (B) and IPN MEA (D). Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO

The stability of the non-modified electrode is not recovered by rinsing it after the end of the stability test, suggesting an irreversible damage on the electrode. This can be due to the modification or deformation of the catalytic layer of the electrode by the precipitate, as was observed by Rolla et al.¹⁶ Inversely, the IPN modified electrode, recovers its capacity to be cycled and is stable for more than 600 additional hours, despite a higher polarization at the end of the first stability test. This confirms that the precipitation of lithium carbonate causes the loss of stability of the modified air electrode, and suggests that the membrane is protecting the electrode from irreversible damage by the precipitate.

4. Conclusion

The results obtained in this chapter show clearly the interest of polymer materials of IPN architecture compared to single polymer networks. The original combination of PECH and PHEMA networks inside an interpenetrating polymer network architecture decrease significantly the PECH polyelectrolyte swelling while preserving a good hydroxide conductivity and anion selectivity. The chemical stability of the polyelectrolyte is also improved by the IPN architecture.

An increase in the DABCO content produces an improvement in the conductivity of the membranes. The measured values appear adequate for the projected application as anion

exchange membrane. Therefore, these membranes have all the characteristics necessary for an anion conducting membrane that could serve to protect the air electrode working in LiOH electrolyte. Under the condition imposed by the lithium-air battery, the longest obtained stability of the air electrode is 650 h when it is modified with a PECH₁₅/PHEMA 68/32 IPN.

The results presented in this chapter have allowed us to confirm that the air electrode can be effectively protected from carbonation by a polymer membrane. This is even more effective than the polymer membrane is chemically resistant to the concentrated lithium hydroxide in which it is immersed. The importance of the IPN architecture compared to single networks has also been shown. Indeed, by limiting the water uptake of the polyelectrolyte network in alkaline medium, the neutral network structure increases the chemical stability of the former. Moreover, the direct synthesis process on the electrode, producing a very good interface between the membrane and the electrode, has also shown effectiveness in the synthesis of IPN. Finally, when the electrode is protected by an IPN membrane, the degradation process is reversible and the assembly can be regenerated, which is not possible on the bare electrode.

To further increase the chemical stability of the polymer membrane and thus that of the modified air electrode, a fluorinated polymer was used as partner network for the PECH. These new associations will be discussed in the next chapter.

5. References

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Chapter IV:
Synthesis of Hydrogenated / Fluorinated
Interpenetrating Polymer Networks

To improve the physicochemical characteristics (mainly selectivity and chemical resistance) of the PECH based interpenetrating polymer networks (IPNs), leading to the increase of the stability in discharge of the IPN-modified air electrode, the association of a polyelectrolyte network with a neutral fluorinated one appears as an interesting strategy. Indeed, it is well known that fluorinated compounds exhibit exceptionally high chemical and thermal stabilities imparted by the strong C-F bond (≈ 513 kJ/mol vs. 347-356 kJ/mol for C-H bond),^{1,2} and the shielding of the polymer backbone by the nonbonding electrons from the fluorine atoms.³ Furthermore, as we have shown in previous chapters, it was preferable to limit the swelling of the protective membrane in order to have better stability and better chemical resistance of the latter. Fluorinated compounds swell less in aqueous solutions than their hydrocarbon counterparts, so they appear as ideal candidates. However, as detailed in Chapter I, a large part of the current research on new polyelectrolyte materials focuses on hydrogenated linear or crosslinked polymers. No hydroxide conductive hydrogenated/fluorinated IPN or semi-IPN have, to our best knowledge, been reported in the literature for anion exchange membrane application. This could be due to the lack of commercial available monomers and to the difficulty in the synthesis of cross-linkable fluorinated precursors. Furthermore, to associate a fluorinated compound with a polyelectrolyte, while retaining the conductivity of the latter on the whole material is a real challenge. Our laboratory has developed an expertise in the synthesis of proton-conducting based IPNs with fluoropolymer-based networks for fuel cell membranes application.^{4,5,6} These original fuel cell membranes show performances comparable to those of commercially available membranes.

In this work, we propose the innovative use of a perfluoropolyether (PFPE) as partner network for the PECH. Solvay Specialty Polymers develops a PFPE product line specifically for use as reactive monomers for polymer modification, Fluorolink[®] in which Fluorolink[®] MD700 is a bifunctional urethane methacrylate PFPE (Figure IV - 1).

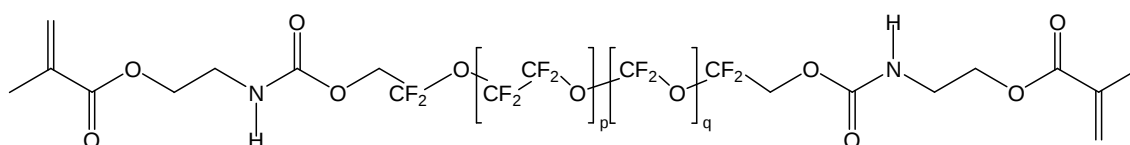


Figure IV - 1: Chemical formula of Fluorolink[®] MD700

Fluorolink ($M_n = 1800$ g/mol) was chosen due to its miscibility with organic solvents such as ethyl acetate and butyl acetate (at 5 - 10 wt.%), and its miscibility with conventional acrylic

monomers. It is also miscible with DMF, the PECH solvent, which was required for the synthesis of the IPN by the *one-pot* method.

The use of Fluorolink[®] MD700 has been reported in the literature to produce nanostructured imprints by means of UV-based nanoimprint lithography,⁷ as elastomeric molds for the fabrication of ordered bulk heterojunction photovoltaic cells,⁸ and for marine antifouling and fouling-release coating.^{9,10} Amphiphilic networks of Fluorolink and poly(ethylene oxide) (PEO) have also been prepared.^{10,11} These networks show bulk morphologies with separate phases from the nanoscopic to microscopic scales. Two glass transition temperatures were detected: the first, at high temperature (30-50 °C) was assigned to the hydrogenated domains, and the second at lower temperature (-115 °C) was assigned to the fluorinated domains. The size of the different domains was between 1 nm and 60 μm, depending on the Fluorolink molar weight and the Fluorolink/PEO proportion. Compared with that of PEO network, the water uptake was reduced from 50 wt.% for the PEO network (750 g/mol between crosslinks) to 3 wt.% for the network containing 70 wt.% Fluorolink. The Young's modulus was simultaneously increased from 40 to 76 MPa. However, to our knowledge, Fluorolink has never been introduced in an IPN architecture.

In this chapter, we will first describe the syntheses of the Fluorolink single network and the PECH₁₅/Fluorolink IPNs. Second, the physicochemical characterizations of these IPNs and the electrochemical characterizations of the IPNs membrane / electrode assemblies (MEA) will be then carried out.

1. Synthesis of Fluorolink Single Network

In this work, Fluorolink[®] MD700 will designate the monomer while we will use the term Fluorolink for the network.

1.1. Synthesis Procedure

Fluorolink[®] MD700 monomer was dissolved in DMF and AIBN was added. This monomer being bifunctional it is not necessary to add a crosslinker, in contrast to the synthesis of PHEMA network. As the crosslinking is carried out by a free-radical polymerization, all materials in this chapter were synthesized in a closed mold.

In a first time, the Fluorolink single network was synthesized with the same procedure used for the PHEMA network. While it is possible to synthesize Fluorolink network without solvent, the synthesis of the single networks were carried out in DMF at different concentrations (20, 50 and 80 wt.%) in order to be close to the synthesis conditions of the forthcoming IPNs. The solutions were degassed under argon for 15 min, placed under vacuum for 5 min to remove all gas bubbles, and finally placed under argon. Initiator (AIBN) was added at a concentration fixed at 4 wt.% with respect to Fluorolink[®] MD700. The solutions were degassed under argon, poured in closed molds made of two silylated glass plates clamped together and sealed with a 500 µm thick Teflon[®] gasket. The mold was heated at 70 °C for 2 h. After synthesis the materials were dried under vacuum. Translucent homogeneous samples were obtained.

In order to confirm the correct crosslink of Fluorolink, soluble fractions contained in the different materials were determined by Soxhlet extraction with DMF for 72 h (Figure IV - 2).

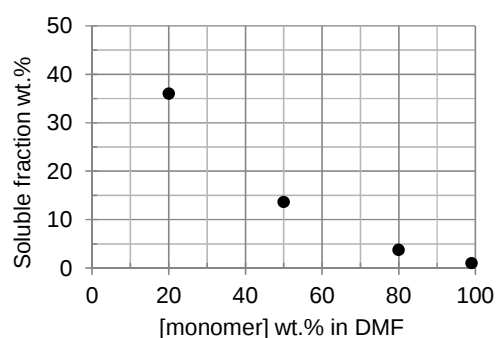


Figure IV - 2: Soluble fraction amount contained in Fluorolink single networks (4 wt.% AIBN) vs. monomer concentration in DMF.

The soluble fraction of the network decreases as the Fluorolink[®] MD700 concentration increases in the reaction solution. The network synthesized from the 20 wt.% Fluorolink[®] MD700 solution in DMF contains a soluble fraction of 35 wt.% and is considered as not correctly crosslinked. In the synthesis of the PECH/Fluorolink IPN, Fluorolink will be added to the PECH solution in DMF, therefore the synthesis of the Fluorolink single network must be improved at low concentrations in DMF. In effect, in the expected IPN, the Fluorolink[®] MD700 concentration depends on the required proportions of the two networks and on the concentration of the PECH solution, which is limited to about 18 wt.% because of spontaneous crosslinking above this concentration (cf. Chapter II § 2.2.2). For example, for the Fluorolink/PECH 50/50 IPN synthesis from a PECH solution at 18 wt.% in DMF, the Fluorolink[®] MD700 concentration must be of 15 wt.%.

Fluorolink networks were thus synthesized from a fixed 20 wt.% monomer concentration in DMF and varying the initiator AIBN wt.% (Figure IV - 3).

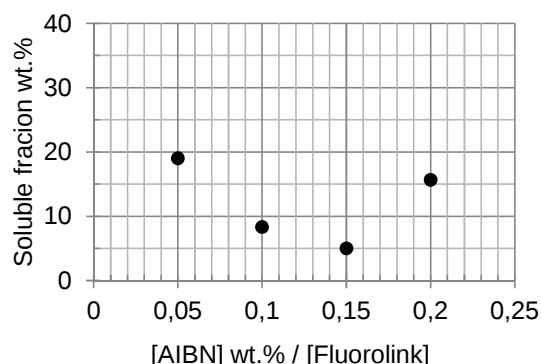


Figure IV - 3: Soluble fraction amount contained in single Fluorolink networks vs. initiator (AIBN) wt.% - [Fluorolink[®] MD700] = 20 wt.% in DMF

While the network synthesized with 4 wt.% AIBN has a soluble fraction of 35 wt.%, a soluble fraction of 5 wt.% was obtained for the network synthesized with 0.15 wt.% initiator. The incomplete crosslinking with 4 wt.% AIBN could be due to radical recombination, which occurs if primary radicals are produced at too high concentrations and/or in a too low monomer concentration. Additionally, in a high initiator concentration, the formation of low molar mass chains is favored. Those chains could be soluble in DMF and thus extracted from the material.¹² With 0.05 wt.% AIBN, the soluble fraction is higher (19 wt.%). This concentration is too low to achieve the complete Fluorolink crosslinking. Subsequently Fluorolink crosslinking will be initiated by 0.15 wt.% AIBN. Under this condition, a translucent homogeneous material was obtained (Figure IV - 4).



Figure IV - 4: Photograph of a Fluorolink single network

1.2. Single Network Characterization

Before measurements, Fluorolink network was dried at 70 °C under vacuum until constant weight. The thermomechanical properties of Fluorolink single network were then measured by DMA (Figure IV - 5).

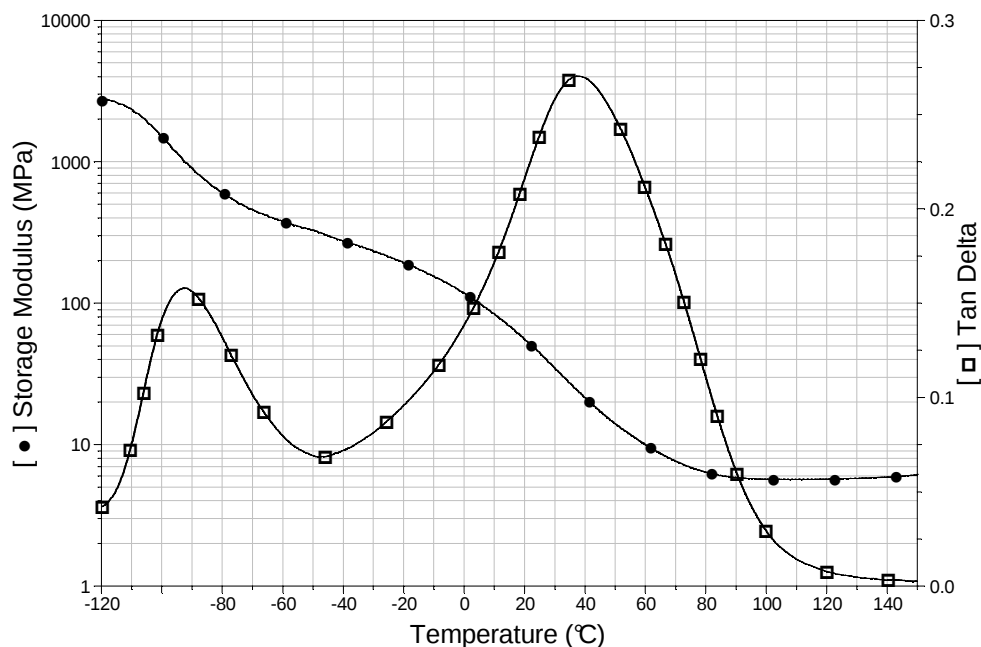


Figure IV - 5: Storage modulus E' (●) and $\tan \delta$ (□) of Fluorolink single network vs. temperature.

Storage modulus (E') and $\tan \delta$ are reported as function of temperature. Two $\tan \delta$ peaks are detected. At lower temperatures ($T_\alpha = -90$ °C), the transition can be attributed to the fluorinated domains in the network and at higher temperatures ($T_\beta = +35$ °C) the transition corresponds to the hydrogenated domains. Consequently, the translucent Fluorolink network is a biphasic material as already reported for similar bifunctional PFPE. Indeed, Bongiovanni et al.¹³ and Priola et al.¹⁴ confirmed by different techniques (UV-visible spectroscopy, DSC, DMA, small-angle X-ray scattering, atomic force microscopy, X-ray photoelectron spectroscopy and optical microscopy) that phase-separated materials were obtained with domain sizes of 1-100 μm .

The two mechanical relaxations are characterized by two drops of E' storage modulus: from 2740 MPa at -120 °C to 230 MPa at -30 °C, and then to ≈ 7 MPa at 80 °C. As a result, this network remains relatively rigid in this temperature range, as required for a polymer network employed as a scaffold in an IPN. One can notice that for the Fluorolink network the second mechanical relaxation expands from around -25 °C to 100 °C whereas that of PHEMA

network starts at 60°C. Thus a Fluorolink based IPN should be less rigid in the dry state at room temperature than a PHEMA based one.

The TGA of Fluorolink and PECH₁₅ single networks were recorded and shown in Figure IV - 6 to assess their thermal resistance.

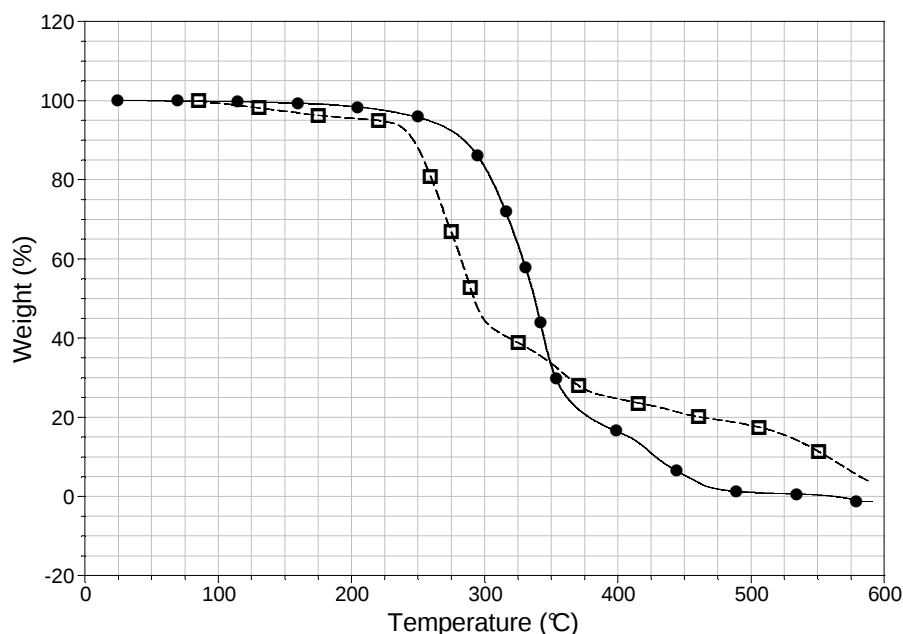


Figure IV - 6: TGA thermograms of PECH₁₅ (□) and Fluorolink (●) single networks - Heating rate: 20 °C/min – synthetic air atmosphere.

Fluorolink network has a higher thermal oxidative stability (250 °C for a weight loss of 5 wt.%) than the single PECH₁₅ network (220 °C), which is already sufficient for the application in aqueous lithium-air cell. Afterwards, a thermal oxidative degradation occurs in two steps as already reported by Bongiovanni et al. in such conditions.¹⁵ As described by these authors, the thermal degradation related to the breaking of urethane bonds and of the acrylic groups cannot be distinguished during the first weight loss. The PFPE chains are highly resistant and their degradation occurs above 300 °C.

In view of the application, the water uptake of the Fluorolink network was quantified by weight measurements and, as expected, it does not swell in water (< 1 wt.% at room temperature). Compared to a PHEMA network (10 wt.% water uptake at room temperature), the Fluorolink network presents a lower water uptake, which should result in a lower water uptake of the IPN. Thus, the chemical stability in aqueous LiOH of Fluorolink material should be higher than that of PHEMA one due to its limited swelling in aqueous solution and the chemical resistance of the PFPE moiety. However, the urethane and ester moieties of the

Fluorolink network are sensible to alkaline hydrolysis, and could reduce the resistance of the network in working conditions. Nevertheless, the ester groups are also present in the PHEMA network, and this network has shown adequate resistance in LiOH. Thus, the behavior of the single Fluorolink network in the presence of 5 M LiOH solution was evaluated qualitatively. In order to accelerate the ageing process, temperature was fixed at 50 °C (Figure IV - 7).

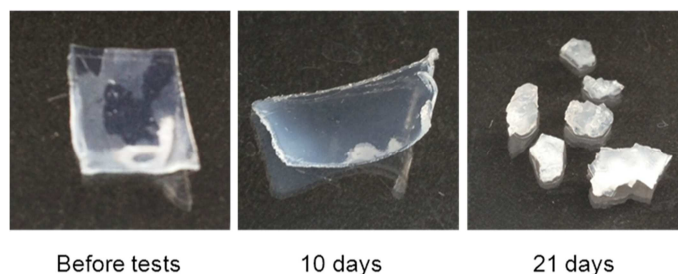


Figure IV - 7: Single Fluorolink network before and after immersion for 10 and 21 days in 5 M LiOH at 50 °C.

After 10 days in 5 M LiOH, the single Fluorolink network maintains its integrity, but after 21 days the material has become very fragile, and it is not possible to remove it from the solution without damage. The water uptake of these fragments is 700 wt.% (instead of < 1 wt.% before the test), but they are still insoluble in dichloromethane. This suggests a decrease in the crosslink density caused by the rupture of the urethane or the ester bonds. Thus, despite the fluorinated nature of this network, the urethane and/or ester moieties of the Fluorolink network can be hydrolyzed in alkaline conditions. Inversely, the PHEMA network does not shows any visible degradation after 21 days in the same conditions (cf. Chapter III § 2.2). These differences can be due to the difference of cross-link densities between the Fluorolink network (1800 g/mol) and the PHEMA one (800 g/mol).

2. Synthesis of PECH₁₅/Fluorolink IPNs

2.1. Synthesis Method

Since Fluorolink[®] MD700 is miscible with DMF, all the IPNs were synthesized by a *one-pot* process. The Fluorolink network was synthesized by free radical polymerization initiated with AIBN at 70 °C. In a second temperature step, the PECH was crosslinked at 100 °C by nucleophile substitution (Figure IV - 8).

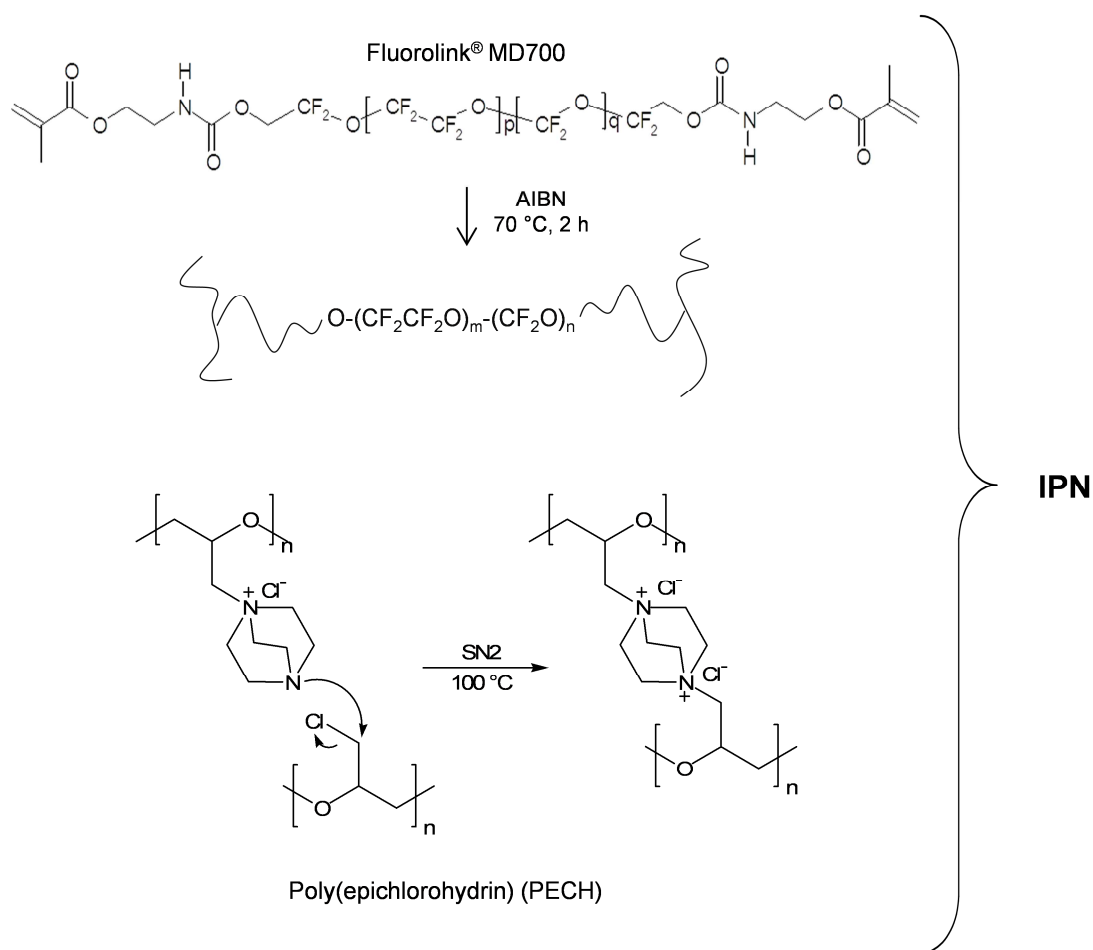


Figure IV - 8: Scheme of PECH/Fluorolink IPN synthesis

In this part, PECH network is always cross-linked with 15 mol % DABCO. The PECH₁₅/Fluorolink IPNs were prepared by dissolving DABCO in the concentrated (18 wt.%) PECH solution and then adding the Fluorolink® MD700 to obtain the desired PECH/Fluorolink weight ratio. Thus, IPNs with different PECH₁₅ network contents ranging from 25 to 90 wt.% were synthesized. All IPN compositions are reported in weight ratio. The IPNs are noted PECH₁₅/Fluorolink y/z IPN where y and z are the weight proportions of PECH and Fluorolink, respectively in the dry final material.

For example, for a PECH₁₅/Fluorolink 70/30 IPN: 10 g PECH solution at 18 wt.% in DMF (1.8 g PECH = 17.3 mmol repeat unit, 1.73 mmol DABCO already grafted) were mixed with 0.097 g DABCO (8.67 mmol) and stirred until complete dissolution. 0.813 g (0.45 mmol) Fluorolink® MD700 were added and the mixture was stirred under argon for 15 min, placed under vacuum for 5 min and then under argon. 1.2 mg AIBN (0.15 wt.% with respect to Fluorolink) were then dissolved in the mixture, stirred under argon for 15 min, followed by 5 min vacuum and was finally placed under argon. The mixture was poured into a mold made

from two silylated glass plates clamped together and sealed with a 500 μm thick Teflon gasket. The mold was placed in an oven at 70 $^{\circ}\text{C}$ for 2 h and at 100 $^{\circ}\text{C}$ for 4 h. The PECH₁₅/Fluorolink 70/30 IPN swollen in DMF were unmolded at room temperature (Figure IV - 9) and dried until constant weight under vacuum (5 mmHg) at 70 $^{\circ}\text{C}$ before testing, unless specified.

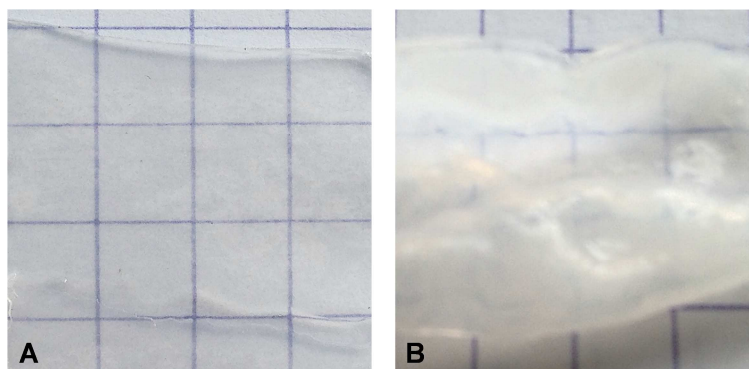


Figure IV - 9: Photos of water swollen PECH₁₅/Fluorolink 70/30 (A) and 25/75 (B) IPNs.

All synthesized IPNs with a PECH₁₅ content superior to 40 wt.% are macroscopically homogeneous in the dry state (translucent) and in the water swollen state (transparent), as shown for PECH₁₅/Fluorolink 70/30 IPN in Figure IV - 9 A. In contrast, the PECH₁₅/Fluorolink 25/75 IPN is macroscopically homogeneous in the dry state, but when it is swollen with water, transparent and opaque domains (in the mm range) appear, as shown in Figure IV - 9 B. Not being macroscopically homogeneous, IPNs containing less than 40 wt.% PECH will not be further characterized.

2.2. Soluble Fraction

To confirm the correct crosslinking of the polymers, the soluble fractions contained in the different IPNs were determined by Soxhlet extraction for 72 h with DMF. The soluble fraction amounts are reported in Table IV - 1.

Table IV - 1: Soluble fraction amounts of single Fluorolink and PECH₁₅ networks, and of different PECH₁₅/Fluorolink IPNs (Soxhlet extraction, DMF, 72 h)

IPN Composition (w/w)	Soluble fraction (wt. %)
Fluorolink network	5
40/60	5
50/50	2
60/40	3
70/30	4
80/20	5
90/10	1
PECH ₁₅ network	4

All analyzed materials show soluble fraction amounts lower than 5 wt. %. Thus, all the polymers can be considered as being correctly crosslinked in the IPNs whatever their composition.

3. Morphology of PECH₁₅/Fluorolink IPNs

The IPN morphology was derived from different analyzes (confocal microscopy, water uptake and DMA) which are now presented.

3.1. Confocal Microscopy

The morphology of a PECH₁₅/Fluorolink 70/30 IPN, synthesized with 0.15 wt.% or 4 wt.% AIBN (before optimization of Fluorolink network synthesis), was studied by laser scanning confocal microscopy. The membranes were dried after synthesis, immersed in a diluted solution of rhodamine B for 24 h, then rinsed until no further coloration on the rinsing solution was observed and then stored in water before analysis (cf. Experimental Part).

The rhodamine B, a water soluble dye, is preferentially absorbed into the hydrophilic PECH phase, and is excluded from the hydrophobic PFPE domains. This point was verified by treating PECH and Fluorolink single networks: dye absorption was only observed in the PECH single network. The rhodamine B was excited at 561 nm and fluorescence collected from 570 to 640 nm (cf. Experimental Part).

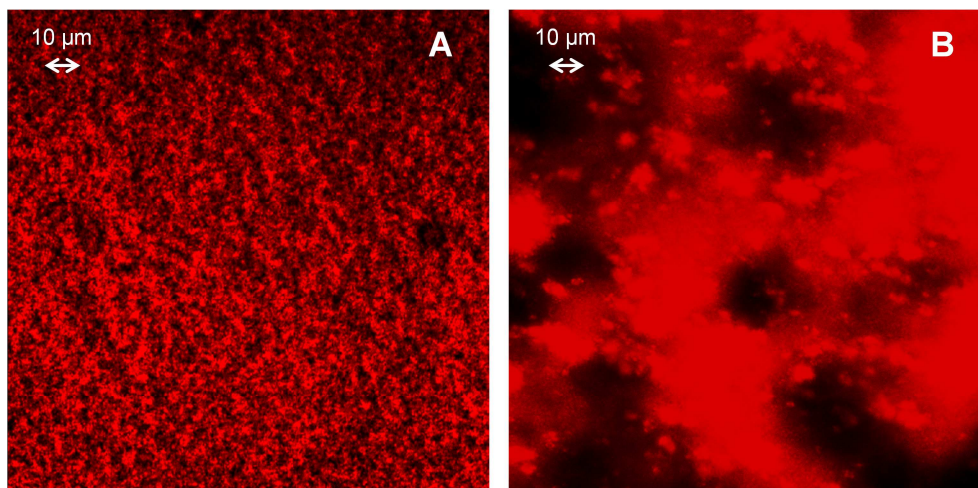


Figure IV - 10: Fluorescence images recorded by laser scanning confocal microscopy for PECH₁₅/Fluorolink 70/30 IPNs synthesized with (A) 0.15 and (B) 4 wt.% AIBN. PECH phase was stained red by rhodamine B. Scale bar: 10 μ m

In the microscopy images of PECH₁₅/Fluorolink 70/30 IPNs, the hydrophilic PECH rich phase is stained red whereas the hydrophobic phase, composed of Fluorolink network, is free of fluorophore and appears in black. So, non-fluorescent and red domains of micrometric size are observed in the PECH₁₅/Fluorolink 70/30 IPN synthesized with 0.15 wt.% AIBN (Figure IV - 10 A) which is in agreement with the translucent aspect of the sample (Figure IV - 9). This phase separation is limited compared to that observed on the amphiphilic Fluorolink/PEO networks (domains from 1 to 100 μ m)¹¹ The IPN architecture shows here all its interest compared with that of co-networks: the PECH-rich and the Fluorolink-rich domains appear continuous for the 70/30 composition. This morphology will be verified by water uptake measurements (cf. § 3.2) and by DMA analysis (cf. § 3.3).

Confocal microscopy has also allowed us to show the importance of the synthesis parameters on the morphology of IPNs. We have previously shown that the initiation of Fluorolink polymerization with 4 wt.% AIBN does not permit to obtain a suitable fluorinated network (cf. § 1.1). Thus, a PECH₁₅/Fluorolink 70/30 IPN was synthesized with 4 wt.% AIBN to compare its morphology to that of the synthesized from the optimized protocol. This IPN shows dispersed black spots (> 10 μ m) in a continuous red stained matrix (Figure IV - 10 B). Hence, the Fluorolink network is dispersed in the PECH matrix. This morphology is in agreement with the important water uptake of this IPN (5000 wt.%).

Another approach to obtain information on the continuity of the various phases is to measure the swelling ratio of the material in a solvent of one of these phases. Consequently, the water

uptakes of IPNs synthesized with 0.15 wt.% AIBN were measured as well. If PECH phase is the only continuous, the uptake is maximum, if it is the fluorinated phase, the uptake will be minimum.

3.2. Water Uptake

For the water uptake measurements (WU), the samples were immersed in 1 M KOH immediately after synthesis (swollen with DMF). They were then rinsed with water until neutral pH and then equilibrated in water for 24 h. The swollen samples were weighted (w_s); they were then dried under vacuum until constant weight, and weighted (w_d). WU (Figure IV - 11) was calculated using eq. II-3.

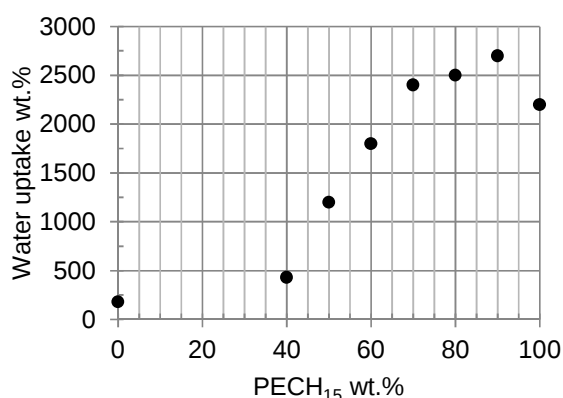


Figure IV - 11: Water uptake of single PECH₁₅ and Fluorolink networks and different PECH₁₅/Fluorolink IPNs vs. PECH weight proportion.

The PECH₁₅ and the Fluorolink networks have a WU of 2200 and 180 wt. % respectively. The WU increases linearly with the increase in the PECH₁₅ proportion, between 40 and 70 wt.% PECH₁₅, which is a typical behavior of continuous PECH network. One can note that PECH₁₅/PHEMA 68/32 IPN presented a water uptake of 1000 wt.% (cf. Chapter II § 2.2) and that the corresponding PECH₁₅/Fluorolink 70/30 IPN shows a water uptake of 2400 %.

At PECH₁₅ concentrations higher than 70 % a plateau is attained at around 2400 wt.% (near the WU of the PECH₁₅ single network) suggesting a discontinuous Fluorolink network. The continuity of the Fluorolink network at low concentrations (higher than 30 wt.%) can be possible because the Fluorolink network is synthesized before the PECH₁₅ network. In general, in the synthesis of IPNs the first network formed is the continuous phase.^{16,17,18}

One can notice that the neutral network, swollen with DMF, also absorbs water if WU measurements are performed immediately after synthesis. Thus, contrary to the expected effect, the fluorinated network does not reduce the water swelling compared to the PHEMA network. This can be explained by the different crosslink density of the two partner networks. In the PECH₁₅/PHEMA 68/32 IPN, the weight between crosslinks (m_c) has been estimated to 800 g/mol (about 6 HEMA units). In the PECH₁₅/Fluorolink 70/30 IPN the weight between crosslink points is given by the Fluorolink[®] MD700 molar weight (1800 g/mol). This lower crosslink density leads to a higher swelling. Another possible reason for the higher water uptake can be the structure of the Fluorolink network imposed by the synthesis conditions. As we saw in § 1.1, the formation of the Fluorolink network is strongly dependent on the monomer concentration during synthesis. In the PECH₁₅/Fluorolink 50/50 IPN, Fluorolink[®] MD700 is dissolved at 15 wt.%. The concentration on monomer is lowered at higher PECH₁₅ proportion in the IPN. This would result in a less densely crosslinked network, and increase the number of pendant chains or oligomers, and thus a higher water uptake is obtained.

3.3. Thermomechanical Properties

The thermomechanical properties of the IPNs were analyzed by dynamic mechanical analysis (DMA). As shown in Chapter II, single PECH₁₅ network displays a broad mechanical relaxation detected from 0 to 140 °C and centered at 79 °C (cf. Chapter II § 3.1). Similarly, we have shown that the fluorinated network presents two mechanical relaxations at -90 and 35 °C (cf. § 2.3). Three representative IPNs are shown in Figure IV - 12 and Figure IV - 13. The IPNs also display two mechanical relaxations. The one at low temperatures can be attributed to the fluorinated domains of the Fluorolink network. The second, at higher temperatures, is attributable to the hydrogenated domains of both the Fluorolink and the PECH network. The relative magnitude of these two transitions appears to be proportional to the amount of each polymer.

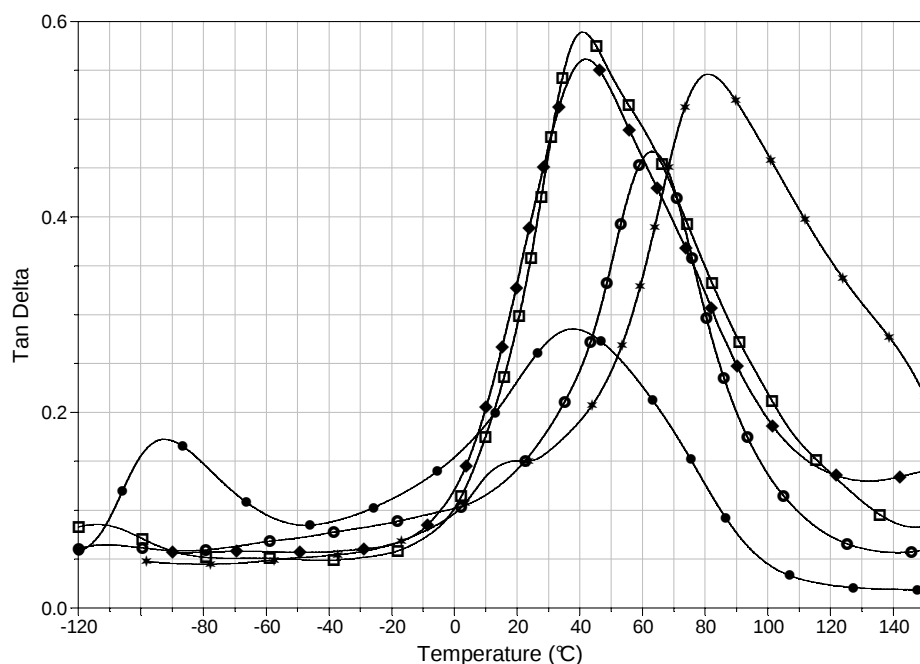


Figure IV - 12: $\tan\delta$ versus temperature of single PECH_{15} (★) and Fluorolink (●) networks, and PECH_{15} /Fluorolink 40/60 (□), 60/40 (◆), 70/30 (○) IPNs

The $\tan\delta$ peak at low temperature, characteristic of the fluorinated domains of Fluorolink is only weakly detected on the PECH_{15} /Fluorolink 40/60 IPN, containing more Fluorolink. The latter disappears for other compositions.

The PECH_{15} /Fluorolink 40/60 and 60/40 IPNs show only one mechanical relaxation centered at +35 °C like on the single Fluorolink network. This relaxation is attributable to the hydrogenated domains of both the Fluorolink and the PECH network. On the PECH_{15} /Fluorolink 70/30 IPN, this relaxation is shifted towards the highest temperature ($T\alpha = 63^\circ\text{C}$). Because the main mechanical relaxations of two networks in the IPN occur in the same temperature range (the difference between the two is 40 °C), it is difficult to attribute the relaxation of each of them in the IPNs.

Additional information was obtained from measurements of storage modulus (E') (Figure IV - 13).

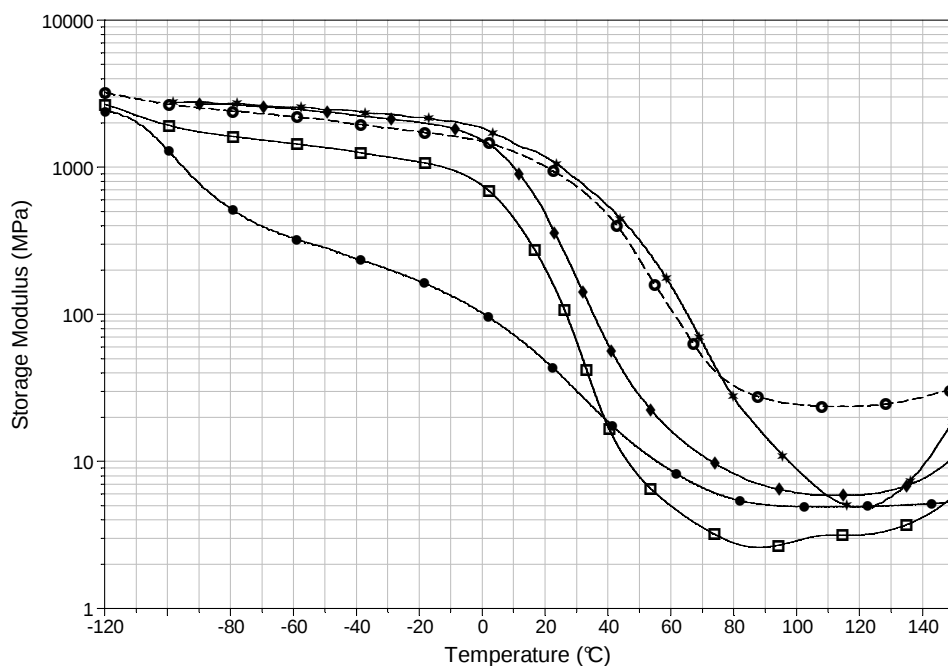


Figure IV - 13: Storage modulus E' versus temperature of single PECH_{15} (★) and Fluorolink (●) networks, and PECH_{15} /Fluorolink 40/60 (□), 60/40 (◆), 70/30 (○) IPNs

Single PECH_{15} network displays a glassy plateau ($E' > 3 \text{ GPa}$) at temperatures lower than 0°C . Above this temperature, the storage modulus values decrease and a rubbery plateau is reached at 100°C ($E' \approx 5 \text{ MPa}$). As previously shown, the single Fluorolink network shows two mechanical relaxations characterized by two drops of the storage modulus, one from $E' = 2740 \text{ MPa}$ at -120°C to $E' = 230 \text{ MPa}$ at -30°C and a second to 7 MPa at 70°C . Between -80 and -20°C , the PECH phase of the IPNs is in the glassy state and the fluorine domains of the Fluorolink network in the elastomeric state. In this area, the Fluorolink network modulus is in the order of 300 MPa . When the proportion of PECH in the IPN network increases from 40 to 70 wt.%, the storage modulus increases from 1300 MPa , to 3000 MPa , equivalent to the modulus of PECH_{15} single network. This is in accord with the reduction of the Fluorolink amount in the IPNs. Above 50°C both polymers are in the amorphous state and no conclusion can be obtained from E' values.

From the above measurements, we can conclude that PECH_{15} /Fluorolink IPNs are biphasic materials, with fluorinated and hydrogenated distinct domains. Analysis by confocal microscopy of PECH_{15} /Fluorolink 70/30 IPN suggests a co-continuity of the two phases, with domain size of about $1 \mu\text{m}$. Water uptake measurements show that the WU increases linearly with the increase in PECH_{15} proportion, between 40 and 70 wt.% PECH_{15} , we can also conclude that both networks are co-continuous in this composition range. The DMA of IPNs,

in the same composition range, shows a single main peak at high temperature, characteristic to the hydrogenated domains measurements. From the three analyses we can conclude that the PECH₁₅/Fluorolink IPNs in the composition range between 40 and 70 % PECH₁₅ show a co-continuous phase morphology. In consequence, the PECH₁₅ network continuity is obtained on a large composition range (from 40 to 90 wt.%). This is required in the IPN for the application since this network has to ensure the hydroxide transport from the electrode to the electrolyte.

4. Physicochemical Characterizations

It is important as a first step to verify that the PECH crosslinking is not modified in the presence of fluorinated network. These crosslink nodes are also the ionic conductors, and are quantified by IEC measurements.

4.1. Ionic Exchange Capacity (IEC)

IEC values were measured as previously detailed, by back-titration of OH⁻ ions in the membrane (cf. Experimental part). IEC of the PECH₁₅/Fluorolink IPNs were measured on non-dried sample after synthesis and the values are reported versus the PECH proportion in Figure IV - 14.

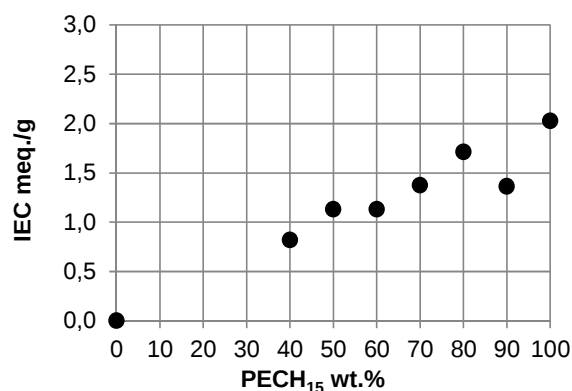


Figure IV - 14: IEC of PECH₁₅/Fluorolink IPNs versus PECH₁₅ network proportion.

The measured values in Figure IV - 14 are lower than the theoretic values. For example, for the PECH₁₅/Fluorolink 70/30 IPN an IEC of 1.4 meq./g is measured instead of the expected 2 meq./g, which would suggest a yield of 70 %. This could also be associated with an incomplete exchange of the Cl⁻ ions in the network. This was already observed for the PECH single network by Stoica et al.¹⁹ who found that the exchange reaction with 1 M KOH was

incomplete, with 0.6 meq./g of Cl^- ions still present in the material. Another reason for the low IEC value could be an incomplete crosslinking of the PECH network, as proposed in the Chapter II.

However, the IEC increases as expected linearly with the PECH_{15} content. This result shows that almost all of PECH network ammonium sites are accessible to the aqueous solution, thus allowing its quantification. This result is again in accordance with morphology where the PECH rich phase is continuous throughout the material. In fact, the linear dependence of the IEC and the PECH proportion in the IPN suggest that the ionic groups of the latter are accessible, not obscured by the Fluorolink network. An IEC superior to 1 meq./g is obtained for PECH_{15} proportions superior to 50 wt.%.

4.2. Ionic Conductivity

Simultaneously, the anionic conductivity values of the single PECH network and of IPNs with various PECH weight proportions were measured (Figure IV - 15). The measurements were carried out on samples non-dried after synthesis, in the OH^- form and swollen in water.

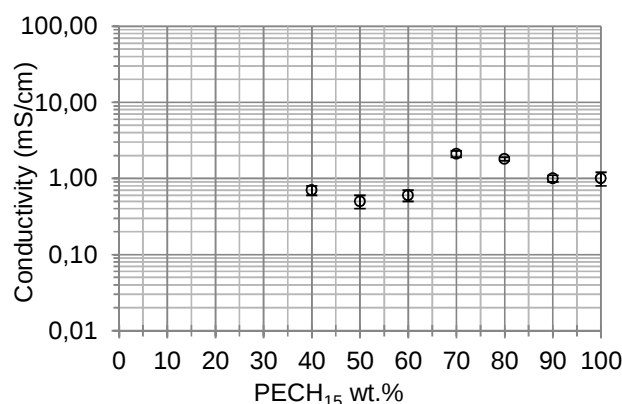


Figure IV - 15: Ionic conductivity of single PECH_{15} network and of different IPNs vs. the PECH weight proportion. Room temperature, OH^- form, water swollen

The anionic conductivity of the single PECH_{15} network in the fully hydrated state is 1 mS/cm. For the PECH_{15} /Fluorolink IPNs a maximum conductivity of approximately 2 mS/cm is obtained for the PECH_{15} /Fluorolink 70/30 IPN. However, no important variations are found with the PECH_{15} proportion in the IPN. These result is equivalent to that obtained for the PECH_{10} /PHEMA IPNs for which all IPNs show an equivalent conductivity of around 1 mS/cm when PECH_{10} proportion is higher than 30 wt.%. Furthermore, the conductivity of

the PECH₁₅/PHEMA 68/32 IPN is the same as that of the PECH₁₅/Fluorolink 70/30 IPN. Thus the fluorinated Fluorolink network does not reduce the conductivity of the IPN compared with hydrogenated PHEMA network.

4.3. Transport Number

The anionic transport number (t^-) delivers information on the ionic selectivity of a membrane under an electric field. The membranes were not dried after synthesis, are OH⁻ exchanged and tested swollen in water. The t^- values of PECH₁₅/Fluorolink IPNs in OH⁻ form are shown Figure IV - 16.

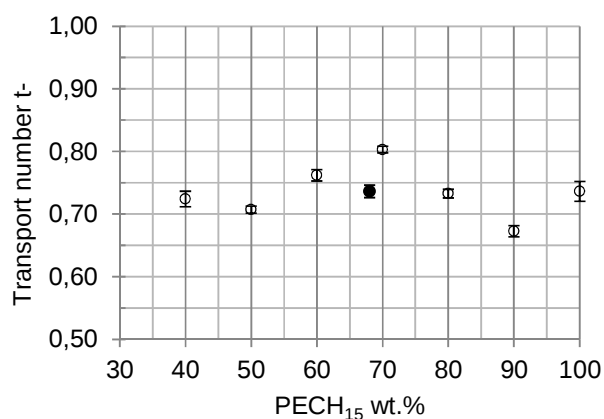


Figure IV - 16: Anionic transport numbers of PECH₁₅/Fluorolink IPNs vs. the PECH₁₅ network proportion (○) and that of PECH₁₅/PHEMA 68/32 IPN (●). IPNs non-dried after synthesis

The anionic transport numbers t^- of PECH₁₅/Fluorolink IPNs vary from 0.65 to 0.8. The highest t^- , and thus the highest selectivity, are obtained between 60 and 80 PECH₁₅ wt.%, with a maximum of 0.80 at 70 % PECH₁₅ network. This value is higher than that of PECH₁₅/PHEMA 68/32 IPN ($t^- = 0.74$), but similar to that of single PECH₁₅ network. The high t^- value obtained at 70 % PECH₁₅ may be due to a good compromise of cationic sites concentration, as shown by the IEC measurements, and the beginning of the water uptake plateau at this composition.

Before assembling these IPNs over the air electrodes, we studied the chemical stability of these materials by soaking them in a concentrated lithium hydroxide solution, in which they will be later immersed in the lithium-air battery.

4.4. Chemical Stability

The stability of PECH₁₅/Fluorolink 70/30 IPN in 5 M LiOH at 50 °C was tested. The samples were dried before the stability test, because when not dried after synthesis they are fragile and the repeated immersion, rinsing and conductivity measurements are not possible. The conductivity of the membrane was monitored during 21 days (Figure IV - 17) and was compared with that of a single PECH₁₅ network and a PECH₁₅/PHEMA 68/32 IPN previously discussed in Chapter III § 1.3.5. Conductivity measurements allow following the possible degradation of ammonium sites according to the mechanisms described in the literature section (cf. Chapter I). The measurements were performed according to the protocol described previously (cf. Experimental part).

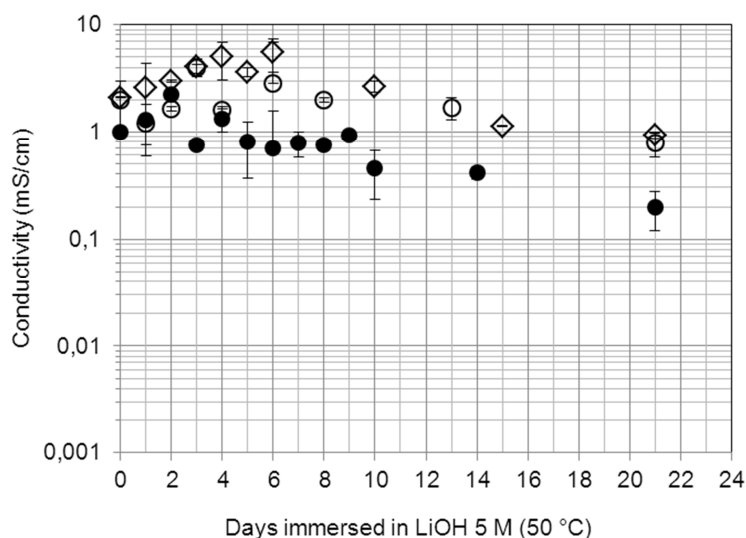


Figure IV - 17: Ionic conductivity vs. immersion time in 5M LiOH at 50 °C of single PECH₁₅ network (●), PECH₁₅/PHEMA 68/32 (◇) and PECH₁₅/Fluorolink 70/30 (○) IPNs

As discussed in chapter II, the PECH single network shows a slight continuous decrease of its conductivity after 5 days of immersion. Inversely, the PECH₁₅/PHEMA 68/32 IPN has an initial conductivity of 2 mS/cm which increases during the first 5 days of tests, followed by a decrease to 1 mS/cm after 21 days. The non-aged PECH₁₅/Fluorolink 70/30 IPN has also an initial conductivity of 2 m S/cm, and an increase in conductivity is also observed during the 5 first days, before decreasing to 1 mS/cm. After 21 days, the conductivity is 1 mS/cm, and we can conclude that there has not been significant degradation of the ionic sites of the membrane. Inversely, the PECH₁₅ network conductivity has decreased to 0.2 mS/cm, and also shows a more pronounced yellowing (Figure IV - 18). While the Fluorolink single networks

lost its integrity under those conditions after 21 days (Figure IV - 7), the Fluorolink based-IPN remains intact, and no noticeable change in mechanical resistance is observed.

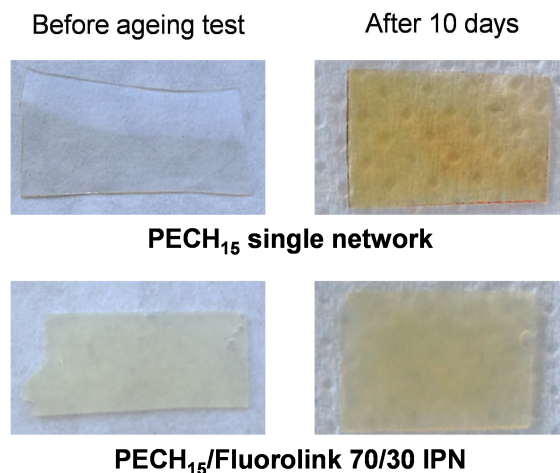


Figure IV - 18: Photographs of single PECH₁₅ network and PECH₁₅/Fluorolink 70/30 IPN before and after ageing test

One can notice that the PECH₁₅/PHEMA 68/32 and PECH₁₅/Fluorolink 70/30 IPNs previously dried, have reduced water uptake of 73 and 80 wt.%, respectively, compared to the PECH single network of 200 wt.%. This is in agreement with the literature as low water uptake has already been reported as a key parameter for long life time of ionic membranes.²⁰

We can conclude that the IPN has a higher stability than either of the single network. The IPN architecture protects the ionic sites of the PECH network. At the same time, the ester and/or urethane groups of the fluorinated network are protected. This is probably an effect of the chemical resistant fluorinated domains. Consequently, the IPN will be hardly affected in the condition used for lithium-air cell at room temperature.

After its characterization *ex-situ*, these new IPNs have been assembled over an air electrode and the assemblies were tested in the half-cell.

4.5. Electrochemical Characterization of PECH₁₅/Fluorolink IPNs MEA

4.5.1. Synthesis Method and Method for Preparing the MEA

The PECH₁₅/Fluorolink IPNs with different compositions were synthesized directly over the catalyst side of the air electrode, as detailed in Chapter II § 4.1.2. The thickness of the membrane was fixed at 500 µm by a Teflon gasket.

First, the good interface between the air electrode and the fluorinated IPN membrane in the MEA was verified by SEM-EDX (Figure IV - 19). Indeed fluorinated polymer based materials are particularly well known for the non-adhering surface properties.

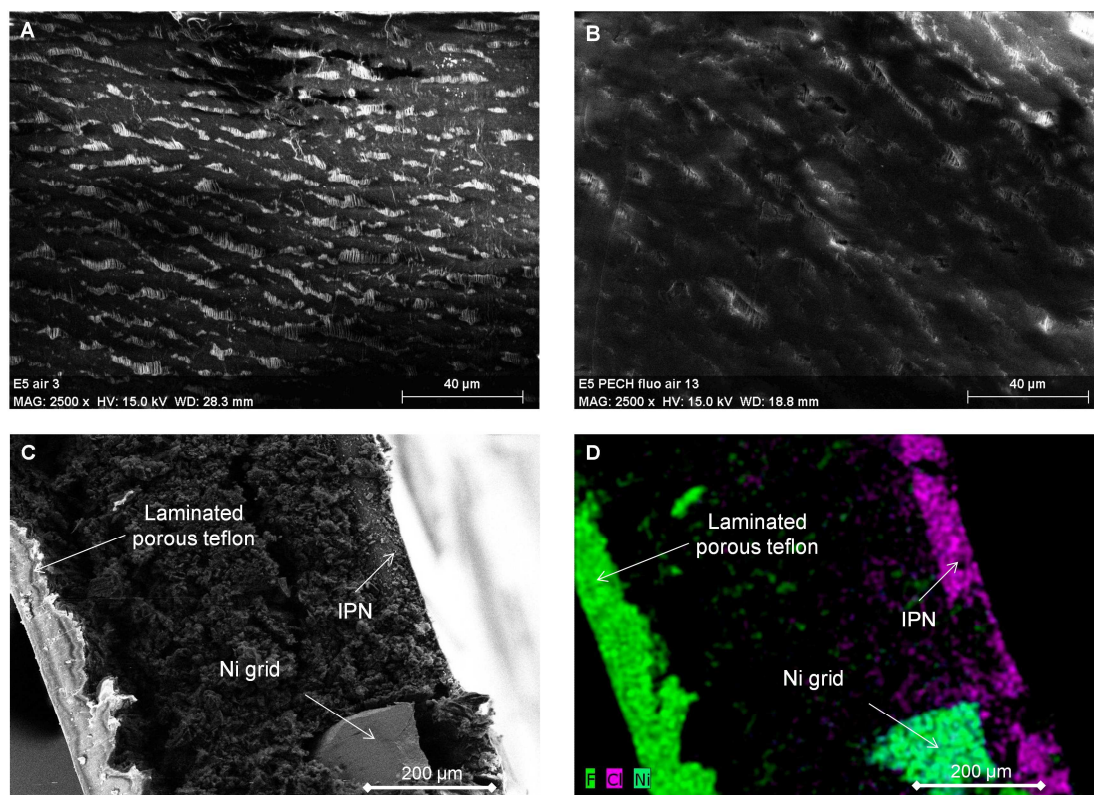


Figure IV - 19: SEM images. Image of the air side of E-5 air electrode, bare (A) and modified with PECH₁₅/Fluorolink 70/30 IPN (B). Cross-section of PECH₁₅/Fluorolink 70/30 IPN MEA (C) and the corresponding EDX analysis (D).

The SEM image of the air side of PECH₁₅/Fluorolink 70/30 IPN MEA (Figure IV - 19 B) displays partially obstructed pores of laminated porous Teflon[®] of the E-5 air electrode (Figure IV - 19 A). In Figure IV - 19 C and D are reported the cross section of the PECH₁₅/Fluorolink IPNs MEA and the corresponding EDX analysis, respectively. The IPN presence is characterized by the Cl signal of PECH. Like for the PECH single network, Cl is highly concentrated on the surface and it also diffuses through the carbon black porosity over more than 200 μm. Fluorine is, as expected, located, in the laminated Teflon[®] layer and the IPN (F signal hidden by Cl in this image). However, in the catalyst layer the fluorine from the IPN and the fluorinated binder cannot be discriminated.

To conclude about these observations, the interface between the air electrode and the fluorinated IPN membrane in the MEA is especially good following this optimized protocol of assembling.

After synthesis, the MEA was unmolded and immersed in 1 M KOH before the half-cell test, to exchange Cl^- ions and synthesis solvent with OH^- and aqueous electrolyte.

Then, to study the additional polarization induced by the presence of the IPNs over the air electrode, the polarization curves of air electrode modified with PECH₁₅/Fluorolink 40/60, 50/50, 70/30 and 90/10 IPNs are recorded (Figure IV - 20) and compared with the polarization of the non-modified air electrode.

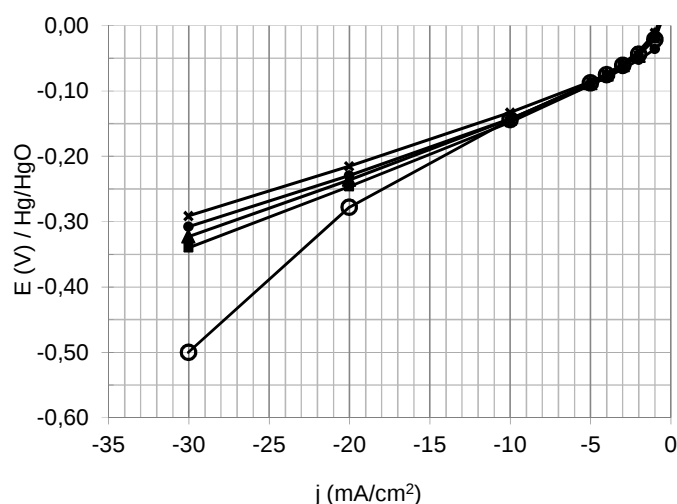


Figure IV - 20: Potential-current density curves recorded on bare electrode (●), PECH₁₅ network (■), PECH₁₅/Fluorolink 40/60 (○), 50/50 (▲), 70/30 and 90/10 (✱) IPN modified electrodes. Electrolyte: 5 M LiOH. Room temperature, atmospheric pressure. Reference electrode: Hg/HgO

The PECH₁₅/Fluorolink IPN modified air-electrodes do not induce a significant increase in polarization except for the PECH₁₅/Fluorolink 40/60 IPN for which the polarization is higher at current densities superior to -10 mA/cm^2 . At -10 mA/cm^2 the non-modified electrode and the electrodes modified with the Fluorolink-based IPNs have a polarization of -140 mV . No polarization difference is found when the IPN contains PECH proportions varying from 50 to 90 wt. % (60/40 and 80/20 IPNs not shown). These last results are in agreement with the previous *ex-situ* conductivity measurements of these polymer membranes ($0.7 - 2.0 \text{ mS/cm}$) which are comparable.

Afterwards, the stability of the different MEA was tested in cycling, at OCV for 10 h and -10 mA/cm^2 for 10 h in 5 M LiOH electrolyte at room temperature with ambient air and atmospheric pressure (Figure IV - 21).

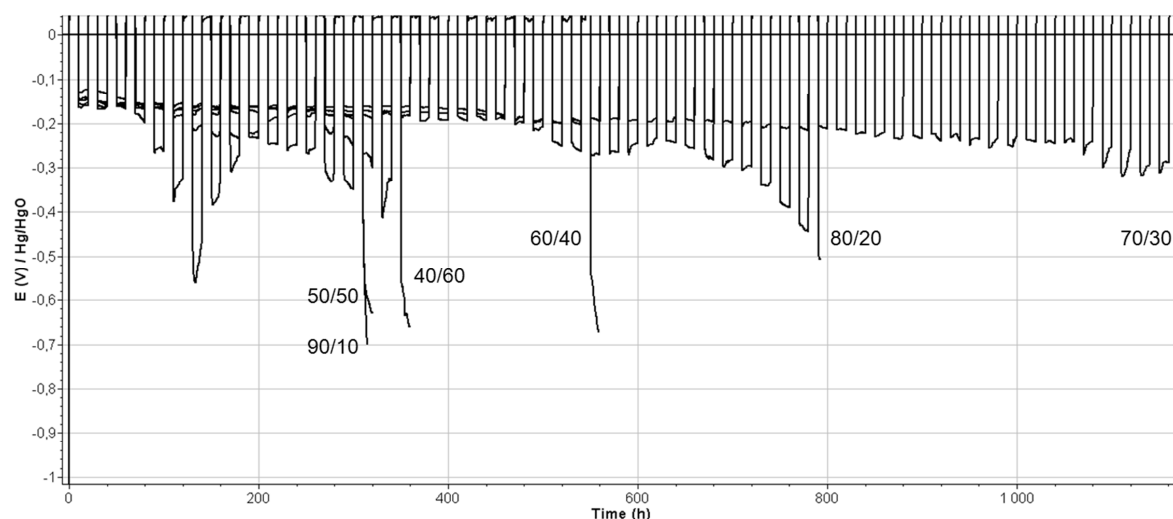


Figure IV - 21: Potential vs. time curves for PECH₁₅/Fluorolink 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 IPN modified electrodes. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO.

Whatever the IPN composition, the polarizations of the assemblies during the first discharges are of the order of -140 mV. It is clear that the stability of the electrode is strongly dependent on the composition of the IPN. The degradation of the electrode performance always results in a sudden increase in the polarization, which appears in all cases after a period of rest.

The stabilities of the PECH₁₅/Fluorolink IPN MEAs, i.e. the time at which the polarization becomes higher than -400 mV, are summarized in Figure IV - 22.

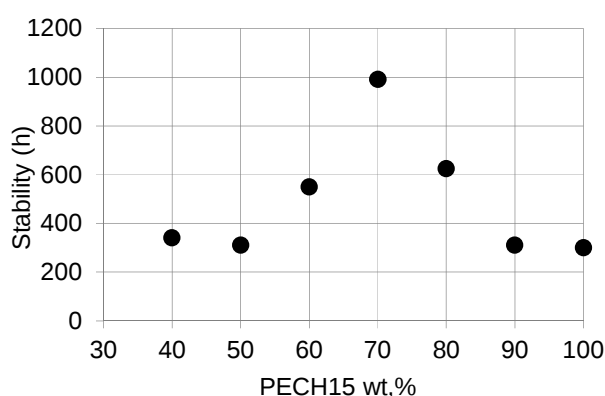


Figure IV - 22: Stability of electrodes modified with PECH₁₅/Fluorolink IPNs versus PECH content. Cycle: OCV for 10 h and -10 mA/cm² for 10 h. Electrolyte: 5 M LiOH. Room temperature, ambient air and atmospheric pressure. Reference electrode: Hg/HgO.

The highest stability, exceeding 1000 h, of the air electrode is obtained when it is modified with a PECH₁₅/Fluorolink 70/30 IPN. This result is in agreement with the characteristics of the 70/30 IPN which shows one of the highest conductivities and the best selectivity,

specifically the highest anion transport number ($t^- = 0.80$). The t^- seems to be the most important parameter influencing the IPN MEA stability. A maximum stability of 1500 h was even obtained in one test for a PECH₁₅/Fluorolink 70/30 MEA. This particular MEA cycling test was interrupted and analyzed.

4.5.2. Analysis of MEA after stability test

After interrupting the tests of a PECH₁₅/Fluorolink 70/30 MEA stable for 1500 h, we analyzed the electrode. A white solid was observed on the air side of the electrode, which covers it entirely (Figure IV - 23 B), and that was not visible before the stability test (Figure IV - 23 A).

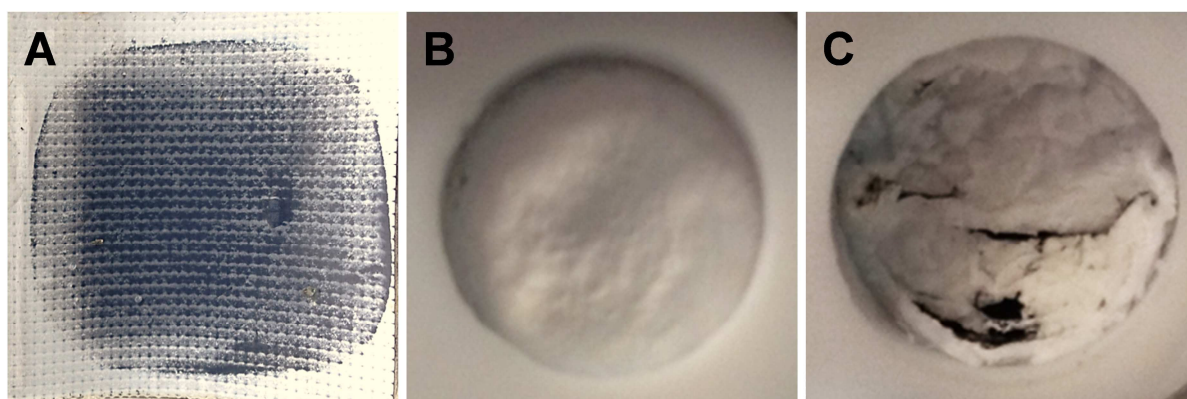


Figure IV - 23: Air-side of PECH₁₅/Fluorolink 70/30 IPN MEA before (A), after 1500 h stability test (B) and after scrubbing of solid formed and rising with water (C)

Under the experimental conditions used, this precipitate may be LiOH becoming from the electrolyte or lithium carbonate due to the reaction between the carbon dioxide of the air and lithium hydroxide from the electrolyte (eq. I-6). This solid was thus analyzed by ATR FT-IR (Figure IV - 24).

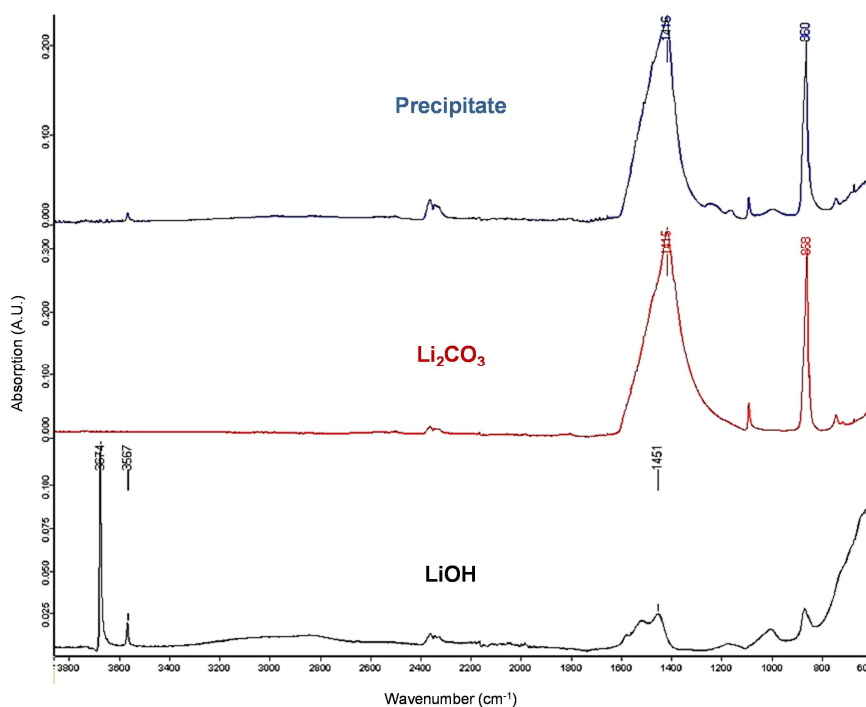


Figure IV - 24: FT-IR ATR characterization of precipitate on the air side of the electrode after 1500 h in stability test (2 cm^{-1} , 32 scans)

The precipitate was identified as Li_2CO_3 as revealed by the strong absorption bands at 1415 and 860 cm^{-1} characteristic of the asymmetric stretch and out of plane deformation, respectively of the carbonate ion.²¹ The solid has been removed from assembly by gently scrubbing the surface (Figure IV - 23 C). Seemingly, the solid precipitation has damaged the porous Teflon film. After scrubbing the solid and rinsing the air side with deionized water, the stability test was resumed, but the polarization of the MEA was higher than -1 V and the test could not be performed. This suggests that further damage has been caused to the electrode and the catalytic layer and/or the membrane by the removal of the precipitate.

In conclusion, best performance (i.e. highest stability) is obtained when the air electrode is modified with the PECH₁₅/Fluorolink 70/30 IPN. The stability of the electrode has been increased from 50 to 1000 h, more than 20 times than for the non-modified electrode.

As we could expect from the physicochemical characterization of the IPNs, the PECH₁₅/Fluorolink 70/30 IPN which presents an adequate conductivity and selectivity presents also the best electrochemical performances, and an air electrode modified with this membrane presented the highest stability of all the modified electrodes tested.

5. Conclusion

In this chapter we demonstrate the interest of the original combination of PECH and Fluorolink networks in an interpenetrating polymer networks architecture. This association increases the chemical stability while preserving a good hydroxide conductivity and anion selectivity.

The biphasic nature of the PECH/Fluorolink IPN in the microscopic range does not seem detrimental to the measured characteristics of the membrane. A PECH₁₅/Fluorolink 70/30 IPN shows the best physicochemical properties: an ionic conductivity of 2 mS/cm², a transport number of 0.80 and an IEC of 1.4 meq./g. Contrarily to what was expected from the fluorinated partner network, the water uptake of the IPN is not reduced significantly. This can be due to the low crosslinking density of Fluorolink network, and to the network structure imposed by the IPN synthesis conditions. However, the water uptake of the IPNs, near that of the single network, does not harm the material properties, which we show were improved by the IPN architecture.

We also show in this chapter that the stability of the modified electrode depends on the IPN composition, though the polarization at -10 mA/cm² is almost independent of the IPN composition. Furthermore, the PECH₁₅/Fluorolink 70/30 IPN membrane/electrode assembly proved to be the most stable, with a stability of more than 1000 h in the test conditions.

The high stability of the air electrode obtained with the PECH₁₅/Fluorolink 70/30 IPN can be explained by the high transport number (0.80) of this network. Additionally, the stability of this modified electrode is nearly twice that of a PECH₁₅/PHEMA 68/32 IPN modified electrode. This improvement in performance could be due to the effect of the fluorinated network in the membrane electrode assembly. As shown by SEM and EDX images, the fluorinated IPN infiltrates in the catalyst layer of the electrode, and the material is even found in the Teflon film air-side of the electrode, without producing an apparent reduction on the gases diffusion. This was not observed with the PECH-PHEMA IPNs modified electrodes. The formation of a superior interface between the network and the electrode can justify higher electrochemical performances.

Finally, best performances (i.e. highest stability) are obtained when the air electrode is modified with the PECH₁₅/Fluorolink 70/30 IPN. The stability of the electrode has been increased from 50 to an average of 1000 h, more than 20 times the stability of the non-modified electrode. Nevertheless, this stability could possibly be increased by optimizing the DABCO proportion in the PECH network. Due to insufficient time this study could not be completed. It should confirm that this particular IPN is of great interest and should be studied more deeply.

6. References

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General Conclusion

Lithium-air battery is one of the most promising technologies for energy storage, due to its high theoretical specific energy. For the particular use in electric vehicles, the aqueous lithium-air battery could allow attaining the same driving range as internal combustion engine vehicles. However, the use of this type of battery with ambient air is limited by the precipitation of lithium carbonates in the pores of the air electrode, product of the reaction of atmospheric CO₂ with the battery alkaline electrolyte. This limitation can be overcome by the protection of the electrode with a solid polymer electrolyte, working as an anion exchange membrane. This polymer membrane ensures the hydroxide ion conduction involved in the electrochemical reaction in the air electrode and also limits the diffusion of the lithium ions from the electrolyte to the air electrode, avoiding thus the formation of insoluble carbonates inside the latter.

Anion exchange membranes used in alkaline fuel cells can be employed. However, few of them are commercially available. They have low mechanical resistance in aqueous electrolyte and their chemical stability in concentrated alkaline solution remains to be demonstrated. To the best of our knowledge, no research has been done on the synthesis of anion exchange membranes associating a crosslinked cationic polyelectrolyte with a crosslinked neutral polymer within interpenetrating polymer networks (IPN) architecture. That is thus the objective of this work. The polyelectrolyte network ensures the anion conduction while preventing the passage of Li⁺ cations, and the neutral network reduces the swelling of the membrane and increases its mechanical and chemical resistances. A bibliographic study has allowed to identify the more appropriated polyelectrolyte network: the poly(epichlorohydrin) cross-linked by 1,4-diazabicyclo-[2.2.2]-octane (DABCO).

In the first part of this work, we have identified and characterized air electrodes under the operating conditions of the lithium air battery. These electrodes, when supplied with untreated air, are stable for only 50 h in rest / discharge cycles at a current density of -10 mA/cm². The synthesis of the PECH network and its assembly on the air electrode were first optimized.

When the PECH network is dried before hydroxide ion exchange, a more selective membrane was obtained. However, this membrane formed a poor interface with the air electrode, which reduced the electrochemical performance. Contrariwise, a good interface in the membrane / electrode assembly (MEA) was obtained by the direct synthesis of a PECH₁₅ network (PECH network modified with 15 mol % DABCO) over the air electrode. The MEA not dried and ion exchanged in 1 M KOH for 3 days displays the highest electrochemical stability, which was

increased from 50 to 350 h, without delamination between the membrane and the electrode. However the membrane is fragile and its water uptake is still significant.

To improve its properties, the PECH network was then combined with a hydrophilic polymer network based on poly(2-hydroxyethyl methacrylate) (PHEMA), in an IPN architecture. The synthesis of these IPNs has been optimized and only one mechanical relaxation was detected on these materials, confirming the desired architecture with good interpenetration of both polymer networks. The PECH₁₅/PHEMA 68/32 IPN showed a water uptake two times lower compared to the single PECH network, while an IEC of 1.3 meq./g preserves good hydroxide conductivity (2 mS/cm) with anion selectivity (transport number = 0.74). The chemical stability in LiOH at 50 °C of the polyelectrolyte network is also improved by the IPN architecture. No significant degradation of the ionic sites in the IPN under those conditions is observed, while the single PECH₁₅ network shows a drop in conductivity after 10 days of immersion. Under the conditions imposed by the lithium-air battery, a stability of 650 h was obtained with the air electrode modified with a PECH₁₅/PHEMA 68/32 IPN. These results have allowed confirming that the air electrode can be effectively protected from carbonation by a polymer membrane. The importance of the IPN architecture compared to single networks has also been shown. Finally, we found that when the electrode is protected by an IPN membrane, the degradation process is reversible and the assembly can be regenerated, which is not possible on the bare electrode.

In order to increase the stability of the IPN-modified electrode, we presented in the last part of this work the original combination of the PECH network with a fluorinated network based on Fluorolink[®] MD700. A PECH₁₅/Fluorolink 70/30 IPN shows an ionic conductivity of 2 mS/cm, a transport number of 0.80, and an IEC of 1.4 meq./g. While the IEC of this IPN is similar to that of a PECH₁₅/PHEMA 68/32 IPN, the selectivity is increased (0.80 vs. 0.74), confirming the interest of the introduction of the fluorinated polymer in the IPN. To our knowledge, this is the first reported association of a fluorinated neutral polymer and a cationic polyelectrolyte in an IPN architecture.

Furthermore, the PECH₁₅/Fluorolink 70/30 IPN / electrode assembly proved to be the most stable, with a stability of more than 1000 h. One of these electrodes was stable for 1500 h, after which the test was voluntarily stopped for analysis. This represents an increase of more than 20 times the stability of the non-modified air electrode. This particularly long stability may arise from the good interface observed between the IPN and the air electrode in this MEA. Indeed, SEM-EDX analysis shows that the PECH₁₅/Fluorolink 70/30 IPN has diffused

through the whole thickness of the air electrode over more than 200 μm deep in the catalytic layer. The known oxygen permeability of fluorinated polymers can also be relevant for the air electrode performance. However, the PECH/Fluorolink IPNs morphology is still to be better characterized. The water uptakes of these IPNs are higher than expected for a partially fluorinated IPN. In particular, the study of the morphology adopted by the IPNs when immersed in electrolytes would be necessary to explain the electrochemical behavior when in operation.

The best performance in our laboratory was obtained on a 0.78 cm^2 air electrode modified with a PECH₁₅/Fluorolink 70/30 IPN. A lifetime of 1500 h (75 cycles of rest / discharge at -10 mA/cm^2) was recorded in saturated (5 M) LiOH electrolyte. Both dried and immersed in 1 M KOH MEA were transferred to EDF R&D to be tested in lithium-air battery (LiO₂ project). Until now, there is not a clear agreement between the results obtained in EDF and LPPI laboratories. Some results are similar while other tests show a much lower performance in EDF laboratory. This confirms the difficulty of the scale-up and the transfer of this new technology (shape the test cell, method for assembling the electrode in the cell, the size of the air electrode...). To overcome these challenges, this study should be continued. For instance, a modification of the IPN membrane to reduce its swelling in the electrolyte could help to improve the results in different tests assemblies and in larger electrode surfaces.

As a perspective, to increase the life-time of a high surface air electrode, it would be interesting to elaborate IPNs with higher transport number, by adjusting the charge density of the polyelectrolyte network or by combining fluorinated polyelectrolytes and fluorinated neutral polymers networks. We showed that the MEA can be regenerated by the removal of the formed carbonate, and thus the chemical resistance can be the limiting factor. The neutral network crosslinking density can be increased to further limit the swelling, to increase the chemical stability, and to increase the mechanical properties for the scale-up of the system.

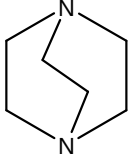
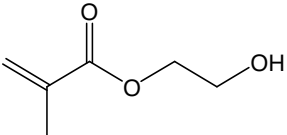
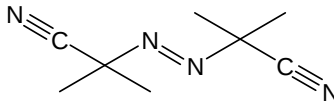
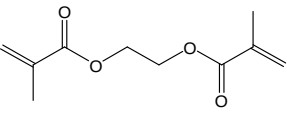
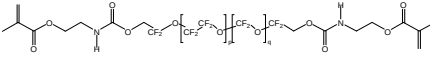
Another aspect that should be studied more deeply is the effect of membrane drying before the anion exchange. We observed that the networks dried after synthesis present a lower swelling behavior than non-dried ones. In addition, the membranes dried before anion exchange were more selective but the corresponding assemblies had much lower performances in half cell and the results were not reproducible due to its delamination. A compromise could be found between complete drying of the assembly that led to destruction of the interface and no drying, for which the best results were obtained. For industrial

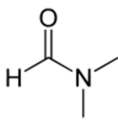
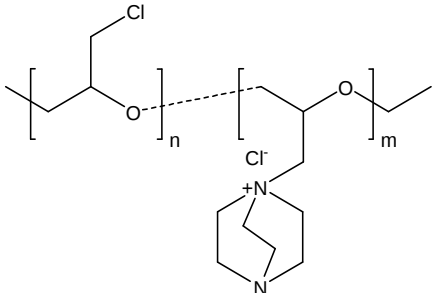
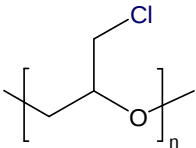
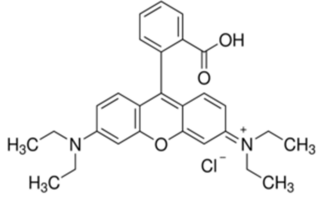
applications it would be preferable to obtain dried assemblies that can be stored for long periods, and be swollen in the electrolyte prior to use.

The stability of the membranes in LiOH can be also subject to more study. In fact, anionic exchange membrane stability has not been studied in the literature in LiOH, and differences appear between NaOH and KOH. The PECH/Fluorolink IPNs are being tested in our laboratory and in EDF as part of aqueous Zn-air battery (AZTEQUE project). In this system, the 8 M KOH electrolyte is expected to be more aggressive for the polymer network than the 5 M LiOH in the Li-air battery. However, promising results are also obtained, which confirms the chemical resistance and adequate electrochemical properties of these fluorinated IPNs. Nevertheless, it is important for the continuation of this work to understand the relationship between membrane morphology and properties, leading to the effective protection of an air electrode under the conditions imposed by the battery.

Annex:
Experimental Part

1. Reagents and Materials

Name Abbreviation CAS No.	Supplier	Molar mass	Physical properties	Structure
1,4-diazabicyclo-[2.2.2]- octane DABCO 280-57-9	Acros Organics	112.2	Solid m.p. 156 - 159 °C sublimation: 20 °C	 $C_6H_{12}N_2$
2-hydroxyethyl methacrylate HEMA 868-77-9	Sigma- Aldrich	130.1	Liquid 1.073 g/mL (25 °C) b.p. 67 °C (3.5 mmHg) Vapor pressure: 0.01 mmHg (25 °C)	 $C_6H_{10}O_3$
Azobisisobutyronitrile AIBN 78-67-1	Acros Organics	164.2	Solid m.p. 103 °C	 $C_8H_{12}N_4$
Ethylene glycol dimethacrylate EGDMA 202-617-2	Sigma- Aldrich	198.2	Liquid 1.051 g/mL (25 °C) b.p. 98-100 °C/5 mmHg Vapor pressure: <0.1 mmHg (21.1 °C)	 $C_{10}H_{14}O_4$
Fluorolink [®] MD700	Solvay Solexis	1800	Liquid R.I. = 1.342 η = 580 cP (25 °C) [F] = 52 wt. %	
Hydrochloric acid HCl 7647-01-0	Fisher Scientific	36.5	36 wt.% solution 1.17 g/mL (25 °C)	HCl
Lithium hydroxide LiOH 1310-65-2	Acros Organics	23.9	Colorless tetrahedral crystals m.p. 473 °C solubility: 125 g/L H ₂ O (25 °C)	LiOH

N,N-dimethylformamide DMF 68-12-2	Acros Organics	73.1	Liquid m.p. -60,48 °C b.p. 153 °C 0.944 g/mL vapor pressure: 2.7 mmHg (20 °C)	 C ₃ H ₇ NO
Poly(epichlorohydrin) modified by DABCO (10-12 mol %) PECH	ERAS Labo, France	103.7	Solution 100 g/L in DMF ~ 1 g/mL	
Polyepichlorohydrin 24969-06-0	Sigma- Aldrich	92.5	Solid soluble in DMF, chloroform	
Potassium hydroxide KOH 1310-58-3	Sigma- Aldrich	56.1	Solid solubility: 1210 g/L H ₂ O (25 °C)	KOH
Rhodamine B 81-88-9	Acros Organic	479.0	Solid m.p. 165 °C soluble in H ₂ O, EtOH, ether	 C ₂₈ H ₃₁ ClN ₂ O ₃

Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. All other chemicals were used without further purification.

Deionized water was used for electrolyte solution preparation and ionic exchange process. The air electrodes (E4 and E5) were purchased from Electric Fuel.

2. Polymer synthesis

The different polymer material synthesis and methods for membrane-electrode assemblies (MEA) were detailed in the different chapters as listed below.

2.1. Synthesis by Solution Casting

PECH network synthesis, solution casting Chapter II § 2.2.1, p. 81

2.2. Synthesis by Reaction Molding

PECH network Chapter II § 2.2.2, p. 82

PECH network with modified DABCO content Chapter II § 3, p. 89

PHEMA network Chapter III § 1.1, p. 118

PECH₁₀/PHEMA IPNs Chapter III § 1.1, p. 118

PECH₁₅/PHEMA IPN Chapter III § 2.1; p. 132

Fluorolink[®] MD700 network Chapter IV § 1.1 p. 146

PECH₁₅/Fluorolink IPNs Chapter IV § 2.1, p. 151

2.3. Membrane Electrode Assembly

2.3.1. Membranes Synthesized *ex-situ*

PECH MEA Chapter II § 4.1.1, p. 97

PECH₁₀/PHEMA IPNs MEA Chapter III § 1.4, p. 129

2.3.2. Membranes Synthesized *in-situ*

PECH MEA Chapter II § 4.1.2 p. 101

PECH₁₅/PHEMA IPN MEA Chapter III § 3.1, p. 137

PECH₁₅/Fluorolink IPNs MEA Chapter IV § 4.5.1, p. 164

All the networks were synthesized between two silylated glass plates for ease of unmolding. The silylation was made by placing the clean glass plates vertically inside a closed desiccator with a beaker filled with 5 mL of chlorotrimethylsilane (CAS 75-77-4, Sigma-Aldrich). The glass plates were left in the desiccator for 24 h at room temperature.

3. Analytical Techniques

3.1. Spectroscopic Methods

3.1.1. Nuclear Magnetic Resonance (NMR)

^1H and ^{13}C NMR spectra were recorded with a Bruker Avance DPX-250 spectrometer (^1H NMR MHz and ^{13}C NMR 62.9 MHz) in deuterated chloroform (Sigma-Aldrich) or DMSO (Sigma-Aldrich) with tetramethylsilane (TMS - Acros Organic) as the internal standard.

3.1.2. Fourier Transform Infrared (FT-IR)

For the FT-IR spectra, a Perkin-Elmer Spectrum One spectrometer equipped with an ATR modulus was used. Spectra were recorded between 4000 and 600 cm^{-1} , by averaging 32 acquisitions at 2 cm^{-1} resolution.

3.2. Microscopy

3.2.1. Scanning Electro Microscopy (SEM) / Energy-Dispersive X-ray Spectroscopy (EDX)

Scanning Electro Microscopy (SEM) was carried out with a Zeiss Ultra 55 microscope, 5kV. Samples were dried under vacuum at 70 °C and analyzed without further treatment. EDX measurements were performed at the same time in this apparatus.

3.2.2. Confocal Microscopy

Images were recorded on a ZEISS (LSM 710) laser scanning confocal microscope. This apparatus is constructed upon an inverted light microscope and employs a “closed-loop” sample scanning stage for sample positioning and image acquisition. Dry samples were immersed in an aqueous rhodamine B solution for marking. Rhodamine B was excited at 561 nm and fluorescence collected from 570 to 640 nm. Light from the laser was directed through polarization optics to control the power and the incident polarization state, prior to directing it into the microscope by reflection from a harmonic beam splitter. The excitation light was focused to a diffraction-limited spot in the sample using a plan-apochromatic 63×/1.4 numerical aperture (NA) oil-immersion objective.

3.3. Electrochemical Methods

3.3.1. Half-cell Characterization of Electrodes

Characterizations were performed in a conventional three-electrode in-house constructed glass half-cell (Figure II - 5). The same method was used for the non-modified and modified electrodes. Air electrode with a 0.78 cm² surface was used as working electrode. Hg/HgO/1 M KOH electrode was used as reference, and a large area platinized titanium grid as counter electrode. Aqueous 5 M LiOH solution was used as alkaline electrolyte. All measurements were made at ambient temperature, under atmospheric pressure with untreated air. The half-cells left at rest for 1 h (for equilibrium) before starting the measurements.

The voltamperograms were recorded at a 2.5 mV/s scan rate from 500 to -1200 mV.

Potential vs. current (polarization) curves were recorded by applying different current densities, in step-wise increases from -1 to -30 mA/cm². Each current was maintained until a stable potential was observed, usually after 5 min. The electrode potential was measured at the end of this period.

Potential vs. time (stability) curves were recorded by cycling the air electrode for 10 h at open circuit voltage (OCV) followed by a 10 h polarization step (-10 mA/cm² current density). This method was chosen to reproduce the behavior of the battery in rest/discharge cycling.

3.3.2. Ionic Conductivity

Ionic conductivity was measured by electrochemical impedance spectroscopy using a BioLogic VSP instrument. The samples were placed between two stainless steel electrodes. Nyquist plots were recorded with a frequency response analysis (FRA) over frequency range of 1000 kHz to 10 μHz with oscillation amplitude of 10 mV. The electrical resistance (*R*) was measured from the intercept of the Nyquist plot at high frequency with the real impedance axis. The ionic conductivity was then calculated using the relation:

$$\sigma(S/cm) = \frac{l}{R \times S}$$

where *l* and *S* denote, respectively, the thickness and the surface of the material between the electrodes. Intrinsic conductivity was measured on water swollen samples in the hydroxide or in the chloride form.

3.3.3. Transport Number

The membrane transport number (t^-) was determined according to a static method derived from Henderson's equation.^{1,2} In this method, the membrane is placed between two cells, each containing 1 and 0.1 M KOH solutions (Figure 1).

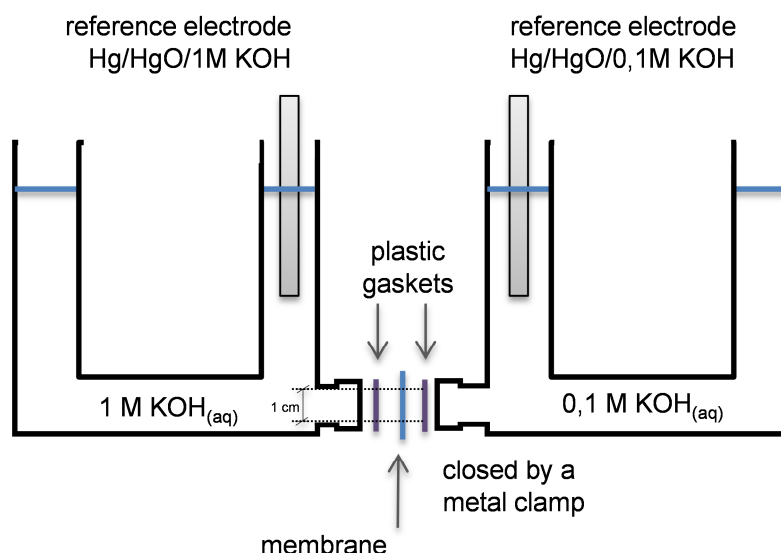


Figure 1: Scheme of assembly for transport number (t^-) measurements

The membrane potential E_M is calculated from the potential difference between the two electrodes:

$$E_{NERST} = \frac{R \times T}{F} \ln \frac{a_1}{a_2} = 57.7 \text{ mV}$$

where F is Faraday constant, R is gas constant, T is temperature, $a_1=0.756$ (1 M) and $a_2=0.0798$ (0.1 M)³ are the activities of the different electrolyte solutions.

Transport numbers are calculated from Henderson's formula:

$$t^- = \frac{1}{2} \times \left(1 - E_M \times \frac{1}{\ln \frac{a_1}{a_2}} \right)$$

¹ AFNOR NF X 45-200 Membranes polymères échangeuses d'ions **1995**.

² Agel, E. *Electrode à air à électrolyte solide polymère alcalin pour piles à combustible et générateur métal-air*, PhD Thesis, Université Paris 7 - CNAM Paris, 2002

³ David R. Lide, ed., *CRC Handbook of Chemistry and Physics, Internet Version 2007, (87th Edition)*, <<http://www.hbcpnetbase.com>>, Taylor and Francis, Boca Raton, FL, 2007.

3.4. Physicochemical Methods

3.4.1. Soluble Fraction

The soluble fraction (the non-crosslinked fraction of the material) of the single networks, IPN and semi-IPN was quantified by extraction of a known weight of dry material (W_0) in a Soxhlet apparatus with the synthesis solvent (DMF) for 72 h. After extraction, the materials were dried under vacuum at 70 °C until constant weight (W_E). The SF was calculated as a weight ratio:

$$SF(wt. \%) = \frac{W_0 - W_E}{W_0}$$

3.4.2. Water Uptake

The water uptake can be expressed as weight %, or as number of water molecules by ionic site. Experimentally, water uptake (WU) was determined by measuring the weight difference of the water swollen material and the dry material. Two methods are used:

When the materials were dried after synthesis: The dried materials were immersed in a 1 M KOH solution for counterion exchange for 24 h. After exchange the materials were rinsed in water until neutral pH and then soaked overnight in water to equilibrium. The water swollen materials were then wiped rapidly and weighted (W_w). They were then dried at 70 °C until constant weight (W_d). The water uptake (WU) was calculated as follows:

$$WU(wt. \%) = \frac{W_w - W_d}{W_d} \times 100 \%$$

When the materials were non-dried after synthesis: After synthesis, the materials (swollen in the synthesis solvent) are immersed in an excess of 1 M KOH solution for 24 h, to achieve the simultaneous removal of the synthesis solvent and the counterion exchange. Afterwards, the samples are rinsed until neutral pH and soaked overnight in water to equilibrium. The soaked materials are then wiped rapidly and weighted (W_w), before being dried until constant weight (W_d). Analogously, the water uptake (WU) is calculated with the above formula.

3.4.3. Ionic Exchange Capacity

The ionic exchange capacity (IEC) gives the number of functional ionic sites per gram of dry material, and can be expressed in meq./g or mmol/g of dry material.

The IEC of the membrane was determined by titration. The membranes in the hydroxide form were immersed for 20 h in 10 mL of an HCl solution of known molarity ($\text{HCl} \approx 0.1 \text{ M}$, titrated with tris(hydroxymethyl)aminomethane (tris) primary standard to determine the exact molarity).

After this period, the HCl solutions (partially neutralized by the OH^- of the membrane) were titrated with a KOH solution ($\text{KOH} \approx 0.1 \text{ M}$, titrated with the above mentioned HCl solution to determine its exact molarity). Titration end points were found with a pH electrode.

The IEC was calculated from the difference between the mol HCl before ($\text{mmol}_{\text{HCl},\text{O}}$) and after immersion ($\text{mmol}_{\text{HCl},\text{E}}$), and the material dry weight (W_d).

$$\text{IEC}(\text{mmol/g}) = \frac{\text{mmol}_{\text{HCl},\text{O}} - \text{mmol}_{\text{HCl},\text{E}}}{W_d}$$

3.4.4. Stability in Saturated LiOH

The stability in a saturated (5 M) LiOH solution is determined by measuring the conductivity of the material after its immersion in this solution. The dried sample, in its OH^- form, of known conductivity is immersed in a 5 M LiOH solution maintained at ambient temperature or at 50 °C. After a defined time the sample is removed from the solution, rinsed and equilibrated in water to remove any excess OH^- and its conductivity is measured. The conductivity of the sample is measured at defined time intervals.

3.5. Thermal Analysis

For all different characterization, when a drying step is indicated, it refers to drying under vacuum (5 mmHg) at 70 °C until constant weight.

3.5.1. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) measurements were performed in a TA instruments Q800 in tensile mode at 1 Hz frequency. Strain magnitude was set at 0.05 %, and preload force at 0.01 N. The tests were made in the linear viscoelastic domain. Temperature was varied from -130 to 200 °C at a scanning rate of 3 °C/min. The set up provides the storage and loss moduli (E'' , E'') and the loss factor ($\tan\delta = E''/E'$).

The DMA is commonly used to detect the presence of different phases in the IPN. In this analysis, E' and E'' are measured as a function of temperature. The mechanical relaxation temperature of a polymer (T_α) is associated with a peak in the curve of $\tan\delta = f(T)$ and a sharp decrease in the curve $E' = f(T)$. The diagram of a binary mixture of incompatible polymers has two distinct transitions corresponding to each phase (Figure 2 b).

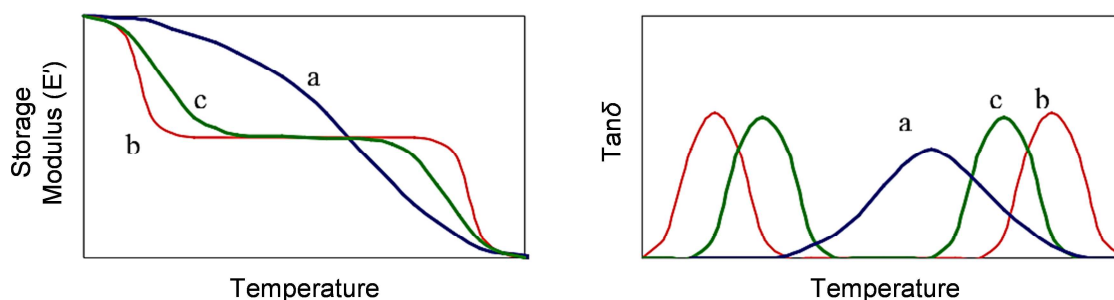


Figure 2: Typical DMA thermograms for (a) miscible, (b) heterogeneous and (c) partially miscible binary mixture

In a biphasic material if there is an interaction between the different polymers, which may disrupt the chain relaxation process at this interface, the peaks are shifted towards each other. If interactions are large enough, an additional $\tan\delta$ peak corresponding to the polymers at the interface can be observed. Thus, when the interface becomes infinite, which corresponds to a homogeneous material, the intermediate peak becomes the predominant or the only observed (Figure 2 c). When the mixture is completely homogeneous across the DMA, a single mechanical relaxation temperature between the mechanical relaxations of the two polymers is detected. DMA analysis therefore provides information on the influence and arrangement of these phases.

3.5.2. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measurements were carried in a TA Instruments Q50 model under argon or synthetic air atmosphere operating from room temperature to 600 °C at 20 °C/min heating rate. The degradation temperatures were measured at 5 % weight loss of the sample.

3.5.3. Rheology Measurements

Rheological measurements were performed with an Anton Paar Physica MCR 301 rheometer equipped with CTD 450 temperature control device with a plate–plate geometry (25 mm diameter). All measurements were recorded at an imposed 0.2 % deformation at 1 Hz frequency at 25 °C on samples that were previously fully hydrated by immersion in water for 48 h. The average value of the shear modulus was measured for 5 samples.

Summary

This work focuses on the synthesis and characterization of polymer membranes to be used as anion exchange membranes for protection on an air electrode in a new lithium–air battery for electric vehicle. In these materials showing interpenetrating polymer networks (IPN) architecture, a hydrogenated cationic polyelectrolyte network, the poly(epichlorohydrin) (PECH), is associated with a neutral network, which can be either hydrogenated or fluorinated. First, the synthesis of the polyelectrolyte network and the membrane/electrode assembly were optimized. Second, a first IPN series associating the PECH network with a poly(hydroxyethyl methacrylate) network was synthesized. Third, the same PECH network was associated with a fluorinated polymer network. All the materials were characterized, and optimal synthesis methods as well as an optimal composition were determined for each association. The IPNs show improved properties compared with the single PECH network. The air electrode protected by these new anion exchange membranes shows improved stability in the working conditions of the lithium-air battery. Specifically, a lifetime of 1000 h was obtained when the electrode was modified with a fluorinated IPN, a 20-fold increase in the lifetime of the non-modified electrode.

Key words: Interpenetrating Polymer Networks; Anion Exchange Membrane; Metal-air battery; fluorinated polymer.

Résumé

Ce travail porte sur la synthèse et la caractérisation de membranes polymères échangeuses d'anions, destinées à la protection de l'électrode à air dans une batterie lithium-air (en vue d'une application pour véhicule électrique). Ces matériaux à architecture de réseaux interpénétrés de polymères (RIP) associent un réseau polyélectrolyte cationique hydrocarboné, la poly(épichlorohydrine) (PECH), à un réseau de polymère neutre qui peut être soit hydrocarboné, soit fluoré. Tout d'abord, la synthèse du réseau polyélectrolyte et son assemblage sur l'électrode à air ont été optimisés. Une première série de RIP associant ce réseau PECH à un réseau de poly(méthacrylate d'hydroxyéthyle) a été synthétisée. Une seconde série de matériaux combinant ce même réseau PECH à un réseau de polymère fluoré a été développée. L'ensemble de ces matériaux a été caractérisé, et pour chaque série de RIP, la méthode de synthèse et la composition ont été optimisées. Les membranes RIP présentent des propriétés améliorées par rapport au réseau simple de PECH. L'électrode à air protégée par ces nouvelles membranes échangeuses d'anions présente une stabilité améliorée dans les conditions de fonctionnement de la batterie lithium-air. Plus précisément, une durée de vie de 1000 h est obtenue lorsque l'électrode à air a été modifiée avec un RIP fluoré, soit une augmentation d'un facteur 20 de la durée de vie de l'électrode non modifiée.

Mots clés: réseaux interpénétrés de polymères ; membrane échangeuse d'anions ; batterie métal-air ; polymère fluoré.

