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UNIVERSITÉ GRENOBLE ALPES

THÈSE

Pour obtenir le grade de

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préparée au sein du Laboratoire du Stockage Électrochimique (CEA/DRT/LITEN/DTS/LSEC) dans l'École Doctorale Ingénierie – Matériaux Mécanique Energétique Environnement Procédés Production

Modélisation Multiphysique de Cellules Sodium Chlorure de Nickel

Thèse soutenue publiquement le **09/12/2015** devant le jury composé de :

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CONFIDENTIAL UNTIL 9th June 2017

I believe that everything happens in this world for a reason, and this reason is usually called science

Facebook wisdom

To Alexandra

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Table of Contents

LIST OF ABBREVIATIONS 11		
INTRODUCTION		
CHAPT	ER 1: THE Na-MCl ₂ BATTERY TECHNOLOGY	
1.1. lı	nvention and developments	17
1.1.1.	The origin	17
1.1.2.	The ZEBRA project: from proof of concept to prototyping	19
1.1.3.	1982-1989: bringing the technology to the next level (Beta R&D and the AAC)	19
1.1.4.	1989-1998 The industrial Scale-up (the AAB years)	20
1.1.5.	1999-2015 From EV applications to large stationary storage systems	23
1.2. C	Operating principles	25
1.2.1.	Key elements and cell reactions	25
1.2.2.	The front reaction hypothesis	28
1.2.3.	Focus on the secondary electrolyte NaAlCl ₄	29
1.2.4.	Additional requirements	32
1.3. T	he FIAMM commercial technology	37
1.3.1.	The ML/3X unit cell: design, constituents and conditioning	37
1.3.2.	Unit cell performances	40
1.3.3.	Environmental impact and health issues	43
1.3.4.	Battery modules: influence of cell failures to packs general design	44
1.3.5.	Battery modules: performances and management	45
1.3.6.	Battery lifetime and ageing	50
1.3.7.	Safety and recyclability	54
1.3.8.	Large energy storage systems: general design and applications	56
1.3.9.	Objectives of the thesis	58

CHAPTER 2: ELECTROCHEMICAL CHARACTERIZATION OF THE COMMERCIAL CELL

2.1 Electrical performances		61
2.1.1	Constant discharge voltage curves	63
2.1.2	Standard charge voltage curves	65
2.2 Cycl	ic voltammetry experiments	69
2.2 Cycl 2.2.1	ic voltammetry experiments Full scan of the cell at very low rate	69 69

8]	Рa	g	e
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2.3 OC	V depe	endence of the temperature	85
2.2.4	Cyc	lic voltammetry with increasing scan rates	82
2.2.3	Con	iclusions	82
2.2.2	Add	litional tests: partial cyclic voltammetry scans	76
2.2	.1.3	Discussions about these first results	73
2.2	.1.2	Full scan peaks analysis	71

CHAPTER 3: 2D MODEL DEVELOPMENT OF THE COMMERCIAL CELL

3.1	Isoth	hermal electrochemical model of the Na-MCl ₂ cell: state of the art	87
3	3.1.1	Porous electrode electrochemical model requirements in molten salts	88
3	3.1.2	The seminal 1D model: governing equations	89
	3.1.2	2.1 Ohms's law for electronic conduction (ϕ 1)	90
	3.1.2	2.2 Ohms's law for ionic conduction (ϕ 2)	90
	3.1.2	2.3 Material Balance	91
	3.1.2	2.4 Charge transfer kinetics	92
	3.1.2	2.5 Molar average velocity of ionic species in the secondary electrolyte	94
	3.1.2	2.6 Porosity and volume fractions changes	95
	3.1.2	2.7 Specificities of the seminal model	95
3	3.1.3	Subsequent works	96
3.2	Integ	gration of the thermal model	99
3	3.2.1	Thermal model requirements for an electrochemical cell	99
3	3.2.2	Potential heat effects in Na-MCl ₂ cells	100
	3.2.3	Focus on the reversible heat	101
3.3	2D m	nodel development	102
3	3.3.1	Geometrical design considerations and meshing	102
3	3.3.2	Parameters and variables of the model	105
	3.3.2	2.1 Active materials microstructural parameters and quantities	106
	3.3.2	2.2 Secondary electrolyte melts properties	107
	3.3.2	2.3 Reference exchange current densities and transfer coefficients	107
	3.3.2	2.4 Thermal parameters and variables	108
	3.3.2	2.5 Geometrical parameters	109
3	3.3.3	Governing equations: practical implementation in Comsol	109
3	3.3.4	Governing equations in domain 1 (negative steel casing)	111
3	3.3.5	Governing equations in domain 2 (negative sodium electrode)	112
3	3.3.6	Governing equations in domain 3 (BASE separator)	112
3	3.3.7	Governing equations in domain 4 (porous positive electrode)	112
3	3.3.8	Governing equations in domain 5 (the carbon felt)	117
	8.3.9	Thermal-electrochemical coupled model	117
3.4	Initia	al simulation strategies	118

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Elec	trochemical two-steps mechanism simulations in isothermal mode	121
4.1.1	Initial tryouts	121
4.1.2	Simulations with constant melt composition (non-isothermal model)	124
4.2 Soli	d state process simulations in discharge mode	126
4.2.1	New working hypothesis	126
4.2.2	Baseline simulation of a constant discharge	127
4.2.	2.1 Baseline simulation for the non-isothermal model	127
4.2.	2.2 Baseline simulation analysis	130
4.2.	2.3 Baseline simulation in isothermal mode	136
4.2.3	Impact of the rate of discharge	137
4.2.4	Impact of the initial temperature	140
4.2.5	Impact of design changes	142
CONCL	USIONS AND PERSPECTIVES	145
APPEN	DIX A: GOVERNING EQUATIONS IN THE SEMINAL PAPER	149
APPEN	DIX B: LIST OF SYMBOLS	155
APPEN	DIX C: ANALYTICAL EXPRESSIONS	159
BIBLIO	GRAPHY	161

List of abbreviations

AAB	AEG Anglo Battery
AAC	Anglo American Corporation
BASE	Beta Alumina Solid Electrolyte
BESS	Battery Energy storage System
BETA	R&D Beta Research and Development
BMI	Battery Management Interface (equivalent to BMS)
BMS	Battery Management System (equivalent to BMI)
BRTC	British Rail Technical Center
CC	Constant Current Phase during charge
CV	Cyclic Voltammetry
DOD	Depth of Discharge
DOE	U.S. Department of Energy
EOC	End of Charge
EOD	End of Discharge
ESS	Energy Storage Solutions
EV	Electric Vehicle
EVS	Electric Vehicle Symposium
F.I.A.M.M.	Fabbrica Italiana Accumulatori Motocarri Montecchio
GE	General Electric
GITT	Galvanostatic Intermittent Titration Technique

12 Page	List of abbreviations
NREL	National Renewable Energy Laboratory (U.S.)
OCV	Open Circuit voltage
ODE	Ordinary Differential Equation
PDE	Partial Differential Equation
PNNL	Pacific Northwest National Laboratory
SBB	Sodium-Beta Batteries
SEM	Scanning Electron Microscopy
SL	Slimline nickel-based cell
SOC	State of Charge
TCB	Thermal Compression Bond
USABC	United States Advanced Battery Consortium
VC	Voltage Control charge phase
ZEBRA	Zeolite Battery Research Africa and also later Zero Emission Research Activities

Introduction

Sodium-metal chloride batteries, which are often referred as ZEBRA batteries, have been implemented for many years now in electric vehicles and are currently gaining growing attention in the field of stationary, grid connected, and off-grid applications. It is in the context of global warming and limitation of carbon dioxide emission that the concept of large grid connected solar and wind energy plants has emerged in the past decade. The deployment of such type of energy production installations has reached a significant level of maturity, and the need to overcome the intermittency factor, and its potential impact on the grid, is becoming more and more critical. Electrochemical accumulators are key devices able to store electrical energy, and ensure a balance between intermittent supply and cyclical daily demand, when the electricity is generated through these green energy alternatives. In the perspective of sustainable development, the choice of the battery technology is of great importance. Abundant and cheap active materials (used or produced in the accumulators) are to be favored, with as less impact on the environment as possible. Storage devices themselves must not emit greenhouse gases, or present a risk to health or safety. In addition, these battery systems must have an important life time and a high cycling capability (several thousand cycles). The Na-NiCl₂ battery technology is a strong candidate to address these issues.

In grid connected solar or wind power plants, the Energy Storage System (ESS) is one component of a larger facility that includes the energy production system itself (solar fields or wind farms), the point of connection to the grid (i.e. the grid energy demand), and all the converters between these components. So, it is necessary to know how to manage the electrical performance of the battery, and how to coordinate the battery operation in synergy with the other devices. For these reasons, it is crucial to have reliable battery management indicators, like its

state of charge and state of health¹, available energy, or ability to meet a power demand at a given time.

Detailed knowledge of the mechanisms at work in discharge, charge, and relaxation phases in ZEBRA batteries are essential to improve the performance of these indicators. This thesis, initiated by the FIAMM Group (a major Na-NiCl₂ battery manufacturer) and the CEA, aims to better understand the electrochemical and thermal behaviors of the commercial cells and battery packs. Because of its inherent features that will be exposed in the first chapter, operando characterization of active materials in the commercial cell at any state of charge would have required to spend a huge amount of time to set up and organize experiments in large scale analytical facilities (neutron diffraction for instance). So, it was decided early on to focus on the physical modeling of the commercial cell to reach our primary objectives. An equivalent circuit modeling approach was also conducted in parallel to provide on the one hand possible inputs to calibrate the physical model, and on the other hand the core of a battery management system that could be implemented in the commercial systems².

In this perspective, most of the experiments required to meet the objectives of my thesis have been conducted in the Laboratory for Electrochemical Storage (CEA/LSEC) and are detailed in this manuscript as follows. In the first chapter, basic concepts related to the Na-MCl₂ technology are described, from the constituents of the cell, to the battery pack level. Characterization of the ML/3X commercial cell is presented in the second chapter. Electrical performances (charge, discharge, and relaxation) have been measured at various current rates and operational temperatures. The identification and quantification of the active materials have been assessed from cyclic voltammetry experiments. The development of the 2D multiphysics model, as well as its full implementation, is described in chapter three. This particular work, which was the main task of my thesis, is based on an exhaustive bibliographic study of the ZEBRA technology. Two important hypotheses are debated in the scientific literature, assuming either a two-step mechanism in solution, or a solid state process between active materials. The originality of my own contribution relies on the fact that I have modeled a mixed Ni/Fe cell, and that I have developed and used a fully coupled electro-thermal model. The simulation results in constant current discharge mode, and the validation of the optimized model are presented and discussed in

¹ The state of health refers to the state of aging of the battery

² This work although carried out successfully will not be disclosed in the present manuscript.

the fourth chapter. The robustness of the model has been put to the test in terms of discharge rates and operational temperatures. The impact of design changes on the cell performance has also been investigated.

The development of a 3D thermal model of the commercial ST523 battery pack (dedicated to the stationary applications described at the beginning of this introduction) was also engaged during my thesis. But as it does not brought any more insights about the physics at work at the cell level, the associated works and results are not included in the present manuscript.

Chapter 1 The Na-MCl₂ battery technology

In this first chapter, the sodium metal halide technology is described in details. Following a historical presentation, the main elements required for basic functioning are reviewed. The actual commercial solutions manufactured by the F.I.A.M.M. group are then introduced, from the cell unit level to large battery energy storage systems (BESS). In the light of this contextual overview, the objectives of my thesis will be exposed.

1.1. Invention and developments

Up to more recent developments, this section mostly highlights Johan Coetzer and Jim Sudworth's recollection of the development of the sodium metal chloride battery, in their 2000 review *Out of Africa: the story of the zebra battery* (1).

1.1.1. The origin

The discovery in the early sixties that beta-alumina ceramics were good ionic conductor at high temperature (2), opened up the possibility of designing electrochemical cells with liquid sodium at the negative electrode, and beta alumina as solid electrolyte membranes³. Weber and Kummer (3), first described in 1967 a new secondary battery that featured a beta-alumina

³ This type of accumulator is often referred as Sodium Beta Battery (SBB)

ceramic as the electrolyte, and liquid sulfur with sodium polysulfide in the positive compartment⁴ (Figure 1).



Figure 1: basic outline of a NaS cell

This type of accumulator provides an open circuit voltage (OCV) of around 2 V. It must be operated at a sufficiently high temperature (250-350 °C) to keep all of the active material in a molten state, and to ensure adequate ionic conductivity of the electrolyte. Because sulfur and polysulfides are insulant materials, an additional conductive media is needed in the positive compartment⁵ that extends from the current collecting plate to the ceramic surface. The sulfur and polysulfides are strong oxidants, whereas sodium is a highly reductive metal. The beta-alumina membrane is impervious to chemical attack by these species, but it shows limited fracture toughness, and this is a significant safety issue. Indeed, the direct reaction between positive and negative molten active materials is highly exothermic and therefore must be controlled. This highly corrosive environment also limits the choice of material for other parts of the cell (casing, leads, seal), and their durability (4). Early works that will lead to the Na-MCl₂ technology (the so called ZEBRA battery), were driven by investigating alternative active materials that do not present these drawbacks.

⁴ It will be further referred as a NaS battery

⁵ Weber and Kummer have proposed the use of a porous graphite felt

1.1.2. The ZEBRA project: from proof of concept to prototyping

ZEBRA research dated back to the mid-seventies. It was first conducted in Pretoria (indeed ZEBRA originally stands for Zeolite Battery Research Africa), where Johan Coetzer and his group started to investigate partly chlorinated transition metal carbides matrix, as an alternative to sulfur compounds. The main benefit of using these metal chloride based materials is that they are non-corrosive, but like the sulfur based species, they are not conductive. The aim of the ZEBRA project was to find a secondary molten salt electrolyte to mediate the transfer of sodium ions between the main solid electrolyte, and the positive current collector. This intermediate molten salt had to be compatible with the latter, and must prevented dissolution of the metal chloride during cell cycling. Indeed, if the transition metal happened to be in ionic form in the melt, it could irreversibly block the ceramic conductive channels. In the early eighties, the binary sodium tetrachloroaluminate molten salt (AlCl₃ + NaCl \rightarrow NaAlCl₄) has been identified as a strong candidate by Roger Bones and his team at the Hartwell Laboratories in the UK, after they have joined the ZEBRA project. Chloroaluminate melts are also referred as the first generation of ionic liquids. In addition to its ionic conductivity and its ability to avoid dissolution of selected metal chlorides⁶, sodium tetrachloroaluminate proved to be an effective asset regarding safety issues (that will be described later in this chapter).

1.1.3. 1982-1989: bringing the technology to the next level (Beta R&D and the AAC)

The beta alumina tubes used for the ZEBRA project were the same one supplied by the British Rail Technical Center in Derby (BRTC, UK) for the development of sodium sulfur battery. After this program was terminated, members of the BRTC team (Jim Sudworth, Roger Tilley, and Hamish Duncan) formed Beta R&D Ltd, to develop potential commercial solutions for sodium beta battery (SBB, i.e. NaS and ZEBRA technologies). The Beta R&D company negotiated a contract with the Anglo American Corporation (AAC) from South Africa to take the ZEBRA concept to the next level of development, and to find viable manufacturing route. The first discloser of this work in the scientific literature, was published by Johan Coetzer in 1986 (5). He proposed a list of transition metal to use as active material (Cr, Mn, Fe, Co, Ni), and presented experimental data concerning FeCl₂/Fe and NiCl₂/Ni cells (with practical specific energy and

⁶ This propriety strongly depends on the melt composition, see section 1.2.3

power up to 130 Wh.kg⁻¹ and 100 W.kg⁻¹ for the first cycles). The viability of the concept was also demonstrated by using multi kWh prototype batteries to power electric cars, over an eighteen month period. This short communication was followed by two more comprehensive papers published in 1987 by the Hartwell Laboratory team on an iron-based cell⁷ (6), and by the Beta R&D/AAC team on nickel and iron-based cell⁸ (7). It is evident from the late eighties scientific literature that the strongest candidates to be used in the positive electrode were iron and nickel (8)(9)(10)(11)(12)(13). The iron cell had the advantage of low cost but the nickel cell was more stable with cycling and gave higher specific power. During this period, efforts have been pursued successfully to optimize initial chlorination of the transition metals, the wetting of the liquid sodium on the beta alumina in the negative compartment, and to identify the additives needed for control of capacity loss and resistance rise. On the other hand, cost effective routes to produce the beta alumina tubes at a large scale production have been developed.

1.1.4. 1989-1998 The industrial Scale-up (the AAB years)

In 1989, AAC formed a joint venture with AEG (then a subsidiary of Daimler Benz), AEG Anglo Batteries (AAB), to industrialize the ZEBRA technology. It was decided to focus on a redesigned slimmer nickel cell to reach the higher power to energy ratio needed for the targeted automotive applications (Figure 2).

⁷ In association with Coetzer and Galloway's ZEBRA Power System Ltd

⁸ Both chemistries were tested in battery systems for electric cars



Figure 2: experimental C-Class Mercedes-Benz with electric drive and ZEBRA battery, 1993

Consequently, the choice of nickel determined the design of all future commercial cell types, with the positive electrode inside the beta alumina tube, as otherwise a nickel cell casing would be needed and this would be too expensive. In 1991, AAB set up a pilot line in Berlin to produce 30 Ah *slimline* cells (denoted SL), using new and more reliable processes to bound the collector nickel parts to the alumina components, and ultimately get a totally sealed cell unit (Figure 3).



Figure 3: ZEBRA cell basic outline from (14)

During the following years, and while testing the battery modules on BMW and Mercedes electric vehicles (EV), other major advances were achieved by modifying the design and content of the unit cell. In 1995, the ceramic-manufacturing plant in UK was able to produce cloverleaf-shaped beta alumina tube (Figure 4) with increased surface area (+50 %). The associated benefit was a significant reduction of the positive electrode mean thickness while keeping the same casing.



Figure 4: ZEBRA cell cross sectional views of slimline (SL) beta alumina on the left and monolith (ML) beta-alumina⁹ on the right (15)

The peak power quality of these *monolith* cells (denoted ML) has also been improved by substituting some of the electroactive nickel with iron (around 20 %)¹⁰. These optimizations have led to a cell with a specific energy in excess of 140 Wh·kg⁻¹, and potentially 100 Wh·kg⁻¹ for a battery pack. These specifications were able to fulfill the EV batteries requirements defined by the United States Advanced Battery Consortium (USABC), such as energy and power density, no maintenance, summer and winter operation, safety, failure tolerance, and low cost potential. This was publicized in a scientific paper written by Cord-H. Dustmann in 1998 (16). Performance advances during the AAB era were also formalized by Roy Galloway and Steven Haslamn, from Beta R&D, in a comprehensive scientific paper (15) published in 1998 too. Figure 5 sums up the

⁹ On the pictures we distinguish metal shims between the casing and the ceramic which function will be described in section 1.3.1

¹⁰ This feature is fully described in section 1.3.2.

Chapter 1

influence of the changes in design and active material on both the specific energy and the specific pulse power at 80 %¹¹ of depth of discharge (DOD) of ZEBRA cells, during the AAB period.



Figure 5: improvements of specific energy and power densities during the AAB era (1)

However the same year, and despite the fact that the ZEBRA technology was ready for commercial volume production, the two parents companies of AAB chose to redirect their strategies away from the EV application field.

1.1.5. 1999-2015 From EV applications to large stationary storage systems

In early 1999, Carlo Bianco the owner of MES-DEA (a major Swiss supplier of components for the automotive market) took this opportunity to purchase the ZEBRA battery IP technology. He installed a new integrated plant in Stabio for the volume production of both the beta alumina tubes and the battery packs (with a projected production capacity potential of more than 30,000 batteries per year). Production started in 2001, with a 32 Ah nickel iron unit cell (denoted ML/3G), and amongst other configurations 32 Ah/64 Ah nominal capacity packs (denoted Z5, 216 cells, 17.8 kWh nominal energy and 32 kW peak power). MES-DEA are part of the CEBI

¹¹ The USABC goal in 1998 regarding the specific pulse power was 150 W.kg⁻¹ at 80 % depth of discharge for a two third open circuit voltage at the end of a 30 s pulse

group of companies and the group's expertise in volume production has been applied to both the cell and battery, resulting in significant weight and cost savings. MES-DEA advances over the years were publicized at the international Electric Vehicle Symposium (EVS) (14) (17) (18) (19) (20), and towards the scientific community in (21) and (22). The latest major improvements to the electrochemical performances of the cell, have been described in 2007 by Alberto Turconi (23). They are related to the composition and granulation of the positive electrode, and their effects on the electrical performances. Indeed and from 2001, MES-DEA pursued a program¹² to enhanced the specific energy density of their unit cells, resulting in the increase from 94 Wh·kg⁻¹ (C-type cell), to 120 Wh·kg⁻¹ (P-type cell), and ultimately 130 Wh·kg⁻¹ for the X-type cell. X-type granules composition is the result of:

- adding small quantities of iron sulfide to prevent capacity loss (enhanced stability with ageing),
- using a different brand of supplied nickel powder, with higher surface area to increase the peak power availability,
- reassessing the iodide additive content and granulometry, to better prevent resistance rise with cycling.

In 2010, the joint venture FZ SoNick, was created between MES-DEA and the Italian FIAMM group. The latter is specialized in automotive parts and one of the world's largest lead acid battery manufacturers. In this partnership, FIAMM aim was to extend the range of potential ZEBRA applications to the stationary energy storage market. Nowadays, FZ SoNick (that became FIAMM SoNick), is an active part of the FIAMM Energy Storage Solutions division (FIAMM ESS), and the company develops combined stationary applications from kWh battery packs (24) (25) (26), to MWh battery systems (27). From the late 2000s however, a new US major player (General Electric), had started to show great interest in the technology through fundamental research, subsequently publicized in several symposia (28) (29) (30) (31) (32). Both automotive and stationary applications were in the scope of GE. They have further move by buying Beta R&D (for a time, beta alumina tubes have been provided by FZ SoNick), and they have developed their own sodium nickel chloride technology brand in 2013, the Durathon[®] battery (33) (34). But despite massive investments (\$170 million in the Schenectady plant nearby

¹² Programme partly funded by the Swiss Federal Office of Energy

Chapter 1

Niskayuna, in the state of New York) and further fundamental research (35) (36), volume production was disrupted in September 2014 due to a lack-of-work order (and GE has scaled back his battery plant in January 2015). This section would not be complete without citing the fundamental works carried out since 2010 at the Pacific Northwest National Laboratory (PNNL, USA) by John Lemmon and Vincent Sprenkle team¹³, to develop laboratory planar cells operating at lower temperatures, and with alternative active materials. By the nature of their subject, these richly documented studies are out of the scope of my thesis although some of their results confirm previous empirical advances (37) (38) (39) (40) (41) (42) (42) (43) (44) (45) (46) (47) (48) (49).

1.2. Operating principles

In this section, I will go back to the basic principles and concepts associated with the sodium metal chloride technology, before focusing on each of its essential parts. If many transition metals have been under investigations during early works (and still are (50)), I will only evoke nickel, iron, and mixed nickel/iron based active material configurations. In the last paragraph, additional features needed to optimize the cycling performance will be reviewed.

1.2.1. Key elements and cell reactions

All electrochemical cells are comprised of three fundamental elements:

- a negative electrode containing the reducing agent that will be oxidized during discharge,
- a positive electrode containing the oxidizing agent that will be reduced during discharge,
- an ion only conductive electrolyte between the positive and negative electrode.

Current collectors at each pole are also needed to transport the electrons in the external circuit during operation, as well as an additional separator to prevent electronic conduction (i.e. short circuit) between the two electrodes. In the case of a fully charged SBB cell (NaS or Na-MCl₂), the negative compartment contains liquid sodium Na_(l), and the electrolyte is a beta-alumina ceramic (or BASE for Beta Alumina Solid Electrolyte). Here, the BASE also acts as the electronic insulant separator. The positive compartment contains one or two transition metal

¹³ Their works was initially supported by the US Department of Energy's Advanced Research Projects Agency-Energy (ARPA-E)

chlorides in solid form MCl_{2(s)}, and molten tetrachloroaluminate NaAlCl_{4(l)} to ensure conductivity continuity. Based on these features, and in the stability window of the secondary electrolyte, the electrochemical reactions occurring at each electrode are (discharge from left to right, M standing for Ni or Fe):

$$MCl_{2(s)} + 2Na^{+} + 2e^{-} = 2NaCl_{(s)} + M_{(s)}$$
 [1]

in the positive electrode, and,

$$2Na_{(1)} = 2Na^+ + 2e^-$$
 [2]

in the negative electrode. The overall reaction of the cell is then given by:

$$MCl_{2(s)} + 2Na_{(l)} = 2NaCl_{(s)} + M_{(s)}$$
 [3]

Solid sodium chloride and pure metals are produced during discharge. In equation [1] and in discharge, sodium ions reactants originates from the tetrachloroaluminate melts, but the overall composition of the latter remains unchanged, as sodium ions are also produced at the negative electrode (equation [2]), and transported through the BASE to the positive compartment. Reverse processes occur in charge mode. To this day, no side reactions have been observed, so the faradic efficiency described by equation [3] is considered to be 100 % in charge and discharge, and for both metals. When M = Ni, the OCV of the cell is 2.58 V at 300 °C. In the case of M = Fe it is 2.33 V. With the Ni/Fe mixed-cell configuration, OCV curves display two plateaus at these two values, but it is not to be interpreted as the simple addition of two separate contributions (see section 2.2.1.3).

The standard operating temperature of a Na-MCl₂ cell is comprised between 260 and 350 °C. With a melting point of 98°C, pure sodium is always in liquid state during cycling. It is in direct contact with the outer negative current collector casing, and separated from the positive active material by the BASE.

In sodium beta batteries, a specific allotropic form of beta alumina is used, the polycrystalline Na₂O,5.33Al₂O₃ β ''-alumina, because it shows better conductive properties¹⁴ than the standard polycrystalline β -alumina Na₂O,11Al₂O₃. β ''-alumina ceramics synthetized for SBB cells are stabilized with MgO or Li₂O (< 1 wt.%). They feature bi-dimensional channels that facilitate the transport of Na⁺ from the negative electrode to the positive compartment (and vice versa).

One of the big breakthrough concerning the positive metal-based material, is the result of the works of Roy Galloway during the AAC era (1). Early on, the ZEBRA cells were assembled in fully charged state by soaking a sintered chlorinated matrix in the secondary electrolyte (Figure 6 (6)).



Figure 6: early Na-FeCl₂ prototype cell (6)

¹⁴ Its conductivity is comparable at 300 °C to standard aqueous electrolyte (51)

The sintered process was not easy, and necessitated the handling of hygroscopic chloride metal and metallic sodium, which was hardly conceivable for a volume production. Galloway demonstrated that the cell could be assembled in the discharge state from pure metal powders and plain sodium chloride¹⁵. Metal powders are use in significant excess relatively to the sodium chloride content to create a permanent electronic conductive matrix between the positive current collector and the internal surface of the BASE. As stated before, the ionic conductive path between these two frontiers are provided by the molten tetrachloroaluminate.

1.2.2. The front reaction hypothesis

There is a consensus in the literature (21) (51) (52) (53) regarding the existence of a reaction front zone that moves from the beta alumina surface towards the central current collector during discharge or charge. That assertion is based on the following points.

- Due to the presence of the invariant metal backbone evoked earlier, electronic conductivity is always possible between the BASE and the positive current collector.
- At fully charged or fully discharged state, the reaction begins on the surface of the beta alumina because the conductive path showing minimal resistance is the metal backbone (100 % electronic conduction).
- When all the charged/discharged active materials near the ceramic have reacted, the electrochemical reaction moves to the next layer, i.e. towards the central collector.
- Between the ceramic and the reaction front, ionic conduction is ensured by Na⁺ displacement in the tetrachloroaluminate melt. Between the reaction front and the current collector, electronic conduction is still ensured by electrons displacement in the metal backbone.
- The overall resistance increases during charge or discharge because the Na⁺ transport path increases.

Considering the Ni/Fe mixed-cell, we can predict that during discharge, when all the nickel active material is consumed, the reaction front will shift back to the electrolyte surface where there is still unreacted iron active material. This process implies a momentary decrease of the cell

¹⁵ The sodium nickel chloride technology is sometimes referred as the table salt battery

polarization resistance. Practical applications of this phenomenon will be describe further in section 1.3.2.

1.2.3. Focus on the secondary electrolyte NaAlCl₄

In addition to its conductive property, the secondary electrolyte has other several key roles in the well-functioning of the cell. To begin with, it is fully compatible with the chlorinated positive electrode and the beta alumina ceramic. And let us remember that it has been chosen in the context of the ZEBRA project because nickel and iron chloride are sparingly soluble in it. But if we go back to the earliest works described in the literature, we found a patent filed by John Werth in 1975¹⁶ (54), describing the broad use of alkali metal chloroaluminate for a SBB battery. In the claims of the invention, one of the criteria that have to be satisfied is that the chosen metal chloride must be soluble to some extent in the alkali metal chloroaluminate. The question here is why molten NaAlCl₄ has been chosen as a good candidate in both cases? In fact and theoretically, the cell can work in both cases, but metal ions such as Fe²⁺, or Ni²⁺ resulting from metal chloride dissolution have proven to be poisoning agents to the ceramic by plugging its conducting channels during cycling (10) (55). Sodium tetrachloroaluminate is a binary molten salt synthesized by mixing AlCl₃ with NaCl. The molar ratio of AlCl₃ in the mixture defines the acidity (AlCl₃ excess) or basicity of the melt. Investigations on the solubility of NiCl₂ (55) in sodium tetrachloroaluminate melts as a function of temperature, have demonstrated that it proved to be minimized in basic melts (molar ratio of NaCl > 50 %), and by keeping the operating temperature under 350 °C. In the case of FeCl₂ and up to 255 °C, the minimum of solubility has been reported to be near the equimolar melt composition (56). To keep this minimum of solubility in broader basic melts compositions, a fluoride additive is added to the positive electrode (see section 1.2.4).

Using from the start a basic melt with excess NaCl has another fundamental consequence. Considering the phase diagram of the melt in Figure 7, we can highlight the operating zone of the cell, between 260 and 350 °C, and roughly between 0.2 (0% of SOC) and 0.5 (100 % of SOC) mole ratio of $AlCl_3^{17}$. Notice that in all basic melts, NaAlCl₄ is indeed in liquid state from 157 °C.

¹⁶ The patent is own by Beta R&D

¹⁷ In the case of a 40 Åh cell



Figure 7: phase diagram of AlCl₃-NaCl melts from FTsalt-FACT salt database

From looking at this intersection zone, we can fairly assume that during operation, the melt is always in a NaCl_(s) saturated state¹⁸. Therefore, in a first approach we can consider that all NaCl_(s)¹⁹ produced in discharge by the electrochemical half reaction [1] will not consecutively dissolve in the melt. In charge mode, the reaction front will move accordingly with the disappearance of solid NaCl in the melt. Considering a full charge, at 100 % of SOC the composition of the melt will be given from Figure 7 by the intersection between the operating temperature ordinate, and the NaCl saturation curve. In the case of a rest period following partial charges, we can expect transitory localized NaCl_(s) phase changes in the melt composition where precipitation in the already charged area will be compensated by dissolution in the non-charged area to balance its spatial distribution (without changing the global quantity of NaCl_(s)) The same kind of process occurs during relax period after partial discharges.

Molten tetrachloroaluminate is also beneficial regarding the cell safety. Figure 8 describes the electrochemical window, and reaction schemes associated to decomposition of the secondary

¹⁸ Especially if high temperatures are avoided at the beginning of discharge or end of charge

¹⁹ In term of global quantity by disregarding the spatial distribution evoked further

electrolyte in case of overcharge, and overdischarge of a nickel-based cell²⁰ (i.e. outside the 0-100 % SOC operating range).



Figure 8: nickel-based cell reactions at 300°C, from (22)

In case of an overcharge, the cell voltage increases to 3.05 V where nickel reacts with the secondary electrolyte as stated in equation [4] (from left to right):

$$Ni_{(s)} + 2NaAlCl_4 = \underbrace{NiCl_{2(s)} + 2AlCl_3}_{positive \ electrode} + \underbrace{2Na_{(l)}}_{negative \ electrode}$$
[4]

As the nickel is in excess in the cell, this reversible reaction acts as a buffer in case of accidental overcharge of the cell. With an iron-based cell, the reaction to consider is described in equation [5], and started at 2.75 V^{21} (6) :

 $^{^{20}}$ For an iron-based cell, the intermediate plateau is situated at 2.33 V

 $^{^{21}}$ The value is given at 250 $^{\circ}\mathrm{C}$

Chapter 1

$$Fe_{(s)} + 3NaAlCl_{4} = \underbrace{FeCl_{3(s)} + 3AlCl_{3}}_{positive \ electrode} + \underbrace{3Na_{(l)}}_{negative \ electrode}$$
[5]

This is also a reversible reaction but operating at this plateau is undesirable as $FeCl_{3(s)}$ is soluble in the melt, leading to BASE poisoning by Fe^{3+} (with cycling, the resistance of the cell dramatically increases). Actually, nickel was first filled in small quantities in iron-based cells, as an additive to prevent reaction [5] (6).

Now in case of an overdischarge, the cell voltage decreases under 1.58 V where the remaining molten sodium and the secondary electrolyte reacts as stated in equation [6] (from left to right):

$$\underbrace{3Na_{(l)}}_{\text{negative electrode}} + \text{NaAlCl}_{4} = \underbrace{4NaCl_{(s)} + Al_{(s)}}_{\text{positive electrode}}$$
[6]

It is a fully reversible reaction provided overdischarge does not exceed 10 % of the full capacity. For a nickel-based or an iron-based cell, this reaction also prevents important polarization of the negative electrode at the end of discharge. It also occurs by direct contact in the event of fracture of the ceramic electrolyte. The metallic sodium is then rapidly consumed and a mixture of sodium chloride and aluminum metal is formed. Although the reaction is exothermic, only a small rise in temperature is observed, and liquid sodium is ultimately neutralized (see also section 1.3.4).

1.2.4. Additional requirements

The adoption of a convoluted shaped BASE has been already presented in section 1.1.4. Here we will begin to discuss the morphology of the positive active material. Disregarding the nature of the metal used as active material in the positive compartment, several features have been added to the cell components and content to optimize the manufacturing route, and electrical performances. Control of the operating temperature will be also addressed.

The morphology of the metal chloride electrode is of high importance regarding the cell available power (electrode surface), energy (passivation of the metal surface) and conductivity. A high-resistance MCl_2 layer is formed for both Fe and Ni on their surface during charge. Whereas this layer may be porous at the beginning, it ultimately sets an upper limit of the electrode area capacity (and thus capacity loading density) by passivation of the metal surface. In the battery field area (lead-acid, lithium-ion, nickel-cadmium), using porous matrix instead of plain metal structure to enhance the power availability is of basic knowledge. But if it is critically important to improve the porosity of the electrode, a balance between small pores to reach higher surface area and large pores to provide effective mass transports has to be found. In the ZEBRA porous matrix described in the literature, conversion ratio from metal to metal chloride has been found to be around 30 % (55) (57) (58).

To stabilize the porosity and matrix structure, hence the electrochemical performance, with cycling and ageing, beneficial effects of some additives have been assessed over the development period of the technology. The addition of small quantities of elemental sulfur (1-5 %) was early on proposed to prevent capacity loss in nickel-based cells (9) (12) (57) (59) (60). Premature capacity loss has been found with nickel active material, and this loss has been diagnosed to relate to the growth of the nickel metal grains within the cathode (9). Ratnakumar *et al.* (60) have reported studies showing that sulfur additive possibly enhance the kinetic of NiCl₂/Ni electrode. Post mortem works on the nickel powder by scanning electron microscopy (SEM) and by energy dispersive X-ray (XRD) analysis (22) confirmed that the presence of sulfur gives a very high surface area. In the late eighties (1), it was discovered that the sulfur needed for control of capacity loss could easily be incorporated as iron sulfide. Sulfur is indeed inserted as FeS (22) in actual commercial cell, and the corresponding quantity of elemental sulfur has been optimized to 1 % of the positive active material content. The role of the sulfur has been debated in the literature, but to this day the mechanism is still not clear (21) (59) (48) (61). For the first charge, it is assumed that Ni is oxidized to NiS at 2.37 V (300 °C), following reaction [7]:

$$\operatorname{FeS}_{(s)} + 2\operatorname{NaCl}_{(s)} + \operatorname{Ni}_{(s)} \to \operatorname{FeCl}_{2(s)} + \operatorname{NiS}_{(s)} + 2\operatorname{Na}_{(l)}$$

$$[7]$$

After that first charge, and with such low amount of sulfur in the cell, there seems to be no redox activity of the sulfur (62) above 2.3 V (i.e. reaction [7] is not reversible). However, sulfur species

have been reported to be electrochemically active between the iron plateau (2.33 V), and the voltage corresponding to the decomposition of the secondary electrolyte (1.58 V) (21). Whatever the mechanism is, by attacking the grain surface of nickel, sulfur inhibits the formation of uniform nickel layer on the grain from the solution. Finally, sulfur has been reported as a good additive to reduce NiCl₂ solubility in tetrachloroaluminate melts (this effect is enhanced if combined with NaBr and NaI additions) (58).

Sodium iodide is another important additive discussed in the literature (28) (63), and used in commercial cells (although NaI additive represents less than 1 % of the positive electrode weight). In 2000, Prakash *et al.* have published a comprehensive paper on the subject (64), and the use of other dopants such as NaBr and NaF (58). They described that sodium iodide addition, especially in combination with sulfur in Na-NiCl₂ cells, significantly increases the usable capacity and reduces the resistance of the cells. But their results have to be carefully interpreted as the effect of iodide doping is not fully uncorrelated from the effect of increased electrode porosity. From recent studies on commercial cells (22), NaI is proven to enhance the NiCl₂ electrode loading by improving the ability to charge at higher rates with voltage above 2.8 V. In accordance with the results published in (64), this effect is interpreted as iodide acting as a charge transfer catalyst at 2.84 V. Possible mechanisms are exposed, but they are not in the scope of my thesis²².

Small quantities of sodium fluoride dopant have been reported to increase the wetting of the ceramic and metals by molten salts (12). But more importantly, the solubility of iron chloride in the molten salt is significantly lowered by the addition of sodium fluoride, and tolerance to overcharge is also enhanced by NaF doping at low levels (5 mol% of the positive active material) (15). Adding sodium fluoride to a nickel-based cell, is also an elegant way to increase furthermore its overall capacity, as it is electrochemically active in the stability window of the secondary electrolyte (OCV = 2.39 V, equation [8]).

²² Indeed, overcharge mode will not be considered for the model, and NaI additive represents 0.4 % of the positive electrode weight
Chapter 1	Page	35
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$$NiF_{2(s)} + 2Na_{(l)} = 2NaF + Ni_{(s)}$$
 [8]

However higher NaF level gives a higher resistance so the capacity increase is limited.

The last additive that I will evoke is consumed during the maiden charge of the cell. By adding a small amount of aluminum in the positive electrode, the low voltage electrochemical reaction described by equation [9] occurs (15):

$$Al_{(s)} + 4NaCl_{(s)} = \underbrace{NaAlCl_4}_{\text{positive electrode}} + \underbrace{3Na_{(l)}}_{\text{negative electrode}}$$
[9]

The corresponding OCV of this reaction is 1.6 V which is much lower than the voltage of the main electrochemical reactions. The sodium generated primes the conductive path in the negative electrode (BASE, metal shims, casing). It also provides additional porosity to the positive solid matrix because solid aluminum metal is replaced by in situ formed sodium tetrachloroaluminate. This additional porosity will be useful to ensure full charge acceptance on this initial charge. And as part of the sodium metal generated during this maiden charge became trapped and inaccessible for further cycling, it minimizes the quantity of inactive sodium²³.

Since the cells are assembled in discharge state, without any liquid sodium in the negative compartment, conducting metal shims were installed between the negative collector casing, and the BASE²⁴. A cross-section of these metal shims can be seen in Figure 4, as well as in Figure 9 below.

²³ This inactive quantity is equivalent to a 2 Ah loss of capacity, not taken into account in the nominal capacity

²⁴ There are four of these metal shims installed around the BASE, one for each lobe



Figure 9: ML/3X cells assembly and cell components from (21)

In the one hand these shims ensure electronic conductivity during the very first charge (or maiden charge), and in the other hand they keep the generated sodium in contact with the BASE along all its useful height by capillarity, in order to sustained high discharge rates. The wetting of the BASE by liquid sodium is further enhanced by using a carbon-based coating on the external surface of the ceramic.

Metal powders²⁵ are added at the bottom of the casing, under the BASE tube. In case of a fracture of the ceramic, these metals are attacked first by the tetrachloroaluminate melt to prevent corrosion of the casing. Like the lateral shims, they also serve as an electronic conducting media at the bottom of the cell.

During cycling, the volume of the solid matrix in the positive electrode changes. For example, during charge, solid sodium chlorides are replaced by metal chlorides that occupy a smaller volume. Thus, the secondary electrolyte level drops a little in the positive compartment. To ensure a constant wetted surface of the positive current collector during cycling (hence

²⁵ FIAMM uses Ni and Al powders

reproducible pulse power), a carbon felt is inserted in the pin-shaped collector²⁶ as shown in Figure 9.

To finish this section, and before describing further the commercial cell, I will give considerations about the operating temperature. Na-MCl₂ cells can theoretically operate from 160 °C, because at this temperature both sodium and secondary electrolyte are in molten state. However, its performance would be very poor as electrical conduction of the BASE under 250 °C (and to a lesser extend conduction of the secondary electrolyte (65) (66)) is very low. From 350 °C, solubilization of the metal chlorides is enhanced (especially for iron chloride), so it is recommended to avoid repeated cycling above 350 °C. Intrinsic safety issues are experienced only when the cell reaches 600 °C, because the volatility of AlCl₃ in the tetrachloroaluminate melt causes pressure increase in the positive compartment, that may eventually lead to the fracture of the BASE.

1.3. The FIAMM commercial technology

The ML/3X cell currently produced by FIAMM SoNick represents in itself the state of the art of the ZEBRA technology, as it sums up the optimizations described in the previous sections. This unit cell is the building block from which all modules and packs configurations are designed.

1.3.1. The ML/3X unit cell: design, constituents and conditioning

The ML/3X commercial cell has a rated capacity of 38 Ah at C/2 rate (19 A), and 40 Ah at C/5 (8 A). The energy delivered during a full discharge at C/2 is 94 Wh. The cell weight is 690 g, and its external prismatic dimensions are 235 mm in height, with a square cross-section of 35.5 mm (Figure 10). Given these values, its specific energy and energy density are respectively 140 Wh/kg, and 317 Wh/L.

²⁶ The shape of the positive current collector derived indeed from the need to immobilize the carbon felt



Figure 10: FIAMM ML/3X unit cell

The cell key structural components are shown in Figure 11.



Figure 11: exploded view of FIAMM ML/3X cell key components

The casing is made of a nickel-coated steel. The cloverleaf-shaped β ''-alumina tube is manufactured from mixing a bohemite precursor (cheaper than using high purity Al₂O₃) with Na₂O (~ 10 wt.%) and Li₂O (<1 wt.%) powders. In the end product, the desired β '' allotropic crystallinity is obtained with a purity greater than 95 %. Volume production processes have been optimized to produce BASE with 1.5 mm thickness. The external surface of the BASE is painted with a carbon conductive formula prior to its insertion in the casing. Figure 12 sums up the top assembly of the cell.



Figure 12: vertical cross-section of the top of a ML/3X cell showing components assembly

The β ''-alumina tube is electrically isolated at the top with an α -alumina ceramic ring. Both ceramics are tied together by a borosilicate glass hermetic seal. The negative casing and positive current collector are laser welded to two nickel collars. These collars are tied to the a-alumina ring by a thermal compression bond (TCB), using a metallic diffusing paste. The α -alumina ring provides electronic insulation between the two collars (i.e. electrodes). The nickel pin-shaped positive current collector is laser welded to the positive collar. The carbon felt is simply put (and hold) inside the pin-shaped collector. Before inserting the BASE, a few quantities of Al and Ni metallic powders are added at the bottom of the casing. The positive active material is produced in an atmospheric controlled room. NaCl, Ni, Fe, FeS, NaF, NaI, and Al powders are dry grinded, blended, and compressed to eventually match the correct grain size and density. These processes are controlled to ensure stable properties (conductivity), and reproducible cell performances. The positive active material is then filled in the ceramic tube on a vibrating table, and the tetrachloroaluminate melt is added at 200 °C, all in dry atmosphere. Finally the nickel end cap (as seen on the top of the cell in Figure 12) is laser welded on top of the new sealed positive electrode. In the positive granules blend, an excess of 70 % of Ni is added relatively to the amount of NaCl. It will be used to create the permanent nickel backbone required to insure electronic conductivity in the entire positive electrode. The content of iron powder added to the mix corresponds to 20 % of the electroactive species, thus roughly 80 % of the available capacity originates from the nickel content.

On the very first charge (maiden charge), sodium is generated at the point of contact between the metal shims and the BASE (according to equation [9]), and aided by the conductive coating, quickly spreads out by capillarity to cover its whole surface. The second part of the maiden charge converts iron sulfide to iron chloride and nickel sulfide (see equation [7], and concerning NiS₂ see section 1.2.4). It is followed by the main reactions: iron to iron chloride first (until complete depletion of iron material), then sodium fluoride to nickel fluoride, to finish with the conversion of nickel to nickel chloride until all sodium chloride has been consumed (nickel is put in significant excess). After that first charge, a part of the sodium produced will be definitively trapped at the bottom of the cell. The amount of aluminum involved in equation [9] is set to correspond to this loss, so because the voltage of the cell will always be higher than 1.6 V (i.e. the reaction described by [9] will never occur in reverse mode), the available capacity of the cell will only depends on Fe, F and Ni based active material. In the ML/3X cell, fluoride electroactive species contributes to around 2 Ah of the available capacity. After the initial charge, the available capacity of the cell improves a little and stabilizes itself during the first ten or eleven cycles. These running cycles are performed in house, before the commercialization. This small improvement of available capacity may originates from the roughening of the current collector surface (55). The sintered nickel backbone is created at this step, and this closely monitored process insures reproducible electrical performances between cells.

1.3.2. Unit cell performances

The discharge curves²⁷ at various rates between C/10 and 1.5C (C being 40 Ah) are shown in Figure 13 (24), for the mean voltage of a ten cells string. The discharge is terminated when a maximum limit of Ah is reached (C/10 and C/5), or when a minimum voltage of around 1.8 V is reached (C/2, 1C and 1.5C).

 $^{^{\}rm 27}$ The charge mode will be described for the pack configuration in section 1.3.5



Figure 13: Discharge curves at various rate for a ML/3X cell, data from (24) are taken from the mean voltage of a ten cells string

Looking at the ten hours discharge curve it is possible to identify two plateaus regions. The first one is associated to the reduction of nickel chloride to nickel metal ($OCV_{NiCl2} = 2.58 \text{ V}$), while the second one is related to the reduction of iron chloride to iron ($OCV_{FeCl2/Fe} = 2.33 \text{ V}$). Even at this low rate, the nickel fluoride 2 Ah contribution between the two plateaus ($OCV_{NiF2/NaF} = 2.40\text{V}$) cannot be distinguished.

By substituting a proportion of nickel by iron, the peak power capability of the cell is significantly enhanced²⁸ (67). Between roughly 0 % and 80 % of DOD, and due to its higher OCV, only NiCl₂ is discharged at a low discharge rate. The FeCl₂ does not take part in the reaction as long as the cell voltage remains above the FeCl₂/Fe OCV. During application of high peak power pulses, the voltage of the cell drops below this OCV, and both NiCl₂ and FeCl₂ are discharged in parallel. During the pulse and until 80 % of DOD, it is FeCl₂ that will mainly contribute because it is still near the BASE interface where the resistance is lower. After the pulse, FeCl₂ is instantly recovered by reaction [10] (21):

²⁸ Another benefit being the lower cost of the cell at a small penalty in terms of specific energy

Chapter 1

$$FeCl_{2(s)} + Ni_{(s)} = Fe_{(s)} + NiCl_{2(s)}$$
 [10]

and iron is available again for the next pulse with the same minimum resistance configuration. The recovery of Fe to FeCl₂ occurs very fast, as long as NiCl₂ is available in the positive electrode (roughly 80 % of DOD). To sum up, iron doping allows peak pulse power which value stays independent of the DOD until all nickel active material is consumed (see Figure 14).



Figure 14: pulse resistance in milliohms of different cell types from (67), 1999, type ML3X can be linked to the iron doped monolith cell family

The segregation of the nickel and iron plateaus described above has to be interpreted carefully when it comes to assign the corresponding capacity contribution. Indeed, post mortem studies (6) (68) (69), and recent in situ analysis (35) (53) (70) have assigned the highest voltage plateau to a mixed metal chloride salt $Ni_{1-x}Fe_xCl_2$. Whenever iron is involved (pure or Ni/Fe mixed cell), the same studies have shown the existence of an intermediary Fe II species, $Na_6FeCl_8^{29}$, that is formed during charge and discharge.

²⁹ It is often referred as the Suzuki phase

1.3.3. Environmental impact and health issues

If we decompose the ML/3X cell in its elemental constituents (parts and active materials), we clearly see that all raw materials used in the manufacturing process are ultimately no threat to the environment, and quite readily available on earth (i.e. not too sensitive nor too expensive). The Na-NiCl₂ technology is indeed often referred as the table salt battery (Figure 15).



Figure 15: FIAMM SoNick sodium nickel chloride technology advertising

Ni is present as active material, in the positive collector and as protective coating in the steel casing. Fe is present as active material and associated with C in the steel casing. Na is present as active material, as oxide in the beta alumina, and as a constituent of the secondary electrolyte. Cl is only present as chloride ions in NaCl, and in the secondary electrolyte. Al is present as salt in secondary electrolyte and as oxide in the beta alumina ceramic. C is present in the steel casing, and is the only constituent of the felt. O is present as oxide in the beta alumina ceramic. Low content additives like Li in the BASE, S, F and I in the positive active material are present in crystal ionic form. During production, safety precautions regarding human handling of NaAlCl₄, NaF, NaI and Li₂O have to be considered. Ni and Fe metal powders are also considered as hazardous material, and have to be kept away from ignition sources (71). Sodium metal and metal chlorides are not handled as they are formed in the sealed cell during the first charge. Because the

technology is commercialized in battery packs form, the topics of safety issues during operation, as well as lifetime and recycling, will be treated in the next section.

1.3.4. Battery modules: influence of cell failures to packs general design

The cells assembly mode in battery packs is in fact dependent of an important intrinsic feature of ZEBRA cells, related to the cell failure mechanism. In the case of β "-alumina fracture (due to mechanical stress or extended overdischarge), the liquid sodium flows through the cracks into the positive electrode chamber, and reacts primarily with the secondary electrolyte. This reaction can be described by equation [6], here it is the direct reaction (equation [11]):

$$\underbrace{\frac{3Na_{(l)} + NaAlCl_{4}}{positive electrode}}_{positive electrode} \rightarrow \underbrace{\frac{4NaCl_{(s)} + Al_{(s)}}{positive electrode}}_{positive electrode}$$
[11]

This reaction is only mildly exothermic, releasing about two-thirds of the energy of the normal electrochemical reaction (71), and obviously produces solid, innocuous products. In addition, the porous matrix structure of the positive electrode reduces the reaction rate of [11], thus heat generation. Aluminum, being electrically conductive and solid at the operating temperature, creates a physical barrier that prevents further reaction but allows electrical conductivity between the cathode and the anode. The formation of this electrically conducting path between the electrodes implied that the cell can be considered as a low resistance shunt in case of BASE fracture (20 to 40 m Ω). This has the additional significant benefit of allowing long chains association of several hundred cells connected in series, without the need for any parallel failure shunts devices, and any complications or risks that might accompany them. Not only the battery is still functional in case of a cell failure, but it has been established that up to 5-10 %³⁰ of cells may fail before the battery can no longer be used. Indeed, one failed cell in a 200 cells string represents only 0.5 % of voltage loss. In battery pack with parallel chains, and in case of failed cells, the presence of iron doping is also beneficial for the balancing between strings during rest periods. The iron active material acts as a buffer, preventing the decomposition of the secondary electrolyte in case of internal circulating currents (21).

³⁰ Depending of the length of the string

In Figure 16, we can clearly see a typical compact association of cells in a FIAMM SoNick 48TL battery pack used for standard 48 V backup systems.



Figure 16: exploded view of a FIAMM SoNick 48TL battery featuring two or more strings of n ML/3X cells

The brazing of the nickel strap between two cells is made with a silver/copper (60 %/40 %) alloy. Through its two subsidiaries, FIAMM SoNick and FIAMM ESS, the company develops packs solutions for the EV market, industrial battery market and on grid energy storage field.

1.3.5. Battery modules: performances and management

Figure 17 and Figure 18 give the rated characteristics and electrical performances of respectively Z5 EV battery packs (or EV5), and the unit pack ST523 used in large stationary energy storage systems (BESS).

		Id.nr.	Z5-278-ML3X-64 30x00006	Z5-557-ML3X-32 30x00007	Z5-278-ML3X-76 30x00129	25-557-ML3X-38 30x00131
		Unit			/	
	Capacity	Ah	64	32	76	38
	Rated Energy	kWh	17.8	17.8	21.2	21.2
	Open circuit voltage					
	0 - 15% DOD	V	278	557	278	557
	Max. regen. voltage	V	313	626	335	670
	Min. op. voltage	V	186	372	186	372
	Max. discharge current	A	224	112	224	112
	Cell Type / nr. of cells		ML3)	V/216	ML3	K/216
	Weight with BMI	kg	11	32	18	32
	Specific energy without BMI	Wh/kg	10	00	11	19
	Energy density without BMI	Wh/I	1	52	181	
	Energy 2 h discharge	kWh	1	16 18		8
	Specific power	W/kg	13	179 169		59
ZEBRA	Power density	W/I	2	273 257		57
SONIC	Peak power	kW	30 30		0	
	2/3 OCV, 30s, 335°C		80%	80% DOD 70% DOD		DOD
	Ambient temperature	°C	-40 ti	0 +50	-40 to	p +50
	Thermal loss	W				
	at 270°C internal temperature		< 1	105	< 1	05
	Cooling		a	ir	8	ir
	Heating time	h	24 h at :	230 VAC	24 h at 2	230 VAC
	Periphery		BMI,	Fan	BMI,	Fan
			HEV Ap	plication	EV App	lication
Star 1	On board generator					
	MAX voltage, up to 70% SOC	V/Cell	2	.7	n.	a.

Figure 17: FIAMM datasheet with specifications of Z5 battery packs with different rated capacity and energy used in EV or HEV applications

ST523 Technical Specification

Electrical Characteristics	
Battery / Chemistry Type	NaNiCl ₂
Constant Power Discharge (Rated)	6.25 kW for 3 hours
Total Number of cells	240
Nominal Current Capacity	38 Ah (100% DOD)
Nominal Energy Capacity	22.5 kWh (100% DOD at C/10)
Round Trip Efficiency	90% round trip efficiency (at 6.25 kW constant power discharge 80% DOD & charging maximum power 6.25 kW)
Operation Voltage	Minimum Nominal Maximum 450 VDC 620 VDC 641 VDC
Max Charge Voltage	700 VDC (DC Bus)
Min Discharge	450 VDC (DC Bus)
Operating Conditions	
Cooling	Not Needed
Heating from cold to operation temperature	Take up to approximately 15 hours
Design Cycle Life	4500 Cycles at 80% DOD

Figure 18: FIAMM datasheet with specifications of the ST523 battery pack used in stationary applications

Notice that EV applications requiring greater peak power availabilities, the corresponding battery packs have an additional cooling system. These EV batteries also feature a better thermal

insulation (with a double wall vacuum system), because it is more critical to minimize the heat losses during more frequent inactivity periods^{31,32} (also see further in this section).

The discharge curves of a single cell displayed in Figure 13 are representative of the discharge performance of a battery pack because the cells are mostly associated in long chains. FIAMM batteries are charged using an I-U profile. First, a constant current is applied with a voltage limitation to 2.67 V/cell, and second, the voltage is maintained in 'floating' mode at 2.67 V/cell until the measured current is lower than 500 or 150 mA (end of charge or EOC criteria)³³. This method insures that whatever was the previous DOD, 100 % of SOC is reached at the end of charge. The more efficient charging currents per cell in term of energy cost and charge duration are in the range between 5 and 8 A. Figure 19 shows that it takes about 11 hours for a complete charge at 5 A, and from 10 A and higher, there is no significant time saving (24).



Figure 19: charging profiles of ML/3X cells as a function of constant charging current (24)

With no side reactions, this technology features 100 % coulombic efficiency, allowing the monitoring of SOC or DOD by a simple measurement of the Ah passed (by coulometry). From an

³¹ Captive active fleets are the actual best market for EV applications

³² These additional features of course generate additional manufacturing and maintenance costs.

³³ In practical BMS, EOC criteria depends of the sensitivity of the current measurements

electrochemical point of view, it is necessary to perform a full charge of the battery regularly, to avoid temporary loss of capacity. Indeed, as the reaction front always moves from the BASE to the central current collector, if the cell is cycled without a full charge phase, discharged active material in the center of the cell (Ni, Fe and NaCl_(s)) will not be solicited for a certain amount of time. And in the case of NaCl_(s), it tends to induce a growth of the NaCl_(s) crystals. In fact, NaCl_(s) is involved in localized dissolutions/precipitations reactions in the saturated secondary melt (reactions controlled by the equilibrium constant of dissolution of NaCl_(s) in NaAlCl_{4(l)}) that lead to its grain growth with time. And these bigger NaCl_(s) crystals with lower surface area are less available for the main electrochemical reactions. If this phenomenon is not irreversible (a few longer full charges can totally dissolve these bigger crystals), it impacts the implementation of the technology since a periodic full charging process has to be scheduled independently of the battery usage³⁴.

The charge process is controlled by the battery management system (BMS, sometimes also referred as the battery management interface or BMI), that measures and supervises the voltage and current, as well as the temperature inside the pack (amongst other data like SOC, and insulation resistance). In particular, by periodic measurements of the overall OCV of a string of cells at 100 % of SOC, the BMS is able to deduct the number of eventual failed cells in the chain. Of course, these BMS (visible at the rear of the packs displayed in Figure 17 and Figure 18) are battery specific. For example Figure 20 shows the EV ZEBRA battery operating scheme, with a BMS that controls the heating and cooling systems, the latter being absent in stationary packs.

³⁴ Sometimes in a multi-packs system, one pack is disconnected to allow this periodic full charging process and is temporary no longer available for normal operations



Figure 20: ZEBRA battery system for EV applications (22)

Cells

By construction, and this is the main advantages of the high temperature batteries, ZEBRA packs are impervious to the external ambient temperature (-40 °C to +70 °C), and do not necessitate air conditioning auxiliary system. The drawback is that the high temperature has to be maintained inside the packs during inactivity³⁵ (or temperature floating mode). In Table 1, we can see that the ambient temperature does not affect the electrical performance of the 48TL80 battery between -20 and +60 °C, with a heat loss flux that never exceed 90 W (these are rather small packs).

Table 1: Influence of external	temperature on the	performances of a 48TL	.80 battery (24)
	1	1	

External	Ah Discharged	Ab abargad	Power Consumption
Temperature	at C/3 rate	All chargeu	in floating condition
-20 °C	78.1	78.3	84 W
20 °C	78.5	78.2	75 W
40 °C	78.2	78.0	70 W
60 °C	78.4	78.5	68 W

If the battery is not plugged, it will use its own energy to maintain a minimum temperature during OCV floating mode, and this process is often inaccurately referred as self-discharge (indeed, there are no electrochemical side reactions involved here). The BMS is implemented to prevent operation outside of specifications, i.e. voltage, current and temperature operating and safety

³⁵ Joule heating is generally sufficient during cycling to keep a sufficient temperature in the pack. This topic will be detailed in chapter 3 in section 3.2.2 of the thermal model

limits. Like most mature battery technologies, there is no need for periodic maintenance intervention during the battery pack lifetime.

1.3.6. Battery lifetime and ageing

The factors which determine cell life, thus battery life, are corrosion, resistance rise, and capacity loss. In the absence of electrical solicitations which is referred as the calendar life, the cell performances degrade only very slowly as demonstrated by the performance of a small battery module (30 Ah) which was put on test in June 1991 (21) (72). This fully charged battery was kept in rest mode over at least 15 years (last data from 2006 were published in 2009), and periodically electrically cycled, with also two freeze/thaw phases per year. The measured capacity has remained unchanged, and Figure 21 clearly indicates that there is no detriment either to the power capability.



Figure 21: mean cell resistance as a function of the discharged capacity from a calendar life test performed on a small 30 Ah module since 1991 (72)

Regarding the electrical performances with ageing, results were reported in the scientific literature for repeated deep cycling (up to 95 % of DOD (24)) and EV continuous profile cycling (between 5 and 80 % of DOD (72)). In the ongoing deep cycling test (last data were reported in

2011), the battery is discharged at the C/5 rate until the low end of discharge (EOD) voltage or capacity criteria, whichever comes first. Recharge is started immediately after the discharge. From Figure 22 it is evident that the battery is still constantly delivering the initial capacity after more than six hundreds cycles. The only noticeable degradation is the decrease of the voltage at the end of discharge due to the increase of the internal resistance (thus a small degradation of the power capability at low DOD).



Figure 22: discharged capacity and voltage at EOD for a 48-TL80 battery as a function of cycle number (24)

It is also noticeable that changing the setting of the operating temperature from 270 to 260 °C logically affects the electrical performances, but without any 'memory' effect when the temperature is switched back to its initial value. The EV profile cycling test mimicking vehicle weekly usage over a period of 7 years (as described in (72)), has been carried out by performing peak pulse power between 5 and 80 % of DOD. Figure 23 shows that after more than 5,000 cycles (in term of equivalent rated capacity), the capacity again remained unchanged, whereas the mean cell power availability has decreased due to internal resistance rise.



Figure 23: remaining cell capacity and cell mean power as a function of rated capacity cycles for a 26 Ah module with ML/4B cells

Numerous tests on the field have also been publicized in the scientific literature regarding EV or HEV applications (19) (20) (72) (73) (74) (75) (76). In the latest report presented at the 2014 IEVC conference (76), a statistical performance analysis has been conducted on a commercial fleet of eight vehicles, equipped with 23.5 kWh Z36 batteries. The mean ageing estimated in percent of initial capacity lost is 3.9 % per year. A replacement of the batteries after five years can be extrapolated when they are no longer capable of delivering 80 % of their initial capacity). These results are indicative of the overall ZEBRA EV technology electrical performances, keeping in mind that these performances have been optimized since the development of the ML/3X unit cell (lower internal resistance with cycling than previous generations (23)). The most recent FIAMM stationary on field systems reports will be evoked in the next section.

From these results, we can affirm that the main effect of ageing is the overall increase of the internal resistance of the cell. This degradation is observed regardless of the fact that there might be recovering schemes. But the mechanisms of ageing are still not clearly understood to this day. Comprehensive laboratory corrosion studies (77), as well as on field post mortem investigations (21) have led to the conclusion that corrosion is not the source of the electrical performances degradation. In fact, signs of corrosion degradation even after 15 years of operation

Chapter 1

are only perceptible on the glass seal, and extend only a few microns into the glass. Investigations on ageing are not easy because we cannot simulate an accelerated ageing by the standard procedures, i.e. increasing significantly the operational temperature. Besides that, operando analytical characterizations of the active material content as a function of DOD are not readily possible without the use of high energy instruments (synchrotron or neutron radiations) capable of crossing the casing and BASE barrier. On the other hand, post mortem room temperature analyses are suggested to misinterpretation due to eventual cooling side reactions. In 2012, Mehdi Hosseinifar and Anthony Petric (78) have tried to simulate accelerated ageing by cycling short strings of ML/3X cells at the limits of normal operation (and slightly above), in terms of temperature (260 and 350 °C) and voltage in charge mode (3.1 V instead of the standard 2.67 V). At both temperatures and in overcharge condition, they have observed a significant to severe internal resistance rise after only one hundred cycles. From post mortem SEM and X-ray diffraction analysis (see Figure 24), they have proposed the hypothesis of a passivation or poisoning of the beta alumina ceramic by surface deposit of AlF₃, impeding the transport of Na⁺ through the BASE.



Figure 24: SEM images of the BASE surface after cycling at 350 °C (left), and positive electrode material adjacent to the BASE after cycling at 260 °C (78)

AlF₃ is not inserted as such during the manufacturing process, so either it is form during cycling, or it is a byproduct originating from the cooling process which is a possibility that cannot be excluded. If complete failure of a cell has not been observed in any test, at 350 $^{\circ}$ C, some cells

have shown a capacity loss. Post mortem analysis indicated that capacity loss was the result of Ni grain growth. If the high temperature condition in itself can be responsible for the phenomenon, another factor that may have contributed to the growth of Ni particles is the formation of the Ni₃S₂ crystal phase on the surface of Ni grains. Ni₃S₂ presence has been detected only after cycling. From section 1.2.4, we know that sulfur is key in preventing the grain growth by poisoning the surface of nickel particles. If formation of Ni₃S₂ compounds consumes sulfur, it can explain why there is not enough sulfur left for the former beneficial mechanism. Like it is stated in (78), verifying such speculations requires a more fundamental understanding of how Ni₃S₂ forms ³⁶, and what are the controlling factors.

1.3.7. Safety and recyclability

The multilayered safety scheme adopted by FIAMM is summed up in Figure 25, and each layer is detailed in the comprehensive National Renewable Energy Laboratory (NREL) report written by David Trickett for the U.S. Department of Energy (DOE) in 1998.



Figure 25: FIAMM battery pack safety strategies diagram

 $^{^{36}}$ Ni₃S₂ is evoked as a product of electrochemical reactions in cyclovoltammetry studies by G. Staikov and P.D. Yankulov in (59), and they have observed a redox activity of sulfur above the NiCl₂/Ni plateau. The latter observation was confirmed the same year in 1991 by Julia Weaving and Walter Orchard (62)

This strategy, which is equivalent of the one use by GE while developing its own Na-MCl₂ Durathon[®] packs, has been successfully put to the test in abusing conditions (34). Extreme scenarios have been considered and experienced (see Figure 26) like complete submersion in salt water (before and after deep penetration of a metallic object), fire exposure, bullet impacts by various types of munitions, overcharge by overvoltage, short circuit testing, high-speed impact in both as-installed and as-shipped conditions, and accidental drop scenarios while in the as-installed condition.



Figure 26: extreme abuse testing with GE Na-MCl₂ prototype battery pack, from (34)

Long story short, no uncontrolled fire or heating, nor explosions were observed. Against all odds, it is recommended to cool down the pack with water in case of fire near the battery, despite the fact that it contains plain sodium³⁷.

The Na-NiCl₂ cells have a potential 100 % recyclability. At the end of their life cycle, all ZEBRA packs are recovered by the FIAMM Company and sent to existing facilities related to the production of stainless steel (see Figure 27).

³⁷ There is very few pure sodium contained in each cell



Figure 27: recycling chart of ZEBRA batteries in a stainless steel plant production, from INMETCO

The recovery efficiency of this process is higher than 50 % (27). In fact, it is the initial supplier of Ni active material³⁸ that bought back the recyclable material, and additionally the material value covers the battery recycling process cost and the transportation from a collection point to the recycling plant (14). At this point, and recollecting all features regarding the active material, structural components, intrinsic safety, and recyclability, the sodium chloride technology can be recognize as a potentially strong candidate for low cost and large scale energy storage.

1.3.8. Large energy storage systems: general design and applications

These past years, FIAMM ESS has developed a 1.5 MWh container unit, with 64 ST523 stationary battery packs connected in parallel, that can be virtually deployed in nMWh systems (see Figure 28).

³⁸ The INMETCO company



Figure 28: from the battery pack level to large energy storage systems

The sodium nickel chloride technology in term of energy availability for stationary applications is positioned for 3 hours rate discharge time (Figure 29). These systems can be used for load levelling, voltage regulation, time shifting, and power fluctuation mitigation of renewable energy sources (wind, solar). FIAMM have communicated initial results regarding on field stationary installations around the world in (27), and is currently involved in a European project to deploy his BESS system in the Tilos Greek island.



Figure 29: Positioning of energy storage technologies, (79)

1.3.9. Objectives of the thesis

If the Na-MCl₂ technology has reached a significant level of maturity, the full understanding of the electrochemical processes involved during operation is still a work in progress. Considerations about operando active material operando analysis and post mortem characterizations presented in this first chapter have led to look for an alternative route to validate the hypotheses exposed in the scientific literature. In this context, an electro-thermal model of the commercial cell has been developed during the thesis, able to put to the test all the mechanisms proposed previously³⁹ and some more. The model has been developed first for the constant discharge mode. Focusing the efforts towards the modeling of an operating commercial cell implied more ambitious goals too. Indeed, there are two simultaneous electrochemical reactions (related to Ni and Fe) to implement, and the results of coupled thermal effects have never been published in the scientific literature.

A multi-physics model is also obviously very attractive from a R&D point of view as it permits to easily predict design and cell contents changes, thus reducing the expenses related to

³⁹ These mechanisms will be detailed in chapter 2

prototype construction and testing. The building of the model has been carried away with this objective in mind.

Ultimately, this type of model represents the state of the art of what can be electronically implemented as battery management system in the field. After the validation step, the objective here is to perform sensitivity analyses to identify the relevant parameters to monitor, i.e. the ones that have a significant influence on the electrical performances of the cell. For instance, by studying the heat effects in the cell, the goal is to develop a thermal model of the pack that can be sufficiently accurate, yet easily implementable in a BMS. Indeed, actual thermal management in the battery is mostly conceived in term of safety (not too high temperature), and power demand issues (not too low temperature). For stationary applications, and especially in association with renewable energies production, thermal management has an important potential for the charge phase efficiency optimization, and minimization of the energy consumption during the OCV floating mode in the view of closed container configurations.

In the next chapter, I will present the electrochemical characterization of the ML/3X unit cell that has given me the means to validate the model proposed in chapter 3, and discussed in chapter 4.

Chapter 2

Electrochemical characterization of the commercial cell

The goal of this chapter is to detail how experimental data were obtained to implement some of the key parameters of the model (initial quantities, OCV as a function of temperature), and for validation purpose. The ML/3X unit cell electrical behavior was fully characterized at INES laboratory. In this chapter, I will begin to present the facilities used to perform these tests, and the main results retrieved. The cyclic voltammetry tests are described in the second section, and proved to be very useful to identify and quantify the active materials involved during charge and discharge phases. I will finish this chapter by focusing on the OCV temperature dependency of the cell.

2.1 Electrical performances

Electrical tests (discharge, charge, cyclic voltammetry, galvanostatic intermittent titration technique (GITT)) were performed with a four-channel (1 A/10 V) Biologic VMP300 test bench. The latter is additionally equipped with four boosters (5 V/10 A) that can be connected in parallel to reach up to 40 A. The cells were cycled in a Nabertherm furnace that fits very well the size of the cell and consequently provides a very homogeneous heating.



Figure 30: ML/3X cell equipped with a K-type thermocouple temperature probe in the Nabertherm furnace

A temperature probe connected to the VMP300 through a cold junction compensation box was inserted inside the furnace against the center of one of the longitudinal face of the cell. To study the thermal behavior of the cells, we had to adjust the oven a bit in order to make it works at a particular setpoint temperature. Indeed, the function of an oven is to keep what is inside at a constant temperature. However, the oven temperature control hides the cell thermal behavior by reducing the heat produced when the cell heats up during operation, and vice versa. To observe any possible change in the cell temperature (reversible and irreversible heats), we disconnected the oven temperature control system and connected its heating resistance directly to an external power supply⁴⁰. This setup gave us the possibility to provide only the constant power needed to compensate the oven heat loss for a specific setpoint temperature, and therefore to precisely measure the cell temperature variations during its operation.

⁴⁰ The furnace temperature probe installed along the internal surface of the furnace was kept functional

Although discharge tests were carried out between 0.4 and 40 A (i.e. between C/100 and 1C), in the perspective of stationary applications, it is interesting to focus on rate comprise between 4 and 20 A. Thus, as a reference to define a full discharge, a capacity value of 40 Ah was selected. It is the maximum discharged capacity C_{max} retrieved at C/2 = 20 A with an EOD criteria of 1.9 V. With this reference, the SOC and corresponding DOD are defined as a function of time in charge by:

$$SOC(t) = \frac{\int Idt}{c_{max}} = 1 - DOD(t)$$
[12]

In discharge, the relation becomes:

$$DOD(t) = -\frac{\int Idt}{C_{\text{max}}} = 1 - SOC(t)$$
[13]

2.1.1 Constant discharge voltage curves

Several 40 Ah full discharges from 100 % SOC were performed on single commercial cells, at various rates ranging from C/10 (4 A) to C/2 (20 A), and from different initial temperatures. These were fresh cells previously subjected to the manufacturer running procedure (including in-house maiden charge). Between these discharges, the cells were resetted to full charge following the I-U procedure described in section 1.3.5. In this charge procedure, several rates were tested between C/10 and C/2 for the constant current phase, as well as different initial temperatures. The OCV curve of the cell was retrieved by GITT, each 1 % of SOC. Measurements have been made consecutive to C/2 discharge pulses, and after a sufficient rest period ending when $\frac{dU_{cell}}{dt} < 1 \text{ mV} \cdot \text{h}^{-1}$. Figure 31 displays some of the experimental discharges curves used for validation purpose.



Figure 31: Voltage curves for open circuit voltage (dotted line) and constant current full discharges (solid lines) from 270°C at C/2, C/5, and C/10 rates

These voltage curves, which are rather identical to the ones published in (24) (see section 1.3.2), are represented alongside the OCV curve. On the latter, we clearly see the two plateaus corresponding in a first approach to Ni active material (75-80 % of DOD or up to 32 Ah), and Fe active material (the last 15 % of DOD or up to 6 Ah). Between these two plateaus we can also observe a third contribution representing approximatively 2 Ah. Indeed, amongst the additives used in the cell (and not considered for the time being in the simulations), the fluorinated additive is electroactive between 2.58 V and 2.33 V (OCV = 2.39 V at 300 °C), and its initial quantity is equivalent to a 2.3 Ah contribution. If at very low rate, we can consider that the iron contribution is distinct from the nickel one, at higher rates (> C/10), we can see that both metal contribute simultaneously. Notice that discharges after full coverage of Ni should present a coup de fouet ('stroke of a whip'') on the beginning of the voltage curves as mass transfer between the bulk and metal surface is impeded. This minimum in voltage at the beginning of the voltage curve is not observed on our experimental data because with a 70 % excess of nickel in the cell we are far from total passivation at 100 % of SOC. With the rates used in this study, and an initial temperature of 270 °C, the cell temperature increases by 10 °C at C/10, and 33 °C at C/2. To get further elements of validation regarding the operational temperature, I have plotted several C/2 discharges, initiated from four different temperatures (260, 270, 280, and 290 °C) in Figure 32.



Figure 32: Voltage curves of C/2 full discharges from different initial temperatures: 260 °C, 270, 280, and 290 °C

As expected, the polarization decreases with increasing temperature because the conductivities of main and secondary electrolytes increase. However we can already notice that the operational temperature does not have a major impact on the voltage curves in the selected operating range (for this technology, C/2 is considered as a rather high rate).

2.1.2 Standard charge voltage curves

Figure 33 displays charges from 0 % of SOC at an initial temperature of 300 °C, plotted alongside an OCV curve obtained from GITT in charge mode at the same temperature. All charges follow the standard FIAMM I-U procedure, with a 150 mA EOC criterion.



Figure 33: voltage curves for complete charges at 5, 10, and 20 A, from 300 °C

On this figure, we can highlight the fact that all the nickel plateaus start before 10 % of SOC (including for the OCV curve). Looking at the discharge curves in Figure 31 we should expect a symmetrical behavior of the active material contributions, i.e. the charging of nickel material after 20 % of SOC. This important hysteresis feature is highlighted in Figure 34 where C/5 discharge and charge curves are plotted on the same graph as a function of SOC:



Figure 34: comparison between charge and discharge voltage curves at C/5 from 270 °C

There is almost 15 % of SOC that can be attributed to the iron active material in discharge, which is not involved in charge in the corresponding SOC range. The assumed mechanisms associated to this phenomenon involving intermediate species (Ni_{1-x}Fe_xCl₂ and Na₆FeCl₈) will be discussed in section 2.2.1.2.

Figure 35 gives insight about the current variations (red curve) during the voltage control phase (VC) following a 5 A constant current phase (CC) from 300 °C, and a 150 mA EOC criteria:



Figure 35: voltage (blue) and current (red) curves for a complete charge at 5 A, from 300 °C

Plotting the charged capacity with respect to the charging time provide quite identical curves to the ones published in (24) (see section 1.3.5), showing that the preferred rates for the CC phase in terms of energy efficiency are indeed between 5 and 10 A:



Figure 36: charged Ah with respect to the charge duration with different CC phases and from $300 \ ^\circ C$

Indeed, the charge duration varies only very slightly between 10 and 20 A, while the power consumption is higher during the CC phase at 20 A.

2.2 Cyclic voltammetry experiments

2.2.1 Full scan of the cell at very low rate

2.2.1.1 Experimental and peaks initial attribution

Cyclic voltammetry tests (CV) were performed using a very slow scan rate of 1 μ V.s⁻¹. The scanned limits were controlled by the cell voltage between 2 and 2.7 V to get all the active material oxidation and reduction signatures⁴¹. CV data treatments such as peak analysis were done using the EC-Lab[®] software. In my situation, I had no means to use a third reference electrode in my commercial cell, so the sodium electrode was used as the counter/reference electrode. It is not the worst case scenario (36), as the sodium negative electrode features negligible overpotential, and its surface (external wetted surface of the BASE) is much larger than that of the positive working electrode (wetted surface of the current collector). Since this setup induces an inaccuracy in the measurement of the working electrode potential, I will only highlight relative data (cell voltage, or half-wave potential for instance) in the following. In

⁴¹ This rate requires 11.5 days for a 1 V range scan.

addition, these voltammograms will be mostly used to evaluate the initial quantity of active material from current peaks areas measurements. Figure 37 shows a full forward (reduction) and reverse (oxidation) scan, starting from the fully charged state at 2.7 V and carried out at 300 °C.



Figure 37: full cyclic voltammogram from a 1 μ V.s⁻¹ scan rate at 300°C starting from 2.7 V with initial peaks assignement

From the bibliography presented in sections 1.2.1 and 1.2.4, we can assign for the time being the oxidation and reduction peaks to the active material labelled in Figure 37. The half-wave potential of the nickel peaks measured here at 300 °C is 2.58 V. The fluorine and iron related peaks are overlapping, but the half-wave potential of the iron peaks (the ones with the greatest magnitude) can be estimated to 2.32 V, and 2.40 V for the half-wave potential of the fluorine peaks. The sulfur peaks features a half-wave potential of 2.17 V. Iodine additives should not be electrochemically active in the chosen window (< 2.7 V).
2.2.1.2 Full scan peaks analysis

Staikov and Yankulov (59) have shown for a pure nickel cell in tetrachloroaluminate melts, that reduction and oxidation peaks exhibit same magnitudes and areas. It is clearly not the case with a Ni-Fe cell with peak heights in reduction and oxidation that are respectively 2.18 and 2.51 A, whereas peak areas correspond to 32.8 and 37.2 Ah, respectively. The capacity contributions from each active material⁴² are summed up in Table 2:

Table 2: cyclic voltammogram peak values obtained with EC-Lab data treatment (in brackets are corrected values)

Active material	Ni	Fe-F	F	Fe	S	Total
peak current red. (A)	2.18		0.32	0.84	0.04	
peak current ox. (A)	2.51		0.14	0.48	0.07	
red. peak area (Ah)	32.8	9.8	~ 2	~ 7.8	0.7	43.3
ov nook aroa (Ah)	37.4	5.0	~ 1	~ 4.9	0.8	44.1
	(36.6)	3.9				(43.3)

The starting point of that experiment was a fully charged cell as defined in the FIAMM standard procedure (500 mA EOC criterion). I am able to reach a higher state of charge in the subsequent charge (+0.8 Ah during the reverse scan), because with such a low scan rate (equivalent to a C/200 rate), some additional active material becomes accessible. Nonetheless, the total capacity will be reset to the 43.3 Ah reference, and the Ni peak area value will be corrected accordingly (37.4-0.8 = 36.6 Ah). The peak area value of Ni in reduction (32.8 Ah) is in accordance with the value deduced from the GITT in Figure 31 (around 32 Ah). The values written in bold in Table 2 show that a part of the iron/fluorine active material reduced in the forward scan has not been subsequently oxidized during the reverse scan. This missing contribution can be estimated to 3.9 Ah. Concerning the labelled Ni peaks, it is the other way around: there is an excess contribution of around 3.8 Ah that can be observed in oxidation.

⁴² In a first approach these contributions are assigned to these elements, but it is not to be taken as "exclusively"

Recalling what was previously stated in section 1.3.2, the Ni peaks cannot be attributed to nickel active material only, but to a mixed metal chloride salt $Ni_{1-x}Fe_xCl_2$ (x ≈ 0.2 at full charge). In addition, when iron is involved an intermediary Fe II species, Na_6FeCl_8 , is formed during charge and discharge. Following equation [1], the positive electrochemical reaction involving iron chloride in discharge can be written as:

$$FeCl_{2(s)} + 2Na^{+} + 2e^{-} = 2NaCl_{(s)} + Fe_{(s)}$$
 [14]

According to (80), this reaction should be seen as the net result of the separate reactions (from left to right in discharge):

$$4\text{FeCl}_{2(s)} + 6\text{Na}^{+} + 6\text{e}^{-} = \text{Na}_{6}\text{FeCl}_{8(s)} + 3\text{Fe}_{(s)}$$
[15]

$$Na_6 FeCl_{8(s)} + 2Na^+ + 2e^- = 8NaCl_{(s)} + Fe_{(s)}$$
 [16]

The potentials of reactions [15] and [16] were reported to be 2.353 and 2.341 V, respectively at 250 °C (13). These reactions, and the one associated to fluorine active material (equation $[\mathcal{B}]$), should occur in the zoomed voltage range of the full scan displayed below, with strongly overlapped peaks:



2.24 2.26 2.28 2.3 2.32 2.34 2.36 2.38 2.4 2.42 2.44 Ucell (V)

Figure 38: zoom on the Fe-F zone of the full voltammogram with associated unbalanced reaction schemes

Notice the broadening of the "Fe"⁴³ peaks at the end of reduction and oxidation in their lower part.

2.2.1.3 Discussions about these first results

06

0.4

0.2 0 () -0.2

-0.4

-0.8

-1

-1.2

Recent interpretations based on operando high energy active material analysis (35) (53) (70) have led to assume the following mechanisms during charge:

- First, iron reacts with solid sodium chloride according to equation [16] (written from right to left) to form Na₆FeCl₈. This reaction progresses swiftly towards the center of the cell, and stops before all iron is consumed. These observations suggest either a passivation phenomenon on the iron surface by the Suzuki phase, or a localized depletion of NaCl_(s) (reaction [16] uses eight moles of NaCl_(s) for one mole of Fe_(s)).
- Then, Na₆FeCl₈ is consumed while a Ni_{1-x}Fe_xCl₂ phase appears with increasing Ni content. At the beginning of this second phase, NaCl_(s) content stays constant before decreasing again.

⁴³ Quotes are used from here because peaks are not exclusively assigned to the referred active material

Notice that each step is mostly described here by focusing on a localized area of the cell. In the overall cell, these reactions are temporally shifted according to the reaction front hypothesis. In the first step, nothing prevents reaction [15] to occur (written in charge from left to right) as soon as the Suzuki phase is produced. But experimental results have shown that no FeCl₂ phase appears during that first step. In the second step, if a mixed Ni_{1-x}Fe_xCl₂ phase appears right away instead of a FeCl₂ or NiCl₂ phase alone, that means that reactions [15] and [17] (equation [1] for nickel active material) proceed in parallel.

$$2NaCl_{(s)} + Ni_{(s)} = NiCl_{2(s)} + 2Na^{+} + 2e^{-}$$
[17]

Reaction [15] allows the oxidation of the remaining iron, and excess $Na_6FeCl_{8(s)}$ supplies $NaCl_{(s)}$ for reaction [17] ($Na_6FeCl_{8(s)}$ can be considered as $FeCl_{2(s)} + 6 NaCl_{(s)}$), which can explain why concentration of the $NaCl_{(s)}$ stays constant for a while.

From (53), the following mechanism is assumed to occur during the initial part of the discharge⁴⁴:

• First, nickel chloride reacts to form nickel and solid sodium chloride according to equation [17] (written from right to left), but the quantity of the latter increases only very slowly. As Na₆FeCl_{8(s)} is also formed during this first step, I can assume that the released NaCl_(s) is used right away by FeCl_{2(s)} from Ni_{1-x}Fe_xCl₂ to form Na₆FeCl_{8(s)} (this last reaction is not an electrochemical process).

And for the second step of discharge, this is what I can propose to interpret the cell behavior during the CV tests:

• When all the nickel chloride has been used, Na₆FeCl_{8(s)} is reduced to iron according to reaction [16]. Following that rationale, reaction [15] does not occur during discharge.

All iron present in $Ni_{1-x}Fe_xCl_2$ can be converted in $Na_6FeCl_{8(s)}$ before being reduced. This can explain why reaction [16] in discharge mode has a higher capacity contribution than in charge mode.

⁴⁴ Experimental data are only available for the first 25 % of DOD

The fluorine content being too low, it has not been addressed in (35), (53) and (70). The difference between its oxidation and reduction peaks shows the same tendency than the iron ones: displaying a higher area in reduction. So my idea was to transpose to the nickel the schemes associated to the iron and its Suzuki phase, using NaF instead of NaCl. Thus in charge, we will have to consider the following unbalanced equations:

$$NaF_{(s)} + Ni_{(s)} = (NaNiF)_{(s)}$$
[18]

$$(NaNiF)_{(s)} + Ni_{(s)} = (NiF_2)_{(s)}$$
 [19]

I have no means to identify the fluorine active material form involved, hence the use of brackets in the equations. In discharge, I will only consider the equivalent of equation [16] (i.e. equation [18] written from right to left).

For the time being, I can sum up the discharge and charge processes using the following table⁴⁵ and figure:

⁴⁵ Ni only contribution is considered identical in charge and discharge.

 Table 3: proposed reaction mechanisms in discharge and charge modes with associated capacity

 contributions based on a 43.3 Ah total capacity

peaks	"Ni"			"F"	"Fe"
reduction reactions and associated contributions		[17] 32.8 Ah		[18] 2 Ah	[16] 7.8 Ah
oxidation reactions and associated contributions	[15] 2.9 Ah	[17] 32.8 Ah	[19] 1 Ah	[18] 1 Ah	[16] 4.9 Ah



Figure 39: assumed mechanisms for each peak during a full scan CV

To validate these hypotheses, complementary CV tests were performed by reducing the scan range on each active material voltage window.

2.2.2 Additional tests: partial cyclic voltammetry scans

The voltage ranges used for these scans are between 2.48 and 2.68 V for the "nickel" peaks (Figure 40), and between 2.24 and 2.46 V for the Fe-F peaks (Figure 41). Within the limits

of the latter window, two additional CV experiments were performed, between 2.24 and 2.40 V to focus on the "iron peaks" (Figure 42), and between 2.34 and 2.46 V for the "fluorine" peaks (Figure 43). All tests were carried out at 280 °C, with the same scan rate of 1 μ V.s⁻¹. Between two experiments, four to five complete charge/discharge cycles were performed to insure identical electrical performances of the cell at the beginning of each CV.

For the nickel area scans, the CV started at 2.68 V in reduction mode (reverse scans from 2.48 V):



Figure 40: cyclic voltammetry on the "Ni" area at 1 $\mu V.s^{\text{-1}}$ and at 280 °C, between 2.48 and 2.68 V

Results here are in accordance with the NiCl₂/Ni only system (59), as we observe reduction and oxidation peaks with identical magnitude (~ 2.5 A) and area, the latter having a mean value of 33 Ah. The peak areas do not differ significantly between scans. At this very low scan rate, we are able to notice a symmetrical elbow at the end of reduction and oxidation (which was also perceptible on the full scan in Figure 37). This phenomenon is probably related to the 2 electrons

charge transfer mechanisms at work for the NiCl₂/Ni electrochemical reaction. This experiment confirms that the excess 3.7 Ah observed in oxidation mode is not directly related to the nickel active material alone. Following my reasoning no iron active material is reduce nor oxidized in this voltage frame.

Regarding the iron-fluorine area scans, the CV started at 2.46 V in reduction mode (reverse scans from 2.24 V), after a linear sweep from 2.7 V. The goal here was to begin the experiment right after the end of the "Ni" plateau reduction.



Figure 41: cyclic voltammetry on Fe-F area at 1 µV.s⁻¹ and at 280 °C, between 2.24 and 2.46 V

After the first scan in reduction mode, peaks areas and maximum currents do not differ significantly between scans. From scan #2, the overall oxidation and reduction peak areas have the same value. The corresponding averaged value for the two last scans is 7.3 Ah, which is 3.3 Ah less than the first scan in reduction (10.6 Ah⁴⁶). Notice that for the "Fe" signal (the peaks

⁴⁶ This value is in accordance with the one obtain in the full scan (9.8 Ah)

on the left-hand side of the voltammogram), and contrary to the full scan in Figure 37, the maximum current peaks have identical magnitude. Other shape characteristics of the "Fe" and "F" peaks will be addressed next. This experiment shows that 3.3 Ah of active material that are reduced in the first scan, are never involved next in the subsequent forward or reverse scans if the overall voltage is kept below the nickel potential range. Following the scheme presented in Figure 39, this missing contribution can be attributed to the fact that reactions [15] and [19] do not occur under 2.46 V.

The "Fe" centered scans have been carried out between 2.24 and 2.40 V, and started at 2.24 V in oxidation mode, after a linear sweep from 2.7 V. The goal was to start the experiment right after the end of the "Fe" plateau reduction.



Figure 42: cyclic voltammetry on Fe area at 1 µV.s⁻¹ and at 280 °C, between 2.24 and 2.40 V

These results for that voltage range are similar to the ones obtained in Figure 41, because for each scan the peaks in reduction and oxidation display the same maximum currents and the same areas. The reducing maximum currents and peaks areas tendency observed between scans was

also noticeable in the previous voltammogram. This trend is probably associated to the reduced percolation of iron active material to the nickel backbone between scans. Indeed, with such a low current density, a maximum of iron active material can be converted into iron chloride on its surface, which in turn cut off contact between small iron grains and the nickel backbone⁴⁷. The fact that for each scan the peak area value is identical in reduction and oxidation confirms that there is only one reaction at work ([16]), if the voltage is kept under 2.40 V. Reaction [15] being hindered, the quantity of active material involved in charge and discharge for reaction [16] is the same (~ 6 Ah). Looking closely at the end of the reduction peak around 2.28 V, we can notice that the broadening of the peak on its lower part observed in Figure 38 and Figure 41 has disappeared completely. Therefore, this phenomenon can be linked to the fluorine content, and we can assume that some active material X oxidized between 2.4 V and 2.46 V (the "fluorine" zone) is reduced around 2.28 V in reduction mode. In Figure 38, we also observe around 2.37 V a broadening of the iron peak in its lower part at the end of oxidation. This broadening is not apparent in Figure 41 and Figure 42, and I have no clear idea of its origin⁴⁸.

The last voltammogram of these complementary tests concerns the "fluorine" area where scans were performed between 2.34 and 2.46 V. The CV started at 2.46 V in reduction mode after a linear sweep from 2.7 V. The goal here was again to begin the experiment right after the end of the "Ni" plateau reduction.

⁴⁷ Nickel is present in such an excess that this phenomenon is not observed on the "Ni" only CV

⁴⁸ All partial scans were carried out with the same fresh cell, but the full scan was obtained from a different cell that was previously cycled for the electrical tests (less than 50 cycles).



Figure 43: cyclic voltammetry on F area at 1 μ V/s and at 280 °C, between 2.34 and 2.46 V

Description of this voltammogram is quite similar to the corresponding part of Figure 41. Indeed, after the first scan in reduction mode, peak areas and maximum currents do not differ significantly between scans. From scan #2, the overall oxidation and reduction peaks areas have the same value. Evaluation of these peaks areas are difficult due to the remaining overlap with the "Fe" reduction and oxidation peaks. It is obvious from the difference between the two firsts scans in reduction that some active material reduced during the first scan is not re-oxidized in the reverse scan (thus under 2.46 V). Also the area of the oxidation "fluorine" peak can be estimated to be around 1 Ah which is twice smaller than the estimated reduction peak for scans #2 and 3. The second most noticeable feature is related to the oxidation peak which is split in two overlapped peaks. In this experiment, the magnitude of the peak on the left-hand side of this split signal increases scan after scan, until it is significantly higher than the right-hand side peak. This behavior differs from what is observed in Figure 41. To further compare these two experiments, Figure 44 displays side by side a zoom on this particular zone (the current scale being identical):





Figure 44: comparison between CV tests on the "fluorine" oxidation split peaks (left zoom from Figure 43, right zoom from Figure 41)

Since the reduction peak comparison does not show any significant differences, this changing behavior can be correlated with the active material that is reduced around 2.28 V (the X active material related to both Fe and F). Perhaps X is oxidized between 2.4 and 2.46 V, more precisely between 2.43 and 2.46 V. Unfortunately, this assumption cannot be validated, and the associated mechanisms remain unclear.

2.2.3 Conclusions

In the perspective of a multiphysics model, theses cyclic voltammetry experiments give us fundamental insights about each active material contribution. Indeed, the capacity contributions play an important role in the tuning of the model, as they will be used to define the initial quantities at the beginning of discharge and charge. For instance, in charge mode, I will use an apparent contribution of "Ni", almost 4 Ah higher than the actual contribution of nickel alone, to take into account the contribution of reaction [15]. The "Fe" contribution will be conversely reduces.

2.2.4 Cyclic voltammetry with increasing scan rates

Figure 45 superimposes the voltammograms obtained by cycling a commercial cell at increasing scan rates between 2 and 36 μ V·s⁻¹.



Figure 45: CV tests carried out at increasing scan rates from 2 to 36 μ V·s⁻¹ at 280 °C, and between 2 and 2.7 V

Anodic and cathodic peak currents have been plotted with respect to the square root of the scan rate for all active materials. As an illustration, results for the "Ni" and "Fe" regions are displayed respectively in Figure 46 and Figure 47.





Figure 46: Ni anodic and cathodic peak current as a function of the square root of the scan rate (the fourth and fifth peaks are beyond 2.7 V)



Figure 47: Fe anodic and cathodic peak current as a function of the square root of the scan rate

For all electroactive species (including F and S), anodic and cathodic peak currents are linear functions of the square root of the scan rate (i.e. they verify the Randles-Sevcik relation), which is usually the signature of systems where linear semi-infinite diffusion transport is predominant.

As previously noted in the literature (80) for a pure FeCl₂/Fe system, if Na₆FeCl₈ is confirmed as an intermediate in both the charge and discharge reactions, it does not appear to

have any effect on the kinetics. In my model, I will treat the "iron" peak as the result of the apparent one step reaction [14] (Fe \rightarrow FeCl₂).

2.3 OCV dependence of the temperature

The open circuit voltage of the FIAMM ML/3X unit cell has been retrieved approximatively every 10 °C between 245 and 350 °C. This experiment was carried to estimate the reversible heat associated to the main electrochemical reaction. These experimental data will be used in the model implementation described in the next chapter, in section 3.2.3. The OCV was measured with a cell at 90 % of SOC⁴⁹. At this value, the mixed potential originates most exclusively from the NiCl₂/Ni system, which was what I was looking for. So, I have obtained a linear relation between the OCV and the temperature:



Figure 48: Open Circuit Voltage of a ML/3X cell with respect to the temperature at 90 % SOC

To quantify the reversible heat in my model, I need the value of $\frac{\partial ocv}{\partial T}$ wich is equal to $-2.16 \cdot 10^{-4}$ V.K⁻¹. This value will be assumed constant for all SOC, including SOC related to the

⁴⁹ With a 70 % excess of Ni, at 90 % of SOC the molar ratio of NiCl₂ in the NiCl₂/Ni system is close to 30 %.

FeCl₂/Fe system (see section 3.2.3). One complementary experiment⁵⁰ has been carried out at 50 % of SOC to validate my assumption. In this case, I have found again a linear relation with $\frac{\partial OCV}{\partial T} = -2.13 \cdot 10^{-4}$ V.K⁻¹, which was less than 1.5 % away from my reference value.

In the next chapter, we will focus on the building of the 2D multi-physics model.

⁵⁰ This type of test is very time consuming as I have allowed at least one day between two measurements to insure stabilized OCV and temperature.

Chapter 3

2D model development of the commercial cell

In this chapter, I will first present briefly the scientific background related to mathematical modeling of an electrochemical device. I will then move to present the state of the art of the Na-MCl₂ cell electrochemical modeling (1D and 2D). The assumed electrochemical mechanisms at work during operation will be highlighted, keeping in mind that all earlier published models were assumed isothermal. The thermal model will be treated separately in the same way, i.e. evoking the general energy balance used in the battery field before detailing which heat effects have to be considered for the ZEBRA technology. Based on these features, the development of my own 2D model of the ML/3X unit cell will be detailed and justified, as well as the incremental initial strategy used for validation of the different hypotheses proposed in the literature.

3.1 Isothermal electrochemical model of the Na-MCl₂ cell: state of the art

The model developed for this thesis relies on fundamental equations from the electrochemistry theory field. These types of models are often referred as mathematical or physic models, in opposition to statistic or equivalent circuit models more commonly used in

commercial battery management systems. Multi-physics models are obviously more complex (thus more expensive to develop), but they are ultimately much more accurate, and once validated, can be used on a more important range of operating conditions. They are not intended to handle directly the in situ management of the batteries, but they are very useful to understand all the physico-chemical phenomena at work during cycling (including ageing processes). The degree of complexity of multi-physics modeling depends on the targeted spatial and temporal scales. At the atomic (10^{-10} m) and particle scale (10^{-7} m) , fundamental thermodynamic phenomena and structural inhomogeneity in the active material can be treated. But modeling at these two scales becomes necessary only when the model at the electrode scale (10^{-3} m) proves insufficient to simulate accurately effects associated to these phenomena⁵¹. The multi-physics model of the cell (i.e. electrode scale) described in this manuscript, is based on the porous electrode theory developed by John Newman and William Tiedemann (81) in 1975. This theory relies on the macroscopic description of porous electrodes, and related models are described by parameters which can be obtained by simple physical measurements. The microscopic inhomogeneities of the pores are disregarded, thus some parameters (like the matrix or liquid phases conductivities) are treated as average quantities through Bruggeman-type relations (82).

3.1.1 Porous electrode electrochemical model requirements in molten salts

At the electrode scale model, we have to consider charge and mass conservation (respectively Ohm's law and Fick's law), as well as the charge transfer processes at the electrode. In the case of a porous electrode, these considerations translate into governing equations related to material balance for solute species, electroneutrality, charge conservation, charge transfer kinetics, and mass transfer process. Determination of the latter in concentrated electrolytic solution requires a description of the movement of ionic species, together with material balance, current flow and fluid velocity. Regarding this topic, Richard Pollard and John Newman have developed in 1979 a general theory to obtain the transport equations for a mixture of two binary molten salts in a porous electrode (83). In order to use their theory in the context of the ZEBRA technology, sodium tetrachloroaluminate melts are considered as a mixture of two binary molten salts with a common ion $A = NaAlCl_4 (Na^+ + AlCl_4) and B = NaCl (Na^+ + Cl^-)$.

⁵¹ These sub-models are then treated as inputs of the electrode scale model

3.1.2 The seminal 1D model: governing equations

A detailed comprehensive mathematical 1D model⁵² of an iron-based cell (Figure 49) has been published in 1990 by Masao Sudoh and John Newman (84).



Figure 49: schematic representation of a sodium-iron chloride cell (84)

This seminal paper provides the theoretical bases that have been subsequently re-used in this field. Regarding the nature and state of the active material, the authors assume the absence of double-layer charging effects in the time frame considered (minutes to hours discharges or charges⁵³). This model predicts the concentration profiles of the ionic species in the melt, the porosity distribution, the local reaction rate, and the terminal voltage as functions of the depth of discharge (DOD). The model features a NaAlCl₄ reservoir domain that corresponds to the early prototype configuration described in Figure 6. Governing equations are listed here in accordance with the seminal paper hypothesis. They originate from transcription of the general results established in (81) and (83), for an iron chloride porous electrode soaked in sodium tetrachloroaluminate melts. Full details regarding how these equations were obtained can be

 $^{^{52}}$ In a 1D model, variables of the model are expressed along only one axis, here any axis of the *x*,*y* plane passing through the center of the cell in Figure 49

⁵³ Relax phases are not studied.

found in appendix A. Initial and boundaries conditions will be addressed in section 3.3.3. In this model, separate expressions for Ohm's law are written for the solution and the matrix phases that are treated as superposed continua in the positive porous electrode.

3.1.2.1 Ohms's law for electronic conduction (ϕ_1)

The current density i_1 in the positive solid matrix phase is associated to potential ϕ_1 and is given by equation [20] (equation [24] in the seminal paper), where $\sigma_e = \sigma \epsilon_{Fe}^{1+\tau}$ represents the conductivity of the iron porous matrix, σ being the plain conductivity of iron⁵⁴.

$$i_1 = -\sigma_e(\nabla \phi_1)$$
^[20]

We should consider the same type of relation in the negative compartment associated to the conductivity of sodium σ_{Na} , but in (84), the corresponding overpotential is rightly assumed negligible.

3.1.2.2 Ohms's law for ionic conduction (ϕ_2)

The current density i_2 in the liquid positive phase is associated to potential φ_2 and is given by equation [21] (equation [7] in the seminal paper⁵⁵), where $\kappa_e = \kappa \epsilon^{1+\tau}$ represents the conductivity of the secondary electrolyte in the porosity of the solid matrix, κ being the temperature-composition dependent conductivity of NaAlCl4.

$$\mathbf{i}_{2} = \frac{\sigma_{e}\kappa_{e}}{(\sigma_{e}+\kappa_{e})} \left\{ \nabla \eta + \frac{r_{s}I}{\sigma_{e}r} + \frac{RT}{F(1-x_{A})} \times \left(1 + \frac{d\ln\gamma_{A}}{d\ln x_{A}}\right) \nabla x_{A} \right\}$$
[21]

The total overpotential of the cell is defined as $\eta = \phi_1 - \phi_2$. The current density *I* is applied at the separator interface ($r_{\rm S}$), so in this 1D model the $\frac{r_{\rm S}}{r}$ factor adapts the current density value at any

⁵⁴ There is a typo in the seminal paper, σ_e being expressed as a function of the total porosity ϵ instead of the porosity of the solid iron backbone ϵ_{Fe} . ⁵⁵ It is written here assuming $t_1^c = x_A$ as proposed in (84)

given radius *r* between r_0 and r_s (see Figure 49). The composition of the secondary electrolyte is given by the mole fraction x_A of NaAlCl₄. The last term of this equation $\left(1 + \frac{d \ln \gamma_A}{d \ln x_A}\right) \nabla x_A$ relates to the spatial variation of the chemical potential associated to NaAlCl₄ ($\nabla \mu_A$, see appendix A). The contribution to the voltage of the ionic conduction in the BASE is simply taken as $I \times R_{sep}$, R_{sep} being the resistance of the ceramic. R_{sep} is calculated assuming that its conductivity κ_{sep} is equal to 0.2κ . In their model configuration, there is a secondary electrolyte reservoir that contributes to the overall voltage of the cell by the term $I \times R_{res}$, R_{res} being the resistance associated to this part of the cell (obviously related to κ).

3.1.2.3 Material Balance

To prevent electrode reactants and products from dissolving into the electrolyte, a NaClrich melt has been adopted, which composition is controlled by x_A . The material balance proposed by Masao Sudoh and John Newman gives the temporal change of this mole fraction in the positive electrode (equation [8] in (84)⁵⁶), where *D* represents the diffusion coefficient of the secondary electrolyte:

$$\epsilon \frac{\partial x_{A}}{\partial t} = \overline{V}_{e} x_{A} R_{I} + \overline{V}_{e} x_{A} \frac{\overline{\nabla} \cdot i_{2}}{F} - \mathbf{v}^{*} \nabla x_{A} + D \nabla \cdot (\epsilon^{1+\tau} \nabla x_{A}) - \frac{\overline{V}_{A} - \overline{V}_{B}}{\overline{V}_{e}} D \epsilon^{1+\tau} (\nabla x_{A})^{2} + \frac{\overline{V}_{e} \nabla \cdot i_{2}}{2F} \nabla x_{A}$$
[22]

Equation [22] is strongly dependent on the average molar volume of the electrolyte $\overline{V}_e = x_A \overline{V}_A + x_B \overline{V}_B$, and takes also into account the reaction rate of the precipitation and dissolution of NaCl, R_I (related to the unknown rate constant k_p). The convective velocity \mathbf{v}^* will be address further in section 3.1.2.5. The last term on the right-hand side of the expression does not appear in the original publication (see appendix A for its origin). This correction was published by Michael Vallance and Ralph White in 2009 (29).

⁵⁶ There is a typo in (84) as the minus sign is missing before the average molar velocity term \mathbf{v}^* .

92 | Page

3.1.2.4 Charge transfer kinetics

At the negative electrode, an expression of the current density with respect to the electrode overpotential is implemented as a boundary condition of the ionic Ohm'law (it is referred as equation [23] in the seminal paper):

$$i = i_{0,N} \frac{nF}{RT} (\phi_1 - \phi_2)_N$$
[23]

This relation results from assuming a negligible overpotential for the negative electrochemical reaction, leading to use linear kinetics. Note that this reaction exchanges only 1 electron, hence n = 1. At the positive electrode, and although main electrochemical reagents and products are ultimately solids, the authors' treatment implies a two-steps mechanism involving solute species (the ferrous complex ions [Fe(AlCl₄)₄]²⁻), between the bulk and surfaces of Fe and FeCl₂. This mechanism is described by Figure 50:



Figure 50: two-steps mechanism associated to FeCl₂/Fe electrochemical reaction as described in (84), after (85)

The kinetic of each step is driven by the associated mass transfer coefficient k_m and k_s . These coefficients are used to establish the local transfer current equation [24] (equation [11] and [12] in (84)), where α_a and α_c represent respectively the anodic and cathodic transfer coefficients:

Chapter 3 Page | 93

$$\nabla \cdot \mathbf{i}_{2} = \mathbf{j} = \frac{e^{\alpha_{a} \frac{F}{RT} \eta} - e^{-\alpha_{c} \frac{F}{RT} \eta}}{\frac{1}{i_{0} a_{m}} + \frac{1}{nF} r_{,e} \left(\frac{1}{k_{m} a_{m}} - \frac{1}{k_{s} a_{s}}\right) e^{-\alpha_{c} \frac{F}{RT} \eta}}$$
[24]

The exchange current density i_0 defined in equation [25] is linked to its reference value $i_{0,ref}$, and to the concentration of the intermediate metal complex concentration $c_{r,e}$, that is assumed constant during operation in the seminal paper ($c_{r,e} = c_{r,ref}$):

$$i_0 = i_{0,ref} \left(\frac{c_{r,e}}{c_{r,ref}}\right)^{1-\beta} \left(\frac{c_2}{c_{2,ref}}\right)^{2\beta}$$
[25]

The value of $c_{r,ref}$ is estimated from assuming a complete complexation of FeCl₂ by Al₂Cl₇, the concentration of the latter in the melt being assessed from data described by Boxall *et al.* in (86), and considered constant. The exchange current density is also related to the change of Cl⁻ concentration c_2 during operation. The reference value of this concentration $c_{2,ref}$ is taken to be its value at saturation $c_{2,sat}$. The symmetry factor β represents the fraction of the applied potential which promotes the cathodic reaction (the FeCl₂ \rightarrow Fe reduction during discharge). Following the two steps mechanism hypothesis, the local transfer current *j* depends on the specific surface areas of iron metal a_m , and iron chloride salt a_s , defined in equations [26] and [27] (equations [A-8] and [A-9] in the seminal paper⁵⁷). Coverage of the active sites by FeCl₂ (related to its volume fraction ϵ_s) and precipitated NaCl (ϵ_p) are also taken into account in equation [26].

$$a_{\rm m} = a_{\rm m,0} \left(\frac{\epsilon_{\rm m} - \epsilon_{\rm m,pass}}{\epsilon_{\rm m,0} - \epsilon_{\rm m,pass}} \right)^{\rm p} \left(1 - \left(\frac{\epsilon_{\rm p} + \epsilon_{\rm s}}{1 - \epsilon_{\rm m}} \right)^{\rm p} \right)$$
[26]

⁵⁷ There is a typo in the seminal paper where $a_{\rm s}$ and $a_{\rm m}$ have been permuted

$$a_{s} = a_{s,0} \left(\frac{\epsilon_{s}}{\epsilon_{s,0}}\right)^{p}$$
[27]

The first term on the right-hand side of equation [26] is the effect of the change in the metal size. The volume fraction of metal ϵ_m takes into account the iron excess put in the positive electrode, while $\epsilon_{m,pass}$ expresses its remaining non passivated volume fraction at full charge (in a way $\epsilon_{m,pass}$ is the minimum value of ϵ_m , so I have decided to refer to it as $\epsilon_{m,min}$). The parameters indexed "0" referred to the maximum values associated to iron metal in fully discharged state $(a_{m,0} \text{ and } \epsilon_{m,0})$, and to iron chloride in fully charged state $(a_{s,0} \text{ and } \epsilon_{s,0})^{58}$. In other words, $\epsilon_{m,0} - \epsilon_{m,pass}$ represents the maximum volume fraction of iron available for the electrochemical reaction. Theoretically at 0 % of SOC, $\epsilon_p = \epsilon_s = 0$, and $\epsilon_m = \epsilon_{m,0}$, so according to [26] $a_m = a_{m,0}$. At 100 % of SOC, $\epsilon_m = \epsilon_{m,pass}$ thus $a_m = 0 \text{ m}^{-1}$. The exponential term p is taken to be 2/3 as a result of assuming regular shaped particles (cubical or spherical).

3.1.2.5 Molar average velocity of ionic species in the secondary electrolyte

The velocity arises primarily from the flux of electrolyte in the solid matrix as its porosity changes. To recall what was stated in section 1.2.4, during cycling the volume of the solid matrix in the positive electrode changes. During discharge, solid sodium chlorides replace iron chlorides, the latter occupying a smaller volume. Thus, the secondary electrolyte level rises in the positive compartment. According to (84), the distribution of the molar average velocity \mathbf{v}^* in the porous electrode is governed by equation [28] (equation [10] in the seminal paper⁵⁹), where \overline{V}_p represents the volume fraction of precipitated NaCl in the melt:

$$\nabla \cdot \mathbf{v}^* = -\nabla \cdot \mathbf{i}_2 \left(\frac{\overline{\nabla}_{Fe} - \overline{\nabla}_{FeCl_2} + 2\overline{\nabla}_B}{2F} \right) + \left(\overline{\nabla}_p - \overline{\nabla}_B \right) \mathbf{R}_I + (\overline{\nabla}_A - \overline{\nabla}_B) \nabla \cdot \left[\epsilon \mathbf{D} (\mathbf{c}_A + \mathbf{c}_B) \nabla \mathbf{x}_A \right] + \frac{\overline{\nabla}_A}{F} \nabla \cdot \left(\frac{x_A}{2} \mathbf{i}_2 \right) + \frac{\overline{\nabla}_B}{F} \nabla \cdot \left(\frac{1 - x_A}{2} \mathbf{i}_2 \right) + \frac{\overline{\nabla}_e}{2} \mathbf{R}_I$$
[28]

⁵⁸ I have deliberately excluded the i index used in (84) (for "initial" value) to avoid confusion

⁵⁹ It is written here assuming $t_1^* = \frac{x_A}{2}$ and $t_2^* = \frac{1-x_A}{2}$ as proposed in (84)

Again, the last term on the right-hand side of the expression $\frac{\overline{v}_e}{2}R_I$ is not accounted in the original paper (see appendix A for its origin). This correction was published by Michael Vallance and Ralph White in 2009 (29), and they have also introduced a Na⁺ flux between the positive domain and the separator as a boundary condition.

3.1.2.6 Porosity and volume fractions changes

The overall porosity ϵ of the positive matrix varies in accordance with the molar volume (thus volume fraction) difference between products and reactants. Its temporal evolution is given by equation [29] (equation [6] in (84)), with a positive sign in discharge and a negative sign in charge:

$$\frac{\partial \epsilon}{\partial t} = \mp \left(\frac{\bar{V}_{\text{FeCl2}}}{2F} - \frac{\bar{V}_{\text{Fe}}}{2F} \right) \nabla \cdot \mathbf{i}_2 \mp \bar{V}_p R_{\text{I}}$$
^[29]

The overall porosity and solid species volume fractions are conditioned by active material initial quantities.

3.1.2.7 Specificities of the seminal model

Heat transfers are not considered in the model, which means that the temperature is assumed constant. The model simulations are not confronted to any experimental data. Before proceeding further, it is important to highlight again the hypotheses proposed in this model that will be questioned in the next sections. First, the electrochemical process is assumed to be a two-steps mechanism involving solute species, in opposition to a solid-solid process between the metal and its salt. This assumption has led to use a complex form of the Butler-Volmer kinetic relation (equation [24]). During operation, the concentration of the intermediate metal complex (the solute species) is considered constant. Furthermore, the kinetic of the chemical reaction of precipitation/dissolution of NaCl (equation [31]) in the saturated melt is considered separately from the main electrochemical reaction (equation [30], rewritten from equation [3]):

$$MCl_{2(s)} + 2Na_{(l)} = 2Na^{+} + 2Cl^{-} + M_{(s)}$$
[30]

followed by

$$Na^{+} + Cl^{-} = NaCl_{(s)}$$
[31]

And as the rate of precipitation/dissolution of $NaCl_{(s)}$ is not known, their model has been developed to take into account variation in the solution composition. Indeed, Na⁺ and Cl⁻ concentrations are locally modified in case of a low kinetic. We have to keep in mind that with an infinitely fast kinetic of precipitation/dissolution, the composition of the secondary electrolyte, related to the variable x_A , can be considered constant.

3.1.3 Subsequent works

In 1990, Bloom *et al.* from Argone National Laboratory (which was one of the pioneer laboratory in developing the Na-MCl₂ technology), have described a mathematical modeling of a nickel-based cell (12). In this rough model, the positive electrode is divided into 10 or 20 elements of equal volume, and the discharge time is divided into 100 equal time samples. Using this discretization procedure, the model does not use the Butler-Volmer equation form. Indeed, the transfer current in each elemental volume, and at any state of charge, is assumed to be proportional to the local overpotential and to the fraction of the original amount of NiCl₂ in the element. Their model does not allow for the solubility of NaCl or NiCl₂, so eventually it has the advantage of being considerably simpler than that of Sudoh and Newman, the necessary calculations being done by spreadsheet software. However, this model only gives insight about changes in the overall electrode resistance. Results were validated with experimental laboratory cells featuring annular electrodes. They concluded that the parameters that have the most significant effects on the cell behavior are the electrode porosity, the sulfur additive content, and the charge rates.

In 1993, Walter Orchard and Julia Weaving (87) have proposed a model of an iron chloride cell suitable for simple geometry (flat-plates cells or plain cylindrical cells). The cathode reaction is considered to be effectively a solid state process, in that the solubilities of FeCl₂ and NaCl are not taken into account. This assumption is supported by another study by Coetzer *et al.* published the same year (80), featuring a functional cell containing no secondary liquid electrolyte. In (80), results suggest that the kinetic of the electrochemical oxidation of iron is drastically improved by the presence of solid NaCl. In (87) the kinetic rate expression is simplified as:

$$j = j_0 \left(e^{\alpha_a \frac{F}{RT} \eta} - e^{-\alpha_c \frac{F}{RT} \eta} \right)$$
[32]

They have based their implementation on the macroscopic porous electrode theory, but the rate of precipitation of NaCl, as well as the effect of the covering salts, are not considered. Some of the simulations were confronted to experimental data obtained from a cylindrical prototype cell. According to the authors, the model is capable of achieving a good fit to experimental data using less parameter than the seminal model. To obtain these optimized simulations, they assumed that the local instantaneous transfer current $j_{0,i}$ was related to the instantaneous local state of charge by the following relation:

$$j_{0,i} = j_{0,ref} (1 - DOD)^{2/3}$$
[33]

From 2008, Sudoh and Newman configuration has been extended to a 2D model of both iron chloride cell (29), and nickel chloride cell (31) (32) by Vallance *et al.*⁶⁰. A few corrections/modifications to the initial model are described as well as its implementation in Comsol Multiphysics[®]. The time-dependent solution displays a reaction front that moves deeper into the positive electrode with increasing DOD. The fact that the positive electrode porous

⁶⁰ These studies emanates from GE R&D.

matrix is assumed homogeneous in (84) is questioned in light of the divergence with experimental data. However, their validation results are only roughly described in uncommented conference presentations and abstracts.

In 2010 Rexed *et al.* (88) introduced a modification of the seminal model related to the non-constant concentration of the metal complex. The kinetic of NiCl₂ dissolution is considered as the rate determining step of the electrochemical process. The model is validated with an experimental low current GITT in charge, discharge, and rest mode. Note that this is the only document that features experimental data from a mixed nickel/iron chloride commercial cell. It is stated in the conclusions that nickel ions concentration at the electrode surface (equivalent to the ferrous complex in the fundamental paper) is a major rate limiting factor during operation.

To finish this section, we will cite the Damla Eroglu and Alan West paper published in 2012 (85), that presents a comprehensive 1D mathematical model of an iron chloride positive electrode. The model is mainly a modification of the seminal model, similar to the one presented by Rexed *et al.* but applied to an iron-based cell. The modification involves changes in the solubility of FeCl₂ with position and time within the cell. Again, a non-constant concentration of the metal complex is proposed, controlled by its equilibrium constant $K_{sp,FeCl}$. The electrochemical reaction rate is obtained in the same way described in (84), but without considering the mass transfer of the ferrous complex between the bulk and the electrode surface:

$$j = \frac{e^{\alpha_a \frac{F}{RT}\eta} - \frac{c_{r,b}}{c_{r,e}} e^{-\alpha_c \frac{F}{RT}\eta}}{\frac{1}{i_0 a_m} + \frac{1}{nF} \frac{1}{r,e} \left(\frac{1}{k_m a_m}\right) e^{-\alpha_c \frac{F}{RT}\eta}}$$
[34]

The main refinement introduced in (85) and (88), is allowing $c_{r,e}$ value to spatially change within the cell as a function of time. In (85), values of $c_{r,e}$, are related to the equilibrium constant of dissolution of FeCl_{2(s)} (K_{sp,FeCl}), and to the concentration of its complexing reagent Al₂Cl₇⁻ which is calculated from changes in the melt composition through x_A (data from (86)):

Chapter 3 Page | 99

$$c_{\rm r,e} = \frac{K_{\rm sp,FeCl} K_{\rm melt}^2 x_{\rm A}^4}{2\overline{V}_{\rm e} (1-x_{\rm A})^2}$$
[35]

In equation [35], K_{melt} is the mole fraction constant of the following equilibrium:

$$2\text{AlCl}_{4}^{-} = \text{Al}_{2}\text{Cl}_{7}^{-} + \text{Cl}^{-}$$
[36]

The reference complex concentration $c_{r,ref}$ is then calculated for $x_A = x_{A,sat}$. The implementation is described in details in (85), but the simulations are not confronted to any experimental data.

We will keep in mind that all of the above mentioned papers, including the seminal paper, consider the cell to be isothermal. Also, none of these studies aim to simulate the two simultaneous electrochemical reactions at work in the commercial mixed-cell.

3.2 Integration of the thermal model

Thermal effects in a ZEBRA cell have been addressed in the scientific literature, but always independently from the electrochemical model. In this section I will give some contextual elements regarding the energy balance in a battery, before considering what is relevant to consider in the thermal model of a Na-NiCl₂ cell.

3.2.1 Thermal model requirements for an electrochemical cell

To list the processes that can be potentially responsible for heat effects in an electrochemical cell, I have used Bernardi *et al.* study on energy balance for battery systems (89). Changes of the battery temperature can be assigned to the following processes:

- electrochemical reactions,
- chemical reactions,
- phase changes,
- mixing,
- electrical work,

• heat exchange with the surroundings.

Therefore, the general energy balance proposed in (89) results from each of the above-mentioned contributions. Phase changes can originate from the temperature evolution, but also from a reaction of precipitation/dissolution at constant temperature.

3.2.2 Potential heat effects in Na-MCl₂ cells

From the above inventory, and following the hypotheses exposed in the seminal paper, we can assume that the relevant processes at work in a ZEBRA-type cell are:

- the main electrochemical reaction described by equation [30],
- the precipitation/dissolution of NaCl_(s) from the melt (equation [31]),
- electrical work,
- heat loss with the surroundings.

~ ~ ~ ~

Using an average heat capacity C_p for the overall cell⁶¹, and according to (89), the corresponding energy balance can be written as the following equation:

$$\underbrace{C_{p}}_{\text{temperature}}^{dT} = I \underbrace{\left[T^{2} d \frac{\frac{\partial CV_{\text{th,avg}}}{T}}{dT} \right]}_{\text{enthalpy of}} + \underbrace{\frac{dn_{\text{NaCl}}}{dt} \left[\Delta H_{\text{NaCl,f}}^{0} + RT \ln \gamma_{\text{NaCl}}^{\text{avg}} \right]}_{\text{enthalpy of NaCl phase change}} + \underbrace{IV}_{\text{electrical}} + \underbrace{Q}_{\text{heat}}_{\text{loss}}$$
[37]

In this relation, $OCV_{th,avg} = E$ represents the theoretical OCV of the cell at equimolar composition, $\Delta H_{NaCl,f}^{o}$ the enthalpy of formation of NaCl (with γ_{NaCl}^{avg} standing for its average activity coefficient), and V the cell voltage. The rate of heat loss *q* is usually related to the heat transfer coefficient *h* (encompassing convective, conductive, and radiative contributions), to the cell external surface area A, and to the ambient temperature T_{amb} . The corresponding relation is given by the heat transfer tr

⁶¹ C_p averaged value is considered constant in the range of temperature and SOC considered

Chapter 3 Page | 101

$$q = hA(T_{\rm amb} - T)$$
[38]

By developing the enthalpy of electrochemical reaction term, equation [37] can be re-written as equation [39], where the cell reversible and irreversible heat contributions are highlighted:

$$C_{p}\frac{dT}{dt} = \underbrace{IT\frac{\partial OCV_{th,avg}}{\partial T}}_{electrochemical reaction}_{reversible heat}} + \underbrace{\frac{dn_{NaCl}}{dt}\left[\Delta H_{NaCl,f}^{o} + RT \ln \gamma_{NaCl}^{avg}\right]}_{chemical reaction}_{reversible heat}} + \underbrace{IV - IE}_{heat} + q \qquad [39]$$

During operation, the irreversible heat originate from the overpotential IV - IE, and from ohmic losses in the electronic and ionic conductive paths. Both reactions (electrochemical and NaCl precipitation/dissolution) constitute reversible heat sources during cycling. The first term on the right-hand side of equation [39] is often defined as the entropic term because as $\Delta S^{\circ} = -\left(\frac{\partial\Delta G^{\circ}}{\partial T}\right)_{\rm P} = zF\left(\frac{\partial OCV_{\rm th,avg}}{\partial T}\right)_{\rm P}$, we deduce that $IT\frac{\partial OC_{\rm th,avg}}{\partial T} = \frac{1}{zF}T\Delta S^{\circ}$.

3.2.3 Focus on the reversible heat

If the general description of the irreversible heat is not dependent on the nature of the battery technology⁶², the reversible heat is obviously specific to the active material involved. Regarding the entropic term, we have investigated works by Cleaver *et al.* (90) (91) on heat transfer in nickel chloride cells⁶³. The $\frac{\partial OCV_{th,avg}}{\partial T}$ term have been evaluated at 90 % of SOC from 200 to 400 °C, and the electrochemical reaction proves to be exothermic in discharge (thus endothermic in charge mode). It is worth mentioning that this reversible heat value does not change significantly if we consider iron active material, because the two metals have similar $\frac{\partial OCV_{th,avg}}{\partial T}$ factor (92). In their studies, the main electrochemical reaction (equation [3]) is considered as a solid state process between the active materials in the positive electrode (NiCl_{2(s)}, NaCl_(s), Ni_(s)), thus neither reaction of precipitation in discharge, nor dissolution in charge are

⁶² It is often summed up as « RI² », with R being the internal or polarization resistance

⁶³ These were commercial SL/08 40 Ah pure nickel cells.

considered for the production or consumption of $NaCl_{(s)}$ (it is already included in the entropic term). At the contrary, precipitation of $NaCl_{(s)}$ from the melt is assumed in the seminal paper, so we need to consider the reversible heat of this phase change during discharge (89). Experimental data were found in a paper published by Hjuler *et al.*(93), regarding the endothermic heat of dissolution of $NaCl_{(s)}$ in sodium tetrachloroaluminate melts around its saturation value, between 175 and 300 °C. Parameter values related to the thermal implementation of the model will be described in section 3.3.2.4.

3.3 2D model development

Now that all the necessary theoretical notions associated to the electro-thermal model of a ZEBRA cell have been exposed, I will describe in this section how the model was implemented in practice, for the ML/3X unit cell. The 2D geometry, partial and ordinary differential equations (PDE and ODE), as well as all the parameters, variables, initial and boundary conditions ⁶⁴ were defined in Comsol Multiphysics® 5.1, a finite element computational software.

3.3.1 Geometrical design considerations and meshing

A multi-physics model is very attractive from a R&D point of view as it permits to predict geometrical design changes without the expenses related to prototype building and testing. With this objective in mind, the geometry of the model was entirely built with the graphic tool of the software, and has been parametrized. For example, it is possible to change the thickness of the BASE by tuning only the associated parameter, without the need to redraw completely this complex cloverleaf-shaped part of the cell. All components listed in Figure 51 are included in the model geometry with their exact dimensions.

⁶⁴ Like initial and boundary conditions.



carbon felt (domain 5)



Figure 51: Cross-section of a FIAMM ML/3X cell with its cloverleaf shaped BASE with the corresponding domains defined in Comsol

The existing rotational symmetry allows reducing the model geometry to the cross-section of a half-cell, and thus saving computation time. This geometry consists of six explicit domains where the governing equations of the model are implemented. The three points, B (near the BASE), C (near the current collector), and I (intermediate position), are used as local probes to monitor spatial changes in model variables. These features are described in Figure 52 (see also Figure 51 for the domain assignments).



Figure 52: 2D cell geometry implemented in Comsol and points used for spatial characterization of the cell: B next to the BASE, C next to the positive current collector, and I intermediate point

Comsol Multiphysics® software solves the system of equations defined by the user, by employing the finite elements method. Results originating from this method rely on the chosen elements distribution and sizing. The meshing of the geometry is particularly critical in our case for domain 4 (the porous positive electrode), as it is the siege of the more complex electro-thermal processes (see section 3.3.7). Figure 53 illustrates this idea, where the meshing used in domains 4, is finer (with smaller elements) than the meshing used in the remaining domains of the cell (in domain 1 the small thickness of the casing imposes the size of the elements).



domains 4 finer meshing

Figure 53: proposed meshing with different element size distribution

However, preliminary tryouts have shown that we can use the "physics controlled" meshing process of the software on all domains with coarse element size without changing substantially the simulation results. As the number of elements is much smaller, for the intermediate tryouts this alternative meshing reduces significantly the computation time (eight minutes instead of half an hour for the most complete version of the model).

3.3.2 Parameters and variables of the model

More than one hundred parameters are used in the model to characterize the geometry, the physico-chemical properties of active material as well as their quantities. Values of many of the parameters and variables needed for our model are available in the literature, and described in details in the seminal paper. For the nickel active material, physicochemical and electrochemical properties have been found in the literature (13) (57) (94) (95). The retained values are listed in appendix B. There are two types of variables: those related to the governing equations (Φ_1 , Φ_2 , x_A , \mathbf{v}^* , T), and the others derived from them through analytical expressions. For example, most of these second type variables are temperature dependent and have been implemented as such (material conductivity, melt density, open circuit voltage...). Their analytical expressions are listed in appendix C. It is nonetheless important to highlight which parameters have been used as adjustable factors in the simulations, and the analytical expression of some key variables.

3.3.2.1 Active materials microstructural parameters and quantities

In the absence of any data regarding in situ particle sizes in the positive electrode after the running cycles, interfacial areas of metal and salts ($a_{m,i,0}$ and $a_{s,i,0}$ parameters) have been treated as adjustable parameters. As a starting point, I have considered the mean particle size of Ni and Fe used by FIAMM as raw material, prior to their insertion into the cell. For the metal salts, we have taken values from the seminal paper for the iron active material, and results from (36)(37)(38) for the nickel active material. As Ni powder used by FIAMM features filament-like microscopic structures⁶⁵, we have allowed the exponential term *p* used in [26] and [27] to be higher than 2/3.

For the discharge procedures starting from 100 % of SOC, the initial values of active materials volume fractions used in our simulations are summed up in Table 4.

Table 4: Initial values used in the simulation (* ideal values after a complete charge)

Initial volume fraction values							
€ _{NiCl2,max}	$\epsilon_{\rm Ni,min}$	$\epsilon_{\rm FeCl2,max}$	$\epsilon_{\rm Fe,min}$	$\epsilon_{\rm p,min}$			
0.18	0.07	0.05	0.008	0*			

These values originate from the cyclic voltammetry peak analysis presented in chapter 0. (section 2.2.3). I have decided to affect the fluorine contribution, in term of volume fraction ($\epsilon_{NiF2,max} = 0.006$), to the nickel volume fraction ($\epsilon_{NiCl2,max} = 0.174_{NiCl2} + 0.006_{NiF2}$). For validation purpose, we can also expect certain values regarding the volume fractions of active materials at the very end of a complete discharge (0 % of SOC after 40 Ah), as displayed in Table 5.

T-1-1-	5 1	. f. 1: 1	1 £		(10	A 1	* : 1 1	-1)
I able	5: end	of discharge	volume trac	tion values	(alter a 40	An discharge,	* ideal v	alues)

Final volume fraction values						
€ _{NiCl2,min}	$\epsilon_{\rm Ni,0}$	$\epsilon_{FeCl2,min}$	$\epsilon_{\mathrm{Fe,0}}$	$\epsilon_{p,max}$		
0*	0.11	0.02	0.013	0.31		

If the fluorine contribution had been implemented separately from NiCl₂, its product would have been NaF ($\epsilon_{\text{NaF, max}} = 0.02$) instead of NaCl in discharge. Here, the value of $\epsilon_{\text{p,max}}$ corresponds to

⁶⁵ In this macroscopic model we have kept the Bruggeman model to describe the porosity.
the normal contribution from NiCl₂ and FeCl₂ (0.29), with the addition of the NiF₂ contribution in the form of NaCl_(s) (0.29 + 0.02). Practical commercial cells are assembled with a 70 % excess of Ni powder, so NaCl_(s) initial quantity defines the nominal capacity of the cell. Thus, the charge process ends way before total passivation of the nickel surface, when there is no more solid NaCl salt in the positive electrode.

3.3.2.2 Secondary electrolyte melts properties

To evaluate the temperature dependency of NaCl saturation limit in the melt, I have used the reference NaCl_(s) liquidus from the FTsalt-FACT phase diagram database (96). According to Figure 7, this source differs slightly from the one used by Sudoh and Newman (93) in our temperature range. The rate constant of precipitation and dissolution of NaCl_(s) is not known in this melt, so I have first implemented the values of k_p used in the seminal paper. The value of the solubility product K_{sp,FeCl} described by Eroglu and West (85) has not been reported in the literature, so they have carried out simulations for values between 10⁴ (corresponding to the seminal paper assumption) and 10⁸ (above this limit FeCl₂ cannot be considered anymore as sparingly soluble in the melt). They have found that 10⁵ is the minimal value to use in order to obtain consistent results (i.e. a convergence of the solver). The way my model is implemented allows me to test each hypothesis, including the absence of precipitation/dissolution of NaCl or FeCl₂.

3.3.2.3 Reference exchange current densities and transfer coefficients

Reference exchange current densities $i_{0,ref}$ and transfer coefficients (α_a and α_c) are treated as adjustable parameters in the model for the cathodic electrochemical reactions. Measurements of exchange current densities at nickel or iron chloride electrodes are reported in the literature (nickel (13) (57) (95), iron (13) (84)), but there is a substantial spread in the results, depending on the methods and the geometry of the electrodes. In Ratnakumar *et al.* (13), the measurement of the exchange current density gives 7.3×10^{-4} A.cm⁻² for the nickel based electrode and 4.3×10^{-4} 4 A.cm⁻² for the iron-based electrode at 220 °C. Their temperature dependency can be estimated considering a 10 % increase for each 10 °C rise of temperature (i.e. around 1 mA.cm⁻² at 270 °C for Ni). In (60), we are in the range of 6.2 to 7.3×10^{-4} A.cm⁻² for a nickel based material at 275 °C. The operational temperature dependency has been treated by using the usual Arrhenius type factor $e^{-\frac{E_A}{RT}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}$. The activation energy parameter E_A has been identified by a fitting process at a reference temperature T_{ref} , and with simulations at different temperatures. For the negative electrochemical reaction, I have used the value of $i_{0,N}$ given in the seminal paper.

In (60), the α_a transfer coefficient is in the range of 0.12 to 0.14. In ref (87), transfer coefficient is taken to be 0.2175 (so must probably a fitted parameter). The transfer coefficients (or apparent transfer coefficients) α_a and α_c as defined by Newman (97) and used in the seminal paper, originally derived from the symmetry factor β following $\alpha_a = (1 - \beta)n$ and $\alpha_c = \beta n$. β represents the fraction of the applied potential which promotes the cathodic reaction (the MCl₂ \rightarrow M reduction in our case during discharge), and *n* is the number of electrons exchanged. This definition differs from the recent IUPAC technical report written by Guidelli *et al.* (98), although the resulting values for α_a and α_c are ultimately the same. Indeed, for Guidelli *et al.* an elementary step involving the simultaneous release or uptake of more than one electron is regarded as highly improbable, so they have proposed a definition of each transfer coefficient independent of *n* (although their sum is related to *n* by $\alpha_a + \alpha_c = \frac{n}{\nu} \frac{66}{\nu}$). Notice that a value around 0.1 for a transfer coefficient like it has been calculated in ref (60) is considered highly improbable in Guidelli paper.

3.3.2.4 Thermal parameters and variables

The heat capacity $C_{p,cell}$, cell density ρ_{cell} , and cell lateral thermal conductivity k_{lat} originate from measurements done at FIAMM facilities. In my model, I am able to use a temperature and SOC dependent value of $C_{p,cell}$. in case it proves to have a significant effect on the simulations results. The heat transfer coefficient h was first considered as an adjustable parameter, and subsequently its value has been validated with experimental data. The electrochemical reversible heat source term has been estimated from OCV measurements at different temperatures and at 90 % SOC (see chapter 0, section 2.3). The eventual NaCl phase change contribution to the reversible heat term is estimated using results presented in (93). For validation purpose, the temperature of the cell surroundings T_{amb} , has been set with experimental data corresponding to the furnace temperature with the cell at 0 % of SOC. This temperature is

 $^{^{66}}$ v is the number of occurrence of the rate determining step in the electrochemical process (only one in our case)

slightly different from the temperature measured at 100 % of SOC as the heat capacity of the cell is not the same.

3.3.2.5 Geometrical parameters

Parameters of the 2D half-cell geometry are very well known and fixed in the implementation. However, in the model three parameters related to the 3D object geometry are needed to simulate the real cell behavior. The first parameter is the surface of the positive collector S_{col} that is involved in the current distribution in the cell (see section 3.3.7), and serves to calculate the corresponding boundary condition (i.e. the current density originating from the positive collector when a current *I* is applied). From construction the value of S_{col} can be estimated roughly, but it will be necessary to adjust its value to match the simulated capacity. For example with a 8 A discharge simulated over 5 h we should consumed the equivalent of 40 Ah of active material.

The second parameter is the height of active material involved in the electrochemical process. This parameter is used for the thermal implementation because by default Comsol normalizes the implemented heat sources in W.m⁻³ by using a dz parameter equal to 1 m. Again from construction the needed value can be roughly estimated as a starting point before doing the necessary adjustments.

The third 3D parameter related to the real cell geometry is the positive electrode volume $V_{\text{electrode}}$, used in the calculation of all active material volume fractions. Its value has been estimated first using the geometry step file provided by FIAMM, and then slightly adjusted during the optimization process.

3.3.3 Governing equations: practical implementation in Comsol

All governing equations have been implemented in Comsol Multiphysics® using its mathematical library of PDEs and ODEs, and heat transfer in solids. Notice that Comsol Multiphysics® provides additional modules for electrical currents, batteries and fuel cells, not used in my work. In addition to the fact that the Na-MCl₂ technology is not included in the Comsol batteries library (although the electrochemistry module allows to consider porous electrodes situations), the objective was to have total control on how the equations were implemented and conditioned.

Ohm's law initial form $\sigma(\nabla \phi_i) = \mp \mathbf{i}_i$ has been transposed in Comsol by using the following general form PDE (where σ is the conductivity of the associated media⁶⁷):

$$\nabla \cdot \sigma(\nabla \phi_i) = \mp \nabla \cdot \mathbf{i}_i$$
[40]

As a consequence of electroneutrality, the total divergence of the current density $(i_1 + i_2)$ is zero. For our macroscopic model, it gives:

$$\nabla \cdot \mathbf{i_1} = -\nabla \cdot \mathbf{i_2} = j \tag{41}$$

Consequently, Ohm's law can always be written:

$$\nabla \cdot \sigma(\nabla \phi_i) = \mp j$$
[42]

Therefore, the local transfer current *j* is the source term in this Ohm's law. The kinetics equations related to local transfer currents j_{M} (M standing for Ni of Fe) were directly implemented as variables in the corresponding domains (see appendix C).

The terminal voltage is defined as:

$$U_{\text{cell}} = \phi_{1,\text{collector}} - \phi_{1,\text{casing}}$$
[43]

Initial condition is $\phi_2 = 0$ V in all domains displaying ionic conduction. From an electrochemical point of view, domain 6 (positive current collector), will be only see as the siege of boundary conditions of governing equations implemented in domain 4 and 5.

 $^{^{67}}$ I will use σ to evoke electronic conductivities, and κ for ionic conductivities.

In a first approach, the heat transfer equation is applied on all domains of the cell as if it was a homogeneous object:

$$\rho_{\text{cell}} C_{\text{p,cell}} \frac{\partial T}{\partial t} + \nabla \cdot (-k_{\text{lat}} \nabla T) = Q_{\text{source}}$$
[44]

The implementation of the irreversible heat loss flux due to the Joule effect in all domains will be described in section 3.3.9.

In a first approach, the fluoride additive contribution was not implemented.

3.3.4 Governing equations in domain 1 (negative steel casing)

In this domain, the only equation to consider for the electrical behavior is the Ohm's law associated to electronic conduction, its source term being null (j = 0, there is no electrochemical reaction):

$$\nabla \cdot \sigma_{\rm Fe}(\nabla \phi_1) = 0 \tag{45}$$

The Dirichlet boundary condition $\phi_1 = 0$ V and the initial condition $\phi_1 = 0$ V are applied at the negative casing (domain 1). The terminal voltage is therefore only defined by the calculated value of ϕ_1 at the current collector interface.

The heat transfer rate with the surroundings is applied on the external surface of the casing using the general convective heat flux expression of Comsol:

$$q = h(T_{\rm amb} - T)$$
[46]

Again, notice that h is able to encompass conductive, convective, and radiative contributions. With a cell operating at 300 °C, we can assume that the heat loss mode is partly convective, and partly radiative.

3.3.5 Governing equations in domain 2 (negative sodium electrode)

In this domain too, the only electrical equation to consider⁶⁸ is the Ohm's law associated to electronic conduction, its source term being also null (j = 0, there is no electrochemical reaction):

$$\nabla \cdot \sigma_{\mathrm{Na}}(\nabla \phi_1) = 0$$
^[47]

3.3.6 Governing equations in domain 3 (BASE separator)

In this domain again, the only have to consider the Ohm's law associated to ionic conduction, its source term being null (j = 0, there is no electrochemical reaction):

$$\nabla \cdot \kappa_{\rm sep}(\nabla \varphi_2) = 0$$
[48]

As explained in section 3.1.2.4, at the interface between the negative electrode and the BASE separator, the Neumann boundary condition is given by equation [23]. This interface is the source of the reversible heat associated to the electrochemical reaction [2]. The implementation of this heat source flux is described in section 3.3.9.

3.3.7 Governing equations in domain 4 (porous positive electrode)

In this domain, we have to consider both Ohm's law associated to electronic and ionic conduction. In our porous media, that gives us for the electronic conduction:

⁶⁸ The electrochemical reaction is considered at the external boundary of domain 3 (BASE)

Chapter	3	Page	113
1		0	

$$\nabla \cdot \sigma_{\rm e}(\nabla \phi_1) = j \tag{49}$$

In our case, $\sigma_e = \sigma_{Ni} \epsilon_{Ni}^{1+\tau} + \sigma_{Fe} \epsilon_{Fe}^{1+\tau}$. At the interface with domain 6 (positive current collector with external surface S_{col}), we have to consider the Neumann boundary condition $\mathbf{i_1} = \frac{l_{exp}}{S_{col}}$, and the initial condition $\phi_1 = U_{exp}(0)$ which is the experimental value of the cell voltage at the beginning of the discharge (t = 0 s). I_{exp} is the current rate applied on the positive electrode in the simulations.

As the ionic conductivity is treated separately from the electronic conductivity in my model (and without the secondary electrolyte reservoir), I have used a modified version of equation [21]:

$$\nabla \cdot \left[\kappa_{e} \left\{ -\nabla \Phi_{2} - \frac{RT}{F(1 - x_{A})} \left(1 + \frac{d \ln \gamma_{A}}{d \ln x_{A}} \right) \nabla x_{A} \right\} \right] = -j$$
[50]

The secondary electrolyte conductivity depends on the total porosity of the solid matrix $\kappa_e = \kappa \epsilon^{1+\tau}$. This equation takes into account variation of the secondary electrolyte composition. The flux of ionic species is set to zero at the interface with the positive collector (domain 6):

$$\nabla \phi_{2,\text{collector}} = 0$$
[51]

A coefficient form PDE is used in Comsol to implement the equivalent material balance presented in the seminal paper with equation [22]:

$$\epsilon \frac{\partial x_{\rm A}}{\partial t} + \nabla \cdot \left(-D\epsilon^{1+\tau} \nabla x_{\rm A} \right) + \left(\mathbf{v}^* + \frac{\overline{v}_{\rm A} - \overline{v}_{\rm B}}{\overline{v}_{\rm e}} D\epsilon^{1+\tau} \nabla x_{\rm A} + \frac{\overline{v}_{\rm e}j}{2\mathbf{F}} \right) \cdot \nabla x_{\rm A} - \overline{v}_{\rm e} \left(R_I - \frac{j}{\mathbf{F}} \right) x_{\rm A} = 0 \quad [52]$$

Considering the full charge state as the starting condition where all NaCl_(s) have been consumed, initial value for x_A is set to $x_{A,sat}(T)$ in this domain. The Neumann boundary condition at the collector interface, the separator interface, and the felt interface is:

$$\nabla \mathbf{x}_{\mathbf{A}} = \mathbf{0}$$
^[53]

I started this work by using the equations established in the seminal paper, for each metal chloride contribution⁶⁹ (M being Ni or Fe).

$$j_{M} = \frac{e^{\alpha_{a} \frac{F}{RT} \eta_{M}} - e^{-\alpha_{c} \frac{F}{RT} \eta_{M}}}{\frac{1}{i_{0,M} a_{m,M}} + \frac{1}{nFc_{T,e,M}} \left(\frac{1}{k_{m,M} a_{m,M}} - \frac{1}{k_{s,M} a_{s,M}}\right) e^{-\alpha_{c} \frac{F}{RT} \eta_{M}}}$$
[54]

Similarly to the seminal model:

$$i_{0,M} = i_{0,\text{ref},M} \left(\frac{c_{\text{r,e},M}}{c_{\text{r,ref},M}}\right)^{1-\beta} \left(\frac{c_2}{c_{2,\text{ref}}}\right)^{2\beta}$$
[55]

⁶⁹ I have use the same transfer coefficient values for both metals

$$a_{m,M} = a_{m,0,M} \left(\frac{\epsilon_{m,M} - \epsilon_{m,M,\min}}{\epsilon_{m,0,M} - \epsilon_{m,M,\min}} \right)^{p_M} \left(1 - \left(\frac{\epsilon_p + \epsilon_{s,M}}{1 - \epsilon_{m,M}} \right)^{p_M} \right)$$
[56]

$$a_{s,M} = a_{s,0,M} \left(\frac{\epsilon_{s,M}}{\epsilon_{s,0,M}}\right)^{p_M}$$
[57]

In the model of the mixed Ni/Fe commercial cell, the total local current density j has been treated as the sum of the nickel and iron active material contributions:

$$j = j_{NiCl2} + j_{FeCl2}$$
^[58]

It has been necessary to use conditional operators in Comsol to express the fact that the iron does not contribute to the total local current density until the cell voltage is lower than the Fe/FeCl₂ equilibrium potential ($U_{cell} < OCV(Fe)$).

$$j = (if (\Phi_1 - \Phi_2) > 0CV_{Fe}, j_{NiCl2}, j_{NiCl2} + j_{FeCl2})$$
[59]

This conditional implementation has also been used in the calculation of iron and iron chloride volume fraction described further. Equations [54] to [59] were implemented as variables in domain 4.

The fifth equation to consider is related to the average molar velocity (equation [28]). My assumption here is that this flux is only perceptible along the vertical axis of the cell and negligible in the plane of our model geometry. In the seminal paper, there is no mention of velocity simulation results, which confirms the fact that its impact on the cell voltage is very

Chapter 3

likely negligible. Thus, I chose not to implement the velocity equation in order to avoid an unnecessary increase of the model computation time.

For each iteration of the time dependent simulation, the following relation⁷⁰ determines how the porosity and all volume fractions are linked:

$$\epsilon = 1 - \epsilon_{\text{NiCl2}} - \epsilon_{\text{Ni}} - \epsilon_{\text{FeCl2}} - \epsilon_{\text{Fe}} - \epsilon_{\text{p}}$$
[60]

Five ODEs have been implemented to calculate changes of volume fraction for NiCl₂, Ni, FeCl₂, Fe, and NaCl during discharge:

$$\frac{\partial \epsilon_{\rm MCl2}}{\partial t} = \frac{\overline{V}_{\rm MCl2}}{2F} j_{\rm M}$$
[61]

for NiCl₂ and FeCl₂,

$$\frac{\partial \epsilon_{\rm M}}{\partial t} = -\frac{\overline{V}_{\rm M}}{2\rm F} j_{\rm M}$$
[62]

for Ni and Fe. And for NaCl:

$$\frac{\partial \epsilon_{\rm p}}{\partial t} = \bar{V}_{\rm p} R_{\rm I} \tag{63}$$

⁷⁰ Implemented as a variable

Each ODE is conditioned by active material initial quantities. In discharge mode, and from 100 % of SOC, these quantities are noted $\epsilon_{\text{NiCl2,max}}$, $\epsilon_{\text{Ni,min}}$, $\epsilon_{\text{FeCl2,max}}$, $\epsilon_{\text{Fe,min}}$, $\epsilon_{\text{p,max}}$ (see Table 4 and Table 5).

Finally, the temperature inside this domain is also dependent of irreversible and reversible heat generation which implementation is described in section 3.3.9.

3.3.8 Governing equations in domain 5 (the carbon felt)

In this domain, we only have to consider both Ohm's laws associated to electronic and ionic conductions:

$$\nabla \cdot \sigma_{\rm C}(\nabla \phi_1) = 0 \tag{64}$$

In our case, $\sigma_{\text{felt}} = \sigma_C \epsilon_C^{1+\tau}$. I have neglected the eventual compression of this felt during discharge, and considered that . Ohm's law associated to ionic conduction is written:

$$\nabla \cdot \left[\kappa_{\rm C} \left\{ -\nabla \varphi_2 - \frac{RT}{F(1 - x_{\rm A})} \left(1 + \frac{d \ln \gamma_{\rm A}}{d \ln x_{\rm A}} \right) \nabla x_{\rm A} \right\} \right] = 0$$
[65]

The secondary electrolyte conductivity in the porosity of the felt is expressed by $\kappa_{\rm C} = \kappa (1 - \epsilon_{\rm C})^{1+\tau}$. Initial value for $x_{\rm A}$ is also $x_{\rm A,sat}(T)$ for this domain.

3.3.9 Thermal-electrochemical coupled model

The way the energy balance is written in equation [39] is not fully satisfactory in the context of a multi-physics modeling as it depends on macroscopic parameters (I and V), and therefore is not locally distributed. From thermal models developed for lithium ion cells (99) (100), the irreversible heat source term Q_{irrev} can be expressed in our case as:

$$Q_{irrev} = j_M \eta_M + \sigma (\nabla \phi_1)^2 + \kappa (\nabla \phi_2)^2 + \frac{2RT\kappa}{F} (1 - x_A) \nabla (\ln c_A) \cdot \nabla \phi_2$$
 [66]

This irreversible heat source is coming on the one hand from the positive electrode overpotential (first term on the right-hand side applied only on domain 4), and on the other hand from the Joule effect in metal constituents and electrolyte (last three terms on the right-hand side). The second term on the right-hand side is only applied in the case of electronic conduction (domains 1, 2, 4, 5 and 6), whereas the third term is only applied in the case of ionic conduction (domains 3, 4 and 5). The last term on the right-hand side only concerns domains 4 and 5.

Looking at the equation we can clearly see how the electrochemical and thermal parts of the model are coupled. Indeed, the heat sources are implemented from variables already defined and used in the electrochemical part of the model, which are themselves temperature dependent.

The reversible heat source flux of the main reaction $Q_{rev,M}$ is also coupled with the electrochemical variable j_M through:

$$Q_{\rm rev,M} = j_{\rm M} T \frac{\partial OCV_{\rm cell,M}}{\partial T}$$
[67]

In the positive electrode, Q_{rev} is generated in the reaction front zone. In the negative electrode, the heat source originates from the external surface of the BASE. The last reversible heat source term $Q_{rev,NaCl}$ is related to the assumed precipitation reaction, and we only know its overall value in kJ.mol⁻¹.

3.4 Initial simulation strategies

Figure 54 sums up this first model implementation:

Chapter 3



Figure 54: summarized diagram of the initial 2D model implementation

The first objective was to put to the test hypotheses proposed in the seminal paper and subsequent works. In this context, the preliminary simulations were run in isothermal mode. The corresponding results have been compared to experimental data originating from constant discharge tests on the ML/3X unit cell. The cell temperature was set to the ambient temperature of the experimental tests. As stated before, the average molar velocity equation was never used in my 2D model. These preliminary tryouts have allowed me to assess the influence of the metal complex concentration $c_{r,e}$, as well as the kinetic of precipitation/dissolution of NaCl_(s) (through the k_p parameter).

Chapter 4

Results and discussions

Initial simulation results presented in the first section of this chapter will be used to propose new working hypothesis. For instance, the seminal two-steps mechanism will be questioned, and simplifications will be considered to establish an implementation of the model based on a solid state process. Influence of the rate of discharge, initial temperature, as well as design changes will be studied to test the robustness of the model and identify the key parameters. The reaction front hypothesis will be also confronted to my simulation results.

4.1 Electrochemical two-steps mechanism simulations in isothermal mode

4.1.1 Initial tryouts

The fundamental hypothesis in the seminal paper refers to the existence of a two-steps mechanism, involving an intermediate metal complex. Concentration of this metal complex $c_{r,e}$ is considered constant ($c_{r,e} = c_{r,ref}$) during operation, most probably for simplification purpose. But basically this concentration is related to the specific surface of the metal chloride salt which decreases during discharge. These variations of $c_{r,e}$ have a direct influence on the exchange current density value through equation [25], and on the local transfer current through equation [34]. In equation [25], the decreasing of the specific surface of metal salt is taken into account in

the term $\left(\frac{c_{r,e}}{c_{r,ref}}\right)^{1-\beta}$ which value is comprised between one ($c_{r,e} = c_{r,ref}$ at 0 % of DOD), and zero ($c_{r,e} = 0$ when all metal chloride has been consumed at 100 % of DOD). Somehow, this term allows us to see equation [25] as a relation of the type $i_0 = f(DOD)$, in the same way that equation [33] is used in (87)⁷¹.

Sudoh and Newman have assumed that the maximum value of $c_{r,e}$ was $c_{r,ref} \sim 10^{-8}$ mol.cm⁻³. This is quite a very low value, and my first attempts using this value proved to be unsuccessful to obtain a simulation result (the software was unable to converge with this initial condition). Notice that the first calculated value of the local transfer current *j* depends of the initial value of $c_{r,e} = c_{r,ref}$, but the latter has no influence on the initial value of the exchange current density i₀. In (85), Damla Eroglu and Alan West have proposed a relation of the type $c_{r,e} = f(x_A)$ through equation [35]. They considered $c_{r,ref} = 10^{-8}$ mol.cm⁻³ by assuming $K_{sp,FeC1} \sim 10^4$ in equation [35] (see section 3.3.2.2). They have estimated that the maximum value of this equilibrium constant of dissolution was 10^8 . From this maximum value, we get $c_{r,ref} \sim 10^{-3}$ mol.cm⁻³ with $x_A = x_{A,sat}$. By using $c_{r,ref} \sim 10^{-3}$ mol.cm⁻³ in the seminal model, I have obtained my first successful simulation. Figure 55 shows the simulation resulting from a C/5 constant discharge (I = 8 A), at 270 °C, with:

- $i_{0,ref,Ni} = i_{0,ref,Fe} = 1 \times 10^{-4} \text{ A.cm}^{-2}$,
- $p_{\rm M} = 2/3$ for both metals,
- $\beta = 0.5$ (thus $\alpha_a = \alpha_c = 1$),
- $c_{\rm r,ref,Ni} = c_{\rm r,ref,Fe} = 10^{-3} \text{ mol.cm}^{-3}$,
- $k_p = 1 \text{ cm}^3 \text{.mol}^{-1} \text{.s}^{-1}$ (dotted curve), $k_p = 0.01 \text{ cm}^3 \text{.mol}^{-1} \text{.s}^{-1}$ (dashed curve)

 $^{^{71}}$ i_{0,i} = i_{0,ref}(1 - DOD)^{2/3}



Figure 55: simulated (black) and experimental (blue) voltage curves for a C/5 constant discharge at 270 °C⁷², with $k_p = 1$ (dotted) and 0.01 (dashed) cm³.mol⁻¹.s⁻¹

At the beginning of the simulated voltage curves, we observed a *coup de fouet* which cannot be attributed to a passivation phenomenon (see section 2.1.1). The higher the values of k_p , the lower the *coup de fouet*, with a total disappearance from 10 cm³.mol⁻¹.s⁻¹. Small values of k_p reflect a low kinetic of the sodium chloride precipitation during discharge. On the one hand, it means that with $k_p = 0.01$ cm³.mol⁻¹.s⁻¹, the effect of covering salt (through ε_p in equation [56]) is attenuated with less precipitation, and as a result, we observe a smaller polarization of the simulated voltage curve (dashed curve). On the other hand, as Na⁺ and Cl⁻ are locally freed without precipitating, significant spatial change in the melt composition are created. Thus ∇x_A in equation [50] varies more abruptly from zero to a higher value at the beginning of discharge in the case of smaller k_p , leading to a more important variation of *j* (*coup de fouet* from the dashed curve). Looking at the experimental voltage curve, we should consider that in fact the rate of precipitation/dissolution of NaCl_(s) is quite high. And because using k_p values beyond the 10 cm³.mol⁻¹.s⁻¹ does not affect the

⁷² For the experimental curve, 270 °C is only the initial temperature as it is not an isothermal process

voltage curves anymore, I have decided to challenge the infinitely fast kinetic hypothesis, right away.

4.1.2 Simulations with constant melt composition (non-isothermal model)

NaCl_(s) is now considered as a reactant or a product of the one-step electrochemical reaction described by equation [1], and is no longer involved in an additional precipitation/dissolution reaction that could affect the melt composition. With a constant composition of the melt, we now have $\nabla x_A = 0$ and $\frac{\partial x_A}{\partial t} = 0$ because $x_A = x_{A,sat}$. Another direct outcome is the fact that the thermal part of the model will not depend on $Q_{rev,NaCl}$. These conditions considerably simplify the model as we remove a major variable (x_A), and we no longer have to deal with its related governing equation (the material balance [52]). In the light of these statements and with $\nabla x_A = 0$, equation [50], [65], and [66] can now be re-written respectively:

$$\nabla \cdot [\kappa_{\rm e}(-\nabla \Phi_2)] = -j \tag{68}$$

$$\nabla \cdot [\kappa_{\rm C}(-\nabla \Phi_2)] = 0 \tag{69}$$

$$Q_{irrev} = j_M \eta_M + \sigma (\nabla \phi_1)^2 + \kappa (\nabla \phi_2)^2$$
^[70]

Regarding the evolution of the volume fraction of $NaCl_{(s)}$, I cannot use equation [63] anymore, because sodium chloride is no longer the result of a precipitation process. $NaCl_{(s)}$ originating directly from the main electrochemical reaction, I have decided to implement the following equation:

$$\frac{\partial \epsilon_{\rm p}}{\partial t} = \frac{\overline{v}_{\rm p}}{F} j$$
[71]

In my model I am able to separate the nickel and iron contribution to the production of NaCl_(s).

At this point, the implementation of the $c_{r,e}$ term is still subject to speculation, and hypotheses used in (85) ($c_{r,e} = f(x_A)$) no longer relevant. Following the idea that the relation giving the exchange current density is of the type $i_0 = f(DOD)$, I have decided to implement the following equation⁷³:

$$i_{0,M} = i_{0,ref,M} \left(\frac{\epsilon_s}{\epsilon_{s,0}}\right)^{p_M} e^{-\frac{E_A}{RT} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}$$
[72]

This way, I have used a close equivalent to the concentration ratio of the salt complex, for instance the volume fraction ratio of the same metal salt which is already implemented in my model. In discharge, this volume fraction ϵ_s decreases from $\epsilon_{s,0}$ to 0, which means that accordingly, the $\left(\frac{\epsilon_s}{\epsilon_{s,0}}\right)^p$ term decreases from 1 to 0. The time dependent value of the complex concentration used in [34] is given by:

$$c_{r,e} = c_{r,ref} \left(\frac{\epsilon_s}{\epsilon_{s,0}}\right)^p$$
[73]

In this equation $c_{r,ref}$ is considered as an adjustable parameter. Figure 56 displays one of the optimized simulation results of a C/5 discharge at 270 °C:

⁷³ The composition of the melt being considered constant, c_2 is also constant with $c_2 = c_{2,sat}$



Figure 56: simulated (black) and experimental (blue) voltage curves for a C/5 constant discharge at 270 °C (constant melt composition)

Results are significantly enhanced by assuming a constant melt composition, although iron contribution to the voltage curve displays a higher polarization than expected. Because I do not have the means to estimate experimentally k_m and k_s , I cannot prove that the mass transfer limitations related to the solute species were the reason I have obtained such a good fit with the model as it was. Thus, I have got rid of these parameters in a new model considering a solid state mechanism hypothesis.

4.2 Solid state process simulations in discharge mode

4.2.1 New working hypothesis

The solid state process model for an iron-based cell has been proposed by Orchard and Weaving (87), after a preliminary studies report (80). In their model, the solubilities of MCl₂ and NaCl are not taken into account. Following the scheme presented in Figure 50, the solid state mechanism implies that the main electrochemical reaction associated to each metal occurs at the interface between the metal and its salt (Figure 57):



Figure 57: solid state process associated to MCl₂/M electrochemical reaction in discharge

In (87), variation of the local transfer current Δj in an element of volume v is directly linked to the applied current in this element through the relation $\Delta I = v\Delta j$. In addition, they do not consider the effect of the covering salts as they only simulate discharge phases. In my model, I have used the specific area of the metal chlorides a_s in the governing kinetic equation, as well as the effect of the covering salts (MCl_{2(s)} and NaCl_(s)) through the expressions proposed in the seminal paper (respectively equations [26] and [27]). For the discharge mode, it gives the following kinetic equation:

$$j_{M} = i_{0,M} a_{s,M} \left(e^{\alpha_{a} \frac{F}{RT} \eta_{M}} - e^{-\alpha_{c} \frac{F}{RT} \eta_{M}} \right)$$
[74]

Notice that the interface between the metal and its salt highlighted in Figure 57 involved in the electrochemical process is taken to be equal to the specific area of the salt in my model, because NiCl₂ is known to form passivating monolayer on the nickel surface (58).

Obviously, the exchange current density $i_{0,M}$ no longer depends on $c_{r,e}$ as it is assumed that the metal complex is no longer an intermediate species.

4.2.2 Baseline simulation of a constant discharge

4.2.2.1 Baseline simulation for the non-isothermal model

The first tryouts with my new working hypotheses have helped me to assess more closely some of the adjustable parameters values. In early simulations, I have tried exchange current density values between 1×10^{-5} and 1×10^{-3} A.cm⁻² for both metals. This range includes all the values proposed in the literature. Regarding the transfer coefficients and their symmetry factor, I have started with $\beta = 0.5$ (thus $\alpha_a = \alpha_c = 1$), and I have subsequently tried values of β comprised between 0.1 and 0.9 ($0.2 < \alpha_a < 1.8$). Adjustable parameter values were identified by a fitting process to the experimental voltage curve resulting from a constant C/5 discharge from 270 °C. The corresponding optimized simulations are displayed in Figure 58 for the voltage curves, and in Figure 59 for the cell surface temperature. The cell simulated temperature is calculated for a centered point on the surface of one of its lateral side as shown in Figure 59 too.



Figure 58: simulated (black) and experimental (blue) voltage curves for a C/5 constant discharge from 270 °C (solid state hypothesis)



Figure 59: simulated (black) and experimental (blue) cell surface temperature curves for a C/5 constant discharge from 270 °C (solid state hypothesis)

The fluorine contribution has been assigned to the iron by increasing its apparent volume fraction (initially $\epsilon_{\text{NiF2}} = 0.037$). The parameters value used to fit closely the experimental curves were the following:

- $i_{0,ref,Ni} = 3 \times 10^{-5} \text{ A.cm}^{-2}$ and $i_{0,ref,Fe} = 7 \times 10^{-5} \text{ A.cm}^{-2}$,
- $p_{\rm Ni} = 1$ and $p_{\rm Fe} = 0.7$,
- $\beta = 0.6$ (thus $\alpha_a = 1.2$ and $\alpha_c = 0.8$) for both metals,
- $\epsilon_{\text{NiCl2}} = 0.18$ and $\epsilon_{\text{FeCl2}} = 0.07$,
- $h = 1.5 \text{ W.m}^{-2}.\text{K}^{-1}$,
- $S_{col} = 48 \text{ cm}^2$.

The S_{col} parameter has been first adjusted to obtain a consumption of NiCl₂ and FeCl₂ corresponding to 40 Ah. The other parameters have been adjusted to fit the form of the voltage curve and its polarization. The $p_{\rm M}$ parameters values are in good correspondence with the particles form of the metal powders used by FIAMM during the cell assembly process. Indeed, iron powders particles are mostly spherical (p = 2/3), while filamentary nickel particles are associated to a higher p value. For the voltage curves, differences between the simulated and

experimental data are kept under 1 % relative error at any DOD. In the case of the surface temperature the maximum relative error is less than 2 %. Both surface temperature curves feature an inflection (increase of temperature is slowed) when iron starts to contribute, although it is more pronounced for the simulated curve. This is characteristic of the fact that the reaction front associated to iron active material starts at the BASE surface where the ionic transportation path, thus ohmic loss, is minimized (see also the ohmic resistance plots in the next section).

4.2.2.2 Baseline simulation analysis

Comsol software solves the system of equations for all variables in any element of the model defined by the meshing procedure. For instance, we are able to monitor the time dependent evolution of all volume fractions, as well as the overall porosity, at the point B located near the ceramic internal surface (Figure 52). Figure 60 shows the result for the baseline simulation (C/5 constant discharge from 270 $^{\circ}$ C).



Figure 60: active material volume fractions and porosity evolution for point B during a C/5 constant discharge from 270 °C (solid state hypothesis)

We can clearly see that the iron contributes only when the simulated cell voltage U_{cell} is lower than OCV_{Fe} (~ 13,000 s or 3.6 h), in accordance to what has been implemented. Figure 61 displays the time dependent evolution of the mean values of all volume fractions, as well as the overall porosity, inside the positive electrode. From this graph, we can extract the volume fraction values of each material at the end of discharge and compare them in Table 6 to the expected value from Table 5.

Chapter 4



Figure 61: active material volume fractions and porosity evolution averaged values inside the positive electrode during a C/5 constant discharge from 270 °C (solid state hypothesis)

Table 6: volume fractions values	at the end of C/5 4	40 Ah discharge
----------------------------------	---------------------	-----------------

Final volume fractions of active material	€ _{NiCl2,min}	€ _{Ni,0}	€ _{FeCl2,min}	€ _{Fe,0}	ε _{p,max}
Expected value	0	0.11	0.02	0.013	0.31
Simulated value	0.004	0.11	0.035	0.014	0.315

The simulated results are quite in accordance with the expected values. Aside from errors originating from the unknown adjustable parameters, differences may be attributed to the following factors:

• Volume fractions are calculated from NiCl₂ and FeCl₂ molar volume and density. If the mixed Ni_{1-x}Fe_xCl₂ active material can be seen as the addition of its constituting metal chlorides, I do not know its exact density and molar volume. Regarding the iron active material (where I have the maximum error), it is more likely that it reacts under its Suzuki form Na₆FeCl₈. However, the latter being only an intermediate it should not have a significant impact on the initial and final volume fraction values.

- The fluorine content is not implemented, and its contribution has been added to the Ni_{1-x}Fe_xCl₂ contribution as if NiF₂ reacts at the same potential. This is not the case as $OCV_{NiF2/NaF} = 2.39 V$ instead of 2.58 V, and its reference exchange density value is expected to be different from the one used with the NiCl₂/Ni couple.
- At the end of discharge, Figure 63 (see further) shows us that the active material distribution is not homogeneous in the cell. So we should assume that in the real cell, the initial active material distribution before discharge was also not homogeneous. For the time being this is something that I have not implemented and put to the test in my model.
- And of course, the experimental results originate from measurements on a 3D cell that features design heterogeneities along its vertical axis. For instance, the terminal negative current collector is localized at the top of the cell on a very small area (less than 1 cm²), and the bottom of the cell contains Al and Ni metal powders instead of sodium to insure the electronic conductivity. In addition, let us bear in mind that the level of sodium in the negative compartment changes significantly during operation of the cell.

In addition to what is presented in Figure 60, the NaCl_(s) volume fraction is monitored in Figure 62 with respect to time at three different points in the cell, B, I, and C:



Figure 62: NaCl_(s) temporal and spatial volume fraction evolution for a C/5 discharge from 270 $^{\circ}\mathrm{C}$

Figure 62 shows clearly that the production of sodium chloride in the cell is not homogeneous. $NaCl_{(s)}$ is produced gradually from the BASE to the central current collector. This observation is in good accordance with the reaction front hypothesis; although the simulated reaction front is quite diffuse (simulated production of $NaCl_{(s)}$ is non null at the beginning of discharge near the current collector). To have a better view of the active material distribution inside the positive compartment, Figure 63 displays 2D plots of $NiCl_{2(s)}$ and $NaCl_{(s)}$ volume fractions at the end of discharge.



Figure 63: NiCl_{2(s)} (left), and NaCl_(s) (right) volume fraction distribution at the end of the baseline discharge

Expected overall final value: 0.31

0

V 0

Expected overall final value: 0

0.28

▼ 0.28

We observe the effects of a diffuse reaction front. If we can consider at the end of discharge that NiCl₂ is fully consumed near the BASE, some of it remains near the current collector. This NiCl₂ distribution will constitute the initial condition for the next charge or rest phase as NiCl₂ is not soluble in the melt. Notice that it is not the case for NaCl_(s), so during a rest phase consecutive to a full discharge some NaCl_(s) near the BASE will dissolve while some NaCl_(s) near the current collector will precipitate, keeping the same overall volume fraction value.

Finally, it is interesting to plot contributions of the BASE and the secondary electrolyte to the ohmic resistance, assuming negligible contributions from electronic conductors (metals and carbon felt contributions are not plotted):



Figure 64: ohmic resistance of the cell (red) and the corresponding contributions from BASE (black) and melt (blue) with respect to time for the baseline simulation

The overall ohmic resistance value of the cell is in accordance to what can be found in the literature: from 7-8 m Ω at 0 % DOD (24), and up to 20 m Ω (72) at 100 % DOD. The most interesting feature, which is in accordance with the reaction front hypothesis, is the temporary decrease of the resistance when iron starts to be involved in the discharge process. Indeed, when the cell voltage reaches the iron OCV (at around 13,000 s thus 3.6 h), the corresponding reaction is enable. If at that time the reaction front related to NiCl₂ was approaching the positive current collector, a second reaction front starts at the BASE surface where there are still iron chlorides to consume, with a minimized ionic transportation path.

4.2.2.3 Baseline simulation in isothermal mode

Figure 65 below displays the result obtained from the baseline simulation, after disabling the heat transfer equation in Comsol. Thus, this simulation runs in isothermal mode (270 °C).



Figure 65: baseline simulation voltage curve (continuous) compared to the same simulation run in isothermal mode (dashed) and to the experimental voltage curve (dotted)

By comparison, we can see that the simulated isothermal voltage curve shows slightly more polarization than the baseline voltage curve. This is not a surprise because as the cell temperature is rising during discharge, we should expect an increased conductivity of the electrolytes (BASE and NaAlCl₄). But it is clear with the rate used in these simulations (C/5), that thermal effects do not have a significant effect on the electrical performances of the cell.

4.2.3 Impact of the rate of discharge

The first tryouts at different rates were tested from the baseline simulation by only changing the current input in the implementation (I = 4 A for C/10 and 20 A for C/2). Results were compared to the corresponding experimental discharge curves in Figure 66:



Figure 66: voltage curve simulations at two different rates from 270 °C, using the baseline implementation

At lower rates (C/10), the model is still able to simulate well enough the voltage curve, but more significant differences appear at the higher rate (C/2) where the model predicts less polarization than what is expected. Note that despite these dissimilarities, I have obtained 40 Ah of discharge capacity at the end of the simulation in both cases. As stated before, the most significant differences do not originate from the thermal part of the model. This lower polarization is surely the result of a lower resistance, which produces less heat as displayed in Figure 67 for the C/2 rate.



Figure 67: simulated (black) and experimental (blue) cell surface temperature curves at two different rates from 270 °C

Both fits can be enhanced slightly by tuning some of the adjustable parameters (mostly p), but I cannot justify these changes by attributing them to an identified process. At C/2, we can see on the experimental curves that the iron consumption is enhanced because as the Ni polarization is higher, we reach the OCV of Fe sooner. The polarization rise observed on the experimental voltage curves (also visible on the baseline simulation at C/5), can be attributed to a more difficult charge transfer at higher rates, or to increasing ohmic losses. Regarding the ohmic losses, they are negligible at the beginning of discharge (almost 100 % electronic conductivity) thus I will not go along with that. In (80), it is recalled that relative contributions of solid and solution phase reactions in an operating cathode will also be expected to depend on the rates of charge and discharge employed, which would strongly influence the local overpotential. CV results at 250 °C from the same studies, suggest that at moderate overpotentials, the solid state processes are favored, whereas at more extreme overpotentials, the assumed reactions of solute species will gain in importance. I have launched tryouts at C/2 with Sudoh and Newman model implementation (the two-steps mechanism with $\nabla x_A = 0$), but I have obtained equivalent results, i.e. significantly less polarization at the beginning of discharge for the simulated voltage curve than what was expected. This higher charge transfer resistance could also be linked to the nature of the active material really involved at the beginning of discharge, Ni_{1-x}Fe_xCl₂ instead of NiCl₂,

and the simultaneous formation of the Susuki phase $Na_6FeCl_8^{74}$. I can suggest that it is related to the diffusion of other solute species, Na^+ from the melt and Cl⁻ from the metal salt for instance, diffusion that features a limitation at higher rates. In the same vein, I cannot rule out the hypothesis of Na^+ depletion inside the beta alumina electrolyte at high rate. Sadly, I did not have time to implement these hypothetical diffusion phenomena in my model to test them.

4.2.4 Impact of the initial temperature

The robustness of the model was put to the test regarding the operational temperature range, by simulating constant current discharges at different rates, and from different initial temperatures. To illustrate these tryouts, I have chosen to display the results for which the initial temperature was the furthest from the baseline simulation. The simulated cell voltage and surface temperature curves of a C/5 discharge from 300 °C are compared to their experimental counterparts in Figure 68:

⁷⁴ Again, it is not here an electrochemical process.



Figure 68: simulated and experimental cell voltage (left) and surface temperature (right) comparison

The simulated voltage curve does not fit the experimental one as well as in the baseline simulation, but the relative error is kept under 2 %. The same can be said for the simulated cell surface temperature. Figure 69 below demonstrate that my model can be validated in terms of temperature dependency, with results obtained with different rates (C/10 and C/2), and from different initial temperatures (280 and 290 °C):



Figure 69: cell voltage and surface temperature comparison for 40 Ah discharges at a) C/10 and from 280 °C, b) C/2 and from 290 °C

In both cases, the relative error is very similar to the one observed from 270 °C in section 4.2.3.

4.2.5 Impact of design changes

I will first illustrate the impact of design change by implementing in my model a thinner beta alumina ceramic (0.5 mm thickness instead of 1.5 mm). In Figure 70 are displayed for comparison purpose, both simulated voltage curves⁷⁵ with these two thicknesses (only this parameter has been changed in the baseline simulation).

⁷⁵ The real cell with a 0.5 mm thickness BASE does not exist, so the corresponding simulation cannot be compared to experimental data


Figure 70: cell voltage curves comparison for BASEs with different thickness (with the C/5 from 270 °C baseline simulation settings)

As expected, the contribution of the electrolyte to the overall polarization is reduced with a thinner thickness.

Being able to test other forms of active material in terms of nature or shape is another interesting aspect of this multiphysics model. For example, I have changed the assumed mean radius of the NiCl₂ particles from 1 to 5 μ m in the baseline simulation to verify the ability of my model to take this parameter into account. Figure 71 displays the simulation result.



Figure 71: cell voltage curves comparison for different NiCl₂ particles mean radius (with the C/5 from 270 °C baseline simulation settings)

The specific area of active material decreases logically with bigger particles, thus I have obtained significantly more polarization in this case⁷⁶. It is interesting to notice that my model is quite sensitive to the mean radius parameter. This is not something that can be directly set during the assembly of the cells because this mean radius is subject to change during the in-house running process (10 to 11 cycles). On the other hand, by using smaller particles size for the nickel active material, the specific active area will increase; but it can have an adverse effect on the constitution and stability of the conductive nickel backbone (poorer percolation, thus poorer conduction).

 $^{^{76}}$ The iron part of the voltage curve is not impacted because I haven't changed the mean radius of $FeCl_2$ in this simulation

Conclusions and perspectives

The initial objective of this work was to obtain an electro-thermal model of the FIAMM ML/3X commercial cell. To reach this objective, I have first started my work by the characterization of the cell electrical and thermal performances. The electrochemical processes have also been characterized and quantified by cyclic voltammetry. Not only these experiments have given me the means to validate my model, but they also proved to be very useful in its initial setting. From previously published studies, I have built a novel comprehensive 2D model based on the commercial cell geometry that could challenge the main hypotheses proposed in the scientific literature. Numerous simulations have been carried out to assess or confirm which parameter or variable had a significant influence on the outcome. As a result, I have presented in this manuscript a simplified and versatile model able to accurately simulate the mixed electrochemical reactions occurring inside the cell. The model has been validated in many operating conditions, over a wide range of rates and temperatures. To date, none of the previous mathematical models published in the literature were able to simulate Na-MCl₂ cell performance in discharge for a mixed active material blend, and in non-isothermal conditions. During the implementation process, I took care of parametrizing the maximum of inputs in my model, including the cell geometrical dimensions. Thus not only I have demonstrated the model ability to predict design changes, but I have made it very easy to implement and test these design changes.

Regarding the electrochemical implementation part of the model, simulations results are in better accordance with the solid state mechanism than the two-steps mechanism involving solute species. And in any case, the model shows that precipitation and dissolution of $NaCl_{(s)}$ are inherent to the electrochemical reaction itself, and should not be considered as a distinct reaction. With a cell that always operates with a saturated secondary melt, this leads to confirm that

composition of the latter remains constant. Simulation results have also confirmed the presence of multiple reaction fronts, one for each metal contribution. If the temperature does not have a significant effect on the cell electrical behavior (which is observed in both experimental and simulated conditions), the current rate has a strong influence on the cell surface temperature during discharge. This thermal behavior dependency on the electrochemical inputs is very well simulated by my model.

The next step of this work will be to deal with charge and rest modes, as well as the simulation of more dynamic profiles (partial discharge from initial SOC \neq 100 %, followed by partial charge with or without rest periods, etc...). In charge mode, the main difficulty will arise from the hysteresis phenomenon presented in section 2.1.2. Although, by following the same strategy used in discharge mode, the reduced contribution of iron during charge and the corresponding increased contribution on the nickel plateau can be implemented as apparent Fe and Ni contributions in the model. Again, the corresponding values would originate from the CV experiments. In relaxation mode, I already know that additional mechanisms will have to be implemented and put to the test. First of all, the local precipitation/dissolution of NaCl_(s), with its associated ions diffusion, is likely to be occurring to homogenize NaCl_(s) concentration in the possibility that some recently produced iron active material will be in presence of remaining NiCl₂ salt at potential that allows the direct reaction between both.

Refinements of this 2D model are of course possible, and also desirable to better simulate for instance high rates of discharge. The true nature of the active materials involved in all reaction mechanisms (Ni_{1-x}Fe_xCl₂, Na₆FeCl₂, and the fluorine species) will have to be considered as well as the identification of their adjusted physical properties (density, molar volume). To assess the intrinsic temperature variations inside the cell, the thermal part of the model can be optimized. by the specification of the particular heat transfer associated to each domain. It would be interesting for instance to confirm that 80 % of the reversible heat is generated in the negative electrode (at the interface with the BASE), and 20 % in the positive electrode (90).

As it is, my 2D model is the intermediate step to get to the 3D model of the ML/3X cell, but more interestingly to develop a 3D model of any battery pack based on these cells. Obviously, with more than 200 unit cells, we cannot imagine using the full form of the multiphysics model for each cell, as the calculation time would be out of proportion. But, by comparing the experimental cell and pack electrical performances, we can observe that the cell electrochemical performances are quite scalable to the pack level using a simple multiplication factor⁷⁷. There is no such simple equivalence with the thermal behavior of the packs (as each cell influences the other ones in its vicinity), which further includes heating and cooling devices. This is why I have finished my thesis work by focusing on the development of a simplified 3D thermal model of a stationary pack (ST523), able to simulate its thermal behavior mainly from the current input and internal electric potential values. This way, a multiphysics model of the pack can be computed to map its temperature by segregating the electrochemical model (the scalable cell model able to give us the overall pack voltage output) and the thermal model, considering a weak coupling between its electrical and thermal behaviors.

⁷⁷ The contribution of the pack wiring can be integrated in this factor.

Appendix A: governing equations in the seminal paper

We will use the seminal paper (84) numeration here to indicate the relevant equation. Equations [7], [8], [10] and [12] are the 4 equations solved regarding the 4 unknowns η , x_A , \mathbf{v}^* and \mathbf{i}_2 . For most of the following demonstrations, let's bear in mind that according to (81) and (83):

- Subscripts 1, 2 and 3 respectively stand for AlCl⁴⁻, Cl⁻ and Na⁺, so z₁ = -1, z₂ = -1 and z₃ = +1
- Therefore j_{in} pore wall flux of active electrochemical species in reaction [2] are only defined for 2, hence j_{1n} and j_{3n} are null. So, according to equation [4]: $aj_{2n} = -\frac{\nabla . i_2}{F} R_I$.
- The melt is considered as $A = NaAlCl_4 + B = NaCl$, with $c_1 = [AlCl_4]$, $c_2 = [Cl]$ and $c_3 = [Na^+]$, Na^+ being the common ion. By definition $c_T = c_1 + c_2 + c_3$ with $c_1 = [AlCl_4]_A$, $c_2 = [Cl]_B$ and $c_3 = [Na^+]_A + [Na^+]_B$. The stoichiometry tells us that $[AlCl_4]_A = [Na^+]_A$ and $[Cl]_B = [Na^+]_B$. Therefore $[Na^+] = c_1 + c_2 = c_3$ and $c_T = 2(c_1 + c_2)$. So indeed $c_3 = \frac{c_T}{2}$. The stoichiometry also tells us that $c_1 = c_A$ and $c_2 = c_B$.
- Our stoichiometry implies that $v_i^A = v_i^B = 1$ and $v^A = v^B = 2$.
- In the reference frame of the common ion Na⁺ velocity (i.e. v₃) $t_1^c + t_2^c + 0 = 1$, therefore assuming $t_1^c = x_A$, indeed $t_2^c = x_B$.
- In the reference frame of the average molar velocity \mathbf{v}^* , the relation between the transference numbers is: $t_1^* + t_2^* + t_3^* = 1$. As $c_3 = \frac{c_T}{2}$, it is assumed that $t_3^* = 0.5$ (contribution of 3 to the current is half of the total current). In the same spirit, as $c_1 = c_A$ and $c_2 = c_B$, it is assumed that $t_1^* = \frac{x_A}{2}$ and $t_2^* = \frac{x_B}{2}$. Hence $\nabla t_1^* = \frac{\nabla x_A}{2}$ and $\nabla t_2^* = \frac{\nabla x_B}{2} = -\frac{\nabla x_A}{2}$ (as $\nabla x_B = \nabla(1 x_A)$).
- By definition, $c_A = \frac{n_A}{v_e} = \frac{\frac{n_A}{n_A + n_B}}{\frac{v_e}{n_A + n_B}}$, so $c_A = c_1 = \frac{x_A}{v_e}$, $c_B = c_2 = \frac{x_B}{v_e}$ and $c_T = 2c_3 = \frac{2}{v_e}$. Also $c_A + c_B = \frac{1}{v_e}$.

All these relations will greatly help simplifies Pollard & Newman general equations used to obtain main equations in the paper.

Equation [7]
$$i_2 = \frac{\sigma_e \kappa_e}{(\sigma_e + \kappa_e)} \left\{ \nabla \eta + \frac{r_s I}{\sigma_e r} + \frac{R T t_1^c}{(F(1 - x_A)x_A)} \times \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right) \nabla x_A \right\}$$

In ref (17) (Pollard and Newman our ref [97]), a modified Ohm's law expression for the superficial current density in the pore solution is established as:

$$\frac{i_2}{\kappa} = -\nabla \Phi_2 - \frac{1}{F} \left[\left(\frac{s_1}{n\vartheta_1^A} + \frac{t_1^C}{z_1\vartheta_1^A} \right) \left(1 + \frac{\vartheta_3^A c_A}{\vartheta_3^B c_B} \right) - \frac{s_3 c_A}{n\vartheta_3^B c_B} \right] \nabla \mu_A \ [32]$$

Here, with our chosen binary electrolyte, any $\vartheta_i^j = 1$ and $\frac{c_A}{c_B} = \frac{c_1}{c_2} = \frac{x_A}{1-x_A}$, and because the electrochemical reaction at the positive electrode depends only of Cl⁻ ions we can eliminate s₁ and s₃ terms from the expression above:

$$\frac{i_2}{\kappa} = -\nabla \Phi_2 + \frac{1}{F} \left[\left(\frac{t_1^c}{1} \right) \left(1 + \frac{x_A}{1 - x_A} \right) \right] \nabla \mu_A$$

Since $\mu_A = RTln(x_A^{\vartheta_1^A}\gamma_A\lambda_A^\circ)$ and assuming that λ_A° is a constant: $\nabla \mu_A = RT \frac{\nabla x_A}{x_A}(\vartheta_1^A + \frac{dln\gamma_A}{dlnx_A})$. As of $-\nabla \Phi_2$, we know that $\eta = \Phi_1 - \Phi_2$ so $\nabla \eta = \nabla \Phi_1 - \nabla \Phi_2$ and

Finally:
$$\frac{i_2}{\kappa} = \nabla \eta - \nabla \Phi_1 + \frac{1}{F} \left[\left(\frac{t_1^c}{1 - x_A} \right) \right] RT \frac{\nabla x_A}{x_A} \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right)$$

In the porous electrode theory of Tiedemann & Newman, solid phases and electrolyte phases are treated as superposed continua. So the global conductivity κ is the result of parallel conductivity between solid phase (σ_e) and electrolyte phase (κ_e), hence a relation of the type: $\kappa = \frac{\sigma_e \kappa_e}{(\sigma_e + \kappa_e)}$.

The remaining term $-\nabla \Phi_1$ account for the potential in the solid matrix at any given radius *r* between r_0 and r_s , and is given through equation [24].

 $\frac{d \ln \gamma_A}{d \ln x_A}$ can be simplified before implementation: starting with equation [A-16]

 $ln\gamma_{A} = \frac{a}{RT} \left[\frac{1-x_{A}}{1+(b-1)x_{A}} \right]^{2} \text{we operate a change of variable } lnx_{A} = y_{A}, \text{ therefore } x_{A} = e^{y_{A}} \text{ and}$ $ln\gamma_{A} = \frac{a}{RT} \left[\frac{1-e^{y_{A}}}{1+(b-1)e^{y_{A}}} \right]^{2}. \text{ Then } \frac{dln\gamma_{A}}{dlnx_{A}} \text{ becomes } \frac{dln\gamma_{A}}{dy_{A}} \text{ and the latter is developed, reduced and}$ expressed as a function of x_A to obtain $-\frac{2a}{RT} \frac{(1-x_{A})x_{A}}{[1+(b-1)x_{A}]^{3}}$ (values of $\frac{a}{R}$, *b* are given in appendix [A-16]).

Equation [8]
$$\varepsilon \frac{\partial x_A}{\partial t} = \overline{V_e} x_A R_I + \overline{V_e} x_A \frac{\nabla . i_2}{F} - v^* \nabla x_A + D \nabla . (\varepsilon^{1+\tau} \nabla x_A) - \frac{(\overline{V_A} - \overline{V_B})}{\overline{V_e}} D \varepsilon^{1+\tau} (\nabla x_A)^2$$

Note that there is a missing minus sign in the original paper equation [8] (see the following demonstration).

In ref (17), a general material balance [22-B] is established as:

$$(c_A + c_B)\left(\varepsilon\frac{\partial x_A}{\partial t} + \upsilon^*\nabla x_A\right) = \frac{c_T}{c_A + c_B}\nabla \cdot \left(\frac{\varepsilon(c_A + c_B)}{c_T}D\nabla x_A\right) + R_{AB} + \frac{i_2}{z_3F}\left(\frac{x_B}{\upsilon_3^A}\nabla t_1^* - \frac{x_A}{\upsilon_3^B}\nabla t_2^*\right)$$

Note again that there are missing * signs in the original paper expression [22-B].

Replacing $\frac{1}{c_A+c_B}$ by $\overline{V_e}$, c_T by $\frac{2}{\overline{V_e}}$ and ∇t_1^* and ∇t_2^* by their expressions this equation can be rewritten as:

$$\varepsilon \frac{\partial x_A}{\partial t} + v^* \nabla x_A = \overline{V_e} \times \nabla \cdot \left(\frac{\varepsilon}{\overline{V_e}} D \nabla x_A\right) + \overline{V_e} R_{AB} + \frac{\overline{V_e} i_2}{F} \left(\frac{x_B}{2} \nabla x_A + \frac{x_A}{2} \nabla x_A\right)$$

The diffusion coefficient is only a function of the temperature and $x_B = 1 - x_A$, so:

$$\varepsilon \frac{\partial x_A}{\partial t} + v^* \nabla x_A = \frac{\overline{V_e} D}{\overline{V_e}} \nabla . (\varepsilon \nabla x_A) + \overline{V_e} D \varepsilon \nabla x_A \times \nabla . \left(\frac{1}{\overline{V_e}}\right) + \overline{V_e} R_{AB} + \frac{\overline{V_e} i_2}{2F} \nabla x_A$$

 $\overline{V_e} = x_A \overline{V_A} + x_B \overline{V_B}$ (equation [9]) so, assuming that $\nabla \overline{V_k} = 0$ (which is true if $\rho_{melt} = f(x_A)$ is constant as $\overline{V_k} = \frac{M_k}{\rho_{melt}}$, note that in real cells x_A is constant = $x_{A,sat}$), we can deduce that $\nabla \overline{V_e} = (\overline{V_A} - \overline{V_B})\nabla x_A$ and as $\nabla \cdot \left(\frac{1}{\overline{V_e}}\right) = \frac{-\nabla \overline{V_e}}{\overline{V_e}^2}$, equation [22-B] is now:

$$\varepsilon \frac{\partial x_A}{\partial t} + v^* \nabla x_A = D \nabla \cdot (\varepsilon \nabla x_A) - D \varepsilon \frac{(\overline{V_A} - \overline{V_B})}{\overline{V_e}} \nabla x_A^2 + \overline{V_e} R_{AB} + \frac{\overline{V_e} i_2}{2F} \nabla x_A$$

Now we will use expression [26], [27] and [28] of Pollard & Newman to develop R_{AB}:

$$R_{AB} = x_B \times a \left(0 - \frac{t_1^*}{-1} \times (0 - 1j_{2n} + 0) - x_A \times a \left(j_{2n} - \frac{t_2^*}{-1} \times (0 - 1j_{2n} + 0) \right) \right)$$
$$R_{AB} = (1 - x_A) \left(-\frac{x_A}{2} a j_{2n} \right) - x_A a j_{2n} + x_A a j_{2n} \left(\frac{1 - x_A}{2} \right)$$
$$R_{AB} = a j_{2n} \left(-\frac{x_A}{2} + \frac{x_A^2}{2} - x_A + \frac{x_A}{2} - \frac{x_A^2}{2} \right) = -x_A a j_{2n} = \frac{x_A}{F} \cdot \nabla i_2 + x_A R_I$$

And $\overline{V}_e R_{AB} = \overline{V}_e \frac{x_A}{F} \cdot \nabla i_2 + \overline{V}_e x_A R_I$.

This results leads to the final expression where Bruggeman expression is used:

$$\varepsilon \frac{\partial x_A}{\partial t} = \overline{V_e} x_A R_I + \overline{V_e} x_A \frac{\nabla \cdot i_2}{F} - v^* \nabla x_A + D \nabla \cdot (\varepsilon^{1+\tau} \nabla x_A) - \frac{(\overline{V_A} - \overline{V_B})}{\overline{V_e}} D \varepsilon^{1+\tau} \nabla x_A^2 + \frac{\overline{V_e} i_2}{2F} \nabla x_A$$

The last term of the expression is not accounted in Sudoh & Newman paper.

Equation [10]:

$$\nabla \cdot v^* = -\nabla \cdot i_2 \left(\frac{\bar{V}_{Fe} - \bar{V}_{FeCl2} + 2\bar{V}_B}{2F} \right) + \left(\bar{V}_p - \bar{V}_B \right) R_I + (\bar{V}_A - \bar{V}_B) \nabla \cdot \left[\epsilon D \left(c_A + c_B \right) \nabla x_A \right]$$
$$+ \frac{\bar{V}_A}{F} \nabla \cdot \left(t_1^* i_2 \right) + \frac{\bar{V}_B}{F} \nabla \cdot \left(t_2^* i_2 \right)$$

In ref (17), a continuity equation [25-B] is established as:

$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot v^* = \bar{V}_A S_A^* + \bar{V}_B S_B^* + \frac{i_2}{z_3 F} \left(\frac{\bar{V}_A}{v_3^A} \nabla \cdot t_1^* + \frac{\bar{V}_B}{v_3^B} \nabla \cdot t_2^* \right) + (\bar{V}_A v^B - \bar{V}_B v^A) \nabla \cdot \left(\frac{\varepsilon (c_A + c_B)^2}{c_T} D \nabla x_A \right)$$

Note again that there are missing * signs in the original paper expression

Let's develop each term from left to right:

• According to [6],
$$\frac{\partial \varepsilon}{\partial t} = \left(\frac{\overline{V}_{Fe} - \overline{V}_{FeC}}{2F}\right) \nabla i_2 - \overline{V}_p R_p$$

• $\bar{V}_A S_A^* + \bar{V}_B S_B^* = \bar{V}_A a \times (-t_1^* j_{2n}) + \bar{V}_B a \times (j_{2n} - t_2^* j_{2n}) = a j_{2n} \left(-\bar{V}_A \frac{x_A}{2} + \bar{V}_B - \bar{V}_B \frac{x_B}{2} \right)$ As $\bar{V}_e = x_A \bar{V}_A + x_B \bar{V}_B$ (equation [9]) $\bar{V}_A S_A^* + \bar{V}_B S_B^* = a j_{2n} \left(\bar{V}_B - \frac{\bar{V}_e}{2} \right)$ So : $\bar{V}_A S_A^* + \bar{V}_B S_B^* = -\frac{\bar{V}_B \bar{V} i_2}{F} - \bar{V}_B R_I + \frac{\bar{V}_e \bar{V} i_2}{2F} + \frac{\bar{V}_e}{2} R_I$ • $\frac{i_2}{z_3 F} \left(\frac{\bar{V}_A}{v_3^A} \nabla . t_1^* + \frac{\bar{V}_B}{v_3^B} \nabla . t_2^* \right) = \frac{i_2}{F} \left(\bar{V}_A \nabla . t_1^* + \bar{V}_B \nabla . t_2^* \right) = \frac{\bar{V}_A}{F} \nabla (i_2 t_1^*) - \frac{\bar{V}_A}{F} t_1^* \nabla i_2 + \frac{\bar{V}_B}{F} \nabla (i_2 t_2^*) - \frac{\bar{V}_B}{F} t_2^* \nabla i_2$

$$= \frac{\bar{V}_A}{F} \nabla(i_2 t_1^*) + \frac{\bar{V}_B}{F} \nabla(i_2 t_2^*) - \frac{\nabla i_2}{F} \overline{(V_A} t_1^* + \bar{V}_B t_2^*) = \frac{\bar{V}_A}{F} \nabla(i_2 t_1^*) + \frac{\bar{V}_B}{F} \nabla(i_2 t_2^*) - \frac{\bar{V}_e \nabla i_2}{2F}$$

$$\bullet \quad (\bar{V}_A \nu^B - \bar{V}_B \nu^A) \nabla . \left(\frac{\varepsilon (c_A + c_B)^2}{c_T} D \nabla x_A\right) = 2(\bar{V}_A - \bar{V}_B) \nabla . \left(\frac{\varepsilon (c_A + c_B)^2}{2(c_A + c_B)} D \nabla x_A\right)$$

$$= (\bar{V}_A - \bar{V}_B) \nabla . \left(\varepsilon (c_A + c_B) D \nabla x_A\right)$$

Now, finally adding again all these terms we found that:

$$\begin{aligned} \nabla . \, v^* &= -\nabla . \, i_2 \left(\frac{\bar{V}_{Fe} - \bar{V}_{FeCl2} + 2\bar{V}_B}{2F} \right) + \left(\bar{V}_p - \bar{V}_B \right) R_I + (\bar{V}_A - \bar{V}_B) \nabla . \left[\epsilon D \left(c_A + c_B \right) \nabla x_A \right] \\ &+ \frac{\bar{V}_A}{F} \nabla . \left(t_1^* i_2 \right) + \frac{\bar{V}_B}{F} \nabla . \left(t_2^* i_2 \right) + \frac{\bar{V}_e}{2} R_I \end{aligned}$$

Again, the last term of the expression is not accounted in Sudoh & Newman paper.

Appendix B: list of symbols

var: value varies during the calculation

Symbols	Definition	Model value
a _{m,i}	Interfacial metal area of electroactive species i (m ² .m ⁻³)	NA
a _{s,i}	Interfacial salt area of electroactive species i (m ² .m ⁻³)	NA
<i>a</i> Ni,0	Initial value of $a_{\text{Ni.}}$ (m ² .m ⁻³)	648,831
<i>a</i> _{Fe,max}	Maximim value of $a_{\text{Fe.}}$ (m ² .m ⁻³)	310,651
<i>a</i> NiCl2,0	Initial value of a_{NiCl2} (m ² .m ⁻³)	5.55×10^{5}
<i>a</i> FeCl2,0	Initial value of a_{FeCl2} (m ² .m ⁻³)	1.39×10^{5}
CA	Concentration of NaAlCl ₄ binary molten salt (mol.cm ⁻³)	var
CB	Concentration of NaCl binary molten salt (mol.cm ⁻³)	var
Cr,e	Concentration of metal complex r at equilibrium (mol.cm ⁻³)	var
Cr,b	Concentration of metal complex r in the bulk (mol.cm ⁻³)	NA
Cr,ref	Reference concentration of metal complex r (mol.cm ⁻³)	var
EA	Activation energy used in the Arrhenius factor (J.mol ⁻¹)	23386
F	Faraday's constant (C.mol ⁻¹)	96485
h	Heat transfer coefficient (W.m ⁻² .K ⁻¹)	1.5
Iexp	Experimental discharge current rate (A)	var
İ0,ref,Ni	NiCl ₂ /Ni reference exchange current density (A.cm ⁻²)	3×10^{-5}
i0,ref,Fe	FeCl ₂ /Ni reference exchange current density (A.cm ⁻²)	7×10^{-5}
i 0,i	Exchange current density for electroactive species i (A.cm ⁻²)	NA
i 1	Current density in the solid matrix phase (A.cm ⁻²)	NA
i 2	Current density in the electrolyte phase (A.cm ⁻²)	NA
j i	Local transfer current relative to electroactive species i (A.cm ⁻³)	NA
j	Local transfer current in the positive compartment (A.cm ⁻³)	NA
K _{melt}	Mole fraction equilibrium constant of $2AlCl_4 = Al_2Cl_7 + Cl_2$	2.37×10^{-6}
Ksp,FeCl	Mole fraction equilibrium constant of $FeCl_{2(s)} + 2Al_2Cl_7 = Fe(AlCl_4)_4^2$	var
<i>k</i> lat	Cell lateral thermal conductivity (W.m ⁻¹ .K ⁻¹)	2

156 | P a g e

<i>k</i> _p	Rate constant of precipitation/dissolution of NaCl (cm ³ .mol ⁻¹ .s ⁻¹)	var
M(A)	Molecular weight of A (g.mol ⁻¹)	191.78
M(B)	Molecular weight of B (g.mol ⁻¹)	58.44
n	Number of electrons exchanged for 1 mol of electroactive species involved (mol)	2 (pos), 1 (neg)
Qrev,M	Reversible heat source term (W.m ⁻³)	NA
Qirrev	Irreversible heat source in the cell (W.m ⁻³)	NA
R	Gas constant (J.mol ⁻¹ .K ⁻¹)	8.314
R _{BASE}	Overall resistance of the BASE (Ω)	NA
Rp	Overall polarization resistance of the cell (Ω)	NA
Scol	Positive collector surface (cm ²)	48
Т	Absolute operating temperature (°C)	var
Tref	Reference operational temperature (°C)	350
Tamb	Temperature in the furnace at 100 % of DOD (K)	var
Uexp	Experimental cell voltage (V)	NA
Ucell	Simulated cell voltage (V)	NA
$\overline{V}_{\rm Ni}$	Molar volume of Ni (cm ³ .mol ⁻¹)	6.6
V _{Fe}	Molar volume of Fe (cm ³ .mol ⁻¹)	7.1
$\overline{V}_{\rm NiCl2}$	Molar volume of metal chloride NiCl ₂ (cm ³ .mol ⁻¹)	36.9
$\overline{V}_{\text{FeCl2}}$	Molar volume of metal chloride FeCl ₂ (cm ³ .mol ⁻¹)	40.1
<i>V</i> _P	Molar volume of precipitated NaCl (cm ³ .mol ⁻¹)	27
XA	Mole fraction of NaAlCl4 binary molten salt	var
x _B	Mole fraction of NaCl binary molten salt	1- <i>x</i> A

Greek	Definition	Model value
α_a/α_c	Transfer coefficients	1.2/0.8
β	Symmetry factor	0.5
E	Total porosity of domain 4	var
€ _{m,i}	Metal volume fraction of species <i>i</i> in domain 4	var
Es,i	Salt volume fraction of species <i>i</i> in domain 4	var
€С	Carbon felt porosity (domain 5)	0.05
€,max	Maximum value of $\epsilon_{}$	See table 4
€,min	Minimum value of $\epsilon_{}$	See table 4
E.,,pass	Value of $\epsilon_{}$ corresponding to total passivation	NA
E,0	Initial value of $\epsilon_{}$ (sometimes it is also the maximum value)	See table 4
η_i	Overpotential relative to eletroactive species i (V)	NA
pcell	Commercial cell density (kg.m ⁻³)	2413.5
τ	Tortuosity factor	0.5
$\sigma_{ m i}$	Electronic conductivity of domain i (S.cm ⁻¹)	NA
Φ ₁	Potential in solid matrix phase (V)	NA
$\mathbf{\Phi}_2$	Potential in electrolyte phase (V)	NA

Appendix C: analytical expressions

Symbol	Definition	Model value
C _{p,cell}	Specific heat capacity (J.kg ⁻¹ .K ⁻¹)	$2.027 I_{\rm exp} t + 0.64T + 127.15$
D	Diffusion coefficient of secondary electrolyte (cm ² .s ⁻¹)	$4.3 \times 10^{-6} \exp\left[\frac{3.035 \times 10^3}{R} \left(\frac{1}{448.15} - \frac{1}{T}\right)\right]$
k _{m,i}	Mass transfer coefficient of metal complex i from the bulk to metal surface (cm.s ⁻¹)	$rac{D(T)}{\delta_{m,i}}$
k _{s,i}	Mass transfer coefficient of metal complex <i>i</i> from metal chloride surface to the bulk (cm.s^{-1})	$\frac{D(T)}{\delta_{s,i}}$
Ksp	Solubility product of NaCl _(s) (mol ² .cm ⁻⁶)	$10^{\left(3.77 - \frac{2.69 \times 10^3}{T} + \frac{0.4129 \times 10^6}{T^2}\right)}$
mв	Apparent mole fraction of B	$0.5436 - 1.972 \times 10^{-4}T + 2.346 \times 10^{-7}T^2$
OCV _{Ni}	Open-circuit Ni cell voltage (V)	$2.705 - 2.16 \times 10^{-4}T$
OCV _{Fe}	Open-circuit Fe cell voltage (V)	$2.524 - 2.16 \times 10^{-4}T$
Qrev,NaCl	Reversible heat source term associated to NaCl phase change (J.mol ⁻¹)	11850 – 63.26 <i>T</i>
RI	Reaction rate for the precipitation of NaCl (mol.cm ⁻³ .s ⁻¹)	$k_p\left(\frac{1-x_A}{\overline{V}_e^2}\right) - K_{sp}(T)$
v *	Molar average velocity (cm.s ⁻¹)	See appendix A
\overline{V}_{e}	Molar volume of secondary electrolyte (cm ³ .mol ⁻¹)	See appendix A
$\overline{V}_{\mathrm{A}}$	Molar volume of NaAlCl ₄ binary molten salt (cm ³ .mol ⁻¹)	$\frac{M(A)}{\rho_{melt}}$
$\overline{V}_{\mathrm{B}}$	Molar volume of NaCl binary molten salt (cm ³ .mol ⁻¹)	$\frac{M(B)}{\rho_{melt}}$
X _{A,sat}	Mole fraction of saturated NaAlCl ₄ binary molten salt	$\frac{1-m_{\rm B}(T)}{m_{\rm B}(T)}$
ρ _{melt}	Melt density	$2.37 - 2.147m_B(T) + 3.197m_B(T)^2 - (2.325 - 7.635m_B(T)) + 9.567m_B(T)^2) \times 10^{-3}$
γA	Activity coefficient of A	See appendix A
$\sigma_{ m Ni}$	Electronic conductivity of Ni (S.cm ⁻¹)	$(27.62 - 6.506 \times 10^{-2}T + 4.268 \times 10^{-5}T^{2}) \times 10^{-4}$
$\sigma_{ m Fe}$	Electronic conductivity of Fe (S.cm ⁻¹)	$(18.16 - 3.961 \times 10^{-2}T + 2.396 \times 10^{-5}T^{2}) \times 10^{-4}$
$\sigma_{\rm Na}$	Electronic conductivity of Na (S.cm ⁻¹)	$\frac{(23.93 - 4.593 \times 10^{-2}T + 2.562 \times 10^{-5}T^2)}{\times 10^{-4}}$
$\sigma_{ m e}$	Electronic conductivity of metal backbone	$\sigma_{\rm e} = \sigma_{\rm Ni}(T)\epsilon_{\rm Ni}^{1+\tau} + \sigma_{\rm Fe}(T)\epsilon_{\rm Fe}^{1+\tau}$

160 | P a g e

Appendix C

	(S.cm ⁻¹)	
$\sigma_{ m felt}$	Electronic conductivity of carbon felt (S.cm ⁻¹)	$\sigma_{\rm felt} = \sigma_{\rm C}(T)\epsilon_{\rm C}^{1+\tau}$
κ	Ionic conductivity of electrolyte (S.cm ⁻¹)	$\epsilon^{1+\tau} [0.145 - 1.827m_{\rm B}(T) \\ + (-0.5715 + 6.358m_{\rm B}(T))] \\ \times 10^{-3}T$
Ke	Ionic conductivity in the matrix porosity (S.cm ⁻¹)	$\kappa_e = \kappa \epsilon^{1+\tau}$
κc	Ionic conductivity in the felt porosity (S.cm ⁻¹)	$\kappa_{\rm C} = \kappa(T)(1-\epsilon_{\rm C})^{1+\tau}$
Ksep	Ionic conductivity in the BASE (S.cm ⁻¹)	$0.44 - 2.325 \times 10^{-3}T + 3.295 \times 10^{-6}T^2$

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