Metal carbodiimides and cyanamides, a new family of electrode materials for Li-ion batteries
Jeethu Jiju Arayamparambil

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Metal carbodiimides and cyanamides, a new family of electrode materials for Li-ion batteries

Présentée par Jeethu Jiju Arayamparambil
Le 29 Novembre 2019

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Chapter 1: General introduction
As we all know, energy can be neither created nor destroyed, it is a quantitative property that is transformed from one form to another in order to perform the work. The modern society is very much dependent on energy and today the world is at a turning point: over the past two centuries, energy demands have increased dramatically, especially in the field of transportation and industry. The major source of energy actually comes from fossil fuels, and the dominant fossil fuels used today by most industrialized and developing countries are oil, coal, and natural gas etc. The enormous use of these energy sources leads - among other things - to the increase of greenhouse gas emissions such as carbon dioxide (CO₂), resulting in global warming and harming of environment and biodiversity.

In the global atmosphere, carbon dioxide ratios for the most part of human history, until industrial revolution and the arrival of the steam age and of the internal combustion engine, oscillated at around 280 parts per million (ppm). In the past decade, the ratio touched 400 ppm, and in 2018 peaked at 414.7 ppm in May, before beginning to fall in the northern hemisphere growing season, to rise again in September. Overall, the average for 2018 was 411 ppm, with an uncertainty factor of 0.6 ppm. Figure 1.1 shows the latest recorded atmospheric CO₂ evolution curve. In May 2019, for the first time in the history more than 415 ppm CO₂ concentration has recorded. Therefore, today energy needs are strongly linked to the environmental crisis. Here comes the importance of clean and sustainable alternative renewable energy solutions such as solar energy, hydropower, wind energy, geothermal energy, biomass energy, etc. However, these technologies have a random and variable energy output, which makes them difficult to manage. It is clear that the advancement of energy storage technologies is required for the effective utilization of renewable energy sources in future smart grids and power management systems.

In 1799 Alessandro Volta presented the first energy storage device known as Volta pile, since then many other storage devices have been gradually developed such as the Daniell cell (1836), the Leclanché cell (1886), lead acid battery, more recently nickel metal hydride batteries, etc. The Li-ion battery (LIB) was first proposed in 1976 by the recent Nobel prize winner Whittingham and in 1991 was commercialized by Sony.
The Ragone plot depicted in Figure 1.2 shows power and energy densities of different electrochemical energy storage technologies. From this figure, it is well clear that the LIB technology dominates in energy densities; such devices possess almost doubled energy density compared to the Nickel-metal hydride technology. Apart from the energy density, LIBs also hold long cycle life and very low self-discharging rates. These characteristics made them a better choice in the portable electronic devices market and we can observe a huge ramp up in their production in the last few years. Today, portable devices contribute around 63% of the world sales and by 2020 global market value can raise up to $213.5 billion. The electric vehicle and smart grid network industries are also pushing hard core researches to improve the performance of LIBs in order to meet their requirements. According to the reports, the energy density of LIBs has increased approximately 3-5% in every year since the past several decades and the current value is still below 200 Wh.kg\(^{-1}\), whereas the target is of 500 - 700 Wh.kg\(^{-1}\). The electrochemical performance of rechargeable LIBs strongly depends on the electrode material’s (anode and cathode) characteristics. These electrode materials play vital role in the electrochemical reaction within the cell, governing the efficiency and durability of the energy storage devices. The current existing lithium ion technology is based on the intercalation chemistry of both anode and cathode materials.
Figure 1.2. Ragone plot of different energy storage technologies.

Commercially used intercalation cathode materials such as layered LiCoO$_2$ (LCO), LiNi$_x$Mn$_y$Co$_z$O$_2$ (NMC), LiNi$_x$Co$_y$Al$_z$O$_2$ (NCA), spinel LiMn$_2$O$_4$ (LMO), and olivine LiFePO$_4$ (LFP), exhibit capacities of up to about 160-250 mAh.g$^{-1}$ whereas for anode materials, graphite (theoretical capacity 372 mAh.g$^{-1}$) is the leading choice. The relatively low specific capacity of intercalation materials limits the increase in the energy density of LIBs. Therefore it is very important to develop high density electrode materials for the future high energy batteries.

Many efforts have been produced in the past decades to develop safer and higher specific capacity anode materials, and numerous candidates from the p-block of the periodic table have been explored such as silicon, tin, antimony, phosphorus as well as their oxides, sulphides, carbonates, etc. Conversion-type anode materials have also been investigated: among them, transition-metal based compounds were found to be very promising as potential alternatives for graphite owing to their high specific capacity. The electrochemical activity of transition metal carbodiimide materials (MNCN, with $M =$ Fe, Mn, Co, Cu, Zn, Ni) was recently reported by different groups for both LIBs and NIBs. The application of transition metal carbodiimides in the field of batteries is still in its starting stage, the detailed understanding of reaction mechanisms of these compounds has not been completely unveiled yet. Moreover, in addition to transition metal carbodiimides, there are possibilities for exploration of other metal cyanamides and carbodiimides as negative electrodes where one can expect combination of different lithiation mechanisms. Therefore,
the main goal of this work is a detailed investigation of electrochemical performance and lithiation mechanisms of inorganic metal cyanamides and carbodiimides as anode materials in LIBs.

The first chapter of this thesis describes the general principle of LIBs followed by a short introduction to carbodiimide and cyanamide materials and their energy applications. The following three chapters describe the main results and discussions of this work. These three chapters, corresponding to three published or submitted papers, describe three different lithiation mechanisms that were identified for metal cyanamides and carbodiimides, namely pure conversion (chapter 2), conversion and alloying reaction (chapter 3) and intercalation plus conversion reaction (chapter 4). The final section of the thesis is devoted to the general conclusion and potential perspectives for inorganic carbodiimide and cyanamide based materials in the field of energy applications.
1.1. General aspects of lithium ion batteries

LIBs have some of the most useful properties among battery technologies. They mainly deliver high specific and gravimetric capacities as well as high voltage and hence high energy density.\(^{38}\)

LIBs consist of a positive electrode (commonly named cathode, since it is the site of the reduction during the discharge) and a negative electrode (also called anode, the site of the oxidation during the discharge) kept apart from each other by a separator soaked with an electrolyte containing a lithium salt.\(^{39}\) The electrolyte allows the transport of Li cations between the two electrodes without electron transports. The separator is needed to hamper any direct contact between negative and positive electrodes, which would lead to a short circuit (direct spontaneous reaction). The basic working principle is shown in Figure 1.3: during the discharge oxidation and reduction reactions spontaneously occur at the anode and the cathode, respectively, inducing a migration of the Li cations through the electrolyte, ensuring the electroneutrality of the two electrodes and compensating the electron flow from cathode to anode via the external circuit. During charge, the reverse reactions are forced with the help of an external charging device, and Li ions move back from the cathode to the anode.

*Figure 1.3. Schematic illustration of the charging process of a LIB.*
In an ideal LIB, these processes should be repeated for an unlimited number of cycles. In practice, some unwanted side-reactions are taking place in parallel with the charge-discharge reactions and cause electrode material as well as electrolyte degradation. Eventually, all these degradations influence the battery performance and even lead to the permanent failure of the cell. Therefore, it is very important to develop cost-effective batteries with prolonged cycle life mainly for large-scale applications such as electric vehicles, portable devices, smart grids, etc.

1.2. Electrode materials

1.2.1. Positive electrode

Positive electrode materials need to operate at high potential and should have fast lithium ions diffusion in order to obtain the fast and safer charging/discharging rates. Composition and atomic structure, which govern many crucial properties such as conductivity and voltage, are essential in the selection of cathode materials. Commonly, layered structure materials are used in LIBs since they allow the two-dimensional lithium ion diffusion in an easy way. Typical commercial layered oxides materials are LCO (lithium cobalt oxide, LiCoO$_2$) and NMC (lithium nickel manganese cobalt oxide). LCO is very attractive in terms of its high theoretical capacity (274 mAh.g$^{-1}$, even though not totally usable), low self-discharge, and good cycling performance. However, it also shows major drawbacks such as its high cost due to the presence of expensive (and lowly abundant) cobalt, low thermal stability and huge capacity fading at high current density. Many other metals (Mn, Al, Fe, Ni, Cr) have been tried as dopants or in partial substitution for cobalt, and some of them have shown promising performance. The substitution of cobalt by nickel was particularly investigated since the resulting material holds the same theoretical capacity of LCO at a lowered cost. However, pure lithium nickel oxide (LNO) was not promising due to its low thermal stability and to the tendency of Ni$^{2+}$ cations to replace Li$^+$ in the Li layers during the synthesis, hence blocking the Li$^+$ diffusion pathway. Partial substitution of nickel with cobalt was one of the effective ways to reduce this cationic disorder. The thermal stability was improved by doping with metals such as Mg, Al, etc. For example, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) was reported and commercially used in batteries such as Panasonic batteries for Tesla electric vehicles.

Lithium manganese oxide (LMO) with a layered structure was also found to be a promising cathode material, considering that manganese is less expensive and less toxic than
cobalt and nickel, and the layered LMO structure has been known for long time.\textsuperscript{47} The performance of LMO was not satisfactory mainly due to (i) the tendency of layered structure to change into spinel structure during Li extraction,\textsuperscript{48} and (ii) Mn leaching during cycling.\textsuperscript{49} Later on, Li(Ni_{0.5}Mn_{0.5})O_2 (NMO) cathode was developed due to its good performance, reduced cost, etc. Cobalt was added to NMO to improve the structural stability leading to LiNi_{x}Co_{y}Mn_{z}O_2 (NMC) cathode materials.\textsuperscript{50} Some studies have reported a high reversible specific capacity of 235 mAh.g\textsuperscript{-1} for microporous NMC.\textsuperscript{51,52}

Another large family of cathode materials is based on large (XO\textsubscript{4})\textsuperscript{3-} anions (X= S, P, Si, As, Mo, W etc.).\textsuperscript{9} Lithium iron phosphate (LiFePO\textsubscript{4}, LFP) with olivine structure is the most representative compound of this group. LFP has excellent thermal stability and high cyclability with few drawbacks such as low ionic conductivity and low average potential. Many efforts such as particle size reduction, carbon coating, cationic doping, etc. were found to be very effective in tackling these drawbacks and hence improving its performance.\textsuperscript{53} Other phosphate with olivine structure including LiMnPO\textsubscript{4} (LMP), LiCoPO\textsubscript{4} (LCP), LiNi_{0.5}Co_{0.5}PO\textsubscript{4} (NCP), Li_{3}V_{2}(PO\textsubscript{4})_{3} (LVP) were also reported, but still require improvements in terms of power, energy density and stability.\textsuperscript{54–57}

\textbf{Figure 1.4. Specific capacities and discharge potentials of commercial LIB positive electrode materials.}\textsuperscript{58}

Conversion-type cathodes (see below for conversion reactions) based on metal fluorides have also emerged as an alternative class of cathode materials due to their high theoretical capacity and intermediate operating potential. However, they suffer from volume
expansion, poor electronic conductivity and polarization. To overcome such limitations, researchers have tried out without frank success electrolyte modifications and incorporation of the active materials in carbon matrices, for example FeF$_3$/CNT, FeF$_3$/graphene, AgCl/acetylene black, etc.\textsuperscript{60-62}

Specific capacities and operating potentials of commercially used positive electrode materials are summarised in Figure 1.4.

1.2.2. Negative electrode

Negative electrode materials have to operate at low electrochemical potential in order to produce a large voltage difference between negative and positive electrodes. Until the 80s, Li metal and its alloys were used as anode materials,\textsuperscript{63} but due to serious safety concerns such as dendrites formation and overheating, carbon graphite was proposed and is currently used as the most common commercial negative electrode material. Besides graphite, many other anode materials have also been investigated. In general, anode materials for LIBs are classified in three groups with respect to their energy storage mechanisms: intercalation, conversion, and alloying.

1.2.2.1. Intercalation materials

In intercalation-type materials, Li$^+$ ions electrochemically intercalate in the interlayer space available in the material. Graphite is the best example of intercalation anode materials. It is a typical layered compound made of hexagonal sheets of graphene with sp$^2$-hybridised carbon atoms as shown in Figure 1.5. The lithium intercalation reaction in graphite can be written as:

$$\text{C}_6 \text{(in graphite)} + x \text{Li}^+ + x \text{e}^- \leftrightarrow \text{Li}_x\text{C}_6 \quad (x < 1)$$

The reversible discharge/charge reaction in graphite proceeds below 0.25 V vs. Li/Li$^+$, and the practical reversible capacity can reach more than 360 mAh.g$^{-1}$ (the theoretical capacity is 372 mAh.g$^{-1}$ or 975 mAh.cm$^{-3}$) with a coulombic efficiency close to 100%.\textsuperscript{32,64} However, during the first discharge some extra capacity is usually observed (around 390 mAh.g$^{-1}$), caused by irreversible side reactions including the electrolyte decomposition and formation of a solid electrolyte interphase (SEI).\textsuperscript{65} The main limitations of graphite anode are its relatively low specific capacity and some safety concerns for cycling at high rates.
Substantive efforts were thus produced to find a better alternative for graphite in order to bring higher capacity and safer operation.

Other intercalation materials are based on lithium transition metal oxides. Titanium is one of the abundant material in earth crust and environmentally friendly. The most commonly used lithium metal oxide is Li$_4$Ti$_5$O$_{12}$ (LTO) which is investigated as a promising substitute for graphite in spite of its low theoretical capacity (175 mAh.g$^{-1}$). It is attractive for merits such as zero-strain during cycling, excellent cycling stability, wide working potential plateau around 1.55 V etc.\textsuperscript{66,67} However, LTO suffers from poor ionic and electronic conductivities and several methods have been developed to improve its electrochemical performances.\textsuperscript{68} TiO$_2$ has also been investigated as anode material. Even though TiO$_2$ shows a relatively low but interesting theoretical capacity (335 mAh.g$^{-1}$), it exhibits excellent safety records, good cycling stability and coulombic efficiency, and high lithiation potential hindering the formation of lithium dendrites at high rates.\textsuperscript{69–71} Various types of TiO$_2$ nanoparticles, nanotubes, nanowires, TiO$_2$-carbon composites etc. have been reported with enhanced electrochemical performance.\textsuperscript{72}

![Schematic representation of graphite structure](image)

\textbf{Figure 1.5. Schematic representation of graphite structure.}\textsuperscript{73}
1.2.2.2. Allo and materials

This group of materials includes elements from the p-block of the periodic table such as silicon (Si), germanium (Ge), tin (Sn), antimony (Sb) and phosphorous (P), which form binary compounds with lithium (usually considered as alloys in spite of the large difference in electronegativity) at low potentials. The reversible reaction is shown below, where M is the anode material:

\[ \text{M} + x \text{Li}^+ + x \text{e}^- \leftrightarrow \text{Li}_x \text{M} \]

Alloying materials are most known for their high theoretical and practical capacities: 4200 mAh.g\(^{-1}\) for silicon (Li\(_4.4\)Si), 1600 mAh.g\(^{-1}\) for germanium (Li\(_4.4\)Ge), 992 mAh.g\(^{-1}\) for tin (Li\(_4.4\)Sn) and 660 mAh.g\(^{-1}\) for antimony (Li\(_3\)Sb). However, all these materials suffer from large volume variations (up to 400%) during the charge and discharge. During cycling, they thus undergo a serious pulverization which results in partial isolation of the active material from electric contact with the current collector and conductive carbon additives. Moreover, alloying materials show a significantly low coulombic efficiency during the first lithiation generally attributed to the formation of SEI. Among all alloying materials, the major attention has been given to the development of silicon anode material mainly because of its low cost and extremely high capacity compared to the other elements.

1.2.2.3. Conversion materials

Materials undergoing the conversion reaction generally (but not always) contain both redox active and inactive elements. Their electrochemical reaction with lithium can be described as:

\[ \text{M}_a \text{X}_b + (b.n) \text{Li}^+ + a \text{e}^- \leftrightarrow a \text{M} + b \text{Li}_n \text{X} \]

where for example M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, and Zn, and X = Sn, Sb, P, O, N, F, S, P, CO\(_3\), PO\(_4\) and NCN and n = formal number of negative charge of X. Several transition metal based compounds have been investigated as possible alternatives for graphite in LIBs owing to their high specific capacity. In spite of such high theoretical specific capacities, high irreversible capacity in the first lithiation and the weak cycling life prevent the practical use of these materials. The main reasons of such limitations rely, inter alia, on the SEI formation as
well as the high volume expansion inherent to conversion materials\textsuperscript{65} exactly like for alloying materials.

Different strategies have been brought forward in order to alleviate the large volume change in conversion-type anode materials. One is to make large surface area structures like mesoporous materials where the pores can provide enough space and flexibility for structural expansion/contraction during the of Li ions reaction\textsuperscript{79–81} Another strategy is to mix carbonaceous materials with conversion reaction materials, the carbonaceous materials can contribute to the capacity and at the same time act as a buffer space to accommodate the structural expansion/contraction\textsuperscript{82} A summary of different types of anode materials and their specific capacity and average discharge potential is shown in Figure 1.6.

![Figure 1.6. Average operating potentials and specific capacities of commonly used anode materials.](image)

**1.2.3. Electrolyte**

The main purpose of an electrolyte is the transport of lithium cations between the electrodes during cycling, but it should also show no electronic conductivity to prevent short circuits. Ideally, the electrolyte should be chemically and electrochemically stable and inert towards all cell components. There are different types of electrolytes used for LIBs, such as liquid electrolytes, polymer electrolytes, ionic liquids, ceramic electrolytes, etc. Among them, liquid electrolytes are the most commonly used because of their high ionic conductivity and lithium solubility. Generally, a liquid electrolyte consists of a lithium salt dissolved in an
organic solvent, where the concentration of the salt is crucial. If the salt concentration is too low, it reduces the conductivity, and if it is too high, it increases the viscosity then reducing the ionic mobility.\textsuperscript{58} Besides the concentration of the salt, the choice of the appropriate solvent is also important since the viscosity of the electrolyte is also influenced by the solvent molecules.\textsuperscript{83–85}

The commonly used salt is LiPF\textsubscript{6} since it dissolves very easily in the solvents and provides decent ionic conductivity. Other salts like LiTFSI, LiBOB, LiClO\textsubscript{4} are also reported, but have many drawbacks like formation of passivation layer on Al current collector, thus limiting their practical use.\textsuperscript{58} The commonly used families of solvents are ethers, esters, and alkyl carbonates. Alkyl carbonate solvents, such as diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC) are the most suitable candidates due to their higher anodic stability. In commercial applications, many additives are also included in the electrolyte. The main targets of these additives are formation of stable SEI layer, reduction of the flammability and prevention of the overcharge.

To summarize, ideally a non-aqueous electrolyte should possess the following properties for the practical use in batteries.\textsuperscript{86}

- High ionic conductivity ($3 \times 10^{-3}$ to $2 \times 10^{-2}$ S/cm) over a wide range of temperature
- Wide stability voltage window.
- Large usable liquid range, typically -40 to 70°C
- Low vapour pressure and low activation energy
- Good ions solvating properties
- Good chemical and thermal stability
- Low toxicity, biodegradable, and cost effective

1.2.4. Separator

Separator is used to prevent the direct physical contact between negative and positive electrodes without hindering the migration of the electrolyte salt in the electrolyte between them. Typically, it is a thin porous film, which consists of, e.g., porous polypropylene with good wettability. The wettability of separators, which can be increased by surface
modifications, is very important because if the pores in the separator remains dry, they will not allow lithium ion transport and will increase the cell resistance.\(^{87}\)

### 1.2.5. Solid electrolyte interphase (SEI)

The SEI is a very complex passivation layer formed on electrode surfaces during the initial cycles by the electrolyte decomposition in contact with the other cell components. The SEI layer is a very critical factor in batteries since it influences battery performance. A good SEI should allow the Li ions transport and act as a barrier between electrode and electrolyte molecules to prevent their further decomposition in contact with the electrode materials at both low and high potentials. However, excessive SEI formation causes lithium trapping, increases ionic and cationic resistivities and reduces the active material surface area especially on the anode side which results in decreasing the reversible capacity and thus battery performance. For this reason, the challenging understanding of SEI formation has a crucial role in the designing of LIBs.\(^{88}\) The performance of a lithium battery is very much related to the SEI properties, the major criteria to be noticed are\(^{86}\):

- SEI should have limited thickness to avoid high internal resistance, low faradic efficiency, and self-discharge.
- SEI layer must have uniform chemical composition and morphology for ensuring the homogeneous current distribution.
- SEI must be adherent to the electrode material and mechanically flexible and stable, especially for alloying and conversion materials.

### 1.3. Carbodiimides in Li-ion batteries

Metal carbodiimides and cyanamides are a unique class of inorganic compounds with the general formula\(^ \ast \) \(M_x(NCN)_y\) (with \(M = \) alkali, alkaline-earth, rare-earth, transition metal or metalloid), generally derived from the parental compound molecular cyanamide, \(H_2N-C≡N\). The \((NCN)^2^-\) anion in these compounds is isolobal with the oxide \((O^2^-)\) anion, and can be termed as nitrogen analogues of the corresponding oxides. Both anions possess similar electronegativities and the crystal structures in some cases can also be comparable for the respective analogue compounds except a small distortion seen in the carbodiimides because

\(^{\ast}\)M can stand for more than one metal such as in LiLa(NCN)\(^2\)}
of the larger size of \((\text{NCN})^2^-\) anion.\(^\text{34}\) There are two electronic forms of the \((\text{NCN})^2^-\) anion: the symmetric linear carbodiimide \((\text{N=C=N})\) and the asymmetric nonlinear cyanamide \((\text{N-C≡N})\). A well-known member of this family is calcium cyanamide \(\text{CaNCN}\), which is widely used as a fertiliser or nitrogen source for the steel industry. Calcium cyanamide has been known for more than one century, and other alkali and alkaline-earth metal cyanamides have been reported starting from late seventies.\(^\text{89,90}\) Main-group elements\(^\text{91–93}\) and transition-metal carbodiimides\(^\text{94–98}\) have been obtained much later starting from 2005, since the synthesis routes were much complex compared to that of \(\text{CaNCN}\).

Over the last decade, due to the close similarity with the corresponding oxides, many researchers have started exploring carbodiimide materials for energy applications, mainly in the fields of catalysis, batteries and supercapacitors. In 2013, \(\text{Ag}_2\text{NCN}\) was applied as an efficient photo-anode material, and later various composites of \(\text{Ag}_2\text{NCN}, \text{PbNCN},\) and \(\text{ZnNCN}\) were also reported for their outstanding photocatalytic performance.\(^\text{99–105}\) Among transition metal carbodiimides, \(\text{CoNCN}\) is known as an efficient semiconductor photo-anode. It was also shown that \(\text{CoNCN}\) and \(\text{NiNCN}\) and their solid solutions in either neutral or basic media exhibit excellent electrocatalytic properties.\(^\text{106–108}\) Very recently, Davi et al. showed that the surface functionalization of \(\text{CuWO}_4\) photo-anodes with manganese carbodiimide \(\text{MnNCN}\) can enhance the photo current by 30%.\(^\text{109}\)

Since 2014 carbodiimides have been studied as negative electrode materials for both \(\text{Li}\) and \(\text{Na}\) ion batteries. \(\text{MnNCN}\) was the very first carbodiimide investigated as anode material in \(\text{LIBs}\), even though the report published in 2014 by Milke et al. claims that \(\text{MnNCN}\) is not electrochemically active.\(^\text{110}\) However, in 2015, the electrochemical activity of several transition metal carbodiimides (including \(\text{MnNCN}\)) vs. both \(\text{LIBs}\) and \(\text{NIBs}\) was confirmed.\(^\text{111}\)

The first investigations of iron carbodiimide showed that the reaction mechanism follows a conversion reaction similar to that of its oxide counter parts.\(^\text{111}\) Although \(\text{FeNCN}\) suffers from a non-negligible initial irreversible capacity and a relatively high operating potential, it exhibits high cycle life and rate capability.\(^\text{33}\) It can maintain a stable capacity for more than 100 cycles for \(\text{LIBs}\) and 240 cycles for \(\text{NIBs}\) and support current densities as high as 30C as shown in Figure 1.7.

In 2016, Eguia-Barrio et al. also reported the electrochemical activity of several transition metal carbodiimides (\(\text{MNCN}, \text{M}=\text{Co, Ni, Fe, Zn, Cu}\)) as anode materials for \(\text{LIBs}\) and \(\text{NIBs}\).\(^\text{34}\) Even though there is an initial capacity loss, all the materials exhibit a high reversible
capacity between 200-800 mAh.g\(^{-1}\) for both NIBs and LIBs. Among them, CoNCN and NiNCN have similar behaviour for both battery systems and exhibit highest irreversible capacities compared to FeNCN, MnNCN, ZnNCN and CuNCN. The first \textit{in situ} characterization of the electrochemical mechanism of FeNCN in LIBs using XRD and \(^{57}\)Fe Mössbauer spectroscopy showed that it occurs according to the following reaction:\(^{33}\)

\[
\text{FeNCN} + 2\text{Li} \rightarrow \text{Fe} + \text{Li}_2\text{NCN}
\]

By analogy, one can speculate that all divalent transition metal carbodiimides should follow a similar general reaction:

\[
\text{MNCN} + 2\text{X} \rightarrow \text{M} + \text{X}_2\text{NCN} \quad (\text{M}= \text{Co, Ni, Fe, Mn, Zn, Cu and X}= \text{Li/Na})
\]

A more detailed study of MnNCN in LIBs by Liu \textit{et al.} in 2016\(^{112}\) confirms a conversion reaction mechanism with a discharge capacity of 725 mA.h\(^{-1}\) at 0.1 A.g\(^{-1}\), much higher than that shown in previous reports and exceeding the theoretical value of 570 mA.h\(^{-1}\),\(^{33}\) with high cycling stability and rate capability. The authors attribute the good cycling performance of MnNCN to the easy reversible phase transition permitted by small MnNCN particles with large surface area. However, the authors neither showed the galvanostatic profile of the first cycle nor explained the observed extra capacity. Interestingly, apart from LIB applications, MnNCN was also studied as anode for Li-ion hybrid capacitors. Against an activated carbon
cathode, it delivers high energy and power densities of 103 Wh.kg\(^{-1}\) and 8533 W.kg\(^{-1}\), respectively\(^{112}\), along with cycling stability up to 5000 cycles at a rate of 5 A.g\(^{-1}\)(Figure 1.8).\(^{112}\)

![Graphs showing cycling stability and rate capability for MnNCN LIBs](image)

*Figure 1.8. Cycling stability tested at 5 A.g\(^{-1}\) and rate capability test for MnNCN LIBs (a,b) and full capacitor (c,d)\(^{112}\)*

Recently, more studies have focused their attention on the performance of transition metal carbodiimides in NIBs\(^{37,113}\), showing a particle size dependence of the capacity taking MnNCN as an example. According to SEM analysis, the electrochemical performance of MnNCN which has a very low potential for Na insertion of \(\sim 0.1\) V vs Na\(^+\)/Na, exhibits a strong dependence on particle size: while micron-sized MnNCN is almost inactive, nano-sized MnNCN delivers at least half of its theoretical capacity. This dependence might explain why MnNCN was found to be inactive in the first report by Milke *et al.*\(^{110}\). Very recently (September 2019), MnNCN nanoparticles with N-doping carbon were used as cathodic electrocatalyst for Li-O\(_2\) batteries.\(^{114}\)

Almost all the transition metal carbodiimides reported until now react electrochemically with lithium and sodium via a conversion reaction as it was shown in the case of FeNCN. To confirm this trend, it is then necessary to extend the investigation of the
reaction mechanism(s) to other carbodiimide compounds using appropriate analytical techniques.

1.4. Objective of the thesis

The main objective of this thesis is to investigate the electrochemical mechanism and performance of metal cyanamides and carbodiimides as anode materials for LIBs and verify whether all of them undergo a conversion reaction as it has been observed until now. Apart from the two-electron conversion reaction seen in the divalent transition metal carbodiimides, one cannot exclude the possibility of combination of conversion with alloying or intercalation processes for other metal carbodiimides and cyanamides. The possible occurring of an intermediate intercalation step in the case trivalent transition metal carbodiimide materials will also be explored. In this respect, the detailed reaction mechanism studies will be carried out employing various complementary *operando* and *ex situ* techniques such as X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Finally, the electrochemical performance of these compounds including cyclability, rate capability, coulombic efficiency, etc., will be confronted and possibly explained in the light of the corresponding electrochemical mechanisms.
Chapter 2: Pure conversion reaction
This chapter is centred on the investigation of cobalt carbodiimide, CoNCN, as negative electrode for LiBs with a focus on electrochemical mechanism and performance. CoNCN has already been reported for its excellence as a catalyst for water oxidation and the ability of CoNCN to store electrochemical energy was evidenced recently. CoNCN offers a theoretical capacity of 541 mAh.g\(^{-1}\). Eguia-Barrio et al. reported a practical reversible capacity, in the second cycle, of 800 mAh.g\(^{-1}\), which is 259 mAh.g\(^{-1}\) larger than the theoretical capacity, with no explanation for such observation. Indeed, no information on reaction mechanism and performance such as long-term cyclability or rate capability, were given. The main goal of this chapter is thus to bring deeper insights on the electrochemical performance and mechanism governing the lithiation/delithiation of CoNCN using operando XRD and XAS.

The work presented here (as for all the subsequent chapters) is the result of a fruitful collaboration between ICGM and RWTH Aachen University. The material was synthesised at RWTH Aachen University, while the electrochemical characterization and operando XRD study were carried out at ICGM. The operando XAS measurements were performed at the ROCK beamline at SOLEIL Synchrotron (Saclay) with the help of Dr Antonella Iadecola (RS2E).

Concerning the electrochemical performance, CoNCN exhibits an excellent capacity retention and rate capability comparable with both CoO and FeNCN. Specific capacity as high as 530 mAh.g\(^{-1}\) can be maintained over more than 400 cycles at 2C current density (540 mA.g\(^{-1}\)). CoNCN displays a better coulombic efficiency compared to both CoO and FeNCN. Operando analyses confirm the reaction pathway as two electron conversion reaction leading to the formation of Co metal nanoparticles upon lithiation. Interestingly, the “CoNCN” recovered after delithiation does not correspond exactly to pristine CoNCN. Its XAS signature might imply an isomerization change from carbodiimide carbodiimide N=C=N into to cyanamide configuration N─C≡N. This work has been the object of a publication recently in the journal ChemElectroChem, which is reported in the following of the manuscript.
Cobalt carbodiimide, CoNCN, as negative electrode for Li-ion batteries: electrochemical mechanism and performance

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2.1. Introduction

Rechargeable LIBs have the highest energy density among all commercially available rechargeable batteries. Even though common negative electrodes based on graphite show excellent charge/lithiation cycling performance, their relatively low energy density and safety issues do not correspond to the requirements of high energy LIB. This still existing need justifies the continuous search for alternative advanced negative electrode materials showing high energy density and long cycle life.30–32 The use of transition-metal compounds has drawn a great attention due to their high specific capacity, and several transition-metal oxides, sulfides, phosphides, etc.11,19–23,26–28,115–124 have been already reported to be electrochemically active at an average potential of 1 V vs. Li⁺/Li. These materials do not react with lithium through the conventional intercalation reaction, but usually undergo a conversion and/or alloying mechanism.32,78,125 For example, Tarascon and co-workers showed that the electrochemical lithiation/delithiation of 3d-transition-metal oxides MO (M = Co, Ni, Cu, etc.) occurs through the reaction:26,126

\[ MO + 2\text{Li} \rightleftharpoons \text{Li}_2\text{O} + M \]
These materials show high reversible capacities of \(~700 \text{ mAh.g}^{-1}\) for at least 100 cycles, which is twice the capacity of carbon-based anodes. Recently, transition-metal carbodiimides, a new family of transition-metal compounds analogous to transition-metal oxides, have been proposed as possible negative electrode materials for LIBs, showing a very promising electrochemical activity vs. lithium and sodium.\textsuperscript{33–35,37,127,128} The carbodiimide group \([\text{NCN}]^2-\) has the same formal charge of the oxide anion \(\text{O}^{2-}\) and a slightly lower electronegativity. In some cases, the crystal structures of metal oxides and carbodiimides are quite similar with some distortion due to the larger size of the \([\text{NCN}]^2-\) group.\textsuperscript{33–35} These similarities have motivated their study as electrode materials in alkali metal-ion batteries. In general, like all electrode materials undergoing conversion reactions, also carbodiimides suffer from high initial irreversible capacity and high operating voltage. Nonetheless, they show relatively higher theoretical capacities than oxides, better cycle life and robust rate capability.\textsuperscript{33,112} For example FeNCN shows outstanding rate capability up to 30C and stable cycling for more than 100 cycles.\textsuperscript{33}

An alternatively interesting metal carbodiimide for energy applications is the cobalt analogue, which already showed very good performance as a catalyst for water oxidation.\textsuperscript{106,107} The ability of CoNCN to store electrochemical energy was evidenced recently,\textsuperscript{33} and it has a theoretical capacity of 541 mAh.g\(^{-1}\). The data reported until now on the electrochemical properties of CoNCN vs. lithium are limited to the two first galvanostatic cycles, without any detail on reaction mechanism and performance. The aim of the current work is to explore the lithiation/delithiation mechanism using complementary \textit{operando} analyses such as XRD and XAS, in order to obtain deeper insights about its performance, including coulombic efficiency, rate capability and capacity retention.

2.2. Experimental details

2.2.1. Material preparation

CoNCN was prepared via a two-step method. The first step consists in the synthesis of the pure auburn-colored cobalt hydrogen cyanamide, \(\text{Co(HNCN)}_2\), starting from cobalt chloride and cyanamide in aqueous ammonia solutions. In the second step, \(\text{Co(HNCN)}_2\) is blended with a mixture of \(\text{LiCl/KCl}\) as a flux and heated up to 400 °C under argon atmosphere in a closed ampule. The melamine produced through the reaction is removed by trapping it in
the cold side of the glass container which is held out of the tube furnace at room temperature. The orange-brown CoNCN powder from the cooled ampoule is washed with water and dried in vacuum.\textsuperscript{96}

2.2.2. Material characterization

The structural and morphological characterization of the as-prepared samples was carried by XRD (PANalytical Empyrean equipped with a Cu Kα source) and scanning electron microscopy (SEM, Hitachi S-4800 scanning electron microscope equipped with a field emission gun). Profile matching and calculation of the cell parameters were refined using the LeBail method.\textsuperscript{129} In situ Fourier transform infrared spectroscopy (FT-IR) analyses were carried out on a Nicolet Magna FTIR spectrometer equipped with a liquid nitrogen cooled MCT-A detector in the Attenuate Total Reflection (ATR) geometry using a specifically designed in situ cell.\textsuperscript{130,131} The cell was obtained by modifying the Raman spectroscopy in situ electrochemical cell used elsewhere,\textsuperscript{132} by replacing the quartz window with the diamond probe of the ATR module. ATR FT-IR spectra were recorded from 600 to 4000 cm\textsuperscript{-1}. The thermal stability of CoNCN was evaluated by thermogravimetric analysis using a NETZSCH Jupiter STA 449 F1 thermobalance with a heating rate of 5 °C.min\textsuperscript{-1} in air flow.

2.2.3. Electrochemical characterization

Electrochemical tests were performed in coin cells with lithium foil as counter and reference electrode in both galvanostatic and cyclic voltammetry (CV) mode. Electrodes were prepared by mixing the CoNCN active material with carbon black and vapor-grown carbon nanofibers (VGCF) as conductive additives, and carboxymethyl cellulose (CMC) as the binder in a weight ratio of 3:1:1. A homogenous aqueous slurry of this mixture was tape-casted over a copper foil at a thickness of 150 µm, dried in air at room temperature and finally at 100 °C in vacuo. Electrode disks punched out of the dried film have an active material loading of \(~\text{1 mg/cm}^2\). Coin cells were assembled in an argon filled glove box vs. Li metal discs using a Whatman glass fiber GF/D separator and an electrolyte solution of 1 M LiPF\textsubscript{6} in ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) (1:1:3 in weight) with 2 % V and 5 % FEC as additives. Galvanostatic lithiation/delithiation cycles were performed using either a Biologic VMP or a MPG-2 system at C/n rate, which is defined here as the reaction of 1 mole of Li per mole of CoNCN in n hours (270 mA.g\textsuperscript{-1}).
**Ex situ** Fourier Transform Infrared Spectra (FT-IR) spectra were collected in the range 4000-650 cm\(^{-1}\) in the Attenuate Total Reflection (ATR) geometry using a specifically built *in situ* cell for protecting the measured samples from the contact with ambient air. The cell was obtained as a modification of the Raman spectroscopy cell used elsewhere,\(^{132}\) by replacing the quartz window with the diamond probe of the ATR module. The samples were mounted in the in situ cell for the FT-IR measurements after cycling and after being washed with PC and dried inside the glow box under Ar.

**Operando** XRD measurements (one pattern per hour) were carried out on self-supported electrodes at C/8 rate in a specifically designed *in situ* cell.\(^{133}\) Co K-edge *operando* XAS measurements were carried out in the transmission mode at the ROCK beamline of Synchrotron SOLEIL.\(^{134}\) A channel-cut Si(111) monochromator with an oscillating frequency of 2 Hz and an energy resolution of 0.7 eV at 8 KeV was used. For these experiments, electrodes were prepared by tape casting the aqueous slurry containing the formulated electrode material directly on the beryllium window of the *in situ* cell.\(^{133}\) The intensity of the X-ray beam was measured by three consecutive ionization detectors, with the *in situ* electrochemical cell placed between the first and the second ionization chambers and a Co metal foil reference between the second and the third one. The homogeneity of the sample was checked before running the electrochemical test. The electrochemical test was started with a current rate of C/8, *i.e.*, in the same conditions of the *in situ* XRD measurement. However, in order to get a complete cycle, the rate had to be accelerated to C/2 for the charge process.

The *operando* XAS spectra were first calibrated in energy using Co foil as reference and then normalized using ATHENA software.\(^{135}\) The whole dataset was then analyzed using a chemometric approach including Principal component Analysis (PCA) and Multivariate Curve Resolution – Alternate Least Squares (MCR-ALS)\(^{136,137}\) described in detail elsewhere.\(^{138}\) In short, PCA is a statistical tool allowing the extraction of the maximum amount of useful information from large datasets by considering each spectrum as a vector in a multidimensional space. By construction, the principal components are the independent (orthogonal) vectors necessary to describe the evolution of the whole set of spectra. Principal components, however, are orthogonal mathematic functions and do not represent pure XAS spectra. Starting from the number of principal components detected by PCA, the MCR-ALS algorithm allows the reconstruction of realistic “pure” components. Such components can
then be treated as real XAS spectra and therefore their EXAFS oscillations can be fitted using the Demeter software package.\textsuperscript{135}

### 2.3. Results and discussions

#### 2.3.1. Pristine CoNCN

The experimental and refined XRD patterns of CoNCN is shown in Figure 2.1. The sharp diffraction profiles indicate the good crystallinity of the powder, and no spurious peaks representing impurities are visible. The cell parameters $a = b = 3.211(1)$ Å, $c = 9.381(2)$ Å, $Z=2$ are in agreement with the known hexagonal structure and space group $P6_3/mmc$.\textsuperscript{96} In this structure, the ions are arranged in a layered manner, each layer consisting of alternate Co$^{2+}$ and NCN$^{2-}$ layers (Figure 2.1 inset).

The NCN$^{2-}$ anions adopt a perfect carbodiimide symmetry ($D_\infty h$ point-group symmetry), that is, linear N=C=N units with C=N bond lengths of $1.226(2)$ Å. The carbodiimide units are oriented parallel to the $c$ axis and are coordinated with six cations in a trigonal prismatic fashion, whereas each metal atom is coordinated by six nitrogen atoms in slightly flattened edge-sharing octahedra sitting in the $ab$ plane.\textsuperscript{96}

![XRD pattern with indexed peaks and crystal structure (inset) of CoNCN.](image)

**Figure 2.1.** XRD pattern with indexed peaks and crystal structure (inset) of CoNCN.

FT-IR and Raman spectra of CoNCN are shown in Figure 2.2(a) and (b), respectively. The asymmetric stretching mode $\nu_{as}$ and the doubly degenerated deformation mode $\delta$ of NCN are visible in the FT-IR spectrum at 2050–2200 cm$^{-1}$ and 648 cm$^{-1}$, respectively, in agreement
with previous reports.\textsuperscript{34,96,106,107} The additional broad band in the range of 1100–1700 cm\(^{-1}\) was not reported by Krott \textit{et al.}\textsuperscript{96} but was observed more recently by Rojo \textit{et al.}, Muller \textit{et al.}, and Ressnig \textit{et al.}\textsuperscript{34,106,107} This broad band can be attributed to melamine polycondensation or to other impurities such as C\(_3\)N\(_4\), which shows bands between 1250 and 1640 cm\(^{-1}\), as well as 810 cm\(^{-1}\) (one band is visible here at 800 cm\(^{-1}\)).\textsuperscript{139} The symmetric NCN stretching mode \(\nu_s\) is visible in the Raman spectrum at 1366 cm\(^{-1}\) whereas the asymmetric one visible as a broad peak centered at 2050 cm\(^{-1}\). According to Müller \textit{et al.}, the peak at 1266 cm\(^{-1}\) can be indexed to the redshifted overtone of the bending mode (2\(\delta\)\(_{	ext{IR}}\) = 2 \times 648 cm\(^{-1}\) = 1296 cm\(^{-1}\)), which occurs with increased intensity as a result of mixing of vibrational states (Fermi resonance).\textsuperscript{106,107} The frequencies at 401 and 201 cm\(^{-1}\) are characteristics to the metal-nitrogen lattice modes. The other two broad peaks seen around 1320 cm\(^{-1}\) and 1600 cm\(^{-1}\) can be assigned to graphitic peaks indicating the presence of \(g\)-C\(_3\)N\(_4\) as an impurity in the CoNCN sample.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{FT-IR (a), Raman (b) spectra, SEM micrograph (c) and TGA curve (d) of CoNCN.}
\end{figure}

The morphology of CoNCN was analyzed by scanning electron microscopy (Figure 2.2c). The SEM results reveal gypsum flower-like morphology with 20–40 nm thick and 3–10 \(\mu\)m long petals. This kind of nanostructured morphology is mainly due to the layered structure of CoNCN, resulting in a relatively high surface area. TGA analysis (Figure 2.2d) shows a continuous weight loss of 5 % between room temperature and 260 °C followed by a drastic loss of 32 % at 330 °C. The initial loss is associated with water or organic molecules desorption from the particle’s surface. The second abrupt loss is due to the decomposition of cobalt carbodiimide into cobalt oxide.\textsuperscript{140}
2.3.2. Electrochemical performance

Galvanostatic and cyclic voltammetry tests of CoNCN vs. Li correspond well to those of typical conversion reactions (Figure 2.3a and b) as in the case of CoO.\textsuperscript{118} During the first lithiation, two well-defined potential plateaus are observed at $\sim 1.1$ and 0.9 V. The first short one around 1.1 V can be associated to the irreversible reaction of lithium with the carbon additive used in the electrode formulation, leading to the formation of a solid electrolyte interphase (SEI, \textit{vide infra}) via electrolyte decomposition, as well as the possible lithium insertion in the residual $g$-C$_3$N$_4$ impurity,\textsuperscript{141-143} whereas the second long plateau can be ascribed to the conversion of CoNCN.\textsuperscript{11,21,144} The initial plateau is however very short compared to the main conversion plateau of CoNCN, implying that the contribution from $g$-C$_3$N$_4$ is minor if not negligible. The gradual potential decrease observed in the last part of the lithiation between 0.5 and 0 V, is very similar to the process described by Laruelle \textit{et al.}, corresponding to the growth of a polymer/gel-like film promoted by the highly reactive metallic nanograins formed during the conversion of transition metal oxides.\textsuperscript{125} This polymer phase is expected to dissolve reversibly once the potential is raised again during the following delithiation. The interaction of such a gel with the metal particles was evidenced in the case of CoO by Grugeon \textit{et al.}\textsuperscript{145} as well as in the case of NiSb$_2$ by Marino \textit{et al.}\textsuperscript{146} The subsequent lithiation processes are completely different from the first one: the two initial plateaus are replaced by an almost continuous potential slope, while two pseudo-plateaus at higher potential (1.7 and 1.3 V) are identified in CV curves. Such difference between first and subsequent lithiations is also typical of conversion reactions, and is caused by the massive and irreversible electrochemical pulverization of the active particle grains going along with SEI formation.\textsuperscript{65,125,147} During delithiation, a continuous slope potential curve is also observed, terminated by a plateau at 2.2 V.

The first lithiation specific capacity of 1155 mAh.g$^{-1}$, significantly higher than the theoretical one (541 mAh.g$^{-1}$), is also typical of conversion reactions, with the excess capacity explained in terms of electrolyte decomposition leading to the formation of SEI.\textsuperscript{22,35,78} The reversible specific capacity, however, drastically decreases starting from the first delithiation. CoNCN exhibits a robust behaviour (Figure 2.3c) with an excellent coulombic efficiency exceeding 99.6 % after 30 cycles, whereas it was only 97 % for FeNCN.\textsuperscript{33} This high coulombic efficiency indicates that no significant irreversible trapping of lithium ions is occurring in the
SEI or in side reactions with the electrolyte, and thus that the SEI layer formed during the first cycles is stable and prevents further irreversible degradation reactions.  

![Graph showing cyclic voltammetry and galvanostatic profile.](image)

**Figure 2.3.** Galvanostatic profile at C/10 ~ 27 mA.g⁻¹ (a) cyclic voltammetry at 0.005 mV/s (b) rate capability and coulombic efficiency vs. cycle number (c) and specific lithiation capacity retention at 2C rate (d) of CoNCN vs. Lithium.  

Finally, concerning rate capability, the capacity decreases with increasing current density as expected. However, even at 4 C rate (1.08 A.g⁻¹), CoNCN retains a specific capacity equivalent to that of graphite (360 mAh.g⁻¹) when the latter is cycled at low current densities (10 mA.g⁻¹), 148,149,150 while at 2 C rate (540 mA.g⁻¹) the CoNCN electrode is capable of delivering more than 420 mAh.g⁻¹. Upon decreasing the current rate from 4 C to 0.1 C, nearly 100 % of the initial capacity is recovered back, highlighting the robustness of CoNCN as anode material unlike the CoO analogue. 149 In terms of cycle life (Figure 2.3d), CoNCN holds a stable capacity around 530 mAh.g⁻¹ over 400 cycles at a current rate of 540 mA.g⁻¹ which is very close to the theoretical value and similar to that of cobalt oxide. It is worth noting that there is a slight increase in the capacity starting from the 200th cycle, which is generally observed in transition metal conversion anode materials. 24,145 Such electrochemical performance points out the excellence of micrometric CoNCN as a negative electrode material in LIBs.
2.3.3. Electrochemical reaction mechanism

The electrochemical reaction mechanism of CoNCN vs Lithium was first investigated by operando XRD (Figure 2.4a). The diffraction peaks of CoNCN disappear during lithiation, leading to a completely amorphous pattern at the end of discharge. No crystalline phase is formed even during the following delithiation, indicating the complete amorphisation/nanostructurati of the electrode. Note that the lithiation process in the in situ cell is usually longer than in coin cells due to its large volume and the consequent larger amount of electrolyte needed, leading to a substantial increase of electrolyte decomposition side reactions.\textsuperscript{124}

![Figure 2.4. Operando XRD patterns of CoNCN (a), associated galvanostatic lithiation/delithiation curve (b) and evolution of the intensity of the main CoNCN diffraction peak (022) with Li reaction (c).](image)

The intensity of the main peak (022) of CoNCN at $2\theta = 18.8^\circ$ remains constant during lithiation down to $\sim1.0$ V (corresponding to the reaction of $\sim1$ Li per mole of CoNCN). This potential corresponds to the first plateau of the first lithiation, and indicates that CoNCN does not react electrochemically with Li in this process. This result confirms that the origin of this first plateau is rather to be found in irreversible reactions of the electrolyte with carbon and
binder additives (*vide supra*). Starting from 0.9 V, the intensity of the diffraction peaks of CoNCN progressively decreases until 0.5 V where a faster decreasing is observed. This behavior suggests a two-steps reaction of CoNCN with lithium.

To complement XRD information, limited to the crystalline part of the electrode, *operando* XAS analysis was performed during the first lithiation/delithiation cycle (Figure 2.5). The electrochemical test was carried out at different current rates starting at C/8, then accelerating it at C/5 and finally at C/2 in order to complete the first cycle within the limited beam time available. Full delithiation was enforced by holding the potential at 3 V at the end of charge. The whole data set consisting of 126 Co K-edge XAS spectra was treated globally using the chemometric approach already described in our previous studies. In short, the number of independent components needed to describe the whole data set of spectra is first obtained by PCA, and in a second step the corresponding pure spectral components are reconstructed by MCR-ALS algorithm by imposing physical and chemical constraints. In this case, PCA analysis indicates that three components are necessary to interpret the evolution of the XAS spectra during the first cycle (see Figure 2.S1). The evolution of the Co K-edge X-ray absorption near-edge structure (XANES) spectra during cycling is shown in Figure 2.5a along with the corresponding electrochemical curve, while the XANES spectra of the three reconstructed components are shown in Figure 2.5b along with spectra at significant states of charge. For technical issues during the experiment, the XAS acquisition was started at 1.26 V instead of 2.5 V. However, as already shown by XRD, the first part of the lithiation is accompanied with the irreversible reactions of the electrolyte with carbon and binder additives. In fact, no difference is observed by comparing the XAS spectra of the pristine CoNCN with that at 1.26 V (Figure 2.S2).

The XANES region being sensitive to both oxidation state and local environment of the cobalt atoms, the evolution of the spectra in Figure 2.5a proves the evolution of the Co oxidation state during lithiation and delithiation. The weak pre-edge feature (zone A) in the spectrum of pristine CoNCN at ~7710 eV, due to the electric-quadrupole forbidden $1s \rightarrow 3d$ transition which becomes visible only in non-centrosymmetric environments, indicates the slightly distorted coordination of CoN$_6$ octahedral sites. With ongoing lithiation, the XANES spectra are gradually modified towards assuming the shape of the spectrum of Co metal, confirming the reduction of Co$^{2+}$ to metallic Co. At the end of lithiation (0.005 V), the corresponding *operando* XANES spectrum resembles to that of the Co metal reference, with a
broader features indicating the nanometric size of the so-obtained cobalt particles,\textsuperscript{146} in line with the absence of any diffraction signature (see Figure 2.4). Upon the following delithiation, the XANES features are again modified, confirming the oxidation of the Co metal nanoparticles. However, the shape of the spectrum obtained at the end of charge does not resemble to that of pristine of CoNCN, indicating that the pristine state is never recovered, as also confirmed by \textit{operando} XRD.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.5}
\caption{Operando Co K-edge XANES spectra collected during the first lithiation/delithiation cycle and corresponding galvanostatic profile (a); Co K-edge XANES spectra of the reconstructed components together with selected states of charge and Co metal as reference (b).}
\end{figure}
Figure 2.6. Evolution of the relative concentrations of the MCR-ALS reconstructed components during lithiation and delithiation of CoNCN. Note that due to some technical issues XAS data between OCV and ~12 hours are missing. This does not affect the conclusions since no significant change is observed in this region.

The XANES regions of the MCR-ALS reconstructed components 1, 2 and 3 are virtually identical to those of pristine CoNCN, to the material at the end of discharge and to the material at the end of charge, respectively. Their evolution during cycling, shown in Figure 2.6, is in line with the direct one-step conversion of CoNCN to Co metal nanoparticles, without the formation of intermediate species. In fact, the intensity of component 2 increases at the expenses of component 1, and reaches its maximum at the end of the long conversion plateau at ~0.7 V, remaining practically stable until the end of lithiation. This finding confirms that the additional capacity below 0.7 V is not due to the metal redox reaction, but rather to a (partially) reversible contribution of the electrolyte (vide supra). A similar effect was reported by Choi et al. in the case of CoO. The back-conversion of Co metal nanoparticles to a new Co(II) species is observed upon delithiation. Indeed, component 2 is gradually transformed during charge into component 3, which is different from the pristine material but can be
attributed to a new Co(II) species. In summary, if the assignment of the first two reconstructed components to pristine CoNCN and to Co metal nanoparticles is straightforward, the analysis of the EXAFS oscillations is necessary to understand the nature of component 3 (vide infra).

Figure 2.7. The Co K-edge $k^2$ weighted EXAFS oscillations of the MCR-ALS reconstructed components in $k$ (a) and $R$ (b) spaces. The black dots represent the data and red line the fit. The FT are not corrected by the phase shifts.

The analysis of the EXAFS oscillations of the three reconstructed components is shown in Figure 2.7, while the corresponding fitting parameters are reported in Table 2.1. The first component fits well to the published structure for CoNCN. Using the first three shells in the fitting procedure, the bond distances perfectly agree with the theoretical values. The different EXAFS oscillations of component 2 reflect the formation of metallic Co nanoparticles, since it can be fitted with a single Co-Co shell at distances slightly smaller than those of bulk Co metal, but with a lower coordination number. As the particle size decreases, the surface-to-volume ratio increases with a consequential increase in the fraction of partially uncoordinated Co atoms at surface sites, hence decreasing the coordination number. By
analogy with CoO, where the cobalt nanoparticles are dispersed in a matrix of Li$_2$O, here it is reasonable to suppose the dispersion of the cobalt nanoparticles in a matrix of Li$_2$NCN.$^{118,124}$

Table 2.1. EXAFS oscillations fitting parameters of the MCR-ALS reconstructed components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Phase</th>
<th>Shell</th>
<th>$S_0^2$</th>
<th>$N_{\text{Theo}}$</th>
<th>$N_{\text{Exp}}$</th>
<th>$R_{\text{Theo}}$</th>
<th>$R_{\text{Exp}}$</th>
<th>$\sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co—N</td>
<td></td>
<td>6</td>
<td>6</td>
<td>2.168</td>
<td>2.138</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>CoNCN</td>
<td>Co—C</td>
<td>0.91</td>
<td>6</td>
<td>6</td>
<td>2.993</td>
<td>2.989</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co—Co</td>
<td>6</td>
<td>6</td>
<td>3.212</td>
<td>3.216</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Co</td>
<td>Co—Co</td>
<td>0.91</td>
<td>12</td>
<td>5</td>
<td>2.501</td>
<td>2.410</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co—N1</td>
<td>6</td>
<td>2.5</td>
<td>1.968</td>
<td></td>
<td></td>
<td>0.009</td>
</tr>
<tr>
<td>3</td>
<td>Co$^{2+}$</td>
<td>Co—N2</td>
<td>0.91</td>
<td>3.5</td>
<td>2.501</td>
<td>2.490</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co—Co</td>
<td>6</td>
<td>6</td>
<td>3.212</td>
<td>3.197</td>
<td>0.024</td>
<td></td>
</tr>
</tbody>
</table>

The coordination number obtained by refining the EXAFS oscillations has largely been used to estimate the size of metal nanoparticles, and many models approximating the shape of the particles and the atomic arrangement inside the particles have been proposed. For Co particles of small size, the fcc structure is expected to be more stable than the hcp one.$^{160}$ For this structure, the following equation can be used assuming homogenous spherical particles of radius $R$, the radius of the cobalt atom $r = 0.125$ nm and a bulk coordination number $N_{\text{bulk}} = 12$:

$$N_{\text{nano}} = \left[ 1 - \frac{3}{4} \left( \frac{r}{R} \right) + \frac{1}{16} \left( \frac{r}{R} \right)^3 \right] \cdot N_{\text{bulk}}$$

This model leads to cobalt particles with a diameter $d = 2R = \sim 0.3$ nm. Using the alternative model proposed by Marinkovic et al$^{161}$, which calculates $R$ as:

$$R = \frac{a}{1.82} \sqrt[3]{N_t}$$

Where $a = 0.3548$ nm is the cell parameter of bulk Co, a diameter $d = \sim 0.7$ nm is obtained. Both models confirm the sub-nanometric size of the Co nanoparticles.
Concerning component 3, one would expect it to be very similar to pristine CoNCN, with modifications directly ascribable to the amorphisation induced by the conversion mechanism. However, component 3 is significantly different from component 1 (Figure 2.7) and its fitting requires a different structural model based on two Co-N (or Co-C, since C and N have the same scattering properties at Co K-edge) paths which are shorter and have lower coordination numbers than those used for pristine CoNCN (Table 2.1). In spite of these differences, this result clearly shows that during delithiation the oxidation of cobalt ions lead to the reformation of new Co-N bonds, thus binding back to the NCN\(^{2-}\) moieties. The difference in the fitting model nevertheless confirms that the structure of pristine CoNCN is not recovered.

More interestingly, the existence of two different Co-N distances may indicate the transformation of the pristine symmetric carbodiimide into asymmetric cyanamide. Additional ex situ FT-IR spectroscopy analyses (cf. Supplementary information, Figure 2.S3) seem to agree with this transformation, indicating a deep modification of the material during the whole discharge-charge cycle. However, cobalt cyanamide has never been obtained and DFT calculations do not predict its formation at ambient conditions. This new form of CoNCN different from the pristine material and indicated in the following as “CoNCN”, observed by both FT-IR and XAS spectroscopies, is made possible by both the electrochemical route and the nature of precursors available in the electrode, i.e., fcc cobalt nanoparticles and Li\(_2\)NCN nanoparticles.

**2.3.4. Proposed mechanism**

By summarizing the results obtained by complementary operando XRD and XAS, a reaction scheme based on a two-electron conversion process (Figure 2.8) can be proposed for the electrochemical reaction of CoNCN with lithium:

\[
\text{CoNCN} + 2\text{Li} \rightarrow fcc\text{Co} + \text{Li}_2\text{NCN } \quad (\text{1st lithiation})
\]

\[
fcc\text{Co} + \text{Li}_2\text{NCN} \Rightarrow \text{“CoNCN”} + 2\text{Li} \quad (\text{subsequent cycles})
\]

Similarly, to all reported transition metal carbodiimides, the lithiation of CoNCN leads also to the formation of Co metal nanoparticles and Li\(_2\)NCN. However, a new “CoNCN” species showing intriguing structural changes is observed at the end of delithiation, possibly implying the formation of a new form of NCN\(^{2-}\) in the cyanamide configuration instead of the
carbodiimide one. *Operando* XRD and XAS results pointed out that CoNCN redox reaction takes place only in the potential domain 1.1–0.7 V. A fraction of the reacted lithium is consumed for the formation of the SEI during the first lithiation, leading to a large first cycle irreversible capacity. Moreover, another fraction undergoes a reversible reaction with the electrolyte forming a polymeric/gel film on the surface of the electrode with a pseudocapacitive character, thus explaining the observed reversible extra capacity, as previously observed for CoO.\(^{125}\) The substantial irreversible capacity observed in the first cycle might however seriously hinder the possible use of CoNCN in full batteries if a practical solution is not found to suppress it.

![Figure 2.8. Schematic diagram of proposed electrochemical mechanism of CoNCN.](image)

### 2.4. Conclusions

The electrochemical performance of cobalt carbodiimide as an anode material in LIBs was evaluated, and its detailed reaction mechanism studied by a combination of complementary *operando* techniques. Concerning the electrochemical performance, CoNCN offers excellent capacity retention and rate capability that are comparable to those of CoO and FeNCN. Specific capacity as high as 530 mAh.g\(^{-1}\) can be sustained over more than 400 cycles at 2C current rate (540 mA.g\(^{-1}\)). The robustness of CoNCN allows the use of very high
current rate (more than 1080 mA.g\(^{-1}\)) without any electrode deterioration. Moreover, CoNCN shows a better coulombic efficiency compared to both CoO and FeNCN.

In the same way as oxides and other conversion anode materials, CoNCN suffers from huge irreversible capacity in the first cycle due to massive electrolyte degradation during the formation of the SEI. During the subsequent cycles, CoNCN presents a reversible extra capacity that relies on the formation of a polymeric gel film on the electrode surface with a pseudocapacitive character. *Operando* XAS confirms the occurrence of the conversion reaction, leading to the formation of Co metal nanoparticles upon lithiation. The “CoNCN” delithiated phase does not correspond to pristine CoNCN, and the formation of NCN\(^{2-}\) ligand in the cyanamide configuration (N─C≡N\(^{2-}\)) cannot be excluded, even though its formation is not expected based on DFT calculations.
2.5. Supporting information

Figure 2.S1. Components from PCA analysis (a) Variance of the components (b) Evolution of the component scores (c).

Figure 2.S2. Comparison between the XAS spectra of the pristine CoNCN with that of spectra at 1.26 V in the operando analysis.
Figure 2.S3. FT-IR difference spectra between the CoNCN at the end of the first discharge and of the first charge, and the spectrum of pristine CoNCN. Positive peaks correspond to the appearance of new absorption bands in the IR spectrum, whereas negative peaks correspond to the disappearance of bands with respect to the spectrum of pristine CoNCN.

The analysis of the infrared spectra, shown in Figure 2.S3, follows well the transformation of the pristine cobalt carbodiimide during the reversible reaction with lithium. During the first discharge, the main feature in the spectrum is the appearance of a new band below 2200 cm\(^{-1}\) and the disappearance of a band at about 2100 cm\(^{-1}\), in line with the transformation of CoNCN (\(v_{as}(NCN) 2090 \text{ cm}^{-1}\))\(^{96}\) into \(\text{Li}_2\text{NCN} (v_{as}(NCN) 2165 \text{ cm}^{-1})\).\(^{89}\) A more complex transformation is observed, on the contrary, at the end of charge: in addition to the great modification of the \(v_{as}(NCN)\) region, several new bands are appearing between 1200 and 1500 cm\(^{-1}\). Such new bands could correspond to the formation of cyanamide-type species, as observed previously, among other, for PbNCN, Ag\(_2\)NCN and HgNCN.\(^{93,100}\) In any case, the spectrum indicates a very large difference between the spectrum of pristine CoNCN and that of the sample at the end of the charge process, indicating a deep transformation of the material during the whole discharge-charge cycle.
Chapter 3: Combined conversion and alloying reaction
This chapter presents a collaborative study on “Electrochemistry of Metal cyanamides and carbodiimides” including ICGM, RWTH Aachen University, and University of Kent.

As mentioned in Chapter 2, the electrochemical lithiation of transition metal carbodiimides (MNCN, with M = Fe, Mn, Co, Cu, Ni)\textsuperscript{33,34,37,112} consists of a two electron conversion process with the formation of Li\textsubscript{2}NCN together with metal nanoparticles, which sets the achievable capacity.\textsuperscript{33} The idea of this chapter is to replace transition metals by some elements having the ability to undergo alloying process after the classical conversion step. Three elements were identified to have this ability and at the same time to form stable carbodiimide compounds: Ag, Zn and Pb. It is worth recalling that even if the three metals are not commonly used in Li-ion technology, they are widely used in industrial energy storage for other technologies such as Pb−acid, Ag−Li, Zn−Ag\textsubscript{2}O, and Zn−air batteries.\textsuperscript{162,163}

PbNCN, Ag\textsubscript{2}NCN and ZnNCN were investigated for the first time as negative electrodes for LIBs. Electrochemical tests and \textit{in situ} XRD confirmed the electrochemical activity of all these materials vs. lithium. However, the massive amorphisation during lithiation prevented the identification of the involved species. Therefore, spectroscopic characterization where carried out using \textit{ex situ} XAS, which is more sensitive to short-range order in solids. The XAS measurements were performed at the beamline B18, Diamond Light Source, via the Block Allocation Group “Materials in Energy Applications” with the help of Prof. Alan Chadwick and Dr. Giannantonio Cibin.

The obtained results clearly evidenced the ability of the selected materials to combine conversion and alloying reactions. Unfortunately, the conversion contribution is highly irreversible for the three compounds, whereas the reversibility of the alloying reaction depends on the metal: it is highly irreversible for PbNCN and Ag\textsubscript{2}NCN which containing the cyanamide group (N≡C= N\textsuperscript{2−}), whereas it is more reversible for ZnNCN which contain the carbodiimide (−N=C=N−) group. In the case of the more covalent, cyanamide-type PbNCN and Ag\textsubscript{2}NCN, the conversion reaction occurs at a higher potential compared to the more ionic, carbodiimide-type ZnNCN, correlated with the nature of bonding in the NCN group and in the phases themselves. This work has been the object of a paper published in the journal ACS Omega, which is reported in the following of the manuscript.
Electrochemical evaluation of Pb, Ag and Zn cyanamides/carbodiimides

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3.1. Introduction

Today’s world is at a turning point, the electricity and the transportation are nowadays crucial from people’s daily life to industry production. This growing demand for energy makes LIBs the best candidate for practically all portable electronic applications. The current choice of negative electrode material for LIBs is graphite due to its appealing properties, such as long cycle life, abundancy, and low cost. However, the graphite anode has two main disadvantages: low energy density and safety. For this reason, there has been a growing interest in developing alternative cost-effective anode material with high energy density and long cycle life.\textsuperscript{31}

Several families of negative electrode materials have been investigated so far, and among them, transition-metal based compounds based on the conversion reaction showed to be a reasonable alternative for graphite owing to their high specific capacity.\textsuperscript{78,164} Compounds with the formula MX where M is a divalent or a trivalent metal and X = O, S, PO\textsubscript{4}, and CO\textsubscript{3} have been reported to be electrochemically active at average voltages around 1 V.\textsuperscript{18–21,23,26,27,116,121,126,145,165–167} In spite of their high theoretical specific capacities, high irreversible capacity in the first lithiation and the short cycle life prevent their practical use in commercial batteries. The main reasons of such limitations rely, \textit{inter alia}, with the nature of the solid
electrolyte interphase (SEI) as well as the high volume expansion inherent to conversion materials.\textsuperscript{125}

Recently, a class of divalent transition-metal compounds, known as transition-metal carbodiimides (MNCN, with M = Fe, Mn, Co, Cu, Zn, Ni) have been reported for their electrochemical activities vs. Li and Na ion by different groups.\textsuperscript{33,34,37,112} In particular, they show an excellent cycle life, even though they suffer from high initial irreversible capacity and relatively high operating potential, like all divalent transition metal-based electrode materials. Despite showing interesting physio-chemical properties, only a limited number of alternative cyanamides/carbodiimides phases have been explored and compared with transition-metal carbodiimides.\textsuperscript{89,92,100,103,168–171}

The aim of this work is thus to study the electrochemical lithiation mechanisms of PbNCN, Ag\textsubscript{2}NCN and ZnNCN by a combination of long-range and short-range techniques, such as XRD and XAS,\textsuperscript{172} and to evaluate their performance as negative electrode materials for LIBs. Contrarily to their transition-metal analogues, these three phases are excellent model materials to investigate the possibility of combining the alloying mechanism of Pb, Ag and Zn with the conversion reaction, possibly leading to higher specific capacities compared to transition-metal carbodiimides. It is worth recalling that even if the three metals are not commonly used in Li-ion technology, they are commonly used in industrial energy storage for others technologies such as Pb-acid, Ag-Li, Zn-Ag\textsubscript{2}O and Zn-air.

### 3.2. Experimental methods

#### 3.2.1. Material synthesis

PbNCN and Ag\textsubscript{2}NCN were prepared by the reaction of an aqueous solution of cyanamide with the corresponding metal salt (lead acetate and silver nitrate for PbNCN and Ag\textsubscript{2}NCN, respectively). The addition of an ammonia solution led to the formation of yellow precipitates, which were then filtered, washed and dried to obtain crystalline lead and silver cyanamide particles.\textsuperscript{168,92} Zinc carbodiimide was prepared by a simple mixing of zinc chloride with cyanamide in excess in ammonia solution for 3 h, yielding a white powder.\textsuperscript{94}
3.2.2. Material characterization

XRD data were collected with a PANalytical Empyrean diffractometer equipped with Cu-Kα source. The measured XRD pattern were refined with the Le Bail method using the FullProf software. The microstructure and the morphology of the samples were observed with a Hitachi S-4800 scanning electron microscope equipped with a field emission gun. Thermogravimetric (TG) profiles were collected by using a NETZSCH Jupiter STA 449 F1 thermobalance with a heating rate of 5°C / min in airflow. Raman spectra were collected using a confocal LabRAM Aramis spectrometer (Horiba), equipped with a HeNe laser, a 1800 grooves/mm grating, and a Peltier-cooled CCD detector. A backscattering geometry with a 50x optical microscope objective under an excitation laser line of 633 nm (HeNe) was used.

3.2.3. Electrochemical measurement

Electrodes were prepared by mixing the active material with carbon black and vapour-grown carbon nanofibers (VGCF) as conductive additives, as well as carboxymethyl cellulose (CMC) as the binder. A homogenous aqueous slurry containing 60% active material, 20% binder and 20% conductive additive (10% CB + 10% VGCF) was prepared by low energy ball milling the suspension for 1 h. The slurry was then tape casted on a copper foil with a thickness of 150 µm, dried first at room temperature and then at 100 °C under vacuum. Finally, homogeneous electrodes with an active material loading of ~1 mg/cm² were cut out from the dried foils and assembled in coin cells in an argon-filled glove box vs. Li metal. The separator was a Whatman glass fibre GF/D, and the electrolyte a solution of 1 M LiPF₆ in ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) (1:1:3 in weight%) containing 2% vinylen carbonate (VC) and 5% fluoroethylene carbonate (FEC) as additives. The electrochemical cells were tested in galvanostatic mode using VMP and MPG Biologic potentiostats at C/n rate (indicating 1 mole of Li reacted in n hours per mole of active material, with n ranging from 0.25 to 10). Cyclic voltammetry (CV) profiles were also measurements with the same potentiostats with a scan rate of 0.05 mVs⁻¹ between 0.005 and 3 V.

3.2.4. Operando and ex situ measurement

Operando XRD measurements were carried out by measuring one pattern per hour on self-supported electrodes at C/8 rate in a specially designed in situ cell. Ex situ analyses
were conducted on electrodes cycled in Swagelock cells, stopped at specific discharge and charge states. The cells were disassembled in an Ar-filled glove box and the electrodes supported on Cu foils placed on a glass slide and covered with a Kapton film with a seal layer of silicone grease to prevent the reaction with air during analysis.

*Ex situ* XAS data were collected at room temperature at B18 beamline, Diamond Light Source (UK). Self-supported Electrodes of 6 mm diameter was prepared with a mixture of 50% active material and 50% carbon additives. The mixture was first loaded into a pellet ring holder of 6 mm and anvil die assembly. This assembly was then placed over the Pellet Press piston, the top lead screw is lowered, and a load of 3 tons applied. After compressing, the formed pellet was removed from the ring holder and dried at 100°C under vacuum. Self-supported pellets were cycled in Swagelok cells, and stopped at different charge/discharge potentials. The cells were disassembled in an Ar filled glove box sealed in airtight bags and transferred to the XAS sample holder. The measurements were carried out at the Zn K-edge, Ag K-edge and Pb L$_3$-edge for electrodes containing ZnNCN, Ag$_2$NCN and PbNCN, respectively. Extended X-ray absorption Fine Structure (EXAFS) spectra were extracted with the standard procedure using Athena and fitted using Artemis, both programs being included in the Demeter software package. Fourier transforms of EXAFS oscillations were carried out from 0.2 to 1.0 nm$^{-1}$ using a sine window. Fitting was performed in the $R$-range from 0.1 to 0.45 nm using $k^1$, $k^2$ and $k^3$ weights.

### 3.3. Results and discussions

#### 3.3.1. Characterization of materials

Figure 3.1 shows the XRD pattern of the obtained Ag$_2$NCN, PbNCN and ZnNCN. All diffraction patterns reveal sharp reflections, suggesting that the powders are highly crystalline in agreement with the previous reports. PbNCN peaks are indexed in the orthorhombic $Pna2_1$ space group (JCPDS No. 72-1116) with lattice parameters of $a = 5.557$ Å, $b = 3.868$ Å, $c = 11.735$ Å and a small amount of lead carbonate hydroxide (~5%). Ag$_2$NCN can be indexed in the monoclinic $P2_1/c$ space group with lattice parameters of $a = 7.315$ Å, $b = 6.010$ Å, $c = 6.684$ Å, and $\beta = 102.29^\circ$ (JCPDS No. 70-5232). Finally, ZnNCN is indexed in the tetragonal $I42d$ space group with lattice parameters $a = b = 8.800$ Å, $c = 5.432$ Å (JCPDS No. 70-4898), like Ag$_2$NCN no crystalline impurities were detected for ZnNCN.
Figure 3.1. XRD pattern with indexed peaks of PbNCN, Ag$_2$NCN and ZnNCN. The red dots correspond to the experimental patterns, the black lines to the calculated patterns, the green sticks to the theoretical Bragg positions and blue lines to the difference between experimental and calculated patterns.

Raman spectroscopy was used to gather additional information about the nature of cyanamide bonding in the three compounds (Figure 3.S1). As reported earlier, the [NCN]$^{2-}$ moiety can exist in two forms: the symmetric form $\equiv N = C = N^{−}$, usually called carbodiimide, and the asymmetric $N \equiv C − N^{2−}$, cyanamide. Four internal vibration modes are expected for both moieties: the symmetric ($\nu_s$) and anti-symmetric ($\nu_{as}$) stretching mode, and two bending modes, which are, usually, degenerated in the gas/liquid phase, giving rise to a single $\delta$ band.
In the case of carbodiimide, only the symmetric stretching ($\delta_{s}$) is active in Raman spectroscopy (and inactive in infrared spectroscopy), whereas all the vibrations of cyanamide ($\delta_{s}$, $\nu_{as}$, and $\delta$) are expected to be active in both Raman and infrared spectroscopy.\textsuperscript{90} Such considerations, which are valid in the gas/liquid phase may however, change in the solid state where some vibrations may become active due to a lowering of the local symmetry in the lattice. For the same reason, also some usually degenerate internal vibrations can split in the solid state. Moreover, the existence of crystallographically different [NCN]\textsuperscript{2−} groups in the lattice may increase the number of observed bands.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.2.png}
\caption{SEM micrographs and TGA curve of PbNCN, Ag\textsubscript{2}NCN and ZnNCN}
\end{figure}

In this case, the crystal structures of the three compounds are rather simple, and a single crystallographic [NCN]\textsuperscript{2−} group exists for ZnNCN, Ag\textsubscript{2}NCN and PbNCN. For the first compound, the two N–C bond distances are equal to 1.2 \AA, indicating the presence of carbodiimide moieties. On the contrary, two different N–C bond lengths exist in the structures of Ag\textsubscript{2}NCN (1.19 and 1.27 \AA) and PbNCN (1.16 and 1.30 \AA), indicating the presence of cyanamide. The different types of [NCN]\textsuperscript{2−} found in these compounds are in full agreement with the results of Raman spectroscopy (cf. Table 3.S1). In fact, the bands corresponding to all the vibrations are visible only in the Raman spectra of Ag\textsubscript{2}NCN and PbNCN, in agreement with the literature.\textsuperscript{34,173} The presence of the three bands is the spectroscopic signature of the asymmetric cyanamide (even though carbodiimide and cyanamide were suggested to coexist in Ag\textsubscript{2}NCN).\textsuperscript{100} Apart from the characteristic peaks of the [NCN]\textsuperscript{2−} unit, additional peaks in the region at $\sim$1000 cm\textsuperscript{−1} in PbNCN may arise from the impurity phase detected by XRD.\textsuperscript{90}. The asymmetric vibration ($\nu_{as}$), however, is absent in the Raman spectrum of ZnNCN, and this absence confirms the presence of [NCN]\textsuperscript{2−} in the form of carbodiimide in this compound.

Figure 3.2 shows typical SEM images and TGA curves (in air) of the as-synthesized Ag\textsubscript{2}NCN (a) PbNCN (b) and ZnNCN (c). PbNCN powder has a flower-like morphology with an
average size distribution around 3–6 µm, whereas Ag₂NCN is made of rectangular particles with a smooth surface, with a size around 300–700 nm in length and 50–300 nm in width. ZnNCN is more cauliflower-like, with homogenous aggregates around 3–6 µm. In terms of thermal stability under air, the three compounds are stable up to an average temperature of 400°C, i.e., stable enough to be used as electrode materials in batteries.

### 3.3.2. Electrochemical properties vs. Li

Cyclic voltammetry (CV) and galvanostatic profiles at C/10 (≈ 10 mA.g⁻¹ for PbNCN and Ag₂NCN, 25 mA.g⁻¹ for ZnNCN) in the potential range 0.005–3.00 V of the first two cycles for the three materials are shown in Figure 3.3. For PbNCN, a reduction peak is observed at 1.35 V during the first lithiation which compares well to the reduction potential of PbO (1.31 V) and hence suggesting an analog conversion of PbNCN into Pb and Li₂NCN. Similarly to PbO, the alloying reactions of Pb occur bellow 0.5 V. During the charge, the oxidation of Pb occurs at a higher voltage (2–3 V). During the second lithiation a slight increase of the reduction potential (1.5 V) is observed and may be explained by an improved electronic/ionic diffusion due to the electrochemically produced nanostructuration of the electrode, commonly observed in conversion/alloying reactions.

Ag₂NCN exhibits a reduction peak at a 1.75 V, in analogy with the first plateau observed in the corresponding galvanostatic profile. Such high reduction potential was also reported long ago by Cignini and Pistoia for the oxide analogue Ag₂O. These authors interpreted the occurrence of two plateaus as a sign of Li intercalation before proceeding conversion reaction. In the case of Ag₂NCN, only one plateau is observed suggesting no significant intercalation step but only the conversion reaction to form metal phase along with Li₂NCN. The other cathodic and anodic peaks at below 1 V can be assigned to the expected alloying reactions. The lower potential peaks of PbNCN are well defined both in cathodic and anodic scan, whereas in Ag₂NCN the anodic scan is better defined with two symmetric peaks at 0.12 V and 0.3 V, and can be ascribed to the expected formation of two different Li-Ag alloys during charge. Considering the second cycle in CV, the higher potential plateau around 1.8 V is completely absent in Ag₂NCN, but in PbNCN it exists with reduced magnitude and this can be seen in the
Figure 3.3. Cyclic voltammetry (0.05 mVs$^{-1}$) and corresponding galvanostatic profile (C/10, corresponding to 1 mole of Li reacted per mole of compound in 10 hours) of (a) PbNCN, (b) Ag$_2$NCN and (c) ZnNCN.

galvanostatic profile as well. This shows that the conversion reaction is not reversible in Ag$_2$NCN in the 0.01–3.00 V range, while it could be partially reversible PbNCN. However, from the combined analysis of both curves of Ag$_2$NCN, the reaction does not seem completed at 3 V, and thus additional reactions occur if the voltage window is extended to higher potentials (cf. Figure 3.52). Indeed, a reduction potential higher than 3 V has been reported for Ag$^+$ to Ag by Li et al.$^{163}$ Such potentials, on the other hand, are very high and beyond the possible
application of such material as a negative electrode, and are thus disregarded in this paper. In the case of ZnNCN, the CV profile is very similar to that of ZnO with virtually no activity above 1.2 V.\textsuperscript{181} The plateau at \(~0.4\) V in galvanostatic profile (0.1 V in CV) can be attributed to a combination of (1) conversion to Zn and Li\textsubscript{2}NCN,\textsuperscript{33,37} and (2) lithiation of Zn to form Li-Zn alloys, in analogy with the reaction mechanism of ZnO.\textsuperscript{165} The peak around 1.4 V in the first anodic scan can be assigned to metallic Zn oxidation and Li\textsubscript{2}NCN decomposition, as observed in the case of ZnO.\textsuperscript{165}

As a general rule, conversion materials suffer from a significant irreversible capacity in the first cycle.\textsuperscript{30,78} The three materials investigated here do not escape this rule, the huge capacities in the initial discharges being only partially reversible (30–50%). The extra initial capacity can be explained in terms of electrolyte decomposition with the expected formation of a solid electrolyte interphase (SEI) and of a polymeric gel-type layer at low potentials.\textsuperscript{146}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_4.png}
\caption{Specific discharge capacity and coulombic efficiency (CE) versus cycle number for PbNCN, Ag\textsubscript{2}NCN and ZnNCN}
\end{figure}
Concerning cyclability, (Figure 3.4) a drastic capacity fading is observed for both PbNCN and Ag$_2$NCN, due to the low reversibility of high potential conversion reaction. Hence the remaining capacity is mainly associated with alloying reactions at low potentials, as confirmed by the separate study of the two potential regions shown in Figure 3.52. In the case of lead, a similar mechanism is observed for the sulphur analogue PbS.\textsuperscript{178} Even though ZnNCN suffers from capacity fading, it exhibits a better performance compared to the other two materials, retaining a capacity close to 350 mAh.g$^{-1}$ after 10 cycles. The results obtained for ZnNCN are in very good agreement with those reported previously.\textsuperscript{33,34,37}

In conclusion, while PbNCN, Ag$_2$NCN and ZnNCN are found to be electrochemically active vs. Li, none of them could compare to the transition-metal carbodiimides in terms of cycle life.\textsuperscript{33}

**3.3.3. Reaction mechanism**

**3.3.3.1. PbNCN**

*Operando* XRD was applied to better understand the electrochemical mechanism of PbNCN while cycling at C/8 (Figure 3.5). To evaluate the reversibility of the conversion before and after the lithiation of lead, the cell was first discharged down to 1 V (first plateau), then charged up to 4 V, discharged to 0.005 V and finally charged again at 4 V. The intensity of the diffraction pattern of PbNCN gradually decreases with the amount of reacted lithium during the first discharge. No new diffraction peaks are observed, and only a gradual broadening around 31.5° (cf. zoom in Figure 3.53(b)) is detected, in line with the formation of amorphous Pb metal.\textsuperscript{182} During the first charge from 1 to 4 V, there is no distinct formation of crystalline PbNCN. However, the modifications of the diffraction pattern suggest the formation of an amorphous and/or nanostructured form of PbNCN: (i) the decrease of the intensity of amorphous Pb at 31.5°, and (ii) the increase of the background intensity in the 20–24° region which includes the (101), (102) and (011) PbNCN diffraction peaks (cf. Figure 3.53(b)). During the second discharge, the main peak of Pb slowly disappears at low potential starting from ~0.5 V, while two new broad humps grow at 25.2° and 35.7°, testifying the formation of poorly crystallized LiPb.\textsuperscript{178,182,183} These profiles reach their maximum intensity at 0.35 V, and then decrease with decreasing potential. Several other weak peak changes occur until the end of the discharge, where two main broad peaks are observed at 22.5° and 37.7°. It is difficult to
distinguish the final phase between Li_{10}Pb_{3} and Li_{7}Pb_{2} since both phases show diffraction peaks at such values of 2θ (Figure 3.5(c)).

Moreover, such broad peaks might also hide the contributions of other coexisting intermediate phases such as Li_{8}Pb_{3} and Li_{3}Pb.\textsuperscript{178,182,183} This lower potential alloying mechanism found to be completely reversible upon next charging by the sequential reformation of all the Li-Pb phases and finally Pb at 0.8V. The high voltage conversion reaction is only partially reversible: the partial oxidation of Pb at this high voltage is testified by the gradual decrease of the intensity of the Pb peak (Figure 3.5(d)), whereas the formation of

Figure 3.5. Operando XRD and associated galvanostatic charge/discharge curve of PbNCN
amorphous PbNCN can be hinted from the growth of a large peak at the typical positions of PbNCN reflections (Figure 3.53(b)).

Complementary information on the mechanism is provided by *ex situ* XAS. Figure 3.6(a) and (b) shows a typical galvanostatic profile for PbNCN and the corresponding Fourier transform of the Pb L$_3$-edge EXAFS spectra, respectively. The EXAFS signal clearly shows the changes starting from pristine PbNCN and the subsequent discharge and charged states.

![Figure 3.6. Galvanostatic profile (a), |χ(R)| plots (b) and fits of the EXAFS R space portion of the ex-situ data of PbNCN in (c). Blue and black circles are experimental real and imaginary parts respectively. Black and red lines are fitted real and imaginary parts respectively.](image)

The intensities of the peaks at 1.59, 2.35, 3.04 and 3.88 Å in the spectrum of pristine PbNCN decrease after the 1$^{st}$ plateau (D1), showing the consumption of PbNCN to form metallic Pb. At D2 position, the shape of the spectrum has changed significantly, and the two peaks of metallic Pb at 1.70 and 3.50 Å dominate the spectrum. At the end of the discharge, the spectrum changes again indicating the formation of lithium-lead alloys. In the first charged state (C3), the reappearance of peaks at 1.70, 3.00 and 3.72 Å and the slight
variation in Pb–Pb peak, point to the partial reformation of PbNCN. The variations in intermediate states C1 and C2 could be linked to alloying and de-alloying of Li-Pb phases.

Figure 3.6(c) shows the fitting results obtained in $R$-space and Table 3.52 shows the corresponding fitting parameters. The pristine state was fitted starting from the orthorhombic structure of PbNCN\textsuperscript{168} and the bond distances coincide perfectly with the theoretical values. For the second and the fourth shell, however, high $\sigma^2$ values are observed, indicating either a slightly disordered or partially amorphised structure, or more probably the presence of some lead carbonate as an impurity. The optimum fit for the next two intermediates D1 and D2 is obtained by using a mix of PbNCN and metallic Pb. The fitting of D2, the very small differences in Pb-Pb distance between LiPb and Pb, and the low X-ray scattering amplitude of Li make the two phases virtually impossible to distinguish by EXAFS. Both fitting considering either the bond distances in LiPb or with the bond distances in Pb provided exactly the same quality of fit. Therefore as seen in the operando XRD we suspect the formation of LiPb at this voltage. The lithium-lead alloy phase formed at the end of discharge was best fitted using the structure of Li$_{10}$Pb$_3$, the high value for $\sigma^2$ indicating a slightly amorphised structure. Upon charging, the first point C1 was fitted well using metallic Pb, and then C2 and C3 were fitted with metallic Pb and PbNCN, which reaches a concentration of 65% at 3.5 V.

According to several reports on the Li-Pb systems\textsuperscript{177,178,182,183}, the lithium-richest formed phase is expected to be Li$_{4.4}$Pb. However, in this case both operando XRD and ex situ XAS analysis agree that lithiation ends with the composition Li$_{3.5}$Pb. Taking into account the consumption of lithium relative to the formation of the SEI during first lithiation,\textsuperscript{146} such composition is compatible with the galvanostatic results, where the $5.5$ reacted Li per mole of PbNCN during the 2\textsuperscript{nd} lithiation can be assumed as $2$ Li for the conversion reaction and $3.5$ Li for the alloying one.\textsuperscript{33}

### 3.3.3.2. Ag$_2$NCN

The lithiation mechanism of Ag$_2$NCN was also investigated by ex situ XRD (Figure 3.7) and XAS (Figure 3.8). At the end of the first reduction plateau at 2 V, the XRD pattern of Ag$_2$NCN has almost vanished at the benefit of broadened peaks at 38.06°, typical of silver metal.\textsuperscript{180} The diffraction pattern of silver persists even at the end of the first discharge, even though a shift in the peak position is observed, possibly due to the insertion of some lithium
in the crystal structure of silver. Indeed, a large solubility domain for lithium in silver, up to about 50 at.% of lithium, is expected from the binary phase diagram of the two metals.\textsuperscript{162} During charge, two additional weak diffraction peaks are observed at 39.4° and 40.5° when reaching 0.3V suggesting the formation of a new Li-Ag alloy that is not observed during lithiation. This new phase is not reported in the previously cited phase diagram, but resembles strongly to the tetragonal AgLi\textsubscript{y} phase, of unknown composition, reported by Morales \textit{et al.} at the end of lithiation of a thin metallic silver film.\textsuperscript{180} During the charge, there is no sign of reformation of Ag\textsubscript{2}NCN up to 3.0 V.

\textit{Figure 3.7.} Ex situ XRD patterns of Ag\textsubscript{2}NCN at different lithiation stages.

The Fourier transform of the Ag K-edge EXAFS spectra of the electrodes at different discharge and charge states along with the corresponding galvanostatic profile is shown in Figure 3.8. Large differences are observed between pristine Ag\textsubscript{2}NCN and all the cycled samples. During the first discharge, the Ag–N shell at 1.6 Å disappears and is replaced by the dominant Ag–Ag shell at 2.01 and 2.77 Å. The slight evolution of the Ag–Ag peak in the following spectra is probably due to the formation of Li–Ag alloys, but no formation of Ag\textsubscript{2}NCN is visible at the end of charge. Fitting results are shown in Figures 3.8 (c) and Table 3.53 summarizes the corresponding fitting parameters. The spectrum of pristine Ag\textsubscript{2}NCN was
perfectly fitted using the monoclinic Ag$_2$NCN crystal structure.$^{92}$ Spectrum collected at 1.1 V during discharge was fitted with 80% metallic Ag and a residual amount (20 %) of Ag$_2$NCN. At the end of the discharge, about half of this metallic Ag is transformed into AgLi.$^{185}$ Similar fits are obtained for the two spectra measured during charging: however, a minor amount (about 25 %) of Ag$_2$NCN has to be added in the fitting strategy in order to obtain a reasonable fit, indicating that small amounts of Ag$_2$NCN could be formed back at 4 V.

![Figure 3.8. Galvanostatic profile (a), |χ(R)| plots (b) and fits of the EXAFS R space portion of the ex-situ data of Ag$_2$NCN in (c). Blue and black circles are experimental real and imaginary parts respectively. Black and red lines are fitted real and imaginary parts respectively.](image)

3.3.3.3. ZnNCN

The ex situ XRD pattern measured for ZnNCN at different states of discharge/charge is shown in Figure 3.9. As seen in the galvanostatic profile, the lithium reaction takes place at $\sim$0.4 V. At 0.2 V, ZnNCN has completely reacted with Li to form only amorphous species. Unfortunately, the main reflection of Zn and of the Cu current collector appear at the same position ($\sim$43.2°) in the diffraction pattern. However, the broadening at the bottom of the peak clearly indicates the formation of amorphous Zn during the discharge (see 3.54).$^{186,187}$ At the end of the discharge, the additional two broad humps around 24.5° and 40° indicate the
formation amorphous Li–Zn alloy. During the following charge, Li–Zn is reversibly consumed, and at the end of delithiation, some diffraction very broadened patterns close to those of ZnNCN are observed at 19°, 28°, 36° and 39°, indicating that the reversible conversion takes place to form an amorphous/nanosized form of ZnNCN. It is interesting to notice that the peaks at 36° and 39° are also clearly seen at lower potentials. Their presence is surprising, and might have several origins: it may come from a different unidentified phase, or from unequal degrees of lithiation, or even from a different phenomenon such as the anisotropic loss of long range order following specific preferential orientations. Additional in situ measurements are thus needed to better clarify their evolution.

![Ex situ XRD patterns of ZnNCN at different lithiation stages.](image)

The Fourier transform of the ex situ Zn K-edge XAS data collected for cycled ZnNCN electrodes are shown in Figure 3.10 along with the corresponding galvanostatic profile. During the first discharge, pristine ZnNCN is slowly converted, as testified by the strong reduction of the intensity of the Zn–N shell for sample D2, coupled to the growth of a new Zn–Zn shell at 2.64 Å, typical of metallic Zn. Virtually no difference is observed between the spectra of samples D2 and D3, indicating that zinc is probably very little involved in the reaction at low potential. This result, therefore, suggests that the additional capacity measured at low potential is mainly due to electrolyte decomposition. Along the following charge, the Zn–N shell starts growing again, indicating the partial recovery of ZnNCN in analogy with previous results on ZnO.
Figure 3.10. Galvanostatic profile (a), $|\chi(R)|$ plots (b) and fits of the EXAFS R space portion of the ex-situ data of ZnNCN in (c). Blue and black circles are experimental real and imaginary parts respectively. Black and red lines are fitted real and imaginary parts respectively.

The results of the fit of the EXAFS spectra are shown in Figure 3.10(c), while Table 3.54 shows the corresponding fitting parameters. The pristine state can be simply fitted starting from the crystallographic parameters of ZnNCN: bond distances coincide perfectly with the theoretical values. Also the spectrum of sample D1 can be directly fitted with the same model, confirming that Zn is not yet involved at this stage, and that all reactions at high voltage are probably connected to the decomposition of the electrolyte and the formation of the SEI, most probably stimulated by the high carbon content of the electrode. Sample D2, discharged at 0.3 V, was fitted using a combination of the first two shells of the metallic Zn and first shell of ZnNCN. In this case, the metallic Zn fraction largely dominates (87 %), and only 13 % of ZnNCN is still contained in the sample at this potential. The relatively high values
of the Debye-Waller factors ($\sigma^2$) observed for the Zn shells indicate a somewhat disordered or amorphised structure.\textsuperscript{146} Sample D3 at the end of discharge cannot be fitted using simply the structure of Zn metal, and an optimal fit is obtained only by including first two shells of LiZn. A phase composition of about half Zn and half LiZn is obtained from the fit. All the charged states were fitted using the combination of metallic Zn and ZnNCN, clearly indicating the formation of ZnNCN already from 0.3 V. It interesting to notice that, unexpectedly, the amount of ZnNCN is larger in sample C1 than in sample D2: this discrepancy can be explained by the presence of some unreacted ZnNCN in C1, given the corresponding conversion plateau slightly shorter than that of the other \textit{ex situ} samples (cf. Figure 3.S9). At the end of charge, more than half of the zinc is transformed back to ZnNCN.

From the above findings, the electrochemical reaction mechanism of Li with ZnNCN can be described as a conversion reaction followed by a partial alloying mechanism. By analogy with well-known FeNCN, upon first discharge zinc carbodiimide is converted to Li$_2$NCN and metallic Zn, and then the newly formed metallic Zn is partially lithiated to LiZn. Upon charging, at least partial back-conversion of Zn to ZnNCN is observed.

### 3.3.4. Capacity fading mechanism

By combining the results of \textit{operando} XRD and \textit{ex situ} XAS along with the electrochemical results, one can try to compare and generalise the electrochemical mechanism of these three materials. Indeed, the lithiation starts with a conversion reaction leading to the formation of metal nanoparticles followed by an alloying reaction. Like all conversion-type materials, huge irreversible capacities in the initial lithiation are observed, probably due to the irreversible electrolyte degradation leading to a SEI layer and the reversible formation an electrolytic polymeric gel.\textsuperscript{146} Upon delithiation, the de-alloying at low potential is completely reversible, leading to the formation of a metal phase. However, only part of such reformed metal is back-converted to the starting material. Contrarily to transition-metal carbodiimides (where the metals do not undergo the alloying reaction), the compounds studied here suffer from a more pronounced capacity fading that seems to concern both conversion and alloying reactions.

PbNCN and Ag$_2$NCN show a fast capacity fading during the early cycles, providing a reversible capacity of less than 200 mAh.g$^{-1}$ already after 20 cycles. In the case of ZnNCN, on the contrary, the capacity fading is less pronounced, delivering capacities exceeding 300
mAh.g\(^{-1}\) after the rate capability test (cf. Figure 3.4). This difference is correlated to the higher voltage of the conversion reaction (Ag, Pb > Zn) and could also be connected to the nature of the [NCN\(^2^-\)] moiety. In fact, for Ag and Pb compounds contain the covalently bonded cyanamide form, whereas [NCN\(^2^-\)] is in the carbodiimide configuration in the more ionic Zn analogue. In this case, the carbodiimide configuration is contained in Li\(_2\)NCN, which is the species formed during lithiation. Therefore, it might be more advantageous to start from a similar configuration, avoiding its continuous modification upon cycling, to gain in reversibility.

Finally, owing to the significant gap between the potentials of conversion and alloying reaction of PbNCN and Ag\(_2\)NCN, it is possible to separate each contribution by selecting the appropriate voltage window (see Figure 3.S2a and 3.S2b). For PbNCN, it is clear that capacity fading is primarily attributed to the conversion reaction since the alloying reaction still delivers 230 mAh.g\(^{-1}\) (the equivalent of 2 Li) after 10 cycles, whereas the conversion reaction delivers less than 50 mAh.g\(^{-1}\) (the equivalent of 0.4 Li). Similar experiment with Ag\(_2\)NCN shows that both conversion and alloying contribution fade at a comparable rate. Such contribution of separation is not possible for ZnNCN since the potentials of the two reactions are virtually identical.

3.4. Conclusions

The electrochemical lithiation of ZnNCN, PbNCN and Ag\(_2\)NCN goes through a two-step mechanism, starting with a conversion reaction followed by alloying. Even though these materials show attractive initial specific capacities (first lithiation), a rapid fading is observed during the early cycles. By the combination of long and short range analytical tools such as operando XRD and ex situ XAS, it was possible to establish a general reaction mechanism than can be written:

1) Conversion reaction: M\(_a\)NCN + 2Li → M + Li\(_2\)NCN (a = 1 or 2; M = Pb, “Ag\(_2\)” or Zn)

2) Alloying reaction: M + xLi → Li\(_x\)M with 1 < x < 3.5

The conversion reaction is found to be partially reversible for the three metals, while the reversibility of the alloying reaction depends on the metal: it is highly irreversible for compounds containing cyanamide bonding (PbNCN and Ag\(_2\)NCN), and more reversible for the
carbodiimide ZnNCN. In the case of PbNCN and Ag$_2$NCN, the conversion reaction occurs at higher voltage compared with ZnNCN, and seems to be correlated with the nature of bonding in the NCN group. Compounds that contain cyanamide bonding show a faster capacity fading (less than 200 mAh.g$^{-1}$ after 10 cycles). By contrast, the carbodiimide ZnNCN could maintain reasonable specific capacity (comparable to that of graphite) for more than 100 cycles.

Compared to carbodiimides of transition-metals, the studied materials show rather bad performance, and no capacity improvement could be observed from the combination of conversion and alloying reaction. On the contrary, a rapid capacity fading is observed especially for PbNCN and Ag$_2$NCN.
3.5. Supporting information

Figure 3.5.1. Raman spectra of PbNCN, Ag$_2$NCN and ZnNCN

Table 3.5.1. Vibrational frequencies of PbNCN, Ag$_2$NCN and ZnNCN

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Figure 3.S2. Low voltage and High voltage cycling of PbNCN (a) & (b) and Ag$_2$NCN (c) & (d) at a c-rate of C/10.

The low and high voltage cycling of PbNCN and Ag$_2$NCN after 10 cycles is shown in Figure 3.S2: the low potential plateau of the PbNCN is found to persist whereas a large fading is observed at high voltage region. For Ag$_2$NCN, the fading is observed in both high and low voltage regions leading to the fastest fading since after only the 4$^{th}$ cycle retained capacity drops below 200 mAh$\cdot$g$^{-1}$. It is worth noting that for Ag$_2$NCN, the reaction continues even after 3.5V, still it invades after a no. of cycles.
Figure 3.S3. Galvanostatic profile and magnification of the operando XRD of PbNCN

Figure 3.S4. Zoom on the 43° region of the ex situ XRD of ZnNCN
Figure 3.55. Comparison of different electrochemical curves of PbNCN (a) Ag₂NCN (b) ZnNCN (c)

A shift in the electrochemical curve of *ex situ* XAS is coming from the difference in the formulation of electrodes, more carbon has been used (50%) in the formulation of *ex situ* XAS electrodes, which causes a larger amount of lithium consumption due to electrolyte degradation at the surface of carbon at the beginning of the first discharge.
Table 3.52. Fitting parameters of the EXAFS portion of the ex-situ data of PbNCN

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Table 3.53. Fitting parameters of the EXAFS portion of the ex-situ data of Ag₂NCN

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Table 3.54. Fitting parameters of the EXAFS portion of the ex-situ data of ZnNCN

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<td>1.990</td>
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75
In the study of Pb, the first coordination shell of spectra D3 and C1 was impossible to fit with reasonable parameters for nitrogen or lithium neighbour shells, and was left out of the fit. In both cases, this contribution seems to derive from oscillations at relatively high values of K (between 8 and 12), and can be largely suppressed by reducing the extraction range in K, as seen in the Figure 3.56. A smaller window in the case space, in fact, suppresses most of the peak at low R.

*Figure 3.56. Original EXAFS spectrum of sample D3 in PbNCN(a) Extraction up to k=12 (b) Extraction up to k=8 (c).*

The spectra of D3 and C1 are those with the lowest overall intensity (Figure 3.57). Therefore, the possible presence of an additional spurious oscillation of possibly of instrumental origin, more visible when the signal intensity is low, might be the cause of these features at low R which cannot be fitted appropriately. In any case, no reasonable fit could be obtained for this feature.
In order to confirm the stability of the electrode materials after soft ball milling, XRD patterns were measured for both ZnNCN and Ag$_2$NCN pristine powders and formulated electrodes. From the patterns shown in Figure 3.8, it is clear that after ball milling both ZnNCN and Ag$_2$NCN also preserve their crystallinity. The additional broad peaks in the electrode patterns come from the Kapton film, which was used to protect the dried electrodes.
Figure 3.59. Galvanostatic profiles of ZnNCN XAS ex situ points D2 (discharged until 0.3 V – blue) and C1 (charged until 0.3 V – Red).
Chapter 4: Combined intercalation and conversion reaction
In this chapter we present the main findings of the study of electrochemical properties of the unique known trivalent transition metal carbodiimide, Cr$_2$(NCN)$_3$. In the previous two chapters, we have introduced two different lithiation mechanisms seen in the cyanamide and carbodiimide materials. In the case of chromium carbodiimide, both theoretical and experimental investigations highlighted a singular lithiation process, which involves both intercalation and conversion reactions.

For the first time both theoretical calculations and experimental investigations allowed a deep examination of the possible reaction pathways for Cr$_2$(NCN)$_3$ upon lithiation. We identified and evaluated via DFT calculations three possible pathways: (i) pure conversion reaction (ii) intercalation reaction and (iii) a combination of the two first pathways. In addition, the chromium lithiation process can follow either the two-step Cr$^{3+}$–Cr$^{2+}$–Cr$^0$ sequence or a direct one-step process Cr$^{3+}$–Cr$^0$. DFT calculations (performed by Dr. Kaixuan Chen from the research group of Prof. Richard Dronskowski at RWTH Aachen University) predict that a sequential intercalation and conversion “Cr$^{3+}$–Cr$^{2+}$–Cr$^0$” pathway is much more favourable than the direct “Cr$^{3+}$–Cr$^0$” conversion. This prediction was validated experimentally by operando XRD and XAS. As for the study of CoNCN (chapter 2), the operando XAS measurement were performed at the ROCK beamline at SOLEIL Synchrotron in Scalay with the help of Dr. Antonella Iadecola (RS2E, Amiens).

In brief, operando XAS confirmed that the lithiation occurs through a two-step process that involves two redox couples (Cr$^{3+}$/Cr$^{2+}$ and Cr$^{2+}$/Cr$^0$). Operando XRD, on the other hand, evidenced that the first of the two process corresponds to the intercalation of lithium in the Cr$_2$(NCN)$_3$ layered structure. This singular mechanism seems to be behind the outstanding electrochemical performance obtained with this compound. Indeed, Cr$_2$(NCN)$_3$ sustains a high specific capacity of 600 mAh.g$^{-1}$ over more than 900 cycles at 2C current rate (240 mA.g$^{-1}$ ) with a coulombic efficiency close to 100%. Such performance is superior to that of the other divalent carbodiimides$^{33}$ and chromium oxide analogue Cr$_2$O$_3$.$^{24,189}$ These results are the object of a publication recently submitted, which is reported in the following of the chapter.
Reversible high capacity and reaction mechanism of $\text{Cr}_2(\text{NCN})_3$ negative electrodes for Li-ion batteries

Jeethu Jiju Arayamparambil$^{1,2,†}$, Kaixuan Chen$^3$, Antonella Iadecola$^4$, Markus Mann$^3$, Xlanji Qiao$^3$, Bernard Fraisse$^1$, Richard Dronskowski$^{3,5,*}$, Lorenzo Stievano$^{1,2,4,*}$, Moulay Tahar Sougrati$^{1,2,4,*}$

$^{†}$These authors contributed equally to this work and should be both considered as first authors.

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$^4$Réseau sur le Stockage Electrochimique de l’Energie, CNRS FR3459, Amiens, France
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(Article submitted for publication in September 2019)

4.1. Introduction

Global energy demand and the necessity to store electrical energy is a hot topic in today’s research. In this context, the development of Li-ion batteries attracts a great amount of attention due to their high energy-density characteristic. The capacities of the commercially graphite-based Li-ion batteries, however, already reach the technological limit (372 mAh.g$^{-1}$), so in the past decades great efforts have been devoted to the development of high-capacity and long cycle life anode alternatives.$^{30-32}$ The main goal of this research is to understand their reaction mechanisms such as to discover safer and higher specific capacity anode materials. In order to achieve that, numerous candidates from the $p$-block of the periodic table have been explored such as silicon, tin, antimony, phosphorous as well as their oxides, sulfides, carbonates, etc.$^{11-28}$ Conversion-type materials have also been widely explored.$^{78,190-192}$ Among them, transition-metal based compounds seem to be potential alternatives for graphite owing to their high theoretical specific capacity. Nonetheless, several problems such as high irreversible capacity in the first lithiation and the weak cycle life prevent their practical use. The main reasons of such drawbacks are the formation of
unstable SEI layers and huge volume expansion during the lithiation and delithiation processes.\textsuperscript{125}

A newer class of transition-metal carbodiimides (MNCN, with $M = \text{Fe, Mn, Co, Cu, Zn, Ni}$) have emerged as promising anode materials for both Li- and Na-ion batteries. In 2016, our group reported the excellent performance of FeNCN with, for example, an impressive rate capability up to 30C and stable capacity for more than 100 cycles.\textsuperscript{33} This paper was followed by other reports exploring the reaction mechanism of transition and main-group metal carbodiimides vs. Li and Na ions.\textsuperscript{34–37,113} Like most transition-metal based anode materials, these materials are expected to react electrochemically with lithium through a conversion reaction but the reaction pathways or mechanisms of these carbodiimides, especially the trivalent ones, are not yet completely clarified.

In this work, we investigate the properties of Cr$_2$(NCN)$_3$ – the only known trivalent transition-metal carbodiimide, to the best of our knowledge – as anode material for Li-ion batteries. It is worth recalling that Cr$_2$O$_3$ – the oxide analogue of Cr$_2$(NCN)$_3$ – has already been studied for its high theoretical capacity and low operating voltage compared to other transition-metal oxides.\textsuperscript{193–198} Cr$_2$O$_3$ reacts electrochemically with Li via a conversion reaction involving one redox couple (Cr$^{3+}$/Cr$^0$). However, the low electrical conductivity, the unstable SEI film, and the large volume change during cycling has hindered its possible application as anode material. This work shows that the electrochemical mechanism of the reaction of Cr$_2$(NCN)$_3$ with lithium is completely different from that of its oxide analogue, and how this difference influences its performances in lithium batteries.

### 4.2. Experimental methods

#### 4.2.1. Material synthesis

Chromium carbodiimide was prepared by metathesis route via the reaction between CrCl$_3$ and ZnNCN. All the synthetic steps were carried out in an argon-filled glove box. The reaction precursors consist of CrCl$_3$ and ZnNCN in a molar ratio of 2:3 and LiCl/KCl (46:54) as a flux. The reactants and flux were initially heated at 300 °C under dynamic vacuum for 12 h and 550 °C for another two days. Then the resulting powder was washed with diluted HCl followed by water and acetone to get the final green-colored Cr$_2$(NCN)$_3$ powder.\textsuperscript{199}
4.2.2. Material characterization

X-ray diffraction (XRD) patterns were collected with PANalytical Empyrean equipped with Co Kα source. The profile fitting was done by using PANalytical high score plus. Morphological characterization was performed by scanning electronic microscopy (Hitachi S-4800 scanning electron microscope equipped with a field emission gun). Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy measurements were done employing a Bruker spectrometer IFS66V equipped with an ATR diamond crystal and a confocal LabRAM Aramis spectrometer (Horiba), equipped with a HeNe laser, an 1800 grooves/mm grating, and a Peltier-cooled CCD detector respectively. Thermal gravimetric analysis was performed using a NETZSCH Jupiter STA 449 F1 thermobalance with a ramp rate of 5 °C/min in air flow.

4.2.3. Electrochemical measurement

The electrochemical tests were carried out in coin-type half cells with a lithium foil as both counter and reference electrode. Electrodes were prepared by mixing 60 wt. % Cr₂(NCN)₃ powder, 20 wt. % conductive additives (carbon black and vapor-grown carbon nanofibers, VGCF) and 20 wt. % carboxymethyl cellulose (CMC) as the binder together with water. The aqueous slurry was then coated over a copper foil via a traditional Doctor blade technique with a thickness of 150 µm, dried at room temperature in air and finally at 100 °C under vacuum for 12 hours. The disc-shaped electrodes were cut from the film with an active material loading of 1 to 2 mg.cm⁻² and mounted in coin cells inside an argon-filled glovebox. Whatman glass fiber GF/D and a 1 M LiPF₆ solution in ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) (1:1:3 in weight) with 2% vinyl carbonate (VC) and 5% fluoroethylene carbonate (FEC) additives were used as was employed as the separator and the electrolyte, respectively. Galvanostatic measurements were performed using Biologic and/or Neware systems at C/n rate (indicating 1 mole of Li reacted in n hours per mole of Cr₂(NCN)₃). Cyclic voltammetry (CV) measurements were performed with a scan rate of 0.05 mV.s⁻¹ between 0.005 and 3 V.

4.2.4. Operando and ex situ measurement

Operando XRD measurements were carried out using self-supported electrodes in a specially designed in situ cell.²⁰⁰ All the Cr K-edge XAS measurements (operando and ex situ) were carried out in the transmission mode at the ROCK beamline¹³⁴ of SOLEIL synchrotron.
For the *in situ* XAS measurements an aqueous slurry containing the formulated electrode material was directly casted on the beryllium window of the specially *in situ* cell\textsuperscript{133}, whereas *ex situ* electrodes were 6 mm diameter pellets recovered from the coin cells cycled until the desired voltage. In XAS experiments, the monochromatic X-ray beam intensity was measured by three consecutive ionization detectors, with the *in situ* cell placed between the first and the second ionization chamber and a Cr metal reference between the second and the third one, respectively, to ensure the energy calibration during the XAS experiment. Electrochemical measurement began initially at C/8 rate, but was later speeded up first to C/5, C/2 and then to C in order to complete the collection of the XAS data of the whole lithiation process within the allocated beamtime. Selected *ex situ* XAS spectra were measured to study the following delithiation. The energy calibration and normalization of the *operando* XAS spectra were performed using the Athena software.\textsuperscript{135} The normalised *operando* spectra were analysed globally using a chemometric approach implying principal component analysis (PCA) and multivariate curve resolution–alternating least squares (MCR–ALS), via a procedure described in detail by Fehse *et al*.\textsuperscript{138} This analysis allows one to extract the pure spectral components that are necessary to describe, via adapted linear combinations, the entire dataset. Such components, as well as the *ex situ* spectra, were finally analysed using the Artemis software.\textsuperscript{135} Fourier transforms of the EXAFS data were performed in the 3-10.5 Å\(^{-1}\) k range, and the fitting was done in the R space up to 3.5 Å.

**4.2.5. DFT simulation**

We performed spin-polarized calculations with projector-augmented-wave (PAW) potentials, as implemented in the Vienna ab-initio simulation package (VASP).\textsuperscript{201} The exchange-correlation parameterization as provided by Perdew–Burke–Ernzerhof (PBE) was adopted. To correctly include the coulombic interactions among the \(d\) levels in the transition metals, we used a Hubbard \(U = 3.5\) eV for Cr, as successfully used in prior research by Jain *et al*.\textsuperscript{202} A plane-wave energy cutoff of 600 eV was set. The Vaspkit was used to generate Γ-centered Monkhorst–Pack \(k\)-meshes with a recommended value of 0.04 \(2\pi/\text{Å}\), which yields, for example, a \(k\)-mesh of \(5 \times 5 \times 1\) (\(7 \times 7 \times 3\)) for the simulated \(\text{Cr}_2(\text{NCN})_3\) (\(\text{Li}_2\text{NCN}\)) unit cell. The Pymatgen tool was employed to establish hundreds of intermediate compounds during the discharge process.\textsuperscript{203}
4.3. Results and discussions

4.3.1. Characterization

The refinement (Figure 4.1) of the XRD pattern of pristine Cr\(_2\)(NCN)\(_3\) powder confirms that it crystallizes in the rhombohedral space group \(R\bar{3}m\) in agreement with Tang et al.\(^{199}\) The crystal packing of alternating layers of cations and anions along the c-axis is similar to other divalent metal carbodiimides. Because of the larger cationic charge, however, the packing of the Cr layers is less dense than in the latter carbodiimides, with each metal atom surrounded by only three Cr neighbours. The chromium coordination by N atoms corresponds to a slightly distorted N\(_6\) octahedron.

The FT-IR and Raman spectra are shown in Figure 4.2(a). The IR results are comparable with those of Tang et al.\(^{199}\), with the asymmetric stretchings of the (NCN)\(^2-\) units visible as a strong peak at 2003 cm\(^{-1}\) and a broad peak between (2050-2150) cm\(^{-1}\). The bending contributions are visible at 633 cm\(^{-1}\) and 695 cm\(^{-1}\). As reported previously and as expected from the \(D_{\infty h}\) point-group symmetry of the N=C=N\(^2-\) carbodiimide moiety, its symmetric
stretches is generally inactive in IR, and active only in Raman spectroscopy. In the case of the N≡C–N²⁻ cyanamide unit, however, such vibrations are active in IR providing bands also in the range 1200–1400 cm⁻¹ but they are absent in this case and rule out the presence of such ligands. From the Raman spectrum, the symmetric NCN vibration is for the first time found as a broad bump in the range of 1300–1420 cm⁻¹. The asymmetric and the deformation band ranges nicely match the IR spectrum values.

![Figure 4.2. FT-IR and Raman (a) spectra. SEM micrograph (b) and TGA curve (c) of Cr₂(NCN)₃.](image)

The SEM image reveals an intergrowth of flakes that look like desert roses petals with a size of several micrometers, as shown in Figure 4.2(b). As reported for other transition-metal carbodiimide materials, Cr₂(NCN)₃ also undergoes a minor initial weight loss (~1.1%) in the 0–350 °C range followed by an abrupt loss (~28%) at 400 °C, as shown from the TGA in Figure 4.2(c). The initial loss is mainly due to the departure of adsorbed water from the surface of the sample, whereas the second one corresponds to the decomposition into chromium oxide. The final weight loss step from 500 to 700 °C can be attributed to the decomposition to form nanocrystalline chromium oxide as seen in the normal transition-metal oxides.

### 4.3.2. Electrochemical performance

The electrochemical performance of Cr₂(NCN)₃ was investigated by cyclic voltammetry and galvanostatic cycling. The cyclic voltammetry results obtained for Cr₂(NCN)₃ between 0.005–3 V at 0.05 mV.s⁻¹ are shown in Figure(a). Like all transition-metal carbodiimides, a significant difference between the first cycle and subsequent ones is clearly visible in the CV profile. This behavior is typical of conversion-type materials which
undergo huge morphological and structural changes during the first lithiation.\textsuperscript{78} Indeed, the sharp and intense cathodic peak (P1) located at 0.43 V is attributed to conversion of micrometric Cr\(_2\)(NCN)\(_3\) particles into a nano-composite made of chromium metal and Li\(_2\)NCN (\textit{vide infra}). During the second and subsequent lithiation processes, the cathodic broadened peak (P2) takes place at higher potential (0.85 V), indicating a lower polarization for the conversion reaction induced by the typical material nanocrystallization. While cathodic scans show only one broadened peak, the anodic ones (P3, P4) exhibit two broadened peaks at 1.5 and 2.5 V associated the oxidation of chromium suggesting a two-step mechanism (cf. inset in Figure 4.3(a)). The minor peaks below 0.3 V are probably due to some (de)intercalation of lithium ions in/from the carbon matrix.\textsuperscript{24,205} While the galvanostatic profile (Figure 4.3(b)) is in good agreement with CV observations concerning the nature of the involved processes, it also highlights the high irreversible capacity during the first lithiation. Indeed, depending on the current density, the initial specific capacity can range from 1200 to 800 mAh.g\(^{-1}\) for C/10 to C/4, respectively, which significantly exceeds the theoretical capacity of 718 mAh g\(^{-1}\). This irreversible extra capacity generally disappears after 10 cycles (see Figure 4.3(c)). This phenomenon is commonly observed in conversion anode materials and constitutes one of their main drawbacks.\textsuperscript{146} It is usually explained, in analogy with transition-metal oxide anode materials\textsuperscript{24,125,205}, by the reversible formation/dissolution of a thin polymeric gel film at the surface of the transition-metal nano-particles (created by the conversion of the initial compound) via the partial degradation of electrolyte components such as alkyl carbonates at low potentials.\textsuperscript{26,125,145,207–209}

Regarding capacity retention and cycle life, after the first 10 cycles the Cr\(_2\)(NCN)\(_3\) electrode stabilizes and maintains a stable capacity exceeding 600 mAh.g\(^{-1}\) for more than 500 cycles when cycled at a current density of 360 mA.g\(^{-1}\) (Figure 4.3(c)), and more than 500 mAh.g\(^{-1}\) are maintained after 950 cycles (Figure 4.51). The coulombic efficiency rapidly reaches an average of 99.2 \% and increases slightly to 99.7 \% after 500 cycles. It is worth noting that the observed increase of capacity around 200 cycles is also commonly observed in transition-metal conversion anode materials.\textsuperscript{24,145}

Another excellent property of Cr\(_2\)(NCN)\(_3\) electrode is its rate capability. Figure 4.3(d) shows that even at 4C (480 mA.g\(^{-1}\)) a capacity as high as 540 mAh.g\(^{-1}\) can be retained without any deterioration of the active material, showing that this anode material can easily manage fast (dis)charging. This excellent capability rate reflects the overall high conductivity (both
electronic and ionic) of the chromium carbodiimide electrode. All these excellent electrochemical features make \( \text{Cr}_2(\text{NCN})_3 \) the best carbodiimide observed until now in terms of capacity and capacity retention.

![Graphs showing cyclic voltammetry and galvanostatic profiles](image)

**Figure 4.3.** Electrochemical performance of \( \text{Cr}_2(\text{NCN})_3 \) vs. Li: (a) cyclic voltammetry (0.05 mVs\(^{-1}\)), (b) galvanostatic profile at C/10, (c) specific capacity at 3C rate, and (d) rate capability versus cycle number.

**4.3.3. DFT study**

In this section, we employed density-functional theory to investigate the detailed reaction mechanism of \( \text{Cr}_2(\text{NCN})_3 \) during the lithiation process. It is well-known that the cell voltage \( \Phi \) of a Li-ion battery significantly decides about its practical application. \( \Phi \) can be computed according to the battery equation. For cathodic \( \text{Cr}_2(\text{NCN})_3 \) in combination with anodic lithium metal, it is written as:

\[
\text{Cr}_2(\text{NCN})_3 + 6\text{Li} \rightarrow 3\text{Li}_2\text{NCN} + 2\text{Cr}
\]

\[
\Phi = -\frac{\Delta G}{zF} \approx -\frac{\Delta E}{zF}
\]
where \( z \) denotes the electron transfer that has been carried by Li cations and \( F \) is the Faraday constant (one mole of electrons). To start with, we tested the influence of the Hubbard \( U \) term on the cell voltage. Not too surprisingly, we obtained a cell voltage of 1.6 V (0.9 V) for \( \text{Cr}_2(\text{NCN})_3 \), which yields a voltage error of 0.5 V (0.2 V) within the PBE (PBE+\( U \)) method, as compared with the experimental 1.1 V. It indicates that the \( U \) correction gives a better coulombic interaction and improves the electrochemical (voltage) data accuracy. Therefore, in the following simulations, we used the PBE+\( U \) for reasons of accuracy.

Table 4.1. Number of the computations to survey the possible Li–Cr–NCN ternary compounds.

<table>
<thead>
<tr>
<th>Structural basis</th>
<th>Space group</th>
<th>Number of calculated compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cr}_2(\text{NCN})_3 )</td>
<td>( \bar{R}3c ) (no.167)</td>
<td>30</td>
</tr>
<tr>
<td>( \text{Li}_2\text{NCN} )</td>
<td>( I4/mmm ) (no.139)</td>
<td>41</td>
</tr>
<tr>
<td>( \text{CrNCN} )</td>
<td>( P6_3/mmc ) (no.194)</td>
<td>51</td>
</tr>
<tr>
<td>( \text{LiCr(NCN)}_2 )</td>
<td>( Pbcn ) (no.60)</td>
<td>32</td>
</tr>
</tbody>
</table>

In order to understand the reaction pathway during a discharge process, one needs to conduct a thorough survey of the possible intermediate compounds, that is, Li–Cr–NCN ternaries. Here, four structural bases were adopted, i.e., \( \text{Cr}_2(\text{NCN})_3 \), \( \text{Li}_2\text{NCN} \), \( \text{CrNCN} \) and \( \text{LiCr(NCN)}_2 \), as shown in Figure 4.S2 in the supporting information. A \( 3 \times 3 \times 1 \) supercell was used for \( \text{Li}_2\text{NCN} \) (or \( \text{CrNCN} \)) and \( 2 \times 1 \times 1 \) for \( \text{LiCr(NCN)}_2 \). For \( \text{Cr}_2(\text{NCN})_3 \), the unit cell was used since the number of atoms included in a unit cell is large enough. Based on these structures, Li insertion and (or) Li/Fe exchange were conducted to create 154 Li–Cr–NCN ternaries at various configurations. The Ewald summation technique implemented in Pymatgen was employed to identify the compound that gives the lowest electrostatic energy at each given configuration, as tabulated in Table 4.1.

As one could suspect from the battery equation, there are two ideal reaction pathways for trivalent carbodiimides upon lithiation. The first one presents a conversion reaction to occur only after a complete intercalation reaction, in other words, sequential intercalation and conversion (denoted as \( \text{Cr}^{3+}–\text{Cr}^{2+}–\text{Cr}^0 \)). The second one indicates a pure conversion reaction from the very beginning to the end of lithiation without any intercalation reaction, that is, one-step conversion reaction (denoted as \( \text{Cr}^{3+}–\text{Cr}^0 \)). In addition, there could
be the third one that combines both, in which the intercalation and conversion reactions occur simultaneously (denoted as “mixing” mechanism).

![Figure 4.4. The phase diagram for Li–Cr–NCN ternaries and (a) schematic chart as regards the different reaction pathways of Cr$_2$(NCN)$_3$ electrode upon lithiation (b).]

These established compounds were then classified depending on which pathway they belong to, as depicted in Figure 4.4. As regards “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0}$”, Li ions intercalate into the Cr$_2$(NCN)$_3$ cathode, without introducing a major structural transformation (at low lithium content). A concomitant reaction occurs in the electrode where Cr$^{3+}$ ions get reduced into Cr$^{2+}$, rather than into elemental Cr$^{0}$. In this stage, the Li–Cr–NCN ternaries share a general formula Li$_x$Cr$_2$(NCN)$_3$ (0 < x ≤ 2). After a full Li intercalation, a conversion reaction dominates, where two Li$^+$ ions exchange for one Cr$^{2+}$ (due to the charge balance) and the ternaries share a general formula of Li$_x$Cr$_{3−x/2}$(NCN)$_3$ (2 < x < 6). For “Cr$^{3+}$–Cr$^{0}$”, no intercalation reaction occurs and a conversion reaction dominates from the very beginning. It means that three Li$^+$ ions exchange for one Cr$^{3+}$ for charge compensation, which yields a general formula of Li$_x$Cr$_{2−$
$x/3(\text{NCN})_3 \ (0 < x < 6)$ for the ternaries. In addition, the compounds that follow the so-called “mixing” mechanism have a more flexible atomic configuration.

Here, we looked at the formation energy to determine whether a certain Li–Cr–NCN ternary is thermodynamically stable.

$$E_{\text{formation}} = E[\text{Li}_x\text{Cr}_y(\text{NCN})_3 + (2 - y)\text{Cr}] - \frac{x}{6}E[3\text{Li}_2\text{NCN} + 2\text{Cr}] - \left(1 - \frac{x}{6}\right)E[\text{Cr}_2(\text{NCN})_3] \quad (3)$$

The ternaries which yield negative formation energies were shown in the phase diagram (Figure 4.4(a)). Most of the stable compounds belong to the “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0\text{r}}$” or the “mixing” mechanism, so the “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0\text{r}}$” pathway is energetically preferred. Following “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0\text{r}}$”, one can observe an inflection point between pure intercalation and pure conversion reactions. At stage (1), two Li ions delivered through the electrolyte and two electrons from the external loop gather at the electrode Cr$_2$(NCN)$_3$ to form Li$_2$Cr$_2$(NCN)$_3$. At stage (2), as the lithiation continues, four Li ions and electrons join into the electrode to eventually form Li$_2$NCN, accompanied with a deposition of elemental Cr$^0$. For the “Cr$^{3+}$–Cr$^{0\text{r}}$” mechanism, however, a direct conversion reaction dominates. During stage (3), six Li ions and electrons entered the electrode with a concomitant deposition of elemental Cr$^0$ (Figure 4.4(b)).

Figure 4.5(a) shows the formation energies of the intermediate compounds with respect to the Li content. The set of ground-state structures giving an energy lower than any other structure of the same composition forms an energy convex hull. The convex hull for the “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0\text{r}}$” (“Cr$^{3+}$–Cr$^{0\text{r}}$”) pathway is displayed with a red solid (blue dotted) line. It shows that at a wide range of Li content, namely the Li–Cr–NCN ternaries following the “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0\text{r}}$” pathway, is much more stable than the “Cr$^{3+}$–Cr$^{0\text{r}}$” counterparts. Resembling the cell voltage, each voltage pair (two stable ternaries with adjacent Li content) gives a voltage plateau. By combining all voltage plateaus along the reaction pathway (energy convex hull), we obtain the corresponding voltage profile depicted in Figure 4.5(b). For comparison, we also present the experimental profile obtained below C/10 rate at the second cycling in a Li-ion battery. The computed stepwise profile for the “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0\text{r}}$” pathway agrees nicely with the experiment and, therefore, confirms the hypothesis that a conversion reaction occurs only after a complete intercalation reaction for Cr$_2$(NCN)$_3$ upon lithiation.

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**Figure 4.5.** The formation energies (and energy convex hull) of the calculated Li–Cr–NCN ternary compounds and (a) voltage profile of Cr$_2$(NCN)$_3$ upon lithiation in a LIB (b).

During the discharge (lithiation) process of the Cr$_2$(NCN)$_3$ electrode, a reduction reaction occurs. The electrochemical reduction potentials of Li$^+$/Li$^0$, Cr$^{3+}$/Cr$^{2+}$ and Cr$^{3+}$/Cr$^{0}$ redox couples are $-3.04$, $-0.42$ and $-0.74$ V, respectively, according to previous literature results. Electrochemically speaking, the more positive the reduction potential of a redox couple, the greater the species’ affinity for electrons and tendency to be reduced. That means a reduction from Cr$^{3+}$ to Cr$^{2+}$ is much more likely to take place than that from Cr$^{3+}$ to Cr$^{0}$, which provides another explanation for the aforementioned assumption.

**4.3.4. Experimental examination**

In order to establish the reaction mechanism of Cr$_2$(NCN)$_3$ vs. lithium and validate the DFT results, combined XRD and XAS *operando* analyses were carried out. *Operando* XRD patterns collected during the first discharge and first charge are plotted as a function of time in Figure 4.6, together with the corresponding galvanostatic profile. At first discharge, the main intense reflections of Cr$_2$(NCN)$_3$, namely (006), (012) and (116), are clearly visible and remain unchanged until the first pseudo plateau. After that, a gradual decrease of intensities is observed, indicating the reaction of Cr$_2$(NCN)$_3$ with lithium.
Figure 4.6. Operando XRD patterns of Cr$_2$(NCN)$_3$ (a) and associated galvanostatic lithiation/delithiation curve (b). Zooms on the (006), (012) (c) and (116) (d) peaks after intensity normalization on the (116) peak position. Evolution of the corresponding cell parameters (e) and volume (f) upon reaction with Li.
At the end of discharge and during the whole charge process, no trace of crystalline products is observed by XRD, so the phases formed are either amorphous or its particles smaller than the detectable range of XRD. This amorphization effect renders the data collected after 20 h non-utilizable. A closer observation of the diffraction peak between OCV and 20 h (after intensity normalization at the (116) reflection), however, shows a slight but clear shift towards low angles (Figures 4.6(c) and 6(d)). The shift is very small between OCV and pattern #13, but becomes more significant between patterns #14 to #20. It is worth noting that the peaks of the beryllium window of the in situ cell serving as an internal calibration standard are not shifted during cycling confirming that the active material’s volume is enlarged by lithium intercalation (see Figure 4.53). In conclusion, the observed change of the lattice parameters supports an intercalation “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0}$” pathway while the amorphization supports the “Cr$^{3+}$–Cr$^{0}$” conversion pathway. Therefore, the only mechanism that can accommodate these two behaviors is the “mixing” pathway predicted by DFT calculation.

Additional short-range information was obtained based on XAS, which is not affected by the loss of crystallinity of the material during reaction. A total of 70 in situ Cr K-edge XAS spectra were collected during the first lithiation, as shown in Figure 4.7(a) along with the corresponding galvanostatic profile. The different current rates in the electrochemical test from C/8 to C were imposed to complete the discharge within the available beamtime. For the same reason, it was impossible to collect in situ data during the subsequent delithiation, and only selected ex situ XAS spectra were collected at different states of charge. Considering the difficulty of accurately analyzing each spectrum separately, a chemometric approach implying PCA and MCR-ALS analyses was carried out in order to extract the maximum useful information from this large data set. A detailed description of this analytical approach is given by Fehse et al. The PCA variance plot showed in Figure 4.54 suggests that at least three components are needed to describe the whole data set. These three pure components were reconstructed thanks to the MCR-ALS algorithm (Figure 4.7(c)). The evolution of the reconstructed components during the discharge is shown in Figure 4.8. The three components, representing the pristine material (Comp. 1), an intermediate species (Comp. 2), and the final discharge product (Comp. 3) where analyzed using standard methods. Component 2 shows its maximum after 40 spectra from the beginning of the discharge, corresponding to the reaction of about 5 Li$^+$ with Cr$_2$(NCN)$_3$. 

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Figure 4.7. The total XAS spectra collected during the first lithiation (a) and the associated galvanostatic profile (b) and XANES regions of the reconstructed components together with the Cr metal reference (b).

The XANES portions of the reconstructed components are very sensitive to the metal valence and coordination. The spectrum of Component 1 is overlapping with that of the pristine Cr$_2$(NCN). Moreover, the pre-edge doublet seen around ~5993 eV is commonly observed for Cr$^{3+}$, in line with the attribution of Component 1 to pristine Cr$_2$(NCN)$_3$. The slight shift towards lower energies observed on going to Component 2 testifies the reduction of Cr$^{3+}$ to Cr$^{2+}$, which is again consistent with the “Cr$^{3+}$–Cr$^{2+}$–Cr$^{0}$” pathway predicted by theoretical calculations (vide supra). Apart from the edge shift, the difference between Cr$^{2+}$ and Cr$^{3+}$ spectra can also be seen in the appearance of an intense shoulder on the absorption edge, usually observed for divalent chromium. Finally, the broad bump at ~5992 eV appearing in Component 3 corresponds well to the formation of Cr metal. However, the comparison of this spectrum with Cr metal reference clearly shows that the conversion is incomplete. Therefore, the final component could correspond to a mixture of Cr$^{2+}$ and Cr$^{0}$. The comparison of the third component to the corresponding ex situ sample discharged at
0.005 V is given in Figure 4.55(b) and both in situ and ex situ spectra give the same information.

\[ E \text{ vs } \text{Li}^+/\text{Li}^0 (\text{V}) \]

![Graph showing the evolution of the concentration of the MCR-ALS components during lithiation of Cr$_2$NCN$_3$.](image)

**Figure 4.8. Evolution of the concentration of the MCR-ALS components during lithiation of Cr$_2$NCN$_3$.**

In contrast to XANES, the EXAFS region of the XAS spectra provides information about the local coordination environment and bond distances around the chromium centers. The EXAFS oscillations in reciprocal \((k)\) space and the magnitude of their Fourier transform in direct \((R)\) space of the reconstructed components are shown in 4.9. Using the model for the pristine Cr$_2$(NCN)$_3$, the central Cr atom is surrounded by 6 N atoms at 2 Å and by 6 C atoms at 2.9 Å, so we need to consider the multiple scattering path due to the Cr—N=C and the single scattering path due to 3 Cr at 3.1 Å. As regards the obtained results for the first four shells of pristine Cr$_2$(NCN)$_3$, the bond distances coincide well with the theoretical values, and the Deby-Waller factors \((\sigma^2)\) hold reasonable values (Table 4.2). Component 2 could be fitted directly with the same pristine structure. The partial conversion of Cr$^{3+}$ to Cr$^{2+}$ seen in the XANES region is indicated here by slightly longer bond distances in the first and second shell without, however, registering major structural changes. It confirms that lithium intercalates into the Cr$_2$(NCN)$_3$ host, leading to the intermediate species Li$_x$Cr$_2$(NCN)$_3$, which possibly contains both Cr$^{3+}$ and Cr$^{2+}$, in line with the theoretical calculations. Finally, Component 3 at
the end of discharge is optimally fitted by combining the first two shells of Li$_x$Cr$_2$(NCN)$_3$ and the first shell of Cr metal, leading to a phase composition corresponding to about 45% Li$_x$Cr$_2$(NCN)$_3$ and 55% Cr. The slightly lower Cr–Cr bond distance compared to bulk Cr metal suggests the formation of disordered and/or nanosized structure of the Cr metal particles, in line with XRD observations and usually obtained results in conversion reactions. The final phase at the end of first lithiation can be thus defined as the mixture of Li$_x$Cr$_2$(NCN)$_3$, Li$_2$NCN (implicitly formed by the complete reaction of pristine Cr$_2$(NCN)$_3$) and Cr metal nanoparticles.

Figure 4.9. Fit of the EXAFS portion of the MCR-ALS components in k (a) and R (b) space. The black circles correspond to the data and red line to the fit respectively.

To investigate the reversibility of the lithiation process, two ex situ electrodes stopped at 1.5 and 3 V through the charge were analyzed. The XANES and EXAFS portions of the ex situ charged samples were analyzed and compared with the spectra at the end of the discharge and pristine material (Figure 4.10). Increasing the voltage from 0 to 1.5 V results in a slight positive shift of the XANES edge corresponding to the partial oxidation of chromium atoms. EXAFS fitting (Figure 4.10(b,c)) of this particular state leads to 78 % Li$_x$Cr$_2$(NCN)$_3$ species with very short Cr–N distances, and 22 % Cr metal. At 3 V, the EXAFS spectrum is very similar to that of the pristine electrode. Its fitting shows that 90% of Cr metal was oxidized back to Cr$^{3+}$.
(and possibly some Cr$^{2+}$). A similar conclusion can be made from the Fourier transform of the ex situ data shown in Figure 4.55(c).

![Figure 4.10. XANES regions of the ex situ spectra (a) Fit of the EXAFS portion of the ex situ charged states in k (b) and R (c) space. The black circles correspond to the data and red line to the fit, respectively.](image)

**Table 4.2.** Fitting parameters of the in situ EXAFS MCR-ALS components and ex situ charged states.

<table>
<thead>
<tr>
<th>State</th>
<th>Phase</th>
<th>Shell</th>
<th>$S_o^2$</th>
<th>N</th>
<th>$R_{Theory}$</th>
<th>$R_{Measured}$</th>
<th>$\sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. 1</td>
<td>Cr$_2$(N CN)$_3$</td>
<td>Cr—N</td>
<td>1</td>
<td>6</td>
<td>2.090</td>
<td>2.054(1)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—C</td>
<td>1</td>
<td>6</td>
<td>2.973</td>
<td>3.034(3)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—N—C</td>
<td>1</td>
<td>12</td>
<td>3.115</td>
<td>3.163(4)</td>
<td>0.010(1)</td>
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<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>1</td>
<td>3</td>
<td>3.161</td>
<td>2.953(1)</td>
<td>0.013(2)</td>
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<td>Comp. 2</td>
<td>Cr$_2$(N CN)$_3$</td>
<td>Cr—N</td>
<td>1</td>
<td>6</td>
<td>2.090</td>
<td>2.061(1)</td>
<td>0.010(1)</td>
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<tr>
<td></td>
<td></td>
<td>Cr—C</td>
<td>1</td>
<td>6</td>
<td>2.973</td>
<td>3.132(2)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—N—C</td>
<td>1</td>
<td>12</td>
<td>3.115</td>
<td>3.195(4)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>1</td>
<td>3</td>
<td>3.161</td>
<td>2.963(1)</td>
<td>0.011(2)</td>
</tr>
<tr>
<td>Comp. 3</td>
<td>Cr$_2$(N CN)$_3$</td>
<td>Cr—N</td>
<td>0.45</td>
<td>6</td>
<td>2.090</td>
<td>2.016(1)</td>
<td>0.009(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.45</td>
<td>3</td>
<td>3.161</td>
<td>3.149(2)</td>
<td>0.005(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.55</td>
<td>8</td>
<td>2.497</td>
<td>2.419(1)</td>
<td>0.029(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.55</td>
<td>6</td>
<td>2.883</td>
<td>2.975(2)</td>
<td>0.009(2)</td>
</tr>
<tr>
<td>1.5 V</td>
<td>Cr$_2$(N CN)$_3$</td>
<td>Cr—N</td>
<td>0.78</td>
<td>6</td>
<td>2.090</td>
<td>2.029(1)</td>
<td>0.011(1)</td>
</tr>
<tr>
<td>charge</td>
<td></td>
<td>Cr—Cr</td>
<td>0.78</td>
<td>3</td>
<td>3.161</td>
<td>3.008(2)</td>
<td>0.008(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.22</td>
<td>8</td>
<td>2.497</td>
<td>2.678(1)</td>
<td>0.011(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.22</td>
<td>6</td>
<td>2.883</td>
<td>2.903(2)</td>
<td>0.005(2)</td>
</tr>
<tr>
<td>3 V</td>
<td>Cr$_2$(N CN)$_3$</td>
<td>Cr—N</td>
<td>0.90</td>
<td>6</td>
<td>2.090</td>
<td>2.036(1)</td>
<td>0.008(1)</td>
</tr>
<tr>
<td>charge</td>
<td></td>
<td>Cr—Cr</td>
<td>0.90</td>
<td>3</td>
<td>3.161</td>
<td>2.967(2)</td>
<td>0.006(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.10</td>
<td>8</td>
<td>2.497</td>
<td>2.687(1)</td>
<td>0.017(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr—Cr</td>
<td>0.10</td>
<td>6</td>
<td>2.883</td>
<td>2.837(2)</td>
<td>0.003(2)</td>
</tr>
</tbody>
</table>
To summarize, the delithiation mainly leads to oxidized chromium (Cr$^{3+}$ and possibly some Cr$^{2+}$) but, as expected, the delithiated phase is not identical to that of the pristine Cr$_2$(NCN)$_3$ owing to structure disorder, amorphization and/or an incomplete oxidation process. Such an ill-defined structure, however, is not an obstacle to achieving outstanding electrochemical performance, due to the nanostructured electrode produced during the first lithiation.

### 4.3.5. Proposed mechanism

Among the three DFT-proposed reaction pathways (intercalation, conversion and a mixing of both), *operando* and *ex situ* XAS and XRD analyses tend to support the mixing pathway, a two-step process involving intermediate species containing Cr$^{3+}$, Cr$^{2+}$ and metallic chromium nanoparticles. The entire reaction can be written as:

**Upon lithiation:**

$$\text{Cr}_2(\text{NCN})_3 + x \text{Li} \rightarrow \text{Li}_x\text{Cr}_2(\text{NCN})_3 \ (x < 2)$$

$$\text{Li}_x\text{Cr}_2(\text{NCN})_3 + (6-x) \text{Li} \rightarrow 2\text{Cr} + 3\text{Li}_2\text{NCN}$$

**Upon delithiation:**

$$2\text{Cr} + 3\text{Li}_2\text{NCN} \rightarrow y \text{“Cr}_2(\text{NCN})_3” + (1-y) \text{Li}_x\text{Cr}_2(\text{NCN})_3 + (6-x+xy) \text{Li}$$

During the first stages of lithiation Cr$_2$(NCN)$_3$ reacts with fewer than two lithium, and Li$^+$ insertion causes a partial reduction of Cr$^{3+}$ to Cr$^{2+}$, leading to the formation of Li$_x$Cr$_2$(NCN)$_3$. Even though it was impossible to determine its exact chemical composition and crystal structure given its low crystallinity, DFT calculations suggest the possible formation of different compositions such as Li$_{0.5}$Cr$_2$(NCN)$_3$, Li$_{5/6}$Cr$_2$(NCN)$_3$, LiCr$_2$(NCN)$_3$ and Li$_2$Cr$_2$(NCN)$_3$ during lithiation. At the end of the lithiation, XAS evidences the formation of metallic chromium nanoparticles, hence implying the concomitant formation of Li$_2$NCN. Even though only partial reactions (intercalation and conversion) can be experimentally observed, they do not compromise the cycling performance of chromium carbodiimide. Last, the extra lithium consumed in the first lithiation is attributed to the partially reversible degradation of the electrolyte leading to an active polymeric gel.$^{125,146}$ Like all conversion materials, the huge irreversible capacity in the first lithiation is still an apparent demerit, to be solved by realizing a real intercalation carbodiimide material, a true challenge both for theory and synthesis.
4.4. Conclusions

In conclusion, we report the electrochemical performance and reaction mechanism of chromium carbodiimide as anode material in Li-ion batteries. \( \text{Cr}_2(\text{NCN})_3 \) offers superior cyclability and rate performance compared with the other divalent transition-metal carbodiimides. It exhibits specific capacity as high as 500 mAh.g\(^{-1}\) that can be sustained over more than 900 cycles at 2C current rate (240 mA.g\(^{-1}\)) with a coulombic efficiency close to 100%. DFT calculations rationalize the outstanding cycling performance of \( \text{Cr}_2(\text{NCN})_3 \) which results from a two-step pathway for the lithium reaction. Instead of pure intercalation or pure conversion, \( \text{Cr}_2(\text{NCN})_3 \) reacts by following a mixing mechanism combining “\( \text{Cr}^{3+} – \text{Cr}^{2+} – \text{Cr}^{0} \)” and “\( \text{Cr}^{3+} – \text{Cr}^{0} \)” pathways. Hence, we propose a two-step process involving two redox couples (\( \text{Cr}^{3+}/\text{Cr}^{2+} \) and \( \text{Cr}^{2+}/\text{Cr}^{0} \)), as also witnessed from experimental \textit{operando} and \textit{ex situ} XRD and XAS analyses. This work opens a new approach for seeking metal carbodiimide electrode materials allowing pure intercalation reactions for future lithium-ion and sodium-ion batteries of high energy, high power, and long life span.
4.5. Supporting information

Figure 4.5.1. Electrochemical performance of Cr$_2$(NCN)$_3$ vs. Li: specific capacity at 2C rate, more than 510 mAh g$^{-1}$ is maintained for 900 cycles.

Figure 4.5.2. The crystal structures of (a) Cr$_2$(NCN)$_3$, (b) Li$_2$NCN, (c) CrNCN and (d) LiCr(NCN)$_2$.

Figure 4.5.3. Evolution of XRD patterns of in situ cell beryllium window during cycling. No shift is observed.
Figure 4.54. Components from PCA analysis (a) XANES (b) EXAFS (c) regions of the reconstructed components.
Figure 4.55. $\chi(R)$ plots of reconstructed MCR-ALS components from operando analysis (a) Comparison between $\chi(R)$ plots of in situ and ex situ discharged states (b) $\chi(R)$ plots of ex situ states in XAS analysis (c).
General conclusions
The main objectives of this work were to investigate the electrochemical mechanisms of inorganic cyanamides/carbodiimides and to evaluate their performance in LIBs. To achieve this goal, we have studied representative candidates from the group of inorganic carbodiimides/cyanamides as anode materials for LIBs. We have then selected three types of compounds, namely: (i) a divalent transition metal carbodiimide \((i.e., \text{CoNCN})\), (ii) carbodiimides/cyanamides with an electrochemically active element expected to alloy with lithium \((\text{PbNCN, Ag}_2\text{NCN and ZnNCN})\) and (iii) the trivalent transition metal carbodiimide \(\text{Cr}_2(\text{NCN})_3\). All the materials were evaluated in their electrochemical reaction with lithium and their reaction mechanisms established via \textit{in situ} and \textit{ex situ} (laboratory and synchrotron) characterization techniques. Concerning the electrochemical performance, \(\text{Cr}_2(\text{NCN})_3\) turned out to be, by far, the best carbodiimide anode material with stable specific capacity of more than 500 mAh.g\(^{-1}\) for more than 900 cycles at 2C rate. \text{CoNCN} has also excellent electrochemical properties since it can sustain a specific capacity higher than 500 mAh.g\(^{-1}\) for more than 400 cycles at 2C rate (Figure G.1). Poor performance was observed for PbNCN, Ag\(_2\)NCN and ZnNCN since the practical capacities are well below the theoretical ones. These phases show also fast capacity fading during the first 20 cycles. Therefore, the idea of exploiting the alloying reaction to bring additional capacity proved to be not successful.

\[\text{Figure G.1. Schematic summary of the figure of merit of the metal carbodiimide/cyanamide electrode materials in Li-ion batteries.}\]^†

^† MnNCN data are those of ref 112, all the others are from this work.
The observed electrochemical performance for the three types of materials seems to be correlated with their different reaction mechanisms. Indeed, the combination of complementary operando and ex situ techniques revealed three different behaviours vs lithium, since three different reaction mechanisms could be identified in theses inorganic carbodiimides/cyanamides: pure conversion, conversion-alloying reaction and intercalation-conversion reaction.

Pure conversion is occurring in the divalent cobalt carbodiimide. The operando XRD and XAS analyses confirm the two-electron conversion process in CoNCN vs. lithium. In this case, no sign of intercalation could be observed. Similarly to all reported transition metal carbodiimides, the lithiation of CoNCN ends by the formation of Co metal nanoparticles and Li$_2$NCN. During the delithiation process, instead of recovering the cobalt carbodiimide (CoN=C=N) operando XAS analyses suggested for the first time the possible formation a new “CoNCN” species showing spectral features of cyanamide configuration (CoN–C≡N)$^+$ together with carbodiimide one. Therefore, the overall mechanism can be written as:

\[
\text{CoN} = \text{C}=\text{N} + 2\text{Li} \rightarrow ^{fcc}\text{Co} + \text{Li}_2\text{NCN} \quad (1^{st}\text{lithiation})
\]

\[
^{fcc}\text{Co} + \text{Li}_2\text{NCN} \Leftrightarrow \frac{1}{2}((1-\gamma)\text{CoN}=\text{C}=\text{N} + \gamma\text{CoN}−\text{C}=\text{N}) + 2\text{Li} \quad \text{(subsequent cycles)}
\]

The possibility of employing carbodiimide/cyanamide materials undergoing both conversion and alloying reactions was proved for PbNCN, Ag$_2$NCN and ZnNCN. All these three compounds have three different types of [NCN]$^{2-}$ symmetry; ZnNCN and PbNCN contain NCN in carbodiimide and cyanamide configuration, respectively, whereas Ag$_2$NCN possesses a mixture of both carbodiimides and cyanamide anions. The lithiation in these materials starts with a conversion reaction leading to the formation of metal nanoparticles followed by the formation of metal-lithium alloys. Upon delithiation, the dealloying takes place more or less reversibly: it is poorly reversible for compounds containing cyanamide bonding (PbNCN and Ag$_2$NCN), and more reversible for the carbodiimide ZnNCN. In contrast, the conversion reaction in all the three materials is very limited irrespective of the metal. In the case of PbNCN and Ag$_2$NCN, the conversion reaction occurs at relatively higher voltage compared with ZnNCN, and seems to be correlated with the nature of bonding in the NCN group. The reaction mechanism for these compounds can then be written as:

\[
\text{CoN} = \text{C}=\text{N} + 2\text{Li} \rightarrow ^{fcc}\text{Co} + \text{Li}_2\text{NCN} \quad (1^{st}\text{lithiation})
\]

\[
^{fcc}\text{Co} + \text{Li}_2\text{NCN} \Leftrightarrow \frac{1}{2}((1-\gamma)\text{CoN}=\text{C}=\text{N} + \gamma\text{CoN}−\text{C}=\text{N}) + 2\text{Li} \quad \text{(subsequent cycles)}
\]

\[\text{‡} \quad \text{This is a schematic representation.}\]
1) Conversion reaction: $M_a\text{NCN} + 2\text{Li} \rightarrow a\text{M} + \text{Li}_2\text{NCN}$ \(a = 1 \text{ or } 2; \text{ M } = \text{Pb, “Ag}_2” \text{ or Zn)}

2) Alloying reaction: $\text{M} + x\text{Li} \rightarrow \text{Li}_x\text{M}$ \(\text{with } x < 3.5\)

Finally, the combination of DFT calculations together with *operando* characterization clearly revealed the co-existence of intercalation and conversion reactions during the lithiation of $\text{Cr}_2(\text{NCN})_3$. For DFT calculations, three possible reaction pathways were considered: intercalation, conversion and a combination of both. As predicted by DFT, *operando* and *ex situ* XAS and XRD analyses support the combined pathway. During the initial step of lithiation $\text{Cr}_2(\text{NCN})_3$ reacts with less than two lithium cations causing a partial reduction of $\text{Cr}^{3+}$ to $\text{Cr}^{2+}$ and leading to a mixed valence compound with the formula “$\text{Li}_x\text{Cr}_2(\text{NCN})_3$”. Even though it was not possible to experimentally determine its exact chemical composition and the corresponding lattice structure given its low crystallinity, DFT calculation suggests the possible formation of different compositions such as $\text{Li}_{0.5}\text{Cr}_2(\text{NCN})_3$, $\text{Li}_{5/6}\text{Cr}_2(\text{NCN})_3$, $\text{LiCr}_2(\text{NCN})_3$ and $\text{Li}_2\text{Cr}_2(\text{NCN})_3$. At the end of the lithiation, XAS evidences the formation of metallic chromium nanoparticles, hence implying the concomitant formation of $\text{Li}_2\text{NCN}$. It was also clear that although the observed reactions (intercalation and conversion) are only partially achieved, they do not compromise the cycling performance of chromium carbodiimide, which shows the highest specific capacity among all other reported cyanamides/carbodiimides vs. lithium. Therefore, the overall mechanism can be described as a two-step process involving intermediate species containing $\text{Cr}^{3+}$, $\text{Cr}^{2+}$ and ending by the formation of metallic chromium nanoparticles and can be written as:

**Upon lithiation:**

$$\text{Cr}_2(\text{NCN})_3 + x\text{Li} \rightarrow \text{Li}_x\text{Cr}_2(\text{NCN})_3 \text{ (x < 2)}$$

$$\text{Li}_x\text{Cr}_2(\text{NCN})_3 + (6-x)\text{Li} \rightarrow 2\text{Cr} + 3\text{Li}_2\text{NCN}$$

**Upon delithiation:**

$$2\text{Cr} + 3\text{Li}_2\text{NCN} \rightarrow y\text{“Cr}_2(\text{NCN})_3” + (1-y)\text{Li}_x\text{Cr}_2(\text{NCN})_3 + (6-x+xy)\text{Li}$$

It is worth noting that whatever the reaction pathway, all the carbodiimide/cyanamide anode materials face the limitation of a significantly low coulombic efficiency during the first cycle. The high capacities in the first lithiation, higher than their theoretical ones, are composed of an irreversible capacity due to the formation of SEI layer and an extra reversible
contribution from the formation of polymeric/gel film on the surface of the electrode with a pseudocapacitive character, which might be partially avoided by limiting the potential of the electrode during the discharge. To overcome these obstacles, however, much effort is needed to clarify the nature and the role of the SEI in the overall performance of this family of materials. A complete picture of the reaction mechanism requires the characterization of Li₂NCN using the appropriate techniques such as XPS, NMR and low energy XAS. Although the studied electrode materials do not fulfil all the requirements for industrial applications, the promising results of this work demonstrate the richness of the chemistry of inorganic cyanamide/carbodiimide materials and underline their potentialities in the field of electrochemical energy storage.
Perspectives
We have investigated the electrochemical performance of several inorganic carbodiimides, and three different types of lithiation mechanisms, pure conversion reaction, conversion-alloying reaction and intercalation-conversion reaction. However, we have not fully explored this family of compounds in batteries, and more research in various aspects is needed to unlock their full potentials as the anode material in next generation batteries and other energy applications. This section is devoted to some future perspective of the current work.

A major challenging aspect of conversion based anode materials is the large voltage hysteresis between the initial charge/discharge cycles due to the continuous growth of SEI layer and electrolyte degradation. This can be seen in the case of both metal cyanamides and carbodiimides, which has to be addressed. Here we have performed all the electrochemical tests on pristine (without any further treatment) metal cyanamide and carbodiimide materials, therefore implementing strategies such as nanostructuration, hetero-atom doping, preparation of carbon composites and surface modifications etc., might not only solve the problems of high irreversible capacity but also enhance the electrochemical performance. For example, an optimized coating introduced by some surface treatments can act as both conductive network as well as protective layer against electrolyte degradation.

Many researchers have already tried out those in the case of transition metal oxides and reported improved performances. Furthermore, it should be pointed out that this proposition would be more significant for materials which have huge capacity fading (PbNCN, Ag$_2$NCN, ZnNCN) because all these materials possess high theoretical capacity. So, proper control of their composition and surface chemistry might in principle bring out future high capacity anode materials. More optimizations in terms of electrode and electrolyte formulation should also be tried to improve their electrochemical performance. To sum up all the parameters affecting the nature and thickness of the SEI need to be explored.

We have discussed the DFT calculation for Cr$_3$(NCN)$_3$ in the chapter4, similarly for other materials also additional calculations are needed. Coupling experimental analysis with theoretical calculation is a great way for understanding the lithiation mechanisms in detail. Such calculations can be used to interpret the battery chemistry at the atomic level (evolution of bond distances, coordination environment, lattice parameters etc.) during lithiation/delithiation, as well as to improve the understanding of the energetics. Theoretical predictions are always a pillar support for the experimental findings.
In this work we mainly investigated the performance and mechanisms of Pb, Ag, Zn, Co and Cr analogues, but many other members of this large family of metal cyanamides/carbodiimides are also reported, and synthesis works leading to new compounds are still in progress by different research groups. Therefore, there is room for exploring other candidates and probability of discovering new materials showing even more interesting performance and probably new reaction mechanisms. Moreover, we have discussed only the reaction mechanism versus lithium, but these materials are already known for their activity towards sodium, so there is a wide scope for discovering the varieties of sodiation mechanisms also. The use of Metal cyanamides/carbodiimides anodes in other promising under development batteries based on K$^+$ and multivalent cations such as Mg$^{2+}$ and Ca$^{2+}$ has not yet been reported, therefore this direction can also be strongly pursued.

Finally, in addition to battery applications, researchers have also explored metal cyanamides/carbodiimides for other energy applications such as photochemical water splitting, supercapacitors, etc. Indeed, all potential applications of this family of compounds have to be studied in detail for moulding future energy materials. In the following section, we introduce a “Frontier” paper published in Dalton Transactions proposing some reasonable directions for future applications of carbodiimides as energy materials. This paper resumes the approaches so far taken by the researchers to investigate the energy applications as well as an insight about tuning the material properties in terms of structural evolution, anionic-cationic nature, etc. In this context, this paper will surely be a useful guide for researches willing to study metal cyanamides/carbodiimides in the future.
Carbodiimides as energy materials: which directions for a reasonable future?

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I. Introduction

Solid-state carbodiimides with the general formula $M_x(NCN)_y$ (with $M =$ alkali, alkaline-earth, rare-earth, transition metal or metalloid) are a class of inorganic compounds originally derived from molecular cyanamide, $\text{H}_2\text{N-C≡N}$, or the highly unstable carbodiimide isomer, $\text{H-N=C=N-H}$. The best-known member of this family is surely CaNCN, a solid material used as a fertiliser or nitrogen source for the steel industry, characterised by a distorted rock-salt structure where the Ca$^{2+}$ ions are octahedrally coordinated to the nitrogen ends of the linear bridging NCN$^2-$ moieties.

While CaNCN has been known for at least one century, other cyanamide derivatives of alkali and alkaline-earth metals were prepared much later, starting from the late seventies. Only in the last two decades, however, main-group element and transition-metal carbodiimides could be prepared and thoroughly characterised. This delay is due to the impossibility of obtaining phases designated as MNCN (with $M =$ Mn, Fe, Co, Ni, Cu) using as simple synthetic routes as for CaNCN. Indeed, the discovery of the theoretical existence of transition-metal carbodiimides as metastable (i.e., endothermic) but still inert compounds occurred prior to their synthesis based on first-principles electronic-structure calculations. This discovery triggered the following synthetic work, which in the very beginning was meant to lead to new oxide-like “correlated” non-oxidic binary compounds. Since then many transition-metal carbodiimides have been prepared thanks to a variety of new chemical routes.
Lately, carbodiimides have been considered for various applications such as corrosion inhibitors, photovoltaic devices, fluorescent light sources and light emitting diodes. Since 2015, several studies have shown the potential use of iron carbodiimides as negative electrodes for LIBs and NIBs. In fact, even though graphite remains the only practical anode material in commercial LIBs, it is characterised by a relatively low specific capacity of 372 mAh.g⁻¹. Therefore, a real need of improving the electrode capacity exists in order to amend the energy performance of lithium-ion cells. Moreover, in the case of NIBs, graphite does not intercalate sodium, and the alternative carbonaceous negative electrode materials that have been proposed, such as hard carbon, are characterised by relatively low specific capacities.

All the carbodiimides studied until now seem to react electrochemically with lithium and sodium via the so-called “conversion reaction” (metathesis) or both conversion and alloying reactions. Typical galvanostatic profiles (1st cycle) and capacity retention are shown in Figure P.1, with in the left panel typical conversion materials and on the right panel materials that show both conversion and alloying reactions. These mechanisms designate the largest families of negative electrodes with high specific and volumetric capacities. They include transition-metal oxides as well as metal phosphides, sulphides and nitrides, all following the “conversion reaction” and for some metals; that can form alloys with lithium; additional specific capacity is achieved via the alloying reaction:

\[
M_aX_b + (b \cdot n) \text{Li} \rightleftharpoons aM + b\text{Li}_nX \text{ (conversion reaction)}
\]

\[
M + m\text{Li} \rightleftharpoons \text{Li}_mM \text{ (alloying reaction)}
\]

where \(M\) = transition metal, \(X\) = p-group element or anion and \(n\) = oxidation state of \(X\) (this mechanism is detailed, e.g., in Ref. 32,78,229–231 and references therein). Based on the available data, materials following only conversion mechanism show better electrochemical performance compared to those with a conversion-alloying mechanism. Among these materials Si(NCN)₂ is the only one to show almost no activity vs. lithium.

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\(^5\) Note that intercalation-conversion reaction has been proved for Cr₂(NCN)₃ after the publication of this review paper.
Figure P.1. Typical galvanostatic profiles for carbodiimides following conversion (top left panel) and conversion-alloying (top right) mechanisms. Specific capacity retention (2nd to 10th cycles, bottom panel). For an easy comparison, the capacities of Cr2(NCN)3 and Si(NCN)2 have been normalised to one NCN group.

Among the materials undergoing the conversion reaction, transition-metal carbodiimides can be viewed as the counterparts of the corresponding transition-metal oxides, where the oxide anion has been substituted by the carbodiimide (or cyanamide, depending on its shape) NCN²⁻ group. Indeed, while oxides are considered the best-known class of compounds among solid-state materials due to the reactivity and the availability of
oxygen, there is a much smaller number of corresponding solid-state nitrogen-based phases. Nonetheless, the solid-state research on nitrogen compounds has clearly advanced in recent years, and it has in particular focused on nitrogen-based pseudo-chalcogenides (beside a few other compounds such as transition metal mixed nitrides.\textsuperscript{231}) In this view, the spatially compact and rigid NCN\textsuperscript{2–} unit with its anionic charge of −2, easily forming bonds via the two nitrogen atoms, can be considered equivalent to a “divalent nitride” anion, hence mimicking O\textsuperscript{2–} but being more covalent in nature because of the less electronegative N atom; a chemically simple but synthetically challenging idea.

The comparison of carbodiimides with the corresponding oxides reveals other interesting physico-chemical properties specific of the former compounds. Cobalt, nickel, and manganese carbodiimides, for instance, were recently identified as non-oxidic water-oxidation electrocatalysts.\textsuperscript{106,233} Moreover, the semiconducting silver cyanamide can meaningfully improve charge carrier separation for photoelectrochemical water oxidation by heterojunction formation.\textsuperscript{105}

II. Improving rate capability: can metastability help?

As mentioned in the introduction, a particular interest for application in batteries has been devoted to 3\textit{d} transition-metal carbodiimides such as those of Fe, Co, and Ni. These compounds are formed from a precursor (\(T(NCNH)_2\) with \(T = \text{Fe, Co, Ni}\)) in a LiCl/KCl flux at 400 °C. Their structure resembles the NiAs type with octahedral coordination for the \(T\) cations and a trigonal prismatic coordination for the linear NCN\textsuperscript{2–} units (Figure P.2).

![Figure P.2. Crystal structure of TNCN (T = Fe, Co, Ni) with octahedral nitrogen (in green) coordination around T (in red) and linearly coordinated carbon atoms (in gray).](image-url)
Clearly, these 3$d$ carbodiimides may be considered the nitrogen analogs of the “correlated” 3$d$ oxides which have been studied by solid-state physics for decades because of their fascinating many-body effects. For the 3$d$ carbodiimides, however, it was realized in 2016 and 2017 that they exhibit an astonishing performance as anode materials in rechargeable LIBs and NIBs. This ability probably goes back to the metastable character of the carbodiimide-based phases. It is very well possible that the discovery of electrochemical activity (and impressive rate capability) just represents the tip of an iceberg to be witnessed for an entire class of compounds. Therefore, further research on the reaction mechanism as well as on related phases is truly required. More precisely, concerted research study focusing on synthesis, reaction mechanism, theoretical modeling, and electrochemical performance of ternary phases whether as anode or cathode materials (some of which are yet to be synthesized) could help revealing and understanding such potentially new properties.

III. Controlling anionic redox at high potential: possible with transition-metal carbodiimides?

During the last five years, huge advances have been made in the understanding of the capacity-fading mechanism of lithium-rich layered oxides. One of the main reasons of this fading is the oxidation of the oxide anions, which contribute to the redox activity at high potential. While this reaction brings an additional specific capacity in lithium-rich layered oxide, it generally leads to the irreversible evolution of oxygen gas implying material destruction and hence a rapid capacity fading (Figure P.3). This mechanism has been tricky to catch since oxygen is contained in almost all battery components such as electrolyte and
binders. Hypothetical phases such as, say, LiM(NCN)₂ and Li₂M(NCN)₂, were they electrochemically active and able to handle excess amount of lithium, might present a different behavior as they are entirely free of oxygen. An interesting and completely unknown aspect will arise since up to date nothing is known about the redox behavior of the NCN²⁻ anion when combined with high potential redox couples such as T⁴⁺/T³⁺.

Fortunately, there is experimental evidence for analogous ternary phases featuring oxidation state +III, at least in the case of several main-group and rare-earth metals. For example, compounds such as LiM(NCN)₂ with $M = \text{Al}^{224}$, $\text{In}^{224}$, $\text{Yb}^{224}$, $\text{Y}^{236}$ and $\text{La}^{236}$, or such as Li₂M(NCN)₂ with $M = \text{Sn}$, $\text{Zr}$, and $\text{Hf}^{237}$ do exist and have been characterized. It is therefore reasonable to believe that chemical analogs with transition metals such as Fe, Co and Mn might be obtainable as well if the right synthetic conditions were found, possibly guided, as said before, by quantum-theoretical calculations. Such theoretical studies might either start from the crystal structures of the already existing ternary compounds or involve genetic algorithms in order to scan the entire ternary phase diagram, such as those used for the prediction of unknown phases, specifically in the case of oxides or other polyanionic battery-related compounds.²¹⁰,²³⁸ Such approach could be extended to NCN-based compounds, helping the search for a viable chemical synthetic route.

In addition to the knowledge of stable crystal structures, first-principles calculations would also help in the prediction of the possible deintercalation and intercalation route of the alkali metal (A) from AM(NCN)₂, providing chemical potential and probing the existence of possible intermediate compounds of the type $A_{1-x}M(NCN)₂$ with $0 < x < 1$. Such compounds are expected to be produced at high potentials, given the high formal oxidation state reached by the transition metals (+IV), just like deintercalation of LiCoO₂ leads to Co⁴⁺, and thus may let one access possible redox processes involving the NCN²⁻ bridging ligands. And yet, everything depends on new synthetic routes to ternaries which must be found. In that spirit, there is the new phase SrZn(NCN)₂, the first example of a ternary post-transition metal carbodiimide which was prepared by a solid-state metathesis reaction.³⁷ Here, tetrahedral coordination is found for zinc, somewhat similar to the oxide analogue SrZnO₂. Likewise, BaZn(NCN)₂ represents the aristotype of the LiBa₂Al(NCN)₄ structure unique to carbodiimide chemistry, also featuring ZnN₄ tetrahedra.³⁸ That is to say that other analogues, now featuring redox-active transition metals at the tetrahedral Zn²⁺ site, should be sought, in parallel with the replacement of alkaline-earth with alkaline metals.
IV. Reaching insertion at low potential starting from trivalent metal carbodiimides

As already mentioned in the introduction, the only mechanism currently observed for MNCN compounds is that typical of conversion reactions, where the divalent metal is reversibly reduced to zero-valent metal nanoparticles. A possible way to avoid the conversion and the complete reduction to the metallic state might be the employment of the $M^{3+}/M^{2+}$ redox couple. In this case, one has to start from solid-state carbodiimides which already contain $M^{3+}$ metals, e.g., compounds dubbed $M_2$(NCN)$_3$, and hopefully intercalate the alkali metal ion theoretically obtaining $AM$(NCN)$_2$-type compounds.

At present, only one such candidate is known, namely Cr$_2$(NCN)$_3$, the first ferromagnetic carbodiimide ever reported. Cr$_2$(NCN)$_3$ is isostructural with antiferromagnetic Cr$_2$O$_3$ (Figure P.4) and adopts a corundum-type structure. Hence, Cr$_2$(NCN)$_3$ is the natural starting point for such research. Fortunately, the rock-solid corundum type seemingly makes Cr$_2$(NCN)$_3$ being an easy material to handle chemically, being astonishingly insensitive to air and humidity.

![Figure P.4. Crystal structure of Cr$_2$(NCN)$_3$ (left) and the coordination environments of the Cr$^{3+}$ ion and the NCN$^{2-}$ ion (right). Reprinted from ref. 12 with kind permission by John Wiley and Sons.](image)

Our first tests on the electrochemical activity of Cr$_2$(NCN)$_3$ with lithium, however, indicate that only the conversion reaction can be observed, with no intermediate formation of stable intercalated species (data not shown). The reason of this lack of intercalation, however, could be related to the particle size of the pristine material. In fact, it is well known...
that micro- and nano-sized materials can exhibit very different activity vs. Li (Figure P.5). By analogy with oxides, one may expect nanostructured $M^{3+}$ carbodiimides to be able to intercalate alkali ions if an optimization of their morphology is considered.

![Figure P.5. Illustration of the effect of particle size (5 nm for nano-Fe$_2$O$_3$) on the electrochemical activity of iron oxide.](image)

V. Carbodiimides for photochemical water oxidation

Surprisingly only at first sight, carbodiimides have recently emerged as novel materials for photochemical energy conversion. Solar-to-hydrogen conversion based on photoelectrochemical water splitting represents a sustainable solution for energy generation. The efficiency is mainly limited by the oxygen evolution reaction (OER), because two chemical bonds need to be broken. Upon illumination of a semiconductor photoanode, exhibiting a valence band edge (VBE) position more positive than the potential for water oxidation (1.23 V vs RHE), the photo generated holes can drive the OER (Figure P.6).

The semiconducting Ag$_2$NCN has a bandgap suitable for solar light harvesting and appropriate VBE position for PEC water oxidation. It has been demonstrated in 2013 that an Ag$_2$NCN photoanode yields photocurrents and maintains its structural stability. Furthermore, the charge carrier separation and hole collection efficiency can be enhanced by forming heterojunctions in type-II band alignment, such as for CuWO$_4$/Ag$_2$NCN photoanodes. The functionalization of a CuWO$_4$ photoanode with Ag$_2$NCN particles improves the photocurrent density from 15 to 45 µA cm$^{-2}$ at 1.23 V vs RHE. The increase of the hole collection efficiency indicates the carbodiimide to be the active species for OER. However, more mechanistic studies are necessary for carbodiimide catalysts in order to determine their role during oxygen evolution.
Figure P.6. Schematic illustration of a photoanode-driven PEC device for water splitting. The photoanode consists of a semiconductor (in yellow) coated with a carbodiimide OER electrocatalyst (in green). Upon illumination, electrons are excited to the conduction band of the semiconductor and migrate to the metallic counter-electrode where water is reduced. Simultaneously, the holes are collected by the MNCN electrocatalyst which subsequently performs the OER.

Cobalt oxides are known as efficient electrocatalysts that can be used for surface modification of semiconductor photoanodes. In 2015 it was shown that the electrocatalytic activity accounts as well for the N-based pseudo-oxides CoNCN, NiNCN and its solid solutions in neutral or basic media. Mixed Co$_x$Ni$_{1-x}$NCN catalysts exhibit an onset potential comparable to cobalt oxides while maintaining the carbodiimide structure in the bulk and on the surface under applied current. Furthermore, it is not necessary to perform $^{18}$O labelling experiments with carbodiimide electrocatalysts. The catalyst can be also used for electroless photocatalytic water oxidation where it displays higher turnover frequency in comparison to the cobalt oxides. This shows up in higher normalized turnover frequency (TOF/$S_{BET}$), based on the surface area $S_{BET}$, during visible-light-driven oxygen evolution reaction. Cobalt carbodiimide exhibits a TOF/$S_{BET}$ of $2.1 \cdot 10^{-1}$ whereas cobalt oxide reaches a significantly lower value of $3.5 \cdot 10^{-3}$.

The electrocatalytic activity of 3$d$ metal carbodiimides does not have to necessarily originate from the carbodiimide structure. We recently showed that functionalizing the surface of CuWO$_4$ photoanodes with MnNCN particles can increase the photocurrent by 30 % and shift the onset potential for the OER cathodically by 100 mV. Contrary to CoNCN, the manganese counterpart transforms in situ to a core-shell structure MnNCN@MnPO$_x$ with a phosphate shell of few nanometres. As such, MnNCN mimics a manganese phosphate catalyst.
while keeping the semiconducting carbodiimide core. This highlights the importance of the surface chemistry for carbodiimide catalysts, and electrochemical activation may be, similar to manganese oxide electrocatalysts, a promising strategy to lower the overpotential for the OER.

These studies show the potential of carbodiimides in photocatalysis although the electrodes in the abovementioned examples contained carbodiimides particles with sizes ranging up to several micrometres. For photoanodes it is essential to ensure short hole diffusion pathways to the electrode-electrolyte interface and to minimize light absorption by the catalyst. These issues will have to be addressed at the level of chemical synthesis and/or particle separation in order to obtain carbodiimides as nanoparticles or nanocoatings.

Studies on the interaction between the carbodiimide catalyst and the complementary semiconductor will be of high importance for the development of future photoelectrodes beyond oxides. For comparison, the best-performing oxide photoanode BiVO₄ shows higher photocurrent if functionalised with platinum instead of iridium oxide; the latter being generally a better OER electrocatalyst. Today, both the electrocatalysis and photochemistry of transition metal carbodiimides/cyanamides are still in their infancy. The reported results and the plethora of materials combination hold promise to new exciting discoveries with respect to energy conversion based on carbodiimide materials.

**VI. Conclusions**

The application of transition-metal carbodiimides and cyanamides in the field of batteries has only just started, showing already interesting properties as negative electrode materials undergoing the conversion reaction. Such properties, however, are currently not sufficient to allow a large-scale application of these materials. New developments are thus necessary, and some possible new ways of investigation have been suggested here. They include, on the one hand, a powerful synthetic effort, but also a necessary theoretical approach to predict and suggest possible new phases and structures.

Once these new materials are synthesised, a combined approach able to investigate both the evolution of the structure and of the physico-chemical state of the redox centres, being them of cationic or anionic nature, is necessary to successfully conclude on the potential future applications of such materials in real energy storage systems. Already now,
however, some of these exciting phases have shown their potential for photochemical water splitting, another hot topic of present-day applied solid-state (materials) chemistry.

Whichever the outcome of these investigations, the study of new transition-metal carbodiimides and of their properties is extremely exciting from the fundamental point of view, promising an excellent future of research on this family of compounds.
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Appendix
A. List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
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<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
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<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EFA</td>
<td>Evolving factor analysis</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FEC</td>
<td>Fluroethylene carbonate</td>
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<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared spectroscopy</td>
</tr>
<tr>
<td>GF</td>
<td>Glass fibre</td>
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<tr>
<td>ICSD</td>
<td>Inorganic crystal structure database</td>
</tr>
<tr>
<td>LCO</td>
<td>Lithium cobalt oxide</td>
</tr>
<tr>
<td>LFP</td>
<td>Lithium iron phosphate</td>
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<tr>
<td>LIBs</td>
<td>Lithium-ion batteries</td>
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<tr>
<td>LMO</td>
<td>Lithium manganese oxide</td>
</tr>
<tr>
<td>LMP</td>
<td>Lithium manganese phosphate</td>
</tr>
<tr>
<td>LVP</td>
<td>Lithium vanadium phosphate</td>
</tr>
<tr>
<td>MCR-ALS</td>
<td>Multivariate curve resolution alternating least square</td>
</tr>
<tr>
<td>NCA</td>
<td>Lithium nickel cobalt aluminium oxide</td>
</tr>
<tr>
<td>NIBs</td>
<td>Sodium-ion batteries</td>
</tr>
<tr>
<td>NMC</td>
<td>Lithium nickel manganese cobalt oxide</td>
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<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
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<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
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<tr>
<td>PAW</td>
<td>Projector-augmented-wave</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew–burke–ernzerhof</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-------------</td>
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<tr>
<td>PCA</td>
<td>Principle component analysis</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interface</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIMPLISMA</td>
<td>Simple-to-use self-modelling analysis</td>
</tr>
<tr>
<td>SVD</td>
<td>Singular value decomposition</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>TOF</td>
<td>Turn over frequency</td>
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<tr>
<td>VASP</td>
<td>Vienna ab-initio simulation package</td>
</tr>
<tr>
<td>VBE</td>
<td>Valence band edge</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>VGCF</td>
<td>Vapour grown carbon fibre</td>
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<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
B. Material synthesis

This Project is the result of a long-term collaboration between RWTH Aachen University and ICGM. All materials were synthesized at RWTH Aachen University.

PbNCN and Ag$_2$NCN were prepared by the reaction of an aqueous solution of cyanamide with the corresponding metal salt (lead acetate and silver nitrate for PbNCN and Ag$_2$NCN, respectively). The addition of an ammonia solution led to the formation of yellow precipitates, which were then filtered, washed, and dried to obtain crystalline lead and silver cyanamide particles.\textsuperscript{92,168} Zinc carbodiimide was prepared by a simple mixing of zinc chloride with cyanamide in excess in ammonia solution for 3 h, yielding a white powder.\textsuperscript{94}

CoNCN was prepared via a two-step method. The first step consists in the synthesis of the pure auburn-coloured cobalt hydrogen cyanamide, Co(HNCN)$_2$, starting from cobalt chloride and cyanamide in aqueous ammonia solutions. In the second step, Co(HNCN)$_2$ is blended with a mixture of LiCl/KCl as a flux and heated up to 400 °C under argon atmosphere in a closed ampule. The melamine produced through the reaction is removed by trapping it in the cold side of the glass container which is held out of the tube furnace at room temperature. The orange-brown CoNCN powder from the cooled ampoule is washed with water and dried \textit{in vacuo}.\textsuperscript{96}

Cr$_2$(NCN)$_3$ was prepared by metathesis route from the reaction between CrCl$_3$ and ZnNCN. All the synthesis steps were carried out in an argon filled glove box. The reaction precursors consist of CrCl$_3$ and ZnNCN in a molar ratio of 2:3 and LiCl/KCl (46:54) as a flux. The reactants and flux were initially heated at 300°C under dynamic vacuum for 12 h and 550°C for another two days. Then the resulting powder was washed with diluted HCl followed by water and acetone to get the final green coloured Cr$_2$(NCN)$_3$ powder.\textsuperscript{199}
C. Material characterization

C.1. X-ray diffraction

X-ray diffraction (XRD) is a characterization technique used for the non-destructive structure analysis. It gives the information about the crystal orientation and inter-atomic spacing. The main principle is, incident beam of monochromatic X-rays interact with the target material and cause the scattering of X-rays from the target material’s atoms. In crystalline materials scattered X-rays undergo both constructive and destructive interference. This process is called diffraction. These interference patterns will be specific to each substance, called fingerprint of the materials. XRD is generally described by Bragg’s equation, 

\[ N\lambda = 2dsin(\theta) \]

Where, \( \lambda \) = X-ray wavelength, \( d \) = lattice spacing, \( \theta \) = Angle between incident beam and scattering plane, \( N \) = Integer.

Here in this thesis XRD data were collected with a PANalytical Empyrean diffractometer equipped with either a Cu or a Co Kα source. In order to process the collected XRD data we used the software PANalytical’s X’pert high score plus which allows to search and match the peaks. The lattice parameters was extracted by refining the data with Le Bail method using FullProf software.
C.2. **Scanning electron microscopy**

Scanning electron microscopy (SEM) makes use of the beam of high energy electrons to generate various signals which carry multiple information such as morphological characters, chemical composition, orientation of material, etc. The narrow beam of electrons emitted by an electron gun are focused on the sample by means of electromagnetic lenses and the interaction between the electrons and the sample causes the formation of secondary electrons of lower energy. These energy signals are then amplified and detected and finally converted into an electrical signal. This process is performed at each point of the sample by scanning the microscope. The set of signals make it possible to reconstruct the topography of the sample and provides a relief image. In general, a modern full-sized SEMs can provide resolution between 1-20 nm and the desktop systems can provide a resolution of 20 nm or more. The SEM analysis in this thesis work was carried out by Hitachi S-4800 scanning electron microscope equipped with a field emission gun.

C.3. **Vibrational spectroscopy**

Vibrational spectroscopy is a non-destructive and non-intrusive method used to observe and characterize the structure of a material and possible to analyze almost all types of samples without degrading them (liquid, solid, paint, membrane, silicon wafer deposition, etc.) Vibrational spectra are generated by the excitation of the vibrational modes in a molecule. Therefore it gives the information about molecular and solid-state structure and interactions between molecules. Infrared and Raman spectroscopy are the two types of vibrational spectroscopy used in this work. The main difference between IR and Raman lies in the way the vibrational modes are excited. IR bands appear in the presence of dipole moments inside the molecule, whereas Raman modes are related to the variation of the polarizability of the bonds during the vibration.

Here in this thesis work, the main information obtained from the vibrational analysis is the nature of N-C-N unit, whether it is carbodiimide (N=C=N) or cyanamide (N≡C-N). There are mainly three types of vibration modes seen in the cyanamide and carbodiimide unit, two stretching modes (symmetrical and anti-symmetrical) and one bending mode (Figure C.2). The symmetric vibrations of carbodiimide group are generally forbidden in IR and active in Raman spectroscopy whereas for cyanamide unit it is active in IR.\(^{90}\)
Figure C.2. Schematic of different types of vibrations in carbodiimide group.

FT-IR and Raman spectroscopy measurements were done employing a Bruker spectrometer IFS66V equipped with an ATR diamond crystal and a confocal LabRAM Aramis spectrometer (Horiba), equipped with a HeNe laser, an 1800 grooves/mm grating, and a Peltier-cooled CCD detector respectively.

C.4. Thermogravimetric analysis

The principle of thermogravimetric analysis (TGA) is to follow the variation of the mass of a sample with respect to the applied temperature in a chamber of controlled atmosphere (inert or oxidizing). Thus, different transformations experienced by the material (evaporation, oxidation, etc.) with the temperature variation can be detected. However, some transformations which do not generate mass variation such as melting or crystallization cannot be directly detected by TGA, and are rather obtained through Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC). In this thesis all the TGA analyses were performed in NETZSCH Jupiter STA 449 F1 thermobalance with a heating rate of 5 °C.min⁻¹ in air flow.
D. Electrochemical characterization

All the electrochemical tests were carried out in coin type half cells with lithium foil as both counter and reference electrodes. Therefore, in this thesis lithiation of carbodiimide materials is called discharge whereas delithiation is called charge.

D.1. Electrode preparation

As described in the Figure D.1 electrodes were prepared by mixing 60 wt. % active material, 20 wt. % conductive additives (carbon black and vapor-grown carbon nanofibers (VGCF)) and 20 wt. % carboxymethyl cellulose (CMC) as the binder together with water. The aqueous slurry was then coated over a copper foil via a traditional Doctor Blade technique with a thickness of 150 µm, dried at room temperature in air and finally at 100 °C under vacuum for 12 hours. Finally, the disc-shaped electrodes were cut from the film with an active material loading of 1 to 2 mg/cm².

Figure D.1. Schematic of different steps involved in electrode preparation.

D.2. Coin cell assembly

The electrochemical cells used for the liquid electrolyte battery design are of Swagelock type 12 mm diameter. The assembly of the cell is carried out in a glove box under an argon protective atmosphere as shown Figure D.2. Once sealed, these cells have the advantage of being sealed and therefore usable outside the glove box. The negative electrode
consists of a metal lithium disc (Aldrich, 99.9%) 10 mm in diameter and 1.5 mm thick. The separator was 12 mm Whatman glass fiber GF/D soaked in electrolyte of 1 M LiPF$_6$ solution in ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) (1:1:3 in weight) with 2% vinyl carbonate (VC) and 5% fluoroethylene carbonate (FEC) additives. In this half-cell, the material studied constitutes the working electrode and acts as a positive electrode.

\[ \text{Specific capacity (Sp. Cap)} = \frac{\text{charge stored}}{\text{mass}} \]

For one mole of material, assuming it provides "x" moles of electrons:

\[ \text{Sp. Cap.} = x \times \text{Na} \times \text{Qe}/\text{Mw} \]

**Figure D.2. Coin cell components.**

**D.3. Galvanostatic cycling**

Galvanostatic cycling is a reliable technique used to measure the electrochemical capacitance of an electrode material by applying constant current and varying potential. During galvanostatic cycling, the discharge and charge current are expressed in terms of current rate. C/n rate indicates that 1 mole of Li reacted in n hours per mole of active material. The galvanostatic profile is the electrochemical signature of the electrode material since each plateau corresponds to the characteristic lithiation reactions. It gives the information such as reversible capacity, nature of lithiation reaction, polarization, etc. In this thesis, Galvanostatic measurements were performed using Biologic and/or Neware potentiostats.

The capacity of the electrode material is normally expressed in mAh.g$^{-1}$ and calculated as per the following formula:

\[ \text{Specific capacity (Sp. Cap)} = \frac{\text{charge stored}}{\text{mass}} \]
Where,

Na = Avogadro’s number
Qe = Charge of an electron (in coulombs)
Mw = Formula mass of cathode material
This value is in coulombs/gram. To convert it to mAhg⁻¹, divide it by 3.6

D.4. Cyclic voltammetry

Cyclic voltammetry (CV) is a powerful electrochemical method commonly used to investigate the redox reactions of molecular species. It measures the current developed in the cell under conditions in a defined potential window. Since the current is directly linked to the number of electrons involved in the chemical reactions, CV can be used for both qualitative and quantitative electrochemical analyses. In this thesis, a Biologic system was used to perform CV measurements.
E. **Operando and ex situ measurements**

E.1. **Operando and ex situ X-ray diffraction**

Operando and ex situ XRD patterns were collected with a PANalytical Empyrean diffractometer equipped with a Cu Kα source. Operando measurements were carried out by measuring one pattern per hour on active material rich self-supported electrodes at the C/8 rate in a specially designed in situ cell\textsuperscript{133} (Figure E.1). A lithium metal disk was used as the negative electrode, separator 20 mm Whatman glass fibre GF/D was placed between the lithium and the working electrode (material studied). The separator was soaked with EC:PC:3DMC + 1M LiPF\textsubscript{6} + 2%VC and 5% FEC electrolyte.

Ex situ XRD analyses were conducted on the normal electrodes with copper foil cycled in Swagelok cells, stopped at specific discharge and charge states. The cells were disassembled in an Ar-filled glove box and the electrodes were supported on Cu foils placed on the XRD holder and covered with a Kapton film with a sealing layer of silicone to prevent the reaction with air during analysis.

![Figure E.1. In situ cell diagram\textsuperscript{133}.](image)

E.2. **Operando and ex situ X-ray absorption spectroscopy**

E.2.1. **Principle**

X-ray absorption spectroscopy (XAS) is a technique used for investigating the electronic or/and geometric structure of matter. The principle of XAS is the photoelectric effect. When a X-ray photon strikes an atom, if the incident energy (E) is sufficient to excite a core electron, the photon is absorbed. This is expressed in the XAS spectra by a drastic increase in the absorption intensity called absorption edge. Therefore, the energies at these
edges correspond to the binding energies ($E_0$) of core shell electrons. An XAS spectrum is generally divided into three sections (Figure E.2):

![X-ray absorption spectrum for CoNCN indicating main three regions.](image)

**Figure E.2.** X-ray absorption spectrum for CoNCN indicating main three regions.

1. **Pre-Edge ($E < E_0$)** - The Pre-edge features are usually due to forbidden electron transitions from core level to higher half-filled or unfilled orbitals ($s \rightarrow p$, or $p \rightarrow d$). Pre-edge gives the information about covalency, coordination symmetry and electronic structure.

2. **X-ray absorption near edge structure (XANES) ($E_0 < E < \sim (E_0 + 50\ eV)$)** - In this region, allowed core electrons transition to non-bound levels occurs. It provides information about the oxidation state of the absorbing atom and its site symmetry.

3. **Extended x-ray absorption fine structure (EXAFS) ($E > \sim (E_0 + 50\ eV)$)** - EXAFS signals are caused by the interference between photo-electron and its scattered image by neighbouring atoms. It provides the information about the co-ordination (distances, number and type of ligands).
E.2.2. Experimental set-up

Operando XAS measurements were carried out in the same in situ cell used for XRD described above and electrodes were prepared by tape casting the aqueous slurry containing the formulated electrode material directly on the beryllium window of the cell. Ex situ electrodes were self-supported. Electrodes of 6 mm diameter was prepared with a mixture of 50% active material and 50% carbon additives. The mixture was first loaded into a pellet ring holder of 6 mm and anvil die assembly. This assembly was then placed over the Pellet Press piston, the top lead screw is lowered, and a load of 3 tons applied. After compressing, the formed pellet was removed from the ring holder and dried at 100°C under vacuum. These pellet electrodes cycled in Swagelok cells, stopped at specific discharge and charge states. The cells were disassembled in an Ar-filled glove box and covered with Kapton film.

XAS measurements were carried out in the transmission mode at the ROCK beam-line of Synchrotron SOLEIL or at the beamline B18, Diamond Light Source. A channel-cut Si (111) monochromator with an oscillating frequency of 2 Hz and an energy resolution of 0.7 eV at 8 keV was used. The intensity of the X-ray beam was measured by three consecutive ionization detectors, with the in situ electrochemical cell placed between the first and the second ionization chambers and a metal foil reference between the second and the third one. The homogeneity of the sample was checked before running the electrochemical test. The electrochemical test was started with a current rate of C/8 as estimated initially for all materials, but then accelerated to get the whole cycle, as the contribution of conductive additives used for electrode preparation slowed down the conversion mechanism. Finally, the operando analysis could be carried out for the first 2 sweeps (first discharge and charge) of CoNCN, and the first sweep and Cr$_2$(NCN)$_3$. The obtained XAS spectra were first calibrated in energy using corresponding metal foil as reference and then normalized using ATHENA software.

Operando X-ray spectroscopy analysis always provides a large set of data and the complexity lies in the approach for treating such a large number on spectra. Therefore an alternative method is needed to interpret and extract the information in a reasonable time. Here is the importance of chemometric approaches, which make use of mathematical methods to obtain as much as possible information from the analytical chemistry results. Principal component analysis (PCA) and Multivariate Curve Resolution-Alternating Least
Squares (MCR-ALS) are two good examples for such chemometric methods. In this thesis we used these two multivariate techniques for the Operando X-ray spectroscopy data analysis.

### E.2.3. Principal component analysis (PCA)

PCA is a factor analysis algorithm that linearly converts an original data matrix of possibly correlated variables into a substantially smaller matrix of uncorrelated variables that contains the most useful information of the original set of variables. The starting matrix of PCA analysis is the experimental data matrix (here in this thesis, the total normalised XAS spectra) and each spectrum in the data matrix is considered as an $n$-dimensional vector where $n$ corresponds to the total number of points within spectrum. The independent vectors called principal components (PC) orthogonal to each other were then computed and expressed in the decreasing order of variance of the data set. The contribution of each principal component to the total variance is generally expressed by the eigenvalues and their respective eigenvectors, the eigenvector with the largest eigenvalue indicates the direction of greatest variation.

The schematic concept of PCA analysis is showed in Figure E.3. Consider a model plane having the space of two variable system which forms two orthogonal principal components. Samples are represented by green stars in the space. The distance between the samples defines their relationship with each other, the nearest samples are considered as more similar ones. The first principal component PC1 shows the maximum amount of variation in one direction whereas the second one PC2 points in to the next most significant variation and so on. In the case of a series of spectroscopic data set, the useful information is contained only in very small number of principal components. The relevant number of principal components can thus be estimated from eigenvalues trajectory; in practice, the principal components linked with noise-related contributions can be avoided. The original experimental, the spectra can thus be reproduced by adapted linear combinations of the principal components and the multiplication factors of principal components in such linear combinations are called scores, according to the general equation:

$$\text{Data} = \text{scores} \times \text{principal components}$$
Practically PCA can be realized by different types of mathematical operations and one of the popular method is Singular Value Decomposition (SVD).\textsuperscript{246} In this thesis, we used this method for all PCA analyses. Figure E.4 shows the PCA_SVD analysis results of Operando Co K-edge XAS of CoNCN vs. lithium. It displays the variance of principle components and evolution of the component scores, this clearly indicates that at least three components are necessary to interpret the evolution of the whole data set consisting of 126 XAS spectra.
Figure E.4. Components from PCA analysis (a) Variance of the components (b) Evolution of the component scores (c).

E.2.4. Multivariate curve resolution-alternating least squares (MCR-ALS)

The orthogonal components obtained from PCA analysis do not have any physical and chemical meaning, they are just orthogonal mathematical functions, not real spectra. Therefore in order to reconstruct the real “pure” components, i.e., the internal reference spectral components needed for interpreting the series of spectra, a different algorithm known as Multivariate curve resolution-alternating least squares (MCR-ALS) has to be used.

MCR-ALS algorithm is used to resolve the mixture analysis problem, it is able to decompose the raw mixed measurements into a scientifically meaningful additive bilinear model of pure contributions.\(^{247}\) Consider a bilinear data matrix \(D\) composed of \(m\) rows and \(n\) columns, MCR-ALS decomposes it into two simpler matrices \(C\) (concentration profile) and \(S^T\) (spectral profile). It can be written as:

\[
D\ (m \times n) = C\ (m \times k) \ast S^T\ (k \times n) + E
\]
E is the error matrix contains residual variation of the data set, mainly noise. The main steps followed in MCR-ALS procedure are depicted in the following Figure E.5.

Figure E.5. The main steps followed in MCR-ALS procedure.

The first step is to find the no. of pure components in order to define the dimension of pure C and $S^T$ matrices. This step is necessary because if the number is incorrect it will hinder the correct resolution of the data matrix (Nested method). The number of pure components can be found by Singular Value Decomposition (SVD) algorithm used for the PCA analysis. In the previous section of PCA, for CoNCN the no of principle components had found as three (higher eigenvalues), the same results from SVD can be obtained here as well. Figure E.6 shows the determination of components by SVD for CoNCN Operando analysis.
Next step is the initial estimation of pure concentration profile ($C$) and pure spectral profile ($S^T$) which are needed for the further ALS iteration algorithm. The main rule for the initial estimation is: it should always start with sensible guesses which obey the constraints will be used in the optimization process. This can be done either manually from the previous knowledge or by using methods like Evolving factor analysis (EFA), pure variable detection via simple-to-use self-modelling analysis (SIMPLISMA) approach, etc. Pure variable detection method can work irrespective of the absence or presence of a structured concentration direction in the data matrix. It selects the most dissimilar rows and columns from a single or multi structure data matrix and then provides the initial estimates of concentration and spectral profiles respectively. The main drawback associated with this method is it is only limited to positive data, for using the negative data, the spectra has to be pre-processed. Evolving factor analysis (EFA) particularly used for the studies where the concentration profiles of the components evolve smoothly in a sequence. It detects the component’s emergence and decay in the data set and then provides concentration profiles by assuming that all the components in the system follow a sequential emergence and decay. EFA is designed for the analysis of single data set, for multisets it should apply separately to each experiment. After, an improved initial estimate adding the individual EFA results can be

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*Figure E.6. Determination of number of components by SVD for CoNCN operando analysis.*
built. In CoNCN case, the initial estimation done by pure variable detection method and EFA method are shown in Figure E.7 (a) and (b).

![Figure E.7](image_url)

**Figure E.7.** Initial estimates by Pure variable detection (a) and Evolving factor analysis (b) methods for CoNCN operando analysis.

After the initial estimation alternating least-squares optimization (ALS) can be started by optimizing iteratively the concentration and spectral profiles $C$ and $S^T$ using the available information to reduce the rotational ambiguity inherent to any data decomposition with MCR. ALS optimization is performing by applying some constraints. Constraints can be defined as some particular characteristics of chemical or mathematical nature obeyed by the pure species for obtaining a final chemically meaningful solution. The most known natural constraints are shown in Figure E.8.
Figure E.8. Common natural constraints in ALS iterations.

**Non-negativity**: This constraint forces the profiles to be formed by only positive values and negative values can be implemented by zeros or with other softer algorithm like negative least squares.

**Unimodality**: Unimodality is applicable when there is a single maximum in the profile. Examples are elution profiles, monotonic reaction profiles etc.

**Closure**: It is called mass-balance condition, typically applied to the concentration profiles when the total concentration of the components is conserved.

**Hard modelling**: This constraint used to fit the concentration profile and/ or spectrum of a component to some parametric physiochemical models.

MCR-ALS analysis of initially estimated concentration and spectral profiles of CoNCN was performed with the constraints non-negativity, unimodality for one of the 3 components and Closure. Constraints applied on concentration profile are showed in Figure E.9.
Once all the constraints are set, ALS optimization begins. The iteration number can be preset according to the convergence criteria or by a threshold defining the difference in the improvement between consecutive iterations. Once the convergence achieved, the MCR results give the real set of concentration profiles and spectra along with quality parameters related to the fit. In the case of CoNCN the convergence was obtained in 7 consecutive iterations with variance of 99.99% as shown in Figure E.10. Evolution of the concentration profiles of three components can be analyzed with the corresponding galvanostatic profile. Starting from 126 total XAS spectra from CoNCN operando analysis the final three pure spectra obtained after MCR-ALS optimization contain all the useful information. These spectra can be realized via specific fitting procedures for the further analysis.
E.2.5. EXAFS data fitting

Modelling of the EXAFS oscillations of the MCR-ALS components were done by using Demeter software package. The Athena program was used for the spectra pretreatment and the background removal, and Artemis was used for the optimization of theoretical model to the measured spectrum. Artemis adjust the structural parameters in the EXAFS equation until a least-squares fit is obtained between the theoretical and experimental spectra. The model can be adjusted as needed (e.g., with different atom types) for make sure the best possible fit between theoretical and experimental spectra.

The special interface in Artemis called “Atoms” converts the crystal structure information into atoms cluster and provides atom positions list in x, y, z coordinates for FEFF computations. In the atom interface window users are allowed to define the crystal structure by specifying the information such as space group, unit cell dimensions, and the fractional positions of the atoms in unit cell etc. Normally, all these information can be extracted from
databases such as CIF files from the Inorganic Crystal Structure Database (ICSD). Once all the input data have been loaded, run the FEFF calculation and then the summary of the calculation will be displayed. Next step is to select the possible paths to include in the structural model and define their mathematical expression for the EXAFS parameters (see the equation below). The parameters includes $N$, $S_0^2$, $\sigma^2$ (amplitude of the EXAFS oscillations) and $\Delta E_0$ and $\Delta R$ (phase of the oscillations).

$$
\chi(k) \sim S_0^2 \sum_j N_j \frac{f_{j}(k)}{kR_j^2} e^{-2Rj\delta(k)} e^{-2k^2\sigma_j^2} \sin \left[ 2kR_j + \delta_j(k) \right]
$$

Where $f(k)$ and $\delta(k)$ are photoelectron scattering properties of the neighboring atom.

$R$ - Distance to neighboring atom.

$N$ - Coordination number of neighboring atom.

$\sigma^2$ - mean-square disorder of neighbor distance.

$S_0^2$ - Amplitude reduction factor

Once the model for the EXAFS parameters has developed, perform the fitting. The fitting results consist of the user defined variables, their fit values, uncertainties in the variables, along with some important information about the model statistics. Statistical parameters are:

- Number of independent points, $N_{idp}$
- Number of variables $N_{var}$
- $\chi^2$(chi-square)
- $\chi^2_v$ (reduced-chi-square)
- R factor.

Among this R factor is the major fit parameter, it is the sum of the squares of the differences between the data and the fit at each data point, divided by the sum of the squares of the data at each corresponding point. For a reasonable fit it should be less than $0.05^{252}$. 

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Abstract

Transition metal carbodiimides (MNCN, with M = Fe, Mn, Co, Cu, Zn, Ni) have been reported for their promising electrochemical performance as anode materials for both Li and Na ion batteries. However, the application of transition metal carbodiimides in the field of energy storage (and conversion) is still in its early stages and despite progress in electrochemical evaluation, much remains to be done in order to establish the reaction mechanisms that govern the reported promising performance. Besides the transition metal carbodiimides, there are still many other inorganic cyanamides and carbodiimides materials to explore. Therefore, the main targets of this PhD work are (i) to assess the possible application of new carbodiimides/cyanamides as electrode materials for LiBs and (ii) to establish the electrochemical reaction mechanisms of these materials via advanced operando techniques and DFT calculations.

Concerning the electrochemical performance, Cr$_2$(NCN)$_3$ turned out to be by far the best carbodiimide anode material with stable specific capacity of more than 500 mAh.g$^{-1}$ for more than 900 cycles at 2C rate. CoNCN and FeNCN have also excellent electrochemical properties since they can sustain a specific capacity higher than 500 mAh.g$^{-1}$ for more than 100 cycles at 2C rate. Poor performance has been observed for PbNCN, Ag$_3$NCN and ZnNCN since these phases show fast capacity fading during the first 20 cycles. These three performance categories correlate well with three different reaction mechanisms established for all the investigated phases.

Up to now, three types of reaction mechanisms have been identified including (i) Combined intercalation and conversion processes in the case of Cr$_2$(NCN)$_3$ as evidenced by both theoretical and experimental methods, (ii) pure conversion reaction in the case of CoNCN and finally (iii) a combined conversion and alloying mechanism in the case of Pb, Zn and Ag compounds. It is worth noting that whatever is the reaction pathway, all the carbodiimide/cyanamide anode materials face the limitation of a significantly low coulombic efficiency during the first cycles. To overcome this obstacle, much effort is needed to clarify the nature and the role of SEI in the overall performance of this family of materials. These promising results reported in this work do not probably yet meet the standards needed to take carbodiimides/cyanamides into the practical applications, but they clearly evidence the rich possibilities offered by this young family of inorganic materials.

Résumé

Les carbodiimides de métaux de transition dePerformance électrochimique des carbodiimides de métaux de transition a été montré des performances électrochimiques prometteuses en tant que matériaux anodiques pour les batteries aux ions Li et Na. Comme tous les matériaux d’électrode à base de métaux de transition, les carbodiimides souffrent d’une capacité irréversible initiale et d’un potentiel de fonctionnement élevés, mais présentent une meilleure tenue en cyclage. L’application des carbodiimides de métaux de transition dans le domaine du stockage (et de la conversion) de l’énergie en est encore à ses débuts malgré les progrès réalisés en terme d’évaluation électrochimique. Il reste encore beaucoup à faire pour établir les mécanismes réactionnels qui régissent les performances prometteuses observées. Outre les carbodiimides de métaux de transition, il reste encore de nombreux carbodiimides inorganiques à explorer. Par conséquent, les principaux objectifs de cette thèse sont (i) d’évaluer la possibilité d’application de nouveaux carbodiimides comme matériaux d’électrode pour les batteries Li-ion et (ii) d’établir les mécanismes réactionnels électrochimiques de ces matériaux au moyen de techniques de caractérisation operando avancées couplées à des calculs DFT.

En ce qui concerne les performances électrochimiques, Cr$_2$(NCN)$_3$ s’est révélé être le meilleur matériau d’anode, avec une capacité spécifique stable de plus de 500 mAh.g$^{-1}$ sur plus de 900 cycles à un régime de 2C. CoNCN et FeNCN ont également d’excellentes propriétés électrochimiques, car ils peuvent maintenir une capacité spécifique supérieure à 500 mAh.g$^{-1}$ pendant plus de 100 cycles à un régime de 2C. Des performances plus modestes ont été observées pour PbNCN, Ag$_3$NCN et ZnNCN car ces phases montrent une chute de capacité sur les 20 premiers cycles. Ces trois catégories de performances sont bien corrélées avec les trois différents mécanismes réactionnels établis pour toutes les phases étudiées.

Jusqu’à présent, trois types de mécanismes réactionnels ont été identifiés, à savoir (i) un processus combinant une étape d’intercalation suivie d’une étape de conversion dans le cas de Cr$_2$(NCN)$_3$, (ii) une réaction de conversion pure dans le cas de CoNCN et enfin (iii) un mécanisme combiné de conversion et d’alliage dans le cas des composés à base de Pb, Zn et Ag. Il convient de noter que, quelle que soit le mécanisme réactionnel, tous les matériaux d’anode carbodiimide sont confrontés à la limitation d’une faible efficacité coulombique au cours des premiers cycles. Pour surmonter cet obstacle, il faut déployer plus d’efforts pour clarifier la nature et le rôle de la SEI dans les performances globales de cette famille de matériaux. Bien que les résultats prometteurs présentés dans ce travail ne répondaient probablement pas aux normes requises pour intégrer les carbodiimides dans des applications commerciales, ils ont le mérite de montrer la richesse de la chimie des carbodiimides et de stimuler davantage de travaux de recherche sur cette famille de matériaux inorganiques moléculaires relativement jeune.