Batteries

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Transition-Metal Carbodiimides as Molecular Negative Electrode Materials for Lithium- and Sodium-Ion Batteries with Excellent Cycling Properties

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Abstract: *We report evidence for the electrochemical activity of transition-metal carbodiimides versus lithium and sodium. In particular, iron carbodiimide, FeNCN, can be efficiently used as negative electrode material for alkali-metal-ion batteries, similar to its oxide analogue FeO. Based on ^{57}Fe Mössbauer and infrared spectroscopy (IR) data, the electrochemical reaction mechanism can be explained by the reversible transformation of the Fe–NCN into Li/Na–NCN bonds during discharge and charge. These new electrode materials exhibit higher capacity compared to well-established negative electrode references such as graphite or hard carbon. Contrary to its oxide analogue, iron carbodiimide does not require heavy treatments (such as nanoscale tailoring, sophisticated textures, or coating) to obtain long cycle life with current density as high as 9 A g^{-1} for hundreds of charge–discharge cycles. Similar to the iron compound, several other transition-metal carbodiimides $M_x(NCN)_y$ with M = Mn, Cr, Zn can cycle successfully versus lithium and sodium. Their electrochemical activity and performance open the way to the design of a novel family of anode materials.*

The battery industry and market grow at an extremely aggressive pace, with lithium-ion technology leading the race. The emergence of new battery materials is linked to the world's increasing appetite for energy storage devices for communication, transportation, and defence systems. Analysts expect a growth in the market of primary-component battery materials from $7.3 to $19.3 billion between 2014 and 2023.[1] In this context, the design of new negative electrode materials made of affordable and abundant elements, with improved electrochemical performances compared to traditional graphite anodes, is crucial.

Among others, materials undergoing a so-called "conversion reaction" (metathesis) form one of the largest families of negative electrodes with interesting specific and volumetric capacities. They include transition-metal oxides as well as metal phosphides, sulfides, nitrides, and alloys (based on Si, Ge, Sn, Sb), all following the "conversion reaction"

$$\mathrm{M}_a\mathrm{X}_b + (b\cdot n)\,\mathrm{Li} \rightleftharpoons a\,\mathrm{M} + b\,\mathrm{Li}_n\mathrm{X} \tag{1}$$

where M = transition metal, X = p-group element and n = oxidation state of X (this mechanism is detailed, for example, in Refs. [2–6] and references therein).

Transition-metal oxides of generic formula MO (M = Fe, Ni, Co), for instance, have many advantages over others, such as low cost, environmental benignity, and high abundance. Since the first report,[7] several groups have investigated FeO and found a low capacity retention.[8,9] Many approaches tried to overcome the shortcomings, for example, by reducing the particle size, designing special nano-architectures, introducing carbonaceous composites or a combination of these approaches (see Ref. [9] and references therein). Nevertheless, such complicated processes with expensive and/or low yield cancel out the intrinsic advantages of FeO, that is, low cost and benignity.

More recently, a class of inorganic negative-electrode conversion-reaction materials characterized by a molecular structure has appeared, such as the well-known metal–organic frameworks (MOF).[10] Cyanamide/carbodiimide compounds with the general formula $\mathrm{M}_x(\mathrm{NCN})_y$ and M = alkali, alkaline-earth, transition metals, or metalloids are a still unexplored family. Its best known member is the commercially available fertilizer CaNCN.[11] More recently, many other metal carbodiimides were successfully prepared.[12–17] Introducing transition-metal carbodiimides was very difficult, at least until their existence was predicted by first-principles electronic-structure calculations.[18] In fact, phases designated as MNCN (with M = Mn, Fe, Co, Ni, Cu) emerged as metastable,

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endothermic compounds. However, since then many transition-metal carbodiimides were prepared thanks to a variety of adequate new chemical routes.[19–23] In a nutshell, carbodiimides are more covalent than their oxide counterparts, as it was clearly shown for MnNCN,[24] and the metal–N bond is lacking significant π interaction.[25] Moreover, plenty of interesting physico-chemical properties are revealed by comparing metal oxides with the respective carbodiimides (such as those shown in refs. [26–29]) and recently, copper and cobalt carbodiimides were applied as non-oxidic water-oxidation heterogeneous catalysts, with a dual photochemical and electrocatalytic activity in neutral and basic media.[30,31] A recent report on the use of carbodiimides in Li-ion batteries claims that MnNCN is not electrochemically active.[32] We will show in the following that the latter claim is unfounded. The aim of this work is to evaluate the potential of carbodiimides as anode materials for Li- and Na-ion batteries. Our results show that, indeed, Cr, Mn, Zn, and Fe carbodiimides are electrochemically active towards Li and Na. The reaction mechanism will be illustrated in detail for FeNCN, the equivalent of FeO in which the oxide anion O^{2-} is replaced by the NCN^{2-} moiety.

The synthesis and the electrochemical test conditions of FeNCN as well as of the other studied carbodiimides are detailed in the Supporting Information. In the same section, the theoretical electrochemical features of FeNCN (specific and volumetric capacity, volume expansion upon lithiation and sodiation) are compared to those of its oxide counterpart, FeO. The galvanostatic cycling of iron carbodiimide versus lithium is summarized in Figure 1.

The voltage composition profile (Figure 1 a) is very similar to that of FeO, with a first lithiation (discharge) taking place following a plateau around 0.6–0.8 V and then a continuous voltage decrease to 0.01 V.[7,8] The following sweeps (first charge and second discharge) are drastically different from the first discharge but completely reversible for the subsequent cycles. This behavior is typical of electrode materials undergoing the conversion reaction,[2,33] indicating deep structural and morphological changes during the first discharge, as will be shown hereafter. During the first cycle, a significant irreversible capacity is observed, underlined by a coulombic efficiency (CE) of about 70 %. This extra capacity can be explained, by analogy to transition-metal oxides, in terms of electrolyte decomposition with the formation of a solid electrolyte interphase (SEI) and a polymeric gel-type layer.[34] Such decomposition reactions are favored by the formation of nanosized grains in the discharged electrode.[34–36] After the first discharge, the CE reaches a higher and stable value close to 97 % (Figure 1 b). During the first charge (and the following cycles), a sloping curve is observed suggesting a single process at an average potential of 1.4 V (arithmetic average of the two potentials evaluated at half-charge and half-discharge), again very similar to FeO.

For the reaction of FeNCN versus sodium, a similar behavior is observed at a lower operating potential of 0.25 V during the first discharge and an average operating potential of about 1 V for the subsequent cycles (Figure 2 a). At C/5 rate, that is, a current of 56 mA g^{-1}, the initial reversible capacities of FeNCN towards Li and Na are 600 and 400 mAh g^{-1}, respectively, which is lower than those obtained for the analogous oxide (750 mAh g^{-1}), in line with the higher molar mass of the carbodiimide compound. Note that these values exceed those usually observed for common negative electrode materials such as graphite (vs. Li) and hard carbon (vs. Na), the latter presenting also a very large irreversible capacity at the first cycle.[37] Moreover, the CE of the FeNCN/Na system is excellent with a value very close to 100 % after the first cycle, meaning that no more Na^+ are irreversibly trapped during the electrolyte degradation (leading to the increase of the SEI) during cycling.

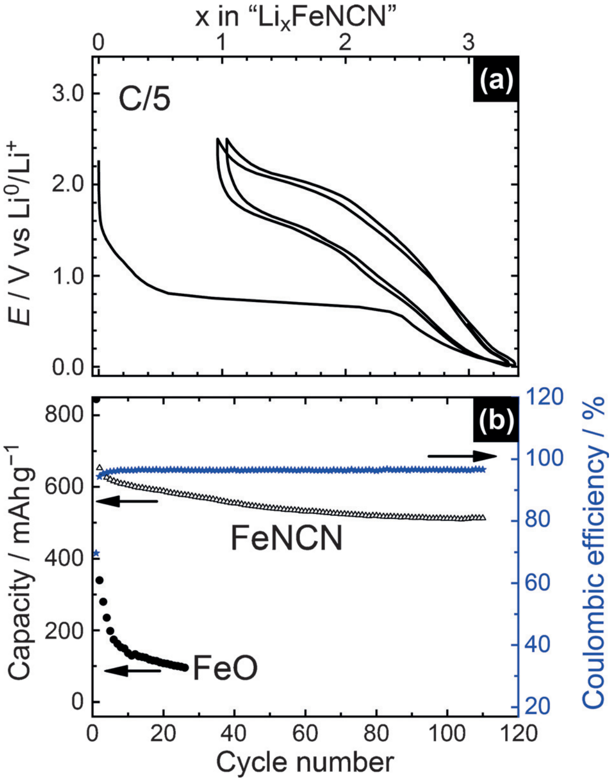

Figure 1. a) Galvanostatic profile and b) specific discharge capacity and coulombic efficiency versus cycle number for FeNCN in a Li half-cell. Specific discharge capacity for FeO in identical conditions is shown in black circles.

This result is remarkable since for other negative electrode materials working with both sodium and lithium, such as Sb, the chemical nature of the SEI layer is thinner in the Li case than in the Na one, leading to a better CE.[38] While the galvanostatic behavior of FeNCN compares well to FeO, the carbodiimide clearly exhibits improved capacity retention versus both lithium and sodium. While the longest cycle life reported for sophisticated FeO composites is 50–60 cycles at current densities between 50 and 400 mA g^{-1},[7,9,39] non-optimized microsized particles of FeNCN maintain a stable capacity, noticeably higher than graphite, for more than 100 cycles at a current density of 56 mA g^{-1} (C/5) versus lithium (Figure 1 b) and more than 240 cycles versus sodium (Figure 2 b). Moreover, in the case of FeO/Li a decrease of about 60 % of the capacity is observed after 25 cycles, whereas only 20 % of the capacity is lost for FeNCN/Li after 50 cycles. An

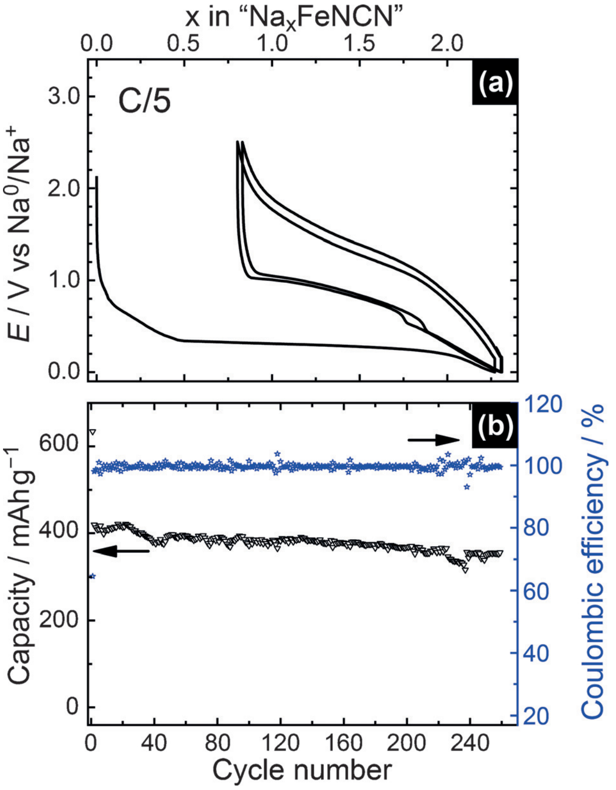

Figure 2. a) Galvanostatic profile and b) specific discharge capacity and coulombic efficiency versus cycle number for FeNCN in a Na half-cell.

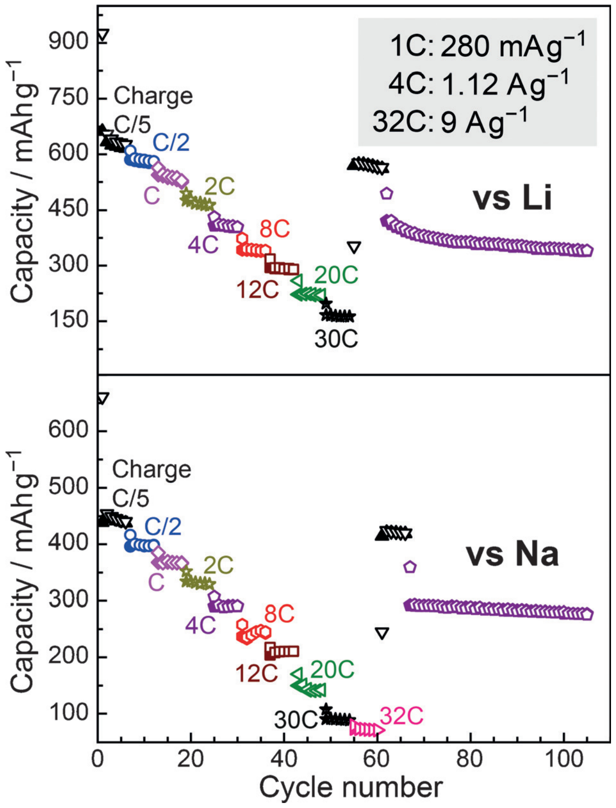

Figure 3. Rate capability of FeNCN vs. lithium (top) and sodium (bottom). Empty and filled symbols are used for discharge and charge, respectively.

additional capacity loss of only 5 % is observed between the 50th and 110th cycle. In the case of sodium, the capacity retention is even better, similarly to the case of Sb:[40] the capacity loss between the 1st and the 50th charge process is only 3 %, with an additional loss of 4 % after 100 cycles. Another interesting aspect is the rate capability, shown in Figure 3. Although the capacity is decreasing with increasing current density, the FeNCN electrode supports well current densities up to 9000 mA g^{-1} (32 C) without any irreversible damage when submitted to high current densities. These observations suggest an intrinsic robustness of FeNCN as anode material auguring that optimization of the material morphology and fine formulation of electrodes and electrolyte will provide excellent performance. Finally, Zn, Mn, and Cr analogues are also found to be electrochemically active and present a good cycling performance as evidenced from the preliminary tests (Supporting Information, Figure S2). The possible application of transition-metal carbodiimides as electrode materials for Li- and Na-ion batteries is in full accord with a previous independent study,[41] and a patent request has been recently filed.[51]

Several complementary techniques were used to elucidate the electrochemical mechanism in this family of materials. The reaction mechanism of FeNCN with lithium was first investigated by operando XRD (Supporting Information, Figure S3). A continuous decrease of the FeNCN pattern intensity is observed along the discharge without observing new diffraction peaks indicating the formation of amorphous phases. This amorphization is irreversible since no diffraction peaks appear during the first charge or the second discharge. To sum up, the good cycling behavior is correlated with irreversible nanostructuration that hinders the possible identification of the phases involved in the reaction by long-range order sensitive techniques such as XRD. We thus used additional short-range techniques such as ^{57}Fe Mössbauer and IR spectroscopy to overcome this issue.

In situ Mössbauer spectra (Figure 4) were acquired at different cycling stages. Spectrum (a) of the initial powder is similar to that previously reported[29] and can be fitted by two components: the main component is a magnetic octet with five resolved lines typical for divalent iron with a combined quadrupolar and magnetic interaction and corresponds to antiferromagnetically ordered high-spin Fe^{2+} (red curve); the weak doublet centered at 0.4 mm s^{-1} is attributed to slowly relaxing Fe^{3+} (gray line), as discussed by Herlitschke et al.,[29] which is most probably due to an impurity, such as an amorphous oxidized Fe(NCNH)$_2$ precursor.

Spectrum (b) collected at the end of the discharge consists of two doublets with similar isomer shifts (about 0.05 mm s^{-1}) and appreciably different quadrupole splittings (0.37 and 0.87 mm s^{-1}). These parameters are characteristic of superparamagnetic iron nanoparticles usually observed at the end of the lithiation of conversion materials, which confirms that Li/FeNCN is most likely converted into Li$_2$NCN/Fe^0.[42,43] At the end of the charge, spectrum (c) can only be fitted using a distribution of magnetically ordered Fe^{2+} components. Thus,

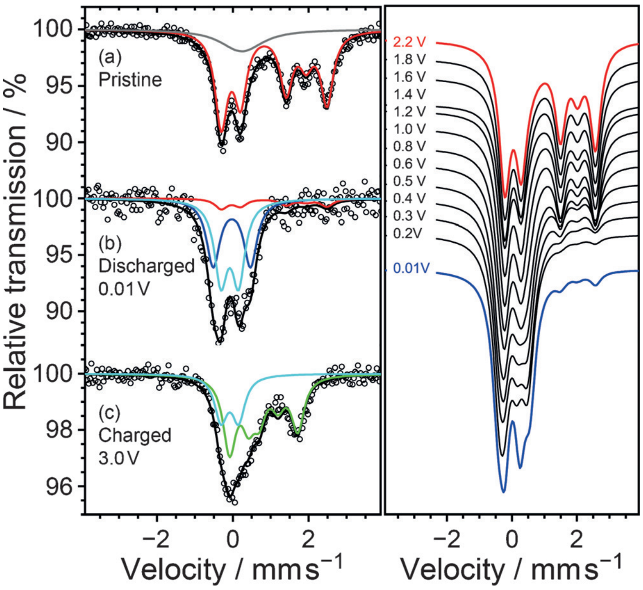

Figure 4. Left: Mössbauer spectra of a a) pristine, b) discharged, and c) charged FeNCN electrode vs. lithium. Fitted spectra obtained during the discharge (right).

the majority of the iron-metal nanoparticles is re-oxidized in the presence of the NCN^{2-} anions to give a Fe^{2+}-containing phase. The lower value of the hyperfine magnetic field (4 Tesla) is in agreement with the reformation of the FeNCN phase in the form of amorphous and/or nanostructured particles, in line with XRD data. Note that the iron oxidation during the charge process is incomplete, since the doublets corresponding to iron nanoparticles are still visible, albeit very weak, at the end of the charge.

Ex situ FTIR spectra of the pristine and cycled electrodes are shown in Figure 5. Pristine FeNCN displays two strong characteristic absorption bands, a narrow one at 642 cm^{-1} and a broad one centered at 2050 cm^{-1} corresponding to the bending (δ) and the asymmetric stretching (ν_{as}) modes of the NCN^{2-} ion, respectively. The symmetrical stretching mode for the linear $N{=}C{=}N^{2-}$ group is missing because it is IR-forbidden.[19] In the spectrum of the formulated FeNCN electrode, many additional bands are present between 900 and 1700 cm^{-1} due to both the carbon additives[44,45] and the carboxymethyl cellulose (CMC) binder[46] used for electrode formulation. Fortunately, both carbon additives and CMC have no absorption band in the range 1900–2200 cm^{-1}, so the main IR band of the carbodiimide is not affected. After full lithiation, 1) the bending band (642 cm^{-1}) has disappeared while a new one, broader and less intense, is observed around 670 cm^{-1}; and 2) the stretching band seems to consist of two unresolved bands around 1980 and 2050 cm^{-1} (Figures 5 b and c). These bending and stretching bands could be the signature of Li_2NCN even though their positions are slightly lower than the bands at 690 and 2165 cm^{-1} reported by Down et al.[14] for Li_2NCN. The difference could be related to the nanostructured nature of the electrode after the delithiation step.

The FTIR spectrum of the charged electrode is quite similar to that obtained for the non-cycled electrode, especially in the range of the asymmetrical stretching band, as evidenced with the zoomed spectra (Figures 5 b and c). However, the NCN stretching band is broad and shifted to lower energies compared to pristine FeNCN, in line with the formation of a nanostructured composite after lithium reaction with FeNCN. Note that both cycled electrodes contain additional absorption bands originating from the electrolyte constituents, such as the PF_6^- anion showing an intense band at 840 cm^{-1}, as well as to other compounds formed by their partial decomposition.[47] In summary, the complete electrochemical reaction of FeNCN with lithium can be formulated as:

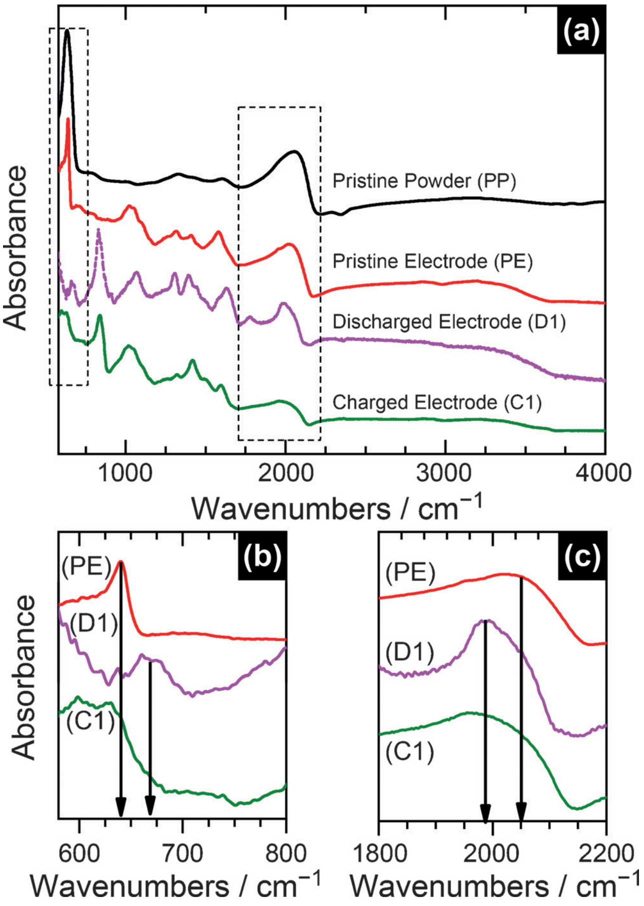

Figure 5. a) FTIR spectra for pristine powder (PP), pristine (PE), discharged (D1), and charge (C1) electrodes. b), c) Zooms around the main IR bands of the NCN^{2-} group.

$$FeNCN_{(s)} + 2\,Li_{(s)} \rightleftharpoons Fe_{(s)} + Li_2NCN_{(s)} \qquad (2)$$

Analogous reactions can be proposed for the other tested transition-metal carbodiimides, that is, MnNCN, ZnNCN, and $Cr_2(NCN)_3$.

This conclusive test of transition-metal carbodiimides as negative electrode materials in Li- and Na-ion batteries showed that both divalent (iron, manganese, and zinc) and trivalent (chromium) carbodiimides are electrochemically active. All studied compounds show galvanostatic behaviors similar to their oxide counterparts. Like oxides, metal carbodiimides exhibit a typical first discharge occurring at a low voltage pseudo-plateau with significant irreversible capacity that probably arises from the electrolyte degradation leading to the formation of an SEI, which is known to take place below 1.3 V.[48–50] This process is accompanied by the complete nanostructuration of the electrode material during the first discharge. The subsequent charge–discharge processes are perfectly reversible, showing a sloping shape at higher voltage. Unlike their oxide counterparts, transition-metal carbodiimides show excellent capacity retention already without any sophisticated pre-treatment or engineering. These excellent cycling properties are probably due to their thermochemical metastability, making them very reactive towards lithiation and sodiation. Moreover, transition-metal carbodiimides demonstrate their robustness since they support cycling at high current rate (up to 32 C, 9000 mA g^{-1}) without any damage of the electrode. The reaction mechanism with lithium was investigated in detail for the case of iron carbodiimide. Operando XRD analyses showed a totally irreversible nanostructuration of the pristine material during the first discharge. ^{57}Fe Mössbauer spectroscopy evidenced the implication of the Fe^{2+}/Fe^{0} redox couple in the redox mechanism, with a complete reduction of the Fe^{2+} cations along the discharge to form nanosized iron-metal superparamagnetic particles (Fe^{0}), which are oxidized during the following charge. Ex situ FTIR analyses agree with the formation of Li_2NCN during the discharge (and its following decomposition during the charge), and underline the occurrence of a typical conversion-reaction (metathetic) mechanism.

In conclusion, on the basis of the reported examples (Fe, Mn, Zn, and Cr), we can generalize that transition-metal carbodiimides represent a new family of efficient negative electrodes for Li- and Na-ion batteries, with an electrochemical mechanism governed by a conversion reaction.[51] This finding paves the way to the exploration of a large choice of materials through partial or total substitution of the oxide anion with the NCN^{2-} moiety in many well-known electrode materials such as titanates or generally oxides, with the hope of new electrochemical properties and improved cycling performances.

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