

Journal of Materials Chemistry A

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COMMUNICATION

Carbodiimides: New materials applied as anode electrodes for sodium and lithium ion batteries

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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Conversely to the electrochemical inactivity claimed for MnNCN, we report here that transition-metal carbodiimides, MNCN (M = Cu, Zn, Mn, Fe, Co and Ni) are electrochemically active materials for electrochemical energy-storage systems. They exhibit high reversible capacities (200–800 mAh/g) for lithium and sodium ion batteries, stored by means of conversion reactions.

At the beginning of the 21st century, exploiting so-called “renewable” energies has become another focus of energy-related research. A severe issue associated with “renewables” is that generation and consumption does not occur at the same time. In principle, however, the energy can be stored in portable or stationary devices such as batteries at production peaks in order to fully take advantage of the stored “renewable” energy when needed [1].

Due to the high energy density of lithium ion batteries (LIB), these devices are at the center of the portable electronic markets. On the other hand, work in sodium ion batteries (SIB) is being developed mostly for stationary applications. The search for new electrode material is important in order to improve the safety and environmental aspects of the battery, lower the costs or improve cycle life or energy density of the

battery. Up to now, graphite is the preferred anode material for lithium ion batteries taking into account its good chemical, thermal and mechanical stability [2], amount of stored energy and price for lithium ion batteries. Nonetheless, for sodium ion batteries [3, 4], sodium ions are not able to intercalate bare in graphite unless the electrolyte solvent, if of sufficient donor number (DN), is co-intercalated [5]. Although there is still no material which can provide as good electrochemical properties for SIB as graphite does for LIB, hard carbons present good performance and seem to be the best anode materials for sodium ion batteries [6]. Moreover, in order to lower the price of the synthetic process, research in organic compounds as terephthalates [7] or polymers as Schiff bases [8] has started. Some inorganics such as red phosphorus [9] or tin [10] and antimony [11] alloys show large plateaus with a high reversible capacity at low voltages but they lead to unsafe products XH_3 ($X = \text{P}, \text{Sb}$) and tin resources are largely depleted. We have decided to investigate transition-metal carbodiimides due to their similarities with the corresponding oxides. Both anions have the same charge (–2) and similar electronegativity values, namely 3.36 for NCN^{2-} and 3.47 for O^{2-} [12]. The lower electronegativity value of the $(\text{N}=\text{C}=\text{N})$ group and larger charge delocalization cause its bond with the transition metals to be more covalent [13] in comparison with the oxide bonds. Also, the structures of transition-metal carbodiimides and oxides are often similar with a small distortion due to the larger size of the NCN group (Figure 1). Most of the metal carbodiimides have a $[\text{N}=\text{C}=\text{N}]^{2-}$ group configuration following the Pearson HSAB principle [14]. The transition metal ions M^{2+} studied in this paper prefer the carbodiimide $[\text{N}=\text{C}=\text{N}]^{2-}$ form than cyanamide $[\text{N}-\text{C}\equiv\text{N}]^{2-}$ configuration [15]. However, H_2NCN has the $[\text{N}-\text{C}\equiv\text{N}]^{2-}$ configuration because the molecule is stabilized through the presence of hydrogen bonds. Moreover, the small molecular weight of the bivalent transition-metal carbodiimides makes them good candidates as anode materials. They have relatively high theoretical capacities (between 254 mAh/g per Li or Na ion in ZnNCN and 282 mAh/g in MnNCN). Analogue oxides such as CuO [16], MnO [17], FeO

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Electronic Supplementary Information (ESI) available: Additional experimental details, spectroscopic study and structural characterization including Figure S1–S3 and Tables S1 and S2. See DOI: 10.1039/x0xx00000x

[18], CoO [19] or NiO [16] react through conversion reaction mechanisms for lithium ion batteries. Nonetheless, for sodium ion batteries, FeO, CoO and NiO seem to be almost electrochemically inactive [20]. Given the similarities between both families and the “softer” chemical character of NCN vs O (bases), an improvement in the electrochemical behaviour may be expected. Up to now, transition-metal carbodiimides MNCN ($M = \text{Cu, Zn, Mn, Fe, Co, Ni}$), were only explored in terms of their magnetic properties. We here report the first electrochemically active carbodiimide materials for both lithium and sodium ion batteries.

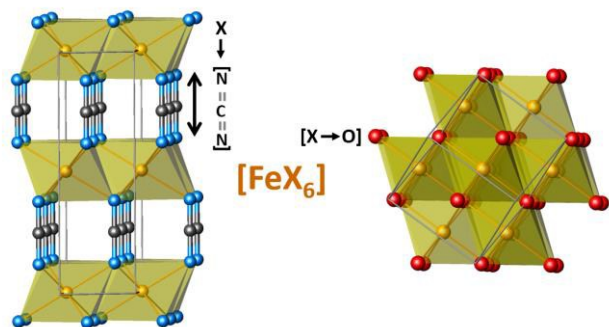


Figure 1. FeNCN (left) and FeO (right) structures. Octahedra of FeX_6 are drawn in both structures. The splitting of the layers of FeX_6 octahedra is pointed in the carbodiimide (left).

Copper [21] and zinc [15] carbodiimides were prepared in aqueous media from metal chlorides and cyanamide. Manganese carbodiimide was prepared by a new metathesis reaction of lithium carbodiimide and manganese chloride in stoichiometric amounts using THF as solvent. Lithium carbodiimide was synthesized with butyl-lithium and cyanamide as precursors with a ratio of 2.4:1. However, iron [22], cobalt and nickel carbodiimide [23] were obtained in two-step reactions. The first step was based on the synthesis of the metal hydrogen dicyanamide in aqueous media using the metal chlorides and cyanamide. The second step is the synthesis of the metal carbodiimide in a sealed glass ampoule. The metal hydrogen dicyanamide is mixed with a mixture of lithium and potassium chloride at the eutectic composition (59:41 mp = 352 °C) and heated up to 400 °C, melamine from disproportionation condensing at the cold end. The synthesized carbodiimides were structurally and electrochemically characterized. MNCN with $M = \text{Cu, Zn, Mn, Fe, Co, and Ni}$ were obtained as pure phase as confirmed by XRD (Figure 2).

CuNCN and ZnNCN reflect a better crystallinity than FeNCN, CoNCN and NiNCN. MnNCN, synthesized by a new metathesis route from Li_2NCN and MnCl_2 , has a very small particle size (6 nm) as deduced from Debye-Scherrer equation. The refined cell parameters of the synthesized carbodiimides are listed in Table S1. Also, the most typical IR bands of carbodiimides (the asymmetrical stretching vibration at 2000–2100 cm^{-1} and the strong deformation at 600–700 cm^{-1}) are all in agreement with the reported values [24]. The infrared spectra can be seen in Figure S1 and the frequencies at

which these bands appear are listed in Table S2. The large shift in the asymmetrical stretching of H_2NCN [24] is due to the cyanamide $[\text{N}-\text{C}\equiv\text{N}]^{2-}$ configuration with the asymmetrical stretching of H_2NCN appearing at 2200 cm^{-1} and being absent in all MNCN.

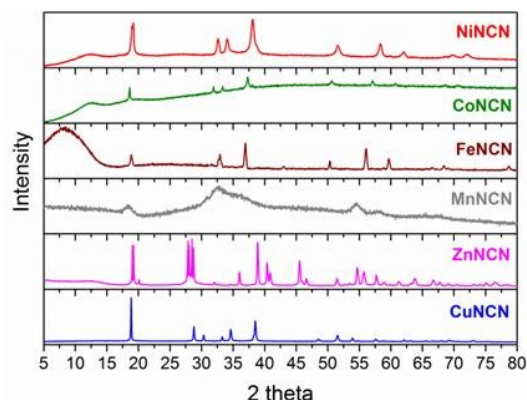


Figure 2. X-Ray diffraction patterns of copper (blue), zinc (pink), manganese (grey), iron (brown), cobalt (green) and nickel (red) carbodiimide.

The electrochemical performance of carbodiimides for SIB and LIB applications is represented in Figure 3. All tested carbodiimides display high reversible capacity values (200–800 mAh/g) for both sodium and lithium ions at voltages down to 0.005 V vs Li^+/Li or vs Na^+/Na . FeNCN, CoNCN and NiNCN showed capacities close to the theoretical ones for the insertion of 2 ions.

Nevertheless, it has to be taken into account that the reduction goes down to 0.005 V vs Na^+/Na , so there is a contribution of the SEI layer formation to the irreversible capacity and also of the insertion into carbon to the reversible capacity since 20% of the electrode is carbon (Figure S2). A small amount of Ketjen black is needed for the materials which react at low voltages to be active. The smaller particle size and higher surface area of this carbon with respect to typical activated carbons provides better percolation enabling materials such as ZnNCN and MnNCN to be electrochemically active.

Herein, each carbodiimide shows its distinct behaviour. NiNCN (red charts in Figure 3) and CoNCN (plotted in green) galvanostatic cycles have very similar properties for LIB and SIB and show the largest reversible and irreversible capacities in the first cycle. While in NiNCN there is a very large plateau at ~ 0.7 V vs Na^+/Na and at ~ 0.9 V vs Li^+/Li , CoNCN has the plateau at 0.9 V vs Na^+/Na and 1.1 V vs Li^+/Li . CoNCN has a reversible capacity of about 600 mAh/g for sodium ion batteries, that is very close to the theoretical one for two electrons (542 mAh/g). For lithium-ion batteries, however, the capacity value is about 800 mAh/g, probably due to the larger contribution of the carbon for Li^+ insertion even if the amount of carbon in each electrode is more or less the same. However, NiNCN has a capacity around 600–700 mAh/g for sodium and lithium ions which is a value close to the theoretical capacity for two electrons (543 mAh/g).

FeNCN, MnNCN, ZnNCN and CuNCN have smaller reversible capacity as well as smaller irreversible capacity in the first cycle. FeNCN also exhibits less polarization and irreversible capacity both

for Li and Na ions (brown lines in Figure 3). It shows a reversible capacity of 450 mAh/g cycling vs sodium with a very large plateau at 0.25 V vs Na⁺/Na, and 550 mAh/g vs lithium which corresponds to the theoretical capacity for transferring 2 electrons for FeNCN.

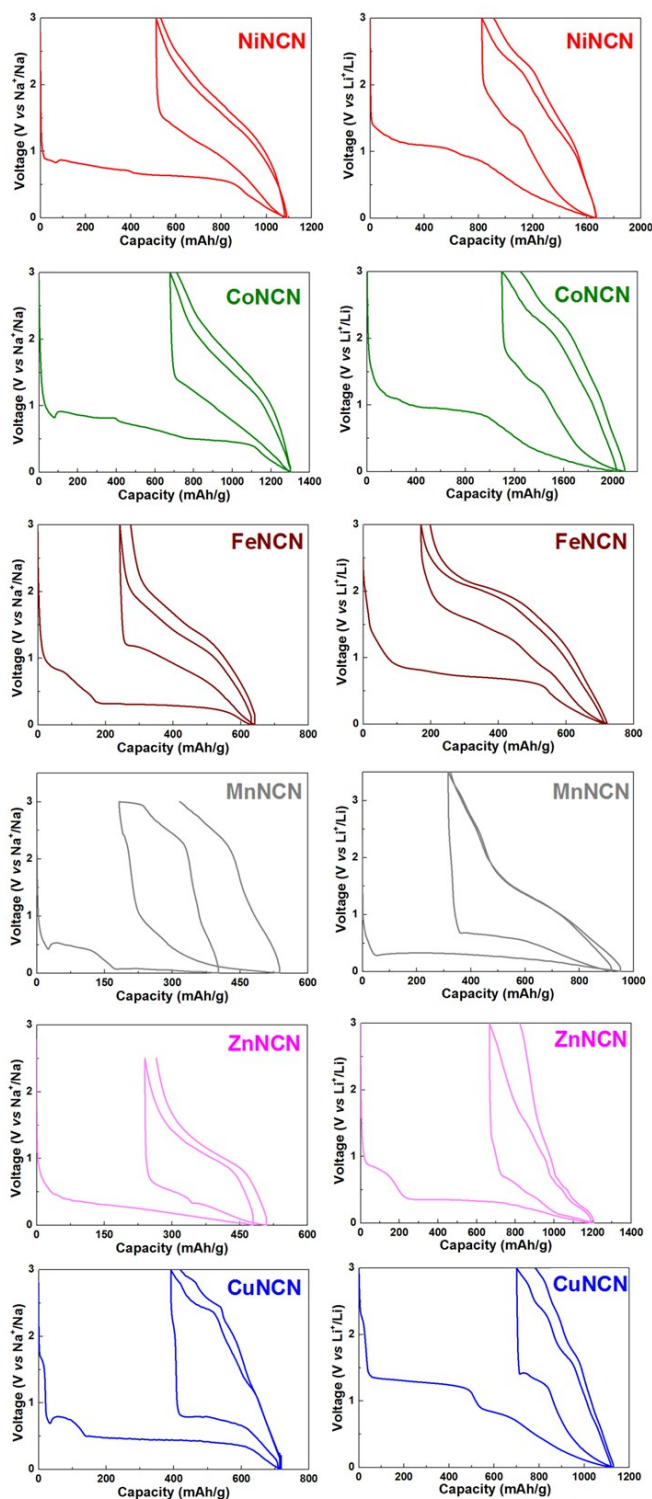


Figure 3. Two first galvanostatic cycles with constant current rate of $C/10$ of CuNCN (blue), ZnNCN (pink), MnNCN (grey), FeNCN (brown), CoNCN (green) and NiNCN (red) for sodium (left side) and lithium (right side) ion batteries. The materials were cycled with a constant current rate of $C/10$ considering $C = 2 \text{ Na}^+$ or Li^+ ions per MNCN unit.

MnNCN exhibits a very different behavior for SIB and LIB. For SIB, it shows a reversible capacity of 200 mAh/g (grey chart of Figure 3 on the left) although with very high polarization. Note that a proportion of high surface area carbon, Ketjen Black, was needed in order to achieve activity vs sodium. On the other hand, in a LIB, (Figure 3 plotted in grey on the right) it provides a very high reversible capacity of 600 mAh/g, very close to the theoretical one for 2 transferred electrons in MnNCN with a plateau at very low voltage of 0.2 V vs Li⁺/Li in the first discharge and at 0.5 V vs Li⁺/Li for the next cycles, with smaller polarization. Also, it is worth mentioning that the MnNCN with a larger crystal size synthesized following the original method [25] is not electrochemically active [26]. ZnNCN, cycling vs sodium and vs lithium (pink lines in Figure 3), has a reversible capacity of 250 mAh/g and one plateau at 0.5 V vs A⁺/A, irrespective of A = Li⁺ or Na⁺, which is unexpected. Finally, CuNCN has a reversible capacity of 300 mAh/g with a big polarization for sodium ion batteries in blue line in Figure 3 on the left, similar to that reported for CuO vs Na⁺/Na [27], and smaller polarization and capacity (250 mAh/g) vs Li⁺/Li in blue line on the right in Figure 3.

In order to better detect the voltages at which the redox reactions of all carbodiimides electrodes occur. $\delta Q/\delta V$ s of all of MNCN are represented in Figure S3a for the first cycle. Along the increase in the number of 3d electrons the average voltage of the reduction reaction of the carbodiimides is also increasing from MnNCN to FeNCN, CoNCN and NiNCN. However, CuNCN and ZnNCN do not follow the same rule because 4s orbitals are involved in the redox reactions [28].

Ex-situ XRD patterns have been collected for all samples at the end of discharge (Figure S4). We present here, as a representative, the in-situ XRD experiment of CuNCN during reduction (Figure 4). When CuNCN is cycled vs Na⁺/Na, at the initial steps of Na⁺ insertion, all the reflections corresponding to CuNCN decrease in intensity during cycling but they are not shifted. This proves that there is no topochemical Na⁺ intercalation through a solid-solution process despite the sloppy character of the voltage curve. Later, during the ~ 0.4 V vs Na⁺/Na voltage plateau, the intensity of the reflections continues decreasing, although not monotonically, meaning that some side processes such as electrolyte decomposition and SEI layer formation occur simultaneously with the electrochemical reaction, although at different rates, in this voltage range. At the end of the discharge the reflections of CuNCN disappear while only a very broad peak appears at $2\theta \sim 44^\circ$. The latter corresponds to the (111) reflection of metallic copper which suggest that a conversion reaction similar to those occurring in oxides is taking place. The carbodiimide reflections were not recovered after the first charge (Figure S5). This suggests that the electrode material reacts towards a smaller particle size and from there, it is impossible to distinguish the products formed. Ongoing spectroscopic studies aim at elucidating the additional products, likely Na₂NCN, formed during the reaction.

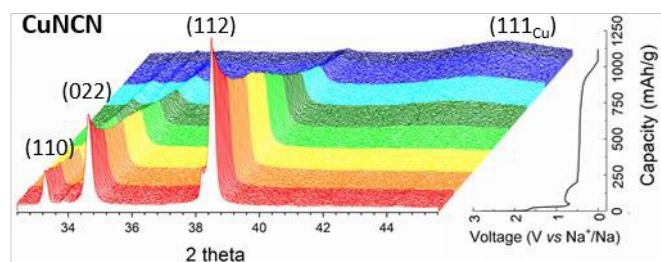


Figure 4. The evolution of the peaks of in-situ powder XRD data according to the first discharge of CuNCN down to 0.005 V vs Na⁺/Na.

In the first charge of CuNCN only one electron seems to be involved during the electrochemical process. The reversible capacity obtained upon cycling is closer to the theoretical capacity for the formation of Cu₂NCN (258 mAh/g) than CuNCN (517 mAh/g) although the formation of Cu₂NCN at the end of the charge has not been confirmed yet by any ex-situ or in-situ analysis. This would be in agreement with the study of mechanism of CuO vs Na⁺/Na [27] where it was observed that during the first discharge, Cu₂O is appearing as intermediate and suggested that the obtained reversible capacity could be due to the formation of Cu₂O upon charge. The number of electrons involved and thus the phases that are formed depends on the nature of the transition metal as well as the alkali ion being intercalated, and therefore a deeper study of each individual system is desired.

Conclusions

In conclusion, transition-metal carbodiimides MNCN (*M* = Cu, Zn, Mn, Fe, Co, Ni) are shown for the first time to be electrochemically active in Li and Na ion batteries. Judging from the large capacity values exceeding to insertion of one alkali atom per formula unit, the hysteresis and fading of voltage profile and given the similarities of carbodiimides to the oxide group, it seems that most *M*(II) binary transition-metal carbodiimides operate through conversion reactions as demonstrated by in-situ powder XRD for CuNCN vs Na⁺/Na. Also, in comparison to the oxides, carbodiimides show higher capacities and smaller hysteresis, especially for FeNCN, CoNCN and NiNCN. This means that carbodiimides improve the electrochemical performance in terms of energy density and efficiency vs oxides, and it opens a new field of inorganic materials that could be explored for their electrochemical performance not only in rechargeable Li and Na ion batteries but also in other electrochemical devices, with many open questions regarding their mechanisms of reactions and future possibilities of transition-metal carbodiimides.

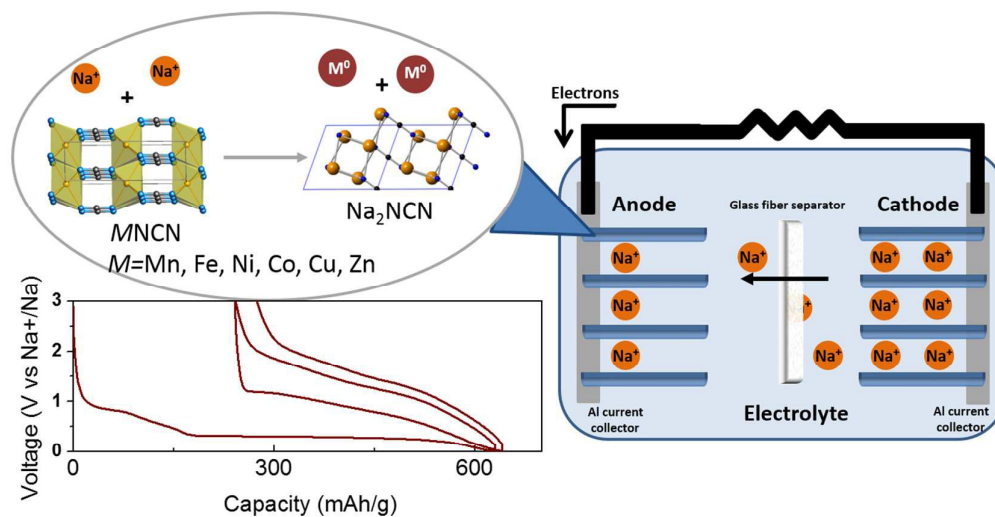
KEYWORDS. Carbodiimides, Na-ion batteries, Li-ion batteries, Anodes, Batteries

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Graphical Abstract

Carbodiimides: New materials applied as anode electrodes for sodium and lithium ion batteries



Carbodiimides for batteries: The family of transition metal carbodiimides $MNCN$ ($M = Cu, Zn, Mn, Fe, Co, Ni$) are shown to be new electrochemically active materials through displacement reactions both for lithium and sodium ion batteries.