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### High voltage supercapacitors based on carbon-grafted NiO nanowires interfaced with an aprotic ionic liquid

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ChemComm

Received 00th January 2012, Accepted 00th January 2012

Cite this: DOI: 10.1039/x0xx00000x

DOI: 10.1039/x0xx00000x

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The report provides a preliminary assessment of the charge storage prerogatives of an asymmetric electrochemical capacitor employing a carbon-grafted NiO electrode interfaced with 1-ethyl-3-methyl imidazoliumdicyanamide as ionic liquid electrolyte. This configuration has been demonstrated to be potentially exploited for developing hybrid supercapacitors providing an as high energy density as 21 WhKg<sup>-1</sup>.

Electric double-layer capacitors (EDLCs or supercapacitors) have been extensively explored as promising energy storage devices in which the charge/energy is stored through ion rearrangement in the interfacial layer between the electrode and electrolyte. Substantial efforts have been dedicated to improve the energy density of EDLCs through design of nanostructured electrodes with a high specific surface area and understanding the interplay between various phenomena defining the performance of these devices.<sup>1</sup>

For EDLCs, room temperature ionic liquids (RTILs) are widely considered the electrolyte of the future. RTILs are solventless electrolytes with many properties that make them attractive for electrochemical energy storage: high chemical and thermal stability, negligible vapor pressure, a broad electrochemical stability potential window and an immense parameter space in terms of ion selection and resulting properties.<sup>2,3</sup>. They are displaced to form alternating layers of cations and anions aligned near a charged surface with the peak densities decomposing to the corresponding bulk values<sup>4</sup>. These alternating layers are accountable for a number of unforeseen electrochemical phenomena at small scales. Larger specific capacitances have been recently achieved through the use of high surface area activated carbon electrodes in combination with different ionic liquid electrolytes.<sup>5</sup>

However it has been shown that not all micropores generated in carbon preparation can be available for EDL formation as in the case of aqueous electrolytes<sup>5</sup>. Largeot et al. observed the "anomalous" increase of capacitance when the pore size of an electrode comes close to the

ionic dimensions<sup>6</sup>. It could be attributed to the formation of ultra-thin EDLs, mainly caused by the absence of solvation shells around RTILs, which also enhances the accessibility of ions to infiltrate nano/sub-nano porous electrodes<sup>7,8</sup>. Increasing specific capacitance through bringing in the faradaic mechanisms was also shown to be a reliable strategy to increase the specific capacitance and in turn the energy density values. Metal oxides such as RuO<sub>2</sub>, MnO<sub>2</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>, metal sulfides, and conducting polymers<sup>9–15</sup> have been used as pseudocapacitor electrode materials. Among these materials, RuO<sub>2</sub> exhibits higher specific capacitance in acidic electrolytes. However, the toxicity and low abundance have necessitated the need to develop other inexpensive materials of comparable performance. NiO is a likely replacement for RuO<sub>2</sub> due to its high theoretical specific capacitance, high chemical and thermal stability and lower cost.<sup>16</sup>

Starting from these remarks, the prospects of using an IL electrolyte in NiO based hybrid supercapacitor shave been preliminarily demonstrated in the present work. A typical aprotic IL, namely 1-ethyl-3-methyl imidazolium-dicyanamide has been examined wherein a highly porous nickel oxide nanowire/carbon network with a pore size roughly close to the anionic radii has been used as anode. It has been assumed that in a similar system dicyanamide ions would form a monolayer surrounded by the charged electrode surfaces<sup>17</sup>.

NiO/carbon composite nanowires were synthesized by following the synthetic route provided in our recently patented procedure.<sup>18,19</sup> Briefly, 0.7M of nickel chloride and 0.7M of ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) were individually dissolved in distilled water and blended under rigorous stirring conditions at room temperature. 1 mL of triethanolamine (TEA) was added to this mixture under stirring. The resultant solution was transferred to a 50 mL Teflon tank and autoclaved at 120°C for 10 h, resulting in a pale green color precipitate. The precipitate was centrifuged and washed with ethanol and dried in air to obtain nickel oxalate nanowires. Camphor blocks were mixed with the nanowire dispersion in methanol in different weight ratio and pyrolyzed in air. In order to synthesize pristine NiO nanowires the nickel oxalate nanowires were annealed at 300°C. Details of the phase,

a)

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Voltage (V)

- 1<sup>st</sup> cycle - 2000<sup>th</sup> yr

dens 1.6 2.4 Voltage (V) 3.2 0.8 1.6 Voltage (V) e) 3.0 d) 35 2.5 2.8 E2 22 /oltage Noltage Fig. 2 CV curves of pure NiO (a) and NC samples (b) at 100 mV/s; CV of NC\_50 at different scan rates; discharge profiles of NC 50 at different currents (c) and comparison between 1<sup>st</sup> and 2000<sup>th</sup> cycles (d).

> The patterns showed an  $I_D/I_G$  ratio of 0.56. (see Fig.1b). The peak at 500cm<sup>-1</sup> corresponds to NiO in the case of NC samples.<sup>23</sup> Fig 1c and 1d show the TEM and HR-TEM images of the nanowire samples. The presence of carbon as a coating is evident from the phase contrast in Fig 1c. Fig. 1d depicts the high magnification examination of these samples revealing the presence of carbon being grafted on the surface wherein the interplanar spacing was measured to be 0.33 nm. On the NiO nanowires it results to be 0.24 nm along the lateral growth direction and both of them are consistent with the identification of (111) plane of as revealed from XRD pattern.

Surface area of the pristine NiO as well as of all the NC samples was calculated from a BET analysis: it has been estimated to be around 74 (for NiO), 89 (for NC 10), 92 (for NC 20), 101 (NC 50) and 91 m<sup>2</sup>g<sup>-1</sup> (for NC\_60) with an average pore size ranging from 0.4 to 0.8 nm (see Fig. SI 3).24

The here referred nanostructured films were thus immersed into an EMI-DCA solution and subjected to a set of exhaustive electrochemical analysis (experimental details are given in ESI). Fig. 2 displays representative cyclic voltammograms (CV) (at 100 mV s<sup>-1</sup> scan rate) of both pure NiO (Fig. 2a) and NC electrodes with different carbon contents (Fig. 2b) in a coin cell configuration. The presence of redox peaks is reasonably attributable to the absorption and desorption of dicyanamide ions from the electrolyte.

We have also investigated the redox activity of NiO in EMI-DCA in a three-electrodes set up. CV measured at a 10 mV/s scan rate in narrower electrochemical window vs. SCE is shown in Fig SI 4b. It clearly highlights the role of redox reactions in determining the electrochemical capacitance of the NiO electrode: both reduction (at around 0.2V) and oxidation (at around 0.9V) peaks (marked with arrows in the figure) are clearly observable. Here the capacitance is mainly based on the redox reaction because the shape of the CVs is distinguished from that of electric double-layer capacitance, which is normally close to an ideal rectangular.<sup>25</sup> XPS analysis of the same electrode in the pristine, charged and discharged state has been also provided to support this.<sup>26</sup> See Fig. SI 4a. Analytical data indicate that NiO is essentially divalent before charging; upon charging it seems to be consistent with the presence of both divalent and trivalent Ni ions, confirming the establishment of a faradaic contribution to the charge/discharge phenomena at NiO/electrolyte interface.



TEA plays a fundamental role in this synthetic route since it acts like a soft template which modulates the degree of solution supersaturation and governs the lattice development mode of the growing nanocrystals by dynamically adhering to specific crystal facets of the nickel oxalate nuclei. A schematic illustration showing the formation mechanism of the nanowires is given in Fig SI\_1a. The final step of the synthesis involves the formation of continuous nickel oxalate nanowires due to Ostwald ripening of the pristine nanocrystals. An increase in reaction time leads to the formation of bundles of nanowires SI 1b). The pyrolytic decomposition of camphor with nickel oxalate results in its dissociation along with the formation of a graphitic layer over the growing NiO nanclusters. In addition to this, in presence of CO and H<sub>2</sub> a partial reduction reaction occurs, leading to the formation of Ni seeds, which can facilitate dispersion of the carbon and serve as catalysts for nucleation sites, thus resulting in the formation of an interconnected graphitic network.<sup>20</sup> Depending on the average amount of carbon in the electrode, which has been calculated from CHN analysis, the samples were designated as NC\_10, NC\_20, NC\_50 and NC\_60, where N, C and number refer to NiO nanowires, carbon and amount of carbon, respectively.

Fig. 1(a) shows typical XRD patterns of the NC nanowires. The diffraction peaks indexed corresponded to cubic phases of NiO (JCPDS (Joint Committee on Powder Diffraction Standards) 78-0429) along with traces of metallic nickel (JCPDS 04-0850) and graphitic carbon (JCPDS 75-2078). The XRD patterns of the nickel oxalate nanowires (JCPDS 01-0299) and pristine NiO nanowires pyrolyzed without camphor are given in the supporting information (see SI 2a, b).

Fig 1 (b) represents the Raman spectra of pure carbon sourced from the pyrolysis of camphor and the NC nanowires<sup>21</sup> showing an enhance intensity of G band. Here CDC and CGN represent camphor derived carbon and carbon grafted NiO, respectively. Two sharp peaks with intensity maxima at 1345 cm<sup>-1</sup> and 1585 cm<sup>-1</sup> correspond to the D and G bands of graphite phase.22



Fig. 1.a) XRD spectrum of an NC\_50 sample; b) Raman spectra of camphorderived carbon (CDC) and carbon-grafted nickel oxide (CGN); c) TEM and d) HR-TEM images of GCN

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Based on these facts a possible redox process is been hypothesized as following:

$$NiO + N(CN)_{2}^{-} \leftrightarrow NiO \cdot N(CN)_{2} + e^{-}$$
(1)

NC\_50 electrodes revealed the best charge storage performance as a consequence of an optimum balance between high surface area and good electronic conductivity.<sup>27</sup> CV plots of NC\_50 with three different scan rates (100, 200 and 500 mVs<sup>-1</sup>) are shown in Fig 2c. As expected, at higher scan rates a less prominent redox pattern can be observed.

We thus used the voltammetric sweep rate dependence to quantitatively determine the capacitive and faradaic contributions to the current response (see Supporting Info).<sup>28</sup> Fig. 2d shows the galvanostatic response of NC\_50 at different discharging currents of 10, 30, 70 and 100 mA. The observed non-linearity in the discharge curve can be attributed to the pseudocapacitance arising out of the redox reaction in the given voltage range<sup>27</sup>.As the current density increases the voltage drop at the onset of the discharge profile becomes more prominent indicating the larger IR drop. Fig. 2e represents the discharge profiles of the system at 1st and 2000th cycles at 20 mA indicating a high cyclic stability with a fade of less than 5%.

The most relevant figures of merits, such as specific capacitance Cs, power density (P) and energy density (E) were then calculated according to DIN IEC 62391-1 (equation S1, S2 and S3)<sup>9</sup>. The maximum capacitance value was calculated to be 1.6 F. The maximum energy and power density values were calculated to be 21 WhKg<sup>-1</sup> and 8.3 kWKg<sup>-1</sup> respectively.

Electrochemical impedance spectroscopy (EIS) measurementswere carried out to determine the charge kinetic properties of the device associated with the above supercapacitive parameters.Fig. 3a and 3b show the Nyquist plot of the as-prepared coin cells based on pure NiO, NC50 and NC60 in the frequency range 100 kHz-0.1 Hz at open circuit potential. The EIS spectra of a pseudocapacitor device usually divided into three segments following three processes; (i) the overall series resistance at high frequency (>1 kHz); (ii) capacitive effects at high and intermediate frequencies (>0.1 kHz); and (iii) Warburg diffusion resulting from the frequency dependence of ion diffusion/ transport in the electrolyte at low frequencies (0.01-0.1 Hz). To elucidate the individual processes and associated impedance parameters the electrical equivalent circuit sketched in Fig 3b has been used, which comprises the series resistance Rs, the electrical double layer capacitance ( $C_{dl}$ ), the charge transfer impedance (R<sub>ct</sub>), frequency dependent Warburg impedance (Z<sub>w</sub>). R<sub>s</sub> is a combination of (i) electrolyte resistance, (ii) intrinsic resistance of the electroactive material, and (iii) the contact resistance between the active material and the current collector that



Fig.3Nyquist plots measured at 0.1V for NiO, NC\_50 and NC\_60 electrodes. The equivalent electrical circuit used to analyze these data is shown in the inset

determines the high frequency off-set of the EIS spectrum<sup>28</sup>.

Pure NiO electrode exhibits a huge charge transfer resistance which completely overwhelms any capacitive effect. These results confirm that introduction of graphitic carbon dramatically facilitates the electron transfer and induces the formation of a double-layer capacitor at the interface. NC\_50 has been confirmed to provide the lowest series resistance among all the here tested electrode compositions.

The charge/discharge prerogatives of the here referred carbon-grafted NiO electrodes can be reasonably understood by assuming the validity of the following assumed conditions<sup>29</sup>: (1) the structure of electrode/ionic liquid interface is to obey the Gouy-Chapman-Stern theory;<sup>30</sup> (2) the EDLC in this electrode/ionic liquid interface is composed of more than one layer of ions with the same/or different signs (i.e., cations or/and anions) arranged in proportion to the charge density of the electrode. The first layer of the ions attached to the electrode surface is called the compact layer (or Helmholtz layer);<sup>31-32</sup> (3) the overall capacitance (Cdl) of such a EDLC in an ionic liquid is approximately equal to the inner or compact layer capacitance (Cc) and the diffuse layer capacitance (Cd) is negligible. According to this model, EMI ions are arranged to form a charged layer in which ethyl chains result to be preferentially aligned towards the C/NiO electrode.33 During the charging process they come to be preferentially adsorbed on the electrode surface due to their high hydrophobicity, whereas the charged moieties (imidazole rings and N(CN)2) could reside away from the electrode surface. Accordingly, DCA<sup>-</sup> ions, which trigger the pseudocapacitive reaction, are likely chemisorbed on the nanostructured electrode during upon discharging, as schematically shown in Fig 4.



Fig. 4 Schematic diagram showing the formation of double layer at the electrode electrolyte interface

In summary, the pseudocapacitive behavior of carbon-grafted NiO-NWs electrodes in an EMI-DCA-based electrolyte has been assessed and their electrochemical properties have been investigated through CV and EIS analysis. Using aprotic IL electrolytes may therefore lead to the development of robust EDLCs which promise to conveniently conjugate power and energy density requirements in a wide range of practical applications.

#### Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, XRD and XPS spectra, BET analysis, electrochemical analysis. See DOI: 10.1039/c000000x/

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