Electronic Supporting Information

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

Morphological and structural characterization. Morphological analyses were performed by using High Resolution Transmission Electron Microscopy (HR-TEM-SAED, Model: JEOL, JEM-2100F) and Scanning Electron Microscopy (SEM; JEOL, JSM-6510). Phase analyses were performed by using X-ray diffractometry (XRD; X'Pert PRO Analytical), Raman spectroscopy (Witec alpha-300) and X-ray Photoelectron Spectroscopy (XPS; Axis Ultra, Shimadzu). Surface area measurements were done by using a BET analyser (Nova Quantachrome). The typical sample weight used was 100–200 mg. Before the measurements, the samples were out-gassed at 200°C overnight under vacuum. All adsorption–desorption measurements were carried out at liquid nitrogen temperature (-196°C). The non-linear density functional theory (NLDFT) method was applied to the N₂ adsorption isotherms to determine the pore size distribution using the Micromeritics software. A Horvath–Kawazoe method was used to extract the microporosity.



Figure SI_1. a) Schematic illusartion showing the formation mechanism of NC samples and b) TEM images of bundles of nickel oxalate nanowires



Figure SI_2. XRD patterns of a) as synthesized nickel oxalate and b) NiO nanowires.



Figure SI_3. Pore size distribution of NiO and NC samples

Electrochemical Analysis

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed by using an electrochemical workstation (Autolab, PGSTAT 302N, Netherlands) to evaluate the capacitance and internal resistance, respectively. Constant-current charge-discharge studies were used to determine the energy and power densities of the electrodes. For all of the above electrochemical studies, a coin cell prototype was used. The working electrode was assembled by coating the slurry of the NiO/NC powder on to a nickel foil current-collector of 16 mm in diameter. The mixture composed of 81 wt % active material, 5 wt % conducting carbon and 14 wt % binder (polyvinylidene fluoride) in an N-methylpyrrolidione (NMP) solvent. The counter electrode was assembled following the same procedure wherein slurry consisted of 85 wt% mesoporous carbon and 5 wt% binder. The electrodes were soaked in the EMI-DCA was used as the electrolyte electrolyte. A polypropylene (PP) film (BATSOL, India) was used as the separator.

In order to further investigate the redox behavior of NiO single electrode studies were also carried out using a three electrode set up consisting of electrophoretically deposited NiO nanostructures, Platinum and standard calomel electrode (SCE) were respectively used as working, counter and reference electrode. EMI-DCA was used as the electrolyte.



Figure SI 4. a) XPS and b) CV curves of a bare NiO electrode

Surface and bulk contributions to the total capacitance: The total charge stored in a rechargeable electrode system like NiO can be divided into two components: i) the faradaic contribution (see equation (i) in the text) and iii) the non-faradaic contribution from the double layer effect primarily arising from the carbon.

These contributions were characterized by analyzing the CV data at various sweep rates and derived using the power law $i = av^b$, where v is the scan rate and a, b are adjustable parameters. The parameter b was determined from the slope of the linear plot of log i vs log v (. In general, slope b=1 for surface redox reactions involving non-diffusion-controlled processes, thus i=av. While for the ideal diffusion-controlled faradaic process, the slope b=1/2 and satisfies Cottrell's equation:

$$i = av^{1/2}$$
 (i)

Therefore, the current response "*i*" at a given potential, V, is the sum of two contributions arising from the redox pseudo-capacitance and intercalation capacity as discussed below.

$$i(V) = K_1 v + K_2 v^{1/2}$$
(ii)

where $K_1 v$ and $K_2 v^{1/2}$ correspond to the current contributions from the capacitive (redox pseudo capacitance plus double layer capacitance) and insertion processes, respectively. Thus, by determining K_1 and K_2 , it is possible to determine the current response due to capacitive and insertion processes at a particular potential.



Figure SI_5. Representative plot showing the relationship of $\log i$ Vs $\log v$ for different voltages of cyclic voltammogram at a) charging and b) discharging



Figure SI_6. Representative plot showing the dependence of slope 'b' (derived from linear fit of log i vs log v) as a function of cell voltage



Figure SI_7. Representative plots of $v^{1/2}$ vs $i/v^{1/2}$ used to calculate the constants K_1 and K_2 at different potentials and sweep rates.



Figure SI_8. Instagram of the charge density accommodated on the different NC samples. Contributions of surface and bulk-controlled processes are differentiated and highlighted

In order to calculate the specific capacitance value the period of time t2–t1 is measured, during which the voltage across the capacitor declines from 80% (V1) to 40% (V2) of the applied voltage V

$$C = \frac{I(t_2 - t_1)}{(V_2 - V_1)M}$$
(S1)

can be attributed to the electrolyte resistance. The power density and energy density were calculated using the following equations.

$$P = \frac{V^2}{4RM}$$
(S2)

$$E = \frac{1}{2M}CV^2 \tag{S3}$$

Where V is the voltage, R is the electrochemical series resistance (ESR), M is the mass of the active material and C is the specific mass capacitance.