Supporting information for

Realizing an Asymmetric Supercapacitor Employing Carbon Nanotubes Anchored to Mn_3O_4 Cathode and Fe_3O_4 Anode

Ankit Kumar,[†] Debasish Sarkar,^{*,†} Soham Mukherjee, Satish Patil, D. D. Sarma and Ashok Shukla^{*}

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bengaluru-560012, India.

*Authors to whom correspondence should be addressed:

E-mail addresses: deb.sarkar1985@gmail.com , debasishs@iisc.ac.in (D. Sarkar), Tel: +91 (080) 2293 2945, and akshukla2006@gmail.com (A. Shukla), Tel: +91 (080) 2293 2795.

[†]Authors contributed equally to this work.

Calculation of Capacitance, and Energy and Power densities

Specific capacitance (C , F/g) is calculated from the Cyclic voltammogram data using the equation:

$$C_a = \frac{\int i dt}{m \Delta V}, \quad (S1)$$

where, i (mA) is the cathodic or anodic current, dt (s) is the time differential, ΔV (V) is the potential window and m (g) is the mass of the active materials only. For calculating areal capacitances, m (g) has been replaced with the area a (cm²) of the electrode material.

From Galvanostatic charge-discharge data, area capacitance (C , F/g) values are calculated from the discharge data of the electrodes using equation:

$$C_a = \frac{i \Delta t}{m \Delta V}, \quad (S2)$$

where, i (mA) is the discharge current, Δt (s) is the discharge time for discharge window ΔV (V) and m (g) is the mass of the active materials only. Here also, mass m (g) has been replaced with the electrode area a (cm²) for calculating areal capacitances.

Gravimetric energy (Wh/kg), equivalent series resistance (ESR) and power densities (P , W/kg) for the assembled ASC cell are calculated using equations:

$$W = \frac{1}{2 \times 3600} C \Delta V^2 \quad (S3)$$

$$ESR = \frac{i R_{drop}}{2 \times i} \quad (S4) \text{ and } P = \frac{\Delta V^2}{4 \times ESR \times m} \quad (S5)$$

where, C is the specific capacitance of the ASC, ΔV (V) is the discharge voltage, and here, m (g) represents the total mass of both of the electro-active materials.

Charge balance between anode and cathode materials prior to assembling the ASC

In ASC cell the mass ratio between cathode (CNT-Mn₃O₄) and anode (CNT-Fe₃O₄) materials is about 1.00:1.40, which is quite similar to the mass ratio of 1.00:1.38 calculated using charge balancing equation as described below.

$$Q_+ (\text{CNT-Mn}_3\text{O}_4) = Q_- (\text{CNT-Fe}_3\text{O}_4) \quad (S6)$$

At a scan rate of 10 mV/s, specific capacitance of CNT-Mn₃O₄ is 453 F/g within the potential window of 0.8 V and 373 F/g for CNT-Fe₃O₄ within the potential window of 0.7 V (-0.2 to -0.9 V).

Therefore, $Q_+ = Q_-$ gives,

$$453 \times m_1 \times 0.8 = 373 \times m_2 \times 0.7$$

$$\Rightarrow \frac{m_1}{m_2} = \frac{1.00}{1.38}$$

, where m_1 and m_2 are masses of CNT-Mn₃O₄ and CNT-Fe₃O₄, respectively.

Figure S1. TEM image of Mn₃O₄ NP anchored on multi-walled CNT surface.

Figure S2. N₂ adsorption/desorption curves for (a) CNT-Mn₃O₄ and (b) CNT-Fe₃O₄ nanocomposites for measuring BET surface area and pore volume; inset figures show corresponding BJH pore size distribution curves.

Description of equivalent circuit for fitting Nyquist plots

In the equivalent circuit constant phase elements (Z_{CPE}) are used to represent electrical double layer capacitance (CPE_{DL}), pseudocapacitance (CPE_p) and the Warburg element (CPE_W). The resistances of the electrode and electrolyte are represented by R_{el} and corresponds to the first high-frequency intersection point of the Nyquist plots with the Z' axis. The semicircular part in the mid frequency region of the Nyquist plot can be represented by a charge transfer resistance (R_{ct}) connected in parallel to the electrical double layer capacitance (CPE_{dl}). An approximate line in the low frequency region correspond to the diffusion related process or Warburg element (CPE_W). Moreover, surface or near surface based fast faradaic reactions delivering pseudocapacitance is represented as CPE_p .

The CPE can be evaluated using the equation:

$$Z_{CPE} = [T_{CPE} (j\omega)^n]^{-1}, \quad (S7)$$

where T_{CPE} and n refer to the CPE coefficient and exponent, respectively, ω represents the angular frequency and $j = \sqrt{-1}$.

Samples	Ohmic resistance (R_{el} , Ω)	Charge transfer resistance (R_{ct} , Ω)	Warburg impedance (R_W , Ω)	Equivalent series resistance (R_{es} , Ω)
CNT	0.791	0.998	1.839	3.628
CNT-Mn ₃ O ₄	1.179	0.634	4.549	6.362
CNT-Fe ₃ O ₄ //CNT-Mn ₃ O ₄ ASC	0.833	2.197	5.810	8.840

Table S1. Resistance values obtained after fitting the Nyquist plots of individual electrode materials as well for the assembled ASC with the equivalent circuit model shown in the inset of Figure 3c.

Figure S3. Variation of rate capability of cathode with increasing mass loading of CNT-Mn₃O₄ composite, varying from 2 – 5.2 mg/cm² (a), and variation of rate capability with increasing mass loading shown explicitly at two different scan rates (b).

Figure S4. Cycling performance of individual electrode materials recorded during 16000 CV cycles at a scan rate of 100 mV/s.

Figure S5. XRD pattern of the sample obtained after decomposing Fe-hexacyanoferrate complex along with the standard XRD patterns for Fe₂O₃ and Fe₃O₄.

Figure S6. Core-level XPS spectra for CNT-Fe₃O₄ nanocomposite material, (a) survey spectrum, (b) O 1s, and (c) C 1s.

Figure S7. (a) GCD curves for the CNT-Fe₃O₄//CNT-Mn₃O₄ hybrid ASC within different potential window ranging from 0.8 V to 2.0 V; (b) shows the variation of calculated Coulombic efficiency against cell potential windows.