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Electronic Supplementary Information

Change Storage Mechanisms of Electrospun Mn_3O_4 Nanofibres for High-performance Supercapacitors

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1. Calculations

1.1 Half-cell electrodes

The specific and areal capacitances of MnO_x half-cell electrodes can be calculated using equations (S1) and (S2)[1];

$$C_{sp}(F/g) = \frac{I \text{ x } \Delta t}{\Delta V \text{ x } m} \quad \text{(S1)}$$

$$C_{Areal}(mF/cm^2) = \frac{I \text{ x } \Delta t}{\Delta V \text{ x } S} \quad \text{(S2)}$$

where C_{sp} is the specific capacitance (F/g), C_{Areal} is the areal capacitance (F/cm^2), I is current, Δt is the discharging time, ΔV is the potential window, m is the mass of active material, and S is a geometrical area of electrode.

1.2 Full-cell supercapacitors

The specific capacitance of the Mn_3O_4 electrode can be calculated from the specific capacitance of the supercapacitor device by the equation (S3);

$$C_{sp,\,CV} = 4\frac{Q}{\Delta V \cdot m} \qquad \text{(S3)}$$

where $C_{sp,\,CV}$ is a specific capacitance determined from CV (F g^{-1}), Q is an average charge in the discharged process (Coulomb, C) of the device, and m is the total mass of active material (g) of the device.

The specific and areal capacitances as a function of applied currents can be calculated from equations (S4) and (S5), respectively[2];

$$C_{sp}(F/g) = 4\frac{I \times \Delta t}{\Delta V \times m} \qquad \text{(S4)}$$

$$C_{Areal}(mF/cm^2) = 4\frac{I \times \Delta t}{\Delta V \times S} \qquad \text{(S5)}$$

The specific energy and maximum specific power can be calculated by the equations (S6) and (S7) from the GCD measurement[1].

$$\text{Specific Energy (E)} = \frac{1}{2}C_{cell}\Delta V^2 \qquad \text{(S6)}$$

$$\text{Maximum Specific Power } (P_{max}) = \frac{V_0^2}{4R_{cell}} \qquad \text{(S7)}$$

where C_{cell} is the cell capacitance, V_0 is an initial voltage of the cell, and R_{cell} is the cell's resistance.

1.3 X-ray absorption spectroscopy

The average oxidation numbers of Mn at the positive and negative electrodes calculated by following equation (S8)[3] are 2.61 and 2.38, respectively.

$$\langle \text{Mn oxidation state} \rangle = \frac{3\text{x}\Delta\text{E of the sample}}{\Delta\text{E of Mn}^{2+}\text{ and Mn}^{3+}} - \left[2\text{x}\left(1 - \frac{\Delta\text{E of the sample}}{\Delta\text{E of Mn}^{2+}\text{ and Mn}^{3+}}\right)\right] \qquad \text{(S8)}$$

1.4 EQCM

The relationship of quartz resonance frequency (Δf) and mass change (Δm) follows Sauerbrey's equation (S9)[4];

$$\Delta m = -\, C_f \cdot \Delta F \qquad \text{(S9)}$$

where C_f is the calibration constant (0.0815 Hz ng^{-1} cm^{-2})

2. XRD

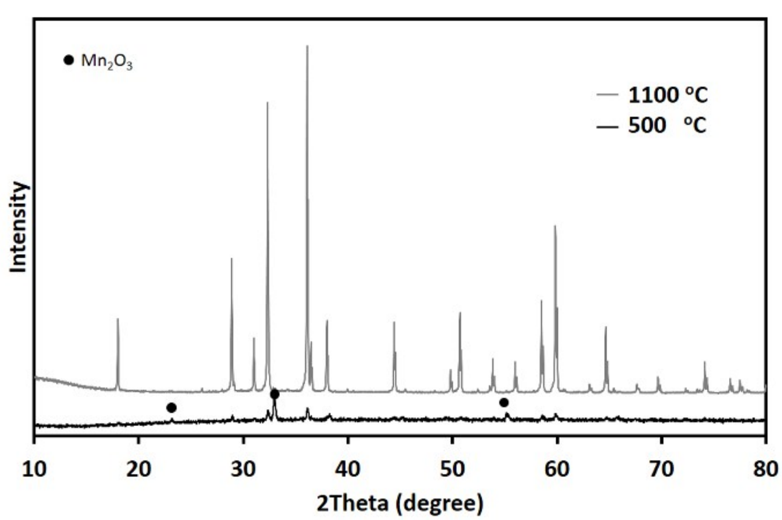

Fig.S1 XRD of MnOx electrospun at 36 wt.% $Mn(OAc)_2$ in PAN after calcined at 500 ^oC and 1100 ^oC.

3. XAS calibration curve

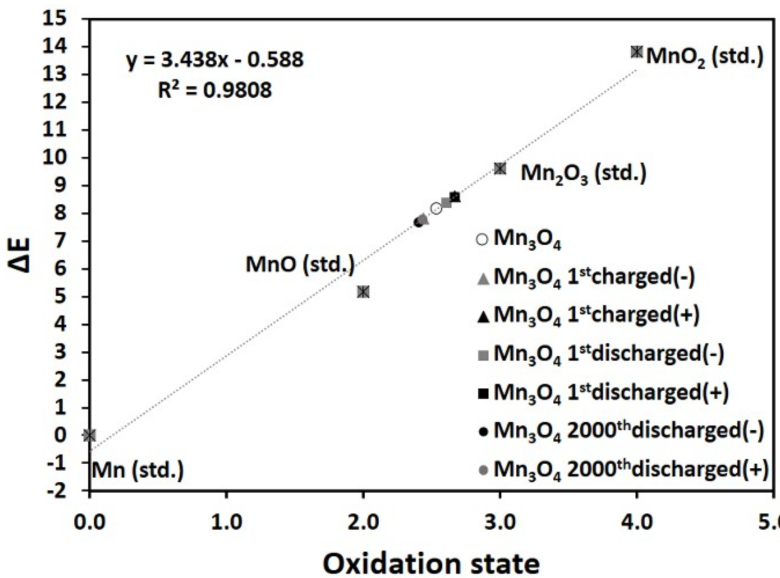

Fig.S2 *Ex situ* high-resolution XAS calibration curve of the manganese oxide compared with the Mn standard compounds including Mn foil, MnO, Mn_2O_3, and Mn_3O_4.

4. Mass ratio by CV

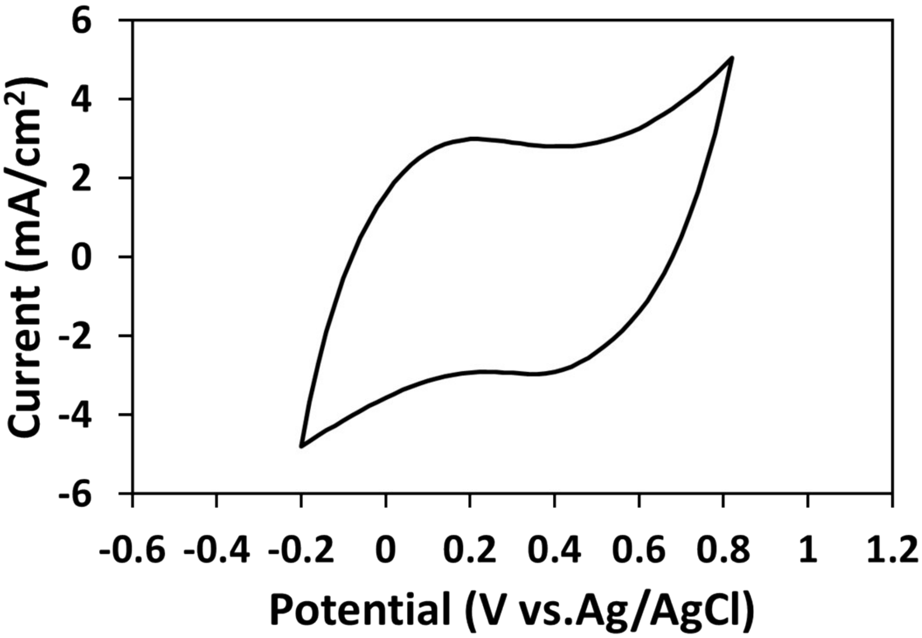

Fig. S3 CV curve of Mn_3O_4 nanofibres in 0.5 M Na_2SO_4 at a scan rate of 50 mV s^{-1}

Positive electrode (Mn3O4 nanofibers).

C^+ = 68.65 F/g

V^+ = 0.76 V

Negative electrode (N-rGO aerogel)

CV curves of N-rGO aerogel were previously reported by our group elsewhere [5].

C^- = 294.95 F/g

V^- = 0.54 V

$$\frac{m^+}{m^-} = \frac{(294.95)(0.54)}{(68.65)(0.76)} = 3.04$$

Table S1. *Ex situ* high-resolution XAS results of the manganese oxide including MnO, Mn_2O_3, and Mn_3O_4

Sample	E(eV)	ΔE(eV)	Oxidation number
MnO std.	6544.17	0	2
Mn_2O_3 std.	6548.61	4.44	3
Bare Mn_3O_4	6547.15	2.98	2.67
Mn_3O_4 1st charge (-)	6546.80	2.63	2.35
Mn_3O_4 1st charge (+)	6547.60	3.43	2.61
Mn_3O_4 1st discharge (-)	6547.39	3.22	2.53
Mn_3O_4 1st discharge (+)	6547.58	3.41	2.51
Mn_3O_4 2000th charge (-)	6546.69	2.52	2.38
Mn_3O_4 2000th charge (+)	6546.77	2.60	2.44

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