Supporting information

High performance flexible all solid state supercapacitor based on MnO_2 spheres coated macro/mesoporous Ni/C electrode and ionic conducting electrolyte

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Calculation

If the capacitances of the two electrodes, i.e. positive and negative, can be expressed as C_p and C_n, respectively, the overall capacitance (C_T) of the entire cell can be expressed as eqn (1):[1]

$$\frac{1}{C_T} = \frac{1}{C_p} + \frac{1}{C_n} \quad (1)$$

In a symmetrical supercapacitor, C_p= C_n=C_0, where C_0 represents the per-electrode capacitance and in this study represents the capacitance of one electrode. So the relationship between C_T and C_0 should be as eqn (2):

$$C_0 = 2C_T = \frac{2I(t - t_{OMC})}{V} \qquad (2)$$

where I, t and V are charged current, t is the discharge time, t_{OMC} is the discharge time of blank OMC membrane on Nickel foam. V is the voltage drop upon discharging (excluding IR drop). As a result, the per-electrode specific capacitance (C_{s0}) and volumetric capacitance (C_{v0}) of MnO_2-MNC electrode is shown in eqn (3) and eqn (4):

$$C_{s0} = \frac{C_0}{m_0} = \frac{2I(t - t_{OMC})}{m_0 V} = \frac{4I(t - t_{OMC})}{m_T V} = 4C_{s-cell} \qquad (3)$$

$$C_{v0} = \frac{C_0}{v_0} = \frac{2I(t - t_{OMC})}{v_0 V} = \frac{4I(t - t_{OMC})}{v_T V} = 4C_{v-cell} \qquad (4)$$

Where m_0 is the mass of active materials in one electrode, m_T represents the total mass of active materials in the whole cell, in which m_T=2m_0. $C_{s\text{-}cell}$ is the specific capacity of the whole cell. V_0 is the volume of one electrode (about 0.08 cm^3). Considering the very low thickness of separator (Celgard 3501, about 50 μm), the total volume of the device v_t≈2v_0. $C_{v\text{-}cell}$ is the volumetric capacitance of the whole device.

The specific energy (E_s) and power densities (P_s) of this supercapacitor can be expressed as eqn (5) and (6):[2]

$$E_s = \frac{1}{2} C_{s-cell} V^2 = \frac{1}{8} C_{s0} V^2 \qquad (5)$$

$$P_s = \frac{E_s}{t} \qquad (6)$$

The corresponding volumetric energy and power density are calculated through eqn (7) and (8):

$$E_v = \frac{1}{2} C_{v-cell} V^2 = \frac{1}{8} C_{v0} V^2 \qquad (7)$$

$$P_v = \frac{E_v}{t} \qquad (8)$$

Measurement of ionic conductivity

Ionic conductivity of PVA-BMIMCl-Li_2SO_4 gel in the supercapacitor is determined from impedance spectrum. The sample is sandwiched between two nickel foam sheets in this measurement. The ionic conductivity σ (mS cm^{-1}) of gel is calculated by the following equation

$$\sigma = L/(R \times S) \times 1000 \qquad (9)$$

where L (cm) is the distance between the two nickel foam sheets, R(Ω) is the bulk resistance, and S (cm^2) is the contact area of the gel and nickel foam sheets during the experiment.

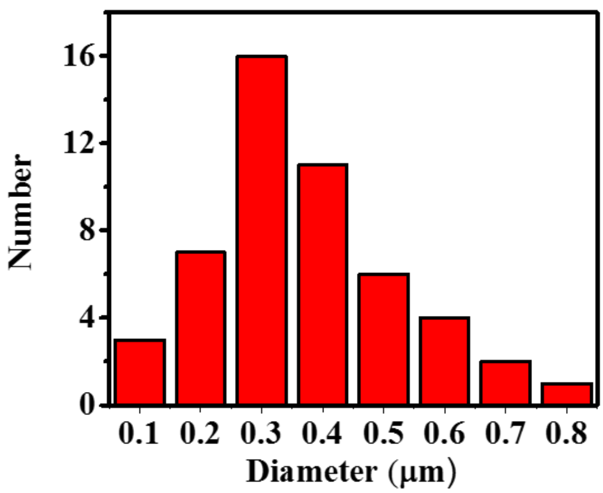

Figure S1. Histograms of diameters for 50 MnO_2 spherical particles.

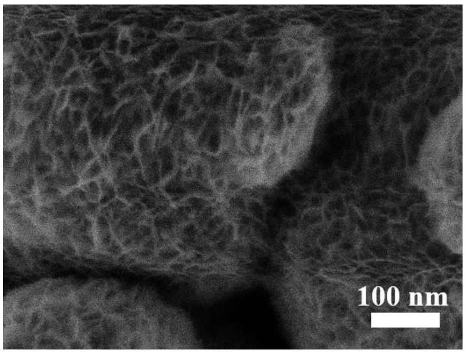

Figure S2. High-magnification SEM image of MnO_2 spheres.

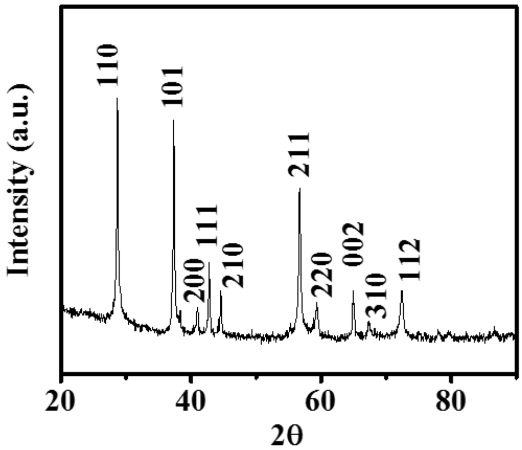

Figure S3. XRD patterns of MnO_2 spherical particles**.**

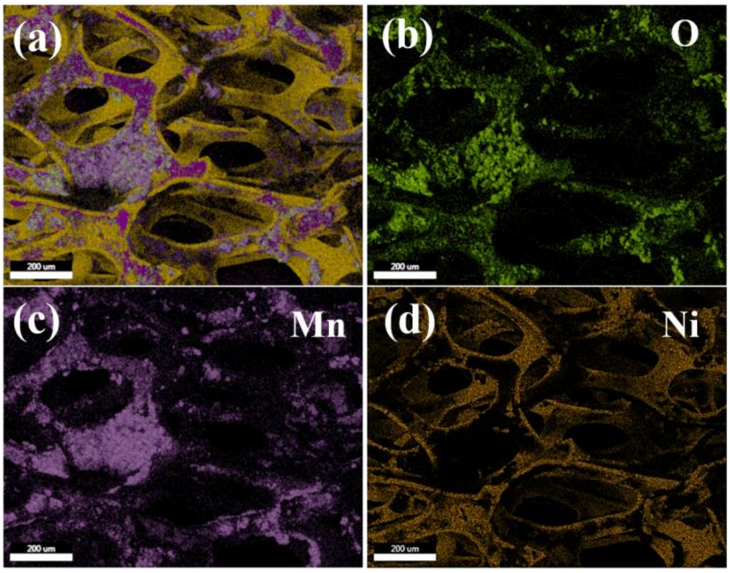

Figure S4. EDX maps of MnO_2-MNC composites: (a) overlapping figures;(b-d) O, Mn and Ni EDX maps.

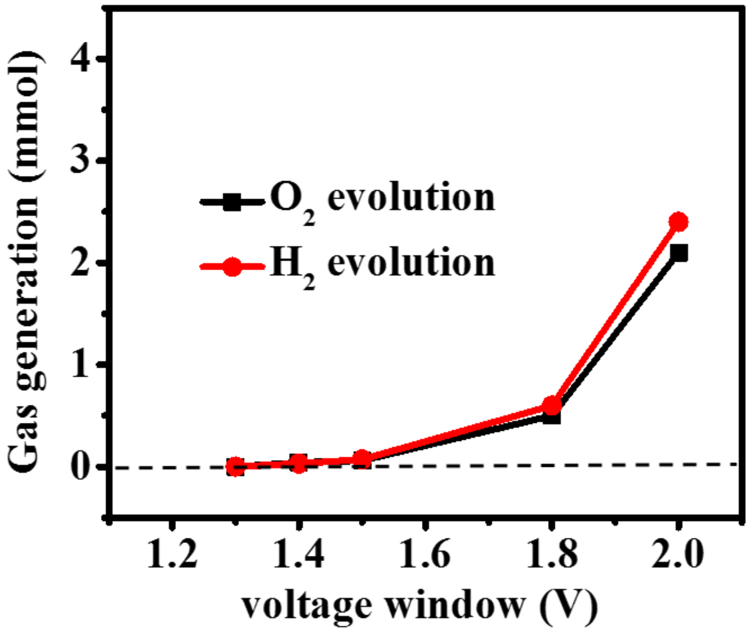

Figure S5. Threshold voltage of water splitting. Determined by H_2 and O_2 accumulation (measured by gas chromatography) in sealed MnO_2-MNC symmetric cell in PVA-BMIMCl-Li_2SO_4 over 24 h under charge-discharge at 1 Ag^{-1}.

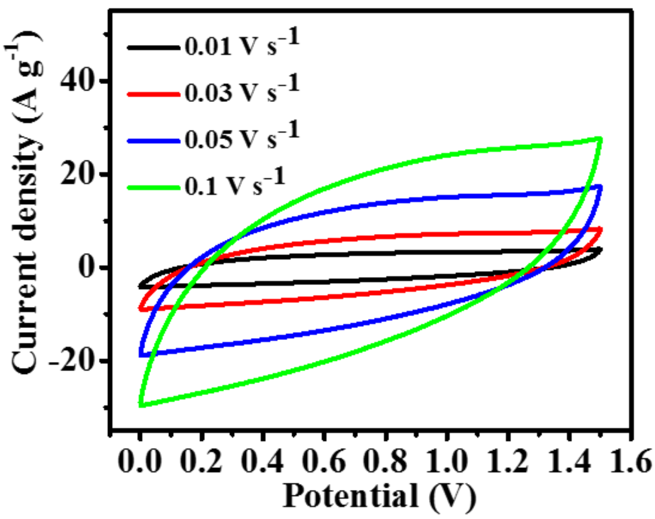

Figure S6. CV curves of MnO_2-MNC symmetrical supercapacitor in different scan rates.

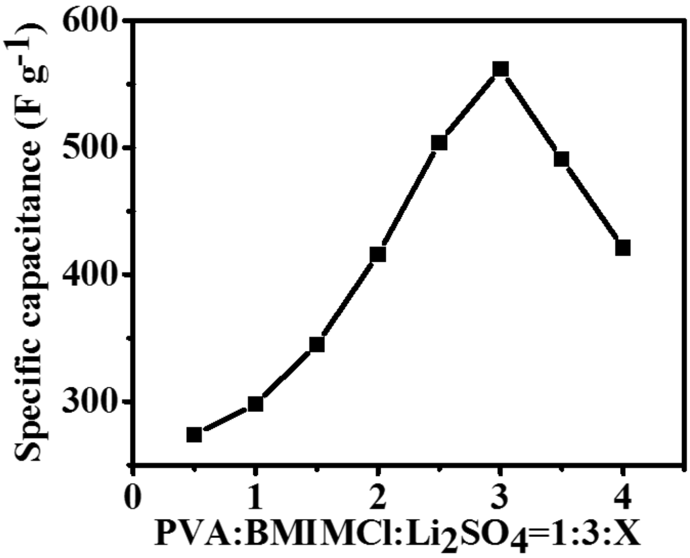

Figure S7. Per-electrode specific capacitance of MnO_2-MNC symmetrical supercapacitor with different gel components.

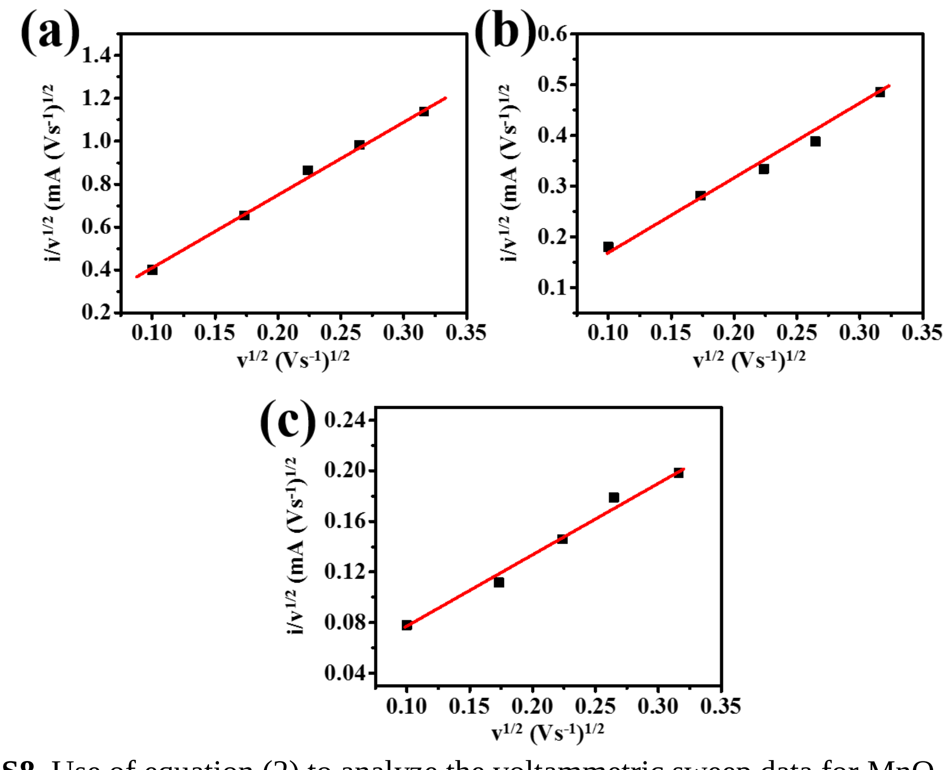

Figure S8. Use of equation (2) to analyze the voltammetric sweep data for MnO_2-MNC (a), MnO_2-MN (b) and MnO_2-MC(c) at a specific potential of 0.5 V, sweep rates varied from 0.01 to $0.1Vs^{-1}$.

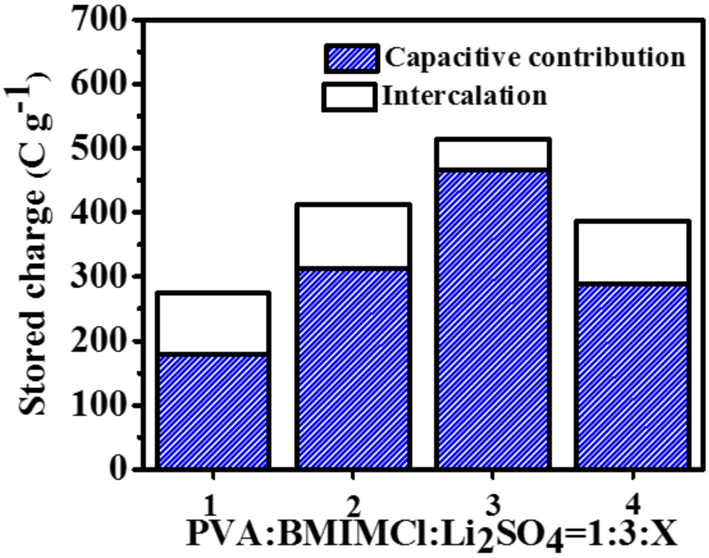

Figure S9. Comparison of charge storage with different concentrated gel electrolyte (at a scan rate of 0.01 V s^{-1}).

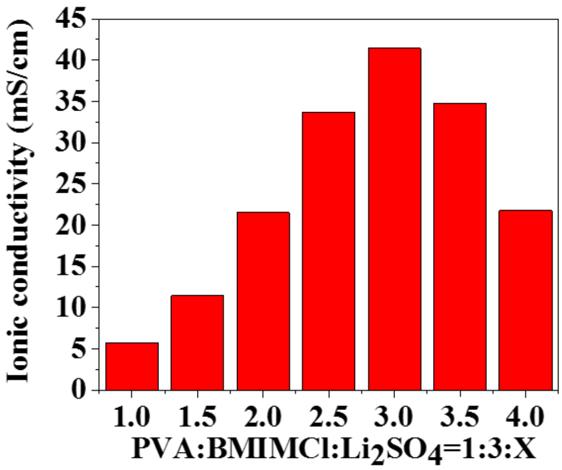

Figure S10. Ionic conductivity of PVA-BMIMCl-Li_2SO_4 with different components.

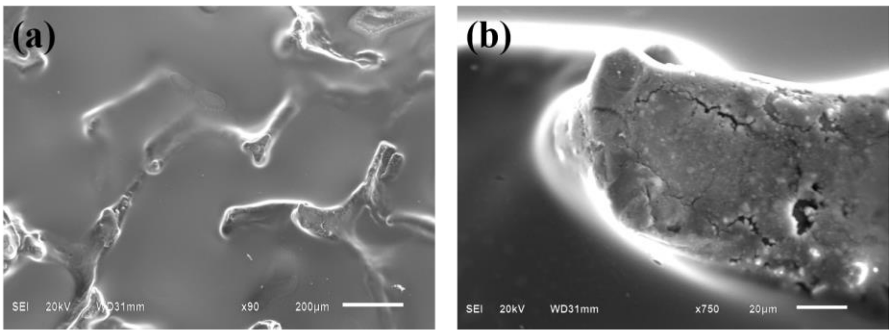

Figure S11. (a,b) SEM image of MnO_2-MNC electrode (combined with gel electrolyte) after 6000 cycles.

References

1. G. Wang, L. Zhang and J. Zhang, *Chem Soc Rev*, 2012, **41**, 797-828.

2. X. Lang, A. Hirata, T. Fujita and M. Chen, *Nature Nanotechnology*, 2011, **6**, 232-236.
3. Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang and X. Duan, *ACS nano*, 2013, **7**, 4042-4049.