Charge storage mechanisms of electrospun Mn$_3$O$_4$ nanofibres for high-performance supercapacitors†

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Mixed oxidation states of manganese oxides are widely used as the electrodes in supercapacitors due to their high theoretical pseudocapacitances. However, their charge storage mechanisms are not yet fully understood. In this work, the charge storage mechanism of Mn$_3$O$_4$ or Mn$^{2+}$$(Mn^{3+})_2$O$_4$ nanofibres was investigated using a synchrotron-based X-ray absorption spectroscopy (XAS) technique and an in situ electrochemical quartz crystal microbalance (EQCM). The average oxidation state of the Mn in the as-synthesized Mn$_3$O$_4$ is +2.67. After the first charge, the average oxidation states of Mn at the positive and negative electrodes are +2.61 and +2.38, respectively. The significant change in the oxidation state of Mn at the negative electrode is due to phase transformation of Mn$_3$O$_4$ to Na$_x$MnO$_{2-x}$·H$_2$O. Meanwhile, the charge storage mechanism at the positive electrode mainly involves the adsorption of counter ions or solvated SO$_4^{2-}$. After the first discharge, the calculated Mn average oxidation numbers are +2.51 and +2.53 at the positive and negative electrodes, respectively. At the negative electrode, the solvated Na$^+$ is desorbed from the electrode surface. At the same time, the solvated SO$_4^{2-}$ is desorbed from the positive electrode. The mass change of solvated Na$^+$ during charging/discharging is ca. 80 ng per cm$^2$ of the Mn$_3$O$_4$ electrode. A symmetric supercapacitor constructed from Mn$_3$O$_4$ nanofibres in 0.5 M Na$_2$SO$_4$ provides a working potential of 1.8 V, a specific energy of 37.4 W h kg$^{-1}$ and a maximum specific power of 11.1 kW kg$^{-1}$ with 98% capacity retention over 4500 cycles. The understanding of the charge storage mechanism of the mixed oxidation states of Mn$^{2+}$$(Mn^{3+})_2$O$_4$ presented in this work could lead to further development of metal oxide-based pseudocapacitors.

Introduction

Supercapacitors have higher specific power (2–10 kW kg$^{-1}$)† than batteries (0.5–1 kW kg$^{-1}$)† and higher specific energy (5–10 W h kg$^{-1}$)† than conventional capacitors (0.01–0.05 W h kg$^{-1}$). Their charge storage mechanisms are based on two phenomena, namely electrochemical double layer capacitance (EDLC) or physisorption of solvated ions on the supercapacitor electrodes, and pseudocapacitance or surface redox reactions. Carbon-based materials, e.g. activated carbon, carbon aerogel, graphene, carbon nanotubes and carbon onions, are extensively used as the electrode materials of electrochemical double layer capacitors. On the other hand, transition metal oxides, e.g. RuO$_2$, NiO, Co$_3$O$_4$, MnO$_2$ and Mn$_3$O$_4$, are widely used as active materials for pseudocapacitor electrodes. Among all metal oxides, manganese oxides are widely employed as pseudocapacitor electrodes because of their relatively low cost, low toxicity, high theoretical capacitance, and environmental compatibility. A number of manganese oxide structures including MnO, Mn$_3$O$_4$, Mn$_2$O$_3$, and MnO$_2$ have been used for high-performance supercapacitors.† Among all structures, Mn$_3$O$_4$ with a normal spinel structure with Mn$^{2+}$ in tetrahedral units and Mn$^{3+}$ in octahedral units with a formula structure of Mn$^{2+}$$(Mn^{3+})_2$O$_4$ (ref. 19) provides high pseudocapacitance. Previously, Mn$_3$O$_4$-anchored graphene sheets produced by a microwave hydrothermal method have exhibited a specific capacitance (SC) of 70 F g$^{-1}$ at 0.2 A g$^{-1}$ in 1 M Na$_2$SO$_4$. A graphene-supported Mn$_3$O$_4$ nanocomposite synthesized by a precipitation method gives a SC of 61 F g$^{-1}$ at 0.1 A g$^{-1}$ in 1 M K$_2$SO$_4$. Mn$_3$O$_4$ nanoparticles (NPs) prepared by ultrasonication and hydrolysis provide a SC of 261 F g$^{-1}$ at 0.4 A g$^{-1}$ in 1 M Na$_2$SO$_4$ (ref. 20). These results show that Mn$_3$O$_4$ nanoparticles have a high specific capacitance. More interestingly, 1D nanofibres of mixed Mn$_3$O$_4$ and Mn$_2$O$_3$ produced by an electrospinning process, which is a simple, efficient, and reproducible method, exhibit a SC of...
360.7 F g⁻¹ at 1 A g⁻¹ in 0.5 M Na₂SO₄. This indicates that 1D nanofibres can enhance both the ion transport pathways and the surface area, increasing the contact area between the electrolyte ions and the surface of the electrodes. The porosity of the nanofibres also plays an important role in the charge storage performance of the supercapacitors. Micropores can help increase the electrochemical double layer capacitance due to their high surface area, while mesopores can enhance electrolyte ion transportation. For example, MnO₃ nanofibres with a pore size of around 10–30 nm provide very good electrolyte diffusion.

However, the charge storage mechanism of MnO₃ is unclear and rather complex. In this work, we have investigated the charge storage mechanism of MnO₃ nanofibres using high-resolution synchrotron-based X-ray absorption spectroscopy (XAS) and electrochemical quartz crystal microbalance (EQCM) techniques. The results here showed that MnO₃ nanofibres produced by an electrospinning process using 10 wt% manganese acetate (Mn(OAc)₂) in polyacrylonitrile (PAN) solution provide higher SCs than other samples. The charge storage mechanism of the MnO₃ nanofibres investigated by XAS involves a phase transformation of MnO₃ to Na₂MnO₃·nH₂O during the first charge. Subsequently, the mechanism is based on surface redox reactions. The mass change of solvated Na⁺ during charging/discharging is ca. 80 ng per cm² of the MnO₃ electrode.

**Experimental section**

**Electrospinning of manganese oxide nanofibres**

Firstly, 1 g of PAN (Mw = 150 000, Aldrich) was dissolved in 10 ml of dimethylformamide (DMF) (Qrec, 99.8%) at 60 °C under stirring and then cooled down to room temperature. Then, 0.052 g of manganese acetate tetrahydrate (Mn(OAc)₂·4H₂O) (Acros, 99.9%) was added into the PAN solution. The PAN/Mn(OAc)₂ solution was subsequently put into a syringe, and the distance between the syringe tip and an aluminium foil collector was fixed at 10 cm. The electrospinning process was subsequently operated at a feed flow rate of 2 ml h⁻¹ and the applied potential was finely tuned to 15 kV. The Mn(OAc)₂ content (0.11 g for 10 wt%, 0.25 g for 20 wt%, 0.42 g for 30 wt%, and 0.56 g for 36 wt%) was also varied to finely tune the homogeneous electrospun nanofibres. Finally, the as-spun nanofibres were dried at ambient temperature for 24 h and calcined at 500 °C with a heating rate of 5 °C min⁻¹ for 2 h.

**Characterization of the electrospun nanofibres**

The morphologies of the as-electrospun nanofibres and as-calcined manganese oxide nanofibres were characterized by SEM-EDX (SEM-EDX, Philips XL30) and TEM (TEM, Hitachi HT7700). The crystalline structure of the as-calcined nanofibres was characterized by XRD (XRD PHILIPS, X’Pert-MPD 40 kV 35 mA, Cu Kα 1.54056 Å) with a 2θ range of 10–80° and a step size of 0.02° s⁻¹. The electronic structure of the nanofibres was characterized by X-ray absorption spectroscopy (XAS), at the Synchrotron Light Research Institute (Thai Public Organization). More details on the XAS measurement procedures can be found in our previous report.

**Electrochemical characterization**

The electrochemical properties of the nanofibres were tested by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) in 0.5 M Na₂SO₄ electrolyte using a Metrohm AUTOLAB potentiostat (PGSTAT 302N). Platinum wire and Ag/AgCl (3 M KCl) were used as a counter electrode and a reference electrode, respectively. In a two-electrode system, GCD was measured using a NEWARE battery tester (GELON LIB., CTS 20V-5A-GGS). The as-calcined MnO₃ nanofibres were mixed with a conductive additive (carbon black, CB) and an adhesive binder (polyvinylidene fluoride, PVDF) at a weight ratio of 6 : 3 : 1 (MnO₃ : CB : PVDF) in N-methyl-2-pyrrolidone (NMP). The mixture was then sprayed onto functionalized-carbon fibre paper with dimensions of 1 × 1 cm² for the three-electrode system and a circle with a diameter of 1.58 cm for the two-electrode system. The mass loading was about 2 mg cm⁻² for each electrode. The electrode was dried at 80 °C for 24 h. The hydrolysed polyethylene (PE) separator was soaked in 0.5 M Na₂SO₄ and inserted between the two working electrodes in a coin case (2016 type). Finally, the symmetric supercapacitor device was fabricated using a hydraulic compression machine at 800 psi. The in situ charge storage mechanism of the MnO₃ nanofibre electrodes was characterized using an electrochemical quartz crystal microbalance (EQCM) with Ag/AgCl (3 M KCl) gel as the reference electrode, Au wire as the counter electrode, and about 0.6–0.7 mg cm⁻² of the sample coated on an Au support (0.67 cm in diameter).

**Results and discussion**

The morphologies of the as-electrospun PAN/Mn(OAc)₂ nanofibres with different Mn(OAc)₂ contents in PAN are shown in Fig. 1. The diameters of the as-electrospun nanofibres are about 400–500, 430–500, 500–600, 900–1800, and 900–1700 nm for 5, 10, 20, 30 and 36 wt% Mn(OAc)₂, respectively.

Fig. 2 shows the morphology of the MnO₃ nanofibres after calcining at 500 °C for 2 h. After the removal of PAN, the diameter of the as-calcined MnO₃ nanofibres is reduced. With increasing Mn(OAc)₂ concentrations, the as-calcined MnO₃ formed larger nanofibres. The diameters of the MnO₃ nanofibres are 60–125, 60–200, 150–250, 300–600, and 300–600 nm for 5, 10, 20, 30 and 36 wt% Mn(OAc)₂, respectively. The presence of Mn and O in the as-obtained nanofibres was confirmed by EDX (Fig. 2f). In addition, it is clearly seen from the TEM images that the MnO₃ nanofibres are formed from connected MnO₃ particles with open pores in the structure. Note that the PAN/Mn(OAc)₂ fibres with rather large diameters cannot be dispersed in solvents and so are not suitable for TEM measurements.

Fig. 3 shows the XRD patterns of the as-calcined MnO₃ nanofibres. The XRD patterns of the MnO₃ produced using 5–20 wt% Mn(OAc)₂ are assigned to MnO₃ (JCPDS 24-0734). In addition, the XRD patterns of the MnO₃ prepared using 30 and 36 wt% Mn(OAc)₂ show mixed crystalline phases of Mn₃O₄ and Mn₂O₃ (JCPDS 073-1826). The Mn₃O₄ and Mn₂O₃ crystallite
sizes are estimated using Scherrer’s equation from the (211) and (222) planes, respectively. The Mn$_3$O$_4$ crystallite sizes are 13.3, 30.7, 42.3, 35.4 and 36.9 nm at 5, 10, 20, 30 and 36 wt% Mn(OAc)$_2$, respectively. Meanwhile, the Mn$_2$O$_3$ crystallite sizes are 30.5 and 30.9 nm at 30 and 36 wt% Mn(OAc)$_2$, respectively. Note that the Mn$_2$O$_3$ phase is easily removed by calcination at high temperature (see Fig. S1†). The formation of Mn$_3$O$_4$ occurs via reactions (1) and (2):\(^{24}\)

\[
\text{Mn(CH}_3\text{COO})_2·4\text{H}_2\text{O} \rightarrow \text{Mn(OH)(CH}_3\text{COO}) + 3\text{H}_2\text{O} + \text{CH}_3\text{COOH} \quad (1)
\]

\[
3\text{Mn(OH)(CH}_3\text{COO}) \rightarrow \text{Mn}_3\text{O}_4 + 2\text{CO}_2 + \text{CO} + 3\text{CH}_4 \quad (2)
\]

Intermediate reactions are proposed as shown in reactions (3) and (4):\(^{22}\)

\[
2\text{Mn(OH)(CH}_3\text{COO}) \rightarrow \text{Mn}_2\text{O}_3 + \text{CO}_2 + \text{CO} + 2\text{CH}_4 \quad (3)
\]

\[
6\text{Mn}_2\text{O}_3 \rightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2 \quad (4)
\]

Fig. 4 shows the electrochemical properties of the as-electrospun PAN nanofibres produced using different Mn(OAc)$_2$ contents. From the CV curves (Fig. 4a), the Mn$_3$O$_4$ nanofibres electrospun at 10 wt% Mn(OAc)$_2$ exhibit the largest area under the curve, leading to the highest capacitance. The SCs of the symmetric Mn$_3$O$_4$ nanofibre supercapacitor at scan rates of 10, 20, 50, 70, and 100 mV s$^{-1}$ are 161, 154, 130, 115, and 98 F g$^{-1}$, respectively. The GCD result in Fig. 4b is in good agreement

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**Fig. 1** SEM images of the as-electrospun PAN nanofibres at different Mn(OAc)$_2$ loading contents: (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, and (f) 36 wt%.

**Fig. 2** SEM and TEM images of the MnO$_x$ nanofibres formed with different Mn(OAc)$_2$ concentrations after calcining at 500 °C: (a) 5, (b) 10, (c) 20, (d) 30, and (e) 36 wt%. (f) The EDX spectrum of the MnO$_x$ nanofibres produced using 36 wt% Mn(OAc)$_2$.

**Fig. 3** (a) XRD patterns of the as-calcined MnO$_x$ nanofibres electrospun at different Mn(OAc)$_2$ loading contents at 15 kV and (b) a crystal structure model of spinel Mn$_3$O$_4$. 

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The specific energy and maximum specific power of the MnO₃ supercapacitor are 37.4 Wh kg⁻¹ and 11.1 kW kg⁻¹, respectively (see the calculation details in the ESI†). The stability of the symmetric supercapacitor based on the as-electrospun MnO₃ nanofibres is shown in Fig. 5d, for which the capacity retention is over 98% after 4500 charge/discharge cycles.

Table 1 summarizes the charge storage performances of MnO₃-based supercapacitors. The theoretical energy density of a supercapacitor can be calculated using the following equation:

\[ E = \frac{1}{2} C V^2 \]

where \( E \) is the energy density, \( C \) is the capacitance, and \( V \) is the voltage. The specific energy and power are calculated from the specific capacitance and maximum specific power, respectively.

Table 1: Charge storage performances of MnO₃-based supercapacitor electrodes

| Materials          | Tested method | Electrolyte                                          | Specific capacitance | Ref. |
|--------------------|---------------|------------------------------------------------------|----------------------|------|
| MnO₃ nanoparticles | GCD at 0.1 A g⁻¹ | 1 M Na₂SO₄                                          | 85 F g⁻¹ (three electrodes) | 35   |
| MnO₃ stacked sheet | CV at 10 mV s⁻¹ | H₂SO₄–PVA (1 : 1 wt) gel electrolyte                 | 127 F g⁻¹ (two electrodes) | 36   |
| MnO₃ nanoparticles | GCD at 0.5 mA cm⁻² | 1 M Na₂SO₄                                          | 322 F g⁻¹ (three electrodes) | 23   |
| MnO₃ nanoparticles | GCD at 0.5 mA cm⁻² | 1 M Na₂SO₄                                          | 113 F g⁻¹ (three electrodes) | 7    |
| As-spun MnO₃ fibres | GCD at 0.3 A g⁻¹ | 1 M Na₂SO₄                                          | 155 F g⁻¹ (three electrodes) | 28   |
| As-spun MnO₂ fibres | CV at 10 mV s⁻¹ | 1 M Na₂SO₄                                          | 161.22 F g⁻¹ (two electrodes) | 37   |
| As-spun MnO₂ fibres | CV at 2 mV s⁻¹ | 0.5 M Na₂SO₄                                         | 63.2 F g⁻¹ (three electrodes) | 38   |
| As-spun MnO₃ nanofibres | GCD at 1 mA (1.25 mA cm⁻²) | 0.5 M Na₂SO₄                                      | 289 F g⁻¹ (two electrodes) | This work |

This work used X-ray absorption near edge spectra (XANES) of the MnO₃-based materials to determine the average oxidation number of Mn at the positive and negative electrodes. The XANES spectra were recorded using a K-edge electron binding energy of 6548.61 eV. The XANES spectra show that the MnO₃-based materials have an average oxidation number of Mn of 3.5 ± 0.2, which is consistent with the theoretical value of 3.5 for MnO₃. The XANES spectra also show that the MnO₃-based materials are stable over 4500 charge/discharge cycles.

To further investigate the charge storage mechanism of MnO₃, the average oxidation number of Mn at the positive and negative electrodes of the device after the 1st charge, the 1st discharge, and the long-term stability test of over 4500 cycles was determined by XAS. The normalized X-ray absorption near edge spectra (XANES) of the MnO₃-based materials are shown in Fig. 6a–c. The K-edge electron binding energies of Mn metal, MnO, Mn₂O₃, and MnO₃ standards are 6539.00, 6544.17, 6548.61, and 6547.15 eV, respectively. After the 1st charge, the
K-edge electron binding energies of Mn at the positive and negative electrodes were in between those of MnO (Mn$^{2+}$) and Mn$_2$O$_3$ (Mn$^{3+}$) at 6547.60 and 6546.80 eV, respectively. The average oxidation numbers of Mn at the positive and negative electrodes calculated using eqn (S8) in the ESI† are 2.61 and 2.38, respectively. Note that the average oxidation state of Mn in the as-calcined Mn$_3$O$_4$ is +2.67 (see Fig. 6d). The decreased oxidation number of Mn, especially at the negative electrode after the 1st charge, when compared with the bare electrode is due to solvated Na$^+$ being inserted into the structure. The charge storage mechanism follows reactions (5) and (6):

$$\text{Mn}_3\text{O}_4 \xrightarrow{1\text{st charge}} \text{Na}_3\text{MnO}_x \cdot n\text{H}_2\text{O}$$  \hspace{1cm} (5)

$$\text{Na}_3\text{MnO}_x \cdot n\text{H}_2\text{O} \leftrightarrow \text{MnO}_x \cdot n\text{H}_2\text{O} + \delta\text{Na}^+ + \delta\text{e}^-$$  \hspace{1cm} (6)

This is because the adsorption of solvated cations can result in a lower binding energy.\textsuperscript{8,40} On the other hand, the partial oxidation of Mn$^{2+}$ to Mn$^{3+}$ at the positive electrode after the 1st charge leads to a slight change in the average oxidation number of Mn. Meanwhile, reduction of Mn$^{3+}$ to Mn$^{2+}$ occurs at the negative electrode, which significantly reduces the average oxidation number of Mn.

After the 1st discharge, the K-edge electron binding energies of Mn at the positive and negative electrode are 6547.58 and 6547.39 eV, respectively. The calculated Mn average oxidation numbers are +2.51 and +2.53 at the positive and negative electrodes, respectively. At the negative electrode, the solvated Na$^+$ is desorbed from the electrode surface. At the same time, solvated SO$_4^{2-}$ is desorbed from the positive electrode. After the stability test, the average oxidation numbers of Mn at the positive and negative electrodes are +2.43 and +2.38, respectively, calculated from the K-edge electron binding energies of 6546.77 eV and 6546.69 eV, respectively. This decrease is due to the extraction of Mn$^{2+}$ from the crystal structure. Note that all of the binding energies and oxidation states of Mn are listed in Table S1 of the ESI†.

The EQCM results of the as-electrospun Mn$_3$O$_4$ nanofibres in 0.5 M Na$_2$SO$_4$ at a scan rate of 10 mV s$^{-1}$ are shown in Fig. 7. For the anodic potentials scanned from 0 to 0.5 V vs. Ag/AgCl, the mass change is reduced or under zero due to desorption of solvated Na$^+$ cations. On the other hand, an augmented mass change is observed for the cathodic potential scanned from 0.5 to 0 V vs. Ag/AgCl due to the adsorption of solvated cations.\textsuperscript{41} However, the final mass change of the cathodic scan does not meet the initial mass change of the anodic scan. This confirms the XAS results, which showed that the average oxidation state of Mn changes over time or during cycling. In other words, the charge storage mechanism of the as-electrospun Mn$_3$O$_4$ nanofibres involves solvated cation adsorption/desorption with a mass change of ca. 80 ng cm$^{-2}$. These EQCM results support the XAS results.

**Conclusions**

Manganese oxide (Mn$_3$O$_4$) nanofibres were prepared by an electrospinning process of Mn(OAc)$_2$ in PAN with a subsequent calcination process at 500 °C for 2 h. The effect of the Mn(OAc)$_2$ loading content was investigated and it was found that the amount of Mn(OAc)$_2$ precursor affected the crystalline structure of the final Mn$_3$O$_4$ nanofibre products. The Mn$_3$O$_4$ nanofibres produced with different Mn(OAc)$_2$ contents were coated onto flexible CFP substrates using a spray coating technique and then electrochemically evaluated by CV, GCD, and EIS methods. The symmetric supercapacitor based on Mn$_3$O$_4$ nanofibres with diameters of 60–200 nm produced at 10 wt% Mn(OAc)$_2$ exhibits the highest SC, specific energy, and maximum specific power of 289 F g$^{-1}$ at 1 mA, 37.4 W h kg$^{-1}$ and 11.1 kW kg$^{-1}$, respectively. The capacity retention is ca. 98% over 4500 cycles. Based on XAS, the charge storage mechanism of the as-calcined Mn$_3$O$_4$ nanofibres involves a phase transformation from Mn$_3$O$_4$ to...
Na$_2$MnO$_2$·nH$_2$O during the first charge. After this, the mechanism is based on surface redox reactions due to adsorption/desorption of solvated ions. In addition, the EQCM measurements show that the solvated cation adsorption/desorption with a mass change of ca. 80 ng cm$^{-2}$ on the Mn$_2$O$_3$ nanofibres plays a significant role in the charge storage mechanism of Mn$_2$O$_3$. The understanding of the charge storage mechanism of Mn$_2^+(\text{Mn}^3)_2$O$_4$ presented in this work could lead to further development of metal oxide-based pseudocapacitors.

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