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## Charge storage mechanisms of electrospun $\text{Mn}_3\text{O}_4$ 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  $\text{Mn}_3\text{O}_4$  or  $\text{Mn}^{2+}(\text{Mn}^{3+})_2\text{O}_4$  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  $\text{Mn}_3\text{O}_4$  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  $\text{Mn}_3\text{O}_4$  to  $\text{Na}_x\text{MnO}_x \cdot n\text{H}_2\text{O}$ . Meanwhile, the charge storage mechanism at the positive electrode mainly involves the adsorption of counter ions or solvated  $\text{SO}_4^{2-}$ . 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  $\text{Na}^+$  is desorbed from the electrode surface. At the same time, the solvated  $\text{SO}_4^{2-}$  is desorbed from the positive electrode. The mass change of solvated  $\text{Na}^+$  during charging/discharging is ca. 80 ng per  $\text{cm}^2$  of the  $\text{Mn}_3\text{O}_4$  electrode. A symmetric supercapacitor constructed from  $\text{Mn}_3\text{O}_4$  nanofibres in 0.5 M  $\text{Na}_2\text{SO}_4$  provides a working potential of 1.8 V, a specific energy of 37.4 W h  $\text{kg}^{-1}$  and a maximum specific power of 11.1 kW  $\text{kg}^{-1}$  with 98% capacity retention over 4500 cycles. The understanding of the charge storage mechanism of the mixed oxidation states of  $\text{Mn}^{2+}(\text{Mn}^{3+})_2\text{O}_4$  presented in this work could lead to further development of metal oxide-based pseudocapacitors.

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## Introduction

Supercapacitors have higher specific power (2–10 kW  $\text{kg}^{-1}$ )<sup>1</sup> than batteries (0.5–1 kW  $\text{kg}^{-1}$ )<sup>1</sup> and higher specific energy (5–10 W h  $\text{kg}^{-1}$ )<sup>2</sup> than conventional capacitors (0.01–0.05 W h  $\text{kg}^{-1}$ ).<sup>3</sup> 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.<sup>2,4–6</sup> On the other hand, transition metal oxides, *e.g.*  $\text{RuO}_2$ ,

$\text{NiO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$ , are widely used as active materials for pseudocapacitor electrodes.<sup>7–12</sup> Among all metal oxides, manganese oxides are widely employed as pseudocapacitor electrodes because of their relatively low cost, low toxicity, high theoretical capacitance,<sup>13</sup> and environmental compatibility.<sup>14</sup> A number of manganese oxide structures including  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$  have been used for high-performance supercapacitors.<sup>13,15–17</sup>

Among all structures,  $\text{Mn}_3\text{O}_4$  with a normal spinel structure with  $\text{Mn}^{2+}$  in tetrahedral units and  $\text{Mn}^{3+}$  in octahedral units<sup>18</sup> with a formula structure of  $\text{Mn}^{2+}(\text{Mn}^{3+})_2\text{O}_4$  (ref. 19) provides high pseudocapacitance. Previously,  $\text{Mn}_3\text{O}_4$ -anchored graphene sheets produced by a microwave hydrothermal method have exhibited a specific capacitance (SC) of 70 F  $\text{g}^{-1}$  at 0.2 A  $\text{g}^{-1}$  in 1 M  $\text{Na}_2\text{SO}_4$ .<sup>20</sup> A graphene-supported  $\text{Mn}_3\text{O}_4$  nanocomposite synthesized by a precipitation method gives a SC of 61 F  $\text{g}^{-1}$  at 0.1 A  $\text{g}^{-1}$  in 1 M  $\text{K}_2\text{SO}_4$ .<sup>21</sup>  $\text{Mn}_3\text{O}_4$  nanoparticles (NPs) prepared by ultrasonication and hydrolysis provide a SC of 261 F  $\text{g}^{-1}$  at 0.4 A  $\text{g}^{-1}$  in 1 M  $\text{Na}_2\text{SO}_4$  (ref. 22) and those produced by chemical precipitation show a SC of 322 F  $\text{g}^{-1}$  at 0.5 mA  $\text{cm}^{-2}$  in 1 M  $\text{Na}_2\text{SO}_4$ .<sup>23</sup> More interestingly, 1D nanofibres of mixed  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  produced by an electrospinning process, which is a simple, efficient, and reproducible method,<sup>24</sup> exhibit a SC of

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360.7 F g<sup>-1</sup> at 1 A g<sup>-1</sup> in 0.5 M Na<sub>2</sub>SO<sub>4</sub>.<sup>25</sup> 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.<sup>25</sup> The porosity of the nanofibres also plays an important role in the charge storage performance of the supercapacitors.<sup>26,27</sup> Micropores can help increase the electrochemical double layer capacitance due to their high surface area, while mesopores can enhance electrolyte ion transportation. For example, MnO<sub>x</sub> nanofibres with a pore size of around 10–30 nm provide very good electrolyte diffusion.<sup>28</sup>

However, the charge storage mechanism of Mn<sub>3</sub>O<sub>4</sub> is unclear and rather complex.<sup>8,29,30</sup> In this work, we have investigated the charge storage mechanism of Mn<sub>3</sub>O<sub>4</sub> nanofibres using high-resolution synchrotron-based X-ray absorption (XAS) and electrochemical quartz crystal microbalance (EQCM) techniques. The results here showed that Mn<sub>3</sub>O<sub>4</sub> nanofibres produced by an electrospinning process using 10 wt% manganese acetate (Mn(OAc)<sub>2</sub>) in polyacrylonitrile (PAN) solution provide higher SCs than other samples. The charge storage mechanism of the Mn<sub>3</sub>O<sub>4</sub> nanofibres investigated by XAS involves a phase transformation of Mn<sub>3</sub>O<sub>4</sub> to Na<sub>6</sub>MnO<sub>x</sub>·nH<sub>2</sub>O during the first charge. Subsequently, the mechanism is based on surface redox reactions. The mass change of solvated Na<sup>+</sup> during charging/discharging is ca. 80 ng per cm<sup>2</sup> of the Mn<sub>3</sub>O<sub>4</sub> electrode.

## Experimental section

### Electrospinning of manganese oxide nanofibres

Firstly, 1 g of PAN (*M<sub>w</sub>* = 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)<sub>2</sub>·4H<sub>2</sub>O) (Acros, 99+%) was added into the PAN solution. The PAN/Mn(OAc)<sub>2</sub> 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<sup>-1</sup> and the applied potential was finely tuned to 15 kV. The Mn(OAc)<sub>2</sub> 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<sup>-1</sup> 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<sup>-1</sup>. 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.<sup>31</sup>

### 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 Na<sub>2</sub>SO<sub>4</sub> 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 MnO<sub>x</sub> 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 (MnO<sub>x</sub> : CB : PVDF) in *N*-methyl-2-pyrrolidone (NMP). The mixture was then spray-coated onto functionalized-carbon fibre paper with dimensions of 1 × 1 cm<sup>2</sup> 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<sup>-2</sup> for each electrode. The electrode was dried at 80 °C for 24 h. The hydrolysed polyethylene (PE) separator was soaked in 0.5 M Na<sub>2</sub>SO<sub>4</sub> 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 MnO<sub>x</sub> 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<sup>-2</sup> 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)<sub>2</sub> nanofibres with different Mn(OAc)<sub>2</sub> 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)<sub>2</sub>, respectively.

Fig. 2 shows the morphology of the MnO<sub>x</sub> nanofibres after calcining at 500 °C for 2 h. After the removal of PAN, the diameter of the as-calcined MnO<sub>x</sub> nanofibres is reduced. With increasing Mn(OAc)<sub>2</sub> concentrations, the as-calcined MnO<sub>x</sub> formed larger nanofibres. The diameters of the MnO<sub>x</sub> nanofibres are 60–125, 60–200, 150–250, 300–600, and 300–600 nm for 5, 10, 20, 30 and 36 wt% Mn(OAc)<sub>2</sub>, 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 MnO<sub>x</sub> nanofibres are formed from connected MnO<sub>x</sub> particles with open pores in the structure. Note that the PAN/Mn(OAc)<sub>2</sub> 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 MnO<sub>x</sub> nanofibres. The XRD patterns of the MnO<sub>x</sub> produced using 5–20 wt% Mn(OAc)<sub>2</sub> are assigned to Mn<sub>3</sub>O<sub>4</sub> (JCPDS 24-0734).<sup>25</sup> In addition, the XRD patterns of the MnO<sub>x</sub> prepared using 30 and 36 wt% Mn(OAc)<sub>2</sub> show mixed crystalline phases of Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> (JCPDS 073-1826).<sup>25</sup> The Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> crystallite



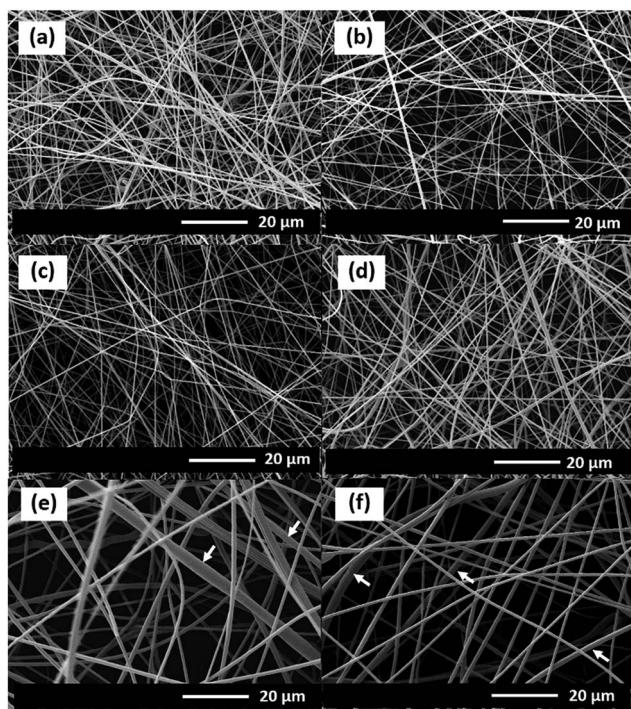


Fig. 1 SEM images of the as-electrospun PAN nanofibres at different  $\text{Mn}(\text{OAc})_2$  loading contents: (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, and (f) 36 wt%.

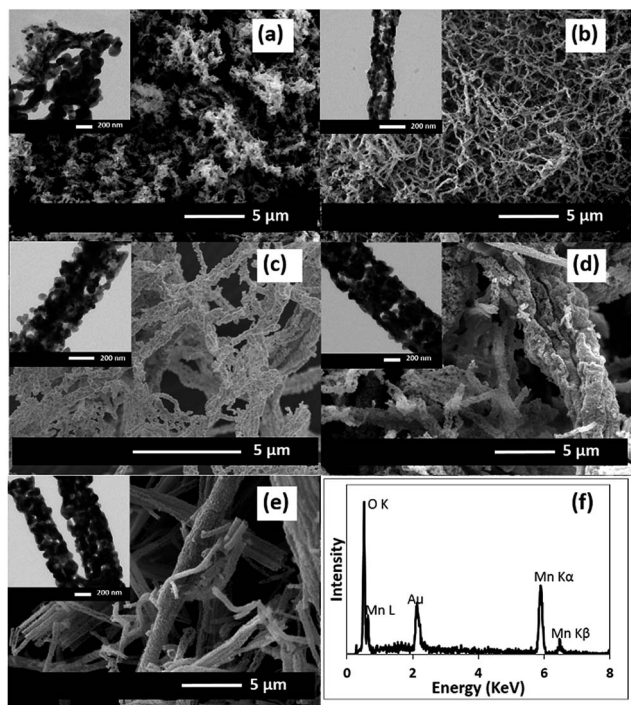


Fig. 2 SEM and TEM images of the  $\text{MnO}_x$  nanofibres formed with different  $\text{Mn}(\text{OAc})_2$  concentrations after calcining at  $500\text{ }^\circ\text{C}$ : (a) 5, (b) 10, (c) 20, (d) 30, and (e) 36 wt%. (f) The EDX spectrum of the  $\text{MnO}_x$  nanofibres produced using 36 wt%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

sizes are estimated using Scherrer's equation from the (211) and (222) planes, respectively. The  $\text{Mn}_3\text{O}_4$  crystallite sizes are 13.3, 30.7, 42.3, 35.4 and 36.9 nm at 5, 10, 20, 30 and 36 wt%

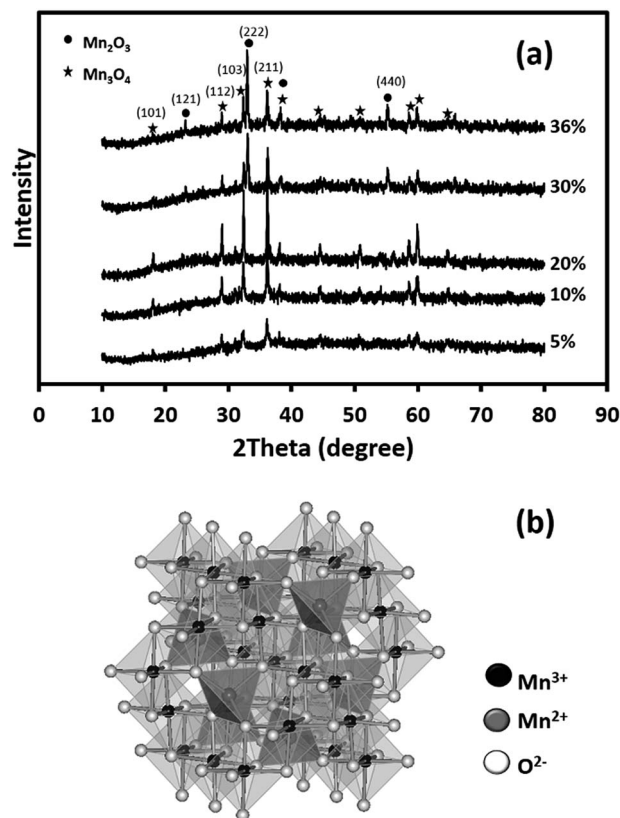
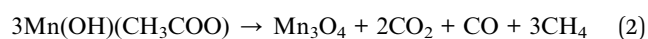


Fig. 3 (a) XRD patterns of the as-calcined  $\text{MnO}_x$  nanofibres electrospun at different  $\text{Mn}(\text{OAc})_2$  loading contents at 15 kV and (b) a crystal structure model of spinel  $\text{Mn}_3\text{O}_4$ .

$\text{Mn}(\text{OAc})_2$ , respectively. Meanwhile, the  $\text{Mn}_2\text{O}_3$  crystallite sizes are 30.5 and 30.9 nm at 30 and 36 wt%  $\text{Mn}(\text{OAc})_2$ , respectively. Note that the  $\text{Mn}_2\text{O}_3$  phase is easily removed by calcination at high temperature (see Fig. S1†). The formation of  $\text{Mn}_3\text{O}_4$  occurs *via* reactions (1) and (2):<sup>24</sup>



Intermediate reactions are proposed as shown in reactions (3) and (4).<sup>32</sup>

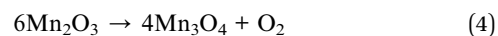
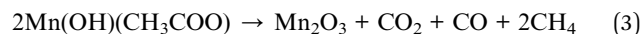


Fig. 4 shows the electrochemical properties of the as-calcined  $\text{MnO}_x$  nanofibres produced using different  $\text{Mn}(\text{OAc})_2$  contents. From the CV curves (Fig. 4a), the  $\text{Mn}_3\text{O}_4$  nanofibres electrospun at 10 wt%  $\text{Mn}(\text{OAc})_2$  exhibit the largest area under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



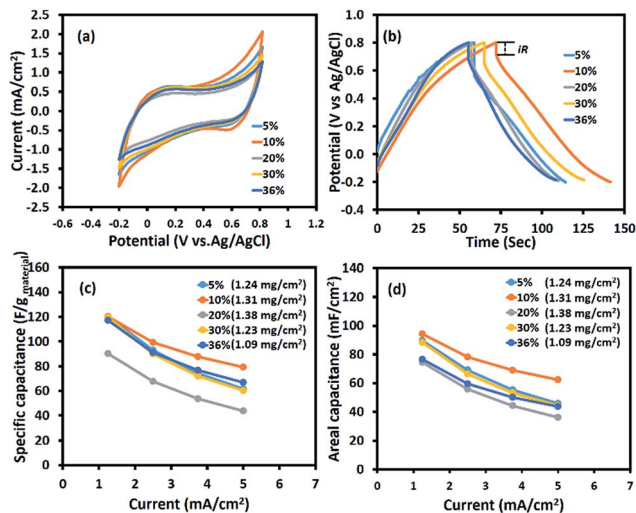


Fig. 4 (a) Cyclic voltammograms at a scan rate of  $10 \text{ mV s}^{-1}$ , (b) galvanostatic charge-discharge curves at  $1.25 \text{ mA cm}^{-2}$ , (c) the specific capacitance vs. applied current, and (d) the areal capacitances vs. applied current of the half-cell  $\text{Mn}_3\text{O}_4$  electrodes in  $0.5 \text{ M Na}_2\text{SO}_4$  electrolyte.

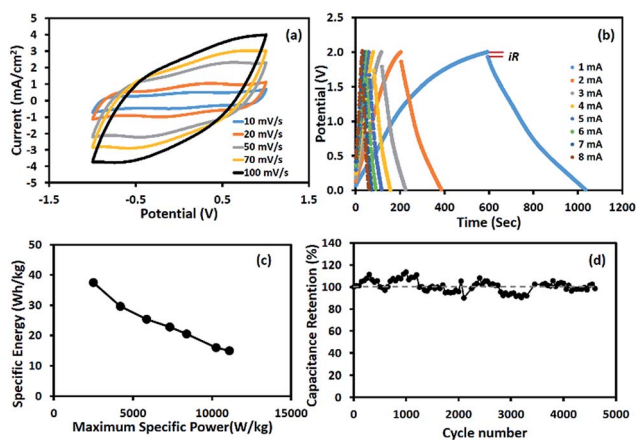


Fig. 5 (a) CV curves, (b) GCD curves, (c) Ragone plot, and (d) capacity retention of the symmetric supercapacitor based on  $\text{Mn}_3\text{O}_4$  nanofibres electrospun at 10 wt%  $\text{Mn}(\text{OAc})_2$  in  $0.5 \text{ M Na}_2\text{SO}_4$ .

with the CV result. The working potential of the electrode excluding  $iR$  drop is *ca.*  $0.9 \text{ V vs. Ag/AgCl}$ . The  $\text{Mn}_3\text{O}_4$  nanofibres produced with 10 wt%  $\text{Mn}(\text{OAc})_2$  content exhibit the highest

capacitance because of their high surface area and 3D porous structure, which enhances the contact area between the electrode and the electrolyte,<sup>25</sup> and their small crystallite size, which can enhance charge transport.<sup>33</sup> Meanwhile, the  $\text{Mn}_3\text{O}_4$  nanofibres electrospun at 20 wt%  $\text{Mn}(\text{OAc})_2$  show the lowest capacitance due to large crystallite size, which leads to poor charge transport. As the conductivity of  $\text{Mn}_3\text{O}_4$  is relatively higher than that of  $\text{Mn}_2\text{O}_3$ ,<sup>25</sup> the  $\text{Mn}_3\text{O}_4$  nanofibres produced at 10 wt%  $\text{Mn}(\text{OAc})_2$  provide a higher SC than the mixed  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  nanofibres electrospun at 30–36 wt%  $\text{Mn}(\text{OAc})_2$ . The specific and areal capacitances of the  $\text{Mn}_3\text{O}_4$  electrodes at different applied currents in  $0.5 \text{ M Na}_2\text{SO}_4$  are shown in Fig. 4c and d, respectively. The charge storage performance of the  $\text{Mn}_3\text{O}_4$  electrodes is under the diffusion limit since their capacitances decrease with increasing applied currents.

The charge storage performance of the symmetric supercapacitor based on the  $\text{Mn}_3\text{O}_4$  nanofibres produced at 10 wt%  $\text{Mn}(\text{OAc})_2$  is shown in Fig. 5. The cyclic voltammograms in Fig. 5a show pseudocapacitive behaviour with a broad peak due to surface redox reactions. The GCD curves in Fig. 5b show a wide working potential of  $1.8 \text{ V}$  excluding  $iR$  drop, which is twice that of the half-cell electrode. The calculated capacitances decrease with increasing scan rates and applied currents due to the limited diffusion of solvated ions.<sup>34</sup> The calculated SC is  $289 \text{ F g}^{-1}$  at  $1 \text{ mA}$  for each cell or  $1.25 \text{ mA cm}^{-2}$ . Table 1 compares the charge storage performances of  $\text{Mn}_3\text{O}_4$ -based supercapacitors. Most previous reports were based on a three-electrode system or half-cell.

The Ragone plot of the device is shown in Fig. 5c. The specific energy and maximum specific power of the  $\text{Mn}_3\text{O}_4$  symmetric supercapacitor are  $37.4 \text{ W h kg}^{-1}$  and  $11.1 \text{ kW kg}^{-1}$ , respectively (see the calculation details in the ESI†). The stability of the symmetric supercapacitor based on the as-electrospun  $\text{Mn}_3\text{O}_4$  nanofibres is shown in Fig. 5d, for which the capacity retention is over 98% after 4500 charge/discharge cycles.

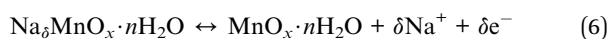
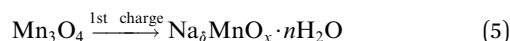
To further investigate the charge storage mechanism of  $\text{Mn}_3\text{O}_4$ , the average oxidation number of Mn at the positive and negative electrodes of the device after the 1<sup>st</sup> charge, the 1<sup>st</sup> discharge, and the long-term stability test of over 4500 cycles was determined by XAS. The normalized X-ray absorption near edge spectra (XANES) of the Mn-based materials are shown in Fig. 6a–c. The K-edge electron binding energies of Mn metal, MnO,  $\text{Mn}_2\text{O}_3$ , and  $\text{Mn}_3\text{O}_4$  standards are 6539.00, 6544.17, 6548.61, and 6547.15 eV, respectively. After the 1<sup>st</sup> charge, the

Table 1 Charge storage performances of  $\text{Mn}_3\text{O}_4$ -based supercapacitor electrodes

Materials	Tested method	Electrolyte	Specific capacitance	Ref.
$\text{Mn}_3\text{O}_4$ nanoparticles	GCD at $0.1 \text{ A g}^{-1}$	$1 \text{ M Na}_2\text{SO}_4$	$85 \text{ F g}^{-1}$ (three electrodes)	35
$\text{Mn}_3\text{O}_4$ stacked sheet	CV at $10 \text{ mV s}^{-1}$	$\text{H}_2\text{SO}_4$ -PVA (1 : 1 wt) gel electrolyte	$127 \text{ F g}^{-1}$ (two electrodes)	36
$\text{Mn}_3\text{O}_4$ nanoparticles	GCD at $0.5 \text{ mA cm}^{-2}$	$1 \text{ M Na}_2\text{SO}_4$	$322 \text{ F g}^{-1}$ (three electrodes)	23
$\text{Mn}_3\text{O}_4$ nanoparticles	GCD at $0.5 \text{ mA cm}^{-2}$	$1 \text{ M Na}_2\text{SO}_4$	$113 \text{ F g}^{-1}$ (three electrodes)	7
As-spun $\text{Mn}_3\text{O}_4$ fibres	GCD at $0.3 \text{ A g}^{-1}$	$1 \text{ M Na}_2\text{SO}_4$	$155 \text{ F g}^{-1}$ (three electrodes)	28
As-spun $\text{MnO}_x$ fibres	CV at $10 \text{ mV s}^{-1}$	$1 \text{ M Na}_2\text{SO}_4$	$161.22 \text{ F g}^{-1}$ (two electrodes)	37
As-spun $\text{Mn}_3\text{O}_4$ fibres	CV at $2 \text{ mV s}^{-1}$	$0.5 \text{ M Na}_2\text{SO}_4$	$63.2 \text{ F g}^{-1}$ (three electrodes)	38
As-spun $\text{Mn}_3\text{O}_4$ nanofibres	GCD at $1 \text{ mA}$ ( $1.25 \text{ mA cm}^{-2}$ )	$0.5 \text{ M Na}_2\text{SO}_4$	$289 \text{ F g}^{-1}$ (two electrodes)	This work



K-edge electron binding energies of Mn at the positive and negative electrodes were in between those of MnO ( $\text{Mn}^{2+}$ ) and  $\text{Mn}_2\text{O}_3$  ( $\text{Mn}^{3+}$ ) 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†<sup>39</sup> are 2.61 and 2.38, respectively. Note that the average oxidation state of Mn in the as-calcined  $\text{Mn}_3\text{O}_4$  is +2.67 (see Fig. 6d). The decreased oxidation number of Mn, especially at the negative electrode is due to solvated  $\text{Na}^+$  being inserted into the structure. The charge storage mechanism follows reactions (5) and (6):



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

After the 1<sup>st</sup> 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  $\text{Na}^+$  is desorbed from the electrode surface. At the same time, solvated  $\text{SO}_4^{2-}$  is desorbed from the positive electrode. After the stability test, the average oxidation numbers of Mn at the

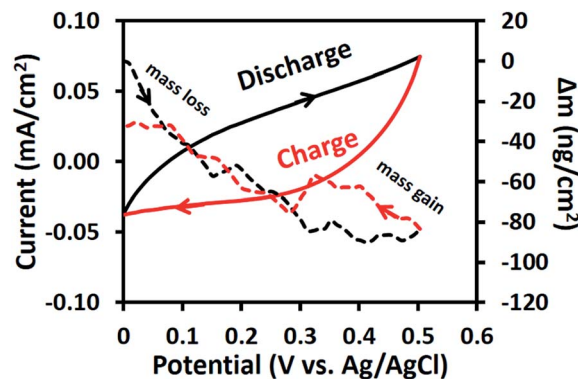


Fig. 7 CV curves and EQCM measurements of the as-electrospun  $\text{Mn}_3\text{O}_4$  nanofibre electrode in 0.5 M  $\text{Na}_2\text{SO}_4$ .

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  $\text{Mn}^{2+}$  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  $\text{Mn}_3\text{O}_4$  nanofibres in 0.5 M  $\text{Na}_2\text{SO}_4$  at a scan rate of  $10 \text{ mV s}^{-1}$  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  $\text{Na}^+$  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.<sup>41</sup> 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  $\text{Mn}_3\text{O}_4$  nanofibres involves solvated cation adsorption/desorption with a mass change of *ca.*  $80 \text{ ng cm}^{-2}$ . These EQCM results support the XAS results.

## Conclusions

Manganese oxide ( $\text{Mn}_3\text{O}_4$ ) nanofibres were prepared by an electrospinning process of  $\text{Mn}(\text{OAc})_2$  in PAN with a subsequent calcination process at  $500^\circ\text{C}$  for 2 h. The effect of the  $\text{Mn}(\text{OAc})_2$  loading content was investigated and it was found that the amount of  $\text{Mn}(\text{OAc})_2$  precursor affected the crystalline structure of the final  $\text{Mn}_3\text{O}_4$  nanofibre products. The  $\text{Mn}_3\text{O}_4$  nanofibres produced with different  $\text{Mn}(\text{OAc})_2$  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  $\text{Mn}_3\text{O}_4$  nanofibres with diameters of 60–200 nm produced at 10 wt%  $\text{Mn}(\text{OAc})_2$  exhibits the highest SC, specific energy, and maximum specific power of  $289 \text{ F g}^{-1}$  at 1 mA,  $37.4 \text{ W h kg}^{-1}$  and  $11.1 \text{ kW kg}^{-1}$ , respectively. The capacity retention is *ca.* 98% over 4500 cycles. Based on XAS, the charge storage mechanism of the as-calcined  $\text{Mn}_3\text{O}_4$  nanofibres involves a phase transformation from  $\text{Mn}_3\text{O}_4$  to

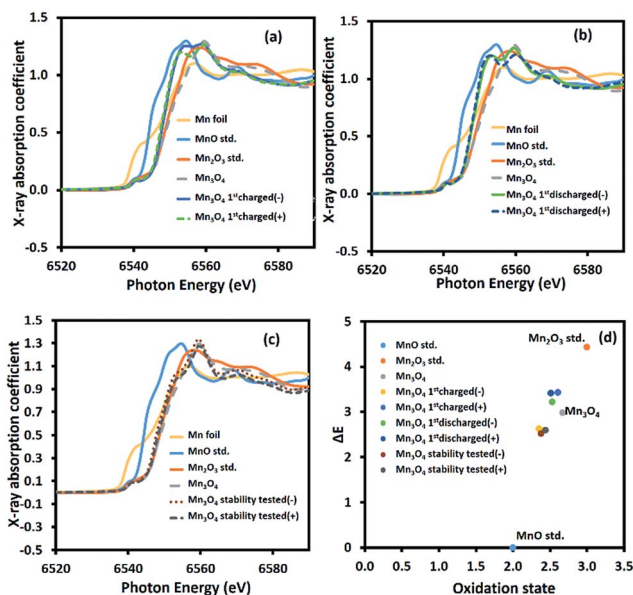


Fig. 6 *Ex situ* high-resolution XAS spectra after (a) the 1<sup>st</sup> charge, (b) the 1<sup>st</sup> discharge, and (c) the stability test, and (d) the average oxidation numbers of Mn in the manganese oxide electrodes compared with the Mn standard compounds.



$\text{Na}_x\text{MnO}_y \cdot n\text{H}_2\text{O}$  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<sup>-2</sup> on the Mn<sub>3</sub>O<sub>4</sub> nanofibres plays a significant role in the charge storage mechanism of Mn<sub>3</sub>O<sub>4</sub>. The understanding of the charge storage mechanism of Mn<sup>2+</sup>(Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> presented in this work could lead to further development of metal oxide-based pseudocapacitors.

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