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1. Introduction

 Mn_3O_4 is a promising charge storage material for applications in cathodes of asymmetric supercapacitor devices operating in a neutral Na_2SO_4 electrolyte.^{1,2} Such devices offer advantages of enlarged voltage windows and enhanced power-energy characteristics. Investigations are focused on the development of advanced techniques for the deposition of nanostructured Mn_3O_4 films¹ and synthesis of Mn_3O_4 nanoparticles^{1,3,4} for the fabrication of bulk electrodes with high active mass. Understanding the capacitive behavior and charging mechanism is crucial for the development of efficient electrodes and devices for practical applications.^{5–7} Particular attention is focused on the charge storage behavior of nanostructured Mn_3O_4 and

Scanning transmission X-ray microscopy studies of electrochemical activation and capacitive behavior of Mn₃O₄ supercapacitor electrodes[†]

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This investigation, which is motivated by promising pseudocapacitive properties of Mn_3O_4 for energy storage in cathodes of supercapacitors, addresses the need to understand both the activation and the charge storage mechanisms of Mn₃O₄ electrodes. Specific activation protocols are shown to result in significant capacitance increase during cycling. For the first time scanning transmission X-ray microscopy (STXM) is used for analysis of Mn_3O_4 activation. STXM analyses at the Mn 2p and O 1s edges provide chemical mapping of different oxidation states with high spatial resolution. Mn₃O₄-carbon nanotube composite electrodes with commercially important high active mass loading of 40 mg cm⁻² are prepared using quercetin dispersant. The catecholate type polyaromatic quercetin facilitates codispersion of Mn_3O_4 with carbon nanotubes and allows enhanced electrode performance at high active mass loadings. Cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic chargedischarge are used for the capacitance monitoring during electrode activation. Two strategies are used for electrode activation in Na₂SO₄ electrolyte: electrochemical cycling at different scan rates and continuous cycling at a fixed scan rate. The capacitance variations are linked to STXM observations, which show gradual oxidation of Mn_3O_4 to form MnO_2 on the particle surface and in the bulk. The pseudocapacitive charge storage mechanism involves in situ oxidation of Mn₃O₄ and redox reactions of Mn^{4+}/Mn^{3+} species on the particle surface and in the bulk.

> composites.⁸ Mn_3O_4 is usually combined with conductive additives for the fabrication of composites with enhanced conductivity and capacitance.⁹⁻¹¹ The charge storage mechanism of Mn_3O_4 electrodes in Na_2SO_4 electrolyte was analyzed in several investigations.^{2,12} The first step involves solvation:¹²

$$\begin{split} \mathrm{Na_2SO_4(aq)} + \mathrm{H_2O} + \mathrm{Mn_3O_4} \to \\ (2 - \delta)\mathrm{Na^+(aq)} + [\mathrm{Na_\delta}\mathrm{Mn_3O_4} \cdot \mathrm{H_2O]^{\delta^+}} + \mathrm{SO_4^{2-}(aq)} \, (1) \end{split}$$

The subsequent charge–discharge steps are based on the reaction: $^{\scriptscriptstyle 12}$

$$Na_{\delta}MnO_{x} \cdot H_{2}O \leftrightarrow MnO_{x} \cdot H_{2}O + \delta Na^{+} + \delta e^{-}$$
(2)

Previously, Mn K-edge X-ray absorption spectroscopy $(XAS)^{12}$ showed that $Na_{\delta}MnO_x$ is formed in the first charge–discharge cycle of Mn_3O_4 cathodes, which resulted in the reduction of the average oxidation state of Mn. Another investigation, using *in situ* XAS at the Mn K-edge, showed reduction of Mn^{3+} to Mn^{2+} at low potentials and oxidation of Mn^{3+} to Mn^{4+} or Mn^{6+} at higher potentials.¹³ Significant changes in lattice constants (a and c) of the tetragonal Mn_3O_4 unit cell were observed during cycling in the positive potential range in the Na_2SO_4 electrolyte.¹³

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Despite the recent progress in the investigation of the deposition mechanism, the charge-discharge behavior of Mn₃O₄ electrodes is not well understood. The understanding of the charging mechanism is complicated due to the electrode activation phenomena. Several investigations analyzed activation of Mn₃O₄ electrodes, which resulted in capacitance increase during initial cycling.2,14,15 A significant increase in capacitance was observed for electrodes with high active mass loading.16-20 The activation process was linked to in situ modification of the electrode microstructure.17,19,21,22 Previous investigations showed that capacitance variations during activation process can be diminished using mixed rhamnolipids as a capping agent for the synthesis of Mn₃O₄ particles and modification of particle morphology.20 However, the origin of the capacitance variation during the activation process and charging mechanism are not well understood. Further analysis of activation behavior is critically important for better understanding of charging mechanism and applications of Mn₃O₄ electrodes in asymmetric supercapacitors.

Scanning transmission X-ray microscopy (STXM) is a promising technique for the investigation of activation behavior of Mn₃O₄ and analysis of the charging mechanism(s). STXM²³⁻²⁵ is a synchrotron-based technique which provides chemically sensitive imaging with high spatial resolution (\sim 30 nm). Chemical contrast is provided by near-edge X-ray absorption fine structure (NEXAFS) spectral signal.²⁶ STXM analytical studies provide spectroscopic identification and quantitative mapping of chemical components with 30 nm spatial resolution in both 2D and 3D projections.23-25,27 Most of the electrochemical applications, particularly energy conversion and storage-related applications are associated with chemical reactions at the electrolyte and electrode interface.27,28 STXM determination of the products of electrochemical reactions, along with quantitative spatial mapping, can provide a mechanistic understanding of electrochemical processes such as supercapacitor charging and discharging.

The objective of this investigation is the application of STXM for the analysis of activation behavior and charging mechanism of Mn₃O₄ based electrodes which contain multiwalled carbon nanotubes (MWCNT) as conductive additives. Investigations were performed using electrodes with high active mass loadings of 40 mg $\rm cm^{-2}$, which is necessary for practical applications. High capacitance was achieved by the use of quercetin as a new catecholate-type dispersant, which facilitated co-dispersion of Mn₃O₄ and MWCNT. Testing results presented below revealed significant increase in capacitance during cycling. We describe the results of Mn 2p and O 1s STXM measurements of Mn₃O₄ -MWCNT samples subjected to different activation procedures. Our findings demonstrate that, as the number of chargedischarge cycles is increased, Mn₃O₄ is partially converted to MnO₂. This was correlated to the steady increase in the obtained capacitance. Testing results provide insight into the mechanism of activation and charge-discharge of Mn₃O₄ electrodes. In this case, the capacitance increase was linked to in situ oxidation of Mn₃O₄ during cycling.

2. Experimental procedures

2.1 Materials, synthesis of Mn_3O_4 particles and electrode fabrication

Quercetin (QC), $Mn(NO_3)_2 \cdot 4H_2O$, isopropanol, NaOH, Na₂SO₄, poly(vinyl butyral) binder (PVB, MilliporeSigma, Canada), multiwalled carbon nanotubes (MWCNT, ID 4 nm, OD 13 nm, length 1-2 µm, Bayer, Germany) and industrial Ni foam current collectors (95% porosity, 1.6 mm thickness, Vale, Canada) were used. A chemical precipitation method^{16,20} was used for the synthesis of Mn₃O₄ nanoparticles from 0.07 M Mn(NO₃)₂ solution in DI water. The pH of the solution was adjusted to pH = 10by aqueous 0.01 M NaOH for the synthesis of Mn₃O₄ nanoparticles. The obtained precipitate was washed with water and ethanol. Ouercetin was used as a co-dispersant for the fabrication of stable suspensions of Mn₃O₄ and MWCNT in isopropanol (see ESI, Fig. S1[†]). The mass ratio of Mn_3O_4 : MWCNT : PVB binder in the suspensions was 80:20:3. The Ni foam current collectors were impregnated with the suspensions. The mass loading of the impregnated material after drying was 40 mg cm^{-2} . The impregnated foams were pressed to 30% of original thickness in order to improve electrical contact of the active material and current collector. Manganese dioxide (MnO_2) , and trimanganese tetraoxide (Mn₃O₄) were purchased from Sigma-Aldrich and used as reference materials for STXM analysis. All reagents were used without further purification.

2.2 Microstructure and electrochemical characterization

Scanning electron microscopy (SEM) investigations were performed using a JEOL microscope, (JSM-7000F, Japan). X-ray diffraction (XRD) analysis was performed using a diffractometer (Bruker D8, Cu-K α radiation, UK) at the scan rate of 1 degree per min. Electrochemical testing of capacitive behavior of the electrodes by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) was performed using a PARSTAT 2273 (Ametek) potentiostat. Galvanostatic chargedischarge (GCD) studies were performed using a BioLogic VMP 300 potentiostat. Testing was carried out using aqueous 0.5 M Na₂SO₄ electrolyte in a 3-electrode electrochemical cell containing impregnated Ni foam as a working electrode, Pt mesh as a counter-electrode, and a saturated calomel electrode (SCE) as a reference.

Electrode capacitance was obtained from the CV, EIS and GCD data by methodology described in the literature^{29,30} and presented as areal (C_S , F cm⁻²) and gravimetric (C_m , Fg⁻¹) capacitance. Integral capacitances were derived from the CV and GCD data in a potential window of 0–0.9 V. CV was performed at scan rates of 2–100 mV s⁻¹. GCD testing was performed at current densities of 3–10 mA cm⁻². Differential capacitances were derived from the EIS data obtained at a voltage amplitude of 5 mV in the frequency range of 10 mHz-100 Hz at an open circuit potential. Analysis of the impedance data was performed using the commercial ZSimpWin software (Ametek) and an equivalent circuit developed for supercapacitor electrodes with high active mass loadings.³¹

 $C_{\rm S}$ and $C_{\rm m}$ were derived from the CV data using the following equation:

$$C = \frac{\Delta Q}{\Delta U} = \frac{\left|\int_{0}^{t(U_{\max})} I dt\right| + \left|\int_{t(U_{\max})}^{0} I dt\right|}{2(U_{\max})}$$
(3)

where ΔQ is charge, I – current and ΔU – the potential range. Capacitance was calculated from the chronopotentiometry data using the equation:

$$C = I\Delta t / \Delta U \tag{4}$$

The complex capacitance $C^*(\omega) = C'(\omega) - iC''(\omega)$ was derived at different frequencies (ω) from the complex impedance $Z^*(\omega)$ = $Z'(\omega) + iZ''(\omega)$:

$$C^{'}(\omega) = \frac{-Z^{''}(\omega)}{\omega |Z(\omega)|^2}$$
(5)

$$C^{''}(\omega) = \frac{-Z^{'}(\omega)}{\omega |Z(\omega)|^2}$$
(6)

The electrode activation was performed using CV at various scan rates (VSR) or at fixed scan rates (FSR). A VSR procedure (VSRP) involved CV at scan rates of 2, 5, 10, 20, 50 and 100 mV s⁻¹. EIS studies were performed after each VSRP. GCD testing was performed after five VSRPs. FSR testing involved 1000 CV cycles at a scan rate of 50 mV s⁻¹.

2.3. Methods: scanning transmission X-ray microscopy

Imaging, spectroscopy and spectromicroscopy measurements were performed using the ambient STXM at the spectromicroscopy (SM) beamline 10ID1 at the Canadian Light Source (CLS, Saskatoon, Canada),32 a brief description of which is presented in ESI, Section S2.† The as-prepared active electrode materials (AEM) and AEM after VSRPs 1-5, or after 100 and 1000 FSR cycles were scratched to separate them from the Ni foam substrate. The AEM particles were drop-cast on formvar coated TEM grids (TED Pella Inc.). The grids were taped to standard trapezoidal STXM sample plates.³³ Spectra, images and image sequences were measured at the Mn 2p and O 1s edges. STXM measurements were performed with the chamber evacuated to $<10^{-2}$ mbar and then backfilled with Helium (He) to a pressure of ~ 100 mbar. During the measurements, the X-ray beam is monochromated to a specific photon energy, then focused by a Fresnel zone plate (ZP) to a 40 nm spot, where the sample is placed (Fig. S2[†]). Images were measured by (x,y) raster scanning the sample while recording the intensity of the transmitted X-rays detected by a phosphor/photomultiplier tube (PMT) detector located behind the sample.^{34,35} Spectromicroscopic data in the form of multi-energy image sequences (stacks³⁶) were obtained at X-ray energies from ~ 10 eV below to ~ 40 eV above the onset of O 1s and Mn 2p absorption. STXM data was analyzed using aXis2000 software.37 The transmitted X-ray flux through the sample (I) was converted to optical density (OD) using the Beer–Lambert Law: OD = $\ln(I_0/I) = \mu(E) \cdot \rho \cdot t$, where I_0 is the incident X-ray flux, measured through an area devoid of the sample but with all other components (windows, zone plate, OSA, formvar); $\mu(E)$ is the energy dependent mass absorption coefficient; *E* is X-ray energy; ρ is sample density and *t* is the sample thickness.²³

After Fourier cross-correlation alignment, the stacks were converted to OD using as I_0 the spectrum from areas of the stack devoid of sample. The OD stacks were then fit to suitable reference spectra, in this case, Mn₃O₄ and MnO₂, which were measured using both STXM and the CLS spherical grating monochromator (SGM) spectroscopy beamline, 11ID1. The results of the reference spectral study are described in ESI (Fig. S2, S3 and Table S1[†]). The Mn 2p spectrum of the commercial Mn₃O₄ sample, measured by both STXM and SGM, was significantly different from that reported in the literature.³⁸⁻⁴⁰ The spectrum of the as-prepared electrode layer was in good agreement with the Mn 2p and O 1s spectra of Mn₃O₄ reported in the literature.38,39 Thus we used the Mn 2p and O1s spectra of the as-prepared material as the reference for Mn₃O₄. The measured O 1s and Mn 2p spectra of Mn₃O₄ and MnO₂ were energy calibrated (see ESI, Section S3[†]) and placed on quantitative intensity scales, corresponding to the OD for 1 nm thickness of each material at its standard density using a method outlined in detail elsewhere.23 These spectra were used in a singular value decomposition (SVD) analysis of the Mn 2p and O 1s stacks from each sample (SVD is a single pass matrix manipulation approximating linear least squares fitting⁴¹). Since quantitative reference spectra are used, the intensity scales of the resulting component maps give the local component thickness in nm.23

3. Results and discussion

3.1 Electrochemical and microstructure characterization

Fig. 1 shows X-ray diffraction pattern of obtained Mn_3O_4 particles. The observed diffraction peaks correspond to data in the JCPDS file 001-1127. It is suggested that the addition of alkali to the $Mn(NO_3)_2$ solutions resulted in the formation of unstable^{42,43} $Mn(OH)_2$, which was oxidized in air to form Mn_3O_4 .



Fig. 1 X-ray diffraction pattern of as-prepared Mn_3O_4 (\bullet -peaks corresponding to JCPDS file 001-1127).

The fabrication of Mn₃O₄ electrodes with high active mass requires the use of conductive additives because Mn₃O₄ exhibits low electronic conductivity. Therefore, MWCNT were used as conductive additives. As-received MWCNT formed large agglomerates with a typical diameter of 0.5 mm. The SEM images of such agglomerates were presented in a previous investigation.44 Nanoparticles of Mn₃O₄ are also prone to agglomeration. Therefore, QC was used as a co-dispersant for Mn₃O₄ and MWCNT. QC was chosen due to its polyaromatic catecholate structure and redox properties. Fig. 2A shows the chemical structure of QC, which includes hydroxylated benzene rings. QC is a polyaromatic molecule, containing a catechol group. It has been widely reported that catechol and related molecules exhibit strong adsorption on surfaces of inorganic particles.45-47 The interest in catechol anchoring groups resulted from the investigation of mussel adsorption on different surfaces, which involved dopamine-type catecholate monomers of proteins.47-51 Fig. 2B shows adsorption of QC on the Mn₃O₄ surface, involving catecholate-type chelating bonding.45 The polyaromatic structure of OC is beneficial⁵² for its adsorption on MWCNT. This mechanism is based on π - π interactions.⁵² Owing to its polyphenolic nature, QC exhibits redox-active properties.53-55 It has previously been shown that catecholatetype redox-active molecules can act as charge transfer medicators, which facilitate charge-discharge reactions of supercapacitor materials.⁵⁶ Moreover, adsorbed catecholate molecules facilitate charge transfer in other processes, such electropolymerization and photovoltaic current generation.45

Sedimentation tests showed enhanced suspension stability of Mn_3O_4 and MWCNT in the presence of QC as a dispersant (see Fig. S1†). Therefore, QC can be used as a co-dispersant for Mn_3O_4 and MWCNT. Fig. 3 shows microstructures of the electrodes prepared with and without QC. The electrodes prepared without QC showed poor mixing of Mn_3O_4 and MWCNT. The SEM image (Fig. 3A) shows large areas containing only MWCNT or Mn_3O_4 . In contrast, the electrodes prepared using QC as a codispersant (Fig. 3B) showed reduced agglomeration and improved mixing of Mn_3O_4 and MWCNT. The improved mixing is beneficial for the fabrication of electrodes with enhanced capacitance. The electrodes prepared using QC were used for electrochemical characterization. Fig. 4A shows CVs at different

В

Fig. 2 . (A) Chemical structure of QC, (B) adsorption QC on Mn_3O_4 by chelation of surface Mn atoms.



Fig. 3 SEM images for as-prepared Mn_3O_4-MWCNT electrodes (A) without QC and (B) with QC. The scale bars in the figures represent 250 nm, and arrows show MWCNT.

scan rates for VSRP 1 and indicate capacitive behavior in a potential window of 0–0.9 V. Fig. 4B compares CVs at a scan rate of 10 mV s⁻¹ for VSRPs 1-5. It is seen that CV area increased from VSRP1 to VSRP5, indicating capacitance increase due to *in situ* activation of the electrodes. Moreover, the CV for VSRP 5 is nearly of rectangular shape, which indicates good pseudocapacitive response.

Fig. 4C and D shows capacitances and impedances for VSRPs 1-5. First cycle at 2 mV s⁻¹ for VSR1 showed a capacitance of 1.5 $F \text{ cm}^{-2}$. The capacitance decreased with increasing scan rate. The activation procedure resulted in capacitance increase from VSRP1 to VSRP5 (Fig. 4C). The capacitance at 2 mV s⁻¹ for VSRP5 was found to be 3.3 F cm^{-2} . The decrease of real part of complex impedance with increasing TP number indicated beneficial decrease of resistance during the activation process (Fig. 4D). The decrease of the imaginary part indicated the increase of capacitance. The analysis of the impedance data using an equivalent circuit for high active mass electrodes³¹ (see ESI, Section S4, Fig. S4⁺) for VSRPs 1-5 showed that changes in the real and imaginary parts of complex impedance resulted from the increase in capacitance and reduction of the charge transfer resistance. The components of complex capacitance were calculated from the impedance data and presented in Fig. 4E and F.

The AC capacitance derived from the impedance data increased with increasing VSRP number. The GCD data acquired after VSRP5 showed (Fig. 5) nearly ideal triangular charge-discharge curves. The capacitance decreased from 4.4 to 4.1 F cm⁻² with increasing current density from 3 to 10 mA cm⁻². The obtained capacitances after VSRP5 were comparable with those reported in previous investigations.^{17,19,22} Higher capacitances can be achieved using special techniques, such as electrostatic heterocoagulation,21 liquid-liquid extraction16 and synthesis in the presence of a capping agent.²⁰ However, to avoid the influence of different factors on Mn₃O₄ particles and with the goal of developing the STXM methodology, a traditional approach was used for the synthesis of Mn₃O₄ and electrode fabrication. This was important for monitoring the chemical modifications of Mn₃O₄ during activation and obtaining better understanding of the charging mechanism.

Another activation strategy was based on continuous cycling at a fast scan rate of 50 mV s⁻¹. Fig. 6 shows a continuous increase in normalized capacitance with increasing cycle number during 1000 FSR cycles. The capacitance for cycle 1 was only



Fig. 4 (A) CVs for Mn_3O_4 -MWCNT electrode at scan rates of (a) 5, (b) 20, (c) 50 and (d)100 mV s⁻¹ for VSRP 1, (B) CVs at 10 mV s⁻¹ for (a–e) VSRPs 1-5, (C) capacitance derived from CV data for (a–e) VSRPs 1-5, (D) Nyquist plot of complex impedance for (a–e) VSRPs 1-5, (E) real and (F) imaginary components of complex capacitances derived from the complex impedance data *versus* frequency for (a–e) VSRPs 1-5.

32.7% of the capacitance for FSR cycle 1000. The capacitance for FSR cycle 100 was 55.7%. Significant increase in capacitance was observed during the first 500 FSR cycles.

3.2 X-ray spectromicroscopy

3.2.1 Mn₃O₄ and MnO₂ reference spectroscopy. Fig. 7A and B present Mn 2p and O 1s spectra of the as-prepared Mn₃O₄ and MnO₂ reference spectra on OD1 intensity scales. The positions and relative intensities of the features in the measured Mn L_{2,3} STXM reference spectra are in agreement in shape with the literature absorption spectra of Mn₃O₄ (hausmannite),³⁸ MnO₂ (pyrolusite)³⁸ and δ -MnO₂.³⁹ However there are discrepancies in the energy scales, with deviations from literature reports greater than 1 eV in some cases. These issues are documented and discussed in ESI, Section S5.† The first sharp peaks in the L₃ spectra of MnO₂ and Mn₃O₄ occur at 641.3 eV and 640.1 eV

respectively, and thus can be used to track sample oxidation. The O 1s \rightarrow Mn3d electronic transitions in the O 1s spectra of MnO₂ and the as-prepared catalyst (Fig. 7B) occur at 529.7 eV and 530.6 eV respectively, again providing a useful tool to track oxidation. The shapes and energy positions of main features in the measured O 1s spectra are similar to those in the O 1s absorption spectra of MnO₂ and Mn₃O₄ reported previously.³⁸

3.2.2 Mn 2p and O 1s results for the MnOx samples. Fig. 8A and B present Mn $L_{2,3}$ and O 1s spectra of as-prepared Mn_3O_4 and MnO_2 in comparison with spectra extracted from STXM stack measurements of the VSRP1, VSRP3 and VSRP5 processed samples. Mn $L_{2,3}$ and O 1s results for samples after FSR100 and FSR1000 cycles are presented in Fig. 8C and D. The Mn $L_{2,3}$ spectra were calibrated as discussed in ESI (Fig. S3 and Table S1†).

The Mn $L_{2,3}$ spectra (Fig. 8A) show that the Mn oxide in the as-prepared material is predominantly Mn_3O_4 showing three



Fig. 5 (A) GCD data for current densities of (a) 3, (b) 5, (c) 7 and (d) 10 mA cm⁻² and (B) capacitance versus current density obtained from the GCD data.



Fig. 6 Capacitance normalized by capacitance value for FSR cycle 1000 versus cycle number for continuous CV cycling at a scan rate of 50 mV s⁻¹.

sharp Mn L₃ peaks at 639.91 eV, 641.23 eV and 641.89 eV which is consistent with the XAS spectrum of an ensemble of the asprepared material measured in TEY mode (ESI Section S6, Fig. S7†), and also with previous reports (Fig. S6B†).^{38,39} At the early stages of the charge/discharge testing procedures (VSR1-VSR5), the Mn 2p spectra showed a noticeable change in the Mn L_{2,3} peak positions, indicating partial conversion of Mn($\pi/\pi\pi$) to Mn(π). On the contrary, the extracted spectra of the electrode material after FSR1000 cycles exhibited the Mn L_{2,3} features characteristic of MnO₂, with sharp Mn 2p \rightarrow 3d peaks at 641.1 (L₃) and 653.7 eV (L₂) and broad peak at (643.5 eV), respectively, indicating a remarkable change in both shape and peak positions compared to the spectra of as-prepared Mn₃O₄ which has a sharp L₃ peak at 640.1 and two broad peaks at (641.4 eV and 642.1 eV), respectively. In addition, the O 1s spectra after VSRP1, VSRP3 and VSRP5 (Fig. 8B) were consistent with the Mn 2p measurements, indicating a significant change in the O 1s \rightarrow 3d features in the 528–534 eV region consistent with partial conversion of the original Mn(π/π) (Mn₃O₄) material to Mn(ν) (MnO₂). The O 1s \rightarrow Mn3d transition in the as-prepared material occurs at 530.6 eV, while after 1000 FSR cycles the O 1s \rightarrow Mn3d transition occurs at 529.9 eV (Fig. 8D). Fig. 9 is an expansion of the low energy O 1s \rightarrow Mn 3d region of the O 1s spectra and the Mn 2p_{3/2} region, showing more clearly the systematic shift in the spectral peak positions with VSRPs 1,3,5 and FSR100, 1000 cycle samples.

The SGM-TEY measurements of Mn 2p spectra presented in Fig. S7[†] showed a remarkable change in the Mn L_{2,3} peak positions of VSRs1, 3, 5 and FSR1000 cycles samples compared to the as-prepared Mn₃O₄, which are consistent with the STXM measurements of the same samples. However, the measured spectra of the VSR and FSR samples are similar, indicating that each consists of a mixture of Mn₃O₄ and MnO₂ species. On the other hand, the O 1s spectra of VSR1, VSR3, VSR5 and FSR1000 cycle samples showed the same O 1s \rightarrow 3d features at 528–534 eV and are similar to the O 1s spectra of MnO₂, while the 536–548 eV region is different with no obvious trend. In contrast, the O 1s spectrum to the as-prepared Mn₃O₄ is very different from the measured spectra of the VSR and FSR samples (3 peaks instead of 2 in the 529–534 eV region).

3.2.3 Mapping of Mn species from the Mn 2p spectromicroscopy of the MnOx samples. The quantitative chemical mapping of the Mn(π/π) and Mn(π) species on the VSRs1, 3, 5 and FSR100 and 1000 cycle samples that derived from fitting of Mn 2p stacks in a photon energy range of 630–670 eV to absolute intensity scale of MnO₂ and Mn₃O₄ reference spectrum showed a steady conversion of Mn(π/π) to Mn(π) by increasing number of cycles.



Fig. 7 (A) Quantitative Mn 2p spectra of Mn(II/III) (dark green) and Mn(IV) (red) on OD1 intensity scales. (B) Quantitative O 1s spectra of Mn(II/III) (dark green) and Mn(IV) (red) on OD1 intensity scales.



Fig. 8 (A) Mn 2p, (B) O 1s absorption spectra extracted from stacks measured for (a) VSRP1, (b) VSRP3 and (c) VSRP5, (C) Mn 2p, (D) O 1s absorption spectra extracted from stacks measured for (f) FSR cycle 100 and (g) FSR cycle 1000 samples.

Fig. 10A presents quantitative chemical mapping of the $Mn(\pi/\pi\pi)$ and $Mn(\pi\nu)$ species in each of VSRs1, 3 and 5, while chemical maps for FSR100 and FSR1000 cycle samples presented in Fig. 10B. Each image is a color-coded composite of quantitative component maps derived by fitting the measured stacks with quantitative OD1 reference spectra of MnO_2 and Mn_3O_4 which are presented in Fig. 7A.

Fig. 11A and B plot the average volume of $Mn(\pi/\pi)$ and $Mn(\pi)$ present for VSRPs1, 3, 5 samples and FSR100 and FSR1000 cycle samples. The chemical mapping and spatial distribution of Mn_3O_4 and MnO_2 shows only a small volume fraction of MnO_2 after VSRP1. Conversely, a considerable increase in MnO_2 contribution was observed after VSRPs 3 and 5. After FSR1000 cycles a 0.6 volume fraction of MnO_2 was obtained.

3.2.4 STXM spectromicroscopy. When compared to published Mn K-edge XAS results,^{12,13} Mn L-edge spectromicroscopy

has the advantages of (i) higher energy resolution, thus achieving better chemical sensitivity - there are remarkable changes in both the Mn 2p and O 1s spectra when the oxidation state changes (Fig. 7); and (ii) nanoscale chemical imaging (Fig. 10). In particular, for the regions studied, it appears that the conversion of $Mn(\pi/\pi)$ to $Mn(\pi)$ occurs to a greater extent in the core of the particles rather than at the edges. This is especially evident for the FSR 1000 cycles sample. The high spectral sensitivity has enabled observation of subtle changes in the Mn₃O₄ supercapacitor electrode material during the activation process. In particular, the improved capacitance can be seen to be the consequence of the increasing fraction of MnO₂. In contrast to the mechanism suggested in previous investigations12,13 we did not observe capacitance decrease during initial cycling (Fig. 6). Very small Mn4+ content (Fig. 11A) in the particles after VSRP1 indicated that oxidation of Mn³⁺ ions on



Fig. 9 Mn L₃ and O 1s \rightarrow 3d features showing conversion of Mn(II/III) to Mn(IV). (A) and (B) present (a) VSRP1, (b) VSRP2 and (c) VSRP3, (C) and (D) present (f) FSR100 and (g) FSR1000 cycle samples in comparison with as-prepared Mn₃O₄ catalyst and MnO₂ reference spectra.

the particle surfaces contributed to pseudocapacitive behavior. Continuous cycling resulted in oxidation of Mn^{2+} species in the bulk and enhanced contributions of bulk material to the total capacitance according to the reaction (2). It should be noted that previous investigations did not show a correlation between capacitance and BET surface area of MnO_2 .^{57,58} It was suggested that some pores accessible by nitrogen gas are not accessible by the solvated ions in the electrolyte. The STXM studies of this work showed that the bulk of the particles contributes significantly to the total capacitance.

Since this work is one of the first applications of STXM to supercapacitor materials, it is appropriate to compare its capabilities to complementary analytical imaging methods being applied to such problems. In terms of spectroscopies, X- ray photoelectron spectroscopy (XPS) is often used to determine oxidation states of metal oxides. In the case of Mn oxides the range of oxidation state shifts from Mn(II) to Mn(IV) is less than 1 eV and the peak positions reported by various authors vary by up to 1 eV (see Table 2 in ref. 59). XPS is a very surface sensitive technique which is an advantage for studying surface dependent phenomena such as the mechanisms of charge transfer in supercapacitors. It is possible to perform XPS imaging, but the typical spatial resolution is 1–2 orders of magnitude lower than that provided by STXM. In terms of imaging, it is clear that electron microscopies such as SEM and TEM provide 1–2 orders of magnitude higher spatial resolution than STXM. However the analytical information provided is generally less sensitive that X-ray absorption. X-ray fluorescence (TEM-EDX) only provides



Fig. 10 Color coded composites of Mn(II/III) and Mn(IV) component maps derived by SVD fitting Mn 2p stacks measured on (A) VSRPs1, 3, 5 (a-c respectively), (B) FSR100 and FSR1000 cycle samples (f and g respectively), scale bar: 0.5 μ m. Color scales are nm thickness. Color wheel indicates color expected for specific combinations of the red and green signals.



Fig. 11 Evolution of Mn(u/uu) and Mn(v) signals of (A) VSRP1, VSRP3 and VSRP5, (B) FSR100 and FSR1000 cycle sample represented in volume fractions.

elemental, not oxidation state, sensitivity. Core level electron energy loss (TEM-EELS) is the direct analog to STXM spectromicroscopy and thus has the same potential for oxidation state determination, but with the advantage of much higher spatial resolution. The most modern implementations of TEM-EELS provide a spectral resolution as STXM, but such measurements can be challenging due to the much greater extent of radiation damage in TEM than STXM.⁶⁰ In addition, since STXM is a photon-in, photon-out method, it is possible to adapt the system to *in situ* and *operando* studies of aqueous electrochemical phenomena such as charge/discharge mechanisms at supercapacitor electrodes. Such studies are currently underway.

4. Conclusions

For the first time scanning transmission X-ray microscopy (STXM) was used for the analysis of Mn₃O₄ activation. The use of OC as a dispersant facilitated fabrication of composite electrodes with high active mass and high areal capacitance. The beneficial effect of catecholate-type polyaromatic QC is related to co-dispersion and efficient mixing of different materials: pseudocapacitive Mn₃O₄ and conductive MWCNT additives. Monitoring the capacitance change by CV, EIS and GCD using VSRP and FSR activation methods and analysis of active material by STXM linked capacitance increase during activation and corresponding Mn₃O₄ oxidation on the surface and in the bulk of the particles. The capacitance increase during activation resulted from the gradual oxidation of Mn₃O₄ and increased contribution of the particle bulk to the total capacitance. The charge storage mechanism involved redox Mn³⁺/Mn⁴⁺ reactions on the particle surface and in the bulk. It is expected that the approach developed in this investigation can be used for the analysis of activation behavior and charge storage mechanisms of other pseudocapacitive materials, such as V2O3.44 In addition, we are actively developing in situ flow electrochemical devices for STXM,^{61,62} which will enable in situ and operando types of studies of supercapacitor electrode materials.

Conflicts of interest

There are no conflicts to declare.

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