

# Journal of Materials Chemistry A

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## Charge storage mechanism of activated manganese oxide composites for pseudocapacitors

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Manganese oxides can undergo an electrochemical activation step that leads to greater capacitances, of which the structural change and mechanism remains poorly understood. Herein we present a wide-ranging study on a manganese oxide synthesised by annealing manganese (II) acetate precursor to 300 °C, which includes *in operando* monitoring of the structural evolution during the activation process via *in situ* Raman microscopy. Based on powder X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron and *ex situ* Raman microscopy, the as prepared manganese oxide was characterised as hausmannite-Mn<sub>3</sub>O<sub>4</sub> with a minor portion of MnO<sub>2</sub>. The activation process of converting as-prepared hausmannite-Mn<sub>3</sub>O<sub>4</sub> into amorphous MnO<sub>2</sub> (with localised birnessite structure) by electrochemical cycling in 0.5 M Na<sub>2</sub>SO<sub>4</sub> was examined. After activation, the activated MnO<sub>x</sub> exhibited capacitive performance of 174 F/g at a mass loading of 0.71 mg cm<sup>-2</sup>. The charge storage mechanism is proposed as the redox reaction between Mn (III) and Mn (IV) at outer surface active sites, since the disordered birnessite-MnO<sub>2</sub> does not provide an ordered layer structure for cations and/or protons to intercalate.

### Introduction

Electrochemical supercapacitors have been widely investigated due to their high charge/discharge efficiency, high-rate charge storage and delivery, as well as long cycle life.<sup>1</sup> Recently, researchers have investigated approaches to increase the specific energy stored in supercapacitors in order to apply to numerous energy storage applications, such as hybrid electric vehicles, starting assistance to fuel cells, and power sources of electronics and cordless electric tools.<sup>1-3</sup> According to the charge storage mechanism, the non-faradaic electrical double-layer capacitors (EDLCs) are based on charge separation (i.e., arrangement of ions/polar molecules) at the electrode/solution interface. The pseudocapacitance originates from the faradaic redox reactions of electroactive species within electrode materials.

The capacitive performance of MnO<sub>2</sub> in neutral aqueous electrolytes has received much attention, due to improving cycle life (at least 10,000 cycles<sup>4-6</sup>), acceptable specific capacitance at moderate scan rates for MnO<sub>2</sub> thin films (100-400 F/g<sup>7-10</sup>), and low cost<sup>10-13</sup>. MnO<sub>2</sub> exhibits more than 0.9 V potential window in neutral media, such as alkali metal chloride<sup>10,14</sup>, alkali metal sulphate<sup>5,12</sup>, and specific lithium salts<sup>15</sup> aqueous electrolytes, without considering the significant enlargement of the cell voltage via the asymmetric design.<sup>16-18</sup> The charge storage mechanism of MnO<sub>2</sub> has been discussed by various analyses, such as X-ray photoelectron spectroscopy (XPS),<sup>13</sup> electrochemical quartz crystal microbalance (EQCM),<sup>19</sup> and *in situ* powder X-ray diffraction (PXRD).<sup>14</sup>

Two mechanisms have been proposed to elucidate the MnO<sub>2</sub> charge storage process. The first is based on the surface adsorption of cations on MnO<sub>2</sub> active sites,<sup>10</sup> while the second involves the intercalation and expulsion of alkali metal cations and/or protons into/from MnO<sub>2</sub> structures.<sup>20</sup> The synergistic effect of MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> has been proposed from our previous work,<sup>21</sup> which demonstrated that the specific current responses for MnO<sub>2</sub>/Mn<sub>3</sub>O<sub>4</sub> composites are superior than individual manganese oxides (MnO<sub>x</sub>), i.e., MnO<sub>2</sub> or Mn<sub>3</sub>O<sub>4</sub> measured on single-crystalline MnOOH nanowires. Alternatively, the activation from hausmannite-Mn<sub>3</sub>O<sub>4</sub> to birnessite-MnO<sub>2</sub> by electrochemical methods has been proposed by a series of PXRD, X-ray absorption spectroscopic (XAS), and *ex situ* Raman spectroscopic analyses.<sup>22-26</sup> The activation process has been proposed as a complex and irreversible process, and the new formed birnessite-MnO<sub>2</sub> is accepted as the material responsible for pseudocapacitive behaviour via the insertion of cations and/or protons.<sup>22,26</sup> The structural disorder of electrochemically activated birnessite-MnO<sub>2</sub> has been previously remarked upon.<sup>23</sup> However, the charge storage mechanism of electrochemically activated birnessite-MnO<sub>2</sub> from hausmannite-Mn<sub>3</sub>O<sub>4</sub> in neutral aqueous electrolytes has not yet been verified.

Raman spectroscopy is a powerful technique for the characterisation of short-range order of surface molecular species (especially for covalent character of the metal-oxygen bond).<sup>27,28</sup> Therefore, Raman analyses have been widely used to characterise various manganese oxides, since they possess a variety of oxidation states and phases.<sup>28-33</sup> The use of *in situ* measurement techniques are important in understanding the

Mn<sub>3</sub>O<sub>4</sub> activation process and charge storage mechanism in neutral aqueous electrolytes since the dried electrodes used in *ex situ* techniques may not represent the true state during electrochemical analyses.

A number of previous works have characterised the conversion of various manganese oxides into birnessite-MnO<sub>2</sub>,<sup>22-26,34</sup> with applicable studies relating to electrochemical activation from Mn<sub>3</sub>O<sub>4</sub> to MnO<sub>2</sub> that are detailed in Table S1. Among these reported works, the as-prepared and electrochemically activated MnO<sub>x</sub> were characterised as pure Mn<sub>3</sub>O<sub>4</sub> and MnO<sub>2</sub> according to various *ex situ* analyses methods, respectively.<sup>22-25</sup> In the majority of studies, the MnO<sub>x</sub> were identified as crystallised hausmannite-Mn<sub>3</sub>O<sub>4</sub> and birnessite-MnO<sub>2</sub>.<sup>22,24,25</sup> Consequently, the crystallinity of activated MnO<sub>x</sub> is presumed to be dependent on the crystallinity of as-prepared Mn<sub>3</sub>O<sub>4</sub>. For example, the applied high temperature thermal reduction of electrolytic manganese dioxide at 1050 °C for 72 hr is believed to be a well crystallised Mn<sub>3</sub>O<sub>4</sub>, which probably results in the highly crystallised birnessite structure after electrochemical activation. In this study, the electrochemical activation of hausmannite-Mn<sub>3</sub>O<sub>4</sub> to in 0.5 M Na<sub>2</sub>SO<sub>4</sub> was characterised by both *in situ* and *ex situ* techniques in order to understand both the activation process and the charge storage mechanism of this promising manganese oxide composite pseudo-capacitive material.

## Experimental

The preparation of MnO<sub>x</sub> material followed our previous work.<sup>17</sup> In short, the manganese (II) acetate tetrahydrate (99.99%, from Sigma-Aldrich) precursor solution annealed at a ramping rate of 1°C min<sup>-1</sup> to 300 °C and then left to cool down to ambient temperature. PXRD was measured using either a Cu K<sub>α</sub> source (λ=1.54 Å, Mac Science, MXP 18) for as-prepared MnO<sub>x</sub> or a Mo K<sub>α</sub> source (λ=0.709 Å, Bruker, D8 advance) for activated MnO<sub>x</sub> in Debye-Scherrer geometry with a capillary diameter of 0.5mm. TEM analyses were conducted on a Philips Tecnai F20 G2 electron microscope at 200 kV, and samples for TEM analyses were prepared by drop casting on copper grids followed by solvent evaporation in air at 80 °C. The surface morphologies of MnO<sub>x</sub> were examined by SEM (JEOL, JSM-6610 at 20 kV). XPS measurements were performed in a standard ultrahigh vacuum surface science chamber (2 × 10<sup>-10</sup> mbar) a PSP Vacuum Technology electron energy analyzer (angle integrating ± 10°) and a dual anode Mg K<sub>α</sub> (1253.6 eV) X-ray source.

For *in situ* Raman cell configuration, the working electrode was free-standing sample film composed of as-prepared MnO<sub>x</sub> (30%), ground carbon black (XC-72, Cabot Corporation, USA, 173 m<sup>2</sup>g<sup>-1</sup>; 20%), and poly(vinylidene fluoride-hexafluoropropylene) co-polymeric binder (Kynar-flex, Arkema) powders (50%). The counter electrode was prepared by casting activated carbon (ACS-679 from China Steel Chemical Corporation, Taiwan, 1635 m<sup>2</sup>g<sup>-1</sup>) onto an Al current collector, while activated carbon free-standing film composed of ACS-679 activated carbon (40%) and Kynar-flex powders (60%) was served as the quasi-reference electrode (QRE).<sup>35</sup> The three-electrode compartments were sealed in the *in situ* Raman cell with adequate amount of electrolyte (4-5 drops).<sup>36</sup> The mass based on Mn<sub>3</sub>O<sub>4</sub> of working electrode and activated carbon of counter electrode were ca. 1 mg and 15 mg, respectively. Note that the potential of QRE were tested in a beaker cell, the cyclic voltammetric (CV) profile of MnO<sub>2</sub>

between -0.1 and 1.1 V was extremely similar to the CV measured against an Ag/AgCl (ALS co. Ltd, Japan, 3 M NaCl, 0.209 V versus SHE at 25°C) in the range between 0 and 1.2 V, indicating that the potential difference of QRE and Ag/AgCl is ca. 0.1 V (Fig. S1). The electrolyte was 0.5 M Na<sub>2</sub>SO<sub>4</sub> degassed with purified argon gas flow before the measurements. *In situ* Raman spectra were recorded with Raman microscope (Renishaw in Via), using a He-Ne laser (632.8 nm) focussed through an inverted microscope (Leica), via a 50× objective lens (Leica). *In situ* Raman spectra were measured at different potentials with an interval of 200 mV, starting from 0.1 V vs. QRE to 1.1 V (positive sweep, PS) and then back from 0.9 V to -0.1 V (negative sweep, NS). Therefore, 12 spectra were obtained from each *in situ* Raman cycle. For each spectrum, the working electrode was pre-polarised for 3 min and held the potential during the spectral acquisition with the range of 250–750 cm<sup>-1</sup>. The formation of Mn<sub>3</sub>O<sub>4</sub> triggered by an increase in lattice temperature due to local heating by laser has been widely reported.<sup>28,29,33</sup> In order to avoid this factor, the laser exposed to sample surface was controlled via the use of an appropriate filter to keep below a maximum power of 0.37 mW.

For *ex situ* Raman experiments, the working electrodes were prepared by casting the slurry composed of as-prepared MnO<sub>x</sub> (70%), XC-72 (20%), and Kynar (10%) onto graphite electrodes. Total mass of each electrode is 0.71 mg, which is used for calculating specific capacitance. An Ag/AgCl and a Pt wire were used as reference and counter electrodes, respectively. The measurements under the three-electrode mode were performed in deaerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> in a sealed beaker cell at 25°C. The cyclic voltammograms were measured at 25 mV s<sup>-1</sup> between 0 and 1.2 V (vs. Ag/AgCl). The MnO<sub>x</sub>-coated working electrodes were potential-cycled for 5, 10, 50, 100, 150, 200, and 500 cycles to elucidate the activation process. After CV cycling, the MnO<sub>x</sub>-coated electrodes were gently washed by deionised-water and dried in 85°C oven overnight.

## Results and discussion

### Chemical synthesised as-prepared MnO<sub>x</sub>

The diffraction pattern of as-prepared MnO<sub>x</sub> (Fig. 1a) corresponds to the PXRD pattern of hausmannite-Mn<sub>3</sub>O<sub>4</sub> from the database (JCPDS CARD 24-0734). Reflections at 18.0°, 28.9°, 32.4°, 36.1°, and 59.8° are recorded, which correspond to face (101), (112), (103), (211), and (224) of hausmannite-Mn<sub>3</sub>O<sub>4</sub>, respectively. The sub-particles of the MnO<sub>x</sub> can be observed by TEM images (Fig. 2b, 2c). From TEM images, the particle size of as-prepared MnO<sub>x</sub> is ca. 6-8 nm. The d-spacing of 0.499, 0.313, 0.281, 0.253, 0.208, 0.182, 0.157, and 0.146 nm can be found and calculated from the selected area electron diffraction (SAED) pattern of as-prepared MnO<sub>x</sub> (Fig. 2a), which are consistent with the d-spacing of hausmannite-Mn<sub>3</sub>O<sub>4</sub>. Moreover, the lattice spacing of 0.50, 0.31, 0.28, and 0.25 nm can be identified from the TEM image (Fig. 2c), which correspond to face (101), (112), (103), and (211) of hausmannite-Mn<sub>3</sub>O<sub>4</sub>, respectively. The diffraction peaks and d-spacing of as-prepared MnO<sub>x</sub> are compiled and compared to



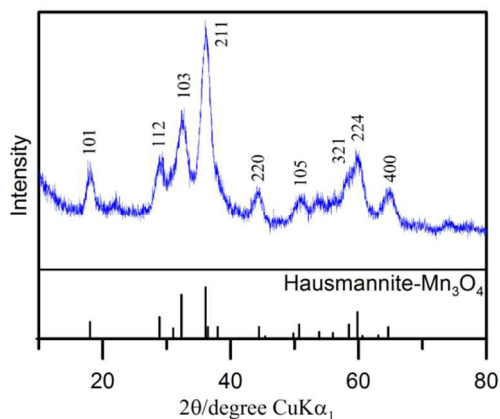


Figure 1. X-ray diffraction pattern of as-prepared  $\text{MnO}_x$ .

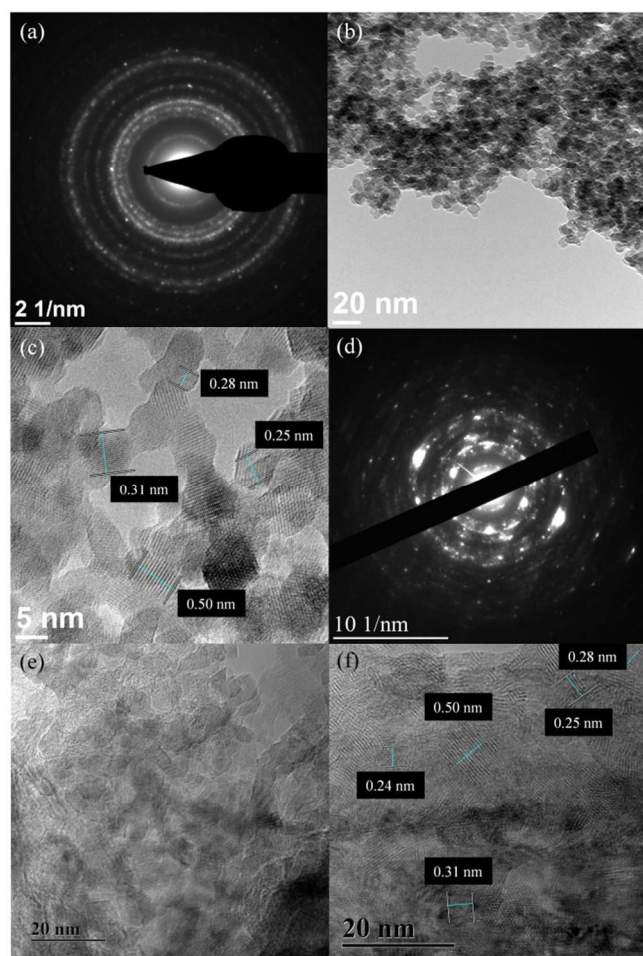


Figure 2. (a, d) SAED pattern and (b, c, e, f) TEM images of (a-c) as-prepared and (d-f) activated  $\text{MnO}_x$ .

hausmannite- $\text{Mn}_3\text{O}_4$  (JCPDS CARD 24-0734) in Table 1, which verifies that the as-prepared  $\text{MnO}_x$  can be considered as consisting of hausmannite- $\text{Mn}_3\text{O}_4$ .<sup>13,37-39</sup> The mean manganese oxidation state of  $\text{MnO}_x$  can be determined by the energy separation between the two peaks of Mn 3s core level spectrum.<sup>13,37-39</sup> It has been reported that more interaction can occur upon photoelectron ejection since a lower valence state implies more electrons in the 3d orbital. Consequently, the

energy separation between the two components of the Mn 3s multiplet will increase.<sup>13,38</sup> The energy separation between these two peaks of Mn 3s spectra is 5.79, 5.50, 5.41, and 4.78 eV for reference sample of  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$ , respectively.<sup>13,38,39</sup> The peak separation is 5.23 eV obtained from Mn 3s spectrum of as-prepared  $\text{MnO}_x$  (Fig. 3a). Therefore, the mean manganese oxidation state of as-prepared  $\text{MnO}_x$  is ca. 3.18 according to the relationship of energy separation and mean oxidation state,<sup>13,38,39</sup> which implies that as-prepared  $\text{MnO}_x$  possesses a minor portion of Mn (IV) since the mean oxidation state of as-prepared  $\text{MnO}_x$  is slightly higher than  $\text{Mn}_3\text{O}_4$  (mean oxidation state = 2.67). XPS is a surface-sensitive measurement, which indicates the mean manganese oxidation state obtained from XPS results is in the proximity to the sample surface. From Mn 2p spectrum of as-prepared  $\text{MnO}_x$  (not shown here), the peaks of Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> are located at 641.91 and 653.31 eV, respectively. From the Lorentz fitting of O 1s spectrum of as-prepared  $\text{MnO}_x$  (Fig. 3b), the peak position at 529.8, 531.3, and 532.5 eV are attributed to Mn-O-Mn (for anhydrous oxide), Mn-OH (hydroxide), and H-O-H bonds (crystalline water), respectively.<sup>13,37-39</sup> The Mn-OH bonds contribute 15% (Table 2), which suggests the as-prepared  $\text{MnO}_x$  exhibit better capacitive performance since the hydrous property facilitates ionic exchange.<sup>37,39</sup>

According to literature,<sup>40</sup> the Raman active bands of hausmannite- $\text{Mn}_3\text{O}_4$  are observed at 289, 315, 370, 477, and 660  $\text{cm}^{-1}$ . Bands at 310-320 and 360-370  $\text{cm}^{-1}$  are the bending mode of  $\text{Mn}_3\text{O}_4$ , while 650-660  $\text{cm}^{-1}$  is the Mn-O breathing vibration of  $\text{Mn}^{2+}$  in tetrahedral coordination.<sup>23,31</sup> In general, the Raman active bands for  $\text{MnO}_2$  are at 500-510, 575-585, and 625-650  $\text{cm}^{-1}$ , which represent Mn-O stretching vibration of  $\text{MnO}_6$  octahedra, Mn-O stretching vibration of the basal plane of  $\text{MnO}_6$  sheets, and the symmetric stretching vibration of Mn-O of the  $\text{MnO}_6$  group, respectively.<sup>23,32</sup> The Raman spectrum of as-prepared  $\text{MnO}_x$  is shown in Fig. 4. The intense peak at ca. 658  $\text{cm}^{-1}$  can be observed, which is the most notable band of  $\text{Mn}_3\text{O}_4$ .<sup>23,31</sup> However, a shoulder around 575  $\text{cm}^{-1}$  can also be found, which provides further evidence that as-prepared  $\text{MnO}_x$  might not be pure hausmannite- $\text{Mn}_3\text{O}_4$ , since a minor portion of  $\text{MnO}_2$  can be found in the spectrum. Moreover, the two peaks at 310-320 and 360-370  $\text{cm}^{-1}$  are not able to be resolved from the background noise. The presence of (a minor portion)  $\text{MnO}_2$  in the as-prepared  $\text{MnO}_x$  might reduce crystallinity of hausmannite- $\text{Mn}_3\text{O}_4$ , which might result in the absence of the bending mode of  $\text{Mn}_3\text{O}_4$ . The results from both Raman and XPS analyses of as-prepared  $\text{MnO}_x$  strongly indicate a minor portion of Mn (IV) is present. According to the above analyses, the as-prepared  $\text{MnO}_x$  can be considered to be hausmannite- $\text{Mn}_3\text{O}_4$  with a minor portion of Mn (IV).

#### Electrochemical activation process of $\text{MnO}_x$

CVs measured at a sweep rate of 25  $\text{mV s}^{-1}$  between 0 and 1.2 V (vs. Ag/AgCl) in 0.5 M  $\text{Na}_2\text{SO}_4$  for controlled cycles are shown in Fig. 5. For the first few cycles, the anodic peak around 1.05 V on the positive sweep can be considered to be the oxidation of  $\text{Mn}_3\text{O}_4$  to higher oxidation state. This anodic peak gradually decreased during cycling, and the cathodic peak around 0.9 V on the negative sweep gradually decreased at the same time. On the other hand, the current responses of the redox peak at ca. 0.4-0.5 V gradually increased during cycling. This peak is related to partial oxidation/reduction between Mn (III) and Mn (IV) according to the Pourbaix diagram.<sup>41</sup> The rectangular CV profile at 500<sup>th</sup> cycle indicates that ideal

Table 1. Comparisons of diffraction peaks and d-spacing calculated from the SAED pattern of as-prepared and activated  $\text{MnO}_x$  with standards (hausmannite- $\text{Mn}_3\text{O}_4$ , JCPDS CARD 24-0734 and birnessite- $\text{MnO}_2$ , JCPDS CARD 18-0802) from database.

|                            | 2 $\theta$ from XRD pattern (degree) | 2 $\theta$ from database (degree) | d-spacing calculated from SAED pattern (nm) | d-spacing from $\text{Mn}_3\text{O}_4$ database (nm) |                          | d-spacing calculated from SAED pattern (nm) | d-spacing from $\text{MnO}_2$ database (nm) |  |
|----------------------------|--------------------------------------|-----------------------------------|---|--|--------------------------|---|---|--|
| as-prepared $\text{MnO}_x$ | 18.0                                 | 18.0                              | 0.499                                       | 0.492  | activated $\text{MnO}_x$ | 0.497                                       |   |  |
|                            | 28.9                                 | 28.9                              | 0.313                                       | 0.309  |                          | 0.308                                       |   |  |
|                            |                                      | 31.0                              |   | 0.288  |                          |   |   |  |
|                            | 32.4                                 | 32.3                              | 0.281                                       | 0.277  |                          | 0.283                                       |   |  |
|                            | 36.1                                 | 36.1                              | 0.253                                       | 0.249  |                          | 0.253                                       | 0.244                                       |  |
|                            | 44.3                                 | 44.4                              | 0.208                                       | 0.204  |                          | 0.242                                       |   |  |
|                            |                                      | 49.8                              |   | 0.182  |                          | 0.210                                       | 0.212                                       |  |
|                            |                                      | 50.7                              |   | 0.183  |                          | 0.182                                       |   |  |
|                            |                                      | 58.4                              | 58.5  | 0.157  |                          | 0.180                                       | 0.158                                       |  |
|                            |                                      | 59.8                              | 59.8  |  |                          | 0.154                                       |   |  |
|                            | 64.7                                 | 64.7                              | 0.146                                       | 0.144  | 0.146                    |   |   |  |

Table 2. Peak position and area percentage of O 1s spectrum of as-prepared and activated  $\text{MnO}_x$ .

| O 1s    |                | Position (eV) |    | Percentage (%) |       |    |
|---------|----------------|---------------|----|----------------|-------|----|
| Mn-O-Mn | as-prepared    | 529.8         | 67 | activated      | 529.9 | 44 |
| Mn-OH   | $\text{MnO}_x$ | 531.3         | 15 | $\text{MnO}_x$ | 531.2 | 37 |
| H-O-H   |                | 532.5         | 18 |                | 532.5 | 19 |

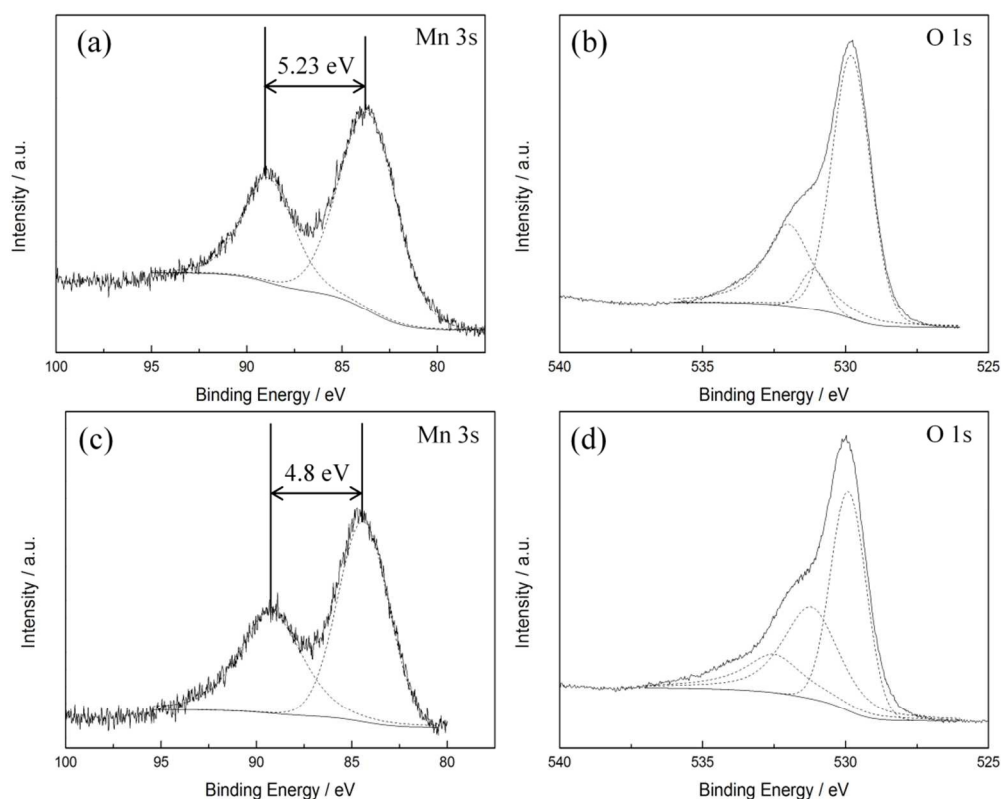


Figure 3. XPS (a, c) Mn 3s, (b, d) O 1s spectra of (a, b) as-prepared and (c, d) activated  $\text{MnO}_x$ .

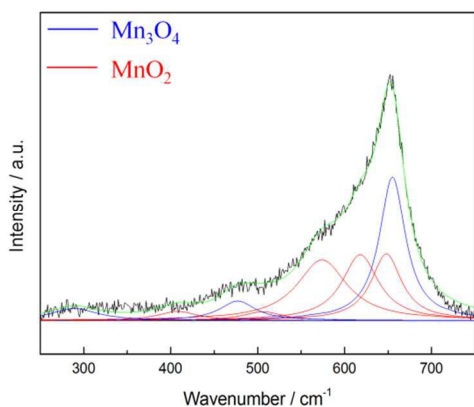


Figure 4. Lorentz fitting of *ex situ* Raman spectrum of as-prepared  $\text{MnO}_x$ . Green line = envelope of total of the fitted peaks.

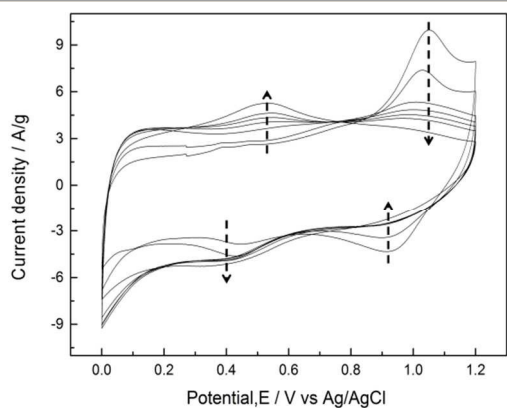


Figure 5. CVs measured at a sweep rate of  $25 \text{ mV s}^{-1}$  between 0 and 1.2 V (vs. Ag/AgCl) in 0.5 M  $\text{Na}_2\text{SO}_4$  for 5, 10, 50, 100, 150, 200, and 500 cycles.

capacitive performances of  $\text{MnO}_x$  can be obtained by potential cycling which has been proposed as an electrochemical activation method.<sup>21</sup> Note that the poor capacitive performance at first few cycles for pure  $\text{Mn}_3\text{O}_4$  (i.e., less than  $20 \text{ F g}^{-1}$ ) has been reported.<sup>22,24</sup> However, the specific capacitance at 5<sup>th</sup> cycle reaches ca.  $130 \text{ F g}^{-1}$  in this work, which confirms that the as-prepared  $\text{MnO}_x$  is composed of a minor portion of  $\text{MnO}_2$  and is not pure  $\text{Mn}_3\text{O}_4$ .

For the 1<sup>st</sup> *in situ* Raman cycle (Fig. 6a), a strong peak located at  $658 \text{ cm}^{-1}$  is visible from PS 0.1 V, PS 0.3 V, and PS 0.5 V. This peak is the characteristics of  $\text{Mn}_3\text{O}_4$  as described above. From PS 0.9 V to NS -0.1 V, this peak slightly shifts to a lower wavenumber (from  $658$  to  $650 \text{ cm}^{-1}$ ) with further applying potential. Besides, the intensity of this peak for the 12 spectra remains in the same level. On the other hand, a descending shoulder from ca.  $650$  to  $550 \text{ cm}^{-1}$  is found from PS 0.1 V. The peak at  $575 \text{ cm}^{-1}$  was gradually formed during the polarisations, and this peak became significant from PS 0.7 V to NS -0.1 V. Since the peak intensity of  $575 \text{ cm}^{-1}$  reached the same level of the peak at ca.  $658 \text{ cm}^{-1}$ , a new  $\text{MnO}_x$  species (i.e.,  $\text{MnO}_2$ ) is believed to be formed. The spectra recorded at the 2<sup>nd</sup> cycle (Fig. 6b) all remain the similar pattern, which indicate that the newly formed  $\text{MnO}_2$  remains stable in the cycled potential window. Therefore the mean Mn oxidation state during further cycling after activation can only be

accessed via other techniques such as X-ray photoelectron spectroscopy or X-ray absorption microscopy.

Lorentz fitting of Raman spectra is used in order to gain a further understanding of this phenomenon. The peaks at  $658$ ,  $477$ , and  $289 \text{ cm}^{-1}$  are related to hausmannite- $\text{Mn}_3\text{O}_4$ ,<sup>40</sup> while the peaks at  $648$ ,  $618$ ,  $575$ ,  $506$ , and  $408 \text{ cm}^{-1}$  are attributed to birnessite- $\text{MnO}_2$ .<sup>33</sup> Note that all the peak positions are fixed except for the peak at ca.  $289 \text{ cm}^{-1}$  (allows from  $283$  to  $289 \text{ cm}^{-1}$ ). The  $\text{Mn}_3\text{O}_4$  peak intensity at  $658 \text{ cm}^{-1}$  gradually decreased, while peaks related to birnessite- $\text{MnO}_2$  (marked as red line in Fig. 7) gradually enhanced during polarisations. The  $\text{Mn}_3\text{O}_4$  peak at  $658 \text{ cm}^{-1}$  dominates for the 1<sup>st</sup> cycle PS 0.1 V and the 1<sup>st</sup> cycle PS 0.5 V. However, the peak at  $648 \text{ cm}^{-1}$  related to birnessite- $\text{MnO}_2$  became stronger than the  $\text{Mn}_3\text{O}_4$  peak at  $658 \text{ cm}^{-1}$  with the positive and negative shifts in electrode potentials. As a result, this peak shifted from  $658$  (1<sup>st</sup> cycle PS 0.9 V) to  $650 \text{ cm}^{-1}$  (1<sup>st</sup> cycle NS -0.1 V) and further remained the same position. The peak intensity ratio of  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$  ( $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4}$ ) is proposed to be an indicator to quantify the degree of activation from  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}_2$  although the different  $\text{MnO}_x$  species show different Raman sensitivities. Here,  $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4}$  is calculated on the basis of the peak intensity of  $575$  and  $658 \text{ cm}^{-1}$  from the fitting results since these two peaks are the best representatives (the strongest signals) for  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$ , respectively.  $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4}$  for as-prepared  $\text{MnO}_x$  is 0.42 (Table S2), and the value increases gradually during the electrochemical polarisations.  $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4}$  is 3.94 for the 2<sup>nd</sup> cycle PS 0.1 V, which is ca. 8 times higher than as-prepared  $\text{MnO}_x$  (Table 3). The mean manganese oxidation state of activated  $\text{MnO}_x$  is ca. 3.94 based on the energy separation (4.85 eV) of Mn 3s core level spectrum (Fig. 3c). Comparing with the mean manganese oxidation state of as-prepared  $\text{MnO}_x$  (3.18), the results support the activation from  $\text{Mn}_3\text{O}_4$  (i.e., Mn (II) and Mn (III)) to  $\text{MnO}_2$  (Mn (IV)) during the electrochemical activation.

According to the fitting results, residual  $\text{Mn}_3\text{O}_4$  can be still observed even at the 2<sup>nd</sup> *in situ* Raman cycle (Fig. 7d). Note that the formed  $\text{MnO}_2$  is stable in the cycled potential window for the 2<sup>nd</sup> *in situ* Raman cycle (Fig. 6b). It therefore be concluded that not all the  $\text{Mn}_3\text{O}_4$  is converted to  $\text{MnO}_2$  in the above electrochemical treatment. Due to the residual  $\text{Mn}_3\text{O}_4$ , the mean manganese oxidation state for the activated  $\text{MnO}_x$  is not exactly equal to 4.0. Hence, it can be concluded that the major portion of hausmannite- $\text{Mn}_3\text{O}_4$  can be activated to birnessite- $\text{MnO}_2$  by the electrochemical treatment. Besides, the residual  $\text{Mn}_3\text{O}_4$  in electrochemically activated birnessite- $\text{MnO}_2$  results in structure disorder of layered birnessite- $\text{MnO}_2$ , which reasonably explains why the oxide derived from  $\text{Mn}_3\text{O}_4$  showed higher cycling stability because of the coexistence of  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$ .<sup>21</sup> *Ex situ* Raman spectra were recorded for all CV-cycled  $\text{MnO}_x$ . From Lorentz fitting results, the correlation between specific capacitance of  $\text{MnO}_x$  and CV cycle number is shown in Fig. 8. Note that the current responses related to the activation from  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}_2$  (the anodic peak around 1.05 V on the positive sweep) are evident in the first few cycles, which decreases gradually during the activation process. The ideal pseudocapacitance of  $\text{MnO}_2$  mainly contributes from the potential window between 0.2 and 0.8 V.<sup>19</sup> The current responses related to the oxidation of  $\text{Mn}_3\text{O}_4$  cannot be considered pseudocapacitance. Therefore, the calculation in Fig. 8 is based on the baseline of 500<sup>th</sup> cycle (stable current responses) between 0.8 and 1.2 V. In general,  $\text{MnO}_2$  is electrochemically active and reversible for supercapacitor applications<sup>10</sup> comparing with  $\text{Mn}_3\text{O}_4$ , which is known as a



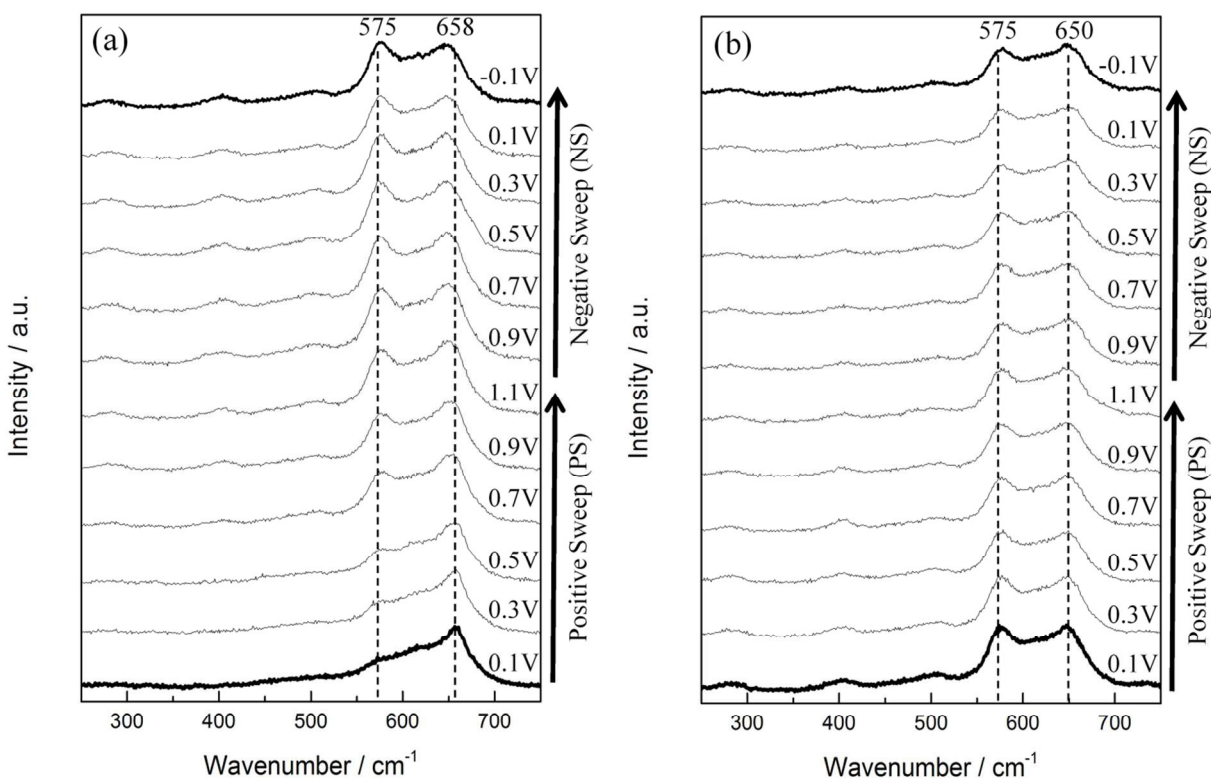


Figure 6. *In situ* Raman spectra series of (a) the 1<sup>st</sup> and (b) the 2<sup>nd</sup> cycle. Each cycle started from 0.1 V (PS 0.1V) and ended at -0.1 V (NS -0.1V).

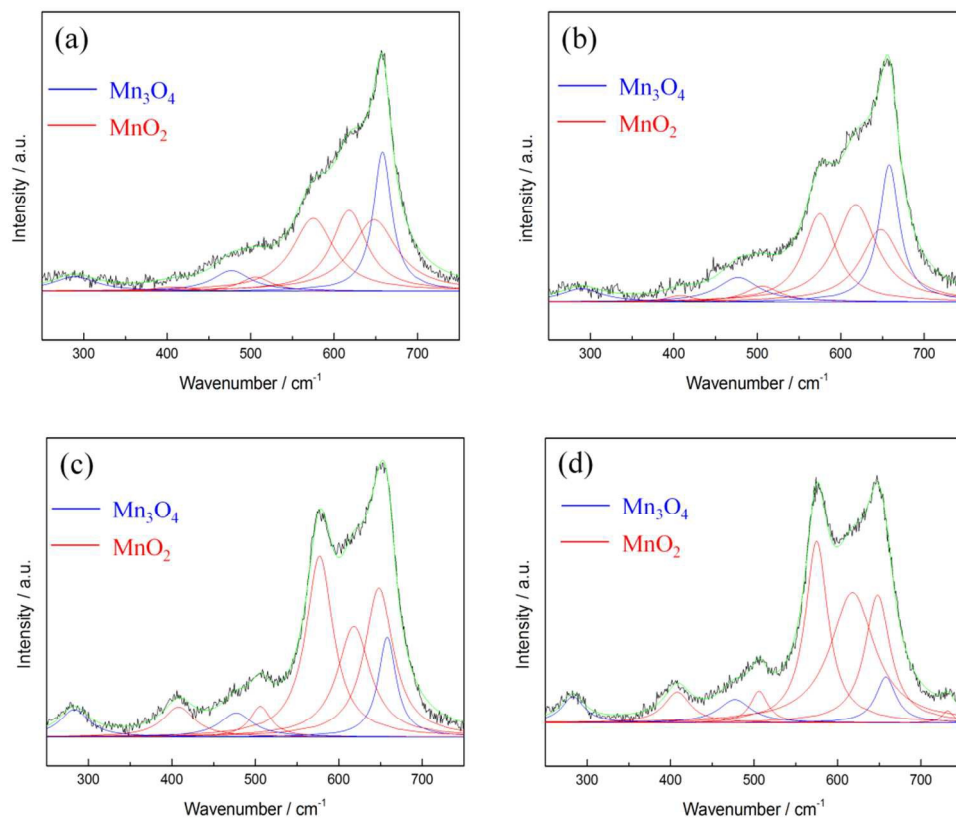


Figure 7. Lorentz fitting of *in situ* Raman spectra (a) 1<sup>st</sup> cycle PS 0.1V, (b) 1<sup>st</sup> cycle PS 0.5V, (c) 1<sup>st</sup> cycle PS 0.9V, and (d) 2<sup>nd</sup> cycle PS 0.1V. Green line = envelope of total of the fitted peaks.

Table 3. Peak position ( $\text{cm}^{-1}$ ) and Full Width at Half Maximum (FWHM,  $\text{cm}^{-1}$  in parenthesis) of the  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  peaks by Lorentz fitting.

|                       | $\text{Mn}_3\text{O}_4$ | $\text{MnO}_2$ | $\text{MnO}_2$ | $\text{MnO}_2$ | $\text{MnO}_2$ | $\text{Mn}_3\text{O}_4$ | $\text{MnO}_2$ | $\text{Mn}_3\text{O}_4$ | $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4}$ |
|-----------------------|-------------------------|----------------|----------------|----------------|----------------|-------------------------|----------------|-------------------------|--|
| 1 <sup>st</sup> cycle | 658                     | 648            | 618            | 575            | 506            | 477                     | 408            | 289                     | 0.52   |
| PS 0.1V               | (27)                    | (66)           | (51)           | (61)           | (45)           | (55)                    | (55)           | (65)                    |  |
| 1 <sup>st</sup> cycle | 658                     | 648            | 618            | 575            | 506            | 477                     | 408            | 284                     | 0.65   |
| PS 0.5V               | (29)                    | (58)           | (60)           | (47)           | (50)           | (60)                    | (40)           | (61)                    |  |
| 1 <sup>st</sup> cycle | 658                     | 648            | 618            | 575            | 506            | 477                     | 408            | 283                     | 1.81   |
| PS 0.9V               | (26)                    | (42)           | (48)           | (40)           | (31)           | (48)                    | (46)           | (43)                    |  |
| 2 <sup>nd</sup> cycle | 658                     | 648            | 618            | 575            | 506            | 477                     | 408            | 283                     | 3.94   |
| PS 0.1V               | (29)                    | (37)           | (64)           | (33)           | (26)           | (48)                    | (38)           | (33)                    |  |

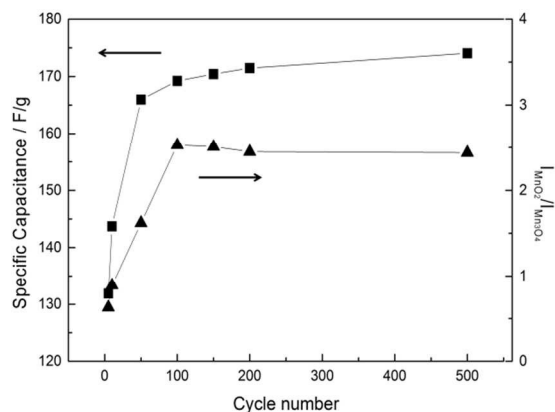


Figure 8. Cycle number dependence of specific capacitance calculated by CV at  $25 \text{ mV s}^{-1}$  and intensity ratio ( $I_{\text{MnO}_2}$  of  $575 \text{ cm}^{-1}/I_{\text{Mn}_3\text{O}_4}$  of  $658 \text{ cm}^{-1}$ ) of  $\text{MnO}_x$ .

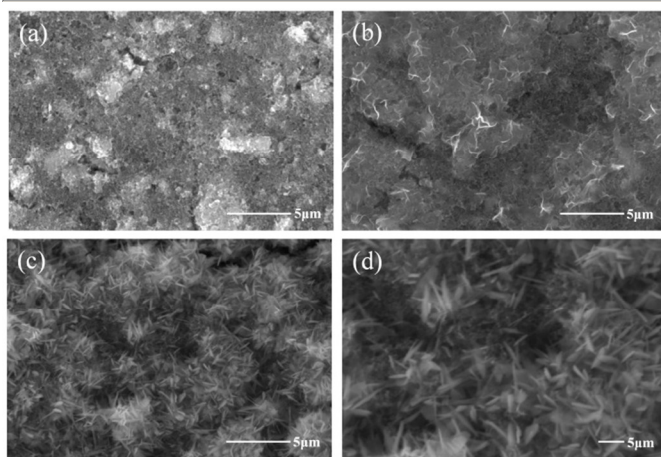


Figure 9. SEM images of (a) as-prepared  $\text{MnO}_x$  and after (b) 100 (c,d) after 500 CV cycles in  $0.5 \text{ M Na}_2\text{SO}_4$ .

relatively electrochemical irreversible material among  $\text{MnO}_x$  species. The specific capacitance of  $\text{MnO}_x$  rapidly increased within the initial 50 cycles, which suggests that the activation from  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}_2$  is relatively fast. With further cycling, the specific capacitance of  $\text{MnO}_x$  gradually increased and reached the stable level (ca.  $170 \text{ F g}^{-1}$ ) from the 150<sup>th</sup> to the 500<sup>th</sup> cycle. Based on the Lorentz fitting of *ex situ* Raman spectra (Fig. S2), the rapid increase of  $\text{MnO}_2$  content ( $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4} = 0.63$  and  $2.53$  for 5<sup>th</sup> and 100<sup>th</sup> cycle, respectively) shows the same trend as capacitance increase. With further cycling to 500<sup>th</sup> cycle,  $I_{\text{MnO}_2}/I_{\text{Mn}_3\text{O}_4}$  remained the

same level (i.e., 2.45). It should be noted that this ratio is lower than that from *in situ* measurements (3.94). Accordingly, the activation from hausmannite- $\text{Mn}_3\text{O}_4$  to birnessite- $\text{MnO}_2$  can be verified by the *in situ* and *ex situ* Raman experiments. The stable electrochemically activated birnessite- $\text{MnO}_2$  can be formed and displays promising pseudocapacitance in  $0.5 \text{ M Na}_2\text{SO}_4$ .

Fig. 9 shows the surface morphology change  $\text{MnO}_x$  during electrochemical activation. A compact surface morphology of as-prepared  $\text{MnO}_x$  can be observed in Fig. 9a, while it gradually changes into a porous surface after electrochemical activation (Fig. 9b-d). It has been proposed that the porous surface layer is the re-deposition of dissolved  $\text{Mn(II)}$  (from hausmannite- $\text{Mn}_3\text{O}_4$  crystalline structure) onto the electrode surface as  $\text{MnO}_2$  during the activation process via CV cycling.<sup>25</sup> The proposed mechanism is reasonable since  $\text{MnO}_2$  can be successfully formed from  $\text{Mn(II)}$  precursor by potentiodynamic method.<sup>12</sup> Besides, the insignificant electrochemical activation of  $\text{Mn}_2\text{O}_3$  comparing with  $\text{Mn}_3\text{O}_4$  has been found.<sup>25</sup> Therefore, dissolution of  $\text{Mn(II)}$  from  $\text{MnO}_x$  crystalline is believed to be the key for the electrochemical activation process. In fact, from the investigation of amorphous  $\text{MnO}_2$  by electrochemical quartz crystal microbalance (EQCM), the porous surface of  $\text{MnO}_x$  (predominate  $\text{MnO}_2$ ) is not only from the re-deposition of dissolved  $\text{Mn(II)}$  during electrochemical activation process but also from the re-deposition (at ca.  $0.8\text{-}0.2 \text{ V}$ ) of dissolved  $\text{Mn(IV)}$  (at ca.  $0.8\text{-}1.0 \text{ V}$ ) during CV cycling.<sup>19</sup> The normalised area of C 1s and Mn 3s XPS spectra of as-prepared and activated  $\text{MnO}_x$  are listed in Table S3. In comparison with as-prepared  $\text{MnO}_x$ , the normalised area ratio (C1s/Mn3s) of activated  $\text{MnO}_x$  reduced from ca. 2.59 to 1.04, indicating the re-deposition of  $\text{MnO}_2$  onto the electrode surface suppressing the intensity of carbon black and polymeric binder.<sup>25</sup> Note that the intensity (counts/second) of XPS spectra strongly depends on the distance between samples and X-ray beam source. Therefore, normalised area (by atomic sensitivity factor) instead of absolute intensity is used in this work. Moreover, from SEM images (Fig. 9d), the porous nanostructure surface forms at the outer surface, while this structure cannot be found in some deeper regions. This suggests the electrochemical activation starts from outermost layer of  $\text{Mn}_3\text{O}_4$  surface and then gradually into the bulk. This finding is consistent with literature, which reported the amorphous and hydrous  $\text{MnO}_2$  is formed in the outer electrode layers and proceeds to grow at the expense of the remaining bulk crystalline  $\text{Mn}_3\text{O}_4$ .<sup>42</sup>



### Electrochemically activated MnO<sub>x</sub> and its charge-discharge mechanism

The activated MnO<sub>x</sub> was characterised by PXRD as amorphous MnO<sub>2</sub> (Fig. S3). The SAED pattern of activated MnO<sub>x</sub> (Fig. 2d) suggests that the electrochemically activated MnO<sub>x</sub> within the electrode composite possess poor crystallised structure since the diffraction patterns do not have well defined rings.

Interestingly, with further analysis, both birnessite-MnO<sub>2</sub> and hausmannite-Mn<sub>3</sub>O<sub>4</sub> crystallites can be found in the activated MnO<sub>x</sub> (Table 1) although no reflections can be observed from diffraction pattern of activated MnO<sub>x</sub>. The d-spacing of 0.242 and 0.210 nm are corresponding to birnessite-MnO<sub>2</sub>. Apart from these two d-spacing found in SAED pattern, others are all related to Mn<sub>3</sub>O<sub>4</sub> residual in the activated MnO<sub>x</sub>. From the TEM images of activated MnO<sub>x</sub> (Fig. 2e), the particle-like MnO<sub>x</sub> structure can be still observed. Compare to as-prepared MnO<sub>x</sub>, the particles and lattices of activated MnO<sub>x</sub> are not well defined. As a result, the activated MnO<sub>x</sub> is believed to have disordered layered birnessite structure; however, there is insufficient long-range order to allow for a PXRD pattern to be observed. Therefore, the structure of the electrochemically activated MnO<sub>x</sub> is determined to be composite material consisting of amorphous MnO<sub>2</sub> (with localised birnessite structure) and a minor portion of residual of hausmannite-Mn<sub>3</sub>O<sub>4</sub>. Amorphous manganese oxide has been considered to be beneficial for supercapacitors since it provides large interlayer distance and surface area-to-volume ratio. The increase contact between the electrolyte and the electrode material improves the utilisation ratio of the material.<sup>43</sup> Besides, the significant increase of Mn-OH (hydroxide) bond in activated MnO<sub>x</sub> (Fig. 3d and Table 2) indicates that the MnO<sub>x</sub> became more hydrous after electrochemical activation. As discussed above, hydrous property of MnO<sub>x</sub> facilitates ionic exchange and exhibits better capacitive performance.<sup>37,39</sup>

The structure transformation from hexagonal to monoclinic due to cation (Na<sup>+</sup>) intercalation into birnessite-MnO<sub>2</sub> has been reported,<sup>44</sup> as well as the subtle change of Raman spectra of birnessite-MnO<sub>2</sub> with and without cation (Li<sup>+</sup> and Na<sup>+</sup>) intercalated in MnO<sub>2</sub> bilayers.<sup>32</sup> The intercalation of alkali-ion into birnessite-MnO<sub>2</sub> bilayers causes local lattice distortion, which results in shorter Mn-O chemical bonds (decrease of the interlayer spacing) and partial reduction of Mn<sup>4+</sup> ions. As a result, the Mn-O symmetric stretching mode moves toward low wavenumber side upon alkali-ion intercalation.<sup>32</sup> However, this peak shift phenomenon due to cation intercalation into layers of birnessite-MnO<sub>2</sub> was not observed by *in situ* Raman during activation process in this work. Moreover, the peak positions of MnO<sub>2</sub> correspond to birnessite-MnO<sub>2</sub> rather than Na-birnessite-MnO<sub>2</sub> from literature.<sup>32,33</sup> Moreover, the peak around 732 cm<sup>-1</sup>, identified as a vibrational mode for non-cation intercalated birnessite-MnO<sub>2</sub>, can be observed by the Raman spectrum of activated MnO<sub>x</sub> (Fig. 7d). This indicates that electrochemically activated birnessite structure might not possess a well-defined layer structure (i.e., structure disordering) to allow cation (Na<sup>+</sup>) intercalation into bilayers.

The XPS Na 1s spectrum of as-prepared MnO<sub>x</sub>, activated MnO<sub>x</sub> and a sodium intercalated MnO<sub>2</sub> sample (Na<sub>0.33</sub>MnO<sub>2</sub>) are shown in Fig. S4. The Na 1s peak was present at 1072.2 eV (FWHM=1.85) for activated MnO<sub>x</sub> and shows ca. 1 eV shift in comparison to Na<sub>0.33</sub>MnO<sub>2</sub> at 1071.2 eV (FWHM=1.77). The binding energy at 1072–1073 eV is related to the Na–F bonding, which is attributed to the Na<sup>+</sup> (from Na<sub>2</sub>SO<sub>4</sub> electrolyte) bonding with co-polymeric binder at F sites.<sup>45</sup> Although the Na/Mn ratio of activated MnO<sub>x</sub> (1.03) is higher

than Na<sub>0.33</sub>MnO<sub>2</sub> (Na/Mn=0.52), the Na element contributes from the Na–F bonding rather than incorporation into the MnO<sub>x</sub> structure after electrochemical measurements.

Based upon the *in situ* Raman and Na 1s XPS analyses, cations are believed to reach the outer surface active sites of electrochemically activated birnessite-MnO<sub>2</sub> and the capacitive behaviour is attributable to the redox reaction between Mn (III) and Mn (IV). The relatively high specific surface area of as-prepared MnO<sub>x</sub> (241 m<sup>2</sup> g<sup>-1</sup>) can provide abundant outer surface active sites. As a result, high specific capacitance of birnessite-MnO<sub>2</sub> can be obtained (i.e., the specific capacitance measured at 500<sup>th</sup> is 174 F g<sup>-1</sup>) by potential cycling, which can be compared with values of similar materials in the literature (Table S4).<sup>22-25</sup> The capacitance normalised to specific surface area (C<sub>SA</sub>) is ca. 72.3 μF cm<sup>-2</sup>, which is higher than the double layer capacitance (ca. 10-20 μF cm<sup>-2</sup>) for high surface area (over 1000 m<sup>2</sup> g<sup>-1</sup>) carbon material.<sup>1</sup> The real C<sub>SA</sub> of electrochemically activated birnessite-MnO<sub>2</sub> should be even higher since the calculation is based on the specific surface area of as-prepared MnO<sub>x</sub> and the material might lose some part of active surface area during electrode preparation. Based on the calculated high C<sub>SA</sub>, the charge storage of electrochemically activated MnO<sub>x</sub> is attributed to the redox reaction between Mn (III) and Mn (IV) (pseudocapacitance).

The one-pot synthesised as-prepared MnO<sub>x</sub> is characterised as hausmannite-Mn<sub>3</sub>O<sub>4</sub> with a minor portion of MnO<sub>2</sub>. The electrochemically activated MnO<sub>x</sub> is characterised as a composite material consisting of localised birnessite structure MnO<sub>2</sub> and a minor portion of hausmannite-Mn<sub>3</sub>O<sub>4</sub>. The improved capacitive performance of activated MnO<sub>x</sub> is attributed to the synergistic effect of poorly crystallised MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> in the composite material, and this work describes routes of generating composite materials that possess greater electrochemical performance.

### Conclusions

Electrochemically activated MnO<sub>x</sub>, from one-pot synthesised hausmannite-Mn<sub>3</sub>O<sub>4</sub>, exhibits a capacitive performance of 174 F g<sup>-1</sup> (at 25 mV s<sup>-1</sup>) and 1.2 V potential window (0-1.2 V vs. Ag/AgCl), which is superior to reported values of comparable materials. Activation from primarily hausmannite-Mn<sub>3</sub>O<sub>4</sub> to predominantly localised birnessite-MnO<sub>2</sub> by potential cycling is verified by both *in situ* and *ex situ* Raman microscopy, XPS and TEM analysis. Due to the structural disordering of electrochemically activated birnessite-MnO<sub>2</sub> and residual Mn<sub>3</sub>O<sub>4</sub>, the charge storage is attributable to the redox reaction between Mn (III) and Mn (IV) at outer surface active sites, rather than cations and/or protons intercalation into layer structures. The improved capacitive performance relates to the synergistic effect of well-dispersed MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> nanoscale domains present within the activated material. Overall we show that the integrated nanoscale structuring of different phases of manganese oxides offers superior properties compared to bulk parent materials, and as such offers an avenue of future supercapacitor materials development.

### Acknowledgements

This research is funded by the National Science Council and Ministry of Science Technology of Taiwan under contract no. 101-2221-E-007-112-MY3, 102-2221-E-007-120-MY3, 103-2911-I-007-515, 103-3113-E-006-009, and also supported by the boost program of the Lower Carbon Energy Research centre

in NTHU. The financial support of this work, by the Ministry of Science and Technology, Taiwan and The Royal Society, UK, is gratefully acknowledged, as well as the Science without Borders Program, Ministério da Educação, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) Brazil; and the Engineering and Physical Sciences Research Council (EPSRC) under grant EP/H000925.

We would like to thank Ming-Guan Chen (Department of Chemical Engineering, National Tsing Hua University, Taiwan). From the University of Liverpool UK, we acknowledge T. Whittles & M. Althobaiti (Stephenson Institute for Renewable Energy) for XPS measurements and Ming Liu (Department of Chemistry) for BET and Tobias Heil (Nano Investigation Centre at Liverpool) for TEM analyses. Part of the work was carried out within the cooperative framework set-up between National Tsing Hua University, Taiwan and University of Liverpool, UK.

## Notes and references

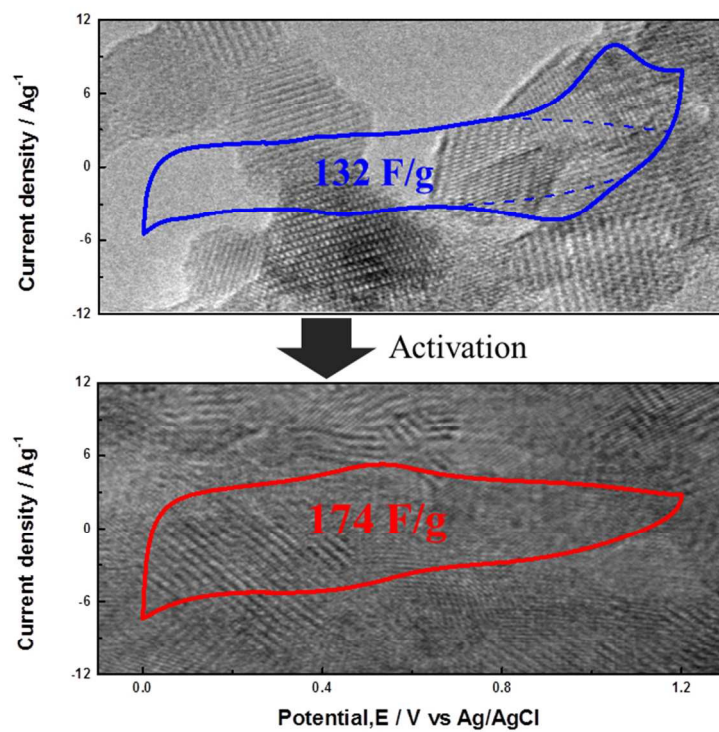
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† Electronic Supplementary Information (ESI) available: Literature comparison, potential of quasi reference electrode measurement, Lorentz fitting of *ex situ* Raman spectra, XPS data and PXRD pattern of MnO<sub>x</sub> after activation. See DOI: 10.1039/b000000x/

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