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### Porous nano-MnO<sub>2</sub>: large scale synthesis via a facile quick-redox procedure and application in a supercapacitor

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A new type of porous nano- $MnO_2$  for supercapacitors has been synthesized for the first time by a facile sonochemistry route from a quick-redox reaction between  $KMnO_4$  and D-glucose. The crystal structure, morphology and chemical composition of the MnO<sub>2</sub> product were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). The results show that the porous MnO<sub>2</sub> nanoparticles in the range 20-50 nm are interestingly composed of nanorods with diameters of about 2 nm and lengths of 4-8 nm. A possible growth mechanism of this nanostructure has been identified based on the experimental results. The electrochemical properties of the porous  $MnO_2$  were investigated in a symmetric capacitor cell using both 1 M Na<sub>2</sub>SO<sub>4</sub> and 9 M KOH aqueous solutions. The results indicate that the MnO<sub>2</sub> electrodes have a good capacitive performance in both cases.

### 1.

Manganese dioxide (MnO<sub>2</sub>), as one of important energy storage materials, has attracted a great deal of attention in many technological applications, such as supercapacitors,<sup>1</sup> zinc manganese batteries,<sup>2</sup> lithium manganese batteries<sup>3</sup> and fuel cells.<sup>4</sup> The advantages of this metal oxide are its low cost, abundance and good environmental compatibility. Recently, increasing demand for light-weight energy storage devices with high energies and power densities has promoted the synthesis of nanoscale MnO<sub>2</sub> (at least one dimension less than 100 nm).<sup>5</sup> Actually, nano-MnO<sub>2</sub> exhibits an electrochemical performance superior to its bulk counterpart because of its higher specific surface area.<sup>6,7</sup> A variety of synthesis techniques have therefore been exploited to obtain nano-MnO<sub>2</sub> with dispersible shapes, including hydrothermal,8 electrodeposition,9 a sol-gel method,10 template synthesis,<sup>11</sup> thermal decomposition,<sup>12</sup> etc. However, complicated operations, time/energy-consuming and expensive reagents always seem to be obstacles for the commercialization of nano-MnO<sub>2</sub>. Hence, the development of quick, simple and

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mild pathways for the synthesis of nano-MnO<sub>2</sub> on a large scale remains a challenge to a large extent.

In past decades, sonochemistry has developed into a powerful technique for generating nanostructured materials with unusual properties.<sup>13,14</sup> The essence of the sonochemical process is the phenomenon of cavitation: the creation, growth and collapse of bubbles that form in liquids. The extremely high temperatures (>5000 K), pressures (>20 MP) and cooling rates  $(>10^7 \text{ K s}^{-1})$ generated during acoustic cavitation within the collapsing bubble lead to many unique properties in irradiated solutions.<sup>15,16</sup> We have previously prepared MnO<sub>2</sub> microspheres based on nanowires by a sonication-assisted hydrothermal synthesis process,<sup>17</sup> while this technology has also been used in the preparation other oxide nanostructures elsewhere.<sup>18</sup>

In the present investigation, we report the large scale synthesis of novel porous MnO2 nanoparticles via a quick and facile sonochemical procedure. In this process, nano-MnO<sub>2</sub> is produced by an inexpensive D-glucose-permanganate redox reaction in the presence of polyethylene glycol (PEG) at ambient pressure. To our knowledge, this is the first report on MnO<sub>2</sub> nanostructures from a D-glucose-permanganate redox reaction, although D-glucose was used previously for the reduction of KMnO<sub>4</sub> to MnO<sub>2</sub> used in chemical analysis,<sup>19</sup> and  $MnO_x$  microstructures have previously been reported from KMnO<sub>4</sub> and simple sugars.<sup>20</sup> The formation mechanism of the porous nano-MnO<sub>2</sub> is investigated. Furthermore, a potential electrode material for supercapacitors, as the electrochemical properties of the nano-MnO<sub>2</sub> are also investigated through a symmetric capacitor cell using both 1 M Na<sub>2</sub>SO<sub>4</sub> and 9 M KOH aqueous solutions.

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Fig. 1 Schematic of synthesis process of nano-MnO<sub>2</sub>.

### 2. Experimental section

In this study, as a green, safe and inexpensive raw material, D-glucose was used to prepare the  $MnO_2$  sample by a quick redox reaction with  $KMnO_4$ . The sonochemical synthesis process was carried out as follows: First, 1.50 g KMnO<sub>4</sub> and 0.05 g PEG-600 were dispersed in 100 ml de-ionized water in a 500 ml beaker. At the same time, 0.50 g D-glucose and 5 ml absolute alcohol were dispersed in 50 ml de-ionized water in another beaker. Then, the D-glucose aqueous solution was poured into the potassium permanganate aqueous solution rapidly. The above mixture was put into an ultrasonic water bath for 10 min in a high-intensity ultrasonic source (100 W and 40 kHz).

During the ultrasonic irradiation, the temperature of the reaction solution rose to around 60 °C. When the reaction was complete, the brown precipitation product was collected and washed thoroughly with de-ionized water and ethanol alternately, and finally dried at 60 °C in a vacuum. The synthesis route schematic is shown in Fig. 1. The conversion rate of this sonochemical synthesis was more than 99.8%.

The morphology and microstructure of the MnO<sub>2</sub> sample were investigated by scanning electron microscopy (SEM) (FEI Quanta 200 FEG, Holand) and TEM (FEI TECNAI G<sup>2</sup> 12, Holand). X-Ray diffraction (XRD) was preformed with a Rigaku D/max 2550 V X-ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The MnO<sub>2</sub> electrodes were prepared in the form of disks (110 ± 10 µm in thickness and 10 mm in diameter) by mixing 80 wt% MnO<sub>2</sub> (18.5 ± 1.5 mg per one) in ethanol with 10 wt% of acetylene black and 10 wt% of binder (polytetrafluoroethylene, PTFE). Electrochemical measurements were performed using symmetric capacitor cells (two-electrode mode), which were assembled with a pair of identical electrodes separated by a piece of microporous separator.



Fig. 2 The XRD pattern of the as-prepared  $MnO_2$ .

### 3. Results and discussion

# 3.1 Crystal structure, morphology and chemical composition of the MnO<sub>2</sub> product

To discover the crystallinity of the as-prepared MnO<sub>2</sub> product, XRD analysis was undertaken, and the resultant XRD pattern is shown in Fig. 2. The two characteristic peaks (311) and (400), at 37 and 66° (marked by  $\checkmark$ ) clearly presented, were confirmed to be MnO<sub>2</sub> (PDF# 42-1169). The weak peak signals observed in the XRD pattern suggest the sample is in a poorly crystalline state with only a short-range crystal form.<sup>21</sup> The low degree of crystallinity of the MnO<sub>2</sub> sample can be attributed to the rapid redox reaction of D-glucose–permanganate during the ultrasound irradiation. Since the reaction rate was high, causing a large number of nuclei to form in a very short period of time and leaving the crystals to grow inadequately, the obtained product was thus poorly crystalline.<sup>22</sup>

Furthermore, the diffraction peaks of the  $MnO_2$  were highlighted using the Peak Paint feature in the JADE software, and the corresponding peak areas were calculated (see Fig. 3). It can be seen that the two broadened diffraction peaks (45 803 and 14 880 area counts) are a strong indication of nanocrystals in the  $MnO_2$ ,<sup>23,24</sup> and the average particle size can be estimated by using the Scherer equation, expressed as follows:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where *D* is the average particle size (nm),  $\lambda$  is the wavelength of the X-rays (0.15406 nm),  $\theta$  is the angle at the peak maximum and  $\beta$  is the width of the peak at half height (peak FWHM). The calculated mean sizes according to the diffraction peaks of (311) and (400) were found to be 2.8 and 4.4 nm, respectively.

Fig. 4(a) shows a low-magnification SEM image of the as-prepared  $MnO_2$  product. It is demonstrated that the product has a three-dimensional (3-D) network structure consisted of a large quantity of  $MnO_2$  nanoparticles (almost 100% in yield). The SEM image with a high-magnification (Fig. 4(b)) reveals that these nanoparticles have a size of ~50 nm and analogous spherical shapes. The  $MnO_2$  nanoparticles synthesized in our case are a uniform dispersion, having no obvious secondary particle agglomerate larger than 500 nm, as reported in the literature,<sup>24–28</sup> indicating a fine nanostructure of  $MnO_2$  in the present study.



Fig. 3 Peak signals from the  $MnO_2$  XRD pattern.



Fig. 4 SEM images (a and b) and TEM images (c and d) of the as-prepared MnO<sub>2</sub>.

Table 1 Compared parameters of MnO<sub>2</sub> nanorods prepared by different methods

MnO <sub>2</sub> nanorods	Present study	Study A <sup>29</sup>	Study B <sup>30</sup>	Study C <sup>31</sup>	Study D <sup>32</sup>
Dimension size/nm	2 × 8	30 × 200	40 × 200	10 × 100	5 × 50
Synthesis route	Sonochemistry	Hydrothermal	Hydrothermal	Template	Microemulsion
Synthesis time	10 min	36 h	12 h	1 h	12 h
Temperature/°C	60	180	160	90	70

TEM observations confirm an exact diameter in the range 20-50 nm for the MnO<sub>2</sub> nanoparticles, as shown in Fig. 4(c). The high-magnification TEM image (Fig. 4(d)) shows that the MnO<sub>2</sub> nanoparticles are composed of many nanorods with diameters of about 2 nm and lengths of 4-8 nm. The MnO<sub>2</sub> nanorods produced in the present study are smaller than those obtained previously by hydrothermal,<sup>29,30</sup> template<sup>31</sup> and microemulsion<sup>32</sup> techniques, whose specific parameters are presented in Table 1. As can be seen from the table, the sonochemical method has more advantages concerning time/ energy savings and high efficiency than the other methods. A similar result was also proved recently in another sonochemistry-derived MnO<sub>2</sub> preparation from potassium permanganate and manganese acetate.<sup>7</sup> It is known that obtaining nanomaterials with a controlled size or shape under mild conditions and with safe precursors at lower

temperatures is an issue in material applications.<sup>16</sup> Consequently, due to the simple process, short reaction time, high yield and safe precursors, the synthesis procedure of nano- $MnO_2$  in our case may be applicable in practical applications.

Particle agglomerates can be classified into two types: soft agglomerate, in which the particles are held together by weak van der Waals forces, and hard agglomerate, in which the particles are chemically bonded together by strong bridges.<sup>33</sup> It is interesting to note that, as shown in Fig. 4(d), the soft agglomerates (overlap and side by side, marked by arrow) of the MnO<sub>2</sub> nanorods resulted in a nearly 10–50-times increase in size to become 20–50 nm nanoparticles, while lots of nanopores (marked by circles) were formed simultaneously from the surface to the inside (namely porous MnO<sub>2</sub> nanoparticles). The pore size is not homogeneous and it varies from



Fig. 5 The EDS pattern of as-prepared MnO<sub>2</sub>.

1–3 nm. Nevertheless, some hard aggregation can be observed (marked by the rectangle), where  $MnO_2$  nanorods have integrated into a solid body by strong chemical bonds due to differences in local reaction conditions (*e.g.* the distribution of surfactant). In addition, one can also deduce from the TEM observations that the  $MnO_2$  nanoparticles interconnect physically into 3-D a network structure in form of a soft agglomerate.<sup>34</sup>

The chemical composition of the obtained  $MnO_2$  product was determined using energy-dispersive X-ray spectroscopy (EDS) analysis attached to the SEM. On the basis of the appearance of the Mn-K $\alpha$ , O-K $\alpha$ , C-K $\alpha$  and K-K $\alpha$  X-ray peaks, one can conclude that the constitutive elements of the sample are Mn, O, C and K, as shown in the EDS pattern (see Fig. 5). Generally, there is always a possibility of potassium ions co-existing in the MnO<sub>2</sub> matrix, arising from potassium permanganate, one of the starting materials.<sup>35,36</sup> Naturally, the C element should be derived from the other starting material, D-glucose. The composition content of the MnO<sub>2</sub> sample is listed in Table 2. It can be seen from the table that the O and Mn content are in absolute superiority, and that the amount of K and C are very negligible for detection using XRD.

SEM-EDS element distribution mapping is a useful technique utilized to identify areas of specific chemical composition, in which several elements on the surface of sample tested can be mapped simultaneously. Fig. 6 shows the SEM-EDS result of the as-prepared MnO<sub>2</sub> product where (a) is the SEM image used in the EDS mapping test and (b) is the resulting image of EDS element distribution based on the SEM image in (a). It can be seen from Fig. 6(a) that well-dispersed, spherical MnO2 nanoparticles are interconnected into a porous network structure. The corresponding EDS mapping images (Fig. 6(b)) of both the Mn and O elements have visible and well-dispersed spot distributions that are consistent with the SEM image, as shown in Fig. 6(a). In addition, the SEM-EDS analysis also indicates that there is little K and C present, in view of the weak spot distribution of the corresponding mapping images.

Table 2 Content of C, O, K and Mn present in the MnO<sub>2</sub> sample

Element	C-Κα	Ο-Κα	Κ-Κα	Mn-Ka	Total
Quality (%)	1.32	45.64	0.78	52.26	100.00
Atom (%)	2.85	71.46	0.521	25.17	100.00



**Fig. 6** The SEM-EDS result of the as-prepared MnO<sub>2</sub>: (a) SEM image used and (b) corresponding images of EDS element distribution mapping.

## 3.2 Reaction courses and the formation mechanism of the MnO<sub>2</sub> product

Generally, it is very difficult to study the exact reaction mechanism of permanganate oxidation to organic substrates due to the multitude of possible oxidation states. The acceptable reaction courses of the permanganate oxidation of D-glucose into  $MnO_2$  are described as follows:<sup>37–40</sup>

$$MnO_{4}^{-} + H^{+} \longleftrightarrow HMnO_{4}$$
(1)

$$\underset{\text{Hom}}{\overset{H}{\underset{\text{Hom}}}{\underset{Hom}}{\underset{Hom}}{\underset{Hom}}{\underset{Hom}}}}}}}}}}}}}}}}}}}}}}}} }$$

$$\mathbf{Mn}(\mathbf{V}) + \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{O}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{O}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}} \underset{\mathsf{HO}}{\overset{\mathsf{HO}}{\longrightarrow}}$$
(4)

$$Mn(IV) + 2H_2O \longrightarrow MnO_2 + 4H^{\dagger}$$
(5)

Eqn (1) represents the protonation of  $MnO_4^-$  to  $HMnO_4$ . This is a critical step in the D-glucose–permanganate redox reaction that indicates that the initial reaction kinetics are dependent on the hydrogen ion concentration.<sup>37</sup> Eqn (2) shows the formation of the D-glucose–Mn(VII) complex, which can decompose into Mn(v) and a glucose-based radical [eqn (3)]. Mn(v) is highly unstable to the glucose-based radical and immediately gets converted into Mn(v) [eqn (4)], and the formation of manganese dioxide can eventually occur in eqn (5).<sup>40</sup>

The mechanism of sonochemical processes are usually based on the formation of the short-lived radical species H<sup>•</sup> and OH<sup>•</sup> [eqn (6)], generated during violent cavitation events.<sup>41</sup> In aqueous solution, H<sup>•</sup> and OH<sup>•</sup> are strong reducing radicals that are able to reduce metal ions.<sup>18,42,43</sup> In our case, the H<sup>•</sup> radical formed in eqn (6) (")))))" symbolizes ultrasonic action) may act as a reducing species, trigger the reduction of K<sup>+</sup> to K and produce a large quantity of hydrogen ions [eqn (7)]. A high concentration of hydrogen ions produced in this step is essential for MnO<sub>2</sub> rapid synthesis within 10 min by sonochemistry. When D-glucose was used for the reduction of KMnO<sub>4</sub> to MnO<sub>2</sub> without ultrasonic treatment, the precipitation was found to be complete only after at least 2 h, even at 80 °C.<sup>19</sup> In addition, the pH of the solution was measured before and after the sonochemical reaction. An increase in the pH from 5.74 before the reaction to 8.62 after the reaction had occurred indicates the generation of  $OH^-$  during the sonochemical process. This is probably due to the reaction between the resulting K and H<sub>2</sub>O [eqn (8)].

$$H_2O )))) OH^{\bullet} + H^{\bullet}$$
(6)

$$\mathbf{K}^+ + \mathbf{H}^\bullet \to \mathbf{K} + \mathbf{H}^+ \tag{7}$$

$$2K + 2H_2O \rightarrow 2KOH + H_2 \tag{8}$$

Up to now, the definite formation mechanisms of MnO<sub>2</sub> nanorod structures have not be well understood and are thought to vary between the different synthesis methods.44 Recently, studies have demonstrated that sonochemistry can promote the synthesis of 1-D metal oxides.<sup>17,45,46</sup> It is well known that there are three regions of sonochemical activity: (i) inside of the collapsing bubble (T > 5000 K and F > 20 MP), (ii) at the interface between the bubble and the liquid ( $T \approx 1900$  K and  $F \approx 8$  MP) and (iii) in the bulk solution under ambient conditions.<sup>18,47</sup> Therefore, we propose that the formation of MnO<sub>2</sub> nanorods in the present study is at the interfacial region where high temperature and high pressure are present. Moreover, the extremely rapid cooling rates ( $> 10^7$  K s<sup>-1</sup>) during acoustic cavitation can effectively prevent the over-growth of the MnO<sub>2</sub> nanorods, this being one key factor in the formation of the poorly crystallized MnO<sub>2</sub>.<sup>6</sup>

Based on the experimental results and discussion above, a possible formation mechanism of the porous MnO<sub>2</sub> nanoparticles is proposed, as presented in Fig. 7. At first under the sonochemical conditions, MnO<sub>2</sub> nanorods grow rapidly according to the series of reaction process described in eqn (1)–(5). Then, the  $MnO_2$  nanorods tend to softly agglomerate and further form MnO2 nanoparticles by van der Waals forces. Finally, under the effect of the surfactant PEG-600, porous MnO<sub>2</sub> nanoparticles consisting of stacked MnO<sub>2</sub> nanorods are generated. During this period, the surfactant PEG-600 acts as an effective dispersant to inhibit the MnO<sub>2</sub> nanorods from hard-agglomerating, otherwise the porous nanoparticles would agglomerate into solid ones later in the reaction. Actually, it has been found that in ultrasound irradiation processes, the surfactant in the reaction system plays an important role in the formation of porous or hollow oxide nanostructures.14,48

# **3.3** Electrochemical properties of MnO<sub>2</sub> electrode in supercapacitor applications

The electrochemical properties of  $MnO_2$  electrodes in 1 M  $Na_2SO_4$  and 9 M KOH aqueous solutions were compared. The galvanostatic charge/discharge curves of the two-electrode



Fig. 7 The proposed growth mechanism of the porous  $MnO_2$  nanoparticles: (1) sonochemical synthesis of  $MnO_2$  nanorods, (2) soft-agglomeration of  $MnO_2$  nanorods and (3) generation of porous or solid  $MnO_2$  nanoparticles.

supercapacitor cells at a current density of 280 mA  $g^{-1}$  are shown in Fig. 8(a) and (b) for 1 M Na<sub>2</sub>SO<sub>4</sub> and 9 M KOH electrolytes, respectively. The typical triangle distributions of the curves prove a good capacitive behavior of the supercapacitors in both electrolytes. At this current density, the single electrode specific capacitance calculated from the discharging plots<sup>12</sup> for the supercapacitor cells in 1 M Na<sub>2</sub>SO<sub>4</sub> and 9 M KOH electrolyte were 198.1 and 401.4 F g<sup>-1</sup>, respectively.

The dependence of the capacitance on the current density of the  $MnO_2$  electrodes in different electrolytes is shown in Fig. 9. It was observed that the specific capacitance decreased with increasing current density (280, 420, 540, 680 and 820 mA g<sup>-1</sup>). At a current density of 820 mA g<sup>-1</sup>, a high value of 196.7 F g<sup>-1</sup> in 9 M KOH electrolyte was obtained, but a lower value of 100.2 F g<sup>-1</sup> was measured in 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte, which indicates that in alkaline electrolyte, the MnO<sub>2</sub> electrodes possess better electrochemical properties than in a neutral electrolyte.

It is well known that the pseudo-capacitive behavior of  $MnO_2$  is a surface reaction: only the surface or a very thin surface layer of the oxide can participate in this pseudo-capacitive reaction.<sup>9,49</sup> The pseudo-capacitance of  $MnO_2$  is based on the reversible redox process that takes place in the redox transition  $Mn^{4+} \leftrightarrow Mn^{3+}$ . The generally accepted reactions for  $MnO_2$  in Na<sub>2</sub>SO<sub>4</sub> neutral aqueous electrolyte are as follows:<sup>35,50–55</sup>

$$MnO_2 + Na^+ + e^- \leftrightarrow MnOONa$$

(MnO<sub>2</sub>) surface + Na<sup>+</sup> + e<sup>-</sup>  $\leftrightarrow$  (MnO<sub>2</sub><sup>-</sup>Na<sup>+</sup>) surface

where the second mechanism is based on the surface adsorption of electrolyte cations on  $MnO_2$ . In the present study, the redox process is mainly governed by the insertion and de-insertion of Na<sup>+</sup> from the electrolyte into the porous nano-MnO<sub>2</sub> matrix.

The redox mechanism of  $MnO_2$  in neutral solution has been well investigated; however, in an alkaline electrolyte such as KOH, it has been rarely reported.<sup>56,57</sup> In the present study, the observed specific capacitance values for the  $MnO_2$  electrode in 9 M KOH is much higher than that in 1 M Na<sub>2</sub>SO<sub>4</sub>. In an alkaline electrolyte, the charge storage process may be completed by the combination of the surface adsorption/ desorption of ions from the electrolyte and proton insertion from water. This could be an interesting extension of the pseudo-capacitance of  $MnO_2$  in aqueous solutions, and the possible reactions are as follows:<sup>10,56</sup>

(MnO<sub>2</sub>) surface + K<sup>+</sup> + e<sup>-</sup>  $\leftrightarrow$  (MnO<sub>2</sub><sup>-</sup>K<sup>+</sup>) surface MnO<sub>2</sub> + H<sub>2</sub>O + e<sup>-</sup>  $\leftrightarrow$  MnOOH + OH<sup>-</sup>

$$MnO_a(OH)_b + nH^+ + ne^- \leftrightarrow MnO_{a-n}(OH)_{b+n}$$

When used for electrode materials, nanostructured metal oxides have been considered to be more beneficial to high capacitance than bulky ones due to their sufficiently high electrode surface area.<sup>5,7,12,58</sup> This may indicate that electrolyte ions can effectively make contact with the active



Fig. 8 Charge–discharge curves of the MnO<sub>2</sub> electrodes in (a) 1 M Na<sub>2</sub>SO<sub>4</sub> and (b) 9 M KOH electrolyte at a current density of 280 mA g<sup>-2</sup>.



**Fig. 9** The dependence of capacitance on the current density of the MnO<sub>2</sub> electrodes in different electrolytes.

electrode materials in nanostructures. We believe that the 3-D porous structure of the nano- $MnO_2$  electrode here can significantly facilitate the penetration of protons and the transportation of electrons,<sup>59,60</sup> thus resulting in a facile redox reaction and a fast charge/discharge in supercapacitor applications. In addition, it is reasonable to suppose that the nanopore structure (1–3 nm) of the  $MnO_2$  electrode could also provide a desirable electric double layer capacitance in symmetric electrode cells with aqueous electrolytes.<sup>1</sup>



Fig. 10 The life cycle of the  $MnO_2$  electrodes in different electrolytes at a current density of 280 mA g<sup>-2</sup>.

The electrochemical stability of supercapacitor cells were examined by charge-discharge cycling at a constant current density of 280 mA  $g^{-2}$  for 900 cycles (see Fig. 10). It was noted that the electrodes had more than 120 F  $g^{-2}$  of electrode specific capacitance in both 1 M Na<sub>2</sub>SO<sub>4</sub> and 9 M KOH electrolytes after 900 cycles. Considering the network structure nature of porous MnO<sub>2</sub> electrodes, the dissolution process should be more sensitive to a high concentration of alkaline solution, which leads to faster capacitance fading within the early 200 cycles in the 9 M KOH electrolyte. Although not perfect compared with the MnO<sub>2</sub> thin films previously reported,<sup>10</sup> this performance is still encouraging, especially in view of the ease of material synthesis. One should also take into account the fact that all of these results were investigated from micron-level electrodes in symmetric cells, which is very close to the actual application environment of supercapacitors.

### 4. Conclusions

In summary, we have accomplished a large-scale synthesis of porous nano- $MnO_2$  via a facile sonochemistry procedure from inexpensive raw materials. The  $MnO_2$  nanoparticles synthesized in this case are highly dispersed and fine nano-structures. The good electrochemical properties of  $MnO_2$  electrodes have been demonstrated both in 1 M Na<sub>2</sub>SO<sub>4</sub> and 9 M KOH aqueous solution. Furthermore, the simple process, high yield and safe precursors of the synthetic procedure indicate that porous nano- $MnO_2$  should be a promising electrode material for supercapacitor applications.

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