# Nanostructured manganese oxides and their composites with carbon nanotubes as electrode materials for energy storage devices\*

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*Abstract*: Manganese oxides have been synthesized by a variety of techniques in different nanostructures and studied for their properties as electrode materials in two different storage applications, supercapacitors (SCs) and Li-ion batteries. The composites involving carbon nanotubes (CNTs) and manganese oxides were also prepared by a simple room-temperature method and evaluated as electrode materials in the above applications. The synthesis of nanostructured manganese oxides was carried out by simple soft chemical methods without any structure directing agents or surfactants. The prepared materials were well characterized using different analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), surface area studies, etc. The electrochemical properties of the nanostructured manganese oxides and their composites were studied using cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopic (EIS) studies. The influence of structural/surface properties on the electrochemical performance of the synthesized manganese oxides is reviewed.

*Keywords*: nanostructures; carbon nanotubes; manganese oxides; supercapacitors; lithium-ion battories.

#### INTRODUCTION

In recent years, the search for new materials for use as electrodes in energy storage devices such as supercapacitors (SCs) and batteries has increased greatly mainly due to the demand for power systems with high energy and power densities. Because of environmental issues and depleting fossil fuels, interest in the development of alternative energy storage/conversion devices with high power and energy densities catering to present-day demands has increased to a greater extent. Of the various energy storage devices, SCs and Li-ion batteries are considered promising candidates for applications ranging from electric vehicles to cellular phones [1]. Li-ion batteries are generally classified based on the electrolyte used, i.e., nonaqueous liquid electrolyte or solid polymer electrolyte. However, the performance of a Li-ion battery is mainly determined by the choice of electrode materials. SCs are broadly classified into two categories, electrical double-layer capacitors (EDLCs) and pseudocapacitors, depending on the nature of charge storage mechanism. EDLCs exhibit a non-faradic reaction with accumulation of charges at the electrode–electrolyte interfaces while the pseudocapacitors show

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faradic redox reactions. In both of these classes of storage devices, the performance is determined by the choice of electrode materials.

Different types of carbonaceous material ranging from amorphous carbons to carbon nanotubes (CNTs) have been used as electrode materials in EDLCs [2-5]. In the case of pseudocapacitors, various noble and transition-metal oxides such as RuO<sub>2</sub>, IrO<sub>2</sub>, NiO, CoO<sub>x</sub>, SnO<sub>2</sub>, and MnO<sub>2</sub> were used as electrode materials [6–10]. Of all the transition-metal oxides studied as pseudocapacitor materials, hydrated RuO<sub>2</sub> has been found to be the most promising material in terms of energy density. However, the high cost of RuO<sub>2</sub> has prompted the research community to focus on other transition-metal oxides such as MnO<sub>2</sub>, NiO, etc., mainly because of the involved cost-effectiveness. In addition, hydrated RuO<sub>2</sub> shows excellent performance mostly in a highly acidic electrolyte such as sulfuric acid. The basic idea behind the choice of highly acidic electrolyte solutions for SC applications mainly relates to the fast charge and discharge, leading to a high power density. This is due to the fact that protons have a better access not only to the surface of the electrode but also to the interior of the electrode than larger alkali ions such as  $K^+$  or Na<sup>+</sup> [6]. Hence, the chemisorption of the H<sup>+</sup> in an acidic-hydrated oxide electrode system is exceptionally fast, leading to a promising pseudocapacitor material [6]. However, the main disadvantage of using a highly acidic electrolyte is the dissolution of metal oxide over a period of cycling time. This leads to SC showing a faster fading in capacitance with respect to cycling. Hence, alternative materials which are much cheaper and more promising in a neutral electrolyte system such as Na<sub>2</sub>SO<sub>4</sub>, KCl, LiCl, etc. have been investigated in recent years [11–13]. Of the various non-noble metals or transition-metal oxides studied, MnO<sub>2</sub> enjoys a place of pride because of its lower cost and environmentally benign nature. Beyond these advantageous properties, MnO2 is very promising in a neutral electrolyte system [11–17].

The Li-ion batteries are considered to be one of the most promising power sources because of the main advantages such as light weight and very high energy density, whereas its disadvantage is lower power density which limits its applicability in various situations especially for electric vehicles. Research for better cathode and anode materials leading to improved electrochemical properties and economical Li-ion batteries is an ongoing pursuit. Most of the commercial Li-ion batteries have  $\text{LiCoO}_2$  as a cathode material [18]. A variety of other cathode materials such as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFePO}_4$ , etc. are extensively studied for a possible replacement of expensive and toxic  $\text{LiCoO}_2$  cathode, making the Li-ion batteries more cost-effective and environmentally benign [19].

The development of new high-rate and -capacity anode materials for Li-ion batteries to match the high-capacity cathodes is of prime importance. There are various anode materials such as metal oxides, carbonaceous materials, phosphates, and sulfides, etc. that are presently envisaged for use in Li-ion batteries [20–24]. The conventional graphitic materials have a theoretical capacity limitation of 372 mAh/g, which very much limits the overall energy density of the Li-ion battery. Alternative anode materials such as CoO, NiO, CuO, SnO<sub>2</sub>, Si, etc. provide very high specific capacity when compared to graphitic materials [20–24]. However, the method of preparation and the microstructure of the material govern the overall performance of the material. Utilizing MnO<sub>2</sub>-based anode materials not only improves the energy density of the material, but also makes the power source environmentally benign and inexpensive.

The topotactic Li insertion/deinsertion reaction varies with the nature of the host. Typically, metal oxide-based anode materials mainly show reversible Li insertion/deinsertion reactions based on the alloying/dealloying of the Li ion and the cation of the metal oxide [20,24]. In the case of graphitic carbon, it can store up to one Li for every six C atoms by a staging mechanism corresponding to the theoretical capacity of 372 mAh/g [24]. However, the disordered C materials can store Li two or three times more than the theoretical value for graphite because of the turbostatic disorder of the graphene sheets [25].

Both single-walled (SWNTs) and multi-walled carbon nanotubes (MWNTs) have been studied for the use as negative electrode material in the Li-ion batteries and the EDLC electrodes for SC applications [26]. Composite formation of a metal oxide and CNT is an interesting alternative for storage device with high energy and power density [27–30].

Manganese oxides as pseudocapacitor electrode materials were synthesized using different techniques such as simple reduction, coprecipitation, sol-gel, thermal decomposition, etc. [11–17]. Various thin-film electrodes of  $MnO_2$  were synthesized via electrochemical and chemical routes [7]. Hydrothermal synthesis has been an interesting technique to prepare materials with different nanoarchitectures such as nanowires, nanorods, nanobelts, nano-urchins, etc. The main advantages of the hydrothermal technique over other soft chemical routes are the ability to control the nanostructures ranging from nanoparticles to nanorods or nano-urchins to nanotubes by properly choosing parameters such as reaction temperature, reaction time, the active fill level in the pressure vessel, and a solvent used for the reaction without any major structure directing agents or templates. In the case of anode properties of  $MnO_2$  in the Li-ion batteries, only a few studies have been reported so far. Ma et al. have reported the electrochemical properties of  $MnO_2$  nanobelts [31]. Electrodeposited  $MnO_2$  thin films in various nanoarchitectures were also studied for the electrochemical Li insertion properties [32,33].

In this paper, we report the synthesis of various nanostructures of manganese oxides by hydrothermal route under mild conditions and further a simple room-temperature (RT) precipitation technique. The change in the nanoarchitectures was achieved by simply tuning the hydrothermal reaction time or changing an alcohol used for the RT precipitation of the  $MnO_2$ . Composites containing  $MnO_2$ and CNTs were achieved either by in situ reactions between the  $MnO_2$  starting material with CNTs or mixing the formed  $MnO_2$  with CNTs during the electrode formation process. Li-ion topotactic reactions in these manganese oxides and their composites will be also reported here. The corresponding variation in morphology, surface property, and electrochemical property as SC electrodes was studied elaborately and discussed.

#### EXPERIMENTAL

#### Synthesis

#### Hydrothermal synthesis of MnO<sub>2</sub>

Hydrothermal synthesis of  $MnO_2$  [ $\overline{3}4$ ] was carried out starting with aqueous solutions of  $MnSO_4 \cdot H_2O$ and  $KMnO_4$  following the procedure reported by Wang and Li [35] with little modification. The wellmixed aqueous solutions of  $KMnO_4$  and hydrated  $MnSO_4$  were transferred to a Teflon-lined pressure vessel (PARR Instruments, USA) and loaded onto an oven preheated to 140 °C. The dwell time for the reaction has been varied from 1 to 18 h in order to optimize the best microstructure for the electrochemical applications. The pressure vessel was allowed to cool to RT naturally after the respective dwell time at 140 °C. The precipitate formed was filtered and washed with distilled water until all the unreacted materials were removed. The washing was done until the pH of the washed water was 7. The precipitated  $MnO_2$  was dried at 100 °C in air. The same amounts of the starting materials were kept in a beaker overnight for the RT formation of an amorphous  $MnO_2$  (a- $MnO_2$ ) precipitate in order to see the structural evolution of the  $MnO_2$  nanostructures from RT to the time-dependent hydrothermal treatment. The synthesized nanostructures were employed as electrodes independently in the pseudocapacitor and the Li-ion battery studies.

#### Room-temperature synthesis of MnO<sub>2</sub>

Manganese oxides were prepared at RT by an addition of different alcohols such as ethanol, methanol, pentanol, isopropanol, glycerol, and ethylene glycol individually to the aqueous solution of  $KMnO_4$  [36]. Typically, 0.5 g of  $KMnO_4$  was dissolved in 30 ml of deionized water. To this  $KMnO_4$  solution, 10 ml of ethanol (for instance) was added drop-wise which led to the formation of brownish precipitate of  $MnO_2$ . The precipitate was filtered and washed extensively with deionized water until the pH of the washed water was 7. Then the precipitate was dried at RT. Similar procedure was followed for the synthesis of manganese oxides with other alcohols as well.

#### Manganese oxide: SWNT composites

The  $MnO_2$ :SWNT composites [37] with different weight ratios of 5 to 40 wt % SWNTs were prepared by a simple precipitation technique developed in our lab [36]. Briefly, the starting materials for the preparation of  $MnO_2$  were  $KMnO_4$  and ethanol. Firstly, the  $KMnO_4$  was made a saturated solution in deionized water. The SWNTs were procured in purified form from Helix Materials, Inc. and used as received. According to their technical data sheet, the diameter distribution is <2 nm and length is 0.5~40 µm and exist as bundles. The purity level is >90 % with the amorphous carbon <5 %. To this saturated solution of  $KMnO_4$ , the SWNTs were dispersed and stirred for 1 h in a magnetic stirrer. After complete homogenization of the mixture, 10 ml of ethanol was added drop-wise under constant stirring. Immediate precipitation of  $MnO_2$  was observed, and the details of the reaction for the formation of  $MnO_2$  have been reported elsewhere [34]. The well-mixed precipitation of  $MnO_2$  and SWNTs were filtered and dried at RT.

#### Structural properties

The phase purity of synthesized materials was characterized using X-ray diffraction (XRD) (Siemens X-ray Diffractometer, Germany). The particle morphology and structural properties of the prepared MnO<sub>2</sub> were further elucidated by scanning electron microscopy (SEM) (Hitachi S 3600N, Japan) and high-resolution transmission electron microscopy (HR-TEM) (JEOL 2010, Japan) studies. Energy dispersive X-ray (EDX) was used to confirm the composition of the formed oxide and the presence of other metal ions such as potassium. The surface properties of the synthesized oxides were studied in detail by X-ray photoelectron spectroscopy (XPS) (Kratos AXIS 165 XPS/SAM, USA). The surface area of the synthesized materials was studied using Brunauer–Emmett–Teller (BET) measurements (Quantachrome Instruments, Model NOVA 2000 Series, USA) [34,36,37].

#### **Electrochemical studies**

Electrodes for evaluating the electrochemical properties of the synthesized  $MnO_2$  were fabricated by mixing the prepared  $MnO_2$  with 20 wt % carbon black (Black Pearl 2000, Cabot Corp., USA) and 5 wt % PVdF-HFP binder. A slurry of the above mixture was made using *N*-methyl-2-pyrrolidone (NMP) as a solvent which was subsequently brush-coated onto a Ni mesh. The mesh was dried at 110 °C in air for 1 h for the removal of the solvent. After drying, the coated mesh was uni-axially pressed to better adhere the electrode material with the current collector. In the case of composites prepared ex situ with  $MnO_2$  and SWNT, the electrode materials were prepared with different weight ratios of CNTs along with the binder [34,36,37].

Cyclic voltammetry (CV) studies were performed using a potentiostat/galvanostat (PGSTAT20, Autolab, EchoChemie, The Netherlands/PARSTAT 2273, EG & G, USA) in a three-electrode configuration with the Ni mesh coated with the  $MnO_2$  as the working electrode, Pt-wire as the counter, and saturated calomel electrode (SCE) as the reference. CV was done between -0.2 and 0.8 V in a 1 M Na<sub>2</sub>SO<sub>4</sub> neutral electrolyte at different scan rates. The specific capacitance was evaluated from the area of the charge and discharge curves of the CV plot. Galvanostatic charge–discharge experiments were performed galvanostatically in a similar set-up as described above, at 200 mA/g between 0 and 1 V. The specific capacitance of the system has been evaluated using the formula [34,37]:

Specific capacitance, C (F/g) = 
$$i\Delta t/m \Delta V$$
 (1)

where *i* is the current used for charge/discharge,  $\Delta t$  is the time elapsed for the charge or discharge cycle, *m* is the mass of the active electrode and  $\Delta V$  is the voltage interval of the charge or discharge. Long-cycle performance was performed in a two-electrode test cell with symmetric electrodes separated by a polypropylene (PP) separator soaked in an appropriate electrolyte.

The electrochemical performance of the MnO<sub>2</sub> and its composites as the Li-ion battery electrode was studied by assembling two-electrode HS-Test Cells (Hohsen Corp., Japan) with Li metal as an anode in a 1 M LiPF<sub>6</sub>+EC+DEC (1:1 in volume) electrolyte (Ferro Corporation, USA). The electrode materials were prepared by mixing the active material with 10 % PVdF:HFP binder (Elf Atofina, France) and 10 % conducting carbon black additive in NMP. The well-mixed slurry was coated on to a copper foil using a hand-held doctor blade. The coated foil was allowed to dry in an oven at 110 °C for 1 h and 30 min. Circular disc electrodes were punched from the foil and used as cathode for assembling the test cells. All manipulations were performed in a glove box (MBraun, UniLab, USA) filled with purified argon. The moisture content and oxygen level were less than 5 ppm inside the glove box. The assembled cells were discharged and charged galvanostatically at different rates from 0.1 to 10 C, between 3.0 and 0.005 V using a Potentiostat/Galvanostat (Autolab PGSTAT30, EcoChemie, The Netherlands). Electrochemical impedance spectroscopy (EIS) studies were performed using the same cell set-up as described above by applying a small perturbation voltage of 5 mV in the frequency range of 100 kHz to 10 mHz at different voltages during the first discharge. Each impedance measurement was made after an equilibration at chosen voltage for 1 h. The analysis of the impedance spectra was performed by equivalent circuit software provided by the manufacturer (Autolab FRA/PGSTAT30, EcoChemie, Netherlands) [38].

#### **RESULTS AND DISCUSSIONS**

#### Hydrothermal synthesis and pseudocapacitance studies of nanostructured MnO<sub>2</sub>

Typical SEM images for the non-hydrothermal  $MnO_2$  and that prepared hydrothermally for 18 h are shown Fig. 1. It can be clearly noticed that the mixing of hydrated  $MnSO_4$  and  $KMnO_4$  immediately leads to the formation of a precipitate of  $MnO_2$  having flower-like nanowhiskers at RT. Hydrothermal treatment at 140 °C for different times showed an evolution of nanorods from a mixture of nanowhiskers and nanorods as discussed elsewhere [34]. The electron diffraction (ED) recorded for the sample prepared for 1 h shows initiation of the nucleation of nanocrystalline particles. However, the lattice fringes are not clearly evolved at 1 h of hydrothermal dwell time. In the case of the material prepared at 18 h, there has been a well-developed crystallinity as shown by the ED studies and well supported by the HR-TEM observations. The lattice fringes are explicitly clear with a d-spacing of 4.8 Å for the (002) plane. There has been a strong correlation with the hydrothermal dwell time with respect to the pore structure and surface area of the  $MnO_2$  nanostructures, which in turn, have a direct effect on the electrochemical properties of the materials. All of these morphological manipulations are the biggest advantage of the hydrothermal technique.



Fig. 1 Typical SEM images of the  $MnO_2$  nanostructures prepared non-hydrothermally at RT (a) and hydrothermally at reaction time of 18 h at 140 °C (b).

#### V. SUBRAMANIAN et al.

The XRD patterns for the prepared  $MnO_2$  at a different time are shown in Fig. 2. The material prepared at RT showed an a-MnO<sub>2</sub> feature having peaks evolving to an  $\alpha$ -MnO<sub>2</sub> structure. Increase in the hydrothermal dwell time correspondingly increased the crystallinity of the formed MnO<sub>2</sub>. There has always been a strong correlation between the crystallinity and the surface area of the system on the electrochemical properties as discussed later.



Fig. 2 XRD patterns for the  $MnO_2$  synthesized by hydrothermal reaction at different time ranging from 1 to 18 h at 140 °C.

 $N_2$  adsorption–desorption studies were performed to determine the specific surface area of the  $MnO_2$  prepared at a different hydrothermal reaction time. The BET surface area was found to be 100 m<sup>2</sup>/g for 1 h hydrothermally treated sample. Interestingly, increase in the hydrothermal dwell time to 6 and 12 h showed an increase in the surface area to 132 m<sup>2</sup>/g and 150 m<sup>2</sup>/g, respectively, which may be attributed to the pore structure of the materials.

XPS studies were performed to identify the oxidation state of Mn in the prepared  $MnO_2$  as this is very critical for any electrochemical application. As evidenced from the Mn3s spectra, the peak energy for the splitting corresponds to values between 4.7–4.8 eV. According to Toupin et al. [14,15], when the oxidation state of Mn is +4, the binding energy (BE) difference is in the range of 4.7–4.8 eV. Therefore, it confirmed the oxidation state of Mn is +4 in the prepared MnO<sub>2</sub>.

Typical CV curves recorded at a scan rate of 5 mV/s for  $MnO_2$  prepared at 140 °C for a different time are shown in Fig. 3. It can be seen from the figures that there has been an ideal capacitive behavior with the plots showing an almost rectangular profile.  $MnO_2$  prepared for 6 h showed the maximum specific capacitance with a value of 168 F/g. There has been an increase in specific capacitance from 140 F/g for the sample prepared at 1 h to 168 F/g for the sample prepared for 6 h which then decreased



Fig. 3 Typical CVs recorded at a scan rate of 5 mV/s for  $MnO_2$  prepared at 140 °C for different hydrothermal reaction time.

to 118 F/g for 12 h and 72 F/g for 18 h. Similar results have been observed in the case of temperaturedependent capacitance for  $MnO_2$  prepared at different temperatures [14,15].

The cycling capability of the  $MnO_2$ -6 h electrode was studied galvanostatically at a constant current density of 200 mA/g and between 0 and 1 V. The galvanostatic cycling is one of the reliable experiments to evaluate the specific capacitance. The specific capacitance was found to be 168 F/g, which is very much comparable to that calculated from the CV studies.

### Alcohol-assisted RT synthesis of MnO<sub>2</sub> and its electrochemical performance as pseudocapacitor material

TEM measurements were performed to study the morphology and microstructure of the prepared manganese oxides using alcohols at RT, and typical micrographs of manganese oxides prepared using ethanol and ethylene glycol are shown in Fig. 4. As can be seen from the figure, the manganese oxides synthesized using ethanol and methanol, which are primary alcohols, show largely agglomerated whiskers in nanoscale. While that from ethylene glycol, isopropanol, and glycerol show particle-like morphology in nanoscale. The time for the precipitation reaction varies with the alcohols used. Except for pentanol, all the alcohols show a reaction time of less than 1 h for complete precipitation. Only in the case of pentanol we have an extended the reaction time of up to 12 h. This is mainly due to the nonpolar nature of pentanol, as discussed later. Moreover, there has been a pronounced color difference among the formed manganese oxides depending upon the alcohol used. The materials synthesized with ethanol, methanol, and pentanol show a brown color precipitate, while that with ethylene glycol, isopropanol, and glycerol show a black precipitate. This is mainly due to the valence state of the formed MnO<sub>2</sub>.

ED studies revealed the formation of crystalline  $MnO_2$ , the lattice fringes can be clearly observed from the HR-TEM studies. The d-spacing of 0.70 nm corresponds to (110) plane of  $MnO_2$  structure.  $MnO_2$  nanostructures synthesized using ethanol showed a surface area of 250 m<sup>2</sup>/g. However, the surface area for the methanol-assisted  $MnO_2$  is 124 m<sup>2</sup>/g. This can be directly related to the whisker size and the porosity of the formed  $MnO_2$ . This clearly indicates that the materials are not only in nanostructured phase but also adequately porous.

#### V. SUBRAMANIAN et al.



Fig. 4 TEM micrographs of manganese oxides prepared at RT using (a) ethanol and (b) ethylene glycol.

All of the manganese oxides from secondary alcohols have a predominantly amorphous phase which has been identified as  $Mn_2O_3$  (Mn in 3+) though there still are a small amount of crystallites which show features corresponding to  $MnO_2$ , confirmed with XRD measurements (not shown here). In the case of ethylene glycol, the particle size is about 10~20 nm, while that from isopropanol and glycerol shows larger particles and highly porous particles, respectively. This observation can be well supplemented from the surface area measurements. Of the three secondary alcohols considered, the glycerol shows the largest surface area of 245 m<sup>2</sup>/g followed by the ethylene glycol with 195 m<sup>2</sup>/g and isopropanol 146 m<sup>2</sup>/g.

The reaction mechanism for the formation of different manganese oxides can be explained as following:  $\text{KMnO}_4$  used here acts as an oxidizing agent in a neutral medium, which is water in the present case. As a typical example, the ethanol is oxidized into acetic acid and permanganate is reduced into  $\text{MnO}_2$  with the formation of KOH. In other words, the formation of KOH must be neutralized by the formation of acetic acid which in turn forms salt and water. However, the reaction mechanism is different when secondary alcohols were used.  $\text{KMnO}_4$  oxidizes the alcohol to a ketone with the formation of  $\text{Mn}_2\text{O}_3$  in the aqueous media.

To confirm the conclusions drawn, XPS studies were performed to evaluate the oxidation state of Mn in the manganese oxides prepared using different alcohols. The typical Mn3s spectra recorded for manganese oxides prepared using ethanol and glycerol are shown in Fig. 5. It was reported earlier [14,15], due to the parallel spin coupling between the 3s electron and the 3d electron during the photoelectron ejection the Mn3s spectra in manganese oxides will exhibit a splitting. The splitting difference in the BE gives important information on the oxidation state of Mn in the prepared MnO<sub>2</sub>. The BE difference values close to 4.8 eV signify the oxidation of Mn in 4+ state [15]. In the present case, the difference in BE for ethanol and methanol was found to be 4.70 and 4.68 eV, respectively, which corresponds to Mn4+, confirming the reaction mechanism discussed above. When a secondary alcohol or acetone was used, the BE difference was much above 5.3 eV, indicating the formation of Mn<sub>2</sub>O<sub>3</sub> [15].



Fig. 5 Typical Mn3s spectra recorded for manganese oxides prepared using (a) ethanol and (b) glycerol.

Figure 6 shows the typical CV curves recorded at a scan rate of 2 mV/s for the manganese oxides prepared using different alcohols. The specific capacitance has been calculated by integrating the area of the CV curves. The rectangular profiles of the CV curves show an ideal capacitive behavior which is very important for a system to be highly reversible. The specific capacitance for the ethanol-assisted synthesis is 202 F/g, which is the highest in the present study. For the methanol-assisted MnO<sub>2</sub>, the specific capacitance was found to be 160 F/g. The main difference in the specific capacitance may be attributed to the difference in the surface area of the synthesized materials. The specific surface area of ethanol was found to be almost double that of methanol. Pseudocapacitance is more related to the actual redox reactions occurring in the system, larger surface area always has a more facile diffusion of electrolyte ions and hence a higher reactivity. Although the profile of the CV curves obtained for manganese oxides prepared using secondary alcohols, ethylene glycol, glycerol, acetone, and isopropanol are similar to that of MnO<sub>2</sub> from ethanol and methanol, the actual specific capacitance values are much



Fig. 6 CVs for the manganese oxides prepared using different alcohols recorded at a scan rate 2 mV/s between -0.2 and 0.8 V in a 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte.

lower. The manganese oxides prepared using secondary alcohols such as pentanol, glycerol, isopropanol, and acetone were 170, 133, 152, and 127 F/g, respectively. The lowest was 113 F/g for the  $Mn_2O_3$  prepared using ethylene glycol. The main reason for the lower specific capacitance is the 3+ oxidation state of Mn, as confirmed from XPS analysis.

The charge–discharge experiments were performed in order to understand the cycling capability of the  $MnO_2$ . Since ethanol-assisted  $MnO_2$  showed the best performance in the present study, the cycling experiment was performed galvanostatically at 200 mA/g, and the typical charge–discharge curves are shown in Fig. 7. The specific capacitance was found to be 205 F/g, which is very much comparable to that calculated from the CV studies.



Fig. 7 Galvanostatic cycling performance of  $MnO_2$  synthesized using ethanol and potassium permanganate at 200 mA/g in a 1 M  $Na_2SO_4$  aqueous electrolyte.

#### MnO<sub>2</sub>: SWNT composites: Supercapacitor studies

Typical TEM micrographs for the pure  $MnO_2$ , SWNTs, and the  $MnO_2$ :20 wt % SWNT composite are shown in Fig. 8. As can be seen from the figure, the mixture of SWNT and a- $MnO_2$  is fairly uniform. It is very important that the mixture of a- $MnO_2$  and SWNTs are homogeneous mainly because the electrical conductivity of the a- $MnO_2$  particles is considerably less when compared to the pure SWNTs. The main reason for the homogeneous mixture of the prepared composites is attributed to the in situ precipitation of a- $MnO_2$  over the entangled SWNTs.



Fig. 8 TEM micrographs for (a) pure MnO<sub>2</sub>, (b) pure SWNTs, and (c) MnO<sub>2</sub>:20 wt % SWNT composites.

The CV curves recorded at a scan rate of 2 mV/s for the pure  $a-MnO_2$  and the composite are shown in Fig. 9. The CV studies showed mirror-like replication below and above the zero line signifies that the system is completely reversible with an instant response upon the reversal of voltage. The specific capacitance calculated from the CV for the pure  $a-MnO_2$  was 202 F/g, while for the pure SWNT it was 22 F/g. Similar results have been observed in the neutral electrolytes such as KCl, LiCl, as well for both  $MnO_2$  and CNTs [30,39,40]. There has been little reasonable decrease in the specific capacitance values as expected when the CNT contents increased, the corresponding values for 5, 10, 20, and 40 wt % SWNTs are 195, 180, 162, and 151 F/g, respectively.



Fig. 9 The CVs recorded at a scan rate of 2 mV/s for pure a-MnO<sub>2</sub> and MnO<sub>2</sub>: 20 wt % composite in a 1 M  $Na_2SO_4$  aqueous electrolyte.

The long-cycle galvanostatic charge-discharge experiments were performed initially at a current density of 200 mA/g for initially few cycles and then ramped up to a high current density of 2 A/g, and the cycling performance is shown in Fig. 10. As can be seen from the figure, when the pure  $MnO_2$ , the pure SWNTs, and the composites were cycled at a high current density of 2 A/g, there was no major reduction in capacitance in the initial cycles for each system. However, the fading started to be very evident for some systems when cycled more than 100 times. It is important to note that the specific capacitance at initial cycles for some a-MnO<sub>2</sub>:SWNT composites (e.g., 5 and 10 wt % SWNTs) is a bit higher than that for the pure  $MnO_2$  at such high current. This is mainly due to improvement in the electronic conductivity of system because of the presence of the SWNTs and also entangled nanotubes because of the higher aspect ratio, which connects the  $MnO_2$  particles at the surfaces and in the interior electrodes. The fading of capacitance was found to be the largest for the pure  $MnO_2$  where the specific capacitance dropped to 10 % of the initial value after 500 cycles. Contrary to the pure MnO<sub>2</sub>, the pure SWNTs showed the maximum stability in cycling when cycled at 2 A/g, as expected. The first cycle specific discharge capacitance for the pure SWNT was found to be 45 F/g when cycled at 2 A/g, and after 750 cycles it was found to be 26 F/g with an efficiency of 81 %. The main reason for the above behavior for the SWNTs is attributed to the sole contribution of the double-layer formation at the electrode-electrolyte interface, which can be quickly charged and discharged.

In the earlier reports on high current capabilities for the a-MnO<sub>2</sub>:SWNT composites, the lack of long cycle performance led to a lot of uncertainties. As we can see from present studies, on the basis of just one cycle, the 5 wt % SWNTs showed the best performance even at a high current of 2 A/g. However, when cycled for more than 100 cycles, they showed a considerable fading in the specific discharge capacitance. Hence, it can be concluded that the presence of CNTs in a composite system improves the electronic conductivity and also reduces the stress induced because of cycling.

EIS is an excellent tool for elucidating complex electrode reactions and the Nyquist plots recorded for the pure a-MnO<sub>2</sub>, a-MnO<sub>2</sub>:10 wt % SWNTs, and a-MnO<sub>2</sub>:20 wt % SWNTs are shown as an inset in Fig. 10. The Nyquist plot typically consists of a high-frequency semicircle and a low-frequency spike. For pure MnO<sub>2</sub>, the low-frequency spike showed an inclination at an angle ~45°. Typically, the high-frequency semicircle is associated with two resistances: (1) the solution or electrolyte resistance (Re) and (2) the particle resistance (Rp). The total resistance in the pure a-MnO<sub>2</sub>, a-MnO<sub>2</sub>:10 wt % SWNTs, and a-MnO<sub>2</sub>:20 wt % SWNTs are 4.07, 2.51, and 1.72  $\Omega$ , respectively. The Re is almost invariant as can be seen from the Fig. 10 (inset), while there has been a decrease in the Rp with respect to the increase of SWNT content. This supports our argument that the presence of SWNTs



Fig. 10 Long-cycle performance of the pure MnO<sub>2</sub>, SWNT, and the composites. Inset: Nyquist plots recorded for the pure a-MnO<sub>2</sub>, a-MnO<sub>2</sub>:10 wt % SWNTs, and a-MnO<sub>2</sub>:20 wt % SWNTs.

indeed decreases the resistance of the system. Also, as can be seen from the inset of Fig. 10, the inclination angle of the low-frequency spike with respect to the X-axis is approaching 90° with the increase of the SWNT content, indicating a higher contribution of capacitance from EDLC phenomena. Another interesting aspect of this composite is the IR-drop in the pure  $MnO_2$  and its composites. During the initial cycles, there has been no obvious IR-drop observed for both the pure  $MnO_2$  and the composite. However, over a cycling period, the IR-drop becomes very prominent for the pure  $MnO_2$ , while there is no such behavior for the composite [37]. This is an important factor that governs a longer and stable performance for the  $MnO_2$ :SWNT composites [37].

#### MnO<sub>2</sub> and MnO<sub>2</sub>: SWNT composites as Li-ion battery electrode material

Interest in the use of oxide materials as anodes in Li-ion batteries has increased since the tin-based materials developed by Fuji film company in the late 1990s. Various other materials such as CoO, NiO, CuO, and MnO<sub>2</sub> were studied for their Li insertion/deinsertion properties.

TEM images of the different  $MnO_2$  used in the present study are shown in Fig. 11. The TEM micrograph of  $MnO_2$  shown in Fig. 11a was synthesized at RT by a simple precipitation technique using ethanol from a mixture of aqueous solutions of  $KMnO_4$  and  $MnSO_4$ . The micrographs shown in Figs. 11b,c are the  $MnO_2$  obtained by calcining the RT- $MnO_2$  shown in Fig. 11a at 300 and 500 °C, respectively. The RT- $MnO_2$  as discussed above has agglomerated nanostructures with plate-like morphology, which on subsequent calcination at higher temperatures (300 and 500 °C) form nanoparticles. The other form of  $MnO_2$  prepared hydrothermally is single-crystal nanorods as shown in the Fig. 11d. XRD studies revealed poor crystallinity of the RT- $MnO_2$ , while there is an appreciable increase for both the heat-treated and the hydrothermally formed  $MnO_2$ .



**Fig. 11** TEM images of the different  $MnO_2$  used in the present study as anode materials for Li-ion battery (a) RT-MnO<sub>2</sub> (b) calcined at 300 °C; (c) calcined at 500 °C and (d) hydrothermal reaction at 140 °C for 48 h. Inset of (d) is the HR-TEM fringes of the nanorods.

The electrochemical studied were performed for the  $MnO_2$  calcined at 500 °C and the  $MnO_2$  prepared hydrothermally for 48 h. The charge–discharge curves for the hydrothermally prepared  $MnO_2$  are shown in Fig. 12. There is a significant first cycle irreversible capacity mainly due to the disproportionate reaction of  $MnO_2$  to Mn and Li<sub>2</sub>O [24,41]. In further cycles, the main reaction is the alloying and dealloying of the Mn and Li as demonstrated from the equations below [24,41].

$$\begin{split} \mathrm{MnO}_{2} + 4\mathrm{Li}^{+} + 4\mathrm{e}^{-} &\leftrightarrow 2\mathrm{Li}_{2}\mathrm{O} + \mathrm{Mn} \\ 4\mathrm{Li} &\leftrightarrow 4\mathrm{Li}^{+} + 4\mathrm{e}^{-} \\ \mathrm{MnO}_{2} + 4\mathrm{Li} &\leftrightarrow 2\mathrm{Li}_{2}\mathrm{O} + \mathrm{Mn} \end{split}$$



Fig. 12 The charge-discharge curves for the hydrothermally prepared MnO<sub>2</sub> in the first cycle.

The cycling experiments were performed for the composite electrodes with two different conducting carbon additives, i.e., (i) SWNT and (ii) carbon black. The electrode prepared using SWNT as a conducting carbon showed improved specific capacity and cycling stability compared to that of the carbon black sample as evidenced from Fig. 13. This is mainly due to the higher electronic conductivity of the entangled SWNT which leads to an improved  $MnO_2$  particle–particle contact because of the high aspect ratio of SWNT bundles.



Fig. 13 The cycling performance of different  $MnO_2$  studied as anode materials for Li-ion batteries in a 1 M  $LiPF_6$ -based nonaqueous electrolyte cycled between 3–0.005 V.

#### V. SUBRAMANIAN et al.

#### CONCLUSIONS

Manganese oxides in different nanostructures were studied for two different promising applications, viz., SCs and Li-ion batteries. Forming composites with SWNTs showed improved electrochemical properties. The following salient conclusions can be made.

The hydrothermal method was successfully employed for the preparation of  $MnO_2$  with different nanoarchitectures by varying the reaction time.  $MnO_2$  nanostructures prepared hydrothermally at 140 °C for 6 h showed the best performance in the SC study with a specific capacitance of 168 F/g when cycled at a relatively high constant current density of 200 mA/g.

Different nanostructured manganese oxides have been synthesized by a simple precipitation technique at RT using different alcohols and potassium permanganate. The surface area of the synthesized manganese oxides ranges from 125 to 250 m<sup>2</sup>/g, and structures ranging from nanowhiskers to nanoparticles were produced depending upon the alcohol used. The synthesized manganese oxides showed excellent pseudocapacitance properties with a specific capacitance ~200 F/g for MnO<sub>2</sub> prepared using ethanol.

Long-cycle performance has been studied for the first time at a high current for the  $a-MnO_2$ :SWNTs composites. The composites were prepared using a simple RT precipitation technique involving KMnO<sub>4</sub>/ethanol and SWNTs. MnO<sub>2</sub>:20 wt % SWNT showed a very good cycling stability with a capacitance value ~140 F/g even when cycled galvanostatically at a very high current density of 2 A/g for more than 1000 cycles.

The hydrothermally synthesized  $MnO_2$  for 48 h at 140 °C showed a rod-like morphology with a diameter of ~30 nm and a length of a few microns. Utilizing SWNT as a conducting additive showed an improved electrochemical performance in both the reversible capacity and the cyclability.

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