

# Composite electrodes for electrochemical supercapacitors

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**Abstract** Manganese dioxide and Ag-doped manganese dioxide powders were prepared by a chemical precipitation method using  $\text{KBH}_4$  as a reducing agent. The powders were studied by X-ray analysis, thermogravimetry, and electron microscopy. Composite electrodes for electrochemical supercapacitors (ES) were fabricated by impregnation of slurries of the precipitated powders and carbon black into porous nickel foam current collectors. In the composite electrodes, carbon black nanoparticles formed a secondary conductivity network within the nickel foam cells. Obtained composite electrodes, containing manganese dioxide and 20 wt% carbon black with total mass loading of  $50 \text{ mg cm}^{-2}$ , showed a capacitive behavior in the 0.5 M  $\text{Na}_2\text{SO}_4$  solutions. The capacitive behavior of the composite electrodes can be improved by mixing of manganese dioxide and carbon black in solutions or using Ag-doped manganese dioxide powders. The highest specific capacitance (SC) of  $150 \text{ F g}^{-1}$  was obtained at a scan rate of  $2 \text{ mV s}^{-1}$ . The electrodes showed good cycling behavior with no loss in SC during 1,000 cycles.

**Keywords** Manganese dioxide · Supercapacitor · Carbon black · Composite · Silver · Nickel foam

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## 1 Introduction

Electrochemical supercapacitors based on  $\text{MnO}_2$  electrode materials are currently attracting significant interest due to the high SC obtained using environmentally friendly aqueous electrolytes [1–3] and low cost of  $\text{MnO}_2$ . The SC of  $\text{MnO}_2$  is believed to be predominantly due to pseudocapacitance as a result of redox processes associated with the surface adsorption of cations or incorporation of cations into the oxide structure [4–7]:



where  $\text{C}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{H}^+$ . Equation 1 indicates that high ionic and electronic conductivity of the active material is necessary to utilize a high SC.

A complicating factor in the application of manganese dioxide for ES is low electronic and ionic conductivity of  $\text{MnO}_2$ . Thin manganese dioxide films ( $\sim 1 \mu\text{g cm}^{-2}$ ) exhibited ideal capacitive behavior [8] in a voltage window of 0.9 V and showed an SC of  $\sim 700 \text{ F g}^{-1}$ . Previous investigations [9] showed that the capacitance decreased from 400 to  $177 \text{ F g}^{-1}$  when the film mass increased from 50 to  $200 \mu\text{g cm}^{-2}$ . It is important to note that the manufacturing of efficient ES requires much higher material loadings. The SC of  $72 \text{ F g}^{-1}$  in the 0.1 M  $\text{K}_2\text{SO}_4$  electrolyte was reported [10] for composite manganese dioxide–acetylene black electrodes with material loading in the range of  $10\text{--}40 \text{ mg cm}^{-2}$ . The SC values obtained are much lower than the theoretical SC [11] of  $1,370 \text{ F g}^{-1}$ .

Numerous investigations have been conducted with the objective to utilize a high SC of  $\text{MnO}_2$  in ES. Impressive progress has already been made in the field of the fabrication of nanostructured porous  $\text{MnO}_2$  materials with high surface area [12–14]. Many successful efforts have been made in the area of the fabrication of composite materials,

where higher electronic conductivity has been achieved by the use of conductive additives, such as carbon black and carbon nanotubes [2, 15–17]. Other studies have been focused on the fabrication of doped manganese dioxide with improved conductivity [18].

Recent studies showed that the conductivity of lithium manganese dioxide can be increased significantly using 1–8 wt% Ag additives [19]. The use of Ag-doped lithium manganese dioxide enabled improved performance of batteries [19]. A similar increase in the electronic conductivity of Ag-doped RuO<sub>2</sub> was reported [20]. The investigation of Ag-doped RuO<sub>2</sub> for application in ES [20] showed much higher SC when compared to the SC of undoped RuO<sub>2</sub>. Therefore, it would be important to prepare and investigate Ag-doped MnO<sub>2</sub> for application in ES.

The aim of this investigation was the fabrication of nanostructured composite manganese dioxide electrodes for application in ES. The results presented below indicate that the use of nanostructured manganese dioxide and nickel foam current collectors enabled good capacitive behavior of composite electrodes at relatively high material loading. The influence of processing conditions, Ag-doping, and electrode composition on the capacitive behavior has been investigated.

## 2 Experimental procedures

KBH<sub>4</sub>, KMnO<sub>4</sub>, and AgNO<sub>3</sub> were purchased from Aldrich. Manganese dioxide was prepared by a chemical reduction method using aqueous solutions [21, 22]. Precipitation was performed by a slow addition of 10 mL of 0.25 M KBH<sub>4</sub> to 50 mL of 0.1 M KMnO<sub>4</sub> solution. The pH of the KBH<sub>4</sub> solution was adjusted to pH = 11 using KOH. HNO<sub>3</sub> was added to KMnO<sub>4</sub> solutions during the reduction reaction to maintain constant a pH of 3 or 6.

KBH<sub>4</sub> has also been utilized as a reducing agent for the precipitation of Ag and Ag-doped manganese dioxide powders. Precipitation was performed at a constant pH = 3 by a slow addition of 10 mL of 0.25 M KBH<sub>4</sub> (pH = 11) to 50 mL of 0.01 M AgNO<sub>3</sub> solution or to mixed 0.1 M KMnO<sub>4</sub> and 0.005–0.1 M AgNO<sub>3</sub> solutions. In all the experiments described earlier, stirring was continued during 1 h after precipitation.

Carbon black (average particle size 15 nm, CABOT) was used as a conductive additive for the fabrication of composite electrodes. Two methods were used for mixing of manganese dioxide powders with carbon black. In the method A, the precipitated powders were washed with water, dried, and mixed with carbon black. In the method B, carbon black was added to the suspension of precipitated manganese dioxide and the mixture was stirred during 1 h, washed with water and dried. The powders prepared using

methods A and B were used for the preparation of slurries and impregnation of current collectors.

INCOFOAM<sup>®</sup> current collectors with a volumetric porosity of 95% were made by Vale Inco using the carbonyl technology [23]. The procedure for the slurry preparation and impregnation of the INCOFOAM<sup>®</sup> was similar to that described in Ref. [23]. The total mass of manganese dioxide and carbon black in the composite electrodes was 50 mg cm<sup>-2</sup>. The impregnated INCOFOAM<sup>®</sup> was roller pressed to ~20% of initial thickness [23].

Electron microscopy investigations were performed using a JEOL 2010F transmission electron microscope (TEM) and a JEOL JSM-7000F scanning electron microscope (SEM). The X-ray diffraction (XRD) studies were performed using a powder diffractometer (Nicolet I2, monochromatized CuK<sub>α</sub> radiation) at a scanning speed of 0.5 ° min<sup>-1</sup>. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in air at a heating rate of 5 °C min<sup>-1</sup> using a thermoanalyzer (Netzsch STA-409). Chemical analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista-PRO, Varian).

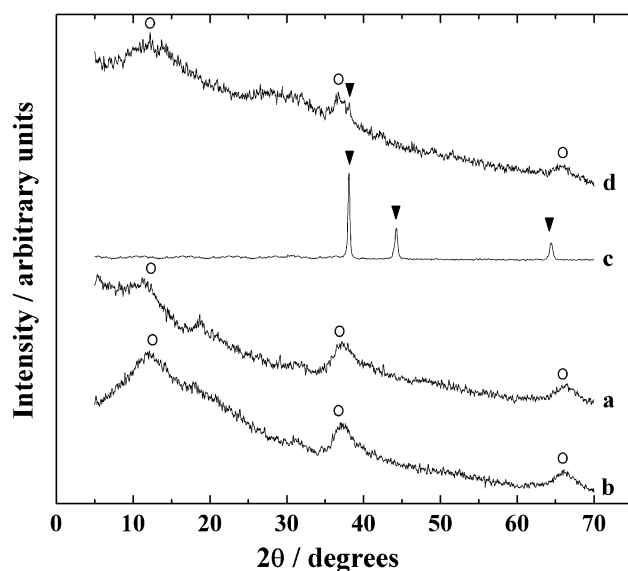
Capacitive behavior of the composite electrodes was studied using a potentiostat (PARSTAT 2273, Princeton Applied Research) controlled by a computer using a PowerSuite electrochemical software. Electrochemical studies were performed using a standard three-electrode cell containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution, degassed with purified nitrogen gas. The counter electrode was a platinum gauze, and the reference electrode was a standard calomel electrode (SCE). Cyclic voltammetry (CV) studies within a potential range of 0–0.9 V versus SCE were performed. The SC was calculated using half the integrated area of the CV curve to obtain the charge (*Q*), and subsequently dividing the charge by the total mass (*m*) of the composite material impregnated into nickel foam, and the width of the potential window ( $\Delta V$ ):

$$C = Q/m\Delta V \quad (2)$$

The complex impedance  $Z^* = Z' - iZ''$  for the composite electrodes was investigated in the frequency range of 0.1 Hz–100 kHz at a voltage of 10 mV.

## 3 Results and discussion

Figure 1 shows X-ray diffraction patterns of powders prepared from different solutions. The X-ray diffraction patterns of the powders prepared from the 0.1 M KMnO<sub>4</sub> solutions showed very small peaks of manganese dioxide. The peaks are very broad and indicate small crystallite size. The X-ray diffraction peaks (Fig. 1a, b) can be attributed to birnessite (JCPDS file 87-1497) structure. The birnessite

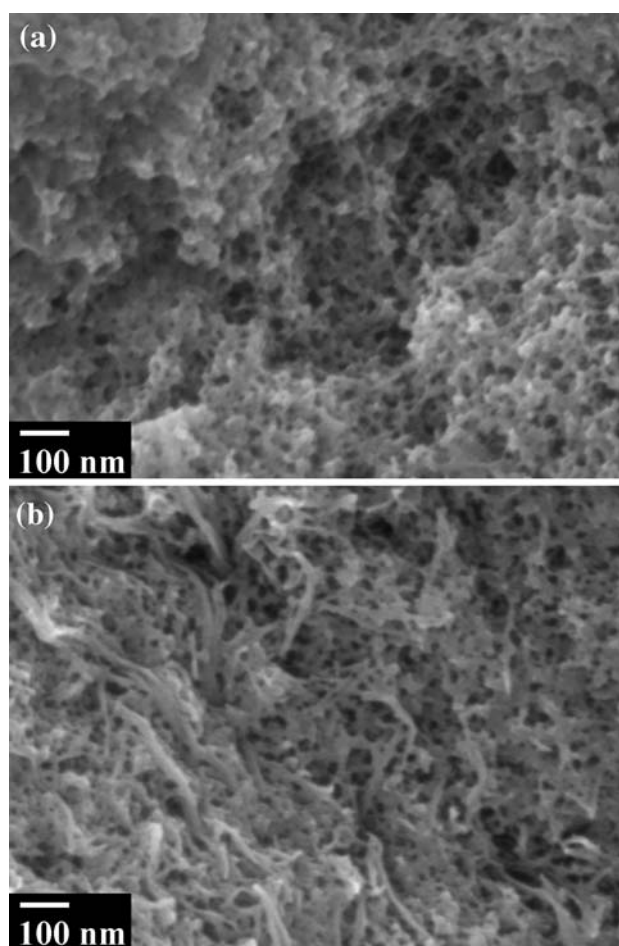


**Fig. 1** XRD patterns of powders prepared from 0.1 M  $\text{KMnO}_4$  solutions at (a) pH = 3 and (b) pH = 6, powders prepared from (c) 0.01 M  $\text{AgNO}_3$  solution at pH = 3 and (d) mixed 0.1 M  $\text{KMnO}_4$  and 0.1 M  $\text{AgNO}_3$  solution at pH = 3

phase has near  $\text{MnO}_2$  composition with manganese oxidation state in the range of 3.6–3.8 [24], which can be described by the formula  $\text{K}_x\text{MnO}_{2+y}(\text{H}_2\text{O})_z$ . It is suggested that as-precipitated powders also contained an amorphous phase. The results obtained are in agreement with literature data for powders prepared under similar conditions [21]. Chemical analysis showed that the powders precipitated from the 0.1 M  $\text{KMnO}_4$  solutions at pH 3 and 6 contained K with the K/Mn atomic ratio of 0.09 and 0.10, respectively.

$\text{KBH}_4$  has been also investigated as a common reducing agent for the co-precipitation of manganese dioxide and Ag and formation of Ag-doped manganese dioxide. According to the literature [25], silver metal nanoparticles can be prepared from  $\text{AgClO}_4$  solutions using sodium borohydride as a reducing agent. The results of our investigation showed that Ag particles can be precipitated from the  $\text{AgNO}_3$  solutions at pH = 3 using  $\text{KBH}_4$  as a reducing agent. Precipitate obtained showed X-ray diffraction peaks (Fig. 1c) of Ag corresponding to the JCPDS file 4-783.  $\text{KBH}_4$  has been further used for co-precipitation of manganese dioxide and Ag from mixed  $\text{KMnO}_4$  and  $\text{AgNO}_3$  solutions. X-ray diffraction pattern of the samples showed small peaks of manganese dioxide and Ag (Fig. 1d). Chemical analysis of the powders precipitated at pH 3 from the 0.1 M  $\text{KMnO}_4$  solutions containing 0.005, 0.01, 0.020 and 0.1 M  $\text{AgNO}_3$  showed Ag/Mn atomic ratio of 0.04, 0.07, 0.15 and 0.29, respectively.

SEM studies of the powders (Fig. 2a, b), prepared from the 0.1 M  $\text{KMnO}_4$  solutions at pH 3 and 6, showed that the powders contained nanoparticles of irregular shape and



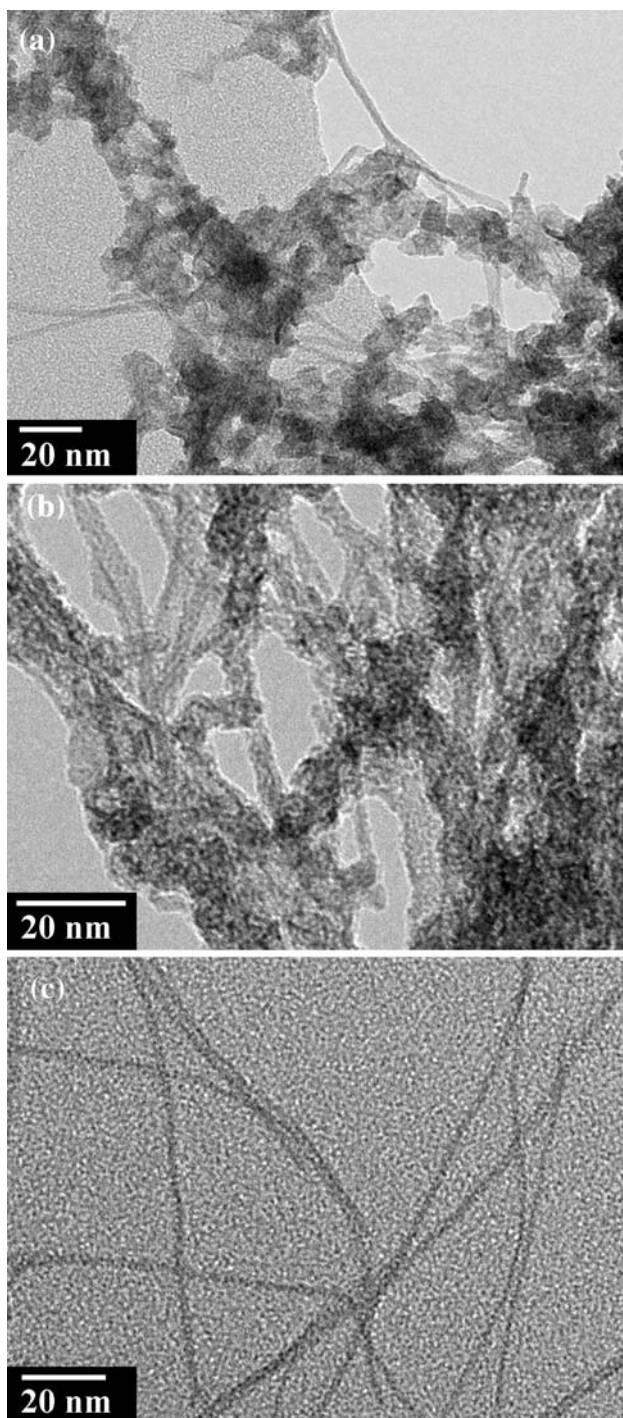
**Fig. 2** SEM images of powders prepared from 0.1 M  $\text{KMnO}_4$  solutions at (a) pH = 3 and (b) pH = 6

nanofibers. Some nanofibers formed bundles, containing several nanofibers. The samples prepared at pH 6 showed much larger content of fibrous particles.

TEM studies (Fig. 3) showed that powders prepared at pH = 3 contained nanoparticles with a particle size of 5–10 nm and nanofibers with diameter of  $\sim 5$  nm and length of 0.1–0.5  $\mu\text{m}$ . It was found that the nanofibers are not individual crystals, but are composed of small nanoparticles with a diameter  $< 5$  nm. The powders prepared at pH = 6 showed significant agglomeration and larger particle size. Moreover, the powders contained large amount of bundles of individual fibrous particles. Figure 3c shows typical image of individual nanofibers prepared at pH 6. The agglomeration of individual particles and larger content of fibers, which formed bundles, is in agreement with the lower surface area reported for the powders prepared at pH = 6 [22].

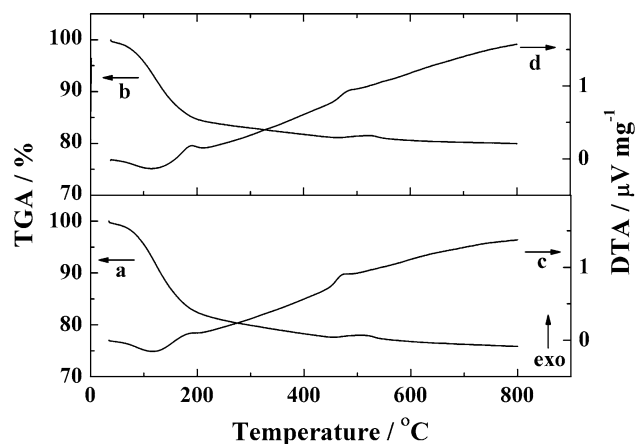
TGA studies (Fig. 4) of the powders showed weight loss mainly below 200  $^\circ\text{C}$  related to dehydration. The corresponding broad endotherms were observed at  $\sim 120$   $^\circ\text{C}$  in the DTA data. Small exotherms at  $\sim 200$   $^\circ\text{C}$  can be





**Fig. 3** TEM images of powders prepared from 0.1 M  $\text{KMnO}_4$  solutions at (a) pH = 3 and (b, c) pH = 6

attributed to crystallization of an amorphous phase. The weight loss at higher temperatures and small exotherm at  $\sim 480^\circ\text{C}$  can be related to the reduction of manganese dioxide and formation of other manganese oxide phases [26, 27]. The total weight loss at  $800^\circ\text{C}$  was found to be 24.2 and 20.0 wt%, for the samples precipitated at pH 3 and 6, respectively.

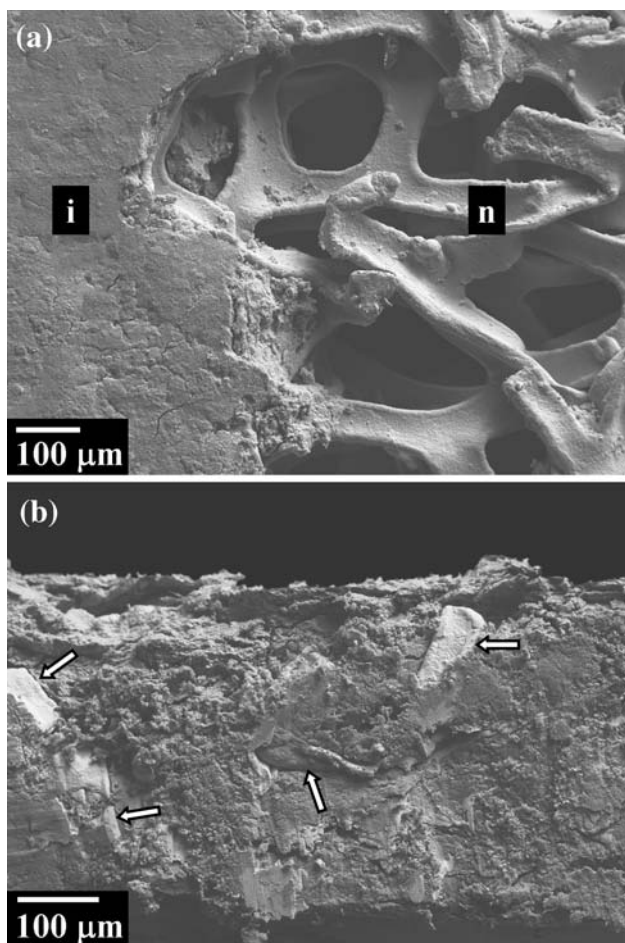


**Fig. 4** (a, b) TGA and (c, d) DTA data for powders prepared from 0.1 M  $\text{KMnO}_4$  solutions at (a, c) pH = 3 and (b, d) pH = 6

The powders of manganese dioxide and composite powders were used for the impregnation of Ni foam current collectors. It is important to note that porous Ni foams are currently used in the industry as advanced current collectors for batteries [23]. In the batteries, Ni foams contain active material within their light weight web. Ni foams provide structural strength, improved electrolyte access to the active material, high electronic conductivity and reduced contact resistance. Electrodes for batteries are produced by pasting a slurry of active material into a porous nickel foam, followed by impregnation, drying, and calendaring. The high porosity and large pore size of Ni foam allows for easy impregnation of the active material slurry into the porous current collectors. However, the increase in foam porosity resulted in reduced electronic conductivity [23]. This problem has been addressed by the use of conductive additives [23], which formed a secondary conductivity network within the nickel foam cells.

Using a similar approach, a slurry containing manganese dioxide, carbon black and binder [23] was impregnated into the INCOFOAM<sup>®</sup> for the fabrication of electrodes of ES. The SEM images of the surfaces of impregnated and non-impregnated areas (Fig. 5a) and cross section of impregnated area (Fig. 5b) of the roller pressed electrode indicated that active material filled the voids in the nickel foam.

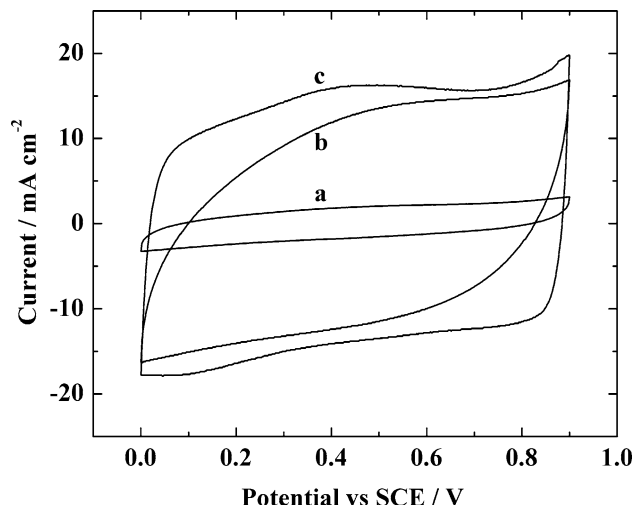
The capacitive behavior of the composite electrodes was studied using cyclic voltammetry. Figure 6 shows typical CVs in the 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte solutions in the potential range of 0–0.9 V versus SCE. The composite electrodes exhibited capacitive-like current–potential response. It is clear from Fig. 6 that there are no redox peaks in the range between 0 and 0.9 V. The composite electrodes, containing powders prepared by method A, showed significantly lower capacitance for manganese dioxide precipitated at pH = 6, as indicated by lower area



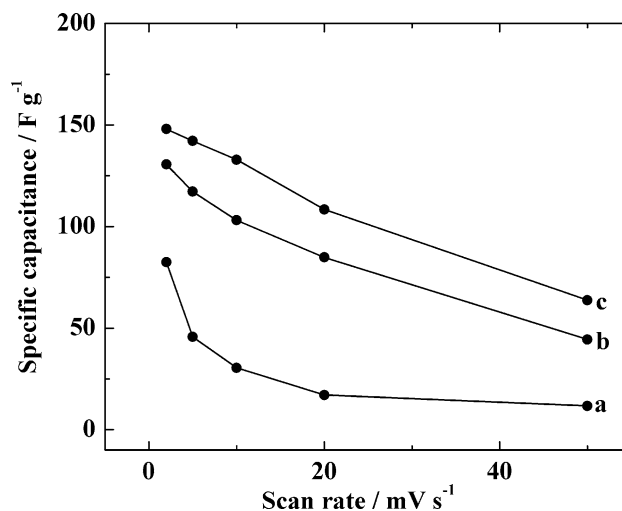
**Fig. 5** SEM images of (a) surface of impregnated (i) and non-impregnated (n) area (b) cross section of impregnated area of the INCOFOAM<sup>®</sup> after pressing. The slurry for impregnation contained manganese dioxide prepared at pH = 3 and mixed with 20 wt% of carbon black using method B. Arrows show INCOFOAM<sup>®</sup>

of corresponding CV plotted in Fig. 6. The different capacitive behaviors of the composite materials can be attributed to the difference in particle morphology. Turning again to the electron microscopy data presented earlier, it is suggested that the formation of fibrous particles and agglomeration of the individual fibers can result in reduced surface area, which, in turn, can result in lower SC. It is also suggested that lower content of fibrous particles in powders prepared at pH = 3 can facilitate mixing of the particles with carbon black and impregnation of nickel foam.

The fabrication of efficient electrodes with high SC requires good mixing of the components and uniform distribution of a conductive phase in the matrix of manganese dioxide. The shape of the CV, obtained using powder precipitated at pH = 3 and mixed with carbon black by method A, deviates significantly from ideal box shape. In contrast, the composite electrode prepared at pH = 3 by



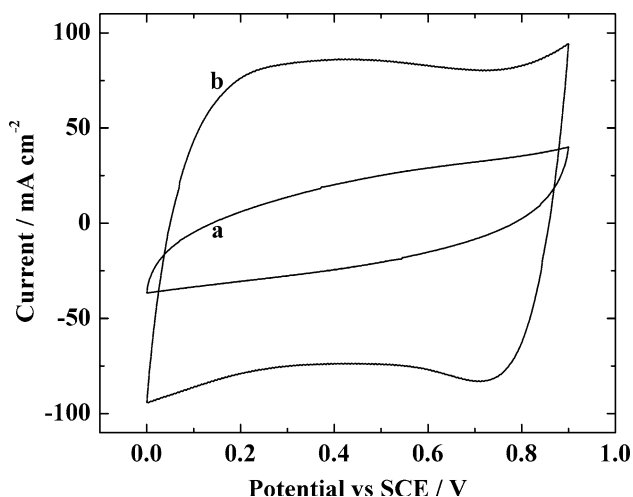
**Fig. 6** CVs at a scan rate of 2 mV s<sup>-1</sup> for composite electrodes containing manganese dioxide prepared at (a) pH = 6 and (b, c) pH = 3 and mixed with 20 wt% of carbon black using methods (a, b) A and (c) B



**Fig. 7** SC versus scan rate for composite electrodes containing (a, b) undoped manganese dioxide and (c) Ag-doped manganese dioxide (Ag/Mn atomic ratio of 0.07) prepared at pH = 3 and mixed with 20 wt% of carbon black using methods (a, c) A and (b) B

method B showed improved shape of the voltage window and higher SC. The SCs calculated from CVs obtained at different scan rates are shown in Fig. 7. The increase in scan rate resulted in a decrease in SC. Significantly higher SCs were obtained for composites prepared using method B, compared to method A. The difference can be attributed to better mixing of the individual components, which can provide improved conductivity of the composite material.

The SC of the composite materials can be improved using Ag additives. Figure 8 compares CVs for the manganese dioxide powder without Ag and powder containing

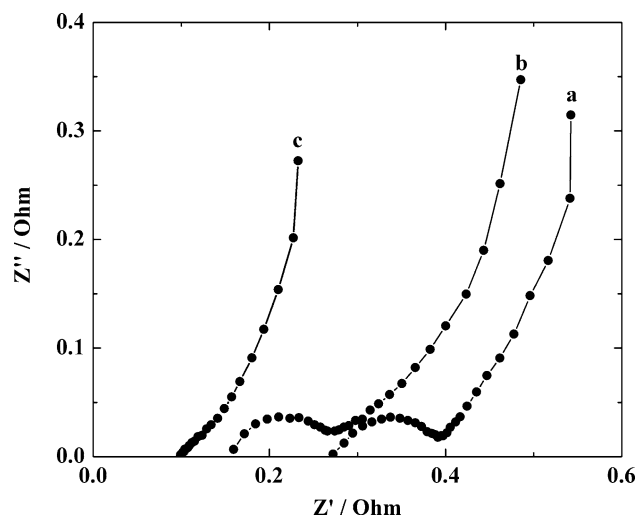


**Fig. 8** CVs at a scan rate of  $10 \text{ mV s}^{-1}$  for composite electrodes containing (a) undoped manganese dioxide and (b) Ag-doped manganese dioxide with Ag/Mn atomic ratio of 0.07 prepared at  $\text{pH} = 3$  and mixed with 20 wt% carbon black using method A

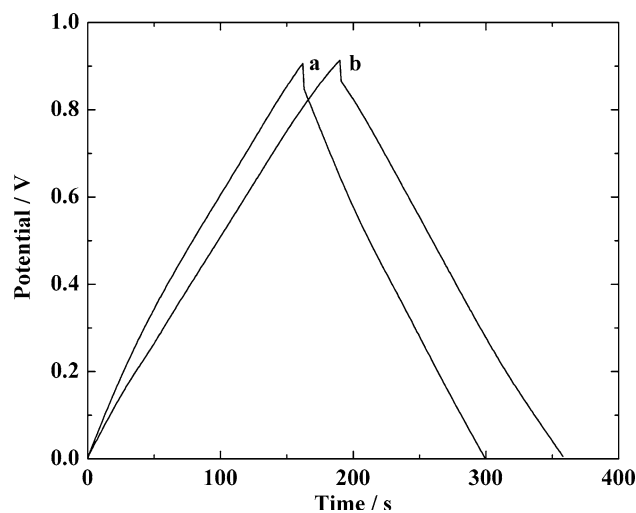
Ag with Ag/Mn atomic ratio of 0.07, mixed with carbon black using method A. The results indicate that Ag additive can improve the capacitive behavior of the composite material, as indicated by the improved shape of CV (Fig. 8) and higher SC (Fig. 7). The highest SC of  $150 \text{ F g}^{-1}$  was obtained at a scan rate of  $2 \text{ mV s}^{-1}$ . The SC decreased with increasing scan rate due to the diffusion limitations in pores of the composite electrodes. It is suggested that the co-precipitation of manganese dioxide and Ag using  $\text{KBH}_4$  as a common reducing agent can result in composite materials with improved conductivity and higher SC. However, the SC of doped manganese dioxide without carbon black was lower than the SC of manganese dioxide-carbon black composite prepared by method A.

Figure 9 shows complex impedance of the composite electrodes measured at a voltage of 10 mV. The composites containing Ag-doped manganese dioxide containing carbon black and undoped material prepared by method B showed lower resistance compared to the undoped composite prepared by method A. The equivalent circuit of ES was discussed in [28]. The high frequency value of the real part of complex impedance has been used for the estimation of the equivalent series resistance of the electrodes. The Ag-doped manganese dioxide-carbon black composites and undoped composites, prepared using method B, showed a resistance of 0.1 and  $0.16 \Omega \text{ cm}^{-2}$ , respectively, which is lower than the resistance of  $0.27 \Omega \text{ cm}^{-2}$  of the composite prepared by method A.

Figure 10 shows charge-discharge behavior of the Ag-doped composite electrodes and undoped electrodes, prepared by method B in the potential range of 0–0.9 V at a current density of  $40 \text{ mA cm}^{-2}$ . The charge and discharge curves are almost linear; however, initial voltage drop was



**Fig. 9** Nyquist plot of the complex impedance  $Z^* = Z' - iZ''$  for the composite electrodes containing manganese dioxide prepared at  $\text{pH} = 3$  and mixed with 20 wt% of carbon black using method (a) A and (b) B and Ag-doped (Ag/Mn atomic ratio of 0.07) manganese dioxide (c) prepared by method A

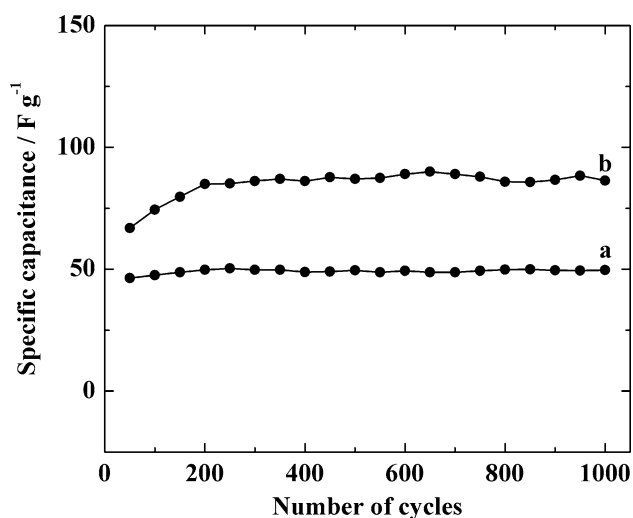


**Fig. 10** Charge-discharge behavior at a current density of  $40 \text{ mA cm}^{-2}$  for composite electrodes containing manganese dioxide prepared at  $\text{pH} = 3$  and mixed with 20 wt% of carbon black for (a) undoped material prepared by method B and (b) Ag-doped (Ag/Mn atomic ratio of 0.07) material prepared by method A

observed in the discharge curve. This can be attributed to electrode resistance, resulting from diffusion limitations in pores. It is suggested that the further optimization of electrode composition and microstructure will result in reduced resistance and improved capacitive behavior.

Figure 11 shows cycling behavior of the composite electrodes in the 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution. The electrodes showed initial increase in SC during first 200 cycles. A similar increase in SC was observed [9] for thin





**Fig. 11** Cycling behavior at a scan rate of  $50 \text{ mV s}^{-1}$  for composite electrodes containing manganese dioxide prepared at  $\text{pH} = 3$  and mixed with 20 wt% of carbon black for (a) undoped material prepared by method B and (b) Ag-doped (Ag/Mn atomic ratio of 0.07) material prepared by method A

films and was attributed to changes in microstructure and oxidation of non-stoichiometric manganese dioxide. However, no loss in SC (Fig. 11) was observed during the 1,000 cycles.

#### 4 Conclusions

Manganese dioxide and Ag-doped manganese dioxide nanoparticles were prepared by a chemical precipitation method using  $\text{KBH}_4$  as a reducing agent. Composite electrodes for ES were fabricated by impregnation of slurries of the manganese dioxide and carbon black into porous nickel foam current collectors. The composite electrodes with a total mass loading of  $50 \text{ mg cm}^{-2}$  showed a capacitive behavior in the  $0.5 \text{ M Na}_2\text{SO}_4$  solutions. The manganese dioxide prepared at  $\text{pH} = 3$  and 6 showed difference in particle morphology, which can explain the higher SC observed for powders prepared at  $\text{pH} = 3$ . The capacitive behavior of the composite electrodes can be improved by mixing of manganese dioxide and carbon black in solutions or using Ag-doped manganese dioxide powders. The highest SC of  $150 \text{ F g}^{-1}$  was obtained at a scan rate of  $2 \text{ mV s}^{-1}$ . The electrodes showed good cycling behavior with no loss in SC during 1,000 cycles.

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