镧掺杂的二氧化锰/碳纳米管电化学超级电容器复合电极

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摘要: 尽管在二氧化锰/多壁碳纳米管($\text{MnO}_2/\text{MWCNTs}$)上获得了较高的比电容, 低电导率仍是制约 MnO_2 负载量或膜厚度提高的主要障碍. 另一个问题是 $\text{MnO}_2/\text{MWCNTs}$ 的循环稳定性远低于活性炭. 所以截止到目前这一新型材料的应用仍然受到很大的限制. 本文采用原位还原的方法制备镧掺杂二氧化锰/多壁碳纳米管电化学超级电容器复合电极材料. 分别通过透射电镜(TEM)、扫描电镜(SEM)、X射线衍射(XRD)和傅里叶变换红外(FTIR)光谱等技术对这些复合材料的形貌与结构进行了分析. 采用循环伏安法、恒电流充放电法和交流阻抗法对其进行了电化学性能的研究. 研究表明, 通过还原 MnO_4^- 可以在 MWCNTs 上形成 La 掺杂 MnO_2 复合材料. La 掺杂降低了复合电极的电阻, 这是因为 La 的引入可以增大 MnO_2 的晶格缺陷, 从而提高材料的电导率以及电极的电化学性能. 因此 La 掺杂是克服 MnO_2 本征导电性差的有效途径之一. 掺杂 La 可以在不增大电极电阻的情况下提高 MnO_2 的负载量或膜厚度. La 掺杂的更重要的作用是使以 $\text{MnO}_2/\text{MWCNTs}$ 作电极的对称电化学超级电容器的循环性能得到显著改善. 此外, La 掺杂也使复合电极的比电容得到一定程度的提高.

关键词: 超级电容器; 多壁碳纳米管; 镧; 二氧化锰; 赝电容

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Lanthanum Doped Manganese Dioxide/Carbon Nanotube Composite Electrodes for Electrochemical Supercapacitors

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Abstract: Although higher specific capacitances have been achieved for manganese dioxide/multi-walled carbon nanotubes ($\text{MnO}_2/\text{MWCNTs}$), the low conductivity of MnO_2 is still the main obstacle in increasing its loading or film thickness. Another problem is that the cycling stability of $\text{MnO}_2/\text{MWCNTs}$ is much lower than that of activated carbon electrodes. Therefore, this new type of electrode material is still limited in application until now. In this paper, lanthanum doped $\text{MnO}_2/\text{MWCNTs}$ composites were prepared by an *in situ* redox method. The surface morphology and phase structure of the as-prepared samples were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectrometry. The electrochemical properties were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS). The La-doped MnO_2 could be formed on the MWCNTs by the reduction of MnO_4^- . The resistance of the composite electrodes decreased because La doping increases the number of imperfections in the MnO_2 lattice, which improves the electrical conductivity and the electrochemical activity of the electrode. La doping is, therefore, an effective way to overcome the intrinsic low electric conductivity of MnO_2 , which facilitates an increase in the loading or the film thickness of MnO_2 without increasing electrode resistance. The major effect of La doping is a significant improvement in the charge/discharge

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cycling performance of a symmetric electrochemical supercapacitor with electrodes composed of $\text{MnO}_2/\text{MWCNTs}$. The specific capacitance of the composite electrodes was improved by La doping.

Key Words: Supercapacitor; Multi-walled carbon nanotube; Lanthanum; Manganese dioxide; Pseudocapacitance

1 Introduction

Electrochemical supercapacitors (ECs) are becoming attractive electrical storage devices in computers, power electronics, and electric vehicles for providing transiently high power.¹⁻³ ECs can be classified into two categories, depending on the energy storage mechanism. One is electrical double layer capacitors (EDLCs), in which activated carbons with high surface area are used as electrode material.¹⁻⁴ The other category is pseudocapacitors, in which fast and reversible Faraday reactions are utilized for charge storage. Metal oxides and conducting polymers are examples of pseudo-capacitive active materials.¹

An active electrode material with high capacitive performance is indispensable to develop an advanced supercapacitor device. Recently, metal oxide-carbon nanotubes (CNTs) composites, such as RuO_2/CNTs , NiO/CNTs , MnO_2/CNTs , have been attracting interest by taking advantage of the excellent electrical conductivity and chemical stability of CNTs and the high capacitance of metal oxides.^{5,6} Among them, MnO_2/CNTs composite has attracted much attention from both the academic and industrial fields due to its high specific capacitance, environmentally friendliness, and cost effectiveness.⁷

Although higher specific capacitances have been achieved on MnO_2/CNTs , the low conductivity of MnO_2 is still the main obstacle for increasing the loading of MnO_2 or the thickness of MnO_2 films.⁸ Another problem is that the cycling stability of MnO_2/CNTs is much lower than that of the activated carbon electrodes,⁹ so that this new type of electrode materials is still limited in applications until now.

Recently, it has been reported that lanthanum has obvious influence on the capabilities of many materials.^{10,11} However, little attention has been paid on the composites of La-doped MnO_2/CNTs .

In this work we have synthesized and employed La-doped $\text{MnO}_2/\text{MWCNTs}$ composites as electrodes for electrochemical capacitors, and electrochemical performances have been investigated. It was demonstrated that La doping led to significant improvements in specific capacitance and cycling stability in a symmetric two-electrode capacitor. Moreover, doping MnO_2 with La is an effective method to overcome the intrinsic low conductivity of MnO_2 , which facilitates the increase of the loading or thickness of MnO_2 films without raising the electrode resistance.

2 Experimental

Commercial multi-walled carbon nanotubes (MWCNTs) (Chengdu Institute of Organic Chemistry) were used to prepare

$\text{MnO}_2/\text{MWCNTs}$ and $\text{La-MnO}_2/\text{MWCNTs}$ composites. The MWCNTs were refluxed in a mixture of concentrated sulfuric acid and nitric acid (3:1, *V/V*) for 30 min, and then washed to neutral using deionized water and dried in an electric oven.

The $\text{MnO}_2/\text{MWCNTs}$ composites were directly synthesized by a redox reaction between the MnO_4^- and pretreated MWCNTs.¹² Firstly, 0.94 g KMnO_4 (99.5%) was dissolved into distilled water to form $0.1 \text{ mol} \cdot \text{L}^{-1}$ solution and heated to 70°C . Then 0.3 g pretreated MWCNTs was added into the KMnO_4 solution. The mixture was stirred at 70°C until the purple color faded away. The $\text{MnO}_2/\text{MWCNTs}$ composite suspension was filtered, washed, and dried at 100°C for 24 h in a vacuum oven.

MWCNTs supported La-MnO_2 ($\text{La-MnO}_2/\text{MWCNTs}$) composites were prepared by a similar method with adding $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (98.0%) and pretreated MWCNTs into the KMnO_4 solution. Several samples with different La:Mn atomic ratios (0.2:9.8, 0.5:9.5, 1:9, 1.5:8.5, 2:8) were prepared, and were marked as $\text{La-MnO}_2(0.2:9.8)/\text{MWCNTs}$, $\text{La-MnO}_2(0.5:9.5)/\text{MWCNTs}$, $\text{La-MnO}_2(1:9)/\text{MWCNTs}$, $\text{La-MnO}_2(1.5:8.5)/\text{MWCNTs}$, and $\text{La-MnO}_2(2:8)/\text{MWCNTs}$, respectively.

The crystallographic structures of the materials were determined by powder X-ray diffraction (XRD) on a diffractometer (D/MAX-IIIC, Rigaku) using Cu K_α radiation ($\lambda=0.15406 \text{ nm}$). The morphology of the composites was examined using a transmission electron microscope (TEM, Philips F-20 TECNAI G², 200 kV). Surface morphological images of the carbon nanotubes were taken by a scanning electron microscope (S-800, Hitachi High-Technologies Co., Japan). Infrared (IR) spectroscopic analysis was carried out using an AVATAR 360 Fourier transform infrared (FT-IR) spectrometer (KBr pellet, wave-number range, $1000\text{--}4000 \text{ cm}^{-1}$).

The electrical conductivity of the composites was measured by ac impedance method on PARSTAT 2273 controlled by a computer. Disk samples were prepared by pressing the powder in a die under 20 MPa to ensure that dense samples were formed.

The active materials, carbon black, and 6% of polytetrafluoroethylene (PTFE) emulsion were uniformly mixed by a mortar and pestle with a ratio of 80:15:5. The mixtures were then rolled to form uniform membranes, and dried at 60°C . The membranes were cut into circular pieces ($\sim 0.5 \text{ cm}^2$) and pressed onto nickel foam to form working electrodes.

The electrochemical properties of the $\text{MnO}_2/\text{MWCNTs}$ and $\text{La-MnO}_2/\text{MWCNTs}$ composites were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy

py (EIS) in three-electrode cells using a PARSTAT 2273 electrochemical station (Princeton applied research Co., Ltd., USA). A Hg/Hg₂SO₄ (saturated K₂SO₄, 0.6151 V *versus* normal hydrogen electrode (NHE)) standard electrode was used as reference electrode. Ni foam was used as counter electrode. The measurements were carried out in 0.1 mol·L⁻¹ Na₂SO₄ (99.0%) aqueous electrolyte with pH 5.4 at room temperature. Charge/discharge cycle tests were performed using a battery testing system (BTS50V50mA, Neware Electronic Co. Ltd.) at different constant current densities. Galvanostatic charge/discharge cycling performances at a constant current of 100 mA·g⁻¹ were investigated for two- and three-electrode systems, respectively.

3 Results and discussion

3.1 Structural characterization

Fig.1(a, b, c) shows the TEM images of the acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composites. It is observed that the diameter of the acid-treated

MWCNTs is around 20 nm and the wall of MWCNTs is smooth. The synthesized products of MnO₂/MWCNTs and La-MnO₂(1:9)/MWCNTs were composed of fibrils of 30 nm in diameter, slightly bigger than the acid-treated MWCNTs. Fig.1 (d) gives the SEM image of La-MnO₂(1:9)/MWCNTs. Energy dispersive X-ray spectra (EDX) in Fig.1(f, g) confirmed the existence of La in the composites. In addition, the K peak in Fig.1 (e, f, g) is attributed to the charging mechanism of MnO₂ with K⁺ by the following reaction:¹³

In a pH neutral solution, the reaction between MWCNTs and MnO₄⁻ is:¹⁴

Thus, MnO₄⁻ was reduced by MWCNTs.

The conductivity of La-MnO₂(1:9)/MWCNTs is 1.1×10⁻³ S·cm⁻¹. It is higher than that of the MnO₂/MWCNTs composite (4.9×10⁻⁴ S·cm⁻¹). The enhancement to the electrical conductivity of the composites is due to the introduction of lanthanum

Fig.1 TEM images of (a) acid-treated MWCNTs, (b) MnO₂/MWCNTs, (c) La-MnO₂(1:9)/MWCNTs; (d) SEM image of La-MnO₂(1:9)/MWCNTs; EDX spectra of (e) MnO₂/MWCNTs and (f) La-MnO₂(1:9)/MWCNTs from TEM; (g) EDX spectrum of La-MnO₂(1:9)/MWCNTs from SEM

into the composites.

Fig.2 shows the XRD patterns of the $\text{MnO}_2/\text{MWCNTs}$ and $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ composites. As shown in Fig.2, except three peaks corresponding to the structure of pristine MWCNTs, there are two broad peaks at 2θ around 37° and 66° . These two peaks can be indexed to birnessite-type MnO_2 (Joint Committee on Powder Diffraction Standards (JCPDS) card No.42-1317).¹² Therefore, the composite should be considered as MWCNTs coated by birnessite-type MnO_2 . In addition, the characteristic peaks of La-doped $\text{MnO}_2/\text{MWCNTs}$ are weaker and broader than those of $\text{MnO}_2/\text{MWCNTs}$. The diffraction peaks of La-doped $\text{MnO}_2/\text{MWCNTs}$ are not apparently shifted in comparison with $\text{MnO}_2/\text{MWCNTs}$ and no diffraction peaks of compounds containing La can be observed. So it is reasonable to suppose that La is dispersed into the lattice of MnO_2 . The ionic radius of La^{3+} (0.106 nm) is much greater than that of Mn^{4+} (0.052 nm), which may increase the imperfection of the crystalline structure of MnO_2 , further enhancing the electrochemical activity of the electrode.

Moreover, the acid treatment may modify the MWCNTs surface with carbonyl and carboxyl hydroxyl groups. As can be seen in the FTIR spectrum of functionalized MWCNTs in the range of $1000\text{--}4000\text{ cm}^{-1}$ (Fig.3), a broad absorption band at 3430 cm^{-1} is attributed to the hydroxyl group.¹⁵ This band might be assigned to the stretching vibration of OH groups¹⁶ and also the $-\text{OH}$ functional groups due to the chemical treatment during the functionalization process.¹⁷ A small peak at 1684 cm^{-1} is associated with the $\text{C}=\text{O}$ stretching of the carboxylic acid ($-\text{COOH}$) group.¹⁸ The peak at 1642 cm^{-1} is due to $\text{C}=\text{C}$ stretching of the CNT.¹⁹ The peak at 1403 cm^{-1} is due to $\text{O}-\text{H}$ bending deformation in $-\text{COOH}$. The peak at 1170 cm^{-1} can be inferred as $\text{C}-\text{O}$ bond stretching.¹⁸ Thus, the generation of $-\text{OH}$ and $-\text{COOH}$ groups on CNTs due to functionalization is observed. These groups are more vulnerable to oxidation,¹⁴ and may initiate the reaction among carbon, KMnO_4 , and $\text{La}(\text{NO}_3)_3$.

3.2 Electrochemical characterization

Fig.4 shows cyclic voltammograms in a three-electrode cell system using the acid-treated MWCNTs, $\text{MnO}_2/\text{MWCNTs}$, and $\text{La-MnO}_2(1:9)/\text{MWCNTs}$. All the acid-treated MWCNTs and

Fig.2 XRD patterns of the as-prepared $\text{MnO}_2/\text{MWCNTs}$ and $\text{La-MnO}_2(1:9)/\text{MWCNTs}$

Fig.3 FTIR spectrum of functionalized MWCNTs

the composites of $\text{MnO}_2/\text{MWCNTs}$ and $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ exhibited square-shaped CV curves that indicated an ideal capacitive behavior.¹ Higher current densities in the CV curves suggest higher specific capacitances. From the CVs, specific capacitance values are calculated using the following formula:

$$C = \frac{1}{v(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV$$

where C refers to the specific capacitance ($\text{F} \cdot \text{g}^{-1}$), v is the potential scan rate ($\text{mV} \cdot \text{s}^{-1}$), $V_c - V_a$ is the sweep potential range during discharging, and $I(V)$ refers to the response current density ($\text{A} \cdot \text{g}^{-1}$).²⁰ The specific capacitances for MWCNTs, $\text{MnO}_2/\text{MWCNTs}$, and $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ electrodes were 34, 117, and $130\text{ F} \cdot \text{g}^{-1}$ at a scan rate of $2\text{ mV} \cdot \text{s}^{-1}$. The composites of $\text{MnO}_2/\text{MWCNTs}$ and $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ showed much higher capacitance than the acid-treated MWCNTs. When compared with the composite of $\text{MnO}_2/\text{MWCNTs}$, $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ showed a higher specific capacitance, which can be attributed to the combination of pseudocapacitance from La-MnO_2 and electrical double layer (EDL) capacitance from MWCNTs.

CVs in a three-electrode cell system recorded for the composite electrodes with various La:Mn atomic ratios are presented in Fig.5A. Although all the composites with different La:Mn atomic ratios exhibited nearly square-shaped CV curves that indicated an ideal capacitive behavior,¹ the composites

Fig.4 Cyclic voltammograms in a three-electrode cell system using (a) acid-treated MWCNTs, (b) $\text{MnO}_2/\text{MWCNTs}$, and (c) $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ measured in $0.1\text{ mol} \cdot \text{L}^{-1}\text{ Na}_2\text{SO}_4$ at a scan rate of $2\text{ mV} \cdot \text{s}^{-1}$

Fig.5 (A) Cyclic voltammograms (CVs) in a three-electrode cell system of the La-MnO₂/MWCNTs composites with different La:Mn atomic ratios measured in 0.1 mol·L⁻¹ Na₂SO₄ at a scan rate of 2 mV·s⁻¹; (B) the specific capacitance obtained from CVs with different La:Mn atomic ratios

with La:Mn atomic ratio of 1:9 exhibited a more squared geometry with a higher enclosed area than others. The variation in the specific capacitances obtained from CVs as a function of La:Mn atomic ratios is plotted in Fig.5B. The specific capacitance was firstly ascending and then descending with the La:Mn atomic ratio. The highest specific capacitance of 130 F·g⁻¹ can be obtained for the composites with the La:Mn atomic ratios of 0.5:9.5 and 1:9. An apparent characteristic of CVs is that the composite with the La:Mn atomic ratio of 1:9 exhibited a nearly rectangular *I*-*V* curve with a steep increment in current within the potential range between -0.4 and -0.3 V, which represents an ideal behavior of supercapacitor.²¹ Therefore, the optimized La:Mn atomic ratio in the La-MnO₂/MWCNTs composite is 1:9.

Fig.6a shows the galvanostatic charge-discharge behavior of two electrode cells built with the acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composite electrodes with applied constant current density of 100 mA·g⁻¹ in a potential range from 0 to +1 V. The sharp drop in electrode potentials with the acid-treated MWCNTs should be noticed. Whereas, the potential drops became lower when doping La in the MnO₂/MWCNTs composite. The specific capacitance was evaluated from the charge-discharge curves, according to the following equation,

$$C_{sp} = \frac{2I}{m(dE/dt)}$$

where *I* is the applied current. *dE/dt* indicates the average slope of these chronopotentiometry curves. *m* is the mass of each electrode. The specific capacitance of the acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composite is ca 31, 120, and 134 F·g⁻¹, respectively. The symmetry of the charge and discharge characteristics of La-MnO₂(1:9)/MWCNTs composites suggests a good capacitive behavior.

The capacitive performance of the La-doped MnO₂/MWCNTs composite was investigated by galvanostatic charge/discharge cycling at different current densities. Fig.6b shows the gravimetric discharge capacitance of the acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs materials at current densities from 0.05 to 1.0 A·g⁻¹ in 0.1 mol·L⁻¹ Na₂SO₄ aqueous solution. It is noteworthy that the capacitance of La-MnO₂(1:9)/MWCNTs is maintained above 86 F·g⁻¹ even at a high discharge current density of 1.0 A·g⁻¹. In contrast, the capacitance of the MnO₂/MWCNTs composite dropped by nearly 60% at a current density of 1.0 A·g⁻¹ (Fig.6b).

The charge transfer process in the La-MnO₂/MWCNTs electrode was investigated by ac impedance measurements at dc bias of 0 V with sinusoidal signal of 10 mV over the frequency range from 10 mHz to 40 kHz. The Nyquist plots in a three-electrode cell system for the acid-treated MWCNTs,

Fig.6 (a) Galvanostatic charge/discharge of two electrode cells built with acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composites at an applied constant current density of 100 mA·g⁻¹ in 0.1 mol·L⁻¹ Na₂SO₄ aqueous electrolyte; (b) gravimetric capacitance vs discharge current density of acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composites; (c) cycling evolution of capacitance of acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composites, measured at 100 mA·g⁻¹ discharge current density in 0.1 mol·L⁻¹ Na₂SO₄ aqueous electrolyte

MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs electrodes are shown in Fig.7. The Nyquist curves can be fitted by a modified Randles circuit²² with a set of resistors and capacitors in series and parallel as shown in the inset of Fig.7. R_s element represents the Ohmic resistance of the electrolyte and the internal resistance of the electrode materials. The semicircle in the high-frequency and mid-frequency regions can be fitted by an interfacial charge transfer resistance R_{CT} and a double layer capacitance CPE_{DL} paralleled to each other. The Warburg element W_o represents the transition part from the high-frequency semicircle to the mid-frequency tail. The straight line parallel to the imaginary axis at very low frequencies is the characteristics of an ideally polarizable capacitance. This capacitance is represented as C_L . The EIS spectra were well fitted by the equivalent circuit (Fig.7). The high frequency value of the real part of complex impedance has been used for the estimation of equivalent series resistance (ESR).

Nyquist plot for the La-MnO₂(1:9)/MWCNTs composite in Fig.7 suggests that the La-MnO₂(1:9)/MWCNTs composite exhibits very low charge transfer resistance. The calculated charge-transfer resistance for the MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs electrode is 3.72, 14.21, and 6.93 Ω , respectively. This supports our argument that the presence of La can decrease the resistance of MnO₂/MWCNTs. The lower the charge-transfer resistance, the higher the specific capacitance. Therefore, it is suggested that the doping of La in the MnO₂/MWCNTs composite improves the charge transfer process in the electrode, which leads to a higher capacitance. These results are in good agreement with the CV plots in Fig.4.

Long cycling life is a key requirement for the supercapacitor electrodes. The composite electrodes of two electrode cells built with MnO₂/MWCNTs and La-MnO₂(1:9)/MWCNTs exhibited a decay in specific capacitance, as shown in Fig.6c. On the contrary, MWCNTs had the highest cycling stability. The capacitance of La-MnO₂(1:9)/MWCNTs electrode is more stable

than that of MnO₂/MWCNTs electrode which suggested the La-MnO₂(1:9)/MWCNTs electrode has a long cycling life. The initial decrease in the specific capacitance of electrochemical electrodes is generally observed and is attributed to the poor mechanical stability of the electrode material. However, the fading was obvious for the MnO₂/MWCNTs composite electrode when it was charged/discharged for more than 1000 cycles. The fading of MnO₂/MWCNTs is attributed to the formation of Mn²⁺ and Mn⁷⁺ species at 1.0 V.²³ It can be inferred that the stability of MnO₂/MWCNTs is improved by doping La³⁺ in such neutral electrolyte. Therefore significant improvement in cycling stability was achieved for the La-doped MnO₂/MWCNTs composites. Our results suggest that doping with La is a prospective method to overcome the intrinsic low conductivity of MnO₂ and increase the specific capacitance and cycling performance of composite electrodes.

It should be pointed out that the performances of manganese oxide were studied in three-electrode systems in positive potential range in most literature,^{14,24–26} while only few reports available on the performance of symmetric two-electrode capacitors evaluated by chronopotentiometry where two manganese oxide electrodes worked in different potential ranges.^{27,28}

Since the pseudocapacitance of manganese oxides in aqueous medium is attributed to reversible redox transitions involving protons and/or cations exchange with the electrolyte following the equation:²⁹

where MnO_x(OH)_b and MnO_{x- δ} (OH)_{b+ δ} indicate interfacial oxy-manganese species at the higher and lower oxidation states, respectively. To avoid the partial dissolution of the electrode, the solubility of either Mn(II) or Mn(VII) in the electrolytic solution should be avoided during charging and discharging the capacitor. From the Pourbaix potential–pH diagram for manganese,³⁰ it is possible to determine that the reactions of Mn(IV) to Mn(II) and Mn(IV) into Mn(VII) occur at potentials of 0.5 and 1.4 V (vs NHE) for pH 5.4, respectively.

As the cyclability of the MnO₂/MWCNTs electrode was fairly steady in the three-electrode system,¹⁴ we presumed that the reason for the poor cyclability of the same electrode in the two-electrode as shown in Fig.6c could be due to the dissolution of negative electrode. Therefore, we have measured the potential of both electrodes when the cell voltage varied between 0 and 1.0 V during the galvanostatic charge-discharge cycling in 0.1 mol · L⁻¹ Na₂SO₄ with a pH of 5.4. For this purpose, we used a three-electrode cell consisting of two MnO₂/MWCNTs composite electrodes, one as the working electrode and the other as the auxiliary one, and a Hg/Hg₂SO₄ reference electrode. Fig.8 presents the variation of the cell voltage during charge-discharge cycling and the potential profile for both positive and negative electrodes. It shows that for the MnO₂/MWCNTs in 0.1 mol · L⁻¹ Na₂SO₄ with a pH of 5.4, the initial potential for both electrodes in the discharged state of the capacitor is 0.08 V (vs NHE). After charging the capacitor to 1.0 V, the potential

Fig.7 Nyquist plots in a three-electrode cell system of acid-treated MWCNTs, MnO₂/MWCNTs, and La-MnO₂(1:9)/MWCNTs composites in 0.1 mol · L⁻¹ Na₂SO₄ aqueous electrolyte. R_s : the Ohmic resistance of the electrolyte and the internal resistance of the electrode materials, R_{CT} : interfacial charge transfer resistance, CPE_{DL} : a double layer capacitance, W_o : the Warburg element, C_L : an ideally polarizable capacitance, R_{leak} : the low-frequency leakage resistance

Fig.8 Galvanostatic charge/discharge cycle ($I=100 \text{ mA} \cdot \text{g}^{-1}$) for the capacitor and for the positive and negative electrodes in a three-electrode cell

The working and auxiliary electrodes of the three-electrode cell are made from the $\text{MnO}_2/\text{MWCNTs}$. The results are presented vs NHE in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{SO}_4$ with a pH of 5.4.

of the positive electrode increases up to 0.54 V, while for the negative one it decreases from 0.08 to -0.45 V (vs NHE). Since the irreversible reduction of Mn(IV) into Mn(II) starts to occur at 0.5 V in a solution with a pH of 5.4,³⁰ it demonstrates that the negative electrode is actually working below this potential, which results in a partial dissolution of the active material in the electrolyte. Hence, the capacitance decrease observed in Fig.6c during the repeated cycling of the capacitor in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{SO}_4$ aqueous solution is due to the deterioration of the negative electrode.

4 Conclusions

La-doping in the $\text{MnO}_2/\text{MWCNTs}$ composite resulted in performance improvement with respect to discharge capacitance and cycling stability. The highest working current density for $\text{La-MnO}_2(1:9)/\text{MWCNTs}$ is above $1.0 \text{ A} \cdot \text{g}^{-1}$, which is higher than that of MWCNTs. The electrochemical performance of the composite electrode was affected by the La:Mn atomic ratio. The electrochemical properties of the composite with a La:Mn atomic ratio of 1:9 reached $130 \text{ F} \cdot \text{g}^{-1}$, which was higher than other composites. La-doped $\text{MnO}_2/\text{MWCNTs}$ is a prospective candidate electrode material for electrochemical supercapacitors.

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