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ORIGINAL PAPER

Electrochemical characteristics of manganese oxide electrodes prepared by an immersion technique

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Abstract In order to control the amount of manganese oxide coated onto a graphite surface, immersion durations were varied. A maximum capacitance of 490 mF cm^{-2} was obtained in 0.5 M NaCl and using an immersion time of 20 min and a current of 1 mA. In addition, for the manganese oxide electrode, the lower the current, the higher the capacitance and the higher the immersion time, the higher the resistance. Furthermore, the chronopotentiometric (CP) charge–discharge curves were symmetrical and featured similar isosceles triangles, which demonstrate high electrochemical reversibility and good stability. Cyclic voltammograms of the manganese oxide electrode demonstrate that its operational stability is high.

Keywords Manganese oxide · Immersion · Chronopotentiometry · Electrochemical capacitors

1 Introduction

Electrochemical capacitors are charge-storage devices which possess higher power density and longer cycle life than batteries [1, 2]. Their applications include hybrid power sources, backup power sources, starting power for fuel cells, and burst-power generation in electronic devices, etc. [3–7]. Electrochemical capacitors are classified into two types, electrical double layer capacitors (EDLC) and pseudo-capacitors according to the energy-storage mechanisms. The capacitance of EDLC arises from the separation of charge at the interface between the electrolyte and the electrode with high surface area inert materials [8]. By contrast, pseudocapacitance arises from fast and reversible redox reactions of electroactive materials with several oxidation states [1, 8–13].

Amorphous hydrous ruthenium oxide prepared by the sol–gel method and annealed at low temperature (<150 °C) has been found to possess a very high specific pseudocapacitance value of 720 F g^{-1} [14, 15]. However, the precursor of hydrous ruthenium oxide is very expensive. Hence, the more economical manganese oxide with a variety of stable valence states appears to be a promising electrode material for electrochemical capacitors. Recently, manganese oxides were prepared by different methods for application as electrode materials in electrochemical capacitors. Hydrous manganese oxide deposited on a carbon substrate at anodic potentials of 0.5 V_{SCE} in 0.25 M manganese acetate solution at 25 °C exhibited maximum specific capacitance of 240 F g^{-1} in 2 M KCl solution at a potential scan rate of 5 mV s^{-1}. The higher the deposition potential, the lower the specific capacitance achieved because of lower porosity and a smaller amount of trivalent manganese oxide [16]. A multi-layer and co-deposition composite electrode prepared by adding carbon powders with higher specific surface area and conductivity into the anodically deposited hydrous manganese oxide possessed about 25% higher specific capacitance than those of plain hydrous manganese oxide electrodes at a scan rate of 150 mV s^{-1} and gave higher retained specific capacitance after 600 cycles galvanostatic charge and discharge [10]. A thin film of amorphous hydrous manganese oxide prepared by the dip-coated sol–gel derived technique involving $KMnO_4$ and $MnCl_2$ was found to exhibit a high specific capacitance of 698 F g^{-1} (at a scan rate of 5 mV s^{-1} and in 0.1 M Na_2SO_4) and long cycle life. However, the discharge

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time achieved is only about 1.1 s at constant current of 0.1 mA and the slope of the constant current discharge curve is not constant [17]. In addition, for pure amorphous hydrous manganese oxide prepared by the co-precipitation method involving $KMnO_4$ and $Mg(CH_3COO)_2$, its faradic reactions take place only in the restricted region near the current collector due to its relatively high resistance and thus co-precipitated carbon-amorphous hydrous manganese oxide shows higher specific capacitance because of more available active sites [18]. Moreover, the ambigel form of manganese oxide synthesized by the sol–gel method reducing $NaMnO_4$ with $Na_2C_4H_2O_4$ offered maximum capacitance of 130 F g^{-1} at a scan rate of 5 mV s^{-1} and in a 2 M NaCl solution [7]. However, the steps of the sol–gel/precipitation/deposition methods for fabricating the manganese oxide electrode are more complicated. A graphite disc electrode was immersed in an acidic solution of $KMnO_4$; the capacitance of the coating only increased to 45 mF cm^{-2} with a deposition time up to 60 min [8]. In addition, from the Pourbaix diagram for manganese [19], at high pH, $Mn(OH)_2$, MnO, etc., which are electrochemically irreversible [17], form. Thus the concentration of $KMnO_4$ was decreased and then pH was decreased after immersion in this experiment. Therefore, a simpler, quicker, and more controllable, one-step immersion process for coating manganese oxide onto a graphite surface was applied to seek maximum capacitance at better/superior conditions (duration for immersion and chronopotentiometry charge–discharge current).

2 Experimental methods

A graphite rod was used as a substrate due to its higher specific surface area (280–420 m^2 g^{-1}, higher than that of carbon nanotubes), lower specific resistance (6.3–7.3, lower than that of activated carbon), and a higher percentage (97.8%, higher than that of activated carbon) of mesopore size distribution [20]. The graphite rod of diameter 6 mm and thickness 1 cm was abraded with SiC paper and then rinsed ultrasonically with de-ionized water for 10 min. It was then etched in 6 M aqueous HCl at room temperature for 30 min and subsequently rinsed ultrasonically with de-ionized water for 10 min. Next, it was degreased ultrasonically in acetone until the surface grease was completely eliminated. It was rinsed with de-ionized water alone and subsequently oven-dried at 50 °C in air and until no weight change occurred. Finally, a graphite electrode was prepared by encapsulating the graphite rod with epoxy resin. After it was oven-dried at 50 °C in air, one of its ends was freed of epoxy resin for electrical connection and the other was abraded with SiC paper for immersion. In addition, carbon in an acidic permanganic potassium solution can be reacted to produce carbon dioxide, manganese oxide, sulfuric potassium and water [8]. This causes carbon loss and underestimates the amount of manganese oxide deposited. Therefore, capacitance normalized to 1 g of manganese oxide is not suitable and the geometric specific capacitance (mF cm^{-2}) is utilized in this research.

The immersion solution was prepared using de-ionized water and reagent grade chemicals by mixing 80 mL of 0.2 M $KMnO_4$ with 20 mL of 2.5 M H_2SO_4. The graphite electrode was immersed in the solution. The immersion durations were 20, 60, and 100 min, respectively. The manganese oxide electrode was then rinsed with de-ionized water and subsequently oven-dried at 50 °C in air.

Electrochemical measurements for the manganese oxide electrodes were performed using an electrochemical analyzer (CH Instruments CHI 608B, USA). The three-electrode cell contained a Ag/AgCl reference electrode, Pt counter electrode and manganese oxide working electrode. The electrolytes were degassed with purified nitrogen gas before chronopotentiometry measurements, and nitrogen was passed over the solution during all the measurements. The solution temperature was maintained at 25 °C by means of a circulating water thermostat (HAAKE DC3 and K20, Germany). Chronopotentiometry (CP) was undertaken with varying currents (1, 2, 3, 4, and 5 mA) and a 0.5 M aqueous electrolyte (NaCl). The CV was taken with a potential scan rate of 10 mV s^{-1}. A potential window in the range 0–1 V was used in all measurements unless otherwise stated.

3 Results and discussion

Figures 1, 2 and 3 show discharge curves of the manganese oxide electrodes at 20, 60, and 100 min immersion with different currents. The discharge curves are approximately straight lines. These demonstrate that the manganese oxide electrodes have stable discharge processes. The capacitance of the manganese oxide electrodes was calculated from the equation, $C = i/(dE/dt)$, where i is the current and dE/dt is the slope of Figs. 1, 2 and 3. The capacitances, as calculated by the above equation, are presented in Table 1. A maximum capacitance of 490 mF cm^{-2} was obtained with an immersion time of 20 min and a current of 1 mA. Furthermore, at any given immersion time, the lower the current, the higher the capacitance. The reason for this behaviour may be that the lower the current, the longer the discharge time (see Figs. 1, 2 and 3), leading to higher capacitance due to $C = i/(dE/dt)$.

In addition, the resistance of the manganese oxide electrode was obtained from the slope of Fig. 4 (i vs. ΔE), where i is the current and ΔE is the potential drop (iR) at

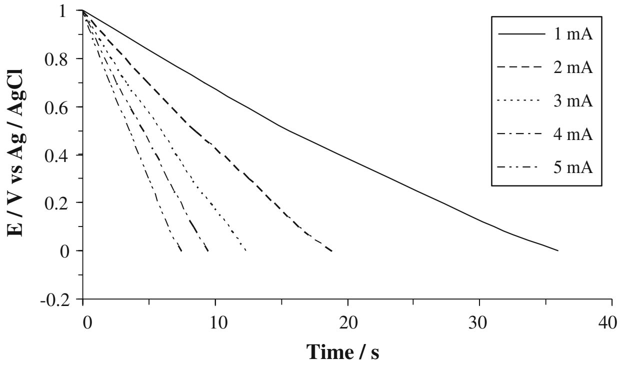


Fig. 1 Discharge curves of the manganese oxide electrode at 20 min immersion time with different currents in 0.5 M NaCl solution

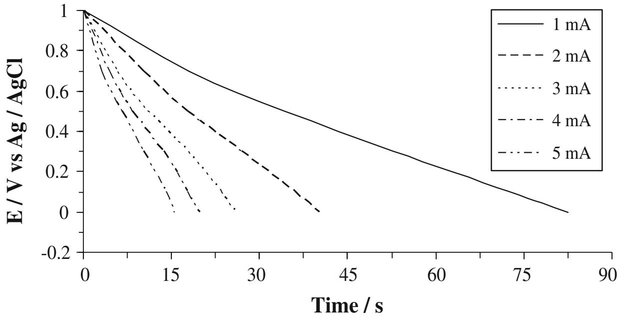


Fig. 2 Discharge curves of the manganese oxide electrode at 60 min immersion time with different currents in 0.5 M NaCl solution

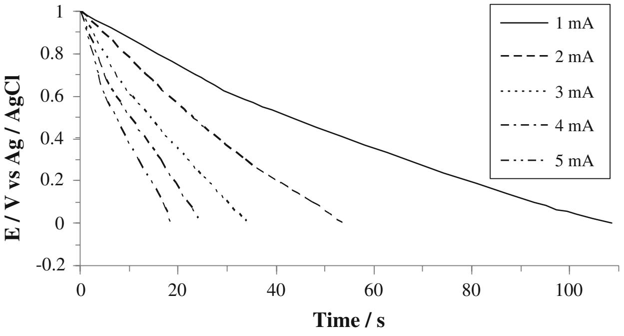


Fig. 3 Discharge curves of the manganese oxide electrode at 100 min immersion time with different currents in 0.5 M NaCl solution

Table 1 Capacitance (mF cm^{-2}), in 0.5 M NaCl solution, of the manganese oxide electrode at different immersing times and currents

Current (mA)	1	2	3	4	5
Immersion time (min)					
20	490	471	471	467	465
60	488	485	480	468	459
100	456	451	443	433	421

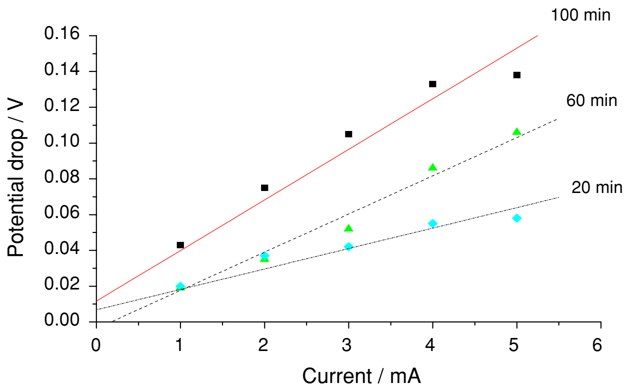


Fig. 4 Effects of different immersion times and currents on potential drop in 0.5 M NaCl solution

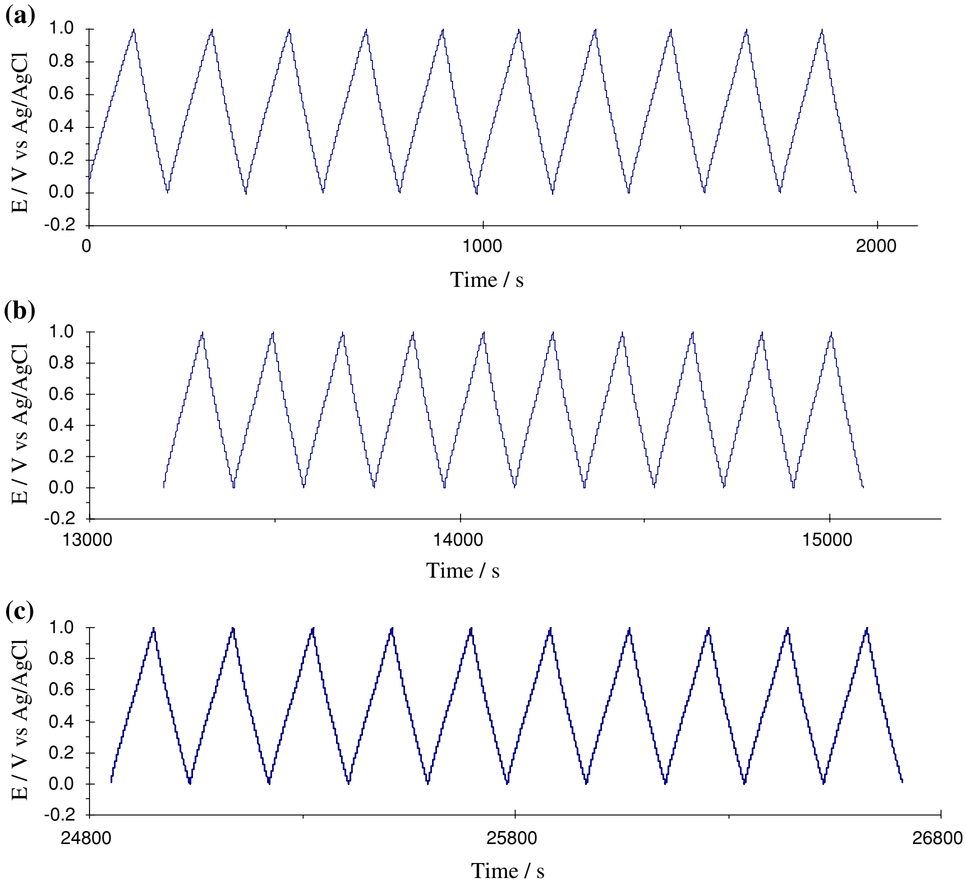
nearly t = 0 in Figs. 1, 2 and 3. The resistances are listed in Table 2 which shows that the higher the immersion time, the more the amount of immersed manganese oxide of lower conductivity, the higher the resistance of the manganese oxide electrode.

Figure 5 shows CP of the manganese oxide electrode with a constant current of 1 mA. Its charge and discharge curves (a: 1st to 10th charge–discharge cycle, b: 71st to 80th charge–discharge cycle, and c: 141st to 150th charge–discharge cycle) are symmetrical and featured similar isosceles triangles. This shows that the manganese oxide electrode has high electrochemical reversibility and good stability. The higher the cycle number, the lower the capacitance; for example 456 mF cm^{-2} for the first charge–discharge cycle and 400 mF cm^{-2} for the 150th cycle. In addition, the electrochemical stability of the manganese oxide electrode was investigated. Figure 6 shows only a small difference between the 1st and 300th charge–discharge cycle; the areas enclosed by the two curves are similar. Thus, the operational stability of the manganese oxide electrode is high. The capacitance gradually decreased with increasing number of charge–discharge cycles and showed <10% loss after 300 charge–discharge cycles. The results of cyclic voltammograms supported those seen in the CP. This picture may be attributed to an irreversible mass loss caused by low dissolution and slow diffusion of active MnOOH (electrolyte changed from transparent to turbid under observation) after cycling [21, 22].

Table 2 The relationship between immersing time and resistance, in 0.5 M NaCl solution, of the manganese oxide electrode

Immersion time (min)	20	60	100
Resistance (Ω)	11	20	28

Fig. 5 CP (**a** 1st to 10th cycles, **b**: 71st to 80th cycles, and **c**: 141st to 150th cycles) of the manganese oxide electrode with constant current of 1 mA in 0.5 M NaCl solution



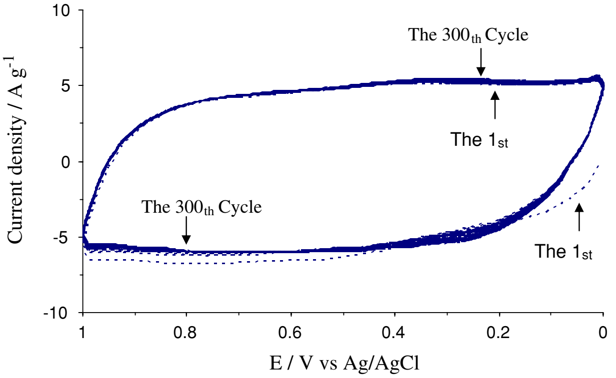


Fig. 6 Cyclic voltammograms, measured in a 0.5 M NaCl solution and 10 mV S^{-1}, of the 1st to 300th cycles of the manganese oxide electrode

4 Conclusion

A simpler, quicker, and more controllable, one-step immersion process for coating manganese oxide onto a graphite surface was applied. A maximum capacitance of 490 mF cm^{-2} was obtained for an immersion time of 20 min and a current of 1 mA. In addition, the lower the current, the higher the capacitance and the higher the immersion time, the higher the resistance of the manganese oxide electrode. Furthermore, CP charge–discharge curves and cyclic voltammograms demonstrate electrochemical reversibility and stability.

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