Electrolytic Manganese Dioxide Structural and Morphological Effects on Capacitive Performance

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A B S T R A C T

Step potential electrochemical spectroscopy (SPECS) has been applied to a range of different electrolytic manganese dioxide (EMD) samples to examine the effects that material composition, structure and morphology have on the performance of these materials as electrochemical capacitor electrodes. The applications of SPECS enabled deconvolution of the electrode behaviour into double layer and diffusional or pseudo-capacitive effects. The technique was even sensitive enough to resolve double layer charge storage associated with either the geometric or porous surface area. The relationships between each of the contributions to total capacitance and the EMD material properties have been described and discussed.

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1. INTRODUCTION

Energy storage is becoming increasingly important due to the growing global demand for energy. This demand, combined with the depletion of non-renewable resources, has increased the need for renewable energy technologies. A major drawback of these technologies is their intermittency; however, this can be overcome with the use of efficient energy storage devices. Electrochemical energy storage devices, particularly electrochemical capacitors, are a promising technology for this, and many other applications.

Electrochemical capacitors (ECs) can store charge in the form of an electrical double layer at the interface between an electrolyte and a polarized electrode [1]. In these devices, charge is stored at the electrode surface, so high surface area materials such as activated carbon are utilized to maximise charge storage. ECs are typified by a high power capability for charging and discharging because charge storage is not limited by the rate of chemical or electrochemical reactions. In addition to double layer charge storage, some electrode materials undergo fast, reversible redox reactions at the interface. These reactions utilize the bulk of the electrode which enables significantly greater charge storage compared to purely double layer capacitance. Since these redox reactions are not technically capacitive, they are known as pseudo-capacitance. Materials which exhibit pseudo-capacitance include conductive polymers [2] and transition metal oxides [3,4].

Manganese dioxide is one such pseudo-capacitive material that has proven to be a good electrode material due to its high performance [5–8], abundance, low cost and low toxicity. The pseudo-capacitive performance of manganese dioxide has been suggested to be largely dependent on its structure [9–11]. Manganese dioxide can exist in many different crystal structures, as it exhibits a range of oxidation states including II, III and IV, which almost exclusively form octahedral arrangements with O^{2-}, OH^- and H_2O species. Hence, the structure of most manganese oxides is based on the $[Mn(O^{2-},OH^-,H_2O)_6]^{z+}$ octahedra. The octahedral geometry can have some distortion depending on the oxidation state, particularly Jahn-Teller distortion of the Mn(III) ion. These octahedral units are arranged to form various structures by either edge- or corner-sharing, which gives rise to a variety of different phases [12].

The pseudo-capacitive reaction of manganese dioxide arises from the reduction of Mn^{4+} ions to Mn^{3+} via electron insertion from the electrical circuit, in parallel with insertion of protons or other cations from the electrolyte to maintain charge neutrality, i.e.:

$$MnO_2 + \Delta H^+ + \Delta e^- \rightarrow MnOOH_\Delta \qquad (1)$$

This process relies on the diffusion of protons and electrons through the crystal lattice away from the interface. Faster rates of proton diffusion have previously been attributed to greater charge storage because more of the bulk material can be accessed [10,13]. It has also been shown that the rate of proton diffusion is heavily affected by the crystal structure [14], meaning certain phases of manganese dioxide are expected to have a greater proportion of pseudo-capacitive charge storage. The crystal structure of manganese dioxide can be easily controlled through synthesis methods

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so, in principle, the crystal structure could be optimized for maximum pseudo-capacitive charge storage. However, it has proven difficult to experimentally determine the effects of crystal structure on pseudo-capacitive charge storage. The different synthesis methods used to obtain specific crystal structures often result in materials with a wide range of specific surface areas (reported values range from $5\,m^2/g$ [9] to $303\,m^2/g$ [15]). Consequently, each manganese dioxide phase has a different double layer charge storage contribution, so the pseudo-capacitive contribution for each phase has not previously been isolated (and vice versa) using conventional electrochemical techniques, such as cyclic voltammetry.

Previous work has demonstrated that step potential electro-chemical spectroscopy (SPECS) is an effective method for separating the contributions from double-layer and pseudo-capacitive charge storage [16–18]. This technique has been successfully used to characterise the charge storage contributions in a range of different manganese dioxide phases [17]. It was found that the magnitude of pseudo-capacitive charge storage varied significantly for different structures, with electrolytic manganese dioxide (EMD; γ-MnO_2) having the highest pseudo-capacitance. The double layer capacitance was found to be affected by the overall specific surface area of the material and it was indicated that both porosity and crystal structure may also be significant influencing factors. Further work, however, is required to differentiate the specific contributions from pore size and crystal structure.

In this work a series of EMD samples were examined. EMD was used because in previous studies it exhibited high diffusional capacitance, which was attributed to specific structural features such as cation vacancies [17]. The samples examined here have differences in their crystal structure (crystallinity, unit cell volume) and material properties (BET surface area, porosity, particle size distribution). Using the SPECS method, the relative contributions from different charge storage processes has been determined. By examining the charge storage mechanism as a function of material properties, the effect of material properties on different capacitive processes has been identified.
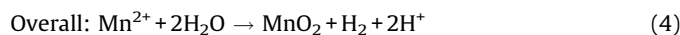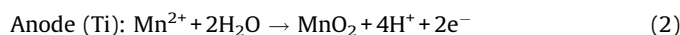
2. EXPERIMENTAL

2.1. Electroactive Material Preparation

The electroactive manganese dioxide phases used in the work were prepared by electrodeposition, and hence were designated as electrolytic manganese dioxide (EMD). They were prepared in an electrolysis cell based on a 2 L Pyrex beaker in a temperature controlled heating jacket. The anode in the cell onto which the EMD was deposited consisted of two $144\,cm^2$ titanium sheets (1 mm thick for mechanical strength) interspersed with three similarly sized copper cathodes. The electrolysis current passed through the cell was dictated by the desired anodic current density (A/m^2). The electrolyte used was based on an aqueous solution of $MnSO_4$ and H_2SO_4. The specific conditions used determine the properties of the resultant EMD, and so Table 1 shows the

Table 1
Synthesis conditions used for the range of EMD materials used in this work.

| Sample	Current Density (A/m^2)	Temperature $(^{\circ}C)$	$[MnSO_4]$ (M)	$[H_2SO_4]$ (M)
EMD1	20	95	0.4	0.6
EMD2	20	95	1.5	0.2
EMD3	60	90	1.0	0.4
EMD4	60	95	0.2	0.4
EMD5	100	95	0.4	0.6

combination of anodic current density, temperature and $MnSO_4$ and H_2SO_4 concentrations that were used to prepare each EMD material. The reactions occurring in the electrolysis cell were:

$$\text{Anode (Ti): } Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \tag{2}$$

$$\text{Cathode (Cu): } 2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

$$\text{Overall: } Mn^{2+} + 2H_2O \rightarrow MnO_2 + H_2 + 2H^+ \tag{4}$$

As can be seen in Eqns (2)–(4), the production of EMD consumes Mn^{2+} and generates H^+. As such, over the course of the electrodeposition process (2–3 days) a solution of 1.5 M $MnSO_4$ was pumped into the cell at an appropriate rate to replenish Mn^{2+} and dilute the H^+ generated. When sufficient EMD had been generated ($\sim$100 g) the current was switch off and the anodes removed from the electrolysis cell and placed into a bath of Milli Q ultra-pure water ($>18.2\,M\Omega.cm$) as a first attempt at extracting any entrained plating electrolyte. After a few hours the manganese dioxide was stripped mechanically from the titanium substrate surface and broken into chunks 1–2 cm in size, and then placed into fresh Milli Q water. The pH of the water was then adjusted (neutralized) over the course of 24 hours to a stable pH in the range 6–7 by the addition of 0.1 M NaOH. The liquid was then decanted off and the chunks of EMD dried in an oven at $60\,^{\circ}C$. The EMD chunks were then milled using a zirconia mill to a $-107\,\mu m$ particle size. This was accomplished by milling the EMD chunks for 1 min before sieving. Those particles not passing through the sieve were returned to the mill. In this way the temperature of the EMD did not become too high to alter the EMD structure. When milling was complete the EMD powder was again suspended in Milli-Q water before the pH was again adjusted over the course of 24 h to a stable value in the range 6–7. The suspension was then filtered, with the collected EMD again dried at $60\,^{\circ}C$.
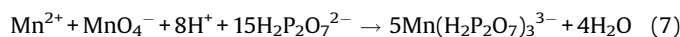
2.2. Material Characterization

EMD is not a stoichiometric material, commonly consisting of cation vacancies, Mn(III) ions and structural water [19,20]. The compositional features of the EMD samples were determined using a potentiometric titration technique used originally by Vetter and Jaeger, and also outlined in Vogel [21]. 0.100 g of the EMD sample was initially dissolved into 25 mL of 0.25 M acidified (10% H_2SO_4) ferrous ammonium sulfate ((NH_4)$FeSO_4$; BDH Chemicals Australia; 99%) solution; i.e.,

$$MnO_x + (2x-2)Fe^{2+} + 2xH^+ \rightarrow Mn^{2+} + (2x-2)Fe^{3+} + xH_2O \tag{5}$$
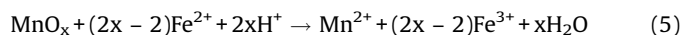
This solution was titrated against a standardized (oxalate method [21]) 0.2 M potassium permanganate ($KMnO_4$; Ajax Finechem; 99%) solution, with the volume of permanganate added denoted as V_1; i.e.,

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \tag{6}$$
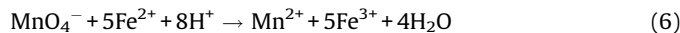
A blank titration of this type was also performed, without any EMD added, and the volume required to reach the end point recorded as V_0. Approximately 20 g of tetra-sodium pyrophosphate ($Na_4P_2O_7$; Ajax Finechem; 99%) was added to the solution resulting from the first titration to stabilize the formation of the Mn(III) complex forming in the subsequent titration. The pH of this solution was adjusted to the range 6–7 by the addition of $\sim$0.20 M sulfuric acid. A second potentiometric titration was performed using the same $KMnO_4$ solution, and the volume required to reach the end point recorded as V_2; i.e.,

$$Mn^{2+} + MnO_4^- + 8H^+ + 15H_2P_2O_7^{2-} \rightarrow 5Mn(H_2P_2O_7)_3^{3-} + 4H_2O \tag{7}$$