Nucleation and Growth of Electrodeposited Manganese Dioxide for Electrochemical Capacitors

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ABSTRACT

In this work the anodic electrodeposition of manganese dioxide from a solution of 0.01 M $MnSO_4$ in 0.1 M H_2SO_4 onto a platinum substrate has been examined in order to determine the mechanism of deposition. Electrochemical data indicates that the dilute acid solution favours the formation of MnO_2 via a MnOOH intermediate (hydrolysis). The electrodeposited material was examined further using AFM and TEM which showed that the oxidation of Mn^{2+} occurs in a number of steps. When a potential is applied, Mn^{2+} is electrochemically oxidised to soluble Mn^{3+}. When the concentration of Mn^{3+} at the electrode reaches saturation, it chemically precipitates onto the electrode as MnOOH, causing an increase in the electroactive surface area. This stage of the deposition is characterised by the nucleation of MnOOH crystallites on the platinum surface. As the deposition proceeds, MnOOH undergoes solid state oxidation to MnO_2. This later stage of the deposition favours the growth of existing MnO_2 crystallites, leading to a decrease in the surface area of the electrodeposited material.

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1. Introduction

Due to increasing demands for energy, high performance energy storage devices have become a necessity. In order for such devices to be commercially viable, they must be able to store large amounts of energy, and then deliver that energy on demand. Chemical energy storage, particularly where the energy can be released electrochemically, is a high grade from of energy storage with efficiencies approaching 100%.

Electrochemical capacitors are a promising energy storage and conversion device, with some such devices already in commercial use. These devices have high power but are limited by their low energy output [1]. Our overall objective is to improve the specific energy density of these devices.

Most commercial electrochemical capacitors, based, for example, on activated carbon electrodes, store energy in the form of charge separation at an electrical double layer. Unlike electrolytic capacitors, which store charge on separated metal plates, electrochemical capacitors store charge at the interface between an electrode and an electrolyte. Furthermore, unlike batteries, conventional electrochemical capacitors do not undergo faradaic reactions at the electrode-electrolyte interface, and since they notionally have no compositional or phase changes, they have a high degree of rechargeability, and hence cyclability [2]. Electrochemical

capacitors perform significantly better than conventional electrolytic capacitors, with some electrochemical capacitor designs demonstrating capacitance values up to 10^4 times higher than electrolytic capacitors [3].

A variety of materials have been employed as electrodes in electrochemical capacitors, including carbon [4,5], conducting polymers [6] and metal oxides [7–9]. Of the metal oxide materials, manganese dioxide has been shown to be a very promising electrode material. This is because, in addition to having desirable electrochemical properties, it is abundant, inexpensive and environmentally friendly [5].

Manganese dioxide electrodes have been found to exhibit very high specific capacitance, in some cases up to 2000 F/g for thin film electrodeposited materials [10]. This high capacitance can be largely attributed to pseudo-capacitance, which arises when, in addition to double layer charging, fast reversible redox reactions occur at the surface of the electrode. In the case of manganese dioxide, this reaction involves the intercalation of cations from the electrolyte; i.e.,

$$MnO_2 + M^+ + e^- \rightarrow MnOO(M) \tag{1}$$

where M^+ is a cation from the electrolyte, such as H^+.

The performance of manganese dioxide, and indeed other electrode materials, has been found to be affected significantly by electrode construction. Electrochemical capacitor electrodes are usually constructed from either a powdered composite mixture, one component of which is the electro-active material, or from a thin film of only electro-active material. Powdered materials are

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usually prepared by thermal or chemical reactions, such as precipitation, or by treatment of a powdered precursor, as in the case of activated carbons. In order for these materials to be used in an electrode, they need to be cast or moulded into a suitable form. This involves combining it with a conductive material, such as carbon black, and a binder, such as PTFE, which needs to be adhered to a conductive metallic substrate. Whilst this method of construction allows large quantities of electrode material to be utilized to create devices with very high capacitance, it does have its disadvantages, notably, lower conductivity.

The alternative to powdered materials are thin films. Thin films are materials with thicknesses ranging from monolayer (fractions of a nanometer) to several microns. Thin film synthesis involves depositing a material directly onto a substrate. Thin films have a number of properties which result in much higher specific capacitive performance compared to powders; namely, very low electrode resistance, lower contact resistance with the substrate, and better electrolyte accessibility. Many of these properties are unique to thin films. It has been observed that as the thickness of thin films increases, their behaviour rapidly approach that of the corresponding bulk material [11]. This trend applies to their electrochemical properties as well, since a number of studies have shown that the performance decreases as the film thickness increases [10,12]. This has limited the performance of thin films, since to be effective, they must be deposited in very thin layers, requiring large surface areas to produce high capacitance. An ideal thin film synthesis method would be one in which greater mass of material could be deposited per unit area, without compromising the performance of the material.

Electrodeposition has been shown to produce thin films with very high capacitance (up to 2000 F/g for manganese dioxide) compared to less than 260 F/g for powdered manganese dioxide [13]. However, this high capacitance has only been observed in very thin deposits, with the performance decreasing as film thickness increases.

In this work, we aim to understand the mechanism by which manganese dioxide films are formed during electrodeposition, particularly the cause of the poorer performance observed in thicker films. Ideally, an understanding of this mechanism will allow us to optimise the deposition conditions so as to deposit larger quantities of material without sacrificing the capacitive performance.

2. Experimental

2.1. Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) was used to characterize the electrochemical oxidation of Mn^{2+} in an acidic environment to form MnO_2. To accomplish this, a clean platinum working electrode (geometric area = 0.785 cm^2) was placed in a solution of 0.01 M $MnSO_4$ ($\geq$99%; Sigma Aldrich) + 0.1 M H_2SO_4 in a 250 mL electrochemical cell. Cleaning of the platinum substrate was achieved by initially immersing the electrode into an acidified (0.1 M H_2SO_4) solution of 5% H_2O_2 to remove any residual manganese oxides by reductive dissolution. This electrode was then polished using a moist 1 µm Al_2O_3 paste on a polishing cloth. After ~2 minutes polishing, the electrode was washed thoroughly with Milli-Q ultra pure water (resistivity ρ > 18.2 MΩ.cm) before being ready for use. Also placed into the electrochemical cell were a saturated calomel reference electrode (SCE; against which all potentials were measured and reported), and a carbon rod (area = 3.5 cm^2) as the counter electrode. The LSV experiment was conducted using a Perkin Elmer VMP 16-channel potentiostat/galvanostat. The potential was swept anodically at a rate of 5 mV/s from the open circuit potential up to 2.0 V vs SCE.

2.2. Chronoamperometry and Electrochemical Quartz Crystal Microbalance (EQCM)

Using the results from the LSV experiments, an appropriate potential was selected to carry out the chronoamperometry experiments. In this case, a diffusion limited potential was chosen, selected based on an assessment of the collected LSV data. In these experiments, the manganese dioxide films were deposited onto a 5 MHz, 1" diameter AT-cut quartz crystal disc with a platinum electrode mounted in a Stanford Research Systems QCM200 Quartz Crystal Microbalance. The deposition electrolyte used was a solution of 0.01 M $MnSO_4$ ($\geq$99%; Sigma Aldrich) in 0.1 M H_2SO_4.

The protocol used was to hold the platinum working electrode at its open circuit potential for 10 s, after which the potential was stepped to the chosen value where it was held for 10-120 s. To assess the reproducibility of the procedure, each set of experiments was repeated eight times, with the resultant standard deviation used to determine the error in the measurements.

2.3. Transmission Electron Microscopy (TEM)

Selected electrode deposits were also imaged using transmission electron microscopy. The electrodes were prepared by first drying the deposited material at ambient temperature. A scalpel was then used to carefully scrape the deposited material off the platinum substrate and into a small beaker. ~10 mL ethanol was added to the beaker and the suspension was ultrasonicated for 10 mins to disperse the material. A small sample of this suspension was pipetted onto a copper TEM grid and allowed to dry at ambient temperature. The grid was then mounted onto a sample holder and examined using a JEOL TEM2100 to obtain high resolution images and electron diffraction patterns.
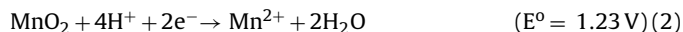
2.4. Atomic Force Microscopy (AFM)

Manganese dioxide electrodes were deposited using the chronoamperometry method outlined in Section 2.2. The material was deposited onto a mirror-finish platinum EQCM electrode for 10, 30 and 120 s. The electrodes were then washed thoroughly with water, and then imaged immediately using an Asylum Research Cypher Atomic Force Microscope in tapping mode. The electrodes were not dried before imaging so as to avoid any material changes due to drying.

3. RESULTS AND DISCUSSION

3.1. Linear Sweep Voltammetry

Figure 1 shows an example of the LSV data collected in this work. The data consists of an anodic voltametric wave starting at ~1.1 V, with a maximum in current at ~1.3 V, superimposed on a wave for the oxygen evolution reaction. This overlap of processes was to be expected given that both anodic reactions have the same standard potential; i.e.,

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad (E^o = 1.23\,V)\,(2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (E^o = 1.23\,V) \qquad (3)$$

The overlapping oxygen evolution reaction is also a complicating factor in determining the active mass of manganese dioxide deposited [14]. To account for this competing reaction the anodic partial current from the Butler-Volmer equation was fit to certain regions of the LSV data so as to allow us to identify what fraction of the total current was due to each process. From this LSV data a