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Manganese dioxide structural effects on its thermal decomposition

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ABSTRACT

In this work, the influence of the structure, composition and morphology on the amount of mass lost from γ-MnO_2 during heat treatment, and the activation energy for this process (from iso-conversional kinetic analysis), was determined using a statistical approach. It was found that the differential thermogravimetric (DTG) data for electrolytic manganese dioxide (EMD) samples typically show two regions of mass loss; water bound to surface sites and structural water at or near the surface removed between ~120 and 200 °C, and bulk hydroxyl groups lost in the range ~200–400 °C. The composition and morphology had the greatest effect on the amount of mass lost; namely, BET surface area and percentage Mn(III) for the first process ($r^2 = 0.92$) and percentage Mn(IV), percentage Mn(III) and cation vacancy fraction for the second ($r^2 = 0.89$). The activation energy for the first processes was most affected by BET surface area, c_0 and crystallite size in the (2 2 1) direction ($r^2 = 0.89$). Relatively poor correlations were found between the amount of water lost and the activation energy for the second process and the material properties measured in this work. This likely relates to the slow kinetics of the first mass loss which complicates the relationships existing for the second.

1. Introduction

1.1. Manganese dioxide as a battery material

The majority of portable consumer batteries produced worldwide use manganese dioxide as the cathode material. While the aqueous Zn/MnO_2 system is the most common battery system in the world, since the 1980s non-aqueous Li/MnO_2 battery systems have found popular application in high power portable consumer electronics [1]. The popularity of manganese dioxide can be attributed to its unique combination of physio-chemical and electrochemical properties, such as a relatively high density and purity, and the spectrum of possible discharge rates maintainable for prolonged periods of time. These characteristics, along with its low cost and low toxicity, make it a difficult material to supersede [2].

1.2. Structure of manganese dioxide

Manganese dioxides form a large and diverse group of compounds due to differences in the crystal structure of these materials, and as such over 30 different compounds have been classified [3,4]. These structural differences influence dramatically both the thermal and electrochemical behaviour of these materials, and hence it is important that we describe in some detail the structures we will encounter in this work.

Manganese in oxidation states II, III and IV prefers almost exclusively an octahedral arrangement, albeit somewhat distorted [5]. This is particularly noticeable for Mn(III) containing species, since it is a Jahn–Teller distorted ion. As a result, the basic structural unit for most manganese oxide and hydroxide compounds is the $[Mn(O^{2-},OH^-,OH_2)_6]^{z+}$ octahedral unit [5]. Assembling these basic building blocks by corner and/or edge sharing arrangements gives rise to the different structures attainable [3,4].

The simplest and most thermodynamically stable form of manganese dioxide is β-MnO_2 (pyrolusite), which consists of corner sharing octahedra in the *a*–*b* plane, and edge sharing octahedra in the *c* direction. The result is a [1 × 1] tunnel structure progressing in the *c* direction. For this tetragonal structure the unit cell parameters are $a_0 = 0.439$ nm and $c_0 = 0.287$ nm [3,4]. Similarly, the ramsdellite structure can be visualized by using both edge and corner sharing in the *a*–*b* plane to form a [2 × 1] tunnel headed into the *c* direction. Ramsdellite has an orthorhombic unit cell with $a_0 = 0.446$ nm, $b_0 = 0.932$ nm and $c_0 = 0.285$ nm [3,4].

γ-MnO_2 is the most commonly used manganese dioxide structure for the alkaline cathode [6], and as the precursor that is heat treated prior to use in the non-aqueous Li/MnO_2 system. The γ-MnO_2 structure is best described as a random microscopic intergrowth between the pyrolusite and ramsdellite forms of manganese dioxide [7]. Other features associated with the γ-MnO_2 structure include cation vacancies, lower valent manganese cations (Mn(III)), and structural water present as protons associated with

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oxide anions so as to compensate for the charge deficiency incurred by cation vacancies and Mn(III) ions [8–11]. As a result the chemical composition of γ-MnO_2 has been described as:

$$(Mn^{4+})_{1-x-y}\cdot(\square)_x\cdot(Mn^{3+})_y\cdot(O^{2-})_{2-4x-y}\cdot(OH^-)_{4x+y} \quad (1)$$

where x and y represent the mole fraction of cation vacancies (□) and Mn(III) ions, respectively. In an unreduced γ-MnO_2 sample typical ranges for x and y are 0.06–0.08 and 0.04–0.12, respectively [12]. Another feature used to explain some features in the X-ray diffraction pattern of γ-MnO_2 is the microtwinning of the (0 2 1) and (0 6 1) growth planes [11]; however, there is conflicting physical evidence as to its actual existence [13].

As a result of the structural and chemical definition given in Eq. (1), considerable structural variation can be found between the multitude of materials that can be loosely classified as γ-MnO_2. The structural features of a given γ-MnO_2 sample are dependant upon both the synthetic method as well as the experimental variables chosen in the materials production process. γ-MnO_2 used, as the cathode-active material is most commonly prepared via electrolysis, and hence termed electrolytic manganese dioxide (EMD) [6]. This is the preferred synthesis method primarily because it leads to a denser material which is desirable for cathode use. Other methods of γ-MnO_2 synthesis are based on oxidation of Mn^{2+} with strong oxidants such as MnO_4^-, $S_2O_8^{2-}$, ClO^- or O_3, reduction of MnO_4^- using reductants such as Mn^{2+}, or acid disproportionation of solid Mn^{3+} species. The original high resolution TEM work on EMD was conducted by Turner and Buseck [14], and it showed definitive evidence in support of De Wolff's microscopic intergrowth model for γ-MnO_2 [7]. More recent TEM work on EMD by Heuer and co-workers [13] has shown the material to consist of needle-like crystallites ~10 nm × 10 nm × 100 nm in size. These needles were then found to be assembled in a somewhat ordered fashion into grains ~200 nm in diameter. These grains were then found to be arranged randomly to form the bulk structure. Also apparent between the crystallites and grains were pores, into which electrolyte is expected to permeate during electrochemical discharge.

1.3. *Thermal treatment of manganese dioxide*

Prior to use in non-aqueous Li/MnO_2 cells the γ-MnO_2 precursor must be heat treated in order to remove water that would otherwise be extracted when inserted into the non-aqueous media, consequently reacting with the metallic lithium anode and causing a decrease in battery performance. The general reaction scheme for the thermal treatment of γ-MnO_2 can be summarised as follows [15]:

$$\gamma\text{-}MnO_2 \xrightarrow{I} \beta\text{-}MnO_2 \xrightarrow{II} Mn_2O_3 \xrightarrow{III} Mn_3O_4 \xrightarrow{IV} MnO \quad (2)$$

Step I corresponds to the loss of water, as well as to a structural transition from the intergrowth γ-MnO_2 phase to the thermodynamically favoured β-MnO_2 phase. Three classes of water have been identified previously using thermogravimetric (TG) analysis; i.e., Type 1 water, which is physisorbed water able to be reversibly removed around 100 °C; Type 2 water, which is comprised of surface bound hydroxyls that are irreversibly removed around 200 °C; and Type 3 water, which are bulk hydroxyl groups removed irreversibly at 300 °C [16,17]. Above 400 °C thermal reduction takes place [18], with Step II occurring in the range 460–570 °C, Step III in the range 700–800 °C, and Step IV above 1300 °C. The mechanism for each of the steps in the thermal decomposition of γ-MnO_2 is known to be related to the origin and history of the material, as well as the conditions under which the reduction takes place [18–23]. For instance, if Step I is carried out in an oxygen containing atmosphere, then oxidation of any Mn(III) present (Eq. (1)) will also occur in addition to water loss and the structural transition.

It is important to note here that Step I is of most interest to the battery industry; i.e., heat treatment up to around 400 °C. The removal of water is of primary importance, and as a consequence of this process, some degree of transition to β-MnO_2 also occurs. However, in order to retain the high electrochemical activity from the Mn(IV) species, it is important that heat treatment is not so intense as to lower the oxidation state of the material; i.e., progress to Steps II, III or IV.

1.4. *This work*

This work focuses on the heat treatment of the γ-MnO_2 precursor required prior to use in non-aqueous Li/MnO_2 systems, and the influence that the starting material structure and morphology have on this process. A better understanding in this crucial area of battery material preparation will aid in optimising the heat treatment process, and in turn improve the overall performance of manganese dioxide as a cathode material in Li/MnO_2 primary cells.

2. Experimental

2.1. *Synthesis of γ-MnO_2*

The samples of γ-MnO_2 used in this work were prepared by anodic electrodeposition, and hence given the designation EMD. The cell used for electrolysis is based on a temperature controlled 2 L glass beaker in which two 144 cm^2 (72 cm^2 on either side) titanium sheets were used as the anode substrate, and three similarly sized copper sheets were used as the cathode substrate. The electrodes were arranged alternately so that each anode was surrounded on both sides by a cathode. The electrolyte was an aqueous mixture ranging from 0.05 to 0.5 M $MnSO_4$ (APS Chemicals, 98%) and 0.01 to 1.0 M H_2SO_4 (Lab-Scan, 98%) maintained at an elevated temperature (90–99 °C). Electrodeposition of the manganese dioxide was conducted with an anodic current density within the range 10–100 A/m^2. Target values within these parameter ranges were chosen so as to make an EMD sample under those conditions. Variation in the EMD properties was generated by choosing different parameters. The deposition reactions are:

$$\text{Anode(Ti)}: Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (3)$$

$$\text{Cathode(Cu)}: 2H^+ + 2e^- \rightarrow H_2 \quad (4)$$

$$\text{Overall}: Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2 \quad (5)$$

The overall process was carried out for three days, during which time the electrolyte Mn^{2+} concentration was of course depleted, while the H^+ concentration increased. To counteract this, and hence maintain a constant electrolyte composition over the duration of the deposition, a concentrated (1.5 M) $MnSO_4$ solution was added continually at a suitable rate to replenish Mn^{2+} and dilute any excess H_2SO_4 added. Under these conditions control of the solution conditions was typically maintained to within ±2%. A total of 17 samples (S1–S17) were examined and compared in this work.

After deposition was complete, the solid EMD deposit was mechanically removed from the anode and broken into chunks ~0.5 cm in diameter, and then immersed in 500 mL of Milli-Q water to assist in the removal of entrained plating electrolyte. The pH of this chunk suspension was adjusted to pH 7 with the addition of 0.1 M NaOH (Sigma–Aldrich, 98%). After ~24 h at a pH of 7 the suspension was filtered and the chunks then dried at 110 °C. After drying, the chunks were milled to a −105 μm powder (mean particle size ~45 μm) using an orbital zirconia mill. The powder was then suspended in ~500 mL of Milli-Q water and its pH again adjusted to 7 with the further addition of 0.1 M NaOH. When the pH had stabilized, the suspension was filtered and the collected solids