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Chronoamperometric characterization of manganese dioxide discharge in alkaline electrolytes

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ABSTRACT

The current response in a chronoamperometric experiment on the alkaline manganese dioxide electrode has been modeled as a composite of two individual discharge processes using a spherical grain diffusion model. This analysis has provided us with the capacity and $A\sqrt{D}$ values for each discharge process, as well as a quantitative means of comparing different EMD samples. This has led to the identification of the domains within the γ-MnO_2 structure in which structural defects such as cation vacancies and Mn(III) ions are most likely to be found.

1. Introduction

1.1. General

The worldwide market for batteries is in excess of $US10 billion per annum. The aqueous alkaline Zn/MnO_2 cell takes up the majority of this market due primarily to the excellent electrochemical properties of the manganese dioxide cathode. As electronic device technology becomes more advanced, the demands placed on the batteries used to power them increases, thus shortening their life expectancy. So as to keep pace with these advances, there needs to be corresponding improvements in battery performance. This work is focused on the performance of the alkaline manganese dioxide cathode where the complex interplay between structural properties and electrochemical behaviour is relatively unknown [1].

1.2. Structural varieties

Many different structural varieties of manganese dioxide have been characterized [2]. The origin of this variety is based on the assembly of the $[Mn(O^{2-}, OH^-, OH_2)_6]^{z+}$ octahedral building block, which manganese in oxidation states of II, III and IV almost exclusively prefers to adopt [3]. Edge and/or corner sharing of this unit allows for the formation of a range of tunnel (*e.g.*, pyrolusite (β), ramsdellite, α-MnO_2) and layered (*e.g.*, birnessite) structures. Intergrowths between these fundamental structures are also common. The most relevant example here is γ-MnO_2, which has essentially been defined as an intergrowth between the ramsdellite and pyrolusite forms of manganese dioxide [4]. Other structural features of γ-MnO_2 that have been characterized include the presence of cation vacancies (□), partially reduced manganese ions (Mn(III)), and structural water included to compensate for the charge discrepancies originating from the previous defects [5–7]. Overall, the chemical composition of γ-MnO_2 can be described as being

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

where x and y represent the mole fractions of cation vacancies and Mn(III), respectively. The significance of γ-MnO_2 is that it is the phase of manganese dioxide preferred for use in the aqueous alkaline manganese dioxide cathode.

1.3. Synthesis of γ-MnO_2

Given the large structural variety of manganese dioxide it is not surprising that a similar number of methods have been developed for its synthesis. In general, these methods are based on either Mn(II) oxidation [8–11], higher valent manganese (Mn(VII/VI/V)) reduction [12–15], or Mn(III) disproportionation [16,17]. γ-MnO_2 can be prepared using a number of approaches, but most often for battery usage it is prepared using electrodeposition, thus giving it the classification electrolytic manganese dioxide (EMD). In this situation a hot (90°–99 °C), acidic (0.05–0.50 M H_2SO_4) solution of Mn(II) (0.05–1.00 M $MnSO_4$) is electrolyzed (10–100 A/m^2) to deposit the EMD onto a titanium anode [18]. Any conditions within these variable ranges will lead to the deposition of γ-MnO_2;

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however, the synthesis conditions for the best performing material in a battery are very narrow indeed.

1.4. Electrochemical discharge of γ-MnO_2 and characterization methods

The currently accepted model for the reduction of γ-MnO_2 in an alkaline electrolyte is based on the initial work by Kozawa et al. [19–23], which has subsequently been refined by others [24–30]. The basis of this model involves concerted proton and electron insertion into the host manganese dioxide structure; *i.e.*

$$(Mn^{4+})_{1-x-y}\cdot(\square)_x\cdot(Mn^{3+})_y\cdot(O^{2-})_{2-4x-y}\cdot(OH^-)_{4x+y}+\Delta H_2O+\Delta e^-\rightarrow(Mn^{4+})_{1-x-y-\Delta}\cdot(\square)_x\cdot(Mn^{3+})_{y+\Delta}\cdot(O^{2-})_{2-4x-y-\Delta}\cdot(OH^-)_{4x+y+\Delta}+\Delta OH^- \quad (2)$$

Protons originate from water decomposition at the solid-electrolyte interface, while electrons come from the external circuit. Given that γ-MnO_2 is a defective intergrowth structure, it is not surprising that these different domains within the material are reduced at different voltages giving rise to a complex discharge curve [24–30]. The exact conditions under which the γ-MnO_2 was prepared influences the nature and proportion of these structural domains, and hence the discharge curve.

When characterizing a solid state electrode such as γ-MnO_2, many methods have been adopted, each providing a range of fundamental information and performance data. A popular electrochemical method that has been used to characterize solid state electrodes is step potential electrochemical spectroscopy (SPECS) [31–39]. The method involves making small sequential cathodic steps on the γ-MnO_2 electrode, followed by an extended rest time during which the current is recorded as a function of time The popularity of this method arises from the fact that it can produce both kinetic (current decay after the potential step) and thermodynamic (equilibrium potentials before the step) data as a function of electrode composition in one experiment. However, the main drawback of SPECS is that it takes approximately two weeks to complete an experiment on one material. This can present a number of problems including electrode stability, lag time between experiments, and possibly even power interruptions during experimentation.

A similar electrochemical method which we have shown [40] to produce complementary kinetic data to a SPECS experiment is large voltage step chronoamperometry, which involves stepping the electrode potential from its initial open circuit value to a final potential where all electroactive species can be reduced. Under these conditions the current that flows is the result of the parallel reduction of the different domains within the γ-MnO_2 structure. In this work an attempt has been made to resolve the total chronoamperometric current into its components for a series of EMD samples produced under a range of synthesis conditions. From this we have determined a number of relationships between the physical properties and the electrochemical performance (kinetics) of the EMD materials.

2. Experimental

2.1. Sample description

The EMD samples used in this work were commercially produced by Delta EMD Australia, Pty Limited. They were prepared electrolytically using a range of synthesis conditions (anodic current density, temperature, and Mn^{2+} and H_2SO_4 concentrations). When deposition was complete, the EMD was removed from the anode, milled to a −105 µm powder, neutralized and washed to remove any remaining electrolyte, and then dried at 110 °C. Using standard analytical techniques the material properties of x in MnO_x [41], Mn(III) (y) and cation vacancy (x) fractions [5–7], pyrolusite content (P_r) [32], and BET surface areas (N_2 as the adsorbate at 77 K) [42] were determined (Table 1).

2.2. Electrochemical cell preparation

The working electrode was prepared by lightly grinding together the manganese dioxide (0.45 g), Timcal SFG6 graphite (4.5 g) and 9 M (37%) KOH (1.105 g). After 5 min of mixing the resulting blackmix was stored in an airtight container for 24 h to allow equilibration to occur.

The electrochemical cell used is shown schematically in Fig. 1. The amount of blackmix corresponding to 0.015 g of manganese dioxide sample was placed into a Teflon-lined C-size battery can. The sides of the can were brushed down, and three separator papers were placed on top of the sample. The sample mixture was

Table 1
EMD sample properties and performance data

Sample	x in MnO_x	P_r	CVF	Mn(III)	BET SA (m^2/g)	OCV (V vs Hg/HgO)	Capacity (C/g)			$A\sqrt{D}$ ($10^4\ cm^3\ s^{-1/2}\ g^{-1}$)	
							Total	Process 1	Process 2	Process 1	Process 2
1	1.964	0.256	0.069	0.068	39.0	0.261	968	584	384	1.48	1.71
2	1.964	0.210	0.079	0.068	80.2	0.295	956	644	312	1.66	1.56
3	1.966	0.300	0.075	0.064	47.3	0.298	1314	1014	300	1.89	1.76
4	1.963	0.100	0.082	0.067	52.4	0.297	936	476	460	1.26	1.33
5	1.954	0.430	0.048	0.087	25.2	0.211	896	797	99	2.04	0.34
6	1.973	0.187	0.078	0.049	22.0	0.317	968	418	550	1.03	1.54
7	1.950	0.359	0.057	0.094	49.3	0.227	950	673	277	1.73	0.31
8	1.967	0.017	0.079	0.061	43.5	0.303	865	492	373	1.35	1.38
9	1.952	0.402	0.054	0.090	31.5	0.217	730	496	234	1.56	0.33
10	1.958	0.323	0.065	0.079	41.5	0.345	914	690	224	1.81	0.69
11	1.963	0.050	0.071	0.069	47.0	0.291	979	670	309	1.63	0.87
12	1.964	0.218	0.076	0.067	42.9	0.284	1079	761	318	1.71	1.70
13	1.973	0.369	0.063	0.050	12.1	0.268	975	529	446	1.25	2.64