

Short communication

Lithium insertion into manganese dioxide electrode in MnO_2/Zn aqueous battery[☆]

Part II. Comparison of the behavior of EMD and battery grade MnO_2 in $\text{Zn}|\text{MnO}_2|\text{aqueous}$ LiOH electrolyte

Manickam Minakshi^{a,*}, Pritam Singh^a, Touma B. Issa^a,
Stephen Thurgate^a, Roland De Marco^b

^a Division of Science and Engineering, Murdoch University, Murdoch 6150, Western Australia

^b Department of Applied Chemistry, Curtin University of Technology, Bentley 6102, Western Australia

Received 5 June 2004; accepted 29 June 2004

Available online 23 August 2004

Abstract

A comparative study of the cathodic behavior of electrolytic manganese dioxide (EMD) and chemically prepared battery grade manganese dioxide (BGM) in $\text{Zn}|\text{MnO}_2|\text{aqueous}$ lithium hydroxide (LiOH) cells has been carried out. The X-ray diffraction (XRD), infrared spectra (IR), thermo gravimetric analysis (TGA) and scanning electron microscope (SEM) investigations showed that the two materials had different phase compositions, water content and particle sizes. The cells with BGM had a higher open circuit voltage (OCV) and discharged at higher voltages as compared to those with EMD. The discharge capacity of BGM was lower compared to that of EMD. On discharge both the materials produced same phase i.e. lithium intercalated manganese dioxide (Li_xMnO_2). This was also confirmed through X-ray photoelectron spectroscopy (XPS) investigation of the discharged products.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Lithium insertion; Battery behavior; Comparison

1. Introduction

The alkaline manganese dioxide battery has advanced to a dominant position in the primary battery market since its introduction in 1960's [1]. γ -Manganese dioxide is a low cost, low toxicity material and its electrochemical characteristics make it an excellent material for use as positive electrode in primary and lithium secondary batteries [2]. Based on the method of production, γ - MnO_2 can be categorized as natural manganese dioxide (NMD), chemical manganese dioxide

(CMD) and electrolytic manganese dioxide (EMD). The γ - MnO_2 polymorph does not denote a unique structure but has been suggested to be either a single phase with considerable disorder [3] or a multi-phase assembly [4]. These materials are made up of varying amounts of pyrolusite (β - MnO_2) intergrowth (1×1 channels) in the ramsdellite (rare MnO_2 material) (2×1 channels) matrix. The pyrolusite is characterized by the De Wolff disorder and the microtwinning defect [5].

γ - MnO_2 is prepared in many different ways. The material produced by electrolytic methods, commonly called as electrolytic manganese dioxide, is the most commonly used form of MnO_2 in batteries. Other forms are also used in batteries but they behave differently. In our previous publication [6], we have shown that EMD undergoes an intercalation

[☆] Part I: J. Power Source 130 (2004) 254–259.

* Corresponding author. Tel.: +61 8 9360 2719; fax: +61 8 9310 1711.

E-mail addresses: minakshi@central.murdoch.edu.au (M. Minakshi), p.singh@murdoch.edu.au (P. Singh).

type of reaction when electroreduced in presence of aqueous lithium hydroxide (LiOH) electrolyte. In this paper, we report our findings on the chemically prepared battery grade manganese dioxide (BGM). The objective is to compare the two materials and to determine whether the BGM behaved in a manner similar to the EMD.

2. Experimental

The EMD and BGM used in this work were purchased from the Foote mineral company and Sigma Aldrich, respectively. The theoretical maximum deliverable electrochemical capacity per unit weight for a one-electron process for both the materials is calculated to be 289 mAh g^{-1} .

The cell design and experimental details were similar to those reported earlier [6]. For X-ray analysis a Siemens X-ray diffractometer using Philips Co K α radiation was used. The FTIR spectrum was recorded by using a Nicolet Magna-IR 850 spectrometer. The EMD and BGM were reportedly mixed thoroughly with KBr (spectroscopic grade). The mixtures were examined by transmission mode FTIR spectroscopy. For each sample an average of 16 scans were recorded. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20). Thermo gravimetric analysis (TGA) of the sample was conducted by using a TA instruments (SDT 2960). Kratos Ultra Axis Spectrometer using monochromatic Al K α (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was carried out at pressures below 1×10^{-9} hPa.

3. Results and discussion

3.1. Characterization of the MnO₂ materials

The EMD and the BGM were characterized by X-ray diffraction (XRD), infrared (IR) spectra, thermogravimetric analysis and scanning electron microscopy (SEM). Fig. 1(a) and (b) show the differences in the X-ray diffraction patterns of the two MnO₂ materials. The XRD peaks of EMD are broad and poorly defined. This is ascribed to non-periodic intergrowth of pyrolusite and ramsdellite structural units [7]. The XRD patterns of the battery grade manganese dioxide material (Fig. 1(b)), contains four diffraction peaks with 2θ angles 16.3, 19.7, 29.7 and 31. Different researchers have reported different 2θ values for this material, which is explained in terms of variation of composition of the constituent ramsdellite and pyrolusite phases [7–9]. The diffraction peaks at the 2θ angle of 29.7 can be assigned to presence of OH bonds in the structure and the peak at 31 to β -MnO₂. The remaining peaks at 16.3 and 19.7 are characteristic of the γ -phase MnO₂.

The FTIR spectra of the EMD and BGM are compared in Fig. 2. The spectral features of both are almost iden-

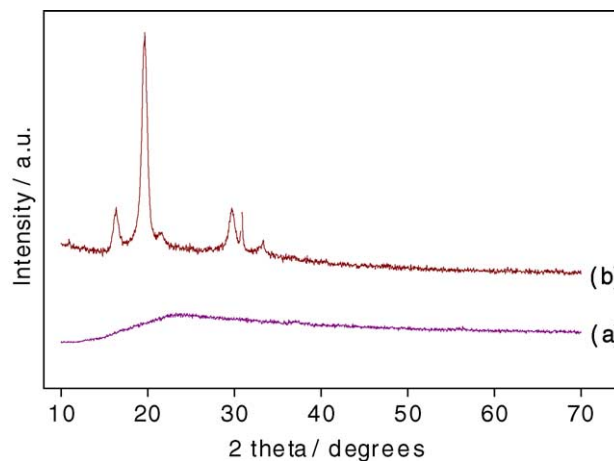


Fig. 1. X-ray diffraction patterns of (a) EMD and (b) BGM before discharge.

tical indicating the presence of similar phases. The region below 1400 cm^{-1} contains peaks due to fundamental vibrations of MnO₆ octahedra and the region above 1400 cm^{-1} contains peaks primarily corresponding to OH vibrations. The absorption band at 3183 cm^{-1} , which is predominant for the battery grade material (Fig. 2 (b)) corresponds to structural or chemically-bonded water [10]. This water is lost on heating as can be seen from Fig. 3. No such loss occurs for the EMD material. Fig. 3 also shows that there is a change in phase of the BGM when heated to around $500 \text{ }^\circ\text{C}$. Thus, while the EMD retains its phase structure on heating the BGM does undergo a phase transformation. This is probably relates to the change of γ -phase to β -phase. The EMD and the battery grade MnO₂ have quite different morphologies. The SEM micrographs of the materials (Fig. 4(a) and (b)) indicate that the battery grade material is less crystalline with finer particle size as compared to the EMD material.

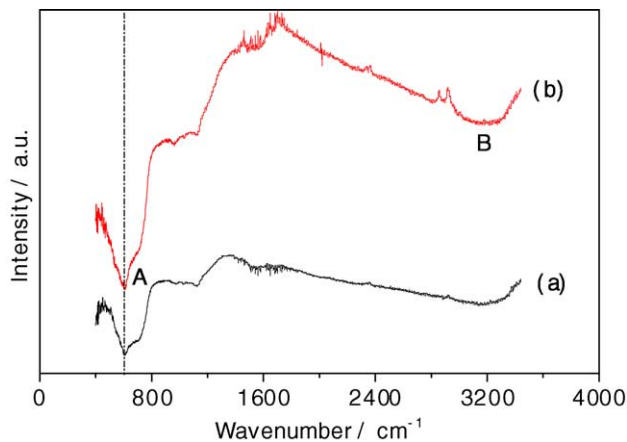


Fig. 2. FTIR spectra of (a) EMD and (b) BGM. (A) Main MnO₂ octahedral vibration and (B) bonded OH.

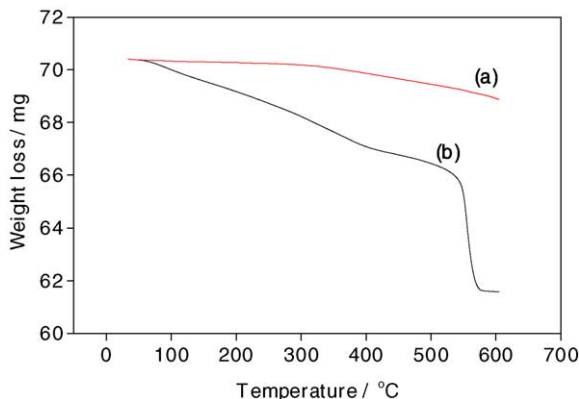


Fig. 3. Thermogravimetric analysis of (a) EMD and (b) BGM.

3.2. Discharge characteristics of Zn|MnO₂|aqueous LiOH cell

Fig. 5 shows the difference in the discharge characteristics of Zn|MnO₂|aqueous LiOH cells containing EMD and the BGM as cathode materials. The OCV of the cell with battery grade MnO₂ is higher and the cell discharges at a higher volt-

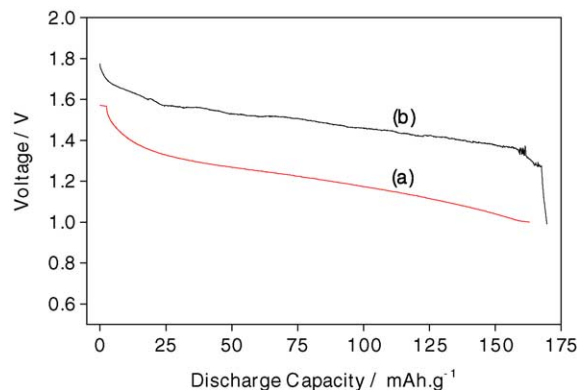


Fig. 5. Voltage vs. discharge capacity of Zn|MnO₂|LiOH (sat.), 1 M ZnSO₄ cells (a) EMD and (b) BGM.

age under identical conditions. However, the active material utilization of the BGM is lower than that for EMD material. In contrast to EMD the BGM shows a sharp drop in voltage when the delivered capacity approaches 165 mAh g⁻¹. The EMD does not show such drop upto that point. This is probably related to the difference in the composition of the two MnO₂ materials with respect to ramsdellite and pyrolusite, water content and surface area. The two MnO₂ materials exhibit quite different rechargeability when subjected to continuous discharge/charge cycles. For example, while a 35% drop in the active material utilization occurred at cycle number 2 for the cell containing BGM. For EMD, the same drop occurred at the 20th cycle. Thus the EMD is more stable to discharge/charge cycling.

3.3. Characterization of the discharged MnO₂ material in Zn|MnO₂|aqueous LiOH cells

The materials that were produced on discharge (electroreduction) of EMD and BGM in Zn|MnO₂|aqueous LiOH batteries was characterized by X-ray diffraction investigation. As noted earlier the XRD patterns of the two starting MnO₂ materials are quite different (Fig. 1). However, as can be seen Fig. 6, the two materials on discharge have almost identical XRD patterns. For the EMD material *d*-spacing of 3.27 Å

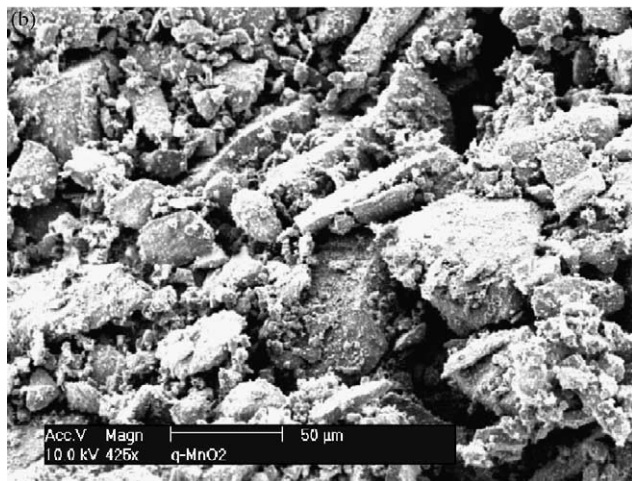
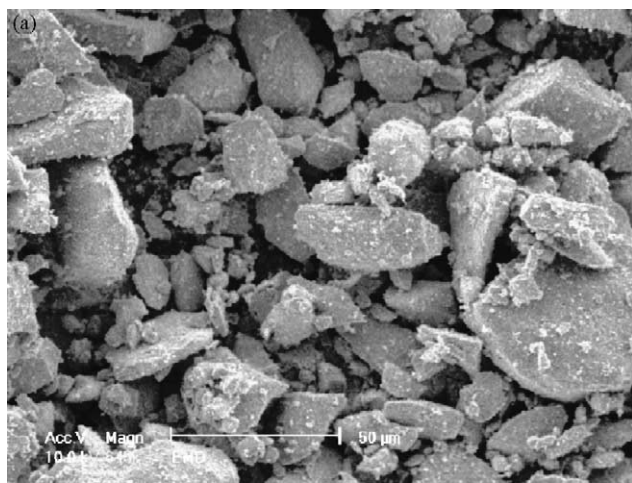


Fig. 4. SEM micrographs of images of (a) EMD and (b) BGM.

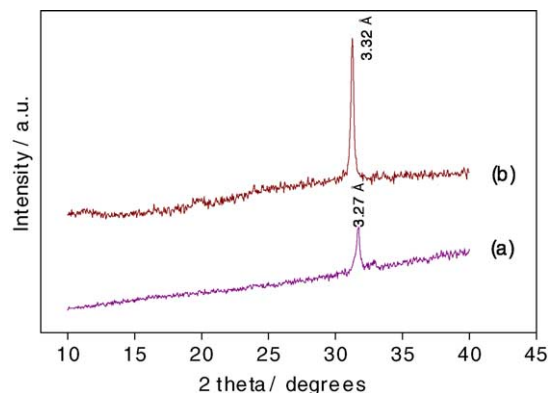


Fig. 6. X-ray diffraction patterns of (a) EMD and (b) BGM after discharge.

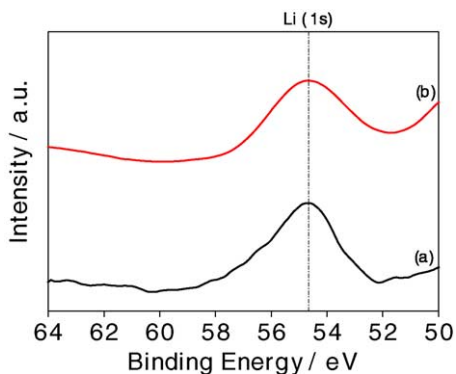


Fig. 7. XPS spectra of Li (1s) for the discharged (a) EMD and (b) BGM.

($2\theta = 31.7$) is ascribed to the formation of Li intercalated MnO_2 phase (Li_xMnO_2) [11]. For the BGM, d -spacing of the peak is at of 3.32 \AA ($2\theta = 31.2$). This difference is to be expected because the two phases could differ in the amount of intercalated lithium.

The XPS spectra of Li (1s) of the two discharged materials (EMD and BGM) are shown in Fig. 7. The peaks are assigned with reference to the values reported in the literature [12,13]. Both the discharged materials show Li (1s) peaks at 54.4 eV , which is attributed to lithium intercalated manganese dioxide (Li_xMnO_2). Thus, both the materials produce the same product on discharge in presence of LiOH.

4. Conclusions

The cathodic behavior of electrolytic manganese dioxide and chemically prepared battery grade manganese dioxide in $\text{Zn}|\text{MnO}_2|\text{aqueous lithium hydroxide (LiOH)}$ is compared. The XRD patterns of the two materials are quite different. The BGM is less crystalline and smaller in particle size compared to EMD. The cells with BGM have higher OCV than those with EMD. The BGM cells discharge at a higher voltage when discharged at the same current density, 0.5 mA cm^{-2} . Even though, the phase composition of the two starting ma-

terials are different on discharge in aqueous LiOH electrolyte both produce the same phase, lithium intercalated manganese dioxide (Li_xMnO_2). As compared to BGM, EMD is more stable to discharge/charge cycling.

Acknowledgements

One of the authors (M. Manickam) is grateful to Murdoch University for research scholarship. The technical support of Doug Clarke, Ken Seymour, Stewart Kelly and Peter Fallon all of Murdoch University is also acknowledged.

References

- [1] D. Linden, Handbook of Batteries, Mc-Graw Hill, New York, 1994.
- [2] E. Macheaux, L.I. Hill, D. Guyomard, The Electrochemical Society, 204th meeting, Abstract 365.
- [3] Y. Chabre, J. Pannetier, Prog. Solid State Chem. 23 (1995) 1.
- [4] A.H. Heur, A. He, P. Hughes, F. Feddrix, Proceedings of the IBA 2000 Manganese Dioxide Symposium, Argonne, May 9–12, 2000.
- [5] P.M. De Wolff, Acta Crystallogr. 12 (1959) 341.
- [6] M. Minakshi, P. Singh, T.B. Issa, S. Thurgate, R. DeMarco, The Electrochemical Society, IMLB 12 meeting 2004, Abstract 161.
- [7] J. Fitzpatrick, L.A.H. Maclean, D.A.J. Swinkels, F.L. Tye, J. Appl. Electrochem. 27 (1997) 243.
- [8] J.G. Kim, J.B. Dixon, C.C. Chusei, Y. Deng, J. Am. Soil Sci. Soc. 66 (2002) 306.
- [9] T. Ohzuku, H. Watanabe, T. Hirai, in: K.V. Kordesch, A. Kozawa (Eds.), The 2nd Battery Material Symposium, vol. 2, Graz, 1985. International Battery Material Association, Cleveland, OH, 1985, p. 145.
- [10] W.C. Vosburgh, J. Electrochem. Soc. 106 (1959) 839.
- [11] E. Levi, E. Zingrad, H. Teller, M.D. Levi, D. Aurbach, E. Mengeritsky, E. Elster, P. Dan, E. Granot, H. Yamin, J. Electrochem. Soc. 144 (1997) 4133.
- [12] K. Kanamura, H. Tamura, S. Shiraishi, Z. Takehara, Electrochim. Acta 40 (1995) 913.
- [13] Perkin Elmer Corporation, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics Division, Perkin Elmer Corporation, USA, October 1992.