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Spectroscopic Study of the Proton Dynamics in Manganese Dioxide Electrode Materials

C. S. Johnson[a], M. M. Thackeray[a], J. C. Nipko[b], and C.-K. Loong[b]

Argonne National Laboratory, Argonne, IL 60439, U.S.A.
[a]Electrochemical Technology Program, Chemical Technology Division
[b]Intense Pulsed Neutron Source Division

Abstract

Proton or lithium diffusion is a critical electrode process that occurs in manganese dioxide electrode materials during cycling of either aqueous (alkaline) or non-aqueous (lithium) batteries. The structural and electrochemical properties of a number of hydrated alpha-phase manganese dioxide compounds (α-$MnO_2 \bullet nH_2O$; $n \approx 0.2$-0.33), the heat-treated products ($n \approx 0$-0.1), as well as their more stable lithia-doped derivatives, α-$[xLi_2O] \bullet MnO_2$ ($0 \leq x \leq 0.25$), have been investigated. Inelastic neutron scattering was used as a means to differentiate and interrogate the key proton or water interactions in these MnO_2 structures. The neutron spectra reveal excitations associated with the hydrogen vibrations centered at 4, 13, 16, 26, 36, 65, 90, 110, 140, 200, 420, and 490 meV in the alpha-phase and 14, 24, 65, 84, 100, 202, and 425 meV in the lithia-doped derivatives. Band assignments were carried out by comparing these frequencies with those reported for structurally similar hydrated γ-MnO_2 compounds and by comparison with infrared data.

Keywords: manganese dioxide, lithium battery, neutron scattering

Correspondence:
Dr. Christopher S. Johnson
CMT, Building 205
Argonne National Laboratory
Argonne, IL 60439-4814

FAX: (630) 252-4167
Email: johnsoncs@cmt.anl.gov

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1. Introduction

Manganese dioxide (MnO_2) materials are increasingly being chosen as the active electrode material in non-aqueous, primary lithium (Li/non-aqueous organic electrolyte/MnO_2), and secondary (rechargeable) lithium-ion batteries (Li_xC_6/non-aqueous organic electrolyte/$Li_{1-x}Mn_2O_4$) [1]. MnO_2 is attractive because of its relatively low cost compared to either nickel in Ni-MH (metal-hydride) or cobalt in lithium-ion ($LiCoO_2$) secondary batteries. Moreover, recent data has demonstrated good performance from MnO_2-based chemistries as well, with cells exhibiting high energy/power density properties [2].

The development of non-aqueous MnO_2 cells has evolved as a result of the use of γ-MnO_2 initially as a primary cathode in aqueous alkaline batteries (Zn/KOH/MnO_2). In the aqueous cell, the discharge process is governed by the diffusion and reaction of protons (H^+) on the surface of the γ-MnO_2 electrode particle. Due to the chemical similarity of Li^+ to H^+, it is reasonable to expect that the behavior of the lithium cation in a non-aqueous cell may be equivalent. In fact, specially heat-treated γ-MnO_2 functions quite well, giving 3 volts in a lithium non-aqueous cell and yielding capacities in the range of 200 mAh/g, equivalent to the insertion of about 0.65 Li per mole of MnO_2 [3] However, these particular materials have limited reversibility which hinders their rechargeability.

Our studies have focused on the preparation and characterization of a class of new alpha-phase (α-MnO_2) materials which possess good rechargeability in terms of capacity and rate in 3 V lithium cells. The objective is to obtain information about the role hydrogen plays in H-bonding and diffusion in these materials. In turn, data from inelastic neutron scattering studies may help us formulate a good comparison between hydrogen and lithium and allow us a better understanding of lithium/MnO_2 batteries. Due to the adverse reaction with metallic lithium or a lithiated negative electrode, the minimization of water in a non-aqueous lithium cell is necessary for its proper operation.

2. Experimental

Hydrated alpha manganese dioxide (α-$MnO_2 \bullet H_2O$; n≈0.2-0.33), its heat-treated product and the subsequent lithium-oxide stabilized product (α-[xLi_2O]MnO_2) were synthesized as previously described [4]. A detailed description of the electrochemical experiments may be found in reference 4.

Inelastic neutron scattering experiments on two hydrated samples (α-$MnO_2 \bullet 0.25H_2O$, α-$MnO_2 \bullet 0.33H_2O$), a dehydrated (α-MnO_2) and partially dehydrated product (α-$MnO_2 \bullet 0.10H_2O$), a subsequent lithium-oxide stabilized (α-[$0.143Li_2O$] $\bullet MnO_2$) product, and a similar deuterated sample (α-$MnO_2 \bullet 0.12D_2O$), were carried out using the HRMECS spectrometer at IPNS. Incident energies of 50, 150, 170, 250, 350, and 600 meV were chosen and the sample temperature was controlled in a range of 6-15 K.

3. Results

Alpha-MnO_2 has a framework structure containing MnO_6 octahedra. It has been commonly believed that the α-MnO_2 structure is stabilized by a foreign cation such as K^+, NH_4^+, or Ba^{2+} within the 2x2 tunnel interstitial space of the framework [5]. From our synthesis method, we have succeeded to synthesize an α-MnO_2 structure devoid of such "stabilizing" cations [6]. The process yields a product which is highly crystalline and dense and which has a tetragonal symmetry (I4/m). The average unit cell parameters, determined from powder X-ray diffraction on 10 separate hydrated samples, are a = b = 9.813 Å and c = 2.850 Å. Analyses of neutron diffraction data by Rietveld profile refinement have shown unequivocally that molecular water (H_2O, or possibly H_3O^+) is present within the 2 x 2 tunnels of the structure and the oxygen atom of the water is located at the center of the tunnel in the (0.0,0.0,0.5) unit cell position [4].

The hydrated α-MnO_2 can be heat-treated at 275 °C in air to remove surface-bound water and water within the 2 x 2 tunnels. Thermogravimetric data collected on this material showed that about 4-5 wt.-% water was present as structural (2x2) tunnel water,

and 2-3 wt.-% was present as surface (interfacial) water. Furthermore, the α-MnO_2 structure itself remains intact at temperatures up to 400°C. Structure analysis of the heat-treated samples confirmed earlier reports that the MnO_2 framework structure remains intact during dehydration [7] and showed that, on average, the unit cell contracts by about 0.5% (a = b = 9.763 Å, c = 2.860 Å).

The α-MnO_2 framework structure can be stabilized by an exchange of the H_2O component in the α-$MnO_2 \bullet nH_2O$ hydrated phase with Li_2O, and that n can reach a value of 0.15 (in nLi_2O) without structural degradation of the α-MnO_2 framework [4]. The unit cell parameters of several samples with varying Li:Mn mole ratios were calculated from powder X-ray diffraction data. The unit cell expands, almost linearly, with increasing lithium content to a Li : Mn ratio of 0.3 : 1 without the appearance of a second phase; with this ratio the unit cell parameters are a = b = 9.932 Å, and c = 2.852 Å. Chemical analysis of lithium-oxide doped products quantitatively verified the reactant Li : Mn mole ratio. The O^{2-} anions occupy crystallographic positions within the 2 x 2 tunnels (Fig. 1); the lithium cations appear to be coordinated octahedrally to the oxygen atoms of the framework structure and those located within the 2 x 2 tunnels [4].

Interactions between the H_2O molecules with the MnO_2 structure are important to address because of their structural equivalency to the Li_2O molecule. These were assessed by inelastic neutron scattering measurements. The inelastic neutron cross-section scattering coefficient of hydrogen is at least one order of magnitude greater than that of manganese or oxygen. Thus, the intensities of bands in the energy transfer spectra are predominantly due to hydrogen interactions within the structure. Fig. 2 shows a representative, baseline-corrected spectrum of α-$MnO_2 \bullet 0.25H_2O$ obtained with a neutron incident energy of 600 meV. Fig. 2 also displays the spectrum of the same sample after heat treatment at 275 °C. This spectrum is essentially featureless in terms of hydrogen interactions and confirms that water is removed from α-MnO_2 on heat treatment. Note that the presence of a large continuum background in the spectrum of the hydrated sample

suggests significant mobility of hydrogen ions. This spectra are similar to a previously reported neutron scattering survey of other manganese oxide structures which have been used in rechargeable lithium batteries [8]. A detailed analysis of the neutron results in conjunction with the electrochemical properties of the Li-inserted MnO_2 system will be given elsewhere.

Acknowledgments

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Figure Caption:

Fig. 1 The positions of the oxygen atoms within the 2 x 2 tunnels of the lithiated α-MnO_2 structure.

Fig. 2 Representative base-line corrected inelastic neutron scattering spectra for α-$MnO_2 \bullet 0.25H_2O$ (open circles) and the same sample after heat treatment at 275 °C (filled circles).

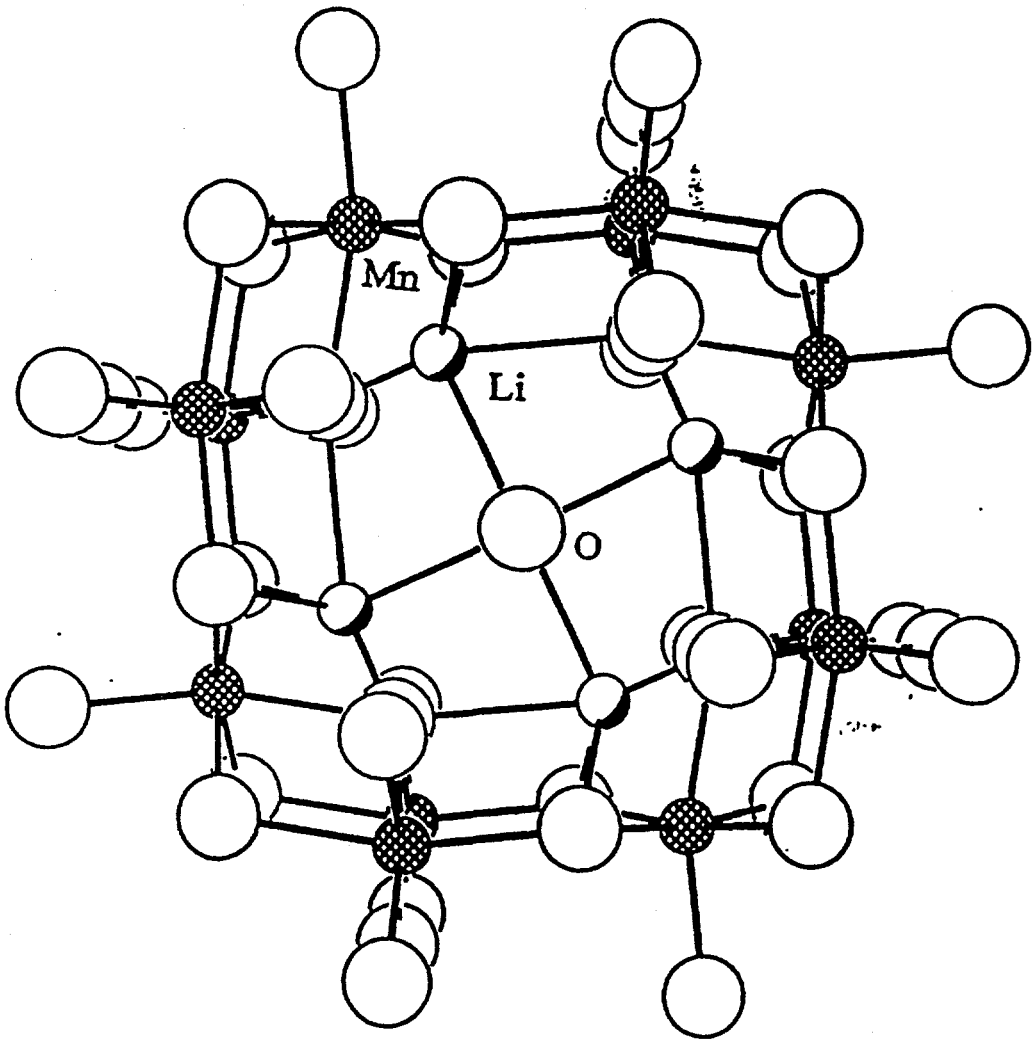

Fig. 1 "Spectroscopic Study of ... " C. S. Johnson *et. al.*

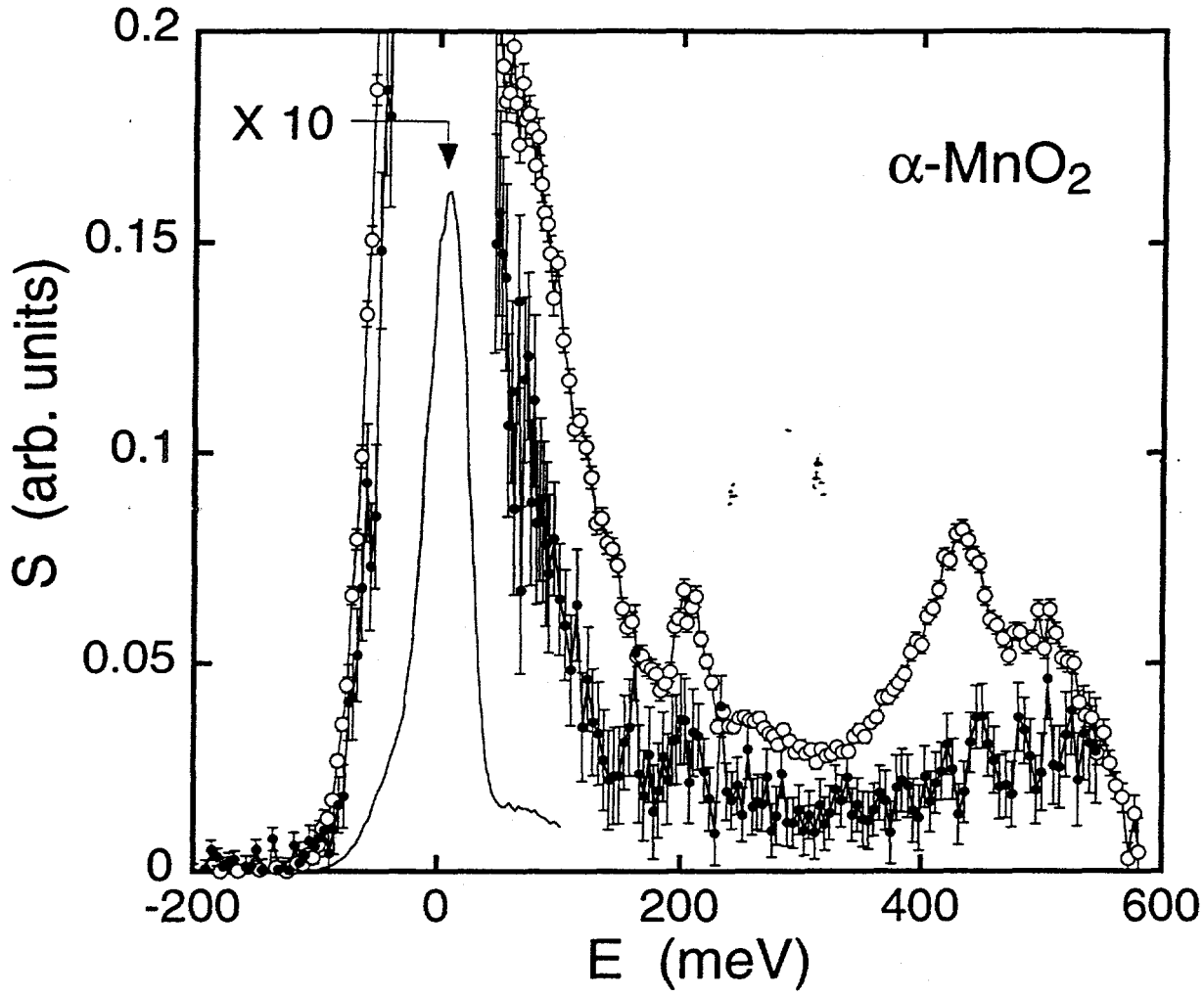

Fig. 2: "Spectroscopic Study of ... " C. S. Johnson et. al.