In-situ Synchrotron X-ray Diffraction Study of the Heat Treated Electrolytic Manganese Dioxide Cathode used in Primary Li/MnO_2 Batteries

Wesley M. Dose[a], Neeraj Sharma[b] and Scott W. Donne[a]

[a]Discipline of Chemistry, University of Newcastle
Callaghan, NSW, 2308, Australia
[b]School of Chemistry, University of New South Wales,
Sydney, NSW 2052, Australia

(scott.donne@newcastle.edu.au)

Manganese dioxide based cathode materials have considerable potential as high power, low cost and safe electrode materials in both primary Li/MnO_2 and secondary Li-ion battery technologies [1, 2]. Prior to use in primary Li/MnO_2 batteries, the MnO_2 must be heated to remove structural water and to form a compound more suitable to lithium intercalation [3]. There are numerous reports in the literature investigating lithium intercalation into heat-treated MnO_2 materials using experimental techniques such as ex-situ lab-based XRD, convergent beam electron diffraction, Li MAS NMR and electrochemical methods [3-5]. However, there is little agreement between these reports on the actual discharge mechanism. This work examines the structural evolution of heat-treated MnO_2 with respect to discharge (and applied current rate) in a real cell environment using time-resolved in-situ synchrotron X-ray diffraction. Additionally, the in-situ results are compared to higher-resolution ex-situ data.

Selected in-situ diffraction patterns showing the structural evolution of the heat-treated MnO_2 discharged at a 4.3 mA/g rate are displayed in Figure 1. The ex-situ diffraction patterns of the heat-treated MnO_2 discharged at 11.4 mA/g, and measured at various degrees of discharge, are shown in Figure 2.

The structural changes observed in the in-situ and ex-situ data as the heat treated MnO_2 is reduced are related with the electrochemical behavior of the battery, and a discharge mechanism is proposed. This is discussed in relation to previously proposed discharge mechanisms for the primary Li/MnO_2 system.

References

[1] J. M. Tarascon, M. Armand, Nature, 414, 359, 2001
[2] C. S. Johnson, J. Power Sources, 165, 559, 2007
[3] T. Ohzuku, M. Kitagawa, T. Hirai, J. Electrochem. Soc., 136, 3169, 1989.
[4] Y. Shao-Horn, S. A. Hackney, B. C. Cornilsen, J. Electrochem. Soc., 114, 3147, 1997.
[5] W. Bowden, C. Grey, S. Hackney, X. Q. Yang, Y. Paik, F. Wang, T. Richards, R. Sirotina, ITE Lett. Batt., 3, 312, 2002.

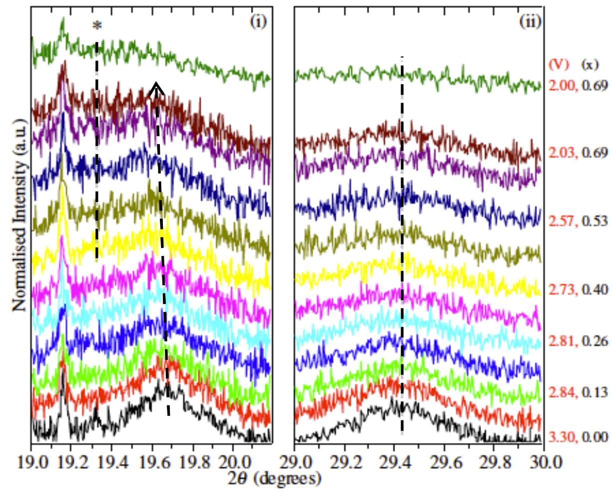

Figure 1: Selected in-situ synchrotron X-ray diffraction patterns collected during the 4.3 mA/g discharge in the regions (i) $19.0 \leq 2\theta \leq 20.2$ ($2.50 \leq d \leq 2.36$ Å) and (ii) $29.0 \leq 2\theta \leq 30.0$ ($1.65 \leq d \leq 1.60$ Å). The 'relaxed' structure for the 0.015 mA and 0.060 batteries measured after 6 and 4 days, respectively (top pattern). There is an emergence of a new phase indicated by (*) and confirmed by ex-situ data.

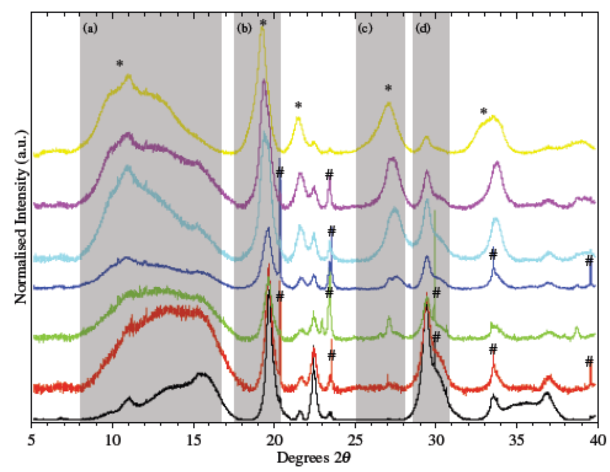

Figure 2: Ex-situ synchrotron X-ray diffraction patterns of heat-treated MnO_2 taken at various degrees of discharge. Shaded areas show 2θ regions which will be further examined in the presentation. Peaks arising from Al foil scraped from the current collector with the removal of the cathode material are marked with (#).