

Erratum

Erratum to ‘Structural and electrochemical studies of  $\alpha$ -manganese dioxide ( $\alpha$ -MnO<sub>2</sub>)’ [Journal of Power Sources 68 (1997) 570–577]<sup>1</sup>

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Errors were inadvertently made by the publisher when printing the above paper.

1. Please note that the affiliations of Argyriou and Christensen were interchanged. The correct version is as above.

2. In the description of manganese dioxide phases, the Greek symbol  $\alpha$  (alpha) was printed several times instead of  $\gamma$  (gamma). The corrected paragraphs read as follows:

**1. Introduction (p. 570)**

Manganese oxides are of interest as insertion electrodes for primary and secondary lithium batteries [1]: (i) heat-treated  $\gamma$ -MnO<sub>2</sub> electrodes are used in commercial 3 V primary cells; (ii) electrodes consisting of an intergrowth structure of lithiated  $\gamma$ -MnO<sub>2</sub> and spinel-related MnO<sub>2</sub> are used in commercial 3 V rechargeable cells, and (iii) the spinel system Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> ( $0 < x \leq 1$ ) is being developed for 4 V rechargeable lithium cells. The rechargeability of 3 V manganese oxide electrodes tends to be limited by the anisotropic expansion and contraction of the crystallographic unit cell when lithium is inserted into, and removed from,  $\gamma$ -MnO<sub>2</sub> or spinel-related electrode structures. Crystallographic distortions in lithiated manganese oxides can be attributed largely to a Jahn–Teller effect, where the concentration of Mn<sup>3+</sup> ions within the oxygen array reaches a critical value, typically when the mean oxidation state of Mn falls below 3.5 [2]. For example, in the 3 V spinel electrode system Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> ( $1 < x \leq 2$ ), the onset of the Jahn–Teller effect at  $x = 1$  results in a tetragonal distortion of the unit cell [3]; the 16% increase in the  $c/a$  ratio is too severe for the crystal structure to tolerate repeated charge and discharge cycles. The practi-

cal consequence of this distortion is, therefore, a pronounced loss in capacity in the spinel cathode during cycling of the cell. Alternative lithium manganese oxide 3 V electrodes exist and offer advantages over the 3 V Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> spinel electrode. A notable example is the intergrowth structure of lithiated  $\gamma$ -MnO<sub>2</sub> and spinel-related MnO<sub>2</sub> which yields superior electrochemical cycling. However, the performance of 3 V MnO<sub>2</sub> electrodes still needs to be improved in terms of both electrode capacity and stability.

**2. Experimental (p. 571)**

The synthesis of hydrated  $\alpha$ -manganese dioxide ( $\alpha$ -MnO<sub>2</sub> ·  $n$ H<sub>2</sub>O;  $n \approx 0.2$ –0.36) was carried out in two steps. In the first step, Mn<sub>2</sub>O<sub>3</sub> was prepared by heating either electrolytic  $\gamma$ -MnO<sub>2</sub> powder (EMD, Kerr-McGee) or chemically prepared  $\gamma$ -MnO<sub>2</sub> (CMD, Chemetals) in air at 700°C. In the second step, Mn<sub>2</sub>O<sub>3</sub> was reacted with 4–8 M H<sub>2</sub>SO<sub>4</sub> at 105°C, which resulted in the disproportionation of Mn<sub>2</sub>O<sub>3</sub> into a soluble Mn<sup>2+</sup> species and the desired  $\alpha$ -MnO<sub>2</sub> product. The reaction temperature can be decreased to 40°C if the time for reaction is increased to days instead of hours. The resulting product was dehydrated at 300°C. The  $\alpha$ -MnO<sub>2</sub> powders were lithiated with  $n$ -butyllithium (25% mole excess) at –40°C or with LiI (50% mole excess) at –40, 25, and 80°C. Li<sub>2</sub>O-doped products ( $x$ Li<sub>2</sub>O · MnO<sub>2</sub>;  $0 \leq x \leq 0.25$ ) were prepared by reaction of  $\alpha$ -MnO<sub>2</sub> with LiOH · H<sub>2</sub>O by wet mixing in methanol, drying the resulting slurry, and firing the final mixture in air at 275°C.

**3.4 Structure analysis of 0.15Li<sub>2</sub>O · MnO<sub>2</sub> (p. 573)**

A neutron diffraction study was conducted on a lithiated  $\alpha$ -MnO<sub>2</sub> sample of composition 0.15Li<sub>2</sub>O · MnO<sub>2</sub>. The structure, as determined from a Rietveld profile refinement is depicted in Fig. 4. A difference Fourier map provided evidence that the oxygen ion from the Li<sub>2</sub>O molecule was

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located at (0.0, 0.0, 0.40), with a site occupancy equal to 0.20(1). This is close to the position that was occupied by the oxygen ion of the H<sub>2</sub>O molecule in the hydrated compound. A subsequent difference Fourier map (after subtraction of all the manganese and oxygen from the structure) indicated that the lithium ions were located at (0.204, 0.078, 0.000), with a site occupancy of 0.19(2). Within experimental error, the final structure analysis yielded a composition of 0.10Li<sub>2</sub>O · MnO<sub>2</sub>, which is considered to be in very good agreement with the anticipated composition of 0.15Li<sub>2</sub>O · MnO<sub>2</sub>, given the low concentration of Li<sub>2</sub>O in the compound and quality of the data. Interatomic Li–O distances showed that the lithium ions were coordinated more strongly with the oxygens of the framework structure than with the oxygens in the (2 × 2) tunnels. (Note that if an oxygen ion completely occupied

the site at (0.0, 0.0, 0.5), then a distorted hexagonal, close-packed oxygen array would result, similar to that found in  $\gamma$ -MnO<sub>2</sub> structures. These data, therefore, indicate that the role of Li<sub>2</sub>O is to stabilize  $\alpha$ -MnO<sub>2</sub> structures, with oxygen occupying sites in the defect oxygen array of the  $\alpha$ -MnO<sub>2</sub> structures, and with the charge-compensating lithium ions occupying newly created interstitial sites. A more detailed description of Li<sub>2</sub>O-stabilized  $\alpha$ -MnO<sub>2</sub> structures has been presented elsewhere [18].

3. The captions for Figs. 7 and 8 were incorrectly assigned. The captions should read:

Fig. 7. The 84th discharge/charge cycle of a Li/1 M LiPF<sub>6</sub>, EC:DMC (1:1)/0.15Li<sub>2</sub>O · MnO<sub>2</sub> button cell.

Fig. 8. Discharge/charge cycle no. 6 of a Li/SPE/0.15Li<sub>2</sub>O · MnO<sub>2</sub> cell at 0.6 mA rate recorded at 60°C.