Thermal Lithiation of Manganese Dioxide: Effect of Low Lithium Concentration ($x \leq 0.3$ in Li_xMnO_2) on Structure and Electrochemical Performance

Joshua Lehr,^a Wesley M. Dose,^a Marina Yakovleva,^b and Scott W. Donne^{a,*}

^aDiscipline of Chemistry, University of Newcastle, Callaghan NSW 2308, Australia

^bFMC Lithium, Bessemer City, North Carolina 28016, USA

The effect of lithium concentration on Li_xMnO_2 ($x \leq 0.3$) materials prepared by co-precipitation/heating is investigated. Lithium concentration determines the phase formed, with three different phases identified in the concentration range. Low levels of lithiation ($x = 0.08$) leads to the formation of a γ/β type MnO_2 material. As the lithium concentration is increased to $x = 0.15$, a lithiated $\gamma\text{-MnO}_2$ like phase is formed. Finally, at $x = 0.28$ tunnel structured monoclinic MnO_2 is obtained. Increasing the concentration of lithium inhibits the formation of the undesired inactive Mn_2O_3 phase, which is formed upon heat-treatment of MnO_2 . At a 5 mA/g charge/discharge rate the monoclinic $\text{Li}_{0.28}\text{MnO}_2$ material gave the best performance, while at 30 mA/g the $\text{Li}_{0.08}\text{MnO}_2$ material proved superior.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.115206jes] All rights reserved.

Manuscript submitted October 18, 2011; revised manuscript received April 5, 2012. Published April 30, 2012.

The development of a range of portable consumer electronic devices over the past two decades has created significant demand for small, high energy, rechargeable batteries. Lithium-ion batteries have, to some extent, met this demand, offering high energy densities and cycle counts.¹ Nevertheless, the development of ever more power hungry devices, coupled with the desire for development of rechargeable batteries for electric cars to stem carbon dioxide emissions continues to drive research and development of superior lithium ion batteries. Much of this work has focused on the development of stable high capacity cathode materials. Research into the use of lithium cobalt oxide (LiCoO_2) and lithium iron phosphate (LiFePO_4) as active positive electrode materials for lithium ion batteries has led to the development of commercial cells integrating these materials.^{1,2} While these cells exhibit excellent cycling, combined with decent capacities of approximately 150 mAh/g, they also have a number of disadvantages. The high toxicity and lack of abundance of cobalt complexes makes LiCoO_2 less than ideal as a cathode active material. Due to poor conductivity, the alternative LiFePO_4 cathode materials require extensive processing making their incorporation into commercial cells costly.¹

Manganese dioxide (MnO_2) is an attractive cathode material due to its abundance, low cost, low toxicity, relatively high conductivity, and high theoretical capacity of 308 mAh/g.³ Furthermore, cells incorporating MnO_2 cathode materials can be produced in the fully charged state. While MnO_2 has been widely used in primary aqueous ($\gamma\text{-MnO}_2$) and non-aqueous ($\beta\text{-MnO}_2$) cells, its integration in secondary lithium ion cells has proven more problematic. Initial investigations were hampered by the evolution of structural water present in $\gamma\text{-MnO}_2$ which severely limits cell rechargeability. Heat treatment of the material was found to remove the structural water,^{4,5} but this was also accompanied by the undesirable transition of the $\gamma\text{-MnO}_2$ structure to a $\gamma/\beta\text{-MnO}_2$ form,^{5,6} and the resulting material was again seen to be unstable to extended cycling.⁷

A number of workers have reported that thermal lithiation of MnO_2 , achieved by heating MnO_2 to temperatures of 300–450°C in the presence of a lithium source, leads to improved capacity retention in non-aqueous cells.^{7–10} Some early work on these lithium manganese dioxide compounds (Li_xMnO_2) found a lithium to manganese ratio of 1:3 (i.e., $x = 0.33$) to be optimum in terms of the performance of the material.^{7,11} In another report¹⁰ an optimum composition of $\text{Li}_{0.38}\text{MnO}_2$ was identified, although materials with this composition consisted of $\text{Li}_{0.33}\text{MnO}_2$ as a component phase. The structure of $\text{Li}_{0.33}\text{MnO}_2$ has been interpreted in a number of ways. Furukawa and coworkers originally proposed a composite structure

of Li_2MnO_3 and $\gamma/\beta\text{-MnO}_2$,⁷ whereas Thackeray and coworkers suggested the material consists of a composite of $\gamma/\beta\text{-MnO}_2$ and a spinel LiMn_2O_4 -like phase.¹² However, neither of these proposals can account for the electrochemical performance or X-ray diffraction patterns of $\text{Li}_{0.33}\text{MnO}_2$.^{10,12,13} These considerations prompted Li et al. to propose the formation of a single $\text{Li}_{0.33}\text{MnO}_2$ phase.¹¹ This proposal is supported by the work of Aurbach and coworkers who found good agreement between experimental data and a simulated XRD pattern for a single phase, tunneled, monoclinic $\text{Li}_{0.33}\text{MnO}_2$ material using the Rietveld method.¹⁵ This result has been supported by subsequent reports.^{14,16}

Unlike $\text{Li}_{0.33}\text{MnO}_2$, thermally prepared Li_xMnO_2 materials with $x < 0.33$ have received little attention with no detailed studies of the effect of x in Li_xMnO_2 on structure and electrochemical performance reported to date. In the present work we investigate the structure and electrochemical performance of thermally lithiated electrolytic manganese dioxide (EMD). The extent of lithiation (x in Li_xMnO_2 , where $x < 0.33$) is varied, and the effect on structure, and electrochemical performance of the material is investigated.

Experimental

Sample preparation.— Lithiation was achieved by suspension of electrolytic manganese dioxide (EMD; Delta EMD, <32 μm particle size) in Milli Q water containing a known quantity of LiOH (99.9%; FMC Lithium). Suspensions containing various (see Table I) lithium to manganese ratios were prepared. After mixing these were placed in a synthetic air (80:20 $\text{N}_2:\text{O}_2$) purged oven at 60°C for several days to allow the water to evaporate and the lithium to precipitate on the EMD surface. Subsequently, the dry LiOH/EMD mixture was heated in a similar synthetic air atmosphere. Beginning at ambient temperature the sample was heated up to 350°C over the course of a 1 hour period. After heating at 350°C for 2 hours, the sample was allowed to cool naturally back to ambient conditions. Heat treated EMD (HEMD) was prepared using the same heat-treatment regime without the prior co-precipitation step.

Chemical characterization.— Inductively coupled plasma - optical emission spectrometry (ICP-OES) was carried out using a Varian Liberty Series II ICP-OES to determine the lithium content. Samples for analysis were prepared by dissolving a known quantity of sample in a solution containing 5% H_2O_2 in 0.1 M HNO_3 . Standards with the same matrix as the samples were used. All calibrations had a correlation co-efficient $R^2 > 0.990$ with at least five standards used. The Mn(III) content of various EMD materials was determined using a potentiometric titration technique as outlined in Vogel.¹⁷

*Electrochemical Society Active Member.

[†]E-mail: scott.donne@newcastle.edu.au

Table I. Comparison between expected and actual lithium content upon thermal lithiation of EMD.

Expected x in Li_xMnO_2 from co-precipitation	x in Li_xMnO_2 from ICP-OES	% Difference
0.019	0.020	2.7
0.037	0.038	2.6
0.074	0.081	8.8
0.148	0.148	0.3
0.220	0.222	1.1
0.300	0.280	7.2

Structural and morphological characterization.— X-ray diffraction (XRD) analysis of the resultant materials was carried out using a Philips 1710 diffractometer with Cu K_α radiation operating at 40 kV and 30 mA. A scan range of 10 to $90^\circ 2\theta$, a step size of 0.05° , and a count time of 2.5 s was used. Divergence and receiving slit widths of 0.1° were also used.

Sample morphology was determined using scanning electron microscopy (SEM) and gas adsorption measurements. SEM was conducted by mounting the sample for study on an appropriate Al stub using double-sided conductive carbon tape. The mounted sample was then carbon coated using an SPI Instruments Carbon Coater, before being examined at a range of different magnifications using a Philips XL30 SEM. Gas adsorption measurements (N_2 as the adsorbate at 77 K) were conducted using a Micromeritics ASAP 2020 unit, on samples that had been previously degassed under vacuum at 120°C for 2 hours. The specific surface area of each sample was then determined using the linearized BET isotherm¹⁸ in the partial pressure range 0.05–0.30.

Electrochemical characterization.— Cathodes were prepared by pressing approximately 250 mg of a 1:8:1 mixture of Li_xMnO_2 :graphite:binder (polyvinylidene difluoride) in a KBr die press under 7.5 MPa (1 kN on 13 mm diameter) for 1 min. After pressing, cathodes were dried at 110°C under vacuum for at least 12 hours prior to being transferred to a Ar filled glove box. Coin cells were assembled (in the glove box) as described previously¹⁹ using a lithium metal anode (FMC Lithium) and the MnO_2 derived cathodes. A 1 M solution of LiPF_6 in 1:1 (v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte. All electrochemistry was carried out using a Princeton Applied Research VMP 16 channel potentiostat/galvanostat. Cycling of the cells was conducted using a constant current charge/discharge protocol. The cells were initially discharged from open circuit potential (~ 3.2 V) to 2.0 V after which they were recharged, at the same rate, until a potential of 3.5 V was reached. The cell was then held at this potential for a further 150 minutes prior to subsequent discharge. This protocol was repeated at least 20 times for each cell.

Results and Discussion

Sample composition.— Table I compares the expected lithium content, based on LiOH and MnO_2 added during co-precipitation, to the empirical lithium content of the materials (after heat-treatment at 350°C for two hours) determined by ICP-OES.

Essentially all lithium co-precipitated with manganese is retained upon heat-treatment, indicating that accurate degrees of lithiation can be achieved by co-precipitation using LiOH, an assumption that is often made, but not verified, in the literature. For convenience the samples will be referred to using the Li_xMnO_2 nomenclature, where x is the moles of lithium per mole of manganese determined by ICP-OES.

Structural analysis.— Figure 1 shows the XRD patterns of the Li_xMnO_2 materials, the parent EMD, and the corresponding non-

Figure 1. XRD patterns of EMD, HEMD and Li_xMnO_2 materials prepared by co-precipitation of EMD and LiOH followed by heating at 350°C for 2 hours. Note that the symbol ($\downarrow$) indicates the formation of the monoclinic Li_xMnO_2 phase.

lithiated HEMD. Comparison of the EMD and HEMD XRD patterns shows the merging of the peaks at $\sim 21^\circ 2\theta$ (110 peak for orthorhombic $\gamma\text{-MnO}_2$) and $\sim 34^\circ 2\theta$ (031 peak for $\gamma\text{-MnO}_2$) to form a single peak at $\sim 28^\circ 2\theta$ (as indicated by the arrows in Figure 1). This change is associated with the conversion of $\gamma\text{-MnO}_2$ (EMD) to $\gamma/\beta\text{-MnO}_2$ during heating.²⁰ The pattern for $\text{Li}_{0.08}\text{MnO}_2$ is similar to that of HEMD, differing only in that it exhibits a slightly stronger peak at $21^\circ 2\theta$. Lithium is known to stabilize the $\gamma\text{-MnO}_2$ structure during heat-treatment.^{21–23} In the case of $\text{Li}_{0.08}\text{MnO}_2$ only a weak stabilizing effect is observed, due to the low concentration of lithium, and hence the material has undergone considerable transformation to $\gamma/\beta\text{-MnO}_2$ upon heat-treatment, as seen by comparison with the EMD pattern which exhibits a more distinct $21^\circ 2\theta$ peak.

Increasing the lithium content from $x = 0.08$ to 0.15 results in strengthening of the $\gamma\text{-MnO}_2$ peak at $\sim 21^\circ 2\theta$, indicating increased stabilization of the $\gamma\text{-MnO}_2$ structure with increasing lithium content. Similar results have been reported by Bowden and coworkers who suspended MnO_2 particles (in some cases pre-treated with H_2SO_4) in LiOH solution. After a specific period of time the solution was filtered and the precipitate heated to 350°C in air.^{21–24} Magic angle spinning (MAS) NMR indicated that immersion of the EMD in LiOH brings about exchange of surface and Ruetschi (associated with cation vacancies²⁰) protons with lithium ions, while Coleman protons (associated with Mn(III))²⁰ are not affected. Subsequent heat-treatment results in migration of lithium ions from the cation vacancy sites to the (1×2) ramsdellite tunnels, leading to the formation of a lithiated ordered intergrowth phase named ‘lithiated manganese dioxide’ (LiMD). XRD patterns of the LiMD indicated preservation of the $\gamma\text{-MnO}_2$ structure after heat-treatment.^{21–23} It was found that the lower limit, in terms of lithium concentration, for the formation of LiMD was $x = 0.125$ in Li_xMnO_2 .²³ This is consistent with the XRD patterns presented in Figure 1 which indicate a lower limit for the formation of the $\gamma\text{-MnO}_2$ -like LiMD at a lithium concentration between $x = 0.08$ and 0.15. Hence, the results obtained in the present work indicate the

Table II. Comparison of lithium and manganese (III) content of selected materials.

Material	$n_{\text{Mn(III)}}/n_{\text{Mn(total)}}$	x in Li_xMnO_2	$(n_{\text{Mn(III)}}/n_{\text{Mn(total)}}) - x$
$\text{Li}_{0.08}\text{MnO}_2$	0.1250	0.0810	0.0440
$\text{Li}_{0.15}\text{MnO}_2$	0.1463	0.1480	− 0.0017
$\text{Li}_{0.28}\text{MnO}_2$	0.2724	0.2800	− 0.0076
HEMD	0.0882	0.00	0.0882
EMD	0.0833	0.00	0.0833

LiMD material reported by Bowden and coworkers can be obtained by a simple co-precipitation/heating procedure, provided the required quantity of LiOH is used.

As the lithium content is increased above $x = 0.22$ the XRD patterns show the disappearance of the (merged) 221/240 peaks situated at $56^\circ 2\theta$, and the emergence of the new 411 peak at $53^\circ 2\theta$. Simultaneously, a further peak is seen to emerge at $\sim 18^\circ 2\theta$, particularly for the $x = 0.28$ sample. Note that the peak at $\sim 18^\circ 2\theta$ is not present for the $x = 0.22$ sample, indicating that there may be a preferred growth axis for this phase. These changes in the XRD patterns have been previously observed upon thermal lithiation with $x \approx 0.3$. As mentioned in the Introduction, this material has been assigned to a single phase monoclinic (c2/m) structure incorporating an ordered alternation of (1×1) and (1×2) tunnels.^{13–15,25} In the present work, Figure 1 indicates this structure is formed using lithium concentrations between $x = 0.22$ and 0.28.

In charge balanced, pure, single phase Li_xMnO_2 materials containing no structural protons, one would expect the amount of lithium and Mn(III) present in the structure to be identical. Hence, comparison of the lithium content (determined by ICP and presented in Table I) and the Mn(III) content (determined by potentiometric titration) can give additional information regarding the phase and purity of the materials, especially since no peaks corresponding to various lithium salts were observed in the diffraction data in Figure 1. Table II compares

the lithium (n_{Li}) and Mn(III) ($n_{\text{Mn(III)}}$) content of selected Li_xMnO_2 materials, EMD, and HEMD. A higher Mn(III) content is observed for HEMD than for EMD, despite the expected removal of Coleman protons (associated with Mn(III) in the structure) during heating at 350°C .²¹ This can be explained by the incorporation of a small amount of amorphous Mn_2O_3 , which is known to form during heating of MnO_2 .²⁶ and would not necessarily be expected to be observed in the XRD patterns at such low levels. The $\text{Li}_{0.08}\text{MnO}_2$ material shows only 0.044 mole of Mn(III) per mole of Mn, after Mn(III) ions associated with lithium have been subtracted from the total Mn(III) content. This indicates $\text{Li}_{0.08}\text{MnO}_2$ has approximately half the Mn_2O_3 content of HEMD, and suggests lithiation inhibits Mn_2O_3 formation. The effect is more pronounced for the $\text{Li}_{0.15}\text{MnO}_2$ and $\text{Li}_{0.28}\text{MnO}_2$ materials, which have near identical Mn(III) and lithium contents, indicating significant amounts of Mn_2O_3 are not present. The absence of Mn_2O_3 in the structure would be expected to improve performance of the material as a cathode active material in lithium ion cells.

Morphological analysis.— Typical images from the SEM analysis on samples prepared in this work are shown in Figures 2a–2d. The starting EMD material (Figure 2a) consists of a range of very jagged irregular particles, covering a wide range of sizes. This very irregular particle shape is as a result of the synthesis process used to make EMD, which includes a high energy milling stage to break the thick anodic EMD deposit (1–2 cm thick) down into a suitable particle size.²⁷ Heat treatment of this starting material apparently has very little effect on morphology, as can be seen in Figure 2b. Similarly, surface lithiation followed by heat-treatment also has little effect on morphology, as seen in Figure 2c and 2d, which were taken from the $\text{Li}_{0.15}\text{MnO}_2$ and $\text{Li}_{0.28}\text{MnO}_2$ samples, respectively.

The BET surface area of the starting EMD sample measured from gas adsorption was $32.2 \text{ m}^2/\text{g}$, which is typical of a commercial EMD sample.²⁷ Heat treatment of this material at 350°C for 2 hours (HEMD) led to a significant decrease in surface area down to $24.3 \text{ m}^2/\text{g}$. This result was expected based on previous work conducted in our laboratory.²⁸ Lithiation and heat-treatment of the EMD

Figure 2. SEM images of (a) starting EMD, (b) HEMD, (c) $\text{Li}_{0.15}\text{MnO}_2$ and (d) $\text{Li}_{0.28}\text{MnO}_2$.

Figure 3. Discharge capacity of cathode at (a) 5 mA/g and (b) 30 mA/g for cathodes containing HEMD (Δ), $\text{Li}_{0.08}\text{MnO}_2$ ($\bullet$), $\text{Li}_{0.15}\text{MnO}_2$ ($\circ$), and $\text{Li}_{0.28}\text{MnO}_2$ ($\blacktriangledown$).

led to samples with BET surface areas within $\pm 3\%$ of the straight heat treated material, with no trend apparent in the results. This allows us to conclude that it is the heat-treatment alone that affects material surface area, rather than lithiation and heat-treatment.

Electrochemical characterization.— The cycling performance of HEMD, $\text{Li}_{0.08}\text{MnO}_2$, $\text{Li}_{0.15}\text{MnO}_2$, and $\text{Li}_{0.28}\text{MnO}_2$ was evaluated at discharge rates of 5 and 30 mA g⁻¹, the results from which are shown in Figure 3 (discharge performance versus cycle number) and Figure 4a–4d (discharge curves from various cycles). At both discharge rates the HEMD control sample (Δ) shows high initial capacity, but exhibits significantly more capacity fade upon repeat cycling than the Li_xMnO_2 phases (cf. Figures 3 and 4a). The high initial capacity of HEMD can be attributed to the large number of intercalation sites in the unlithiated MnO_2 structure, while more rapid capacity fade for unlithiated material compared to Li_xMnO_2 phases, has been previously reported.^{7,9}

At a discharge rate of 30 mA g⁻¹ the $\text{Li}_{0.08}\text{MnO}_2$ material ($\bullet$) exhibits the best cycling of the four materials tested, giving a stable capacity of ~ 120 mAh/g after 20 cycles. The superior performance of $\text{Li}_{0.08}\text{MnO}_2$ is somewhat surprising considering structural similarities to HEMD, and indicates low levels of lithiation can effectively stabilize the structure during cycling. At both discharge rates the $\text{Li}_{0.15}\text{MnO}_2$ ($\circ$, LiMD) phase exhibits a drop to a low capacity after the first cycle. However, subsequent capacity gain was observed with final capacities close to that of the other materials obtained after 10–20 cycles. We attribute this behavior to a phase change occurring during cycling, perhaps somewhat similar to that observed during some of our previous work in this area.²⁹ In this article we reported on

Figure 4. Selected discharge curves for (a) HEMD, (b) $\text{Li}_{0.08}\text{MnO}_2$, (c) $\text{Li}_{0.15}\text{MnO}_2$ and (d) $\text{Li}_{0.28}\text{MnO}_2$ (30 mA/g discharge rate).

the phase transformations that a HEMD (β - MnO_2) sample undergoes when chemically (rather than electrochemically) reduced. In particular, the parent structure showed evidence for (i) structural expansion as a result of lithium intercalation, (ii) partial structural transformation into LiMn_2O_4 , and (iii) the formation of $\text{Li}_2\text{Mn}_2\text{O}_4$ presumably as the result of LiMn_2O_4 reduction. For the samples reported here, the $\text{Li}_{0.28}\text{MnO}_2$ ($\blacktriangledown$) material shows the best performance at a low charge/discharge rate of 5 mA g^{-1} , with a stable capacity of 160 mA g^{-1} observed over 10 cycles. It is worth noting that the varying cycle profiles of the three lithiated materials is further evidence that three distinct phases are formed at these different lithium concentrations (Figure 3).

The overall performance of the Li_xMnO_2 materials prepared in this work is quite good in comparison to the existing positive active materials used in Li-ion systems. This is particularly true when considering that these materials can be produced at a fraction of the cost of other comparable materials. In comparison to the performance achieved compared to other similar studies¹⁰ it is apparent that our materials demonstrated slightly inferior performance; i.e., $\sim 150 \text{ mAh/g}$ compared to 170 mAh/g .¹⁰ To justify and explain this difference we would highlight the differences in EMD precursors used for the respective syntheses, in particular the fact that the mean particles size of EMD used in Reference¹⁰ was $\sim 25 \mu\text{m}$ compared to $\sim 45 \mu\text{m}$ used in this work. There are abundant references in the literature where the effects of particle size and crystallite size are significant in determining the performance of a battery active material; e.g., LiFePO_4 is at present a common example.

Conclusions

The effect of lithium concentration on the structure and performance of Li_xMnO_2 ($x < 0.3$) materials, prepared by co-precipitation and heat-treatment, was investigated. Distinct phases, exhibiting different structural features and electrochemical cycling profiles were observed. As the lithium content is increased from $x = 0$ (HEMD) to 0.15 less conversion to the γ/β - MnO_2 phase is observed upon heat-treatment, with the γ - MnO_2 phase almost completely retained at $x = 0.15$. As the lithium content is increased above $x = 0.15$, the monoclinic tunnel structure Li_xMnO_2 phase is formed. Increasing lithium content was also seen to inhibit formation of the undesirable Mn_2O_3 product with no formation of this phase observed when $x \geq 0.15$. All lithiated materials exhibited equivalent, or better, performance than unlithiated HEMD, at cycle rates of both 5 and 30 mA/g . At 5 mA/g the monoclinic $\text{Li}_{0.28}\text{MnO}_2$ material gives a slightly higher capacity after ten cycles than the other materials. However, at a higher rate of 30 mA/g lithiated $\text{Li}_{0.08}\text{MnO}_2$ material exhibited the best cycling of the materials. This is a somewhat surprising result considering structural similarity to HEMD, and indicates low levels of lithiation can

effectively stabilize the MnO_2 structure to repeat cycling. Materials with this low level of lithiation have not been significantly investigated and warrant further study.

Acknowledgments

The authors acknowledge FMC Lithium for providing the funding for this project.

References

1. J. M. Tarascon and M. Armand, *Nature*, **414**, 359 (2001).
2. M. S. Whittingham, *Chemical Reviews*, **104**, 4271 (2004).
3. C. S. Johnson, *J. Power Sources*, **165**, 559 (2007).
4. H. Ikeda, T. Saito, and H. Tamura, *Manganese Dioxide as Cathodes for Lithium Batteries, Manganese Dioxide Symposium Cleveland, Ohio, USA, 1975*; A. Kozawa and R. J. Brodd, Eds. I.C Sample Office: Cleveland, Ohio, USA, 1975; pp 384.
5. F. Tedjar and J. Guillon, *Thermochim. Acta*, **181**, 13 (1991).
6. F. Petit, J. Durr, M. Lenglet, and B. Hannoyer, *Mater. Res. Bull.*, **28**, 959 (1993).
7. T. Nohma, T. Saito, N. Furukawa, and H. Ikeda, *J. Power Sources*, **26**, 389 (1989).
8. T. Nohma, Y. Yamamoto, K. Nishio, I. Nakane, and N. Furukawa, *J. Power Sources*, **32**, 373 (1990).
9. M. Yoshio, H. Nakamura, and Y. Y. Xia, *Electrochim. Acta*, **45**, 273 (1999).
10. J. R. Dahn and B. M. Way, US Patent 4,959,282 (1991).
11. L. Li and G. Pistoia, *Solid State Ionics*, **47**, 231 (1991).
12. M. M. Thackeray, M. H. Rossouw, A. Dekock, A. P. Delaharpe, R. J. Gummow, K. Pearce, and D. C. Liles, *J. Power Sources*, **43**, 289 (1993).
13. Y. Xia, K. Tatsumi, T. Fujieda, P. P. Prosinski, and T. Sakai, *J. Electrochem. Soc.*, **147**, 2050 (2000).
14. B. Banov, A. Momchilov, M. Massot, and C. M. Julien, *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, **100**, 87 (2003).
15. E. Levi, E. Zinigrad, H. Teller, M. D. Levi, and D. Aurbach, *J. Electrochem. Soc.*, **145**, 3440 (1998).
16. Y. J. Wei, H. Ehrenberg, K. B. Kim, C. W. Park, Z. F. Huang, and C. Baetz, *J. Alloys Compd.*, **470**, 273 (2009).
17. G. H. Jeffery, J. Bassett, J. Mendham, and R. C. Denny, *Vogel's Textbook of Quantitative Chemical Analysis*, 5 ed., John Wiley & Sons: New York, 1989.
18. S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
19. T. Nohma, S. Yoshimura, K. Nishio, Y. Yamamoto, S. Fukuoka, and M. Hara, *J. Power Sources*, **58**, 205 (1996).
20. Y. Chabre and J. Pannetier, *Prog. Solid State Chem.*, **23**, 1 (1995).
21. Y. Paik, W. Bowden, T. Richards, and C. P. Grey, *J. Electrochem. Soc.*, **152**, A1539 (2005).
22. W. Bowden, C. P. Grey, S. Hackney, F. Wang, Y. Paik, N. Ilchev, and R. Sirotna, *J. Power Sources*, **153**, 265 (2006).
23. W. Bowden, T. Bofinger, F. Zhang, N. Ilchev, R. Sirotna, Y. Paik, H. Chen, C. Grey, and S. Hackney, *J. Power Sources*, **165**, 609 (2007).
24. N. Ilchev, W. Bowden, P. Christian, P. R. Moses, and K. Brandt, *ITE Letters on Batteries, New Technologies and Medicine*, **2**, 349 (2001).
25. P. He, J. Y. Luo, X. H. Yang, and Y. Y. Xia, *Electrochim. Acta*, **54**, 7345 (2009).
26. A. A. Abdul, M. H. Askar, and G. A. Kolta, *Electrochim. Acta*, **17**, 291 (1972).
27. C. B. Ward, A. I. Walker, and A. R. Taylor, *Progress in Batteries and Battery Materials*, **11**, 40 (1992).
28. A. P. Malloy, G. J. Browning, and S. W. Donne, *J. Coll. Interface Sci.*, **285**, 653 (2005).
29. W. M. Dose, J. Lehr, and S. W. Donne, *Mat. Res. Bull.*, in press (2011).