

Characterization of tin oxide/ LiMn_2O_4 thin-film cell

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Abstract

An amorphous, thin film of tin oxide is tested as an anode to replace lithium metal in a thin-film battery. Tin oxide shows irreversible discharge capacity in its initial state, and this gives rise to capacity loss on the first charge–discharge process. Thus, in terms of electrochemical properties, lithium metal is better than tin oxide as an anode for a thin-film battery. In some applications, however, thin-film batteries must withstand high fabrication temperatures (over 250°C to 260°C). Lithium metal film cannot be applied in such conditions due to its low melting point (181°C). Tin oxide is not only able to endure high fabrication temperatures but can also preserve its capacity for a large number of cycles after the initial discharge process. In this study, a thin film of amorphous tin oxide has been prepared by means of a sputtering method. Its suitability as an anode for a thin-film battery is examined. A thin film of LiMn_2O_4 , prepared by a sol–gel method is used for the cathode. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Thin-film batteries have many applications such as smart cards, CMOS-based integrated circuits and micro-devices [1–3]. In some cases, the batteries must withstand temperatures as high as 250°C to 260°C, so that they can be integrated into circuits using the solder reflow process [2]. Until now, lithium film has usually been used as the anode material [3–17]. Lithium metal film, however, is not stable in a high process temperature due to its low melting point (181°C). This paper examines a tin oxide thin film as an anode electrode to overcome the high-temperature problem. It is known that a tin oxide thin film has good reversibility at high current densities, and can be easily prepared by various methods such as magnetron sputtering, evaporation of elemental tin in an oxygen atmosphere, chemical vapour deposition, and ultrasonic spray pyrolysis [18,19]. On the other hand, tin oxide shows irreversible capacity loss on the first cycle because it is decomposed to

amorphous Li_2O and metallic tin [18–23]. Hence, the capacity of a cell containing tin oxide as the anode electrode is less than that of a cell containing lithium metal as the anode electrode.

In a previous work [3], we reported the fabrication of an LiMn_2O_4 thin film by a sol–gel method, and examined the electrochemical properties of an Li metal/ LiMn_2O_4 thin film cell. The present work is focused on the electrochemical properties of cell containing LiMn_2O_4 thin film as a cathode and a tin oxide thin film as an anode. The tin oxide thin film was fabricated by a sputtering method and its elemental properties were characterized by X-ray diffraction and scanning electron microscopy.

2. Experimental

$\text{Si}(100)$ wafers covered with 1000 Å of thermally grown oxide were used as the substrate. A current-collector of platinum (800 Å) was deposited on the SiO_2/Si wafer by RF-magnetron sputtering. LiMn_2O_4 thin films were prepared on the $\text{Pt}/\text{SiO}_2/\text{Si}$ substrate by a spin-coating technique. The solution was spin-coated on substrates and

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dried at 310°C for 10 min to evaporate the solvents and remove the organic materials. The as-deposited films were annealed at 750°C in flowing O₂ for 10 min for crystallization. The fabrication process for the LiMn₂O₄ thin film has been reported in a previous paper [3].

The tin oxide thin film was prepared by an RF-magnetron sputtering method. A 4-in. tin sample and a gas mixture of ultra pure (99.999%) Ar and O₂ were used as target and the reactive gas, respectively. The tin oxide thin film was deposited at room temperature, 100°C, 200°C, 300°C and 400°C on Pt/SiO₂/Si substrate. The film thickness was controlled by the deposition time. Identification of the phases in the films was carried out by X-ray diffraction with CuKα radiation using an automated Rigaku X-ray diffractometer. The film morphology was observed by means of scanning electron microscopy.

For electrochemical measurements, the LiMn₂O₄ and tin oxide thin film was placed in an open beaker cell which contained 1 M LiClO₄ in propylene carbonate (PC), and was located inside an argon atmosphere glove box. Charge–discharge tests were controlled with an EG&G Electrochemical Analysis System (model 273A). The initial charge–discharge curve of the LiMn₂O₄ thin film and tin oxide thin film were measured using lithium foil as a counter electrode.

The initial discharge curve of the tin oxide thin film/1 M LiClO₄ in PC/LiMn₂O₄ thin film cell was investigated with a constant current density of 100 μA cm⁻². The LiMn₂O₄ thin film and tin oxide thin film were used as the cathode and the anode, respectively (two electrode cell). The rechargeabilities of the cell were also analyzed by performing a cycle test at the same current density (100 μA cm⁻²) in the potential range 4.3 to 3.0 V.

3. Results and discussion

3.1. Properties of tin oxide thin film

The X-ray diffraction patterns of tin oxide thin films deposited at room temperature, 100°C, 200°C, 300°C and 400°C are given in Fig. 1. There are no diffraction peaks of tin oxide in the film deposited at room temperature; this shows the film to be amorphous. On increasing the deposition temperature, however, the crystallinity of the tin oxide film improves and (110), (101), and (211) peaks are observed. Peaks marked with S correspond to the substrate silicon wafer and platinum layer. Electron micrographs at high magnification (see Fig. 2) show the tin oxide to have a very small grain size, i.e., about 0.02 to 0.04 μm. The films have a relatively smooth and dense surface.

The capacity and reversibility of tin oxide thin films deposited at various temperatures were investigated vs. a metallic lithium electrode. After the initial discharge process, the test cell was cycled 100 times at a current density

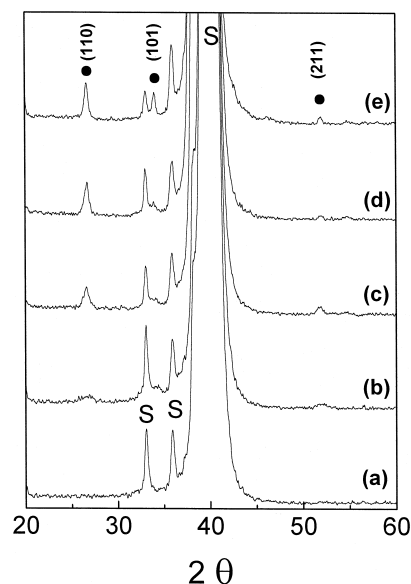
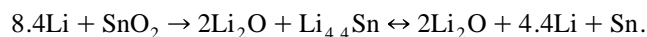


Fig. 1. X-ray diffraction patterns of tin oxide thin films deposited at (a) room temperature; (b) 100°C; (c) 200°C; (d) 300°C; and (e) 400°C.

of 300 μA cm⁻² between 1.1 and 0.1 V. The results are given in Fig. 3. On increasing the deposition temperature to 300°C, the capacity of the tin oxide thin film increases. The capacity of the film deposited at 400°C was, however, smaller than that of the films deposited at 200°C and 300°C. The reversible capacity is about 35% of the initial discharge capacity, which is due to the initial decomposition reaction of tin oxide [18–23]. It is known that as lithium is titrated into tin oxide (SnO₂) in the first discharge process, the initial reaction involves the decomposition of SnO₂ into amorphous Li₂O and metallic Sn. With further lithium titration, a series of Li–Sn binary alloys form, until the final Li–Sn alloy composition of Li_{4.4}Sn is reached. The charge process would be the reverse process, except that some fraction of the lithium ions can be removed from the Li₂O [23]. The total process is summarized by [21]:



Hence, the reversible charge and discharge capacity after the first discharge process is smaller than the initial discharge capacity. The reversible portion of the capacity is only the portion of the alloying/dealloying process between lithium and tin ($2\text{Li}_2\text{O} + \text{Li}_{4.4}\text{Sn} \leftrightarrow 2\text{Li}_2\text{O} + 4.4\text{Li} + \text{Sn}$).

As shown in Fig. 3, the films display good reversibility after the initial process. An anode prepared in situ during the initial reaction must be able to handle the enormous stresses induced by the volume change occurring in the tin–lithium alloy, and the tin–lithium system must remain in electrical contact during this transformation [19].

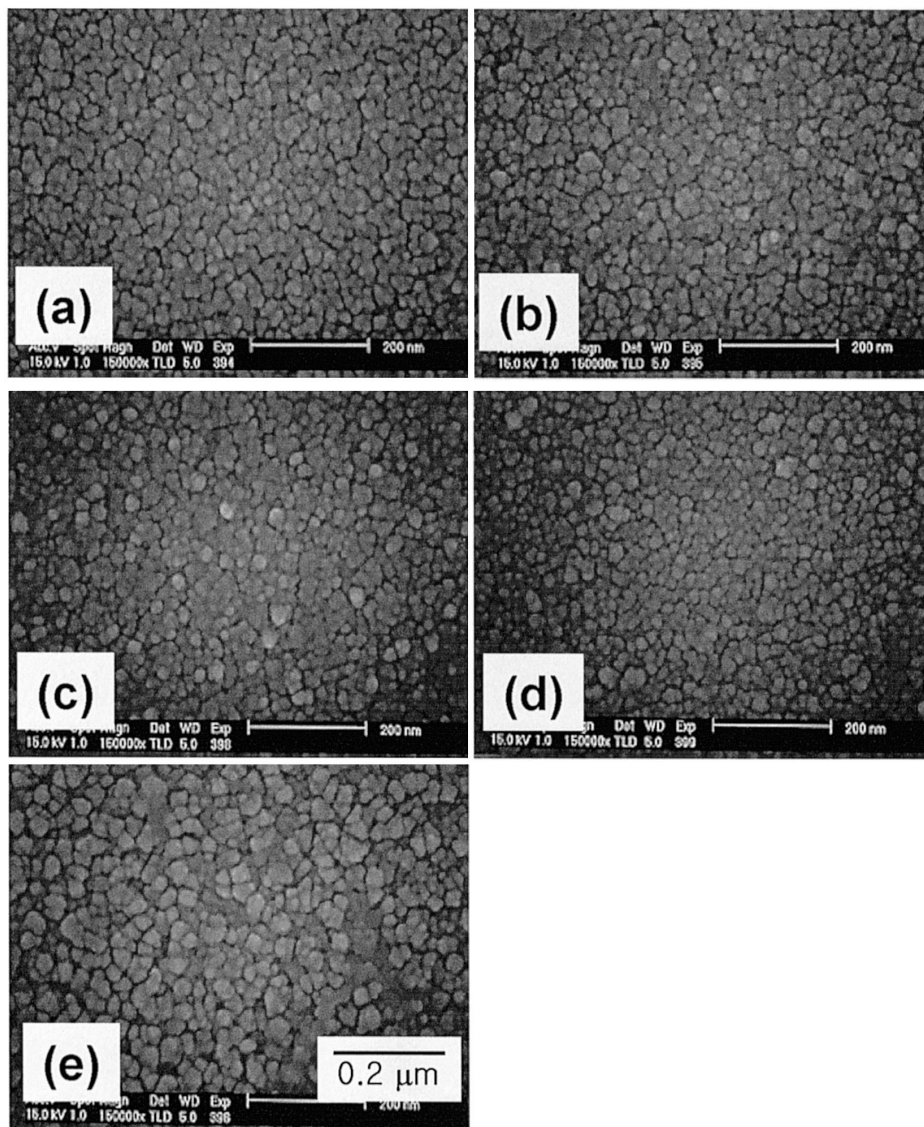


Fig. 2. Electron micrographs of tin oxide thin films deposited at (a) room temperature; (b) 100°C; (c) 200°C; (d) 300°C; and (e) 400°C.

3.2.. Electrochemical properties of tin oxide (anode material) / LiMn_2O_4 (cathode material) thin-film cell

Typical initial charge and discharge curves of tin oxide and an LiMn_2O_4 thin film are given in Fig. 4. In the initial discharge curve of the tin oxide thin film (Fig. 4a), a voltage plateau near 1.1 V is observed. It is believed that the plateau region is related to the reaction of lithium with oxygen bound to metallic Sn to form Li_2O and very small metallic Sn regions [22]. The majority of the discharge reaction by the alloy process occurs below 0.4 V after a sharp decline from the plateau region. As has been reported [3,5,6], the charge and the discharge curves of the LiMn_2O_4 thin film display a voltage plateau near 4.0 and 4.2 V, respectively (Fig. 4b).

As stated earlier, tin oxide thin films have irreversible capacity. In other words, during the initial reaction process

of the cell containing tin oxide as anode material, some fraction of the lithium ions extracted from the cathode are used up for the decomposition of tin oxide into Li_2O and metallic tin. This reaction is not reversible. Hence, only the fraction of lithium ions which reacts with metallic Sn for the formation of an Li–Sn alloy is reversible. The initial charge curve of the cell in such case is shown in Fig. 5a. The tin oxide thin film deposited at room temperature (thickness: 200 Å) was used for preparing the tin oxide/ LiMn_2O_4 thin film cell. The long voltage plateau in the 3 V range means that the two voltage-plateau region of about 4 and 4.2 V of the LiMn_2O_4 thin film overlaps with the 1.1 V plateau region of the tin oxide thin film. This shows that almost all of the lithium ions extracted from the LiMn_2O_4 thin film are used up for the decomposition of tin oxide to Li_2O and metallic tin. The cell yields a very small discharge capacity (Fig. 5b).

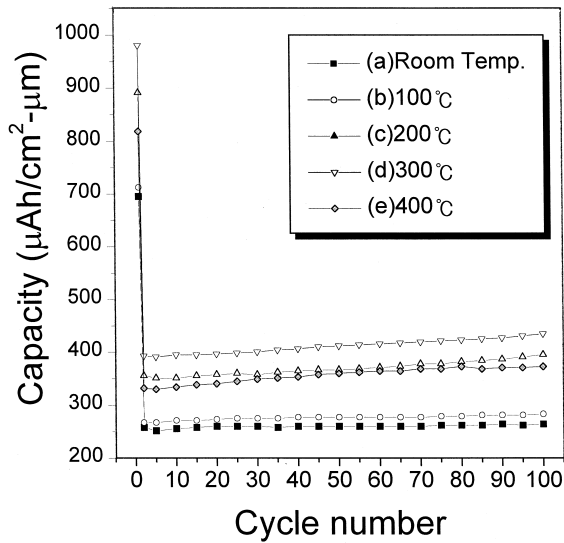


Fig. 3. Comparison of cycling behaviour of tin oxide thin films deposited at (a) room temperature; (b) 100°C; (c) 200°C; (d) 300°C; and (e) 400°C.

Thus, the amount of lithium ions required for the initial process of the tin oxide thin film should be adjusted to almost the same amount of lithium ions extracted from the LiMn_2O_4 thin film. This can be achieved by controlling the amount of cathode and anode material, i.e., the ‘material balance’ between the two electrodes. This is very important for the application of a tin oxide thin film as an anode.

The initial discharge capacity per volume of the tin oxide thin film is many more times the charge capacity per volume of the LiMn_2O_4 thin film. Hence, the thickness of the tin oxide thin film should be decreased to a very thin

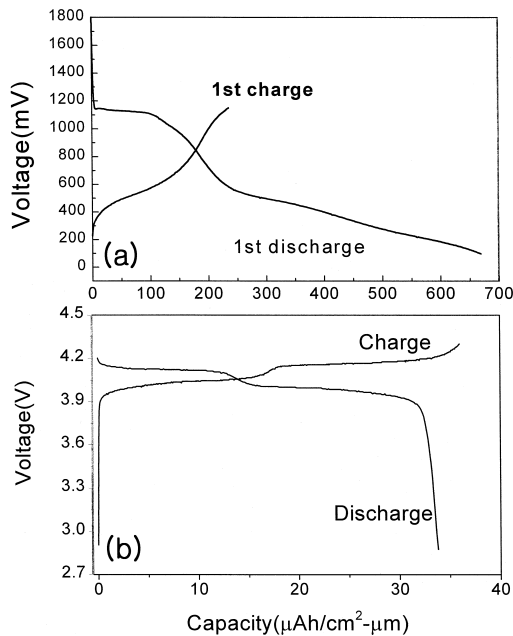


Fig. 4. Typical initial discharge–charge curves for cell of (a) Li/1 M LiClO_4 –PC solution/tin oxide thin film; (b) Li/1 M LiClO_4 –PC solution/ LiMn_2O_4 thin film.

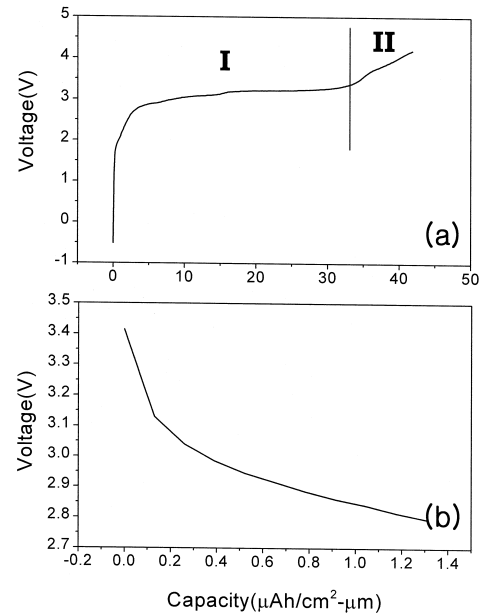


Fig. 5. (a) Initial charge curve and (b) discharge curve of tin oxide thin film/1 M LiClO_4 –PC solution/ LiMn_2O_4 thin film cell (material imbalance state between cathode and anode).

level for ‘material balance’. In this work, the thin film deposited at room temperature was used for fabrication of the tin oxide/ LiMn_2O_4 thin film cell. The thickness of the tin oxide film was about 100 Å, which is suitable for meeting the material balance with an LiMn_2O_4 thin film (thickness is 2000 Å). If a tin oxide film deposited at a higher temperature is used, the thickness of the film should be decreased to below 100 Å. This is very difficult to

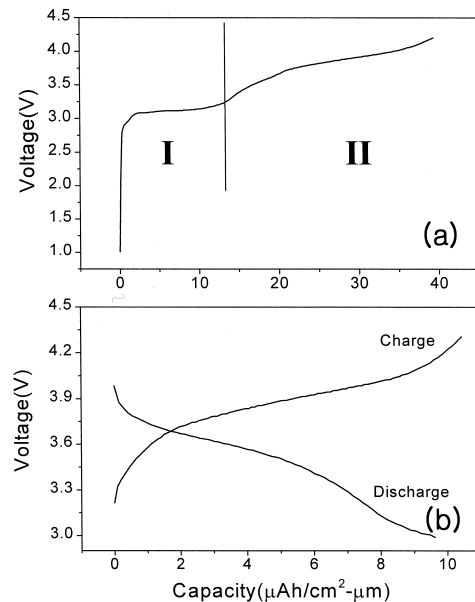


Fig. 6. (a) Initial charge curve ; (b) charge–discharge curve after the initial process of tin oxide thin film/1 M LiClO_4 –PC solution/ LiMn_2O_4 thin film cell (material balance state).

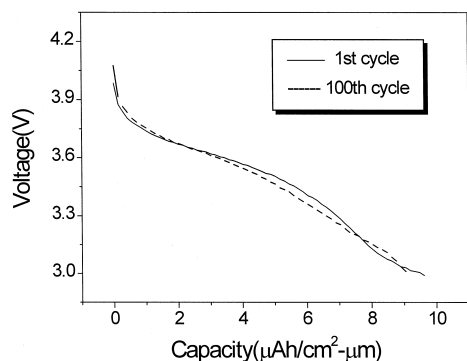


Fig. 7. Comparison of discharge curves between first and 100th cycle of a cell of tin oxide thin film/1 M LiClO₄-PC solution/LiMn₂O₄ thin film in the voltage range of 4.3–3.0 V.

control. Nevertheless, it is possible that a tin oxide thin film deposited at high temperature can be used if the thickness of the LiMn₂O₄ thin film is increased up to two to three times, while maintaining its material balance.

The initial charge curve for a tin oxide/LiMn₂O₄ thin film cell is shown in Fig. 6a. The 3 V plateau is decreased to about 30% of the total charge capacity. After the 3 V plateau, the voltage slowly increases. The charge–discharge curve, after the initial reaction, is presented in Fig. 6b. The discharge capacity is about 30% of the Li/LiMn₂O₄ thin film cell.

The tin oxide/LiMn₂O₄ thin film cell was cycled between 4.3 and 3.0 V at a current density of 100 μA cm⁻². The discharge curve is given in Fig. 7. The solid line is the initial discharge curve of the cell, and the dotted line is that of the cell after 100 cycles. Only a small degradation is observed after 100 cycles at room temperature, which shows the possibility of using tin oxide thin film as an anode for thin-film batteries.

4. Conclusions

A tin oxide thin film is deposited by a sputtering method and tested as an anode for a thin-film battery. The capacity of the tin oxide thin film increases as the deposition temperature is increased to 300°C. The film deposited at 400°C shows lower capacity than the film deposited at 200°C or 300°C. The capacity loss during the initial discharge process is observed in the tin oxide film, and is due to the decomposition reaction from tin oxide into Li₂O and metallic tin. Regardless of the deposition temperature, the tin oxide thin film displays good reversibility after the initial process.

In the preparation of a tin oxide/LiMn₂O₄ thin film cell, the correct material balance between anode and cath-

ode is very important to prevent capacity loss. From the control of the material balance, a tin oxide/LiMn₂O₄ thin film cell with suitable capacity has been obtained. The discharge capacity of this cell is about 30% of that of an Li/LiMn₂O₄ thin film cell. The capacity loss after 100 cycles is small, however, and indicates that the tin oxide thin film can be used as anode for a thin-film battery, which should be able to withstand a high process temperature (i.e., 250°C to 260°C).

References

- [1] S.D. Jones, J.R. Akridge, *J. Power Sources* 54 (1995) 63.
- [2] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans, *Proceeding of the 12th International Conference on Solid State Ionics*, in press.
- [3] Y.J. Park, J.G. Kim, M.K. Kim, H.T. Chung, W.S. Um, M.H. Kim, H.G. Kim, *J. Power Sources* 76 (1998) 41–47.
- [4] J.B. Bates, G.R. Gruzalski, N.J. Dudney, C.F. Luck, X. Yu, *Solid State Ionics* 70/71 (1994) 619.
- [5] K.-H. Hwang, S.-H. Lee, S.-K. Joo, *J. Power Sources* 54 (1995) 224.
- [6] K.-H. Hwang, S.-H. Lee, S.-K. Joo, *J. Electrochem. Soc.* 141 (1994) 3926.
- [7] J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B.S. Kwak, X. Yu, R.A. Zuhr, *J. Power Sources* 54 (1995) 58.
- [8] S.J. Lee, J.K. Lee, D.W. Kim, H.K. Baik, *J. Electrochem. Soc.* 143 (1996) L268.
- [9] K.A. Striebel, C.Z. Deng, S.J. Wen, E.J. Cairns, *J. Electrochem. Soc.* 143 (1996) 1821.
- [10] P. Fragnaud, R. Nagarajan, K.M. Schleich, D. Vujic, *J. Power Sources* 54 (1995) 362.
- [11] P. Fragnaud, D.M. Schleich, *Sens. Actuators, A* 51 (1995) 21.
- [12] S.D. Jones, J.R. Akridge, *J. Power Sources* 54 (1995) 63.
- [13] S.D. Jones, J.R. Akridge, F.K. Shokoochi, *Solid State Ionics* 69 (1994) 357.
- [14] L. Chen, J. Schoonman, *Solid State Ionics* 67 (1994) 17.
- [15] A.A. Vanzomerem, E.M. Kfilder, J.C.M. Marijnissen, J. Schoonman, *J. Aerosol Sci.* 25 (1994) 1229.
- [16] J.B. Bates, D. Lubben, N.J. Dudney, F.X. Hart, *J. Electrochem. Soc.* 142 (1995) L149–L151.
- [17] C.H. Chen, A.A.J. Buysman, E.M. Kelder, J. Schoonman, *Solid State Ionics* 80 (1995) 1.
- [18] W. Liu, X. Huang, Z. Wang, H. Li, L. Chen, *J. Electrochem. Soc.* 145 (1998) 59–62.
- [19] T. Brousse, R. Retoux, U. Herterich, D.M. Schleich, *J. Electrochem. Soc.* 145 (1998) 1–4.
- [20] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2943–2948.
- [21] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2045–2052.
- [22] K. Wan, S.F.Y. Li, Z. Gao, K.S. Siow, *J. Power Sources* 75 (1998) 9–12.
- [23] J. Wolfenstine, J. Sakamoto, C.-K. Huang, *J. Power Sources* 75 (1998) 181–182.