

Short communication

# Morphological differences between lithium powder and lithium foil electrode during discharge/charge

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## Abstract

The dissolution/deposition behaviors of a lithium powder electrode during discharge/charge were examined by scanning electron microscopy (SEM) observation, and compared with those of a lithium foil electrode. For the lithium foil electrode, the dissolution/deposition of lithium was localized in limited areas on the lithium surface, and then the resulting lithium dendritic growth was accelerated after repeated cycling. On the other hand, for the lithium powder electrode, the dissolution/deposition of lithium was distributed throughout the entire body of the lithium electrode, and the lithium dendritic growth was considerably suppressed. Also, the shape of electrodes was maintained as a mixture of the porous powder particles even after several cycles. The effects of current density on the morphological changes and dissolution/deposition behaviors were also observed.

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**Keywords:** Lithium dissolution/deposition behaviors; Lithium metal battery; Lithium powder; Dendritic growth

## 1. Introduction

While rechargeable batteries using lithium metal as the negative electrode theoretically offer the greatest promise, they have encountered difficulties reaching the market place, because of safety and cycleability issues. These problems are associated with the reactivity of lithium and the growth of dendrites at the lithium anode during cycling [1].

In order to solve these problems, the use of pure lithium metal powder was proposed for the anode material. By using such an electrode, the cycling efficiency was remarkably improved and the lithium dendritic growth during charging was considerably suppressed [2,3]. However, the morphological behaviors and dissolution/deposition mechanisms of lithium powder electrodes during discharge/charge have not yet been studied in detail.

Lithium dendritic growth is intimately associated with the morphology of the lithium surface during cycling. Extensive research has been undertaken to clarify these correlations. Therefore, the lithium dissolution/deposition behaviors of lithium foil electrodes have been widely studied in various fields [4–8]. However, it was presumed that the lithium dissolution/deposition behaviors of lithium powder electrodes were completely different from those of lithium foil electrodes, because of the porous characteristics of the former.

In this paper, the morphological changes in lithium powder electrodes during discharge/charge were examined by scanning electron microscopy (SEM) observation. The morphologies of the lithium powder electrodes were observed at various cycle numbers and current densities. The results were also compared with those of lithium foil electrodes.

## 2. Experimental

Lithium powders were made by the droplet emulsion technique (DET). The details of the DET method have been presented elsewhere in the literature [9–11]. The lithium powders

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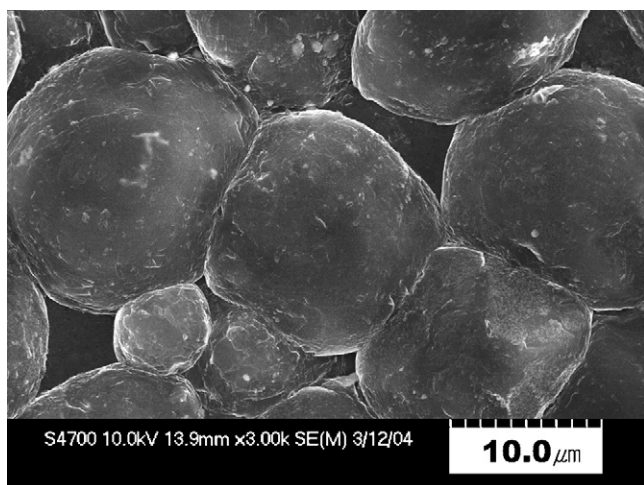


Fig. 1. The typical microstructure of the as-prepared lithium powder electrode.

made in this study were about 10  $\mu\text{m}$  in diameter. To prepare them in electrode form, the lithium powders were compacted to a coin shape (16 mm diameter) by applying a pressure of approximately 15 MPa. The typical microstructure of the compacted lithium powder electrode is shown in Fig. 1. As shown in Fig. 1, the porous characteristics of the lithium powders were clearly observable. The porosity of the lithium powder electrode was about 11.8% [12], and the surface was as large as six times of that of foil [13].

Two kinds of lithium electrodes were used as the working electrode. One was the as-received lithium foil electrode

obtained from Cyprus Co. (U.S.A., purity 99.9%). The other was a compacted lithium powder electrode manufactured in the lab. As a counter electrode, commercially available MCMB (meso-carbon microbead) 6–10 powders (Osaka Gas, Japan) were used. The electrolyte was LP30 Selectipur (Merck, Germany) and consisted of ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1) containing 1 M  $\text{LiPF}_6$ . Polypropylene was used as a separator. All of the lithium samples were prepared for coin type cells (2032 coin cell, cell diameter 20 mm, height 3.2 mm).

The discharge/charge tests were conducted for both the lithium foil and compacted lithium powder electrodes. The coin cells were discharged with a cut-off voltage of 0.01 V, and then charged with an upper potential limit of 2.0 V.

The cells were cycled at a constant current density ( $C/10$  rate) corresponding to a current density of  $0.1 \text{ mA cm}^{-2}$  during discharge/charge. After cycling, the lithium electrodes were washed with pure dimethyl carbonate to remove the residual electrolyte and dried in an argon-filled glove box at room temperature. To observe the morphological changes associated with the dissolution/deposition of lithium on the lithium electrodes, the morphology of the lithium electrodes was investigated after the first and fifth cycles using field emission scanning electron microscopy (Horiber 7200-H).

Also, to examine the influence of the current density on the lithium interfacial morphology, the same experiments were carried out at  $C/1$  rate ( $1 \text{ mA cm}^{-2}$ ), and the resulting lithium interfacial morphology was compared with that obtained at  $C/10$  rate.

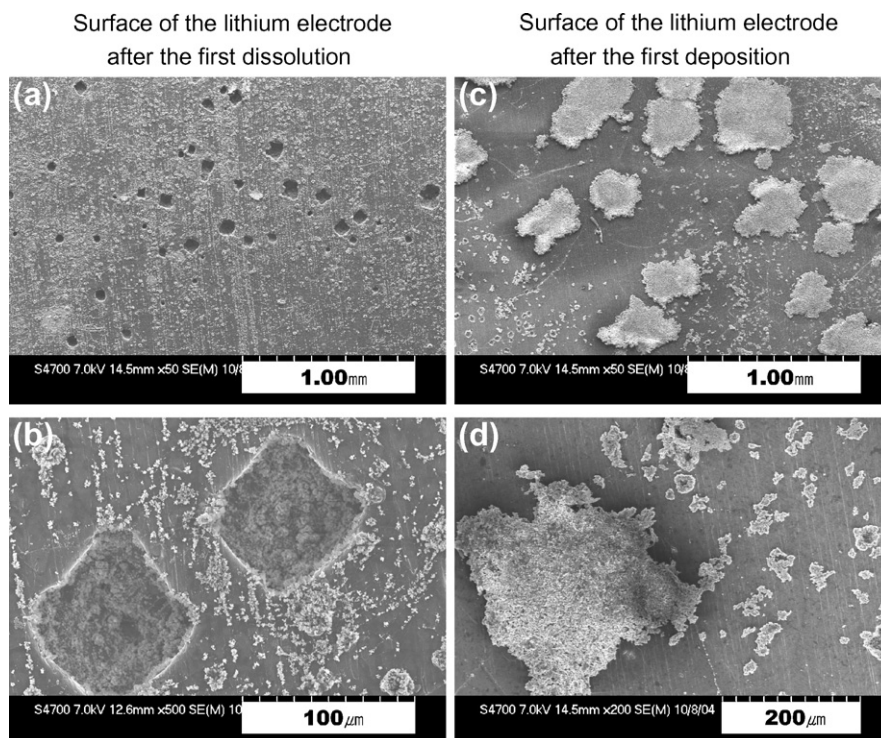


Fig. 2. The typical SEM images on the surface of the lithium foil electrode after the first dissolution (a and b) and deposition (c and d) at  $C/10$  rate in EC + DMC (1:1) electrolyte containing  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ ; by high magnification (b and d).

### 3. Results and discussion

The two different lithium electrodes (foil and powder) were discharged/charged at  $C/10$  rate ( $0.1 \text{ mA cm}^{-2}$ ). After the first dissolution/deposition, the morphology of the lithium electrodes was observed by scanning electron microscopy.

Fig. 2 shows the SEM images of the surfaces of the lithium foil electrode after the first dissolution and deposition at  $C/10$  rate. For the lithium foil electrode, many scattered pits were localized in limited areas on the lithium surface after the first discharge, due to the localization of the current distribution (Fig. 2a and b). After successive charging, lithium ions seemed to be deposited in these pits, but only sparsely, so that the surface appeared to be swelled and protruded (Fig. 2c and d). At high magnification, the morphology of these deposits resembled that of a mass, in which a bunch of dendrites were twisted and aggregated [6–8].

Fig. 3 shows the SEM images of the surfaces of the lithium powder electrode after the first dissolution and deposition at  $C/10$  rate. In this case, the lithium ions were uniformly dissolved from almost all of the individual powder particles during discharge, including those located in the interior, and the connection between the particles was not lost (Fig. 3a and b). After successive charging, the lithium ions appeared to be deposited even in those pits which formed as a result of the previous dissolution of the powders (Fig. 3c and d). In other words, for the lithium powder electrode, the lithium ions were dissolved/deposited not non-uniformly but uniformly over the entire body of the lithium electrode. Therefore, even after repeated dissolution/deposition, the individual powder particles kept virtually their original shape.

The morphology of the lithium surface was investigated after the fifth cycle, in order to observe the morphological changes as a function of the cycle number. Fig. 4a–c show the SEM images of the lithium foil electrode after the fifth dissolution at  $C/10$  rate. After the fifth dissolution, based on many observations, the density of the pits in the surface was found to increase but their size remained similar to that observed at the first dissolution. As shown in Fig. 4a, the scattered pits with a diameter  $100\text{--}200 \mu\text{m}$  were observed, and in Fig. 4b and c, pits which were covered with lithium deposits in the previous depositions are also shown. That is, the lithium deposits which formed during the previous cycles were not completely dissolved, and some of them remained unchanged, which meant that additional pits were newly created on the lithium surface in this dissolution. If lithium is deposited at these sites after successive charging, it might grow in the form of dendrites. Fig. 4d–f shows the SEM images of the lithium foil electrode after the fifth deposition at  $C/10$  rate. It was observed that lithium was deposited at the sites of the undissolved mass and that the mass seemed to grow (Fig. 4d and e). On the other hand, undeposited pits were still observed even after the fifth deposition (Fig. 4f). For the lithium foil electrode, similar results have reported in other literature [14]. From these results for the lithium foil electrode, it was presumed that lithium dissolution/deposition was limited to restricted areas and resulted in lithium dendritic growth after repeated cycling.

Fig. 5 shows the SEM images of the lithium powder electrode after the fifth dissolution and deposition at  $C/10$  rate. After the fifth dissolution, the lithium interfacial morphology on the lithium powder electrode was scarcely changed in com-

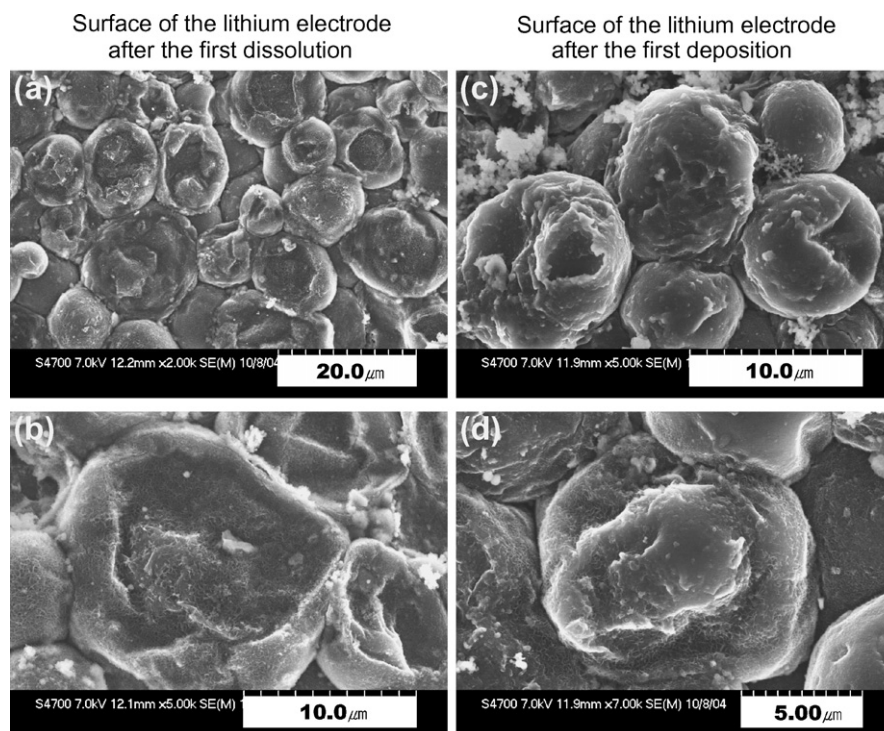


Fig. 3. The typical SEM images on the surface of the lithium powder electrode after the first dissolution (a and b) and deposition (c and d) at  $C/10$  rate in EC + DMC (1:1) electrolyte containing  $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ ; by high magnification (b and d).

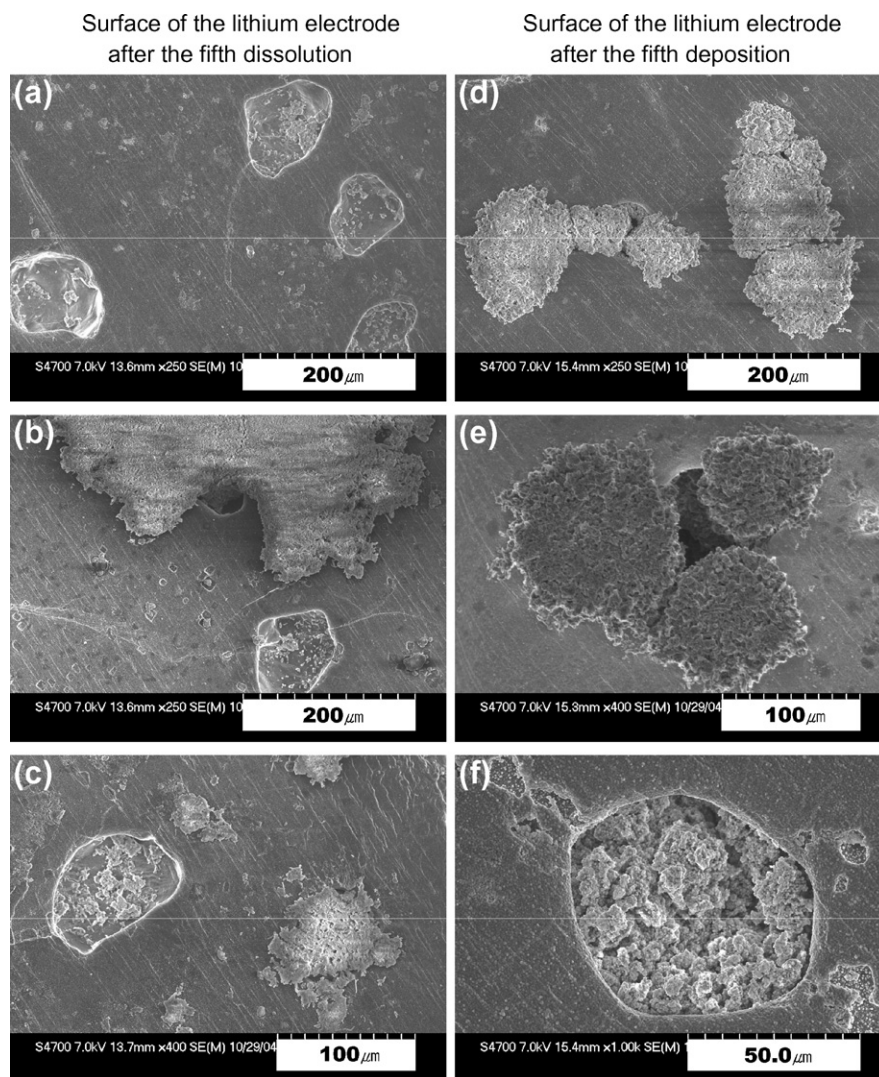


Fig. 4. The typical SEM images on the surface of the lithium foil electrode after the fifth dissolution (a–c) and deposition (d–f) at  $C/10$  rate in EC+DMC (1:1) electrolyte containing  $1 \text{ mol dm}^{-3}$  LiPF<sub>6</sub>; taken at different locations of the electrode (b, c, e and f).

parison with that observed after the first dissolution (Fig. 5a and b). That is, the lithium ions were not non-uniformly dissolved, but still uniformly dissolved over the entire body of the lithium powder electrode, and the previously formed lithium deposits did not remain as they did in the case of the lithium foil electrode. After the fifth deposition, lithium ions were found to be repeatedly deposited in those pits which formed as a result of previous dissolution, in a similar manner to that observed after the first deposition (Fig. 5c and d). However, in comparison with the first deposition, quite small deposits of a particle-like shape were generated. It seemed that the lithium deposits were built up little by little during the repeated discharge/charge. Nonetheless, the shape of the individual lithium powder particles was mostly maintained without any lithium dendritic growth occurring, even after the fifth cycle. From these results, it was concluded that, for the lithium powder electrode, the lithium dissolution/deposition takes place in a much more uniform manner on the surface of each powder particle and throughout the entire electrode. Therefore, the dendritic growth of lithium was sig-

nificantly suppressed. Nevertheless, the changes in the lithium interfacial morphology and dendritic growth mechanism of the lithium powder electrode need to be examined after a much greater number of cycles.

To examine the influence of the current density on the lithium interfacial morphology, the morphology of the lithium powder electrode was observed after the first cycle at  $C/1$  rate ( $1 \text{ mA cm}^{-2}$ ). Fig. 6 shows the SEM images of the lithium powder electrode after the first cycle at  $C/1$  rate. At this rate, the entire surface of the lithium was covered with deposits of a rice-like diamond shape quite unlike the interfacial morphology observed at  $C/10$  rate (Figs. 3d and 5d). Generally, during electroplating, the formation mode of the surface morphology is dependent on the current density [15]. Therefore, the deposition mechanism of the lithium electrode is altered by changes in the current density as observed in the case of electroplating. However, the changes in the deposition mechanism need to be studied in detail for a wide range of current densities.

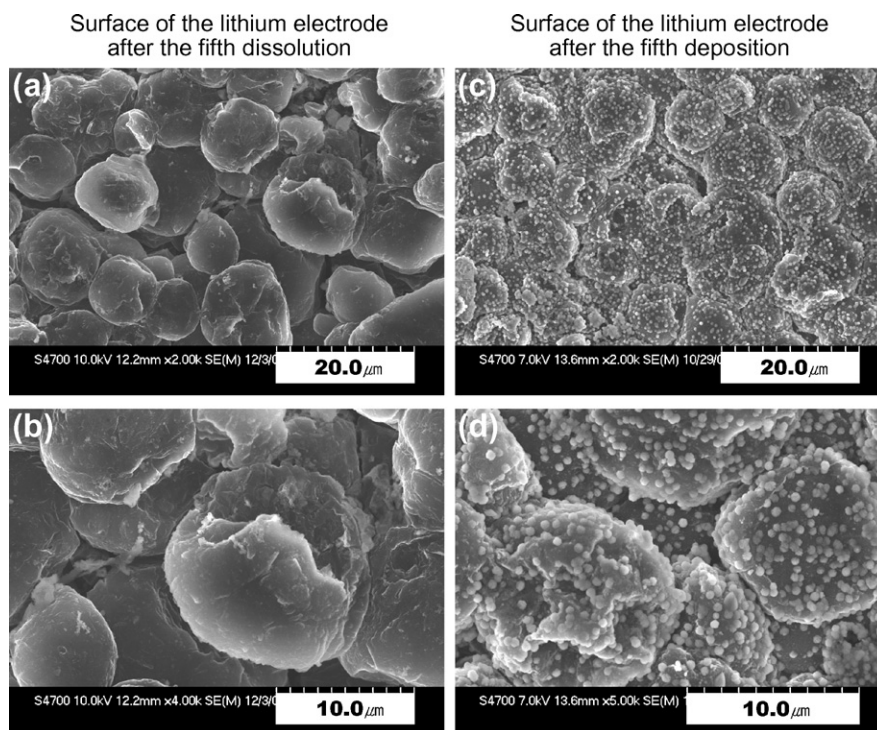


Fig. 5. The typical SEM images on the surface of the lithium powder electrode after the fifth dissolution (a and b) and deposition (c and d) at  $C/10$  rate in EC + DMC (1:1) electrolyte containing  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ ; by high magnification (b and d).

Surface of the lithium powder electrode after the first cycle at  $C/1$  rate

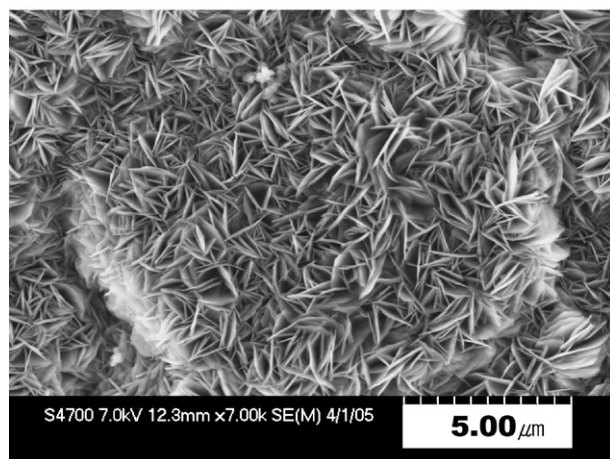


Fig. 6. The typical SEM images on the surface of the lithium powder electrode after the first cycle at  $C/1$  rate in EC + DMC (1:1) electrolyte containing  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ .

#### 4. Conclusions

The morphological changes and lithium dissolution/deposition behaviors of the lithium powder electrode during discharge/charge were examined by scanning electron microscopy observation at a constant current density ( $C/10$  rate), in comparison with those of the lithium foil electrode.

For the lithium foil electrode, many scattered pits were non-uniformly created on the lithium surface during discharge.

The lithium ions were sparsely deposited at first, and then concentratedly deposited on the previously formed lithium deposits after repeated cycling. For the lithium powder electrode, on the other hand, the lithium ions were uniformly dissolved from almost all of the individual powder particles, and deposited in those pits which formed as a result of the previous dissolution of the powders. Therefore, even after a few cycles, the shape of the porous powder particles was retained. In conclusion, the lithium dendritic growth was accelerated in the lithium foil electrode, but suppressed in the lithium powder electrode after repeated cycling.

In addition, for the lithium powder electrode, it was observed that the lithium interfacial morphology varied with the current density. However, the changes in the lithium interfacial morphology and dendritic growth mechanism need be examined in detail after a much greater number of cycles and with a wider range of current densities.

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#### References

- [1] S. Tobishima, Y. Sakurai, J. Yamaki, J. Power Sources 68 (1997) 455.
- [2] J.S. Kim, W.Y. Yoon, Electrochim. Acta 50 (2004) 529.
- [3] W.S. Kim, W.Y. Yoon, Electrochim. Acta 50 (2004) 541.
- [4] F. Orsini, A. Du Pasquier, B. Beaudoin, J.M. Tarascon, M. Trentin, N. Langenhuizen, E. De Beer, P. Notten, J. Power Sources 76 (1998) 19.

- [5] K. Saito, M. Arakawa, S. Tobishima, J. Yamaki, *J. Power Sources* 72 (1998) 111.
- [6] H. Ota, X. Wang, E. Yasukawa, *J. Electrochem. Soc.* 151 (2004) A427.
- [7] N.S. Choi, Y.M. Lee, W. Seol, J.A. Lee, J.K. Park, *Solid State Ionics* 172 (2004) 19.
- [8] X. Yang, Z. Wen, X. Zhu, S. Huang, *Solid State Ionics* 176 (2005) 1051.
- [9] M.S. Park, W.Y. Yoon, *J. Power Sources* 114 (2003) 237.
- [10] W.Y. Yoon, J.S. Paik, D. LaCourt, J.H. Perepezko, *J. Appl. Phys.* 60 (1986) 3489.
- [11] J.H. Perepezko, I.E. Anderson, in: T.J. Rowland, E.S. Machlin (Eds.), *Synthesis and Properties of Metastable Phases*, 9A, TMS-AIME, Warrendale, 1980, p. 31.
- [12] J.H. Chung, W.S. Kim, W.Y. Yoon, S.W. Min, B.W. Cho, *Second International Conference on Polymer Batteries and Fuel Cells Meeting Abstracts*, Las Vegas, Nevada, 13 June, 2005.
- [13] W. S. Kim, M.S. Thesis, Korea University, 2005.
- [14] J. Yamaki, S. Tobishima, K. Hayashi, K. Saito, Y. Nemoto, M. Arakawa, *J. Power Sources* 74 (1998) 219.
- [15] X. Cui, D.C. Martin, *Sens. Actuators A* 103 (2003) 384.