

Electrochemical properties of LiFePO_4 thin films prepared by pulsed laser deposition

Chihiro Yada^a, Yasutoshi Iriyama^{a,*}, Soon-Ki Jeong^b,
Takeshi Abe^a, Minoru Inaba^c, Zempachi Ogumi^a

^a Department of Energy & Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University Katsura Campus, Nishigyo-ku, Kyoto 615-8510, Japan

^b Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^c Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

Available online 31 May 2005

Abstract

Lithium iron phosphate (LiFePO_4) thin film electrodes were prepared by pulsed laser deposition (PLD). The thin films were annealed at various temperatures under argon gas flow and the influence of annealing temperature on their electrochemical performance was studied. The thin films annealed at 773 and 873 K exhibited a couple of redox peaks at 3.4 V (versus Li/Li^+) that are characteristics of the electrochemical lithium insertion/extraction of LiFePO_4 . Atomic force microscopy (AFM) observation revealed that the film annealed at 773 K (*773 K-film*) consisted of small grains with 50 nm in thickness, and the grain size increased with an increase of annealing temperature. Because of its small-sized grains, the *773 K-film* showed high rate capability and the discharge capacity at 10 μA maintained 65% of that at 25 nA. However, the discharge capacity of the *773 K-film* was ca. 10% smaller than that of the film annealed at 873 K, indicating that annealing at 773 K is slightly insufficient to obtain well-crystallized LiFePO_4 . From these results, it was concluded that a point of optimization between high rate capability and capacity would be found between 773 and 873 K.

© 2005 Elsevier B.V. All rights reserved.

Keywords: LiFePO_4 ; Pulsed laser deposition (PLD); Thin film; Rechargeable lithium battery

1. Introduction

Lithium iron phosphate (LiFePO_4) is a promising candidate for positive electrode materials in rechargeable lithium batteries because of its environmental benignity, thermal stability, and low cost [1]. It has been pointed out that one of the drawbacks of LiFePO_4 is poor electronic conductivity, which prevents full use of its theoretical capacity (170 mAh g^{-1}). Hence, several studies to overcome this problem have been reported so far [2,3]. In contrast to these studies, electrochemical lithium insertion/extraction properties of LiFePO_4 , such as lithium diffusion in the active material and charge transfer reaction rate at the electrode/electrolyte interface, have

not been clearly understood, although they also should play important roles in its charge–discharge performance.

Thin film electrodes are useful to investigate electrochemical properties of active materials in detail. This is especially true for poorly conductive active materials because the thickness can be reduced to a value at which the poor electronic conductivity does not significantly affect the electrochemical behavior. However, studies on the fabrication of LiFePO_4 thin film electrodes and their electrochemical properties have not been reported so far [4,5].

In this study, we prepared LiFePO_4 thin film electrodes by pulsed laser deposition (PLD) and investigated the dependency of annealing temperature on their electrochemical performance. We revealed that both rate capability and capacity of LiFePO_4 thin films can be optimized when they are annealed at $773 \text{ K} < T < 873 \text{ K}$.

* Corresponding author. Tel.: +81 75 383 2485; fax: +81 75 383 2488.
E-mail address: iriya@elech.kuic.kyoto-u.ac.jp (Y. Iriyama).

2. Experimental

The target of LiFePO_4 for PLD was prepared by a solid state reaction using $\text{LiOH}\cdot\text{H}_2\text{O}$ (99.95%, Aldrich), $(\text{CH}_3\text{COO})_2\text{Fe}$ (99.995%, Aldrich), and $\text{NH}_4\text{H}_2\text{PO}_4$ (99%, Wako Pure Chemical) as raw materials. The target used for PLD was rich in lithium and phosphorus to the stoichiometric composition to compensate the loss of these elements during deposition. The mixture was first calcined at 723 K for 12 h under argon gas flow and was ground again. The resultant powders were pressed into a pellet and then sintered at 1073 K for 24 h under argon gas flow.

Thin films of LiFePO_4 were prepared with a conventional PLD system. The films were deposited on platinum plates or basal planes of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics, STM-1 grade) for 30 min at room temperature. The films were then annealed at 673–973 K for 3 h under argon gas flow. Hereafter, the film annealed at T K is referred to as T K-film. The resultant films were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). XRD measurements were also conducted to clarify the crystal structure of the annealed thin films. Unfortunately, films deposited for 30 min gave no clear diffraction peaks even when they were annealed at 973 K. Hence, films deposited for 120–180 min were specially fabricated on glass substrates or basal planes of HOPG for XRD measurements.

Electrochemical properties of the films were studied by cyclic voltammetry (CV) and charge–discharge tests. These tests were performed using a three-electrode cell. The thin

film electrodes prepared by PLD were used as working electrodes. The counter and reference electrodes were lithium foil. The electrolyte solution was $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ dissolved in propylene carbonate (PC). Cyclic voltammetry was carried out at 5 mV s^{-1} between 2.0 and 4.5 V (versus Li/Li^+). Charge–discharge tests were performed at a constant current (25 nA – $10 \text{ }\mu\text{A}$) between 3.0 and 4.0 V. All of these electrochemical measurements were conducted in an argon-filled glove box.

3. Results and discussion

Cyclic voltammograms of the thin films annealed at 673–973 K are summarized in Fig. 1. When the films were annealed at 673 K, a couple of broad anodic and cathodic peaks were observed at around 3.0 V. Because as-deposited film also exhibited nearly the same voltammogram, these broad peaks are probably due to the electrochemical lithium insertion/extraction properties of an amorphous lithium iron phosphate phase [6]. Annealing at 773 and 873 K (Fig. 1(b and c)) drastically decreased the current peak at around 3.0 V and produced only a couple of anodic and cathodic sharp peaks at 3.4 V. These redox reaction peaks are characteristics of electrochemical lithium insertion/extraction reactions of LiFePO_4 [1]. Other redox peaks were not observed in these two voltammograms, indicating that the films annealed at 773–873 K consisted of single-phase LiFePO_4 and did not contain impurity phases such as $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$, LiFeP_2O_7 , and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ [1]. On the other hand, when the films were

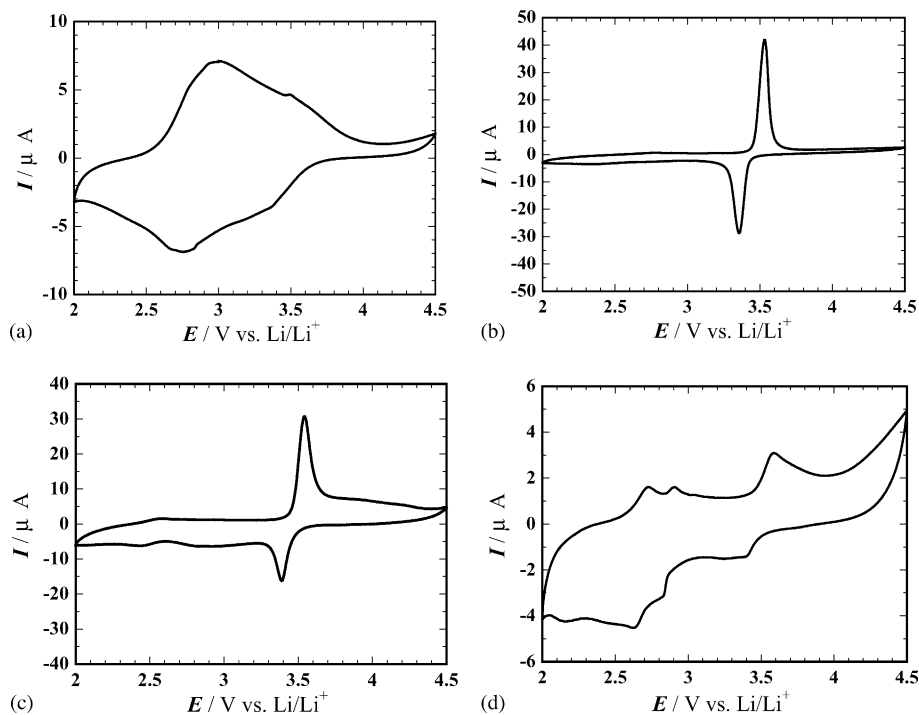


Fig. 1. Cyclic voltammograms of the films annealed at (a) 673 K, (b) 773 K, (c) 873 K, and (d) 973 K. The films were deposited on platinum substrates for 30 min and then annealed at different temperatures for 3 h under argon gas flow; $v = 5 \text{ mV s}^{-1}$.

annealed at 973 K, the peak current at 3.4 V greatly decreased and, alternatively, broad peaks appeared again at around 3.0 V. The peak at 3.4 V completely disappeared when the films were annealed at temperatures higher than 973 K, and some couples of sharp redox peaks newly appeared in the range of 2.6–3.0 V.

Fig. 2 shows the variation of XRD patterns (30° – 40°) of the films deposited for 180 min with annealing temperature in the range of 673–973 K. Diffraction peaks observed at $2\theta = 35.6^\circ$, 36.6° , and 37.9° on the XRD pattern of the 773 K-film are indexed as the (1 3 1), (2 1 1), and (1 4 0) reflections of LiFePO_4 , respectively. On the other hand, the 673 K-film gave no visible diffraction peaks in this range, which indicates that the 673 K-film was not well crystallized or was in an amorphous state. The 973 K-film exhibited visible diffraction peaks; however, some diffraction peaks marked by asterisks were not assigned to any of the reflections of LiFePO_4 , indicating that impurity phases were formed in the 973 K-film. Because the 773 K-film had nearly the stoichiometric composition ($\text{P}/\text{Fe} = 0.99$ and $\text{Li}/\text{Fe} = 0.98$) [5], the impurity phase would be formed by the decomposition of LiFePO_4 through reactions with residual oxygen in argon gas. These results can qualitatively explain the CVs of the films annealed at different temperatures shown in Fig. 1.

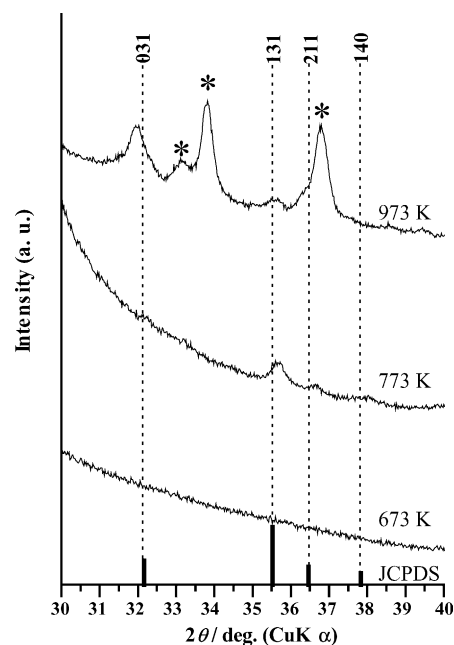


Fig. 2. XRD patterns (30° – 40°) of thin films annealed at different temperatures. The films were deposited on basal planes of HOPG or glass substrates for 120–180 min at room temperature and then annealed for 3 h under argon gas flow. JCPDS data (No. 40-1499) is shown for comparison.

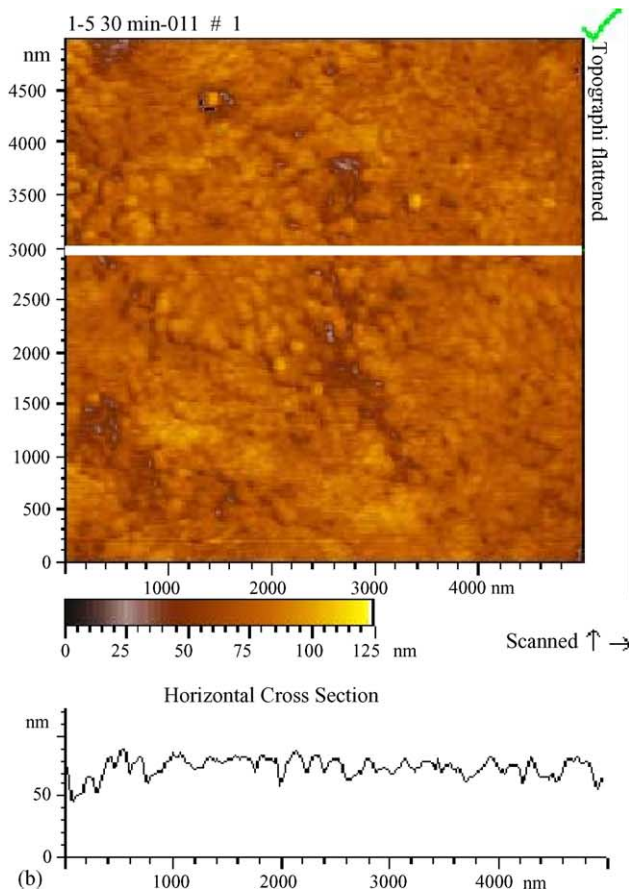
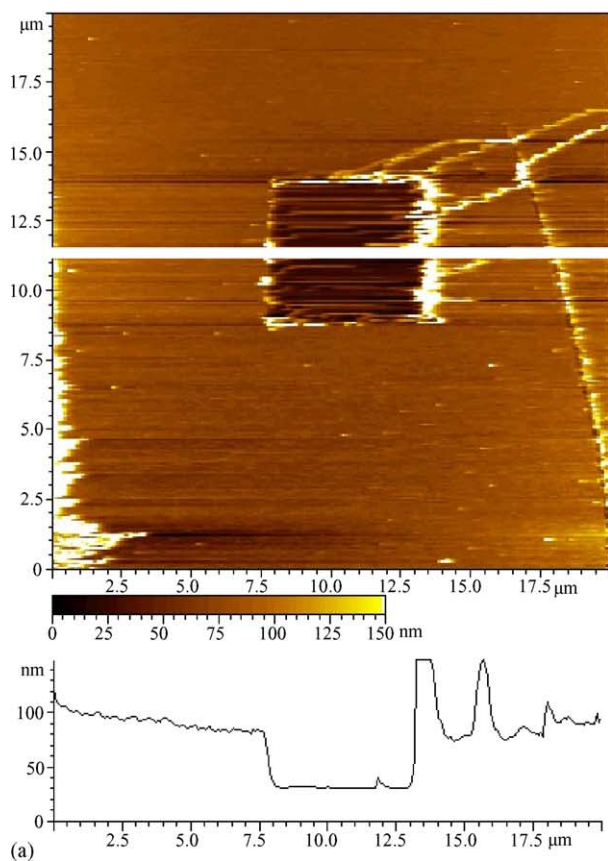


Fig. 3. AFM images of the films deposited on basal planes of HOPG for 30 min: (a) as-deposited film (before annealing) and (b) after annealing at 773 K under argon gas flow for 3 h. The height profiles were measured along the white lines in the images.

Surface morphology of the film electrodes was studied by AFM. Fig. 3(a) shows the AFM image of an as-deposited film fabricated on a basal plane of HOPG for 30 min. The AFM observation was performed by the contact mode, in which the AFM tip was constantly in contact with the surface during scanning. Hence, the AFM tip can scrape off the film by its repeated scanning of the surface. In Fig. 3(a), the $5\ \mu\text{m} \times 5\ \mu\text{m}$ area is seen as a square hole, where the films were scraped off during repeated scanning. A flat plane is observed below the scraped film, which is probably the atomically flat basal plane of HOPG. It is also seen that the scraped films accumulated at the right side of $5\ \mu\text{m} \times 5\ \mu\text{m}$ area on the film surface. The height profile of the surface revealed that the thickness of as-deposited film was ca. 50 nm, and the film covered the substrate uniformly. When the film was annealed at 773 K for 3 h, the substrate was covered with small grains with ca. 50 nm in thickness (Fig. 3(b)).

Fig. 4 shows TEM images of the films annealed at 673–973 K. The films were directly deposited on Au micro grids, and microstructure of the film was observed at the edge of the grid (seen as black shaded area in Fig. 4). As shown in these images, grain growth in the film was clearly observed when the film was annealed at 873 K or higher. This means that small-sized grains are expected when the film is annealed at temperatures lower than 873 K. Fig. 5 shows magnified images of the surface structure of the 773 K- and 873 K-films. In both images, a layered structure with an interlayer spacing of 0.43 nm was observed, which is in good agreement with the (0 1 1) planes of LiFePO_4 . Clear facet planes were not formed in the film surface in contrast to the case of *c*-axis oriented LiCoO_2 thin film [7]. It should be noted that the electrode surface was covered with an amorphous layer for each film. The thickness of the amorphous layer seemed to increase when annealing temperature was increased as shown in Fig. 5. From the results of CVs, it is speculated that this amorphous layer is a decomposition product of LiFePO_4 .

Charge–discharge curves of the 773 K- and 873 K-films between 3.0 and 4.0 V are shown in Fig. 6. Flat potential profiles at 3.4 V correspond to the couple of sharp redox peaks at 3.4 V in Fig. 1(b and c). The theoretical capacity of the film calculated from the film thickness (50 nm), the density of LiFePO_4 ($3.6\ \text{g cm}^{-3}$), and the geometric electrode area ($0.13\ \text{cm}^2$) is roughly estimated to be $0.4\ \mu\text{Ah}$, which was in good agreement with the capacity obtained experimentally at 25 nA for both films. The discharge capacity obtained at 25 nA of the 873 K-film was ca. 10% larger than that of the 773 K-film, indicating that the 773 K-film was poorly crystallized than the 873 K-film. However, the 773 K-film exhibited better rate capability than the 873 K-film. The relative discharge capacities obtained at different current densities to the capacity at 25 nA are summarized in Fig. 7. The capacities at $10\ \mu\text{A}$ of the 773 K- and the 873 K-films maintained ca. 65 and 50%, respectively, to those at 25 nA. The 773 K-film was formed by small-sized grains, which could sustain enough electronic conductivity, decrease the diffusion length of lithium ion in the active material, and also reduce the charge-transfer re-

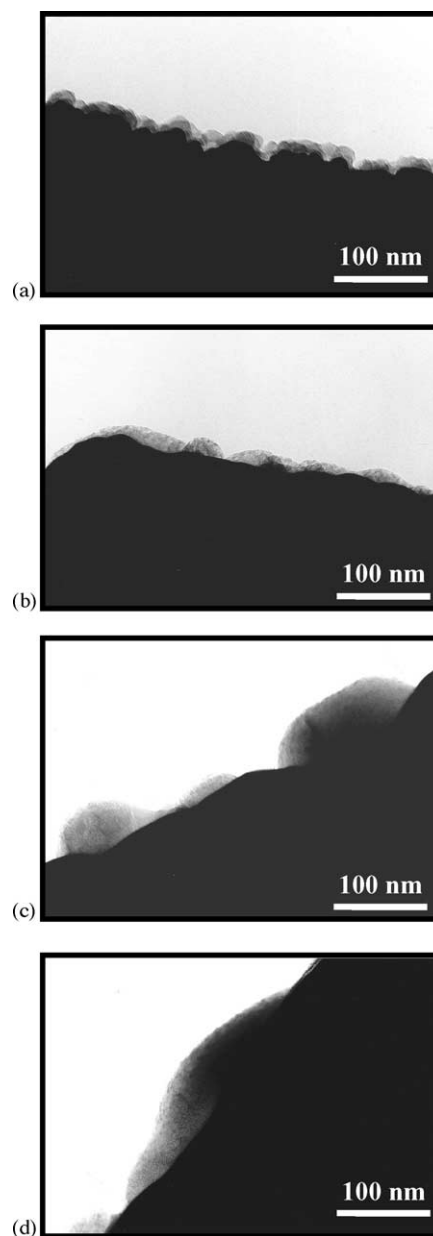


Fig. 4. TEM images of the films annealed at different temperatures: (a) 673 K, (b) 773 K, (c) 873 K, and (d) 973 K. The films were deposited on Au micro grids directly for 30 min and then annealed under argon gas flow.

sistance at the electrode/electrolyte interface. The difference in rate capability of these two films is probably due to these structural advantages of the 773 K-film. From these results, it is reasonable to expect that a point of optimization between high rate capability and large capacity would be found between 773 and 873 K. Quite recently, we confirmed that the 823 K-film obtained larger capacity than that of the 873 K-film and also showed high rate capability than that of the 773 K-film.

Yamada et al. have synthesized LiFePO_4 powders at various conditions and reported that LiFePO_4 powders are optimized on their electrochemical properties when they are

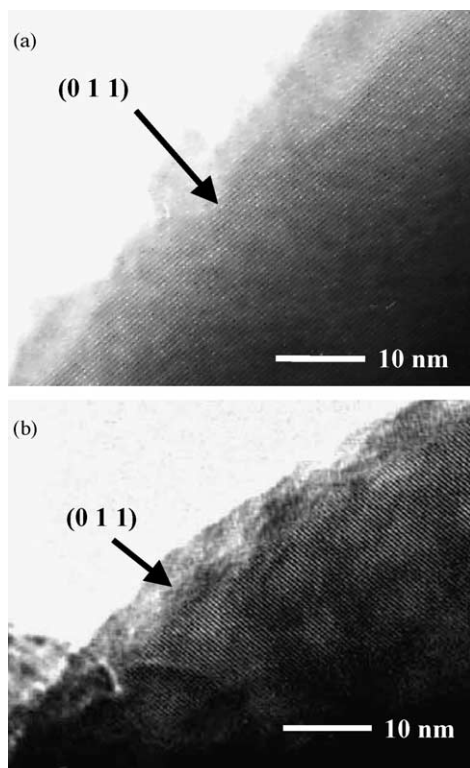


Fig. 5. TEM images of LiFePO₄ thin films annealed at (a) 773 K and (b) 873 K.

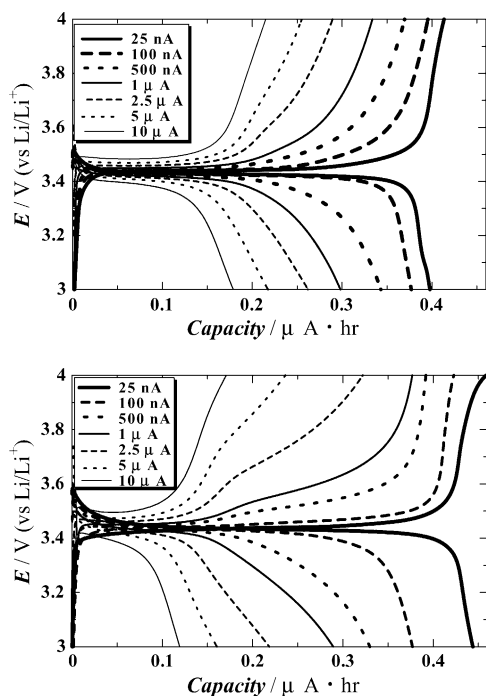


Fig. 6. Charge–discharge curves of LiFePO₄ thin films annealed at (a) 773 K and (b) 873 K. The curves were measured at different current densities (25 nA–10 μA) between 3.0 and 4.0 V.

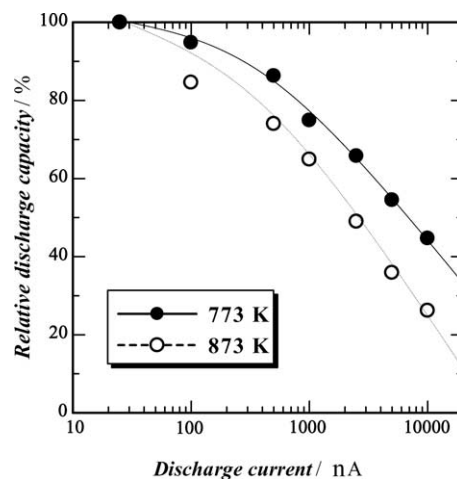


Fig. 7. Rate capability of LiFePO₄ thin films annealed at 773 K (shown by closed circles) and 873 K (shown by open circles). The discharge capacities at different current densities were normalized with the discharge capacity at 25 nA as a standard.

sintered at 823 K [8]. They attributed this optimization to non-crystalline phase formation at $T < 773$ K and undesirable particle growth at $T > 873$ K. Although their preparation method is different from that used in the present study, electrochemical properties of LiFePO₄ thin films can be optimized when they are annealed at $773 \text{ K} < T < 873 \text{ K}$. This optimization is probably due to a compromise between small-sized grains and well-crystallized structure of the film electrode. As was discussed earlier, suppression of an amorphous layer formation on the electrode surface may be another important factor to improve the electrochemical properties of LiFePO₄.

4. Conclusions

Olivine-structured LiFePO₄ thin film electrodes were prepared at various conditions, and their electrochemical and structural properties were studied. The films annealed at 773–873 K gave only a couple of redox peaks at 3.4 V in cyclic voltammograms between 2 and 5 V, which is characteristics of electrochemical lithium insertion/extraction reaction of LiFePO₄. The films annealed at 673 K or lower were not well crystallized or were in an amorphous state, while those annealed at 973 K or higher were not of single-phase LiFePO₄ and contained an impurity phase. The film annealed at 873 K gave a larger discharge capacity than that annealed at 773 K. Unfortunately, grain growth in the film electrode occurred at 873 K, and thereby the rate capability of the former film was poorer than the latter one. These results indicate that a point of optimization between high rate capability and large capacity would be found between 773 and 873 K. This optimized annealing temperature was also in good agreement with the results for LiFePO₄ powder reported by Yamada et al. [8]. These results will give

an important insight to fabricate LiFePO_4 used in large-size rechargeable lithium batteries requiring high rate capability and large capacity. Extended studies on the interfacial reactions of LiFePO_4 by using optimized thin film electrodes will be reported in the near future.

Acknowledgements

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan, and also by a Grant-in-Aid for 21st COE Program for a United Approach to New Materials Science from the Ministry of Education, Culture, Sports, Science, and Technology.

References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] F. Croce, A. D'Epifanio, J. Hassoun, A. Deptula, T. Olczac, B. Scrosati, *Electrochem. Solid State Lett.* 5 (2002) A47.
- [3] S.-Y. Chung, J.T. Bloking, Y.-M. Chiang, *Nat. Mater.* 1 (2002) 123.
- [4] F. Sauvage, E. Baudrin, M. Morcrette, J.-M. Tarascon, *Electrochem. Solid State Lett.* 7 (2004) A15.
- [5] Y. Iriyama, Y. Yokoyama, C. Yada, S.-K. Jeong, T. Abe, M. Inaba, Z. Ogumi, *Electrochem. Solid State Lett.* 7 (2004) A340.
- [6] Y. Okazaki, T. Yamamoto, S. Okada, J. Yamaki, The 71th Meeting of the Electrochemical Society of Japan, Yokohama, Japan, March 2004 (Abstract 2H02).
- [7] Y. Iriyama, M. Inaba, T. Abe, Z. Ogumi, *J. Power Sources* 94 (2001) 174.
- [8] A. Yamada, S.C. Chung, K. Hinokuma, *J. Electrochem. Soc.* 148 (2001) A224.