



Electrochemical Deposition and Modification of LiFePO_4 for the Preparation of Cathode with Enhanced Battery Performance

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LiFePO_4 was deposited onto substrate surface during Au electrodeposition. Formation of this $\text{LiFePO}_4/\text{Au}$ mixed film leads to better electrochemical performance of the LiFePO_4 , because Au modifies its low conductivity. This simple electrochemical method also provides an opportunity for the incorporation of modifying materials such as metal oxides during a mixed-metal codeposition process. Interestingly, it is possible to use a similar method to coat the electroactive material surface with modifier. After the deposition of the electroactive film, a thin layer of metal oxide was additionally coated on the film surface. The results obtained from the experimental investigations show that the LiFePO_4 cathode prepared by the simple electrochemical method proposed has an excellent battery performance, including higher specific capacity, less capacity fading, and faster diffusion process. The LiFePO_4 cathode prepared shows only a 10% capacity fading after 1000 cycles at 80°C , while approaching its theoretical capacity at this condition.

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Because the desired design of lithium batteries is based on film electrodes, finding an appropriate method for the deposition of highly stable films of electroactive materials is an active area of research. The available methods satisfying the requirements for this purpose are commonly high technological methods. Among them, radio frequency (rf) sputtering is the most interesting method, as modifying material can be simply incorporated into the electroactive film during the sputtering. More recently, mixed-metal codeposition has been introduced as an efficient method for the deposition of LiMn_2O_4 film for lithium battery applications.^{1,2} The latter method has some valuable advantages from both fundamental and applied points of view, because it is very simple and provides new opportunities for improving the battery performance. In this paper, we show that this method has additional advantages when applied for cathode materials with weak electrochemical performance. In fact, LiMn_2O_4 has an excellent electrochemical behavior with a good redox system, but its battery performance, such as stability at elevated temperatures, should be improved for commercialization. Upon such achievements, LiMn_2O_4 is the most promising alternative to available LiCoO_2 cathodes. However, it should be noted that there are other candidates for cathode material in lithium batteries with peculiar advantages, but they suffer from weak electrochemical performance. For instance, olivine-type compounds are interesting materials for the preparation of cathodes of lithium batteries, but they have weak redox systems.³ LiFePO_4 is the best example and prototype of this class of cathode materials.⁴⁻¹⁰ Here, it is aimed to use the mixed-metal codeposition method for the preparation of LiFePO_4 film electrode to improve its battery performance, and also its weak electrochemical activity. This introduces the usefulness of the method and shows its practical interest; deep investigations are excluded in this preliminary report.

Experimental

LiFePO_4 was synthesized by an available solid-state reaction well established previously and widely applied in the literature.⁶ To this aim, Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{HPO}_4$ were weighted in stoichiometric amounts and homogenized with a mixer. To decompose the oxalate and the phosphate, the mixture was placed in a tubular furnace and heated at 320°C for 10 h. To avoid iron oxidation, the synthesis was performed in a nitrogen atmosphere. The mixture was then sintered for 24 h at temperature 550°C . The crystallographic structure was confirmed by X-ray. Because the synthe-

sis procedure was followed as previously reported, the results were similar to those reported in the literature.⁶ On the other hand, as the deposition methods have no significant influence on the structure of the electroactive material attached, the crystallographic structures of the LiFePO_4 of different electrodes were similar.

Four LiFePO_4 film electrodes were fabricated for the present study in accordance with the following procedure for the deposition of the electroactive material: (1) depositing the LiFePO_4 by conventional rf sputtering with a strength of 80 W, (2) depositing the LiFePO_4 during Au codeposition, as a small amount of LiFePO_4 particles were dispersed within an Au plating bath, (3) adding a small amount of metal oxide as modifier to the LiFePO_4 film during mixed-metal codeposition, and (4) covering the latter electrode with a thin layer of metal oxide by electrochemical deposition. The experimental details regarding the Au plating bath and mixed-metal codeposition can be found in our previous papers.^{1,2} The typical metal oxide employed throughout this research as both incorporating and covering agent was silver oxide. According to the procedure of mixed-metal codeposition, appropriate electrolyte salt was added to the depositing cell. However, the silver particles deposited immediately transform to silver oxide in the experimental condition. On the other hand, incomplete oxidation of silver does not make any difficulty.

Because attachment of the electroactive material is accompanied by the deposition of Au, the common approach of weighing the electrode before and after deposition process is not a reliable method for estimating the amount of the electroactive material, which is needed for the calculation of specific capacity of the cathode material. To this aim, the amount of the electroactive material attached to the substrate surface was estimated by weighing the cathode material dispersed within the plating bath before and after the deposition, which is a simple approach. The LiFePO_4 film electrodes were investigated in a Coin type cell containing Li anode. The electrolyte solution was a 1 M LiPF_6 in ethylene carbonate:dimethyl carbonate (EC/DMC) 3:7. Charge/discharge tests were carried out using a battery cycler. The electrochemical experiments for recording chronoamperograms were performed using a homemade potentiostat connected to a computer running CorrView software. Differential scanning calorimetry (DSC) was performed from 100 to 450°C using $\alpha\text{-Al}_2\text{O}_3$ as reference. The electrochemical cell was disassembled in a glove box to remove the charged cathode. The cathode was cut and hermetically sealed into an aluminum sample plan.

Results and Discussion

Electrochemical performance of the LiFePO_4 films.—Figure 1 shows typical charge/discharge characteristics of the LiFePO_4 film

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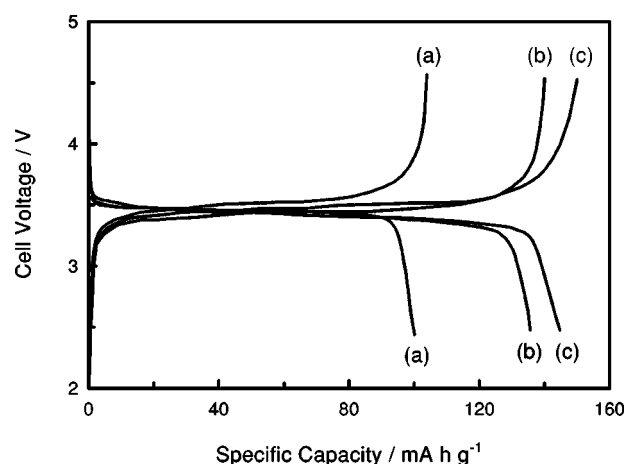


Figure 1. Charge/discharge profiles of the LiFePO_4 film electrodes prepared by (a) sputtering deposition, (b) simple Au codeposition, and (c) mixed-metal codeposition. The curves were recorded with $C/2$ at room temperature.

cathodes prepared by sputtering and mixed-metal codeposition methods. The results show that the LiFePO_4 film electrode prepared by the mixed-metal codeposition method has higher specific capacity in comparison with that deposited by sputtering method. This is an excellent result for the practical performance. Different factors can be responsible for this improvement. A possible problem for the sputtering deposition of electroactive materials is the mechanical strokes inducing in the course of the deposition process, which may affect the structure of the solid material and squeeze the film formed. Thus, low sputtering strength is employed to avoid such effects, because the diffusion process is weaker in the condensed solid formed by high sputtering strengths. Whereas, this mechanical squeezing is not applicable for the codeposition method, and the electroactive particles dispersed on the substrate electrode distantly are able to assist the diffusion process. This is indeed a mechanical aspect of the deposition methods compared.

It is known that LiFePO_4 strongly suffers from weak electrochemical activity at high current densities due to its low electrical conductivity.⁵ Thus, electrochemical performance of LiFePO_4 can be improved by increasing its electrical conductivity. Among different modifying materials proposed for this purpose, metal particles are most promising.^{4,6} Of course, this approach is different from that experienced in the present study, because metal particles are usually added during synthesis, whereas in the present case, the Au particles form between the depositing particles. However, with a similar mechanism, the Au particles dispersed within the electroactive film (or in a sense *vice versa*), increase the film conductivity in favor of better electrochemical performance of the electroactive material.

A typical charge/discharge profile of the LiFePO_4 film electrode prepared by simple Au codeposition method is also illustrated in Fig. 1 (curve b). By comparing the results, it can be understood that not only the existence of Au improves the electrochemical performance of LiFePO_4 , but also the incorporation of metal oxide additionally improves it. In other words, mixed-metal codeposition has an additional advantage in comparison with simple Au codeposition. This issue has not been taken into account in previous reports, and dispersion of metal oxides has not been used to improve the electrochemical performance of LiFePO_4 , whereas this approach has been widely employed for improving cyclability of LiMn_2O_4 . This can be attributed to the fact that metal oxides can coat the LiMn_2O_4 particles to avoid Mn dissolution, but this failure is not applicable for LiFePO_4 . In the present case, metal oxide particles dispersed within the electroactive film also improve the electrochemical performance of LiFePO_4 . In fact, less rigid structure of metal oxide, or in other expression porous solid formed during the codeposition process, provides a better opportunity for the diffusion of Li ions.

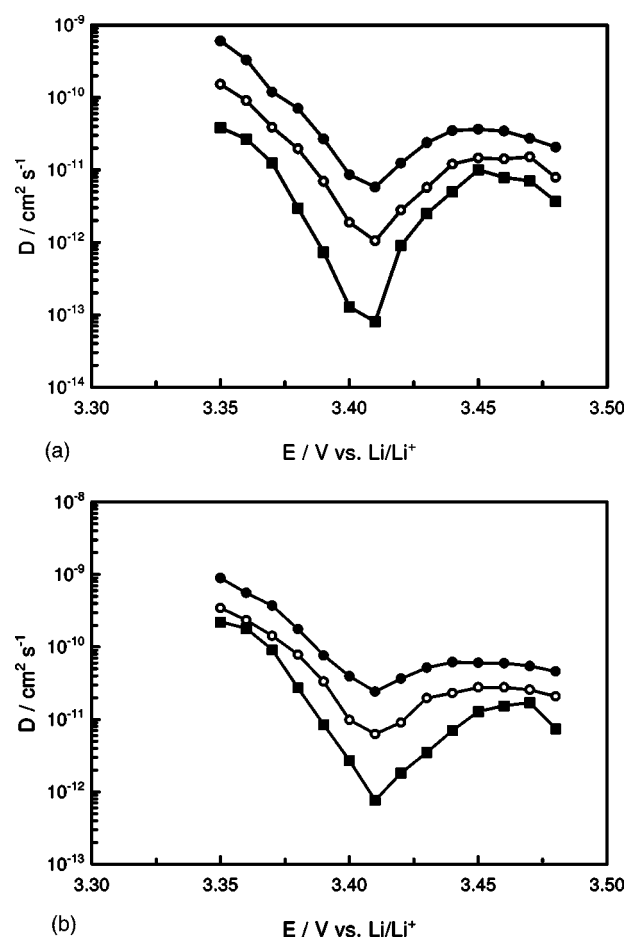


Figure 2. Variations of the diffusion coefficient as a function of applied potential for the LiFePO_4 electrodes prepared by (■) sputtering deposition, (○) simple Au codeposition, and (●) mixed-metal codeposition; recorded for the lithium (a) insertion and (b) extraction into/from the LiFePO_4 .

This issue has been described for different tasks of metal oxide modifier to improve battery performance of a film-based cathode.¹¹

Diffusion process.—In the preceding section, it was demonstrated that the electrochemical performance of LiFePO_4 could be significantly improved by depositing the LiFePO_4 particles via mixed-metal codeposition method. This effect was attributed to a better diffusion process occurring in the latter film prepared. However, without appropriate experimental results proving this, such hypothesis remains were speculation. The diffusion coefficients of both insertion and extraction of Li ions into/from different LiFePO_4 films prepared were estimated in the potential range of the battery performance.

For this purpose, the values of the diffusion coefficient were determined from chronoamperometric measurements at different potentials. This is a common method in this context, and the detailed procedure can be found in the previous reports.^{12,13} However, careful attention should be paid to such measurements, because the Li insertion/extraction in the system under investigation occurs along a flat potential at 3.5 V vs. Li/Li^+ . Thus, the diffusion coefficients should be measured in a narrow range of potential. The results are reported in Fig. 2. It is obvious that the results provide strong evidence for the hypothesis proposed above. The improvement made in the electrochemical performance of LiFePO_4 is due to the stronger diffusion process occurring in the LiFePO_4 film prepared by mixed-metal codeposition.

Although it seems that the electroactive particles are swallowed by rigid matrix of the Au film codeposited, it is possible to use an

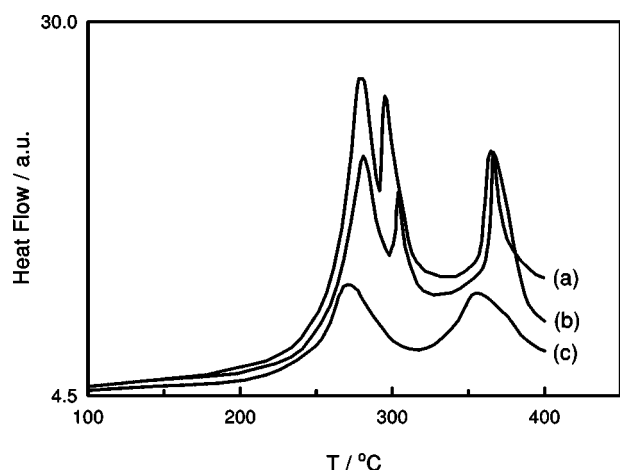


Figure 3. DSC scans of the LiFePO₄ film electrodes prepared by (a) sputtering deposition, (b) simple Au codeposition, and (c) mixed-metal codeposition. The temperature was scanned with a rate of 10°C/min. The electrodes were charged to 4.5 V vs. Li/Li⁺.

additional approach to prepare 3D structure of the electroactive film deposited,^{14,15} which leads to stronger diffusion.¹⁵ Another interesting feature of the codeposition method is related to its applicability for fundamental studies. For instance, the investigations performed regarding the diffusion process should be conducted for a film-based electrode, because the existence of various organic additives incorporated into composite electrodes may significantly affect the electrode kinetics. Thus, the codeposition method proposed is efficient to immobilize the electroactive particles on a substrate surface to investigate the electrochemical performance of the electroactive material.

Coating the LiFePO₄ film.—By assuming that metal oxides are applicable modifying materials to improve battery performance of LiFePO₄, another advantage of the electrochemical deposition method proposed is the ability for coating the electroactive film. Combination of these two approaches may lead to superior performance of the cathode.¹¹ To this aim, similar deposition process is performed but in the absence of Au plating bath and LiFePO₄ particles. In other words, a thin layer of metal oxide is deposited onto the electroactive film electrochemically. Contrary to LiMn₂O₄, LiFePO₄ is not subject to dissolution at elevated temperatures, and, thus, there is no need to improve its cyclability with surface modification. However, avoiding surface contact of electroactive films with electrolyte solutions is always favorable, as its particular advantage is described below.

From the practical point of view, safety issues must be taken into account before commercialization of a new battery. An important problem in this context is that the large short-circuit current in high-energy lithium batteries raises the local temperature and induces oxygen release from the cathode. The oxygen released as a result of this failure reacts with the organic electrolyte, which leads to gas evolution. This is very hazardous, as it may be accompanied by fire and perhaps explosion. This is indeed an important safety problem of available lithium batteries. Although an interesting advantage of LiFePO₄ as a cathode materials is that all oxygen ions form strong covalent bonds with P⁵⁺ to form the (PO₄)³⁻ tetrahedral polyanion, and their extraction is difficult, this important safety issue should be improved.

Figure 3 shows typical DSC scans of different LiFePO₄ electrodes in a charged state in the temperature range 100–400°C. The conventional LiFePO₄ film electrode prepared by sputtering method displays substantial exothermic peaks in the temperature range corresponding to the oxygen generation from cathode decomposition. The appearance of such peaks strongly depends on the synthesis

method and experimental conditions, and various exothermic peaks at about 270 and 360°C with different values for the total heat flow have been reported by various researchers.^{6,8,9} The total heat flow value was 312 J g⁻¹.

When comparing the results obtained with those of other cathode materials reported in the literature, the superior advantage of LiFePO₄ over other cathode materials can be found. Because DSC analysis is strongly dependent on the surface structure and the amount of residual electrolyte, it is important to take this into account. It is necessary to compare various electrodes with similar surface structures, though it is not always possible to achieve this similarity. Very large differences in DSC peaks for the system under investigation provide a reliable opportunity for comparative study. It is obvious that the heat evolution for LiFePO₄ is significantly lower than those of LiCoO₂ and LiNiO₂,¹⁶ but it is approximately equal to that of LiMn₂O₄. Note that LiFePO₄ has a superior thermal stability in comparison to LiMn₂O₄, because the discharged form of LiMn₂O₄, λ-MnO₂, loses oxygen to form Mn₂O₃, but this failure is not applicable for LiFePO₄.

The thermal stability of such olivine-type cathode materials is of interest to produce batteries with high tolerance to extreme temperatures. Thus, attention should be paid to this problem to improve their thermal stability as much as possible. Figure 3 shows that covering the LiFePO₄ surface with a metal oxide cover will significantly hinder the occurrence of the exothermic reaction of the cathode material with the electrolyte solution. Interestingly, the LiFePO₄ film electrode by mixed-metal codeposition even in the absence of the metal oxide-retaining layer has a lesser heat evolution. This suggests that the metal oxide particles dispersed within the electroactive film also reduce the exothermic reaction to some extent. In fact, it is another advantage of mixed-metal codeposition and incorporation of metal oxide modifier.

Cyclability at elevated temperatures.—As stated above, a particular advantage of LiFePO₄ is its excellent thermal stability. Thus, further improvement of this property may lead to the preparation of a desired cathode for specified application. For instance, large-scale lithium batteries for electric vehicles or loading systems may be operated at elevated temperatures, and lithium batteries in consumer products may be stored at elevated temperatures (*e.g.*, in unventilated vehicles). Therefore, it is of practical interest to improve such specified properties in appropriate candidates, rather than conducting the research to obtain better alternative for common lithium batteries. In this direction, although LiFePO₄ has a good thermal stability, it must be improved further to meet the requirement for specified application of lithium batteries at elevated temperatures.

In fact, LiFePO₄ is just such a promising candidate for lithium batteries with high-temperature performance, rather than an alternative to common lithium batteries. In addition to good thermal stability of LiFePO₄, its electrochemical performance is also improved at elevated temperatures due to a faster diffusion process. Because the low capacity of LiFePO₄ at higher current densities is due to limiting interface diffusion within a single grain,⁴ this limitation will be overcome at elevated temperatures due to the enhancement of the Li diffusion. Unfortunately, in addition to the Li diffusion rate, the rate of other less desirable reactions also increases at elevated temperatures, which results in capacity fading. Thus, it is only possible to claim LiFePO₄ as an excellent cathode material for high-temperature lithium batteries by overcoming the latter problem.

According to the literature, cyclability studies of the LiFePO₄ cathode at elevated temperature are usually restricted to few cycles. Thus, it is usually claimed that LiFePO₄ has a good cyclability at elevated temperature, because the specific capacity of LiFePO₄ usually increases during the first hundred cycles (Fig. 4). While LiFePO₄ cathodes are subject to severe capacity fading at higher numbers of cycles (Fig. 4), this can be attributed to the significant changes in the physical structure of the electroactive film appearing upon numerous charging/discharging,¹⁷ and particularly at

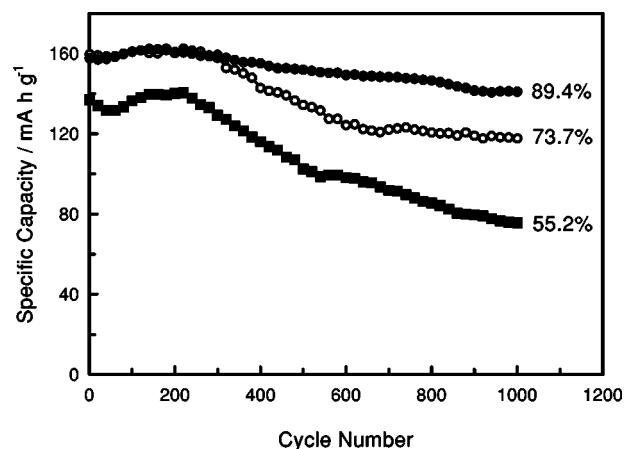


Figure 4. Cyclability data of the LiFePO_4 film electrodes prepared by (■) sputtering deposition, (○) simple Au codeposition, and (●) mixed-metal codeposition for charging/discharging with 2C rate at an elevated temperature of 80°C . The percentage of the capacity retained after 1000 cycles is noted for each case.

elevated temperatures. The metal oxide particles incorporated within the electroactive film and the metal oxide-retaining cover coated on the film surface can reduce the occurrence of such structural changes. Particularly, the metal oxide retaining cover can avoid interfacial reaction of the electroactive material with the electrolyte solution. However, investigating such structural changes requires a different strategy of research. Of course, this is a well-known advantage of metal oxide covers acting as retaining wall. For instance, it has been reported that coating LiCoO_2 with a metal oxide cover can reduce severe changes of lattice constant in the course of cycling.^{18,19}

The results obtained from cyclability studies of LiFePO_4 show that the preliminary charging/discharging cycles improve the electrochemical performance to achieve higher capacity. This suggests that the preliminary Li insertion/extraction processes modifies the film structure leading to easier Li diffusion. Upon further cycling (usually higher than 200 cycles), the Li insertion/extraction causes destruction of the film structure resulting in capacity fading. From a practical point of view, such behavior calls for in depth investigations of cyclability (which is not usually reported in the literature) to claim LiFePO_4 as an acceptable cathode material. However, from a fundamental standpoint, further investigations of the diffusion process from a statistical point of view and its influence on the structural changes is of great interest, and the future researches should be conducted in this direction.

It should be emphasized that the method proposed was employed to improve cyclability of a prototype cathode material with excellent cyclability. The improvement of other systems with weak cyclability will be more obvious. For instance, modification of chemical structure of LiFePO_4 with substituting metals^{3,8} results in severe prob-

lems in cyclability. On the other hand, problems regarding direct contact of the electroactive material with the electrolyte solution are truly serious for 5 V cathode materials. It has been reported that Fe in high-voltage performance of 5 V cathodes may be subject to over-oxidation to form mixed valency state of, e.g., $\text{Fe}^{+3.5}$, which is extremely reactive to oxide in the electrolyte salt.²⁰ Fortunately, the retaining layer of metal oxide is able to avoid such unfavorable reaction.²⁰

Conclusion

It was demonstrated that mixed-metal codeposition method is of interest for the preparation film-based cathodes from both fundamental and applied points of view. This provides an opportunity for the deposition of electroactive particles without physical structure destruction, which is of interest for fundamental researches in this context, e.g., investigating the diffusion process. On the other hand, mixed-metal codeposition is an efficient method for the preparation of cathodes with enhanced battery performance.

For a typical case investigated here, LiFePO_4 film cathode prepared by this method by incorporation of silver oxide within the electroactive film and coating the film surface with a retaining layer of the same modifying material. The LiFePO_4 film cathode is indeed a promising candidate for high-temperature lithium batteries with high specific capacity (approaching the theoretical capacity), excellent cyclability, and safety due to thermal stability. Although, the method proposed is able to improve battery performance of the LiFePO_4 cathode both at room and elevated temperatures, this cathode material is better suited for high-temperature performance rather than room temperature batteries.

References

1. A. Eftekhari, *J. Electrochem. Soc.*, **150**, A966 (2002).
2. A. Eftekhari, *J. Power Sources*, **124**, 182 (2003).
3. A. Yamada, M. Hosoya, S.-C. Chung, Y. Kudo, K. Hinokuma, K.-Y. Liu, and Y. Nishi, *J. Power Sources*, **119-121**, 232 (2003).
4. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1188 (1997).
5. N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier, and M. Arbab, *J. Power Sources*, **97-98**, 503 (2001).
6. A. Yamada, S. C. Chung, and K. Hinokuma, *J. Electrochem. Soc.*, **148**, A224 (2001).
7. F. Corce, A. D'Epifanio, J. Hassoun, A. Deptula, T. Olczac, and B. Scrosati, *Electrochem. Solid-State Lett.*, **5**, A47 (2002).
8. G. Li, H. Azuma, and M. Tohda, *J. Electrochem. Soc.*, **149**, A743 (2002).
9. M. Takahashi, S. I. Tobishima, K. Takei, and Y. Sakurai, *Solid State Ionics*, **148**, 283 (2002).
10. P. P. Prosini, M. Lisi, D. Zane, and M. Pasquali, *Solid State Ionics*, **148**, 45 (2002).
11. A. Eftekhari, *Solid State Ionics*, **167**, 237 (2004).
12. A. Eftekhari, *Electrochim. Acta*, **47**, 495 (2001).
13. A. Eftekhari, *J. Power Sources*, **126**, 221 (2004).
14. A. Eftekhari, *Electrochim. Acta*, **47**, 4347 (2002).
15. A. Eftekhari, *Solid State Ionics*, **161**, 41 (2003).
16. J. R. Dahn, E. W. Fuller, M. Obrovac, and U. von Sacken, *Solid State Ionics*, **69**, 26 (1994).
17. A. Eftekhari, *Electrochim. Acta*, **48**, 2831 (2003).
18. J. Cho, Y. J. Kim, and B. Park, *Chem. Mater.*, **12**, 3788 (2001).
19. Y. J. Kim, T.-J. Kim, J. W. Shin, B. Park, and J. Cho, *J. Electrochem. Soc.*, **149**, A1337 (2002).
20. A. Eftekhari, *J. Power Sources*, **124**, 182 (2003).