



Surface Modification of Thin-Film Based LiCoPO₄ 5 V Cathode with Metal Oxide

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The electrochemical performance of LiCoPO₄ as a 5 V cathode material for lithium batteries was investigated in LiBF₄ electrolyte. It was demonstrated that using this electrolyte salt significantly improves the electrochemical behavior of LiCoPO₄, as it is accompanied by a faster diffusion process. In addition, another approach, viz., surface/chemical modification of the cathode with a metal oxide, was employed to reduce capacity fades appearing at elevated temperatures. To this aim, a thin layer of Al₂O₃ was deposited on the cathode surface by a sputtering method. The results obtained from experimental investigations are indicative of the fact that both approaches significantly improve cyclability of the cathode. Such improvements provide a satisfactory cyclability for LiCoPO₄ to be used as a 5 V cathode material.

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During the past decade, lithium batteries have been widely used as power sources for portable electronic devices such as cellular phones and laptops because of some valuable advantages of lithium batteries over other types of rechargeable batteries. One of these advantages is the high-voltage performance of lithium batteries, as commercial batteries usually provide voltages in the range of 3–4 V. The high-voltage performance occurs because of the negativity of the lithium anode due to the formal potential of the Li/Li⁺ redox system (although other anodes have also been used with potentials close to that of the lithium anode).

More recently, some cathode materials with high redox potential have been proposed,^{1–12} which can be used for the fabrication of 5 V lithium batteries. Two main examples of this class of cathode materials are LiM_xMn_{2–x}O₂ (M = Cr, Fe, Co, Ni, and Cu)^{1–9} and LiMPO₄ (M = Mn, Ni, and Co).^{10–12} The former materials were discovered by substituting Mn ions in LiMn₂O₄ with other transition metals to improve the cyclability of LiMn₂O₄ at elevated temperatures for the fabrication of conventional 4 V lithium batteries. The latter ones have been proposed by introducing LiMPO₄ compounds as candidates for cathode materials for lithium batteries.¹³

However, there are some disadvantages and unsolved problems for this class of cathode materials (5 V) with an olivine-type structure. For instance, the most common example of these compounds, LiFePO₄, suffers from a significant difference between the theoretical and practical capacities, which is due to poor diffusion of lithium ions through LiFePO₄/FePO₄ interfaces and its poor electrical conductivity (LiFePO₄ can be considered as an insulating phase). This can be partly improved by adding small amounts of carbon^{14,15} or metals,¹⁶ increasing the conductivity of the cathode material. Decreasing the particle size is an efficient way to overcome the diffusion limitation problems for LiFePO₄.¹⁷

However, based on the comparison of different examples of LiMPO₄ (M = Fe, Mn, Ni, and Co), Okada *et al.* have shown that LiCoPO₄ has the highest redox potential.¹¹ LiCoPO₄ is the only example of this class of material that is suitable for 5 V performances. LiFePO₄ and LiMnPO₄ are good candidates for 4 V cathode materials in accordance with their redox potentials, *i.e.*, 3.6 and 4.1 V vs. Li/Li⁺, respectively. However, due to the presence of cobalt instead of iron, LiCoPO₄ has higher electrical conductivity and faster lithium diffusion in comparison with LiFePO₄.

Interestingly, even the famous class of 5 V materials, *e.g.*, LiM_xMn_{2–x}O₄, does not have a higher redox potential in comparison with LiCoPO₄. LiCoPO₄ can be considered as one of the best examples of 5 V cathode materials, because of its high specific

capacity and voltage. However, some problems still should be overcome before commercialization of this cathode material. Generally, there is insufficient technology for the fabrication of a 5 V lithium battery for use in practical applications. For example, the nonaqueous medium needed for the 5 V performance is still problematic, because of the instability of common electrolytes at such a high-voltage performance. This problem exists for all 5 V cathode materials. Also, the electrochemical performance of LiCoPO₄ is not well studied in the literature. To our knowledge, there are only two brief communications^{10,12} devoted to the battery performance of LiCoPO₄ and a comparative study of different LiMPO₄ cathodes in a short manuscript.¹¹ The main problem for LiCoPO₄ as a cathode material is its significant capacity fades at elevated temperatures. This is a common problem for all 5 V cathode materials. Following numerous researches devoted to the investigation of the capacity fading of LiMn₂O₄, attention has been recently paid to the capacity fading of LiM_xMn_{2–x}O₄ spinels as 5 V cathode materials.^{7–9} However, such investigations are not usually performed for LiMPO₄ cathode materials, and studies of such novel materials are still in a preliminary stage.

Experimental

LiCoPO₄ was synthesized according to the method proposed by Lloris *et al.*¹² Briefly, the cobalt ammonium phosphate precursor CoNH₄PO₄ was prepared by precipitation according to the following process. First, 10 mL of 30% NH₃ solution was added to 100 mL of a 0.2 M CoCl₂ · 6H₂O solution. Then, 50 mL of a 0.5 M (NH₄)₂HPO₄ solution was slowly added to the preceding solution. This process was performed under continuous stirring until the precipitation was accomplished. The product was filtered and washed several times with water and absolute ethanol, then dried at 80°C for 12 h. To prepare LiCoPO₄, a solid-state reaction was performed between CoNH₄PO₄ and LiOH · H₂O (10% more than the stoichiometric amount needed for the reaction), following by annealing at 400°C for 12 h. Additional annealing as performed in Ref. 12 was carried out after the deposition processes via annealing at 400°C for 10 h.

The LiCoPO₄ synthesized was deposited on an Al current collector using the sputtering technique with a 100 W strength. The amount of the electroactive material attached was about 25 μg, and it was about 500 nm thick. A modified cathode was also prepared by covering the LiCoPO₄ film cathode with a thin layer of Al₂O₃ deposited by reactive sputtering of an Al target. The sputtering procedure employed was conventional and similar to those widely applied in the literature for the preparation of thin films of common cathode materials such as LiCoO₂. The thin-film based LiCoPO₄ cathode prepared was also similar to other sputtered cathode materials with a conventional porosity and physical structure. There was no special feature in the sputtering deposition of this 5 V cathode material. All

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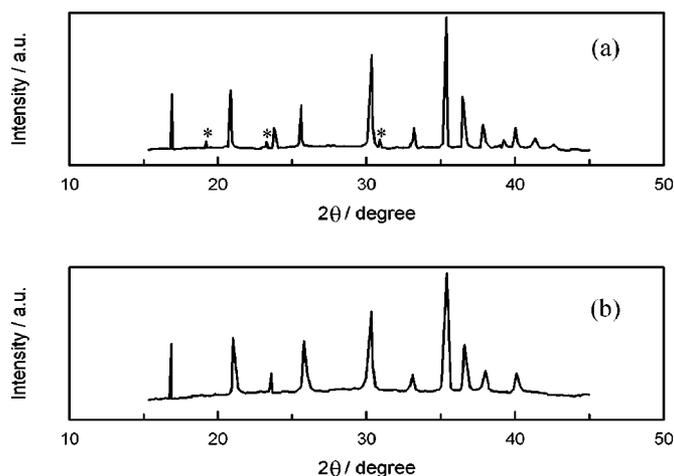


Figure 1. XRD patterns of (a) unmodified and (b) Al_2O_3 -modified LiCoPO_4 particles.

investigations reported here correspond to thin-film based cathode material, except the X-ray diffraction (XRD) patterns reported in Fig. 1, which were obtained from as-prepared cathode material to investigate the synthesis process and inspect the existence of modifier material.

The battery performance was investigated in a two-electrode cell containing the LiCoPO_4 thin-film cathode and a lithium foil as both counter and reference electrodes. The electrolyte was prepared from 1 M LiBF_4 as the electrolyte salt in 1:1 ethylene carbonate (EC) dimethyl carbonate (DMC) solvent. All chemicals including EC and DMC were of analytical grade. The electrochemical measurements were performed using a homemade potentiostat/galvanostat connected to a computer running CorrView software. The battery performance of the lithium secondary cell containing the LiCoPO_4 thin-film cathode was investigated using a battery cycler. Depth profile data were obtained by Ar ion-beam sputtering (4 keV).

Results and Discussion

At the first stage of the research, the influence of surface modification of individual particles on the material characterization was investigated. To this aim, the surface of individual particles of LiCoPO_4 was modified by the metal oxide modifier according to a common surface/chemical modification (cf. Ref. 18). The characterizations of both unmodified and Al_2O_3 -modified LiCoPO_4 indicate well-defined orthorhombic olivine-type structure with the space group $Pmnb$ (Fig. 1). However, because of the use of excess reactant for the synthesis process, impurities of Co_3O_4 and Li_3PO_4 are detected (shown by asterisks in Fig. 1a). The XRD patterns of the Al_2O_3 -modified LiCoPO_4 shows peak broadening without any impurity phase, indicating that the Al_2O_3 particles are coated on the LiCoPO_4 as an amorphous or nanophase. In addition, as the XRD patterns show no peak of any Al_2O_3 phase, it can also suggest the formation of a solid solution ($\text{LiCo}_{1-x}\text{Al}_x\text{PO}_z$), as indicated by depth profiling.

Depth profiling by sequential Ar^+ -ion sputtering and X-ray photoelectron spectroscopy analysis is a common way to determine surface layer thickness and to measure elemental concentrations as a function of depth. To inspect the general structure of the modifier material coated on the cathode material, depth profiling was employed to monitor the amounts of main elements at different depths of the thin-film cathode. The sputter rate was estimated to be 1.8 nm/min. The distribution of Al across the film deposited is presented in Fig. 2. The Al atoms are distributed at a thin layer about 10 nm thick on the surface. The decreasing concentration gradient of Al is indicative of the formation of a solid solution of $\text{LiCo}_{1-x}\text{Al}_x\text{PO}_z$ at

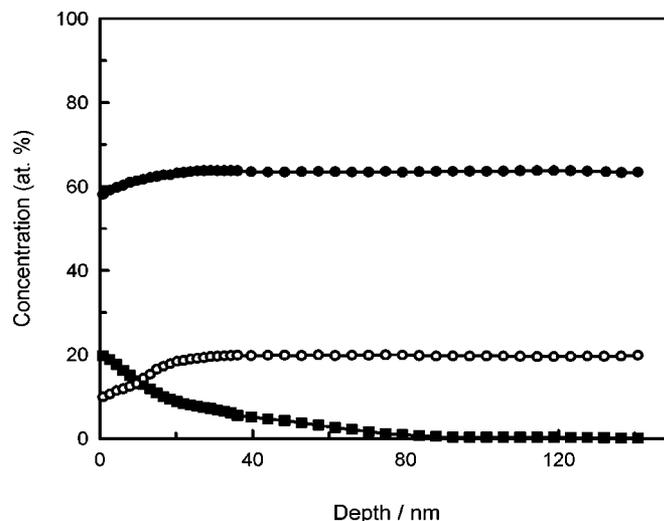


Figure 2. Concentration/depth profile of an Al_2O_3 -coated LiCoPO_4 film electrode: Al (■), Co (○), and O (●). Li and P are not presented.

the $\text{LiCoPO}_4/\text{Al}_2\text{O}_3$ interface. The results are in agreement with those reported for Al_2O_3 coating of LiCoO_2 .¹⁹ This issue has been extensively studied for a LiMn_2O_4 cathode when the Al_2O_3 modifier was placed beneath, within, and upon the cathode material.¹⁸

The electrochemical properties of high-voltage cathode materials are not well described in the literature, because such studies are related to composite electrodes, and it is difficult to reveal the electrochemical properties resulting from the active material alone in the presence of an organic polymer binder and high surface area carbon. However, there has been much focus on the preparation of thin-film cathodes for the fabrication of microbatteries. Thus, it is of interest to conduct the research based on a thin-film cathode. Figure 3 shows a typical cyclic voltammogram (CV) characteristic of the LiCoPO_4 film electrode in the LiBF_4 electrolyte. The curve shows a well-defined CV displaying a better reversible behavior accompanied by lower peak separation in comparison with that reported in Ref. 10. This may suggest a faster electron transfer occurring for the LiCoPO_4 film electrode prepared.²⁰ The CV displays a redox couple

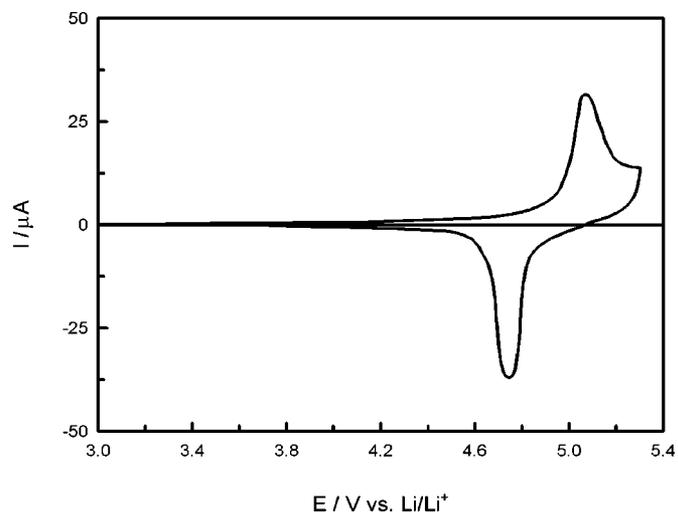


Figure 3. Typical CV of the LiCoPO_4 film electrode in 1 M LiBF_4 electrolyte. Scan rate 0.05 mV s^{-1} . The current is normalized for 1 mg of the cathode material.

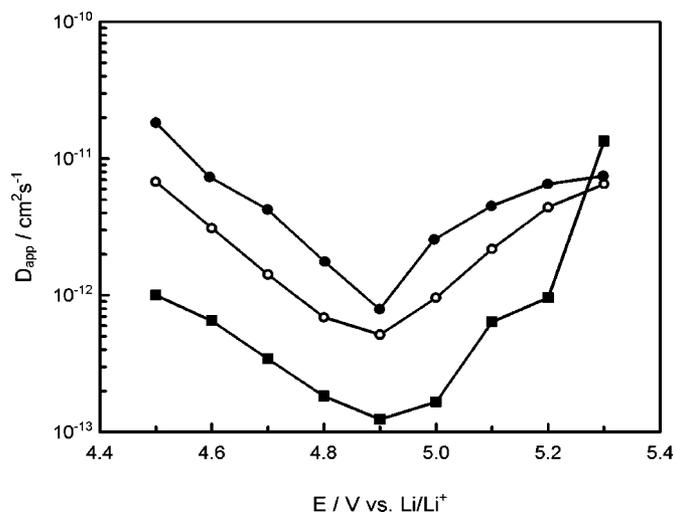


Figure 4. The diffusion coefficient as a function of electrode potential determined for various cases: (■) the LiCoPO₄ cathode in LiPF₆ electrolyte, (○) the LiCoPO₄ cathode in LiBF₄ electrolyte, and (●) the Al₂O₃-modified LiCoPO₄ cathode in LiBF₄ electrolyte.

occurring at about 4.9 V vs. Li/Li⁺. In addition, it is observable that the electrolyte is stable at this potential region (up to 5.3 V).

To investigate the efficiency of the approaches employed in this research, three different cases were compared: (i) the unmodified LiCoPO₄ film electrode in LiPF₆ electrolyte (as a conventional case), (ii) the unmodified LiCoPO₄ film electrode in LiBF₄ electrolyte (to investigate the influence of the electrolyte), and (iii) the Al₂O₃-modified LiCoPO₄ film electrode, prepared by coating the unmodified LiCoPO₄ film electrode with a thin layer of aluminum oxide, in LiBF₄ electrolyte (to investigate the influence of surface/chemical modification and the combination of two different approaches employed). The investigation of surface/chemical modification approach in LiPF₆ electrolyte was too meaningless to be reported here. We attempted to make two different comparisons between the cases (i) and (ii) and between (ii) and (iii); however, the data are presented together to avoid repetition.

To compare the rate of the diffusion process for different cases, the diffusion coefficients were estimated for these different cases. A series of diffusion coefficients at different electrode potentials were determined by a chronoamperometric technique according to a method described previously.²⁰ Figure 4 presents the diffusion coefficients for three cases at different electrode potentials. For the three different cases, the variations of the diffusion coefficient as a function of electrode potential were similar to the conventional potential dependency of the diffusion coefficient, displaying minima for the diffusional constant at the potentials consistent with the peak current in the CV. According to the results (Fig. 4), the diffusion coefficient is higher in the electrolyte medium containing LiBF₄ (comparison of cases i and ii). However, surface coating of the LiCoPO₄ cathode increases the diffusion coefficient. We emphasize that the values measured at high potential are not reliable because of the significant electrolyte instabilities at high potentials.

The typical charge/discharge characteristics of three different cases are illustrated in Fig. 5. Observe that the LiCoPO₄ cathode displays a better battery performance associated with a higher specific capacity in LiBF₄ electrolyte in comparison with common LiPF₆ electrolyte. The difference in the electrochemical performances of a cathode material at different electrolyte components can be attributed to the influence of electrolyte components to form different solid films at the cathode surface. As the Li intercalation process is partly controlled by the Li migration through the films formed on the electrode surface, different solid film properties such

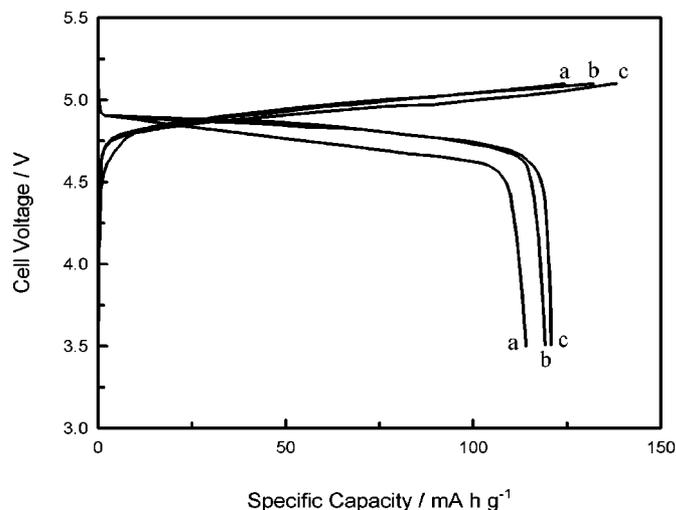


Figure 5. Charge/discharge profiles of the secondary cells fabricated using (a) the LiCoPO₄ cathode in LiPF₆ electrolyte, (b) the LiCoPO₄ cathode in LiBF₄ electrolyte, and (c) the Al₂O₃-modified LiCoPO₄ cathode in LiBF₄ electrolyte. Rate C/10.

as ionic conductivity, compositions, and structures lead to different charge-transfer processes.

The other approach employed in this research was also efficient at improving the battery performance of the cathode. When comparing the unmodified and modified electrodes in the same electrolyte (LiBF₄ as the better medium), the Al₂O₃-modified LiCoPO₄ cathode provides a higher specific capacity than that of the unmodified LiCoPO₄ cathode because of a faster Li diffusion through the LiCoPO₄/Al₂O₃ interface. This can be attributed to the existence of easier diffusion paths due to the formation of the LiCo_{1-x}Al_xPO₄ solid solution. Enhanced Li diffusion due to the formation of such a solid solution has also been reported for the formation of an LiCo_{1-x}Al_xO₂ solid solution.^{19,21,22} The results obtained from battery performances of three different cases indicate that both approaches, *viz.*, choosing electrolyte salt and modification with Al₂O₃ film, significantly increase the specific capacity of the cathode material, and a combination of these approaches can be used to obtain an excellent performance of the LiCoPO₄ cathode. Interestingly, a combination of these two approaches leads to an excellent value of the specific capacity for LiCoPO₄, comparable to that reported based on the addition of carbon,¹² which is the most common (and efficient) approach for improving the specific capacity of LiMPO₄ cathode materials.

A serious problem for the cathode materials of lithium batteries is capacity fading at elevated temperatures. As a rechargeable device, there is a considerable requirement for good cyclability. Thus, investigations of cyclability and reducing the capacity fades at elevated temperatures are active areas of research in this context. Such phenomena can be attributed to dissolution of low-valent metals generated in the electrochemical redox of the cathode (*e.g.*, Mn dissolution in the form of Mn²⁺ due to the existence of Mn³⁺ in the Mn³⁺/Mn⁴⁺ redox system of LiMn₂O₄; it is based on the reaction: Mn⁴⁺ + Mn³⁺ → MnO + Mn⁴⁺). Such failures are stronger for 5 V cathode materials because of new problems appearing during 5 V performance; however, less attention has been paid to this problem in the literature. Figure 6 shows cyclability data for the different cases under investigation.

A comparison of curves (■) and (○) in Fig. 6 clearly shows the importance of electrolyte on the cyclability of a 5 V cathode material. Weak cyclability of the LiCoPO₄ cathode in LiPF₆ electrolyte is due to instability of LiPF₆ at elevated temperatures, as the common lithium batteries suffer from this failure. The thermal stabilities of

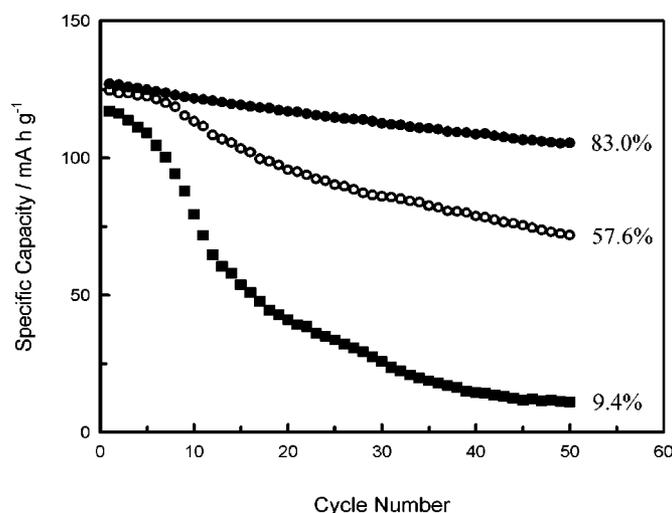


Figure 6. Cyclability data of three cases under investigations obtained from charge/discharge profiles related to (a) the LiCoPO_4 cathode in LiPF_6 electrolyte (\blacksquare), (b) the LiCoPO_4 cathode in LiBF_4 electrolyte (\circ), and (c) the Al_2O_3 -modified LiCoPO_4 cathode in LiBF_4 electrolyte (\bullet). The values noted for the curves are the percent capacity after 50 cycles.

LiPF_6 and LiBF_4 as two electrolyte salts for lithium batteries have been compared in the literature.²³ However, avoiding direct reaction of the cathode active material at the electrolyte/electrode interface due to the presence of an intervening layer of Al_2O_3 is a reason for good cyclability of the Al_2O_3 -modified LiCoPO_4 cathode. In this direction, solid electrolytes, which are not subject to such severe electrolyte oxidation at the cathode surface, are good candidates for 5 V lithium batteries.²⁴

XRD patterns of the thin-film cathode material (Fig. 7) are similar to those of the original material (Fig. 1), except for an Al peak that occurs because of the current collector. To inspect the surface structural changes occurring in the course of cycling, XRD patterns of the modified and unmodified cathodes were compared before and after successive charge/discharge cycling. The unmodified cathode shows severe peak broadening, which is probably due to the microstructural defects or local strain formed in the course of cycling. It is also accompanied by the appearance of impurity peaks. Because the changes in the XRD patterns of the modified electrode after cycling are significantly less than the changes of the unmodified electrode (Fig. 7), one can conclude that the modifier layer is able to avoid the possible side reactions due to decomposition of the electrolyte on the electrode surface in the course of the high-voltage performance. It has been reported that formation of carbonaceous films on the cathode surface, which hinders Li migration, is an important reason for the capacity loss of 5 V cathode materials, as claimed by Sun *et al.*⁸

However, because increasing the surface area of LiMPO_4 cathode materials is an approach for improving their electrochemical performances⁷ and because of the complex surface of cathode materials associated with high fractal dimensions,²⁵ it is of interest to cover the cathode surface with such a thin layer to avoid side reactions on the cathode surfaces.

To understand the source of capacity fading of LiCoPO_4 and the reasons for such improvements provided by the approaches employed, it is useful to investigate the capacity fading of LiCoPO_4 for charging/discharging at different voltage regions. The cyclability data obtained from the charge/discharge characteristics of three cases under investigation for different voltage regions are summarized in Table I. Such investigations can help us to understand the reason for the appearance of capacity fading of the LiCoPO_4 cathode material.

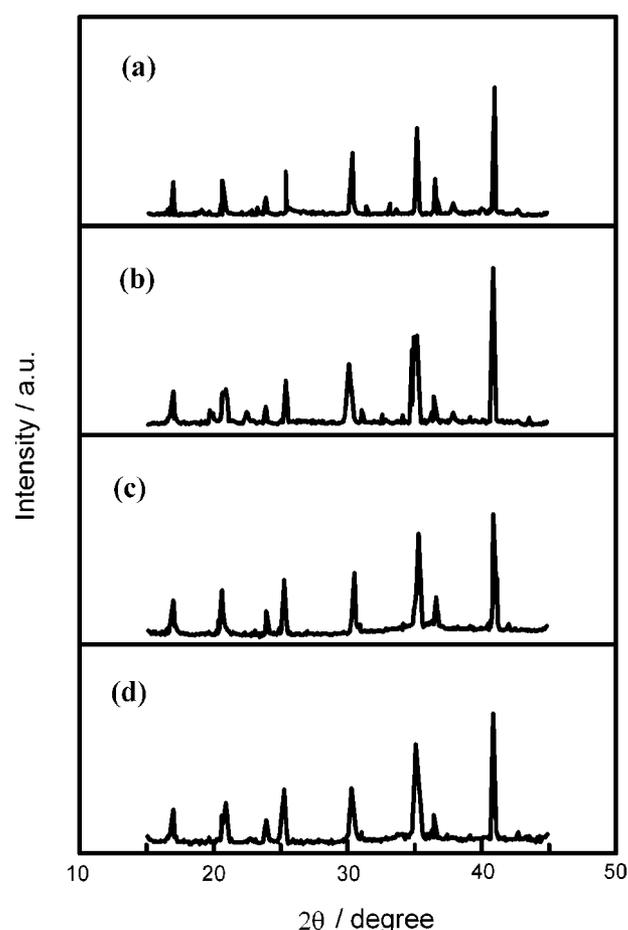


Figure 7. XRD patterns of (a) uncoated and (b) Al_2O_3 -coated LiCoPO_4 thin-film cathodes before electrochemical experiments (as-deposited electrodes) and (c,d) corresponding patterns after 50 successive charge/discharge cycles under the conditions described in Fig. 5.

As can be seen, cyclability of the cathode is good for charging/discharging at low voltages in comparison with that observed for

Table I. Cyclability data obtained from charge/discharge characterizations of three cases: (1) the LiCoPO_4 cathode in LiPF_6 electrolyte, (2) the LiCoPO_4 cathode in LiBF_4 electrolyte, and (3) the Al_2O_3 -modified LiCoPO_4 cathode in LiBF_4 electrolyte. $T = 55^\circ\text{C}$.

| Voltage Region | | Case 1 | Case 2 | Case 3 |
|----------------|--|--------|--------|--------|
| 3.5-5.1 V | Initial capacity (mAh g^{-1}) | 117.0 | 124.6 | 127.0 |
| | Capacity after 50 cycles | 11.0 | 71.8 | 105.5 |
| | Percent capacity fading | 90.6% | 42.4% | 16.9% |
| 2.5-5.1 V | Initial capacity (mAh g^{-1}) | 120.3 | 125.9 | 128.2 |
| | Capacity after 50 cycles | 9.1 | 70.3 | 104.2 |
| | Percent capacity fading | 92.4% | 44.1% | 18.7% |
| 4.1-5.3 V | Initial capacity (mAh g^{-1}) | 121.8 | 128.3 | 130.5 |
| | Capacity after 50 cycles | 4.1 | 48.6 | 95.4 |
| | Percent capacity fading | 96.6% | 79.7% | 26.8% |

cycling at high voltages. This suggests that metal (Co) dissolution cannot be the reason for the weak cyclability of LiCoPO_4 cathode material, as Co dissolution occurs at low voltages due to the existence of low-valent Co. Therefore, one can conclude that the appearance of significant capacity fading of LiCoPO_4 is related to its 5 V performance, due to the electrolyte instability.

It is of interest to determine if the electrolyte instability is the reason for the appearance of such capacity fades or if the involvement of the cathode material in a side reaction occurring at high voltage is responsible. By comparing the unmodified LiCoPO_4 film electrode with Al_2O_3 -modified LiCoPO_4 film electrode, this question can be answered. Assuming that the electrolyte instability is only related to the high-applied voltage, there should not be a difference between the unmodified and modified electrodes (or just a tiny difference), as the electrolyte instability at high-voltage performance is appropriate for both of them. However, from the data presented in Table I, the metal oxide covering significantly improves cyclability by reducing the capacity fades appearing at high voltages.

We can say that coating the cathode material with a thin film of Al_2O_3 avoids the involvement of the LiCoPO_4 in a side reaction occurring at the electrolyte/electrode interface (which is strong at high voltages), because the Al_2O_3 film acts as a semimembrane allowing the Li intercalation/deintercalation process. We call the film a semimembrane, because a perfect membrane just allows the transfer of counter ions, whereas the electrolyte solution can also be incorporated within the film to reach the electroactive material. Thus, oxidation of the electrolyte can also occur in the presence of the metal oxide layer. This can be judged from the XRD patterns illustrated in Fig. 7. Although the pattern changes in the course of cycling are less for the modified cathode, they are still significant, suggesting structural changes of the cathode material, probably due to the electrolyte oxidation. In other words, the metal oxide is a semimembrane, because it reduces direct contact of the electrolyte solution with the electroactive material (but does not avoid it completely).

Coating the cathode surface with a thin film of aluminum oxide improves the battery performance in two ways. First, the metal oxide formed on the electrode surface avoids direct contact of the high-valent Co generated by the redox system of LiCoPO_4 with the electrolyte to participate in a side reaction causing the electrolyte decomposition. This effect has been extensively described for a known 5 V cathode material ($\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$).⁹ Second, the $\text{LiCo}_{1-x}\text{Al}_x\text{PO}_z$ solid solution formed at the $\text{LiCoPO}_4/\text{Al}_2\text{O}_3$ interface provides faster Li diffusion. Thus, as the modifier material deposited on the cathode material is in the form of Al_2O_3 at the outer part and $\text{LiCo}_{1-x}\text{Al}_x\text{O}_z$ at the inner part (the $\text{LiCoPO}_4/\text{Al}_2\text{O}_3$ interface), it can be considered as both surface and chemical modification. Such behavior has also been reported for the incorporation of metal particles into cathode material, which provides an opportunity for surface modification of individual particles.^{26,27}

Since the completion of the original draft of this paper, West and co-workers²⁸ have published a paper devoted to the preparation of thin-film based LiCoPO_4 cathode in this *Journal*. Despite the same subject, the strategy of the study here is different than that employed in Ref. 28. That paper discusses fundamental issues on the preparation of thin-film based cathodes using LiCoPO_4 and corresponding material characterization; whereas, this paper attempts to improve the battery performance of this 5 V cathode material. Both papers emphasize the usefulness of thin-film based cathodes for 5 V per-

formance. In any case, the early paper²⁸ is of great interest in this context.

Conclusion

It was demonstrated that capacity fading of LiCoPO_4 as a 5 V cathode material from the family of LiMPO_4 compounds is mainly due to electrolyte instability at 5 V performance as a result of the occurrence of side reactions at the electrolyte/electrode interface. This problem can be overcome by two different approaches, as examined here. First, one can use an electrolyte with higher stability in comparison with the common LiPF_6 electrolyte. Although there is still no ideal electrolyte as an alternative to this common electrolyte, it was shown that LiBF_4 has significantly better stability for 5 V performance. On the other hand, because such instability is related to the involvement of the electrolyte salt in a side reaction with high-valent Co generated at high-voltage performance, coating the cathode material with a thin layer of metal oxide (e.g., Al_2O_3) can avoid direct reaction of the high-valent Co at the electrolyte/electrode interface. However, the Al_2O_3 film formed on the cathode surface does not hinder the Li intercalation/deintercalation. Moreover, the formation of a $\text{LiCo}_{1-x}\text{Al}_x\text{PO}_z$ solid solution at the $\text{LiCoPO}_4/\text{Al}_2\text{O}_3$ interface provides a faster Li^+ diffusion.

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