Short communication

Li-ion diffusion kinetics in LiCoPO$_4$ thin films deposited on NASICON-type glass ceramic electrolytes by magnetron sputtering

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ABSTRACT

LiCoPO$_4$ thin films were deposited on Li$_{1+x+y}$Al$_x$Ti$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$ (LATSP) solid electrolyte by radio frequency magnetron sputtering and were characterized by X-ray diffraction and scanning electron microscope. The films show a (1 1 1) preferred orientation upon annealing and are chemically stable with LATSP up to 600 °C in air. An all-solid-state Li/PEO$_{18}$-Li(CF$_3$SO$_2$)$_2$N/LATSP/LiCoPO$_4$/Au cell was fabricated to investigate the electrochemical performance and Li-ion chemical diffusion coefficients, $\tilde{D}_{Li}$, of the LiCoPO$_4$ thin films. The potential dependence of $\tilde{D}_{Li}$ values of the LiCoPO$_4$ thin film was investigated by potentiostatic intermittent titration technique and was compared with those of the LiFePO$_4$ thin film. These results showed that the intercalation mechanism of Li-ion in LiCoPO$_4$ is different from that in LiFePO$_4$.

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1. Introduction

Since pioneered by Amine et al. [1], olivine-type lithium cobalt phosphate, LiCoPO$_4$, has received great interest as a candidate cathode material for Li-ion batteries due to its high electrode potential of 4.8 V vs. Li/Li$^+$ and it can be easily synthesized in air. LiFePO$_4$ only gives a 3.5 V electrode potential vs. Li/Li$^+$ and must be synthesized in an inert atmosphere even though both belong to the olivine-type family [2,3]. The reported discharge capacity of LiCoPO$_4$ was less than 136 mA h g^{-1} [4,5], which is lower than the theoretical value of 167 mA h g^{-1}. It seems that the low discharge capacity of LiCoPO$_4$ can be attributed to its low electronic conductivity of around 10^{-10} to 10^{-9} S cm^{-1} [6,7]. Although the electronic conductivity can be significantly increased by introducing a second phase Co$_2$P by heat treating LiCoPO$_4$ in Ar, the discharge capacity of LiCoPO$_4$ is still unsatisfactory [6,8–10]. The discharge capacity of LiFePO$_4$ almost reached its theoretical value when measured in a quasi-open-circuit mode. As a result, the discharge capacity of LiCoPO$_4$ should not be simply controlled by its electronic conductivity.

As is generally accepted, the poor rate capability of LiFePO$_4$ is partly due to the slow diffusion through the LiFePO$_4$/FePO$_4$ two-phase interface. Similarly, a two-phase model was also suggested by Bramnik et al. [11,12] using in situ and ex situ XRD to explain the Li extraction/insertion mechanism in LiCoPO$_4$. However, the XRD results showed that the crystalline phase was only a lithium-poor phase; no "CoPO$_4$" phase was identified even though LiCoPO$_4$ was fully charged. In addition, two successive voltage plateaus were often observed during the charge of LiCoPO$_4$ [5,11–14]. Nakayama et al. [13] proved that it was not related to the irreversible side reactions and suggested that it might be due to an increase in electrochemical polarization around $x = 0.3$ in Li$_{1-x}$CoPO$_4$. Nevertheless, the exact mechanism for the two-plateau charge profile is still controversial, and in other cases, a one-plateau charge profile was reported [15–17]. LiFePO$_4$ exhibits only one-plateau charge profile in the two-phase region. Therefore, it is reasonable to infer that the different electrochemical behavior can be ascribed to the different Li-ion diffusion character.

In our present work, LiCoPO$_4$ thin films were prepared by radio frequency (RF) magnetron sputtering on Li$_{1+x+y}$Al$_x$Ti$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$ (LATSP) solid electrolyte. Li-ion chemical diffusion coefficients were measured by potentiostatic intermittent titration technique (PITT) using the all-solid-state Li/PEO$_{18}$-Li(CF$_3$SO$_2$)$_2$N/LATSP/LiCoPO$_4$/Au cell. Eftekhari [16] showed that the $\tilde{D}_{Li}$ values of LiCoPO$_4$ depended on the electrolyte used. The author also pointed out that the $\tilde{D}_{Li}$ values measured at high voltages were not reliable due to the decomposition of the electrolyte. The LATSP used in our case is electrochemically stable at the high voltage. Therefore, the $\tilde{D}_{Li}$ values at high voltages are reliable when LATSP is used. The $\tilde{D}_{Li}$ values of LiCoPO$_4$ were compared with those of LiFePO$_4$ to clarify the different Li-ion diffusion behaviors between LiCoPO$_4$ and LiFePO$_4$.

2. Experimental

The glass ceramics plates, $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ (0.15 mm in thickness), provided by OHARA Inc., were used as the solid electrolyte for the following experiments. LATSP was selected as the solid electrolyte because of its high Li-ion conductivity at room temperature [18,19]. $LiCoPO_4$ was prepared by the two-step solid-phase reactions using stoichiometric amount of Li_2CO_3, $Co(OCOCH_3)_2\cdot4H_2O$ and $(NH_4)_2HPO_4$ as the starting materials. The mixture was pressed into pellets and heated at 400 °C for 5 h. The reaction product was then ground and pressed again into pellets and headed at 800 °C for 24 h. The $LiCoPO_4$ thin films (8 mm × 8 mm) were deposited on the LATSP substrates (10 mm × 10 mm) by RF magnetron sputtering using an Ulvac SCOTT-C3. The target (50 mm in diameter) used for sputtering was prepared by cold pressing $LiCoPO_4$ powder. $LiCoPO_4$ sputtering was carried out for 2 h in pure Ar with a working pressure of 2 Pa. The power used for $LiCoPO_4$ sputtering was 50 W, and the distance between the substrate and the target was 10 cm. Au was then deposited on the $LiCoPO_4$ by RF magnetron sputtering in pure Ar for 30 min as a current collector to form a LATSP/$LiCoPO_4$/Au electrode. The as-prepared electrodes were then annealed for 1 h in air to improve crystallization. The structure of the films was characterized by X-ray diffraction (XRD) using a RINT2000/PC diffractometer with Cu Kα radiation. The cross-sectional morphology of the films was observed by scanning electron microscopy (SEM) using a Hitachi S-4000.

An Li/PEO_{18}-Li$(CF_3SO_2)_2$N/LATSP/$LiCoPO_4$/Au cell was fabricated to investigate the electrochemical performance and Li-ion chemical diffusion coefficients of the $LiCoPO_4$ thin film. To prevent the reaction between Li and LATSP, a polyethyleneoxide (PEO)-based solid polymer film, PEO_{18}-Li$(CF_3SO_2)_2$N, was inserted between them. The polymer electrolyte was prepared by our previously reported method [20]. Galvanostatic cycling of the cells was carried out at a current density of 1 μA between 3.5 and 5 V. Cyclic voltammetry (CV) was performed between 3.5 and 5.1 V at a scan rate of 0.1 mV s^{-1} using a Solartron 1287 electrochemical interface. For the PITT measurements, a potential step of 10 mV was applied and the current was recorded as a function of time. The procedure was repeated between 4.7 and 5 V. In this work, PITT method was chosen because it is a useful tool even for the electrode reactions involving a two-phase process [21]. All the electrochemical measurements were performed at 50 °C.

The electrochemical behavior of $LiCoPO_4$ was compared with that of $LiFePO_4$. The $LiFePO_4$ powder was prepared by solid-phase reactions of stoichiometric Li_2CO_3, $FeC_2O_4\cdot2H_2O$ and $(NH_4)_2HPO_4$ at 700 °C for 6 h in an Ar/H_2 mixture (2% H_2). The $LiFePO_4$ thin films were sputtered under the same conditions as $LiCoPO_4$ and were annealed for 1 h in the Ar/H_2 mixture (2% H_2). An Li/PEO_{18}-Li$(CF_3SO_2)_2$N/LATSP/$LiFePO_4$/Au cell was also fabricated to investigate the electrochemical performance and Li-ion chemical diffusion coefficients in the $LiFePO_4$ thin films. Galvanostatic cycling of the cells was carried out at 1 μA between 2.8 and 4.1 V. CV was performed between 2.8 and 4.1 V at a scan rate of 0.1 mV s^{-1}. PITT measurements were conducted between 3.4 and 3.7 V with a 10 mV potential step. All the electrochemical measurements were also performed at 50 °C.

3. Results and discussion

The as-deposited film by sputtering is generally in an amorphous state. The film was annealed to improve the crystallization. Therefore, it is crucial to investigate the chemical stability between the sputtered film and the LATSP solid electrolyte during the heat treatment. Previous studies showed that some electrode materials, such as the $LiMn_2O_4$ thin film (up to 600 °C) [22], the $Li_4Ti_5O_{12}$ thin film
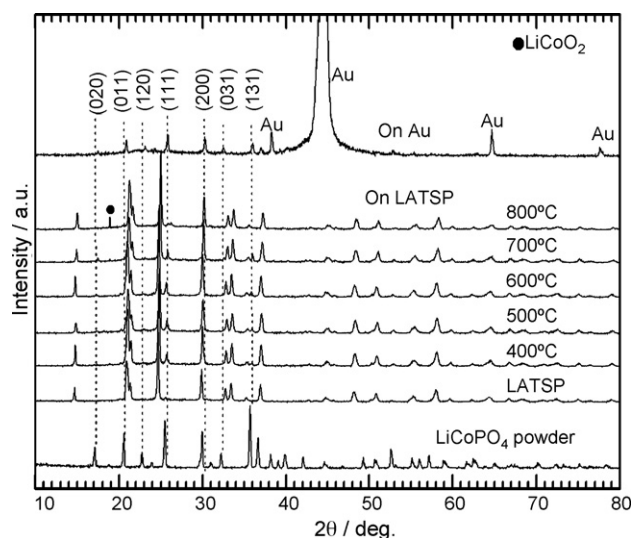

Fig. 1. XRD patterns of the $LiCoPO_4$ thin films on LATSP annealed at different temperatures and on Au annealed at 600 °C in air.

(up to 600 °C) [23], the $Li_3Fe_2(PO_4)_3$ and $LiCoPO_4$ powders (up to 900–1000 °C) [5], showed chemical stability toward NASICON-type solid electrolyte. As shown in Fig. 1, the $LiCoPO_4$ thin film shows a sharp peak at $2\theta = 25.5°$ by annealing at 600 °C in air, which is indexed to the (1 1 1) diffraction peak of $LiCoPO_4$. The $LiCoPO_4$ thin film deposited on LATSP exhibits a (1 1 1) preferred orientation upon annealing. The $LiCoPO_4$ thin film was also sputtered on Au substrate for comparison. The $LiCoPO_4$ thin film on Au, which was sputtered under the same conditions and annealed at 600 °C, shows similar XRD patterns as the $LiCoPO_4$ powder. It suggests that the orientation of the $LiCoPO_4$ thin film depends on the substrate used. When annealed at 700 °C, the peak becomes broad and is slightly shifted to a high angle, indicating some interfacial reactions take place between $LiCoPO_4$ and LATSP. At 800 °C, a new peak at around $2\theta = 19°$ appears, suggesting that the interfacial reactions become significant at elevated temperature. The new peak is suggested to be (0 0 3) peak of $LiCoO_2$. The LATSP/$LiCoPO_4$/Au electrodes annealed at 600 °C were used in the following electrochemical experiments. The interfacial stability between $LiFePO_4$ and LATSP upon annealing in the Ar/H_2 mixture (2% H_2) was also checked. As shown in Fig. 2,
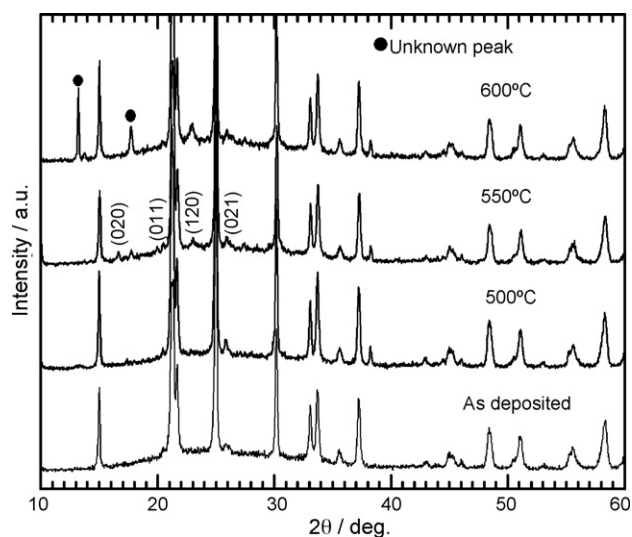

Fig. 2. XRD patterns of the $LiFePO_4$ thin films on LATSP annealed at different temperatures in an Ar/H_2 mixture (2% H_2).
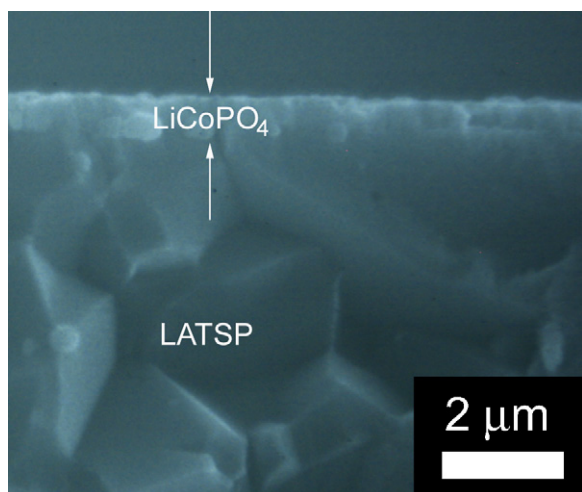
Fig. 3. Cross-sectional SEM image of the LiCoPO$_4$ thin film on LATSP after annealing at 600 °C for 1 h.

the LiFePO$_4$ film is chemically stable toward LATSP up to 550 °C. At 600 °C, some unknown peaks appear, indicating chemical reactions take place between LiFePO$_4$ and LATSP. Thus, we used the LATSP/LiFePO$_4$/Au electrodes annealed at 550 °C in the following electrochemical experiments.

Fig. 3 shows the cross-section SEM image of the LiCoPO$_4$ thin film sputtered on the LATSP followed by heating at 600 °C for 1 h. Note that the film is dense and the thickness is estimated to be about 0.7 μm. The relative density of the film was estimated to be about 80% by the weight gain and the density of the LiCoPO$_4$.

Fig. 4(a) shows the charge and discharge profiles of the LiCoPO$_4$ thin film for the first three cycles. It is clear that the film exhibits different charge profiles between the first and following cycles; the first charge curves give only a plateau at around 4.9 V vs. Li/Li$^+$, while the second and the third ones give two successive plateaus at around 4.8 and 4.9 V, respectively. Similar behavior was observed by Nagata et al. [5] and Bramnik et al. [12], where the composite electrodes composed of LiCoPO$_4$, acetylene black and polymer binder were used. The structural rearrangement in LiCoPO$_4$ may take place during the first charge process of the LiCoPO$_4$ thin film. Note that only a sloping line can be observed between 4.6 and 4.9 V during the discharge process, indicating that the mechanisms for Li-ion re-insertion into "CoPO$_4$" and extraction from LiCoPO$_4$ are different. Fig. 4(b) shows the CV plots of the cycled LiCoPO$_4$ thin film. Note that in addition to an obvious peak at 4.95 V, a small shoulder
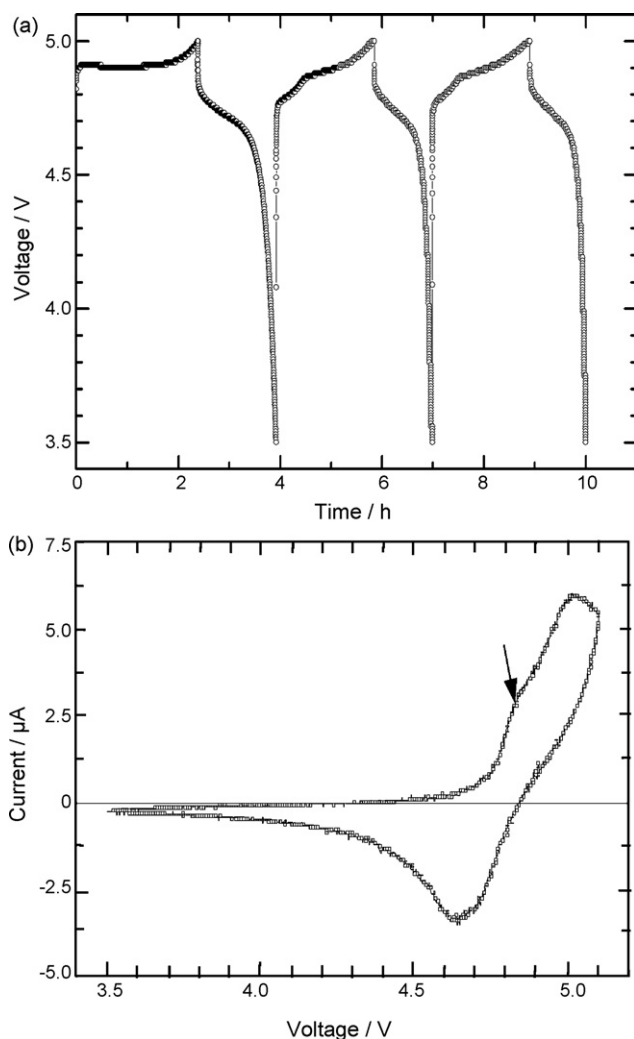

Fig. 4. Charge and discharge profiles at 1 μA (a) and CV at a scan rate of 0.1 mV s^{-1} (b) of the LiCoPO$_4$ thin film annealed at 600 °C for 1 h.
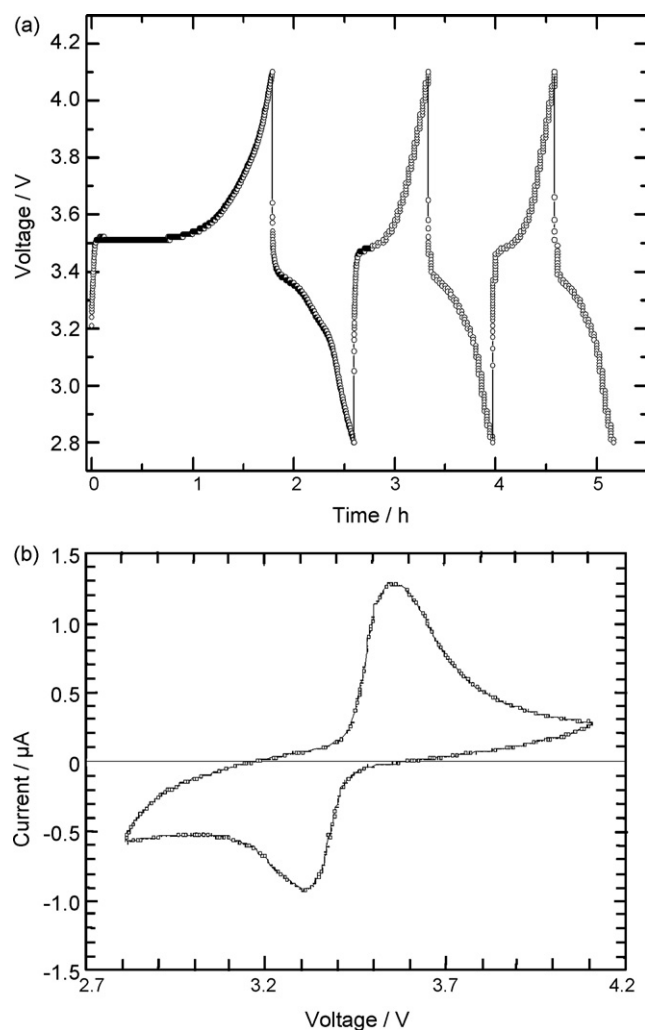

Fig. 5. Charge and discharge profiles at 1 μA (a) and CV at a scan rate of 0.1 mV s^{-1} (b) of the LiFePO$_4$ thin film annealed at 550 °C for 1 h.
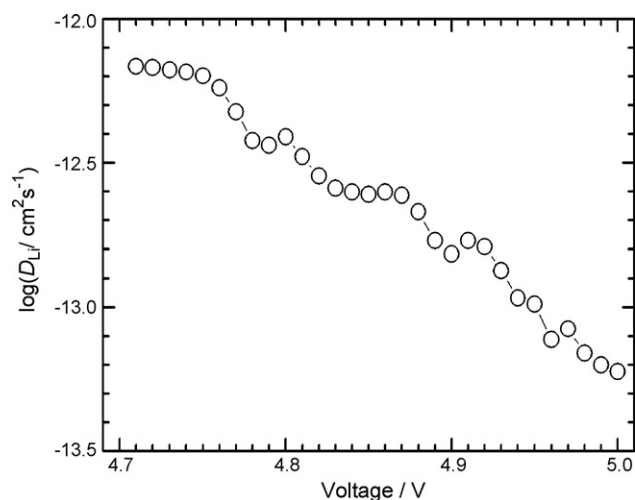
Fig. 6. Potential dependence of Li-ion chemical diffusion coefficients in the cycled LiCoPO$_4$ thin film by PITT.

at around 4.8 V is observed as indicated by the arrow. The small shoulder corresponds to the first charge plateau in Fig. 4(a). The asymmetry between the cathodic and anodic CV plots implies that the Li-ion diffusion in LiCoPO$_4$ thin film obeys a different mechanism between charge and discharge processes. In contrast, both the charge–discharge curves and the CV plots of the LiFePO$_4$ thin film show that the process of Li-ion extraction and re-insertion is reversible as shown in Fig. 5, even though the charge and discharge plateaus are not well developed due to the large interfacial resistance between LiFePO$_4$ and LATSP caused by annealing.

The Li-ion chemical diffusion coefficients, $\tilde{D}_{Li}$, in the LiCoPO$_4$ thin film are measured with the help of PITT [21] method, in order to clarify the different electrochemical behaviors between LiCoPO$_4$ and LiFePO$_4$. As shown in Figs. 4 and 5(a), the voltage exhibits a sloping profile with time rather than a flat plateau expected for the typical charge–discharge curves of LiFePO$_4$ and LiCoPO$_4$. Therefore, we measured the chemical diffusion coefficients at a wide potential region for both the films. Fig. 6 shows the $\tilde{D}_{Li}$ values as a function of the electrode potentials for the LiCoPO$_4$ thin films measured by PITT. For the LiCoPO$_4$ thin film cycled for three times between 3.5 and 5 V, the $\tilde{D}_{Li}$ value decreases monotonously from 7×10^{-13} cm^2 s^{-1} at 4.71 V to 6×10^{-14} cm^2 s^{-1} at 5 V. The

decrease of $\tilde{D}_{Li}$ value with the increasing electrode potentials means that the Li-ion diffusion is hindered by extracting Li-ion from LiCoPO$_4$, which can explain the relatively low capacity of LiCoPO$_4$. Theoretical calculation by first-principle method also showed that Li-ion diffusion coefficients in LiCoPO$_4$ is 4 orders higher than in "CoPO$_4$" [24].

Fig. 7 compares the $\tilde{D}_{Li}$ values vs. voltage curves between the cycled LiCoPO$_4$ and the cycled LiFePO$_4$ thin films. The $\tilde{D}_{Li}$ values of LiCoPO$_4$ decrease monotonously between 4.7 and 5.0 V even though they are higher than those of LiFePO$_4$. By contrast, the $\tilde{D}_{Li}$ values of the LiFePO$_4$ thin film show slight change with cell voltage in the voltage range 3.5–3.7 V. These chemical diffusion results suggest that the lithium extraction mechanism in LiCoPO$_4$ is different from that in LiFePO$_4$; that is, Li$_{1-x}$CoPO$_4$ has multiphases, contrasted to two phases of LiFePO$_4$ and FePO$_4$.

4. Conclusions

LiCoPO$_4$ thin films were deposited on the LATSP electrolyte. The films show a (1 1 1) preferred orientation upon annealing and are chemically stable with LATSP up to 600 °C. The chemical diffusion coefficients of LiCoPO$_4$ were determined by PITT and were compared with those of LiFePO$_4$ on the LATSP. The $\tilde{D}_{Li}$ value of cycled LiCoPO$_4$ decreases from 7×10^{-13} cm^2 s^{-1} at 4.71 V to 6×10^{-14} cm^2 s^{-1} at 5 V upon charging. On the other hand, the $\tilde{D}_{Li}$ value of LiFePO$_4$ showed no significant dependence on the cell voltage in the range 3.5–3.7 V vs. Li/Li$^+$. We could conclude that the Li-ion de-intercalation mechanism in LiCoPO$_4$ is different from that in LiFePO$_4$.

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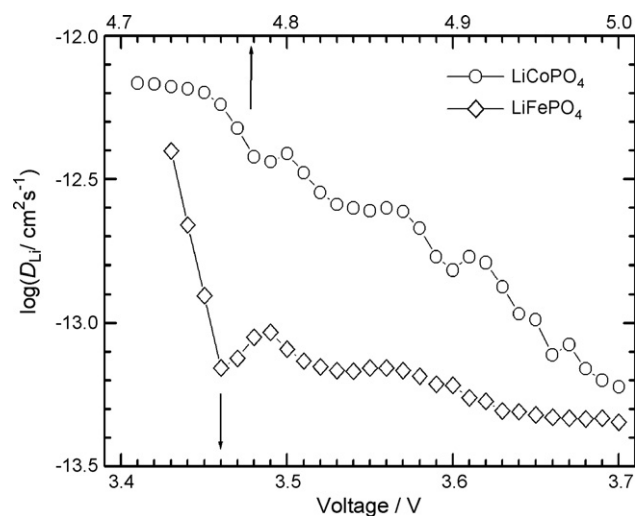[24] D. Morgan, A. Van der Ven, G. Ceder, Electrochem. Solid-State Lett. 7 (2004) A30.

Fig. 7. Comparison of Li-ion chemical diffusion coefficients in the cycled LiCoPO$_4$ and the cycled LiFePO$_4$ thin films by PITT.