

Crystalline $\text{Li}_3\text{PO}_4/\text{Li}_4\text{SiO}_4$ Solid Solutions As An Electrolyte For Film Batteries Using Sputtered Cathode Layers

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Abstract

Crystalline solid solutions of 1:1 $\text{Li}_3\text{PO}_4/\text{Li}_4\text{SiO}_4$ were synthesized and tested electrochemically using thin film, physical vapor deposited electrodes. After cathode deposition, the electrolyte/cathode structures were annealed at 700°C for 2 hours—a process that resulted in cathode crystallization without encouraging deleterious interfacial reactions. Results indicate that the electrolyte functioned well in this configuration. Test cells were taken through multiple charge/discharge cycles at different rates and temperatures and demonstrated a marked enhancement in performance parameters in comparison to previous reports. It is suggested that this material could function well in Li batteries fabricated using proper form factors.

Introduction

Promising results have been published in the literature several times since at least 1977 indicating that an inorganic solid-state crystalline compound consisting of a solid solution of Li_3PO_4 and Li_4SiO_4 could possibly serve as a functional lithium battery electrolyte.^{1,2} The result is of significant interest in part because most reported Li-ion conducting solid state materials are at least partially amorphous or glassy in nature. A fully crystalline, high-temperature annealed, electrolyte is appealing for solid state systems where a high-temperature process step is desirable for cathode improvement and electrode/electrolyte interfacial quality enhancement. Most recently, a “thick film” battery system was suggested, using a $500\ \mu\text{m}$ thick tape-cast, porous $\text{Li}_3\text{PO}_4/\text{Li}_4\text{SiO}_4$ electrolyte.¹ Results indicated that a 1:1 ratio of $\text{Li}_3\text{PO}_4:\text{Li}_4\text{SiO}_4$ had a conductivity of 2.8

$\times 10^{-6}$ S/cm at room temperature, with a significant increase at elevated temperatures. Though this value is much lower than that found for state-of-the-art liquid electrolytes, it is similar to that of glassy inorganic thin-film solid-state electrolytes such as LiPON, which is routinely used in the production of thin film batteries.³ A nominally conventional powder-based LiCoO₂ cathode and a Li foil anode were combined to create a working battery. Though these results served as an apt proof of concept, the attained capacities and discharge rate capabilities were extremely low: total capacities of less than about 8 μ Ah/cm² were obtained despite the fact that the cathode and anode masses were large enough to supply *at least* an order of magnitude more.

Concurrently, many studies on physical vapor deposited thin film electrodes, particularly cathode layers, have been performed. Typically, these films require a relatively high-temperature (> 500 °C) anneal step after deposition that serves to crystallize and orient the material for optimal performance. Our experiment, then, was to combine the LiSiPO solid state electrolyte (SSE) with vapor deposited electrode layers. In this study, a LiCoO₂ cathode was sputter-deposited directly onto a thin SSE plate. The cathode/SSE structure was then annealed to 700°C, and a Li anode film was evaporated onto the reverse side of the SSE to create a complete test cell. The results indicated a significant improvement in electrolyte and cell performance compared to those cells that used traditional cathode and anode configurations with a similar SSE material.

Experimental

The LiSiPO SSE material was created by mixing stoichiometric amounts of Li₃PO₄, Li₂CO₃, and SiO₂ to provide a 50/50 atomic % LiPO₄/Li₄SiO₄ compound. The powders were ball milled for 30 minutes in an Ar filled glove box, followed by cold pressing (1% PVDF in cyclopentanone binder solution used to keep the material cohesive before annealing) at approximately 25,000 psi, and calcinating at 1100°C for 2 hours in air. The resulting pieces were 100 to 500 μ m thick and 1 cm in diameter. Half cell test structures

were fabricated by sputter-depositing a Pt blocking electrode on one side of the electrolyte chip and thermally evaporating a thin film of Li on the anode side. Full test cells were fabricated by sputter-depositing a 100-nm -thick LiCoO_2 layer and 200 nm thick Pt current collector onto the SSE. The entire structure was annealed for 2 hours at 700 °C before anode deposition. The materials were characterized using x-ray diffraction, scanning electron microscopy, impedance spectroscopy, and cyclic voltammetry. Details of the deposition chamber, film deposition techniques, and analysis techniques commonly used in our labs are published elsewhere.⁴

Results and Discussion

Figure 1 shows a diffraction pattern collected from the LiSiPO SSE material. The diffraction pattern is consistent with that expected from an orthorhombic phase, as has been reported previously, though a second phase also appears to be present.² A refinement on the pattern yields the following lattice parameters: $a = 5.0067 \text{ \AA}$, $b = 5.25496 \text{ \AA}$, $c = 6.12569 \text{ \AA}$, and $\beta = 90.508^\circ$. These values are similar to those published for a monoclinic solid solution with a Li_3PO_4 mole fraction of 0.4 to 0.5.² There are several weak peaks that may be caused by a yet unknown second phase. The inset in figure 1 shows a limited 2θ range plotted to depict more clearly both the accuracy of the fit as well as scattering from a possible second phase.

The results of the AC impedance analyses are shown in figure 2. The conductivity of the material ranged from $8 \times 10^{-5} \text{ S/cm}$ at 19°C to 0.009 S/cm at 95°C, corresponding to a Li diffusion activation energy of 0.51 eV. This value is nominally lower than the 0.54 eV reported from a similar LiSiPO electrolyte materials fabricated elsewhere.¹ Even with the improvement reported here, however, this electrolyte would need to be no thicker than 10 μm if it were to be used in a practical battery system.

Figure 3 shows cross-section SEM images of the $\text{Au/LiCoO}_2/\text{LiSiPO}$ interfacial areas after annealing at 700°C. The micrograph in Figure 3(a) shows that the sputtered current collector and cathode layers are fully conformal to the relatively rough surface of

the LiSiPO chip. The higher magnification image in figure 3(b) indicates that there is a clean interface between the LiCoO₂ and the LiSiPO. It is also evident in these images that the LiSiPO is not fully dense, having small dispersed pores instead. Such a microstructure should not be conducive to facile ion diffusion through the bulk crystal material, and so it is likely that a fully dense LiSiPO sample would conduct Li ions through its thickness more easily.

Typical discharge data at different temperatures and rates are given in figure 4. The capacity of the cell was found to be nearly double the room temperature value at 80°C. The discharge curves were consistent with those typically reported from sputtered/annealed crystalline LiCoO₂ layers, with several minor discharge plateaus between 3.5 and 4.0 V consistent with those observed for this material elsewhere. The charge/discharge rate was 3 μA/cm² and was approximately a C/2 rate for this cell. The total capacity realized at 80°C was 45 μAh/cm²μm (where the μm indicates cathode layer thickness), or 65% of the maximum capacity observed in optimized thin film LiCoO₂ cathode solid-state cells. Though the cell was rate limited due to low electrolyte conductivity, the performance is remarkable considering the fact that the SSE was hundreds of microns thick. The cycle life of similar cells as cycled at both room temperature and 80°C is shown in figure 5. This degree of capacity loss is not unusual for solid-state batteries cycled at elevated temperatures and is commonly associated with degradation of the cathode layer.⁵

The above results indicate that the electrochemical properties of a test cell using a fully crystalline SSE were enhanced when thin-film electrodes were conformally deposited onto the bulk, pressed electrolyte. Annealing the electrode/electrolyte composite served to crystallize the cathode layer, as evidenced by the defined discharge plateaus associated with fully crystalline electrode material. The effects of the anneal step on the cathode/electrolyte interface are not known, and are under examination. In the previous study cited, the electrolyte was tape cast from a LiSiPO slurry, resulting in

relatively porous, discontinuous material. Though this morphology is appealing in principle, the reality of using powder-based cathode materials is likely to cause interfacial issues. Further, bulk transport of Li ions through a crystalline material is likely to be impeded when manifested in a highly porous microstructure.

Conclusions

These results show that batteries using sputtered thin film cathodes and a bulk solid-state electrolyte consisting of a crystalline solution of Li_3PO_4 and Li_4SiO_4 can perform similarly to cells using alternative glassy electrolytes such as LiPON. The fact that much of the practical LiCoO_2 cathode capacity was realized when using a solid state electrolyte hundreds of microns thick indicates that the electrolyte material, if created in the proper form factor (i.e. very thin), could function well in a practical setting. The SSE was stable in the presence of Li and also showed no evidence of reacting with a Li-based cathode even when a composite electrolyte/electrode sample was annealed to 700°C . For this reason, further investigation of the $\text{Li}_3\text{PO}_4/\text{Li}_4\text{SiO}_4$ SSE material is warranted.

References

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Figure Captions:

Figure 1: X-ray diffraction from a 50/50 $\text{Li}_3\text{PO}_4/\text{Li}_4\text{SiO}_4$ annealed pressed powder sample. Fitting to an orthorhombic unit cell yielded the indicated lattice parameters. The predicted lines based on this refinement are drawn the inset plot graphs.

Figure 2: Impedance spectroscopy results taken from a Pt/SSE/Li half-cell test structure. Data analysis shows that the Li-diffusion activation energy is 0.51 eV.

Figure 3: Scanning electron micrographs of the SSE/ LiCoO_2 /Au interfacial areas. (a) The sputtered and annealed cathode layer was nominally conformal to the surface of the SSE. (b) Shows a close up of the interfacial area, circled is an area where a clean electrode/electrolyte interface is visible.

Figure 4: Discharge data from a cell taken at 25 and 80 °C. Approximately 65% of the expected cathode capacity is delivered at 80°C. The inset graph shows a rate study, where significant capacities are present even at a discharge rate of 0.1 mA. Cell area was 0.25 cm².

Figure 5: Cell cycle life at 80°C and room temperature. There was a much more pronounced fade at 80°C, a result consistent with other solid state systems using a sputtered, crystalline LiCoO_2 cathode film.

Figures

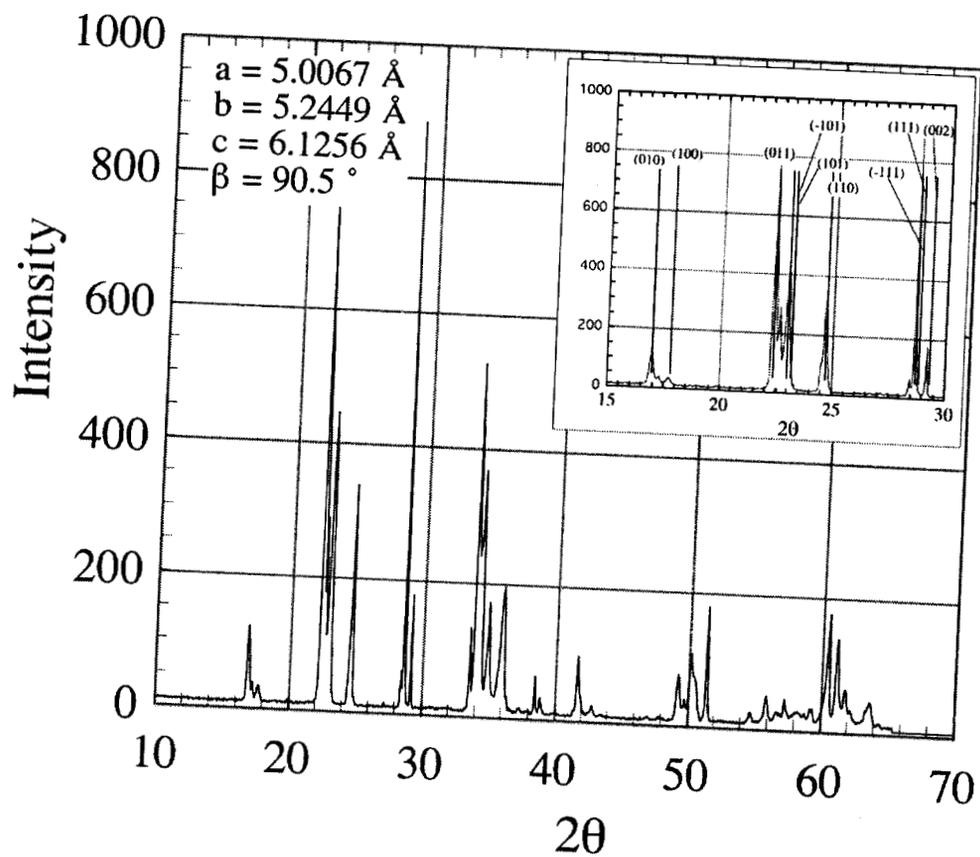


Figure 1

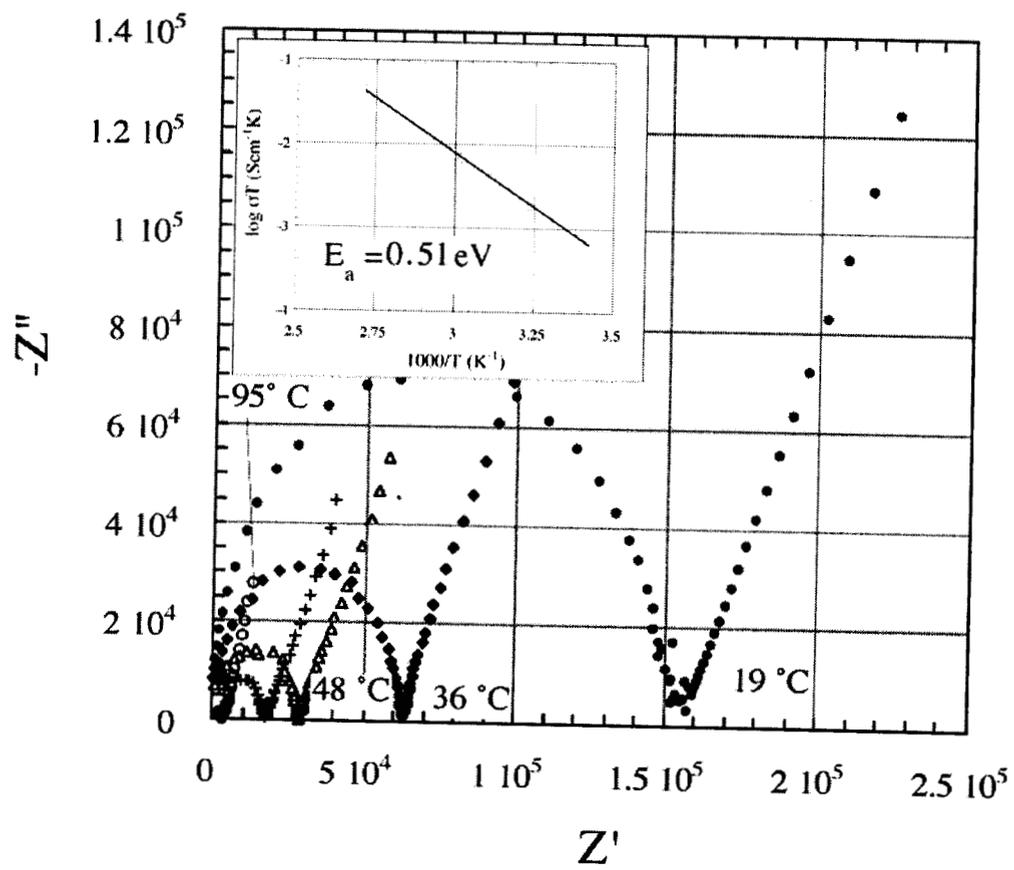


Figure 2

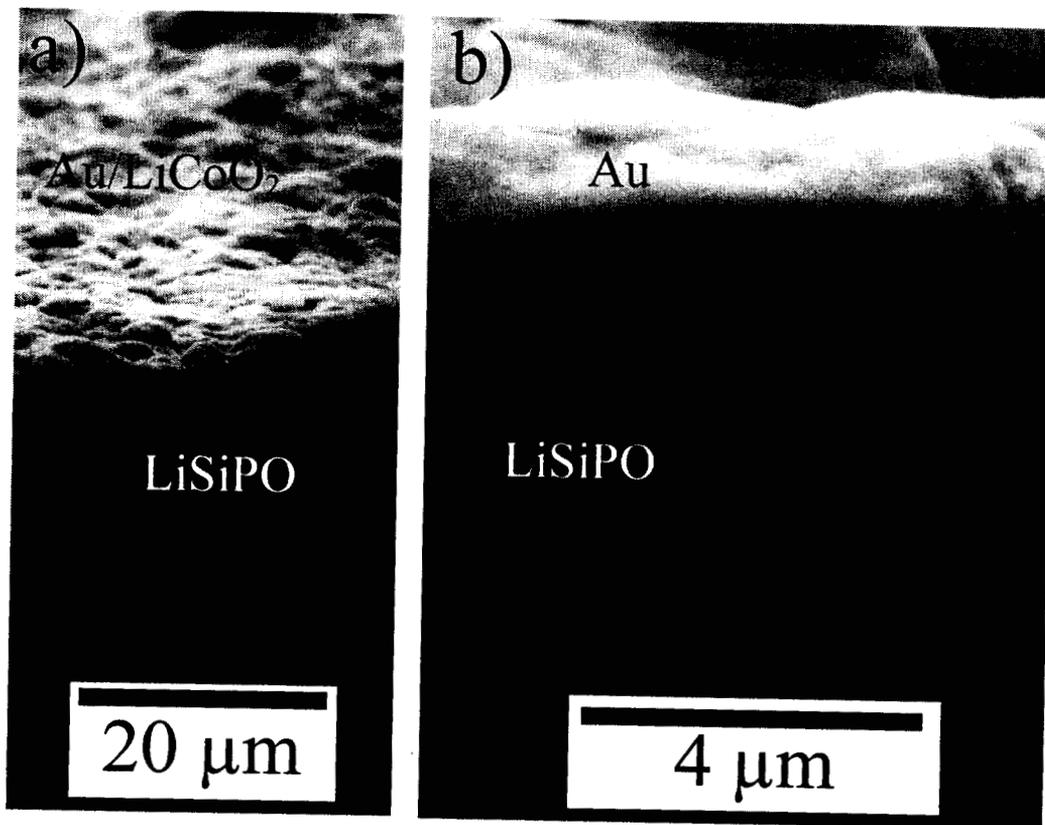


Figure 3

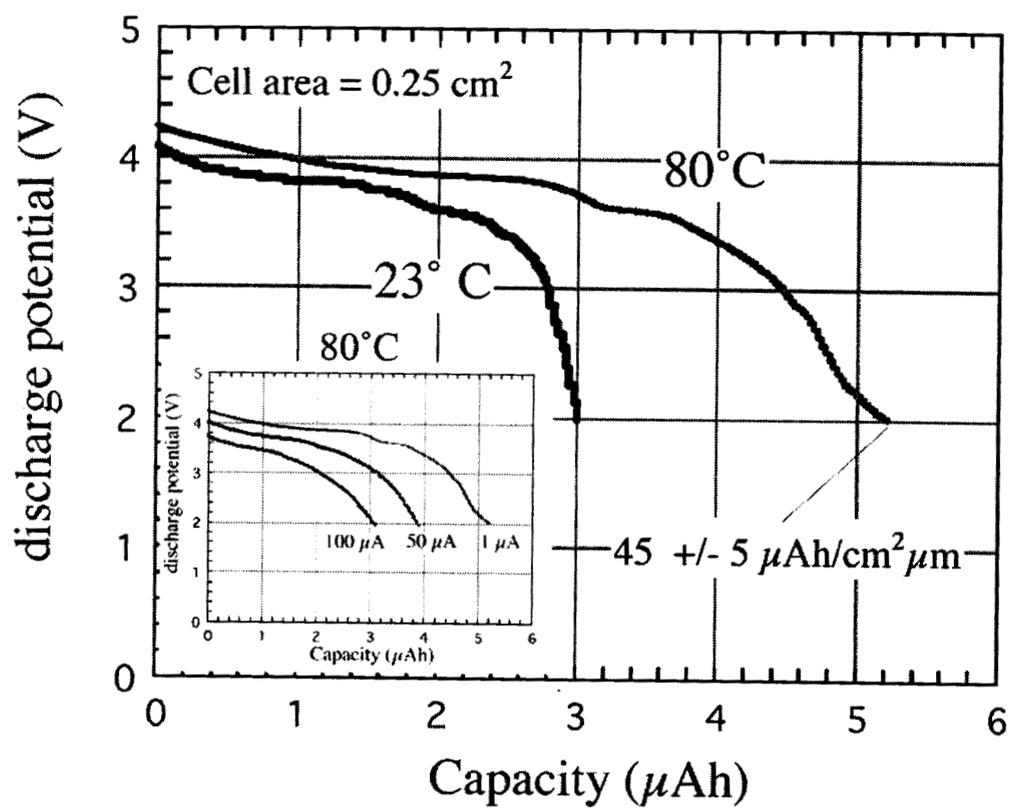


Figure 4

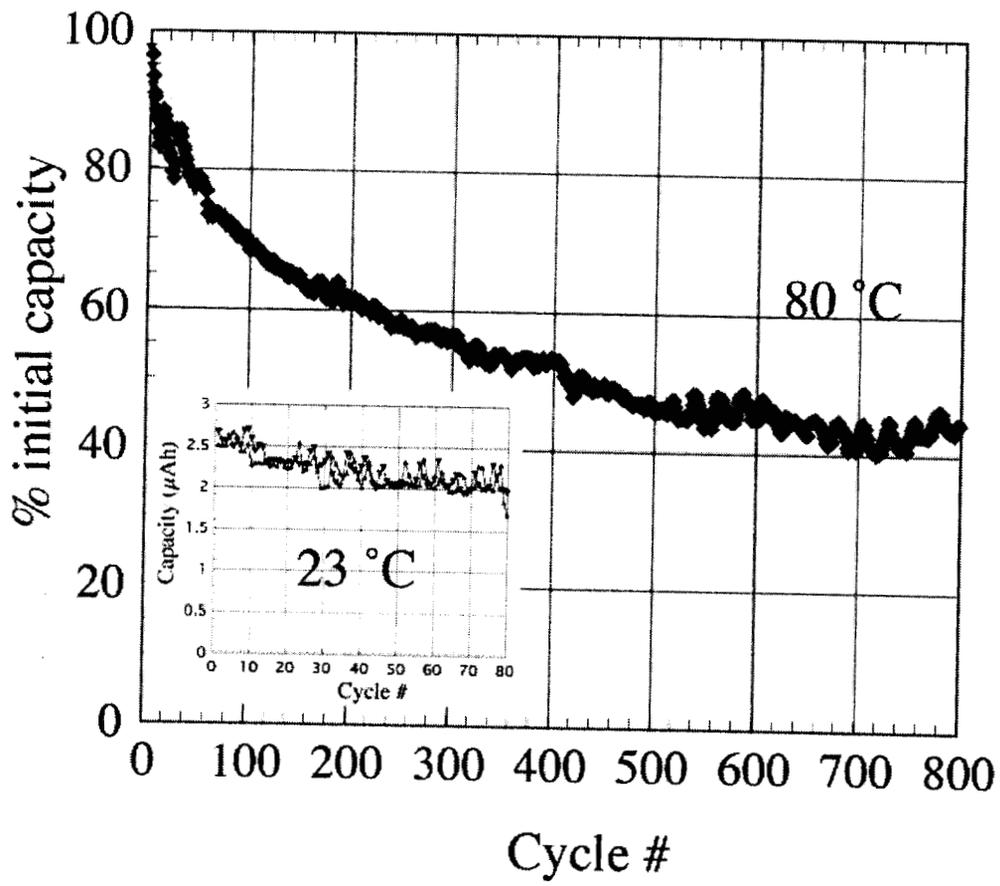


Figure 5