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Li₄SiO₄-Li₃PO₄ solid solutions as ceramic electrolytes in Li metal cells

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Batteries based on lithium metal have the highest theoretical energy densities of all known technologies.¹ However, their application is plagued with issues associated with the cycling of the Li electrode, such as dendrite formation and high reactivity with other cell components. The use of protective layers in the solid state that conduct ions but are electronically insulating has been proposed as a possible solution.² Consequently, several phases are being investigated for this purpose.³ It is preferable to work with phases that do not contain redox active transition metals, which can form electronically conductive products upon reduction by lithium. For this reason, we have selected the Li₄SiO₄-Li₃PO₄ system for further study.

This system can form two different solid solution structures over the full composition range. Both structures are reported to be more ionically conductive than Li₄SiO₄ or Li₃PO₄.⁴ As reported, solid solutions with 50-60 mol% Li₃PO₄ have the highest conductivities in the Li-Si-P-O system, with a value of $\sim 4 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$, and the lowest activation energies (0.51 and 0.52 eV respectively).⁵ Borate-based phases are commonly used as sintering agents, with some formulations such as 42.5Li₂O:57.5 B₂O₃ (mol%) (LB) reported to have good ionic conductivity as well.⁶ For this work, we systematically evaluated the changes in conductivity as a function of composition, sintering temperature, and addition of the LB sintering agent on the Li₄SiO₄-Li₃PO₄ system for potential application as a ceramic protective layer in Li metal batteries.

Li₄SiO₄-Li₃PO₄ solid solutions were prepared by solid state reaction. X-ray diffraction (XRD) was used to characterize the phases. Die-pressed pellets from different compositions containing 40, 50 and 60 mol% Li₃PO₄ (40LP, 50LP and 60LP) and 60LP with the addition of 0.2, 0.5, 1, 2 and 5 wt% LB were sintered at different temperatures (700-1000°C) and their morphologies, conductivities and activation energies were analyzed. The conductivities of 40LP, 50LP and 60LP (porosity < 10%) are within the same order of magnitude ($10^{-6} \Omega^{-1} \text{cm}^{-1}$) at room temperature. For example, 60LP pellets sintered at 900°C showed the highest conductivity with $4.5 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and an activation energy of 0.49 eV. The addition of 0.2 and 0.5 wt% LB into 60LP decreases the sintering temperature significantly (see Fig. 1) without any deterioration in ionic conductivity or activation energy. The sintering range gets narrower with increasing lithium borate.

The electrochemical stability of the prepared phases against lithium was studied in Li-Li symmetric cells with well-sintered pellets from 60LP and 60LP with 0.5wt%LB as electrolyte. The symmetric cell was heated at 90°C for 4 hours to improve the interfacial contact between lithium and solid electrolyte. After heating, the contact resistance remained stable. Both Li-Si-P-O and Li-Si-P-B-O solid electrolytes were found to have a stable

voltage profile during cycling, with no deleterious reactions observed.

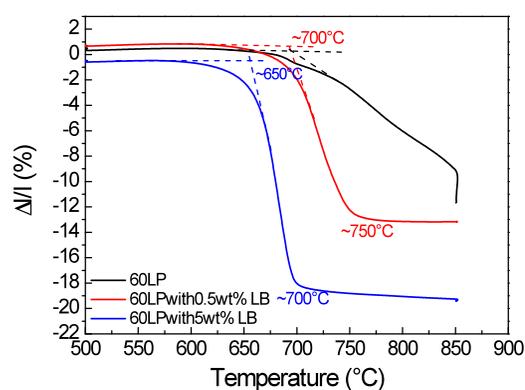


Fig. 1 Sintering curves collected for pellets of 60LP with different amounts of LB.

Additional insight on the electrochemical stability of the phases was obtained from Li/liquid electrolyte/60LP cells. The dQ/dV plots in Fig. 2 show that no redox reaction occurs on the phospho-silicate between 0.0 and 3.0 V, with the activity observed due exclusively to the presence of 30% of a carbon black conductive additive.

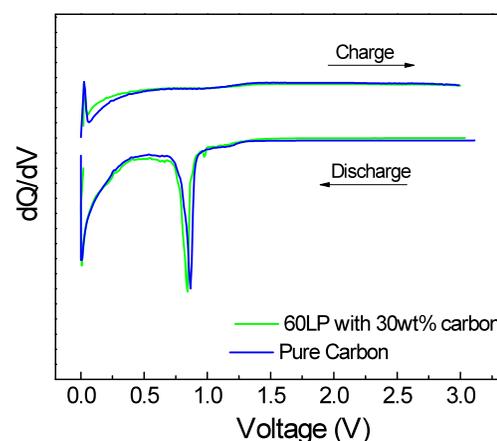


Fig. 2 dQ/dV plots collected from the cell with pure carbon and 60LP with 30 wt% carbon as cathode and lithium as anode.

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