Li_4SiO_4-Li_3PO_4 system as protective layer in Li-metal batteries

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The application of Li-metal batteries 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.[1] 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 Li_4SiO_4-Li_3PO_4 system for further study.

Li_4SiO_4-Li_3PO_4 system can form two different solid solution structures over the full composition range. Both structures are reported to be more ionically conductive than Li_4SiO_4 or Li_3PO_4.[2] Borate-based phases are commonly used as sintering agents, with some formulations such as $42.5Li_2O{\cdot}57.5\ B_2O_3$ (mol%) (LB) reported to have good ionic conductivity.[3]

Li_4SiO_4-Li_3PO_4 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% Li_3PO_4 (40LP,50LP and 60LP) and 60LP with the addition of various amount of LB were sintered at different temperatures (700-1000°C) and their morphologies, conductivities and activation energies were analyzed. 60LP pellets sintered at 900°C showed the highest conductivity with $4.5x10^{-6}\ \Omega^{-1}cm^{-1}$ and an activation energy of 0.49 eV. The addition of 0.5 wt% LB into 60LP decreases the sintering temperature significantly without any deterioration in ionic conductivity or activation energy.

Various methods such as sol-gel and radio frequency sputtering were used to deposit thin films with the compositions such as 60LP with 0.5wt% LB onto Al_2O_3 substrates. Heat-treatment was carried out in order to get dense or crystalline films. The films have been characterized by XRD, scanning electronic microscope (SEM)/energy dispersive X-ray Spectroscopy (EDS). The amorphous and crystalline thin films were compared in terms of morphology and conductivity.

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. Additional confirmative insight on the electrochemical stability of the phases was obtained from Li/liquid electrolyte/60LP cells.

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