Solid-state lithium batteries using thio-LISICON solid-state electrolytes

Christopher P. Rhodes,* Yongzhu Fu, Matthew Mullings, Kyle Uselton and Jenifer Cross

Lynntech, Inc. 7610 Eastmark Dr., College Station, TX 77840

*chris.rhodes@lynntech.com, 979-693-0017

Rechargeable lithium batteries with higher energy densities and improved safety/abuse tolerance are needed for numerous applications including electric vehicles, consumer electronics, and military devices. The energy densities of current lithium-ion batteries are limited by the relatively low capacities of current anodes and cathodes. In addition, current lithium-ion batteries utilize flammable organic solvent-based electrolytes which result in safety hazards, particularly during abuse/overcharge conditions.

Solid-state lithium batteries which utilize a solid-state electrolyte rather than a liquid electrolyte can potentially provide higher energy density cells and eliminate safety issues (e.g. explosions, fires, leaking) of current Li-ion batteries. Current thin-film solid-state lithium batteries based on Lithium Phosphorous Oxynitride (LIPON) electrolytes have shown reasonable cycle life (cells containing metallic Li have been cycled ≥1000 times),[1] however LIPON has a low ionic conductivity (~10^{-6} S/cm at 25 ºC). The low ionic conductivity of the electrolyte limits performance particularly at low temperatures and necessitates that the electrolyte be very thin for reasonable performance. In addition, thin-film solid-state batteries have limited capacities based on the limitations of the thickness of the electrodes within the thin-film design. To achieve higher energy and power density solid-state batteries, advanced solid-state electrolytes (e.g. high ionic conductivity, extremely low electronic conductivity, and chemical/electrochemical stability) and advanced solid-state composite electrodes (e.g. low resistance, high capacity) are needed.

Solid inorganic lithium-ion conductors based on thio-LISICON (LIthium SuperIonic CONductor) have shown among the highest reported ionic conductivities (>10^{-3} S/cm at 25 ºC)[2, 3] of any solid-state inorganic lithium-ion conductors.[4] Thio-LISICON materials, generally described by the formula, $Li_xM_{1-y}M'_yS_4$ (M = Si, Ge, and M′= P, Al, Zn, Ga, Sb) have been synthesized with various compositions using both high temperature and low temperature, planetary ball milling routes.[2, 3] The low temperature planetary ball milling process yields thio-LISICON materials which show high ionic conductivities (3.2 x 10^{-3} S/cm at room temperature)[3] and wide electrochemical stability windows (up to 10 V vs Li).[5]

To provide highly conductive solid electrolytes, thio-LISICON materials with various compositions were synthesized using a low temperature, planetary ball milling and subsequent heating step. Characterization of the material was performed to determine structure and ionic conductivity. The solid material showed high ionic conductivities of > 10^{-3} S/cm at 25 ºC. Using this solid-state electrolyte, multiple solid-state batteries were fabricated using Li metal anodes and various cathodes with different compositions. Initial work showed that the composition of the composite electrode plays a critical role in the battery performance, as supported by previous studies.[6] The solid-state batteries were successfully cycled. Additional work is currently underway to optimize battery fabrication and performance using the highly conductive solid electrolytes.

References

1. Neudecker, B. J.; Dudney, N. J.; Bates, J. B., *J. Electrochem. Soc.* **2000,** 147, (2), 517-523.
2. Kanno, R.; Maruyama, M., *J. Electrochem. Soc.* **2001,** 148, (7), A742-A746.
3. Mizuno, F.; Hayashi, A.; Tadanaga, K.; Tatsumisago, M., *Adv. Mater.* **2005,** 17, (7), 918-921.
4. Knauth, P., *Solid State Ionics* **2009,** 180, 911-916.
5. Minami, K.; Hayashi, A.; Tatsumisago, M., *Solid State Ionics* **2008,** 179, 1282–1285.
6. Mizuno, F.; Hayashi, A.; Tadanaga, K.; Tatsumisago, M., *J. Electrochem. Soc.* **2005,** 152, (8), A1499-A1503.