Effect of aluminium doping on the ionic conductivity of Li_2S-GeS-P_2S_5 solid electrolyte system

S. Amaresh, Kwang Jin Kim, Min Chul Kim, P. Sennu, Shin Ho Kim and Yun Sung Lee*

Faculty of Applied Chemical Engineering, Chonnam National University, Gwangju – 500 757, South Korea
*E-mail: leeys@chonnam.ac.kr

Organic electrolyte used in lithium ion batteries is stable up to certain voltage limit (4.5V). The battery operation has been hindered because of the decomposition of organic electrolyte and the reaction products thereof. Various solid electrolytes like NASICON, Garnet type have been developed for lithium ion conduction to overcome the safety issues namely leakage and inflammability. The major requirements of solid electrolytes are to provide high lithium ionic conductivity, allow lithium mobility between electrode-electrolyte interface and negligible electronic conductivity, not to mention the chemical stability at anodic and cathodic environments. [1] All solid state batteries having less weight, high energy density and flexibility can be developed based on utilization of solid electrolyte for lithium ion conduction. Commercialization of solid state batteries can be achieved when the solid electrolytes reach equivalent conductivity values of liquid electrolytes. The sulfur based lithium ionic conductors present in Li-Ge-P-S system have shown remarkable ionic conductivity. The sulfide crystalline lithium superionic conductor, thio-LISICON, such as solid solutions in the system Li_4GeS_4–Li_3PS_4, exhibits high ambient temperature conductivities over 10^{-3} Scm^{-1}. [2, 3] Recently, $Li_{10}GeP_2S_{12}$ solid electrolyte has shown very high ionic conductivity of 10^{-2} S cm^{-1} at room temperature. [3]

In this work, we developed thio-LISICON analogue based on a similar Li_2S-GeS-P_2S_5 system and the effect of aluminium doping have been evaluated. An attempt to develop aluminium based thio-LISICON system was also made, which can maintain the high lithium ionic conductivity and also reduces the cost of solid electrolytes. A symmetric coin cell assembly using lithium as non-blocking electrodes were used for ionic conductivity measurements. The obtained powders showed excellent ionic conductivity at room temperature. The stability of the solid electrolyte against metallic lithium as counter and reference electrode with stainless steel acting as working electrode shows that the thio-LISICON analog produced was stable up to 5V without any noticeable peaks for any side reaction. The stability of solid electrolyte has been tested in various organic solvents like ethylene carbonate, di-ethyl carbonate, di-methyl carbonate, etc for checking the feasibility of developing solid state battery. The conversion of metastable precursor to thermodynamically stable crystalline solids during increased temperature treatment can be responsible for such high ionic conductivity. These solid electrolytes can be applied to a solid state lithium rechargeable battery for developing a highly safe energy storage system. The obtained results will be presented in detail.

References:

1) C. Julien, G.-A. Nazri, in: Solid State Batteries: Materials Design and Optimization, Kluwer Academic Publishers, Dordrecht, 1994, p. 579.
2) R. Kanno, M. Murayama, *J. Electrochem. Soc.* 148 (2001) A742.
3) N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* 10 (2011) 682.