



Comparison of Li^+ and Na^+ alkali-cations on the ionic transport properties of solid-polymer electrolytes intended for secondary batteries

D.H.K.T. Dassanayake, J.H.T.B. Jayamaha, V. Jathushan and K. Vignarooban*
Department of Physics, Faculty of Science, University of Jaffna, Jaffna 40000, Sri Lanka
* vigna@univ.jfn.ac.lk

Abstract

Battery chemistries beyond lithium-ion such as sodium-ion batteries (SIBs) are becoming popular these days due to the limited availability and high cost of lithium raw materials. Designing suitable electrolytes is of critical importance for the development of SIBs. $\text{PEO}_{10}\text{LiClO}_4$ is a very commonly used solid-polymer electrolyte (SPE) in secondary lithium-ion batteries. It is quite generally accepted that replacing LiClO_4 with NaClO_4 in a SPE will reduce the ambient temperature ionic conductivity, essentially due to the larger size of Na^+ compared to that of Li^+ . In this work, two SPEs $\text{PEO}_{10}\text{LiClO}_4$ and $\text{PEO}_{10}\text{NaClO}_4$, which are Li^+ and Na^+ conducting respectively, were synthesized by using standard solvent-casting method employing acetonitrile (CH_3CN) as the solvent and characterized by using experimental techniques such as EIS, CV, LSV and DC polarization to quantitatively compare the effect of alkali-cations (Li^+ and Na^+) on the electrochemical properties of these SPEs. Both SPEs showed similar electrochemical properties except the ionic conductivity and the activation energy values. Li^+ and Na^+ ion conducting SPEs showed an ambient temperature ionic conductivity in the order of 10^{-4} and 10^{-5} S cm^{-1} , respectively, whereas the electrochemical stability window obtained from the LSV and CV studies remained almost equal (3 V) for both types of SPEs. DC polarization tests on SS/SPE/SS configuration showed that both SPEs are dominantly ionic conductors with almost equal ionic transference numbers ($t_{\text{ion}} \sim 0.99$) and negligible electronic conductivity. Ionic conductivity vs inverse temperature followed Arrhenius behavior with activation energies of 0.48 and 0.62 eV (at $T < T_m$) respectively for Li^+ and Na^+ conducting SPEs. Higher activation energy of Na^+ conducting SPE agrees well with its lower conductivity in comparison to its Li^+ counterpart.

Keywords: Lithium-ion batteries; Sodium-ion batteries; Solid-polymer electrolytes; Electrochemical impedance spectroscopy; Ionic conductivity

Acknowledgement: This research was supported by the Accelerating Higher Education Expansion and Development (AHEAD) operation of the Ministry of Higher Education funded by the World Bank (DOR Project # 62).