

Free Volume Characteristics and Ionic Conductivity in PEO-Based Solid Polymer Electrolytes: a Positron Annihilation Spectroscopy Study

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With the global surge in energy demand in power electronics and portable battery technology during recent years, Li-ion batteries are at the forefront of research in terms of battery chemistry, electrode materials, electrolyte, separator, and compatibility among different components [1]. Device miniaturization, weight reduction and enhanced safety can be accomplished by consolidated function of electrolyte and separator in these batteries using Solid Polymer Electrolyte (SPE) [1-2]. Although SPE is regarded as a critically safer substitute to the contemporary organic liquid electrolytes in next generation power devices, the practical incorporation has been impeded by its limited room temperature ionic conductivity [2]. To circumvent the issue, comprehensive investigation of the underlying mechanism at molecular level is important in order to design solid polymer electrolyte meeting industry standards and requirements. However, a common consensus among researchers has not been reached yet regarding the factors governing enhanced ionic conductivity in SPE. Poly(ethylene oxide), PEO, added with Li⁺ ion source is a highly felicitous and most widely studied semicrystalline polymer as SPE in Li ion batteries [3-4]. Apart from most prevalent view of ionic conductivity being greatly influenced by amorphous fraction in semicrystalline polymer [1], many studies suggest that segmental dynamics and free volume assisted migration of ion (inter and intra-chain hopping) takes place in PEO based polymer electrolytes [4]. Positron Annihilation Spectroscopy (PAS) is an established technique to investigate free volume characteristics and distributions through its annihilation parameters in SPE [4]. Segmental dynamics of polymer can be characterized by complementary Broadband Dielectric Spectroscopy (BDS) technique. During recent years, we have been actively engaged in studies on PEO based SPEs focusing on discerning the exclusive role of incorporating passive fillers (viz. silica, alumina) and Lithium salt (viz. LiTFSI) on free volume characteristics using PAS techniques [4-6]. Recently, we have investigated evolved microstructural modification in complex ternary PEO-silica-LiTFSI SPE using PAS and complementary techniques [7]. Interplay between segmental dynamics, free volume and semicrystalline morphology governs conductivity in these SPEs. Passive nano size fillers, by virtue of interfacial interaction and nanoconfinement effect, alters the semicrystalline morphology and free volume structure of PEO electrolytes. The role of interfacial interaction in the enhancement of ionic conductivity via an alternate ion conduction pathway along the interface is also evident from our study on alumina nanorod laden SPEs [8].

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