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Ionic liquid dispersed Li^+ ion oxide glasses and glass-ceramics: Assessment of electrical transport and thermal stability

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ABSTRACT

Effect of ionic liquid (BMIM BF_4) dispersion on Li^+ ion oxide glass and glass-ceramics has been investigated. Addition of ionic liquid in a very small amount (0.5–5 wt.%) enhances the ionic conductivity significantly. For a typical glass composition $60Li_2SO_4$-$40(0.5Li_2O$–$0.5P_2O_5)$, with grain size of ~50 nm, dispersion of ~5 wt.% ionic liquid leads to a conductivity rise of ~2–4 orders of magnitude. Structure of ionic liquid dispersed glass and glass-ceramic composites has been investigated by X-ray diffraction and FE-SEM, and thermal properties by DSC. It has been revealed by a galvanic cell method, impedance spectroscopy and dc polarization technique that these composites are essentially ionic in nature. Based on these investigations, a model for electrical transport has been proposed according to which Li^+ ions are the majority charge carriers in these composites. The model suggests that ionic liquid acts like a filler between the glass/glass-ceramic grains and Li^+ ions mainly migrate through these channels. These composites appear promising for Li^+ ion battery applications.

1. Introduction

Li^+ ion oxide glasses and glass-ceramics have been thoroughly investigated in last three decades due to their thermal stability, highly amorphous framework, predominant Li^+ ion conductivity and potential candidature for low dimensional as well as high temperature device applications [1–4]. However, poor ionic conductivity of these amorphous systems at room temperature is a major hurdle for their direct use in Li^+ ion battery applications [1–7]. There have been several attempts in order to enhance the ionic conductivity of glasses and their glass-ceramics. Some interesting fast ionic glass-ceramics in oxide systems have also been developed by precipitation of Li^+ ion NASICON crystallites (e.g., $LiTi_2(PO_4)_3$) during glass-ceramic formation [7–10]. Nevertheless, in spite of high ionic conductivity, application of these glass-ceramics to devices is still a challenge mainly due to constraints related to size and content of these crystallites in the glass matrix [7–10].

Recently, it has been demonstrated [11–14] that ionic liquid addition to a glassy ionic system increases the conductivity notably. The mechanism of such an anomalous rise in the conductivity is however under exploration. Nevertheless, application of novel materials like ionic liquid is promising in the field of solid state ionics. Ionic liquid is an organic salt normally exists in molten state, at/near room temperature and consists of organic cations and anions. It reveals interesting properties such as high thermal stability, good mechanical properties, negligible volatility and, especially, relatively high ionic conductivity in its liquid state [15,16,37]. Ionic liquids have also been used as a liquid electrolyte for lithium batteries previously [17–20].

Interestingly, ionic liquids, viz. [BMIM][BF_4], [EMI][BF_4], BmImCl etc. have also been used to enhance the ionic conductivity of solid polymer electrolytes [21–34]. For example, Liew et al. [26] added 1-butyl-3-methylimidazolium chloride (BmImCl) in a polymer PVdF–HFP–$LiClO_4$ and found highest conductivity of $\sim 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at room temperature with 80% content of BmImCl [26]. Further, Hashmi et al. [28–30] studied a series of ion conducting solid polymer electrolytes dispersed with ionic liquid which exhibited a room temperature conductivity $\sim 10^{-4}\ \Omega^{-1}\ cm^{-1}$. It is suggested that ionic liquid in polymers acts like a plasticizer that decreases the crystallinity of the polymer matrix [28–30]. In another interesting work, An et al. [31] successfully prepared functional ionic liquid-polymer electrolytes with ionic conductivity $\sim 10^{-4}\ \Omega^{-1}\ cm^{-1}$. The electrochemical cells prepared with these electrolytes exhibited higher reversible capacity and long cycle life. A mixed ionic liquid-organic electrolyte has also been investigated by Guerfi et al. [32] and found improved safety and electrochemical performance of Li-ion battery. Likewise, Jin et al. [33], adding ionic liquid, synthesized a novel gel polymer electrolyte that exhibited good thermal stability, high anodic oxidation potential and good interfacial stability with lithium electrode. The cyclic performance of the battery fabricated using this electrolyte was also found to be improved.

Recently ionic liquid-composite solid ionic systems have also been synthesized. For example, it was demonstrated that when ionic liquid

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[BMIM][BF_4] is added into a composite SiO_2–LiTf, conductivity shows a notable rise and exhibits a maximum value of ~0.5×10^{-2} Ω^{-1} cm^{-1} at room temperature [34].

Synthesis of composites of ionic liquid with ionic glasses has also been attempted recently. Hayashi et al. [11] in a novel approach found that ionic liquid [EMI][BF_4] can dissolve the Li^+ ion conducting sulfide glasses and a composition $70EMIBF_4$–$30Li_{1.4}P_{0.6}S_{2.2}$ that exists in liquid state found to be exhibiting an ionic conductivity ~10^{-3} Ω^{-1} cm^{-1} at room temperature. Hayashi et al. [12] also synthesized solid composites by dispersion of ionic liquid in ionic glasses. Addition of 10 mol% of [EMI][BF_4] ionic liquid into $50Li_2SO_4$–$50Li_3BO_3$ oxide glassy matrix leads to significant enhancement in ionic conductivity and influences the glass transition temperature. A maximum conductivity value of ~10^{-4} Ω^{-1} cm^{-1} is obtained at room temperature which is three orders of magnitude higher than that of the pristine glass. In another investigation, Dabas et al. [13] studied the effect of ionic liquid in Li^+ ion conducting glasses and obtained a conductivity of ~10^{-5} Ω^{-1} cm^{-1} for the composition 1[EMI][BF_4]-99($0.5Li_2O$–$0.45P_2O_5$–$0.05Nb_2O_5$). It has been also reported in one of our recent study that addition of ionic liquid [BMIM][PF_6] in $60Li_2SO_4$-40($0.5Li_2O$–$0.5P_2O_5$) glassy matrix leads to significant enhancement in the conductivity [14]. For a composition with 5 wt.% of IL, predominant ionic conductivity of ~10^{-5} Ω^{-1} cm^{-1} was reported at room temperature [14]. Ionic liquids were also dispersed in some novel ceramic systems to improve ionic transport. Recently, $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$ (BCN18) treated with ionic liquid (BMIM BF_4) reveals bulk conductivity ~10^{-5} Ω^{-1} cm^{-1} at 23 °C which is ~7 orders of magnitude higher than that of BCN18. Ionic liquid found to decrease the grain-boundary impedance of solid electrolytes. BCN18-ionic liquid composite shows a mass loss at 280–400 °C [35].

It is apparent from above studies that ionic liquid addition in polymers, gels and glasses influences the electrical transport very significantly. Present work was undertaken essentially (i) to systematically characterize the ionic liquid dispersed glasses and glass-ceramics and (ii) to understand the mechanism behind the high ionic conductivity in these novel composites.

2. Experimental

Glassy samples of the composition $60Li_2SO_4$-40($0.5Li_2O$–$0.5P_2O_5$) (abbreviated as 60LSLP) were prepared by conventional melt quenching as described elsewhere [36]. Glass-ceramics were prepared by annealing glassy sample well above the crystallization temperature for 5 h and subsequent furnace cooling. The glass and glass-ceramic samples of this composition were abbreviated as 60LSLP-G and 60LSLP-GC, respectively. Ionic liquid [BMIM][BF_4] [37] was chosen due to its low melting point that provides a wide range of thermal stability for composites. This ionic liquid (hereafter IL) was then carefully added (in wt.%) into fine ground glass/glass-ceramic powder and mixture was again thoroughly ground for 20 min. The uniform IL-glass/glass-ceramic composites thus obtained in various compositions were pelletized and used for measurements. The IL content was kept below 5 wt.% in order to prevent its leakage from pellets.

The thermal stability of these composites was studied by Thermo gravimetric Analysis (PerkinElmer 4000). The structural characterization was carried out by X-ray diffraction (Rigaku Miniflex II) and Field emission type scanning electron microscopy (FEI-Nova NanoSEM 450). The electrical conductivity (σ)-temperature (T) cycles were obtained using a computer interfaced HIOKI 3532-50 LCR meter at a control heating rate of 1 °C/min. Low temperature impedance spectroscopy measurements (42 Hz–5 MHz) were also performed using Novo control bridge in the temperature range of − 100 °C to 27 °C. Ionic nature was examined by a conventional galvanic cell method and dc polarization technique.

3. Results and discussion

3.1. X-ray diffraction (XRD)

At the outset, X-ray diffraction studies were carried out to examine nature of the IL composites. XRD pattern for pristine 60LSLP glass (Fig. 1a) and its composite with IL (Fig. 1b) apparently confirm glassy/amorphous nature of both samples. Further, by annealing 60LSLP above its crystallization (~430 °C) glass-ceramic was obtained. Fig. 1c–d shows XRD patterns for pure glass-ceramic and IL-glass-ceramic composite, respectively. The peaks mainly correspond to $LiPO_3$ and Li_2SO_4 compounds. Apparently, IL dispersion does not change the nature of the XRD patterns. These results suggest that IL addition neither leads to formation of any new compound, nor affects the amorphous/glassy nature.

3.2. Thermogravimetric analysis (TGA)

TGA was carried out on pure IL and IL-composites, viz. 5IL-95(60LSLP-G) and 5IL-95(60LSLP-GC) at a heating rate of 10 °C/min in nitrogen atmosphere (Fig. 2). In case of both pristine 60LSLP-G and 60LSLP-GC samples there is no significant weight loss till 500 °C. Weight loss is evident for pure IL at ~400 °C. Whereas, for 5IL-95(60LSLP-G) and 5IL-95(60LSLP-GC), a sharp endothermic dip was observed at ~290 °C and 300 °C, respectively due to the evaporation of IL. Thus, the IL-glass and glass-ceramic composites are thermally stable at least up to ~290 °C. As no new thermal event in IL-solid composites is witnessed, it essentially also suggests no thermally unstable new phase formation.

3.3. Electrical transport

Ionic transport was examined by three important techniques. Firstly, in order to confirm the ionic nature of IL-glass and glass-ceramic composites, Cole–Cole/Nyquist plots were obtained in the frequency range 42 Hz–5 MHz. The Nyquist plots for 5IL-95(60LSLP-G) and 5IL-95 (60LSLP-GC) composites at three different temperatures are shown in Fig. 3. A depressed semicircle followed by inclined line at low frequencies is evident. Further, the diameter of semicircles gradually decreases with temperature rise. The inclined line at low frequencies may be attributed to interfacial polarization that suggests predominant ionic transport in the IL-composites.

Secondly, cells of the type Li/composite/$LiCoO_2$ were carefully prepared in a dry nitrogen glove box and open circuit voltage (OCV) was measured for a short time. Interestingly, the OCV was found to be close to ~3.7 V which is a value reported for typical $LiCoO_2$/Li cells [38]. Therefore, ions are again confirmed as majority charge carriers.

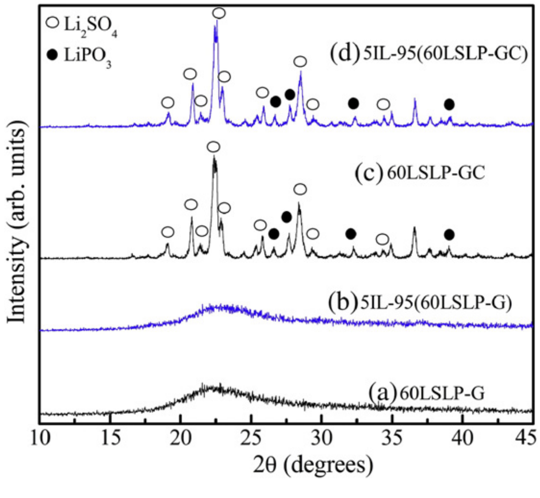

Fig. 1. X-ray diffraction patterns for (a) pristine glass, (b) IL-glass composite, (c) pristine glass-ceramic and (d) IL-glass-ceramic composites.