Ionic Transport and Dielectric Properties of polymer PEO based Organic-Inorganic Hybrid Ionogels

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Abstract-In the present paper, comparative performance of the organic-inorganic hybrid ionogels (HIGs) obtained by in-situ production and dispersion of silica (SiO_2) nanoparticles within the PEO polymer matrix with lithium salt (LiTf) and ionic liquid (EMIMTf) are being reported. Impedance measurements revealed that ionic conductivity of the pristine HIG film is found to increase upon addition of LiTf or EMIMTf. The HIG film consisting of 10wt.% EMIMTf gives ionic conductivity values of ~ 1.22×10^{-7} S/cm (at 30 ^{o}C) and 1.09×10^{-4} S/cm (at 100 ^{o}C), along with significantly high electrochemical stability window of ~2.87 V. Additionally, impedance data of the HIGs are utilised to study the different ionic transport parameters like ionic mobility (μ), Charge carrier density (N), and diffusion (D) using loss tangent (tan δ) spectra which showed that the addition of lithium salt/ionic liquid is the responsible factor for controlling overall ionic transport mechanism in such systems.

Keywords-Hybrid ionogels, Silica nanoparticle, Ionic conductivity, electrochemical stability

I. INTRODUCTION

Due to worries about the depletion of fossil fuel supplies and the resulting rise in demand for renewable energy sources. The current wave of research in the scientific community word-wide is mainly focussed on the development of cost effective solid state electrochemical energy storage and conversion devices such as batteries, fuel cells, supercapacitors, solar cells etc. [1,2]. From many studies, it can be seen that electrolyte is a critical factor that significantly affect the performances of these solid-state portable energy storage systems because it favors the fast ionic transport between the electrodes of an electrochemical devices [3]. Earlier, liquid electrolytes are generally used in the fabrication of these electrochemical devices by dissolving the ionic salts into suitable polar solvents. However, their wide applications are commonly diminished by certain problems such as electrolyte leakage, corrosion, and packing issues [4]. Therefore, the special configuration design of electrolyte materials in thin and flexible formed as solid polymer electrolyte (SPE) is considered to be one of the most effective strategy [5]. Although, these solid electrolytes have been thoroughly examined and effectively used in the development of numerous electrochemical devices, they have poor electrochemical stability in addition to low conductivity at room temperature. Thus, a lot of research is being done to create solid electrolytes that have both high ionic conductivity and good mechanical strength [6-8]. Recently, an inventive technique that involves indirectly modifying the polymer orientation and conformation by combining organic and inorganic materials simultaneously to form "*organic-inorganic hybrid ionogels*". When compared to the individual properties of each component, the primary advantage of such hybrid systems is the synergistic interaction of the organic and inorganic components, which produces materials with superior features and functionalities [9-10].

The present study is focused on studying the comparative performances of the physico-chemical and electrical transport properties of the organic-inorganic hybrid ionogels (HIGs) consisting of polymer PEO, lithium salt LiTf and ionic liquid [1-ethyl-3-methylimidazolium trifluoromethane sulfonate, (EMIMTf)] with in-situ produced and dispersed SiO_2 nanoparticles into flexible polymer matrix. Various experimental techniques, which includes, complex impedance spectroscopy, and electrochemical measurements have been employed to characterise the synthesized organic-inorganic hybrid ionogels "HIGs".

II. EXPERIMENTAL

A. Materials

For the preparation of different organic-inorganic hybrid ionogels (HIGs), polymer PEO of average mol. wt. 6 x 10^5 g/mol as host matrix, Lithium trifluoromethanesulphonate, (LiTf), purity ≥ 99.9% as dopant salt and ionic liquid, 1-ethy-3-methylimidazoliumtrifluoromethanesulfonate(EMIMTf), purity≥ 98.0% has been used as dopants. Tetraethylorthosilicate (TEOS), purity≥99.0% as silica source. 3-(glycidyloxypropyl) trimethoxysilane (GLYMO), purity≥ 98% has been used as crosslinking agent. All the chemicals are analytical grade and procured from the Sigma Aldrich. Analytical grade methanol and hydrochloric acid used in the synthesis process and have been used as received.

B. Synthesis of organic-inorganic hybrid ionogels

Organic-inorganic hybrid ionogels (HIGs) were synthesized by using sol-gel technique followed by solution casting method. Briefly, this technique involves the combining an inorganic precursor solution with an electrolyte solution made of organic polymers. In order to prepare inorganic portion of the hybrid ionogels, a mixture of GLYMO and TEOS was hydrolysed in a reaction vessel at a molar ratio of 1:5 for an hour at 50 °C. Further, the above mixture was added with the requisite volume of HCl solution (0.3M HCl solution in distilled water) drop by drop to start the hydrolysis process under stirring. Thus obtained prehydrolyzed sol was added to the appropriate ratios of the PEO or PEO+LiTf or PEO+EMIMTf solution in methanol and stirred for another four to five hours until a viscous slurry was obtained. Finally, the obtained viscous slurry solution has been casted in polypropylene dishes and dried at room temperature to get the free standing thin films of organic-inorganic hybrid ionogels (HIGs). The sample codes and their constituents has been given in Table 1.

Sample Codes	*Composition*
IL	*1-ethy-3methylimidazoliumtrifluoro methanesulfonate (EMIMTf)*
HIG-0	*PEO/SiO_2 (in-situ)*
HIG-10Li	*PEO/SiO_2/10wt.% LiTf*
HIG-10IL	*PEO/SiO_2/10wt.% EMIMTf*

Table 1: Sample codes for different synthesized organic-inorganic hybrid ionogels (HIGs)

C. Characterization techniques

The ionic conductivity and dielectric measurements of the HIGs was conducting by utilising electrical impedance spectroscopy technique with the help of Novacontrol Broad Band Dielectric spectroscopy in the temperature region 30 to 100°C in the frequency range between 1Hz to 20MHz. The electrochemical measurements were performed by utilising an electrochemical workstation CHI 608E, USA. To assess the electrochemical stability window of the prepared hybrid ionogels (HIGs), the cyclic voltammetry (CV) measurements was employed at a scan rate of 5 mV/sec on the cell SS/PGE/SS. Further, the ionic transport number (tion) of the prepared hybrid ionogels were measured using DC polarization technique on the cell configuration SS|PGE|SS at applied voltage 0.75 V.

III. RESULTS AND DISCUSSION

A. Ionic Conductivity Studies

Impedance spectroscopic technique is used to study the electrical conductivity and ion dynamics behavior of the mobile change present in the polymer electrolyte system and their interfaces [11]. In impedance spectroscopy, the real and imaginary parts of complex impedance were measured simultaneously at various frequencies. The complex impedance (Z^*) can be expressed as:

$$Z^{*} = Z' + jZ''\text{……………..(1)}$$

where Z' and Z'' are the real and imaginary parts of the complex impedance, respectively. The bulk resistance, R_b can be estimated from the Cole-Cole plot (Figure 1) of negative imaginary part ($-Z''$) versus real part (Z') of complex impedance at the intersection of the arc and real impedance axis.

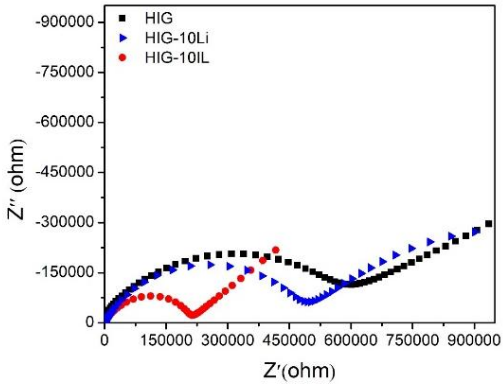

Figure 1: Cole-Cole plots for (a) HIG, (b) HIG-10Li (c) HIG-10IL at 30°C.

The bulk electrical conductivity of the organic-inorganic hybrid ionogels (IGs) can be calculated by using the relation was calculated by using the expression:

$$\sigma = \frac{t}{R_b \times A} \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Where, R_b is the bulk resistance, t is the thickness and A is the cross section area of the samples.

Each cole-cole plot displays two distinct regions: an inclined spike in the low-frequency range and a depressed semicircle in the high-frequency range. The high-frequency semicircle represents the bulk characteristics of the polymer electrolyte, which corresponds to the parallel combination of capacitance and bulk resistance. The low-frequency spike reflects the formation of double-layer capacitance at the electrode-electrolyte interface, resulting from ion migration at the interface [12]. As the IL(EMIMTf) or lithium salt (LiTf) concentration of 10 wt%, doped to hybrid electrolytes, the ionic conductivity rises due to the increase of mobile charges within in the matrix.

Composition dependent ionic conductivity (σ) of different organic-inorganic hybrid ionogels are shown in Figure 2.

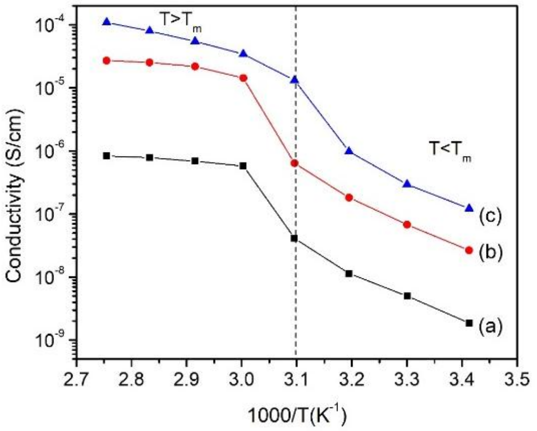

Figure 2: Composition dependent ionic conductivity for different organic-inorganic hybrid ionogels (IGs) at room temperature.

It is evident that room temperatures ionic conductivity of the synthesized hybrid gels rises as the IL or lithium salt incorporated in the pristine hybrid matrix PEO/SiO_2 i.e. HIG. This is because the increase in the amorphicity of the hybrid ionogel films and a greater number of free ions available for conduction [13]. The organic-inorganic hybrid ionogel (HIG-10Li) containing 10 wt% EMIMTf has an ionic conductivity of 1.22 x 10^{-7} S/cm at room temperature (30°C), which is higher than lithium salt incorporated hybrid ionogel. This suggest that IL is more effective plasticizer as compared to the lithium salt.

Figure 3, displays a temperature-dependent ionic conductivity plots for various organic-inorganic hybrid ionogels with dopant lithium salt (LiTf) & ionic liquid (EMIMTf) along with pristine hybrid ionogel PEO/SiO_2.

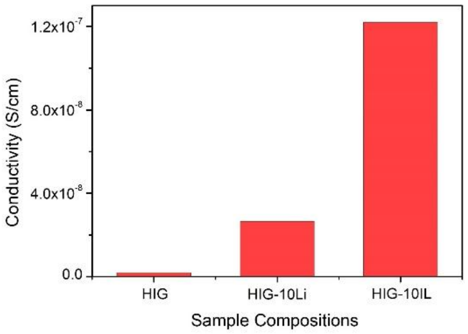

Figure 3: Temperature dependent ionic conductivity of (a) HIG (b) HIG-10Li and (c) HIG-10IL

It is evident that ionic conductivity follows an Arrhenius-type thermally activated process and rises linearly below the melting temperature (T_m). The semi-crystalline to amorphous phase change of the PEO at T_m is linked to the abrupt increase in ionic conductivity that is visible as T_m approaches. The temperature dependent ionic conductivity flows Arrhenius type behaviour:

$$\sigma = \sigma_o \exp(-E_a / kT) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where, σ_o is pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is temperature (in K). The activation energies for various organic-inorganic hybrid ionogels lies between 0.37 to 0.35 eV (at $T < T_m$) and 0.22 to 0.11 eV (at $T>T_m$). The value of activation energy has been found to be least for highest conducting hybrid ionogel.

B. *Loss tangent and ion transport studies*

Figure 4, shows the variation with frequency of tan δ (ε″/ε′), where ε′ and ε″ are the real and imaginary components of the dielectric constant at different concentrations for HIG, HIG-10Li and HIG-10IL. On evaluating the loss tangent (tan δ) as a function of frequency, the dielectric relaxation parameter of the hybrid polymeric based ionogels can be determined [14].

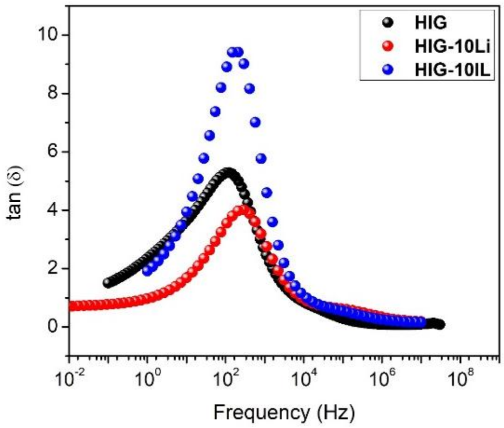

Figure 4: Loss tangent (tan δ) vs. frequency plot of (a) HIG (b) HIG-10Li (c) HIG-10IL

As frequency increases, tan δ rises and reaches its maximum value at a specific frequency, after which it decreases rapidly as the frequency continues to rise. The relaxation time τ, can be calculated using the equation $\tau = 1/(2\pi f)$, where f is the frequency corresponding to the relaxation peak. Further, the peak position of the pristine hybrid electrolyte membrane shifts to higher frequencies as the hybrid electrolytes incorporated with lithium salt or ionic liquid. The estimated relaxation time from tan δ vs. frequency plots are found to decrease with varying frequency suggested an enhancement in chain flexibility/backbone mobility of the organic-inorganic hybrid ionogels [15]. The change in the maxima of the loss tangent value ($\tan\delta_{max}$) of hybrid ionogels and corresponding shifts in the peak position (f_{max}) is the signature of the appearance of dielectric relaxation processes occurring in all the studied hybrid ionogels.

The ionic conductivity of hybrid ionogels is mainly depending on mobile charge carrier density '*N*' and ionic mobility 'μ'. Further, bulk d.c. conductivity, σ_{dc} is directly depends on ionic mobility (μ) and charge carrier number density (N) as given by the following relations: $\sigma_{dc}=N\mu q$. Both polymeric chain backbone mobility/flexibility as well as number of mobile charge carrier 'N' increases with the concentration of dopants IL or LiTf. The transportation of ions in polymeric based organic-inorganic hybrid ionogels takes place from one site to another site via the segment motion of the organic polymeric chain which is followed by jump/hopping mechanism. Furthermore, the conduction process in such systems are well explained in terms of diffusion coefficient (D), ionic mobility (μ) and charge carrier number density (N). Trukhan model [16] has been used to evaluate the charge carrier number density (N) by applying the Nernst-Planck equations of diffusion from the value of dielectric loss tangent tan(δ) [17]. The expression for the estimation of diffusion coefficient from tan (δ) spectra maximum value is: $D = \frac{2\pi f_{max} t^2}{32\,(tan\delta_{max})^3}$ where, t is the thickness of the sample and f_{max} is the frequency corresponding to the maximum *tan(δ)* value. The charge carrier number density (*N*) expression is estimated using the equation $N = \frac{\sigma_{d.c.}\,K_B T}{D q^2}$, where K_B is Boltzmann's constant, *q* is the elementary charge, *T* is the absolute temperature, σ_{dc} is bulk d.c. conductivity obtained from impedance or cole-cole plots. The estimated values of D, N and μ for different organic-inorganic hybrid ionogels HIG-10Li and HIG-10IL are listed in Table 2. From Table 2, it can be seen that values of N and D respectively obtained for IL-containing hybrid ionogel is found to be 4.00 x 10^{20} /cm^3 and 1.22×10^{-7} cm^2/sec, which is slightly higher than lithium salt (LiTf) incorporated ionogel sample as indicated in Table 2. From the above study, it can be seen that transport properties (electrical conductivity and dielectric relaxation). It can be seen The higher values of transport parameter i.e. N, D and μ obtained for IL-incorporated ionogel support enhance chain flexibility or larger polymeric backbone mobility, which support higher segmental motion due to the plasticization effect of IL.

Table 2: The values of diffusion coefficient (D), charge carrier number density (N), and ionic mobility (μ) for prepared organic-inorganic hybrid ionogels.

Sample codes	σ_{dc} (S/cm)	D *(cm^2/sec)*	N *(/cm^3)*	μ *(cm^2/V. sec)*
HIG-10Li	2.72×10^{-8}	5.23×10^{-4}	8.45×10^{-19}	2.00×10^{-9}
HIG-10IL	1.22×10^{-7}	2.90×10^{-3}	4.00×10^{20}	1.91×10^{-9}

C. Dielectric Studies

A dielectric spectroscopy was performed to know the interaction of an alternating external electric field with the constituents of polymer electrolyte sandwiched in-between two stainless steel electrodes. SPE film has several functional groups which may form a complex with the dopant like salt and plasticizers. Hence such materials respond differently in the presence of high range time varying electric field. Therefore, different types of polarization mechanism namely electronic, ionic/atomic, orientation and interfacial polarization will appear in terms of a dielectric relaxation/resonance frequency [18]. In the presence of an external electric field the dielectric materials gets polarized and provides the material characteristics information in terms of complex dielectric permittivity (ε*) as a function of angular frequency (ω= $2\pi f$) and stated as:

$$\epsilon_{\omega}^{*} = \epsilon' - j\epsilon" = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} - j\frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} = \frac{1}{j\omega C_0 Z^*} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where ε′→ real part of the complex permittivity represent the polarizability/dielectric constant of the material, ε′′→ imaginary part of the complex permittivity associated with energy loss due to polarization and ionic conduction, C_0 is the capacitance of free space and its value is $C_0 = \frac{\varepsilon_0 A}{t}$, ε_0 is the permittivity of free space and f is the frequency of applied ac field. Impedance spectroscopy technique is used to study the dielectric properties of organic-inorganic hybrid ionogels, such as the dielectric constant (ε') and dielectric loss (ε''), which is illustrated in Figure 5.

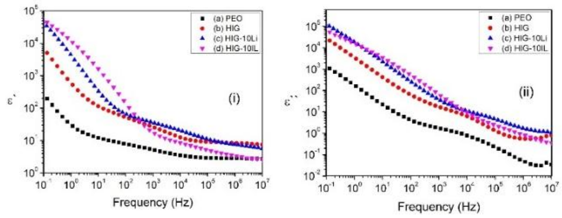

Figure 5: (i) Dielectric permittivity (ε′) and (ii) dielectric loss (ε″) vs. frequency plots for (a) PEO (b) HIG (c) HIG-10Li and (d) HIG-10IL at room temperature (30°C).

The dielectric constant (ε') and dielectric loss (ε') spectra clearly show a decrease in their values with increasing frequency. This behavior may be attributed to the alignment of dipoles in the direction of the applied electric field, leading to a reduction in space charge polarization. At high frequencies, the dielectric constant (ε') and dielectric loss (ε') become independent of the frequency and gives static dielectric constant value of the material [19].

D. Ionic transport number

The total ionic transference number (t_{ion}) of these organic-inorganic hybrid ionogels has been evaluated using transit ionic current (TIC) measurement (or dc polarization) technique using the symmetrical cell "SS| hybrid ionogel sample |SS" (where SS corresponds to stainless steel). The ionic transference number (t_{ion}) has been obtained by using the following equation [20]:

$$t_{ion} = I_t - I_e / I_t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where, I_t is the initial total current and I_e refers to the final stabilized current after the polarization. Typical plots of polarization current vs. time for hybrid ionogel HIG-10IL is shown in Figure 6 and similar plots have also been obtained for other organic-inorganic hybrid ionogels. The ionic transport number (t_{ion}) for HIG-10IL has been estimated using eqn. 5 and Figure 6 is about 0.994. This confirms the overall electrical conductivity is due to the movement of ions in the hybrid ionogel.

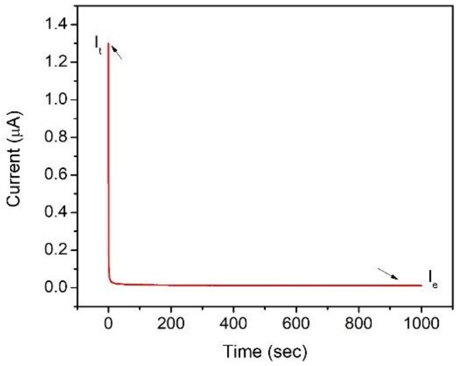

Figure 6: d.c. polarization curve for HIG-10IL at ambient temperature (~30°C)

E. Electrochemical studies

The electrochemical stability window of an electrolyte is a crucial factor in determining its suitability for use in energy storage and conversion devices [21]. The electrochemical experiment was carried out by placing the HIG-10IL film between two blocking stainless electrodes with cell configuration (SS/HIG-10IL/SS) to access the electrochemical stability window of the prepared organic-inorganic hybrid ionogels. The results show that the stability window of the highest conducting hybrid ionogel i.e. HIG-10IL, which is approximately found to be 2.87 V as obtained by linear sweep voltammetry (LSV) technique (Figure 7a). This value is sufficiently wide voltage range for the most energy storage applications. Similarly, Cyclic voltammetry (CV) analysis was conducted to assess the electrochemical performance of the Electric Double Layer Capacitor (EDLC) using HIG-10IL hybrid ionogel, (as indicated in Figure 7b).

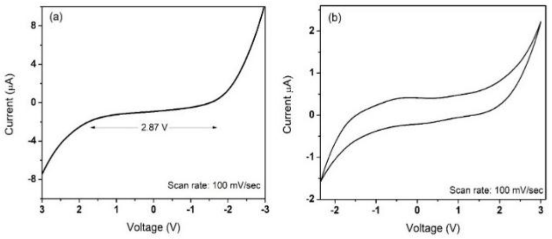

Figure 7: (a) LSV and (b) CV curves for hybrid ionogel HIG-10IL obtained at room temperature

The CV curve obtained for the EDLC was measured at a scan rate of 100 mV/s. Notably, no peaks were observed within the optimized potential range, indicating the absence of redox reactions in this voltage window. This is a positive sign, as it suggests that the electrolyte is functioning in a capacitive mode, which is characteristic of EDLCs (Electric Double Layer Capacitors).

IV. CONCLUSION

A series of organic-inorganic hybrid ionogels (OIHGs) "PEO/SiO_2" consisting of lithium salt (LiTf) and ionic liquid (EMIMTf) have been prepared and studied. The addition of salt or ionic liquid along with the in-situ production and dispersion of SiO2 nanoparticle have been found effective in reducing the degree of crystallinity (hence increasing the flexibility) of the matrix and resulted in improving the ionic conductivity of hybrid the film. The hybrid electrolyte film with the addition of 10 wt.% of EMIMTf, exhibits maximum room temperature ionic conductivity of $\sim 1.22 \times 10^{-7}$ S/cm and having wide electrochemical stability window (ESW) of ~2.87 V. The ionic conductivity increases with temperature and follows Arrhenius type thermally activated behavior both below and above T_m. The values of ionic transference number (i.e., t_{ion}) for the ionic liquid incorporated hybrid ionogel HIG-10IL has been found to be ∼0.994 confirming the predominant ionic conduction in the hybrid system.

V. ACKNOWLEDGMENT

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REFERENCES

[1] M. Armand, F. Endres, DR MacFarlane, H. Ohno, B. Scrosati, Ionic-liquid materials for the electrochemical challenges of the future, *Nature Materials* 8 (2009) 621-629.

[2] X. Liang, X. Wu, Y. Wang, X. Li, Q. Gai, J. Mao, Study on Preparation and Performance of PEO-PVDF Composite Binder for Lithium ion Batteries, *Int. J. Electrochem. Sci.* 15 (2020) 8471-8478.

[3] X. Zhou, Y. Zhou, L. Yu, L. Qi, K. S. Oh, P. Hu, S. Y. Lee, and C. Chen, Gel polymer electrolytes for rechargeable batteries toward wide-temperature applications, *Chem. Soc. Rev.* 53 (2024) 5291-5337.

[4] H. Kim, J. Hong, K. Y. Park, H. Kim, S. W. Kim, K. Kang, Aqueous Rechargeable Li and Na Ion Batteries, *Chem. Rev*. 114 (2014) 11788–11827.

[5] X. Shan, Z. Song, H. Ding, L. Li, Y. Tian, A. P. Sokolov, M. Tian, K. Xu, and P. F. Cao, Polymer electrolytes with high cation transport number for rechargeable Li–metal batteries: current status and future direction, *Energy Environ. Sci.* 17 (2024) 8457-8481.

[6] W. Na, A. S. Lee, J. H. Lee, S. S. Hwang, S. M. Hong, E. Kim, C. M. Koo, Lithium ion capacitors fabricated with polyethylene oxide-functionalized polysilsesquioxane hybrid ionogel electrolytes, *Electrochim. Acta* 188 (2016) 582-588.

[7] A. J. Nagajothi, R. Kannan, S. Rajashabala, Electrochemical Performance of Plasticized PEO-LiTf Complex-Based Composite Gel Polymer Electrolytes with the Addition of Barium Titanate, *Ionics* 24 (2018) 1407-1414.

[8] J. O. Kweon, S. T. Noh, Thermal, thermomechanical, and electrochemical characterization of the organic–inorganic hybrids poly(ethylene oxide) (PEO)–silica and PEO–silica–$LiClO_4$, *J. Appl. Polym. Sci.* 81 (2001) 2471-2479.

[9] T. Babkova, R. Kiefer, and Q. B. Le, Hybrid Electrolyte Based on PEO and Ionic Liquid with In Situ Produced and Dispersed Silica

for Sustainable Solid-State Battery, *Sustainability* 16 (2024) 1683.

[10] D. G. Kim, J. Shim, J. H. Lee, S. J. Kwon, J. H. Baik, J. C. Lee, Preparation of solid-state composite electrolytes based on organic/inorganic hybrid star-shaped polymer and PEG-functionalized POSS for all-solid-state lithium battery applications, *Polymer* 54 (2013) 5812-5820.

[11] K. A. Nath, K. Prasad, K. P. Chandra, and A. R. Kulkarni, Impedance and a.c. conductivity studies of $Ba(Pr_{1/2}Nb_{1/2})O_3$ ceramic, *Bull. Mater. Sci.* 36 (2013) 591-599.

[12] B. A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices, J. Phys. Chem. C 122 (2018) 194-206.

[13] F. Wu, N. Chen, R. Chen, L. Wang, L. Li, Organically modified silica-supported ionogels electrolyte for high temperature lithium-ion batteries, *Nano Energy* 31 (2017) 9-18.

[14] T. Dam, S. N. Tripathy, M. Paluch, S. S. Jena, D. K. Pradhan, Investigations of Relaxation Dynamics and Observation of Nearly Constant Loss Phenomena in PEO_{20}-$LiCF_3SO_3$-ZrO_2 Based Polymer Nano-Composite Electrolyte, *Electrochim. Acta* 202 (2016) 147-156.

[15] A. Munar, A. Andrio, R. Iserte, V. Compan, Ionic conductivity and diffusion coefficients of lithium salt polymer electrolytes measured with dielectric spectroscopy, *J. Non Crystalline Solids* 357 (2011) 3064-3069.

[16] V. Compan, T. Smith Sorensen, R. D. Calleja, E. Riande, Diffusion coefficients of conductive ions in a copolymer of vinylidene cyanide and vinyl acetate obtained from dielectric measurements using the model of Trukhan, *J. Appl. Phys.* 79 (1996) 403-411.

[17] Y. Wang, C. N. Sun, F. Fan, J. R. Sangoro, M. B. Berman, S. G. Greenbaum, T. A. Zawodzinski, A. P. Sokolov, *Phys. Rev. E* 87 (2013) 042308.

[18] D. K. Pradhan, R. N. P. Choudhary, B. K. Samantaray, Studies of Dielectric Relaxation and AC Conductivity Behavior of Plasticized Polymer Nanocomposite Electrolytes. *Int. J. Electrochem. Sci.* 3 (2008) 597-608.

[19] F. Frenzel, R. Guterman, A.M. Anton, J. Yuan, F. Kremer, Molecular Dynamics and Charge Transport in Highly Conductive Polymeric Ionic Liquids, *Macromolecules* 50 (2017) 4022-4029.

[20] M. J. Reddy, P. P. Chu, T. Sreekanth, U. V. S. Rao, PEO:KIO_3 Polymer electrolyte system- its application to solid state electrochemical cell, *J. Mater. Sci: Materi. Electron.* 12 (2001) 153-156.

[21] S. Tanwar, N. Singh, and A. L. Sharma, High-performance symmetric supercapacitor based on activated carbon-decorated nickel diselenide nanospheres, *J. Mater. Sci.* 57 (2022) 20335-20350.