Molten Li Salt Solvate-Silica Nanoparticle Composite Electrolytes with Tailored Rheological Properties

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ABSTRACT

Nanocomposite electrolytes comprising molten Li salt solvates (MLSs) and inorganic fillers provide liquid-like processing and reasonably high Li ion transport properties. Thus, they can be potentially used as thermally-stable and mechanically-robust electrolytes. In this study, nanocomposite electrolytes exhibiting two distinct non-Newtonian rheological responses, i.e., shear thinning and shear thickening behaviors, were prepared using glyme- and sulfolane-based molten Li salt solvates and hydrophilic fumed silica without any surface modification of the silica. The rheological responses strongly depended on the anionic structure of the MLSs. The MLS-silica composites containing bis(trifluoromethanesulfon)amide (TFSA) and BF₄ anions formed a shear thinning gel and shear thickening fluid, respectively. The characteristic rheological properties (elastic modulus for the shear thinning gel and the maximum peak viscosity and critical shear rate for the shear thickening system) were extensively tailored by the silica content in addition to the chemical structure of the MLSs, while the changes in their ion transport properties were moderate even in the presence of silica fillers.

1. Introduction

The development of clean energy storage and conversion devices is becoming crucial to create a sustainable society. Thus, the research and development of Li secondary batteries underwent exponential growth in the past decade. However, with aggressive increases in the size of these energy devices for electric vehicles and stationary devices, the risk of short circuit from the contact between electrodes and the consequent explosion from the exothermic reaction give rise to safety concerns. Therefore, the creation of electrolytes with high thermal stability and high resistance to mechanical abuse has become an essential requirement to ensure safety in these large-scale devices. While the use of solid electrolytes prepared from ceramic and polymeric materials can ensure sufficient mechanical strength, they often have difficulties related to the formation of electrode/electrolyte interfaces, large area processing, and inferior transport properties. In this context, the nanocomposites of liquid electrolytes and inorganic fillers are of interest because they can be easily prepared and provide adequate mechanical strength and compliance, liquid-like processing, and high ionic conductivity.

The nanocomposite electrolytes can be divided into two classes in terms of their non-Newtonian rheological behaviors, i.e., a shear thinning colloidal gel and a shear thickening liquid electrolyte. The shear thinning colloidal gels behave like a soft solid in the absence of shear; however, they can flow under sufficient shear. In contrast, the shear thickening liquid electrolytes exhibit a reversible and drastic increase in viscosity upon the application of mechanical stress. These non-Newtonian electrolytes can be potentially used as a safer alternative to conventional electrolyte systems for use in Li secondary batteries. Indeed, colloidal gel electrolytes were found to improve the charge-discharge cycle performance of Li secondary batteries and eliminated the electrolyte leakage. Shear thickening electrolytes with the unique impact resistance property (i.e., a drastic increase in the mechanical resistance under a large shear force) can provide an effective strategy to prevent cell failure or explosive exothermic reaction that occurs from short circuit during high impact events in electric vehicles without increasing additional weight or volume like metallic physical protection packages which are conventionally used. Several studies have elucidated that composites prepared from incorporation of suitable solid particles in electrolytes are capable of withstanding mechanical abuse while exhibiting good electrochemical properties. Veith et al. have found that electrolytes formulated by addition of silica nanoparticles in 1.2 M LiPF₆ ethylene carbonate/dimethyl carbonate solution could tolerate impact energy up to 5.65 J while maintaining good cycle performances of Li ion batteries. However, these nano-composite electrolytes were prepared with conventional organic electrolytes and still face flammability concerns. In addition, the shear thickening systems often require complicated surface modification of fillers to ensure the colloidal stability in electrolyte solutions.

We investigated molten Li salt solvate (MLS) electrolytes where almost all the solvent molecules strongly coordinate with the salt cation, resulting in a negligible amount of free solvents in the system. In addition to the remarkable properties, resembling those of ionic liquids (ILs), including high thermal stability and less-flammability, MLSs were found to exhibit some unique features relevant to Li ion battery applications, such as enhanced oxidation stability, inhibiting Al corrosion suppression, improved rate capability, and poor solubility of electrochemically-active ionic species (e.g., polysulfides and superoxides). These features render them as a superior alternative to conventional organic electrolytes for usage in Li-S, Li-air, and Li-ion batteries.

We previously found that both the shear thinning gels and shear thickening fluids were obtained from the dispersions of silica nanoparticles in aprotic ILs (AILs) and protic ILs (PILs). The two distinct rheological responses of the IL-silica nanocomposites were tuned via simple variations in the ionic structure of the ILs. These IL-nanoparticle hybrid systems with unique colloidal stabilization behavior and remarkable rheological properties have shown potential in diverse applications, such as catalysts, separation...
technology, shock resistant materials, electrochemical sensors and electrolytes. As Li ion conducting liquid electrolytes, MLSs were found to be superior to AIL-Li salt binary electrolytes in terms of Li ion conductivity and charge-discharge rate capability of Li/LiCoO2 cells. However, to the best of our knowledge, few studies have focused on the transport and rheological properties of MLS-metal oxide composite electrolytes. In this paper, we show an easy approach to separately prepare the shear thinning gel and shear thickening electrolyte with high thermal stability by using commercially available hydrophilic silica and a series of glyme- and sulfolane-based MLSs with BF4 or bis(trifluoromethylsulfonyl)imide (TfSA) anions.

2. Experimental

Dehydrated triglyme (G3) and tetraglyme (G4) were provided by Nippon Nynkaizai. The dried LiTfSA was received from Solvay, Japan. Battery-grade sulfolane (SL) and LiBF4 were purchased from Kishida Chemical. All chemicals were used as received without further purification. The solvents and either LiBF4 or LiTfSA were mixed at a given molar ratio in a glove box filled with argon gas (VAC, [H2O] < 1 ppm) to prepare the MLSs. Aerosol 200 (supplied by Nippon Aerosil, with a primary particle diameter of approximately 12 nm) was used as the silica nanoparticle; it was dried for 24 h in a vacuum oven at 120°C prior to use. The samples were prepared gravimetrically, and the volume fractions were calculated from the bulk density values of fumed silica (2.2 g cm⁻³) and MLSs (1.42 g cm⁻³ for [Li(G3)][TfSA], 1.22 g cm⁻³ for [Li(G4)][BF4], 1.424 g cm⁻³ for [Li(SL)2][BF4] and 1.568 g cm⁻³ for [Li(SL)2][TfSA]). Suspensions of the silica particles in the MLSs with a volume fraction of the silica particles (Vs) were prepared using a conditioning mixer (AR-250, THINKY) by mechanical mixing for 20 min to ensure homogeneous mixing, followed by degassing for 3 min to remove the air bubbles from the samples. The composites did not undergo any phase transitions within the range of room temperature to 80°C.

Rheological measurements were performed with a rheometer (Physica MCR301, Anton Paar) under dry air conditions at 30°C. The experimental procedure for rheological measurements has been reported in detail in our previous work. The ionic conductivities were obtained from the complex impedance spectra, measured using a Hewlett Packard 4192A LF impedance analyzer in the frequency range of 5 Hz to 13 MHz at an oscillation voltage of 0.01 V. These measurements were performed in a cell with stainless-steel electrodes. The cell constant of the conductivity cell was determined using a solution of 0.01 M KCl at 25°C. Before the measurement, the samples were thermally equilibrated at each temperature for 1 h using an SU-261 constant temperature oven (ESPEC, Japan).

3. Results and Discussions

The addition of silica nanoparticles in the MLSs yielded a soft solid-like gel or liquid suspensions depending on the anionic structures of the electrolytes (Fig. S1). The [TfSA]-based MLSs were quasi-solidified by adding silica particles, thereby suggesting that the collective flocculation of silica particles results in a percolating network throughout the volume of the electrolyte (i.e., formation of a colloidal gel). In contrast, the suspensions in [BF4]-based MLSs remained stable in all the studied compositions. Therefore, it was suggested that there are no percolating networks of the silica aggregates in the [BF4]-based MLSs. These observations concur with our previous findings regarding the anion dependent sol/gel states for imidazolium-based AIL-silica composites; i.e., the silica suspensions in [C2 mim][TfSA] ([C2 mim]: 1-ethyl-3-methyl imidazolium) and [C2 mim][PF6] ([C2 mim]: 1-butyl-3-methyl imidazolium) formed a quasi-solid gel with approximately 3% of silica content whereas the suspensions in [C4 mim][BF4] behaved as a viscous fluid even with 15–20% of silica content. The macroscopic difference in the MLS-silica composites is attributable to the morphological difference in the aggregation/dissociation state of the silica nanoparticles. In a previous study, the hydrogen bonds between the ions and the silica surface were found to play an important role in determining the colloidal interactions and consequently, the stability of nanoparticles in a dense ionic medium, such as ILs; however, there exist complicated competitions between the cation-anion and nanoparticle-ion interactions. Molecular dynamic simulations of the ILs confined between amorphous silica slabs suggested that the surface silanol groups of silica are more engaged in hydrogen bonding with the anions for [C2 mim][BF4] in comparison to [C4 mim][PF6]. The extensive hydrogen bonding ability of [BF4]-based ILs with silica was considered to be responsible for the formation of a robust solvation layer of the ILs around the silica surface, which gave rise to the effective repulsive force to confer the colloidal stability in high-ionic-strength media where the electrostatic force does not contribute to interparticle repulsion.

Figure 1 shows the effect of variations in the shear rate on the shear viscosity of the MLS-silica composites at Vs = 0.08. The dispersions containing [TfSA]-based MLSs exhibited a similar change in the viscosity in response to the application of shear, i.e., both exhibited a significantly high shear viscosity (> 2 × 10⁸ Pa s) at a low shear rate of 1 s⁻¹, and the viscosity decreased with the increasing shear rate. This shear thinning behavior results from the breaking of the aggregating network structure. In contrast, the [BF4]-based MLS-silica composites demonstrated a much lower and less shear rate-dependent, Newtonian-like viscosity in the low shear rate region, suggesting that the silica particles are well dispersed. However, the viscosity of the [BF4]-based MLS-silica composites increased by more than one order of magnitude above a certain shear rate and reached a maximum value (i.e., shear thickening) due to the aggregation of the silica particles. The shear viscosity eventually decreased at a higher shear rate as a result of further breaking of the transient aggregates. The rheological properties of the MLS-silica composites were determined primarily by the anionic structure of the MLS, i.e., the [TfSA]-based MLS-silica composites form a shear thickening colloidal gel whereas the [BF4]-based MLS-silica composites serve as a shear thickening liquid electrolyte. A colloidal gel was obtained even at Vs = 0.04 for both [Li(G3)][TfSA] and [Li(SL)2][TfSA]. The soft solid-like behavior of the [TfSA]-based MLS-silica composites was rheologically confirmed from the elastic (G') modulus, which was larger than the
viscous (G') modulus via oscillatory shear measurements (Fig. S2). As evident in Fig. 2, the elastic modulus (G') can be tuned by the silica content and enhanced to almost 10^3 Pa at V_{silica} = 0.12 of [Li(G3)][TFSA]-silica composites. This G' value of the silica-based gel electrolytes is comparable to that of the reported colloidal gels of ILs\textsuperscript{15} and organic electrolytes;\textsuperscript{27} however, it is much higher than that of previously reported polymer-based gel electrolytes of the MLSs (G' in the order of ~10^2 Pa) at a similar solid content.\textsuperscript{28} The G' values were lower for the [Li(SL)\textsubscript{2}][TFSA]-silica composites in comparison to those of the [Li(G3)][TFSA]-silica composites. This suggests weaker attractive interactions between the silica particles in [Li(SL)\textsubscript{2}][TFSA].

Seminal works by Fedkiw and Khan et al. on silica-based colloidal gels containing an organic liquid electrolyte demonstrated inhibition in the growth of lithium dendrites,\textsuperscript{29} stabilization of Li metal surface,\textsuperscript{30} and improved cycle ability of metallic Li batteries.\textsuperscript{6} The high mechanical strength of the present MLS-based colloidal gel electrolytes may also contribute to the above appealing features in battery systems. The silica-based quasi-solid electrolytes containing the MLSs can indeed be employed for highly safe 100 Wh-class all-solid state Li-ion batteries, as demonstrated by Unemoto et al.\textsuperscript{31}

Figure 3 displays the V_{silica}-dependence of the shear thickening behavior for the [BF\textsubscript{4}]-based MLS-silica composites. With increasing V_{silica}, the maximum peak viscosity increased and the critical shear rate, at which the viscosity starts to increase, systematically shifted to a lower shear rate for both systems. Similar V_{silica}-dependence of the shear thickening behavior was observed for the [G\textsubscript{2}mim][BF\textsubscript{4}]-silica composites.\textsuperscript{15} In comparison to the [Li(G4)][BF\textsubscript{4}]-silica composites, the [Li(SL)\textsubscript{2}][BF\textsubscript{4}]-silica composites exhibited higher maximum viscosity and lower critical shear rate at the same V_{silica}. Previous studies suggest that the shear thickening behavior is primarily affected by the hydrodynamic forces and the extent of interparticle interactions in the dispersed particles; the former depends on the initial viscosity of the dispersant media, while the latter has an impact on the critical shear rate.\textsuperscript{20} For a higher viscosity of [Li(SL)\textsubscript{2}][BF\textsubscript{4}] (743 mPa s)\textsuperscript{22} than [Li(G4)][BF\textsubscript{4}] (314 mPa s),\textsuperscript{15} stronger hydrodynamic forces are expected for [Li(SL)\textsubscript{2}][BF\textsubscript{4}], which lead to higher maximum viscosities of the [Li(SL)\textsubscript{2}][BF\textsubscript{4}]-silica composites in the shear thickening region. A higher critical shear rate of the [Li(G4)][BF\textsubscript{4}]-silica relative to the [Li(SL)\textsubscript{2}][BF\textsubscript{4}]-silica suspensions implies stronger anion-silica interactions in [Li(G4)][BF\textsubscript{4}]; the surface solvation layer of [Li(G4)][BF\textsubscript{4}] can break apart at higher critical shear rates (and larger shear stress) to form silica particle aggregates. This may be ascribed to competing molecular interactions, such as stronger Li ion-solvent interaction with multidentate G4 and the resulting weaker anion-Li interactions in [Li(G4)][BF\textsubscript{4}]. Consequently, the shear thickening behavior, namely the maximum viscosity (in the range of 2.8–5.5 ×10^3 Pa s) and the critical shear rate (in the range of 0.32–10^3 s\textsuperscript{-1}), can be tailored by both the silica content and the solvent types of the MLSs. In addition, owing to the inherently high viscosity of the MLSs, the [BF\textsubscript{4}]-based MLS-silica composites achieved very high maximum peak viscosities, exceeding 10^3 Pa s, which is more than one order of magnitude greater than the values reported for the shear thickening electrolytes using silica particles and carbonate-based organic electrolytes.\textsuperscript{6,9} Ding et al.\textsuperscript{11} and Veith et al.\textsuperscript{7} reported an improved mechanical protection performance of the pouch cells of the Li-ion batteries using carbonate-based shear thickening electrolytes. The shear thickening behavior of the [BF\textsubscript{4}]-based MLS-silica composites, which outperformed the organic electrolyte-based shear thickening electrolytes, would enable the further enhancement of the impact resistance properties of Li secondary batteries.

Figure 4 shows the ionic conductivity of the MLS-silica composites with different values of V_{silica}. Despite the distinctive changes in the rheological properties discussed above, the conductivity of the composites exhibits only moderate changes in comparison to that of the MLS. This is in contrast to the reduction in conductivity for the polymeric systems; i.e., more significant decrease (40\% loss) in conductivity was observed for a polymer-based gel membrane of the MLSs at a similar solid content of 10\%.\textsuperscript{28} The small decrease in conductivity of the present colloidal systems is attributed to the decrease in charge carrier density and obstruction of ion movement in the presence of the silica network. In a recent study on PIL-silica composites, we found a significant increase in the conductivity of the shear thickening composites of the methanesulfonate salt of protonated 1,8-diazabicyclo[5.4.0]undec-7-ene ([DBU][MSA]) and the silica particles within a certain composition range.\textsuperscript{18} Strong hydrogen bonding was assumed to exist between the silica surface and the ions to contribute toward an increase in the charge carrier density and efficient ionic correlations, thereby leading to conductivity enhancement. The absence of the notable conductivity enhancement in the MLS-silica composites suggests that the interaction of the silica surface with [BF\textsubscript{4}] anion does not significantly alter the ionic environment in an effective way to enhance the charge carrier concentration or correlations of ionic motions.

As shown in Fig. 4, the conductivity reduction is less prominent in the case of [BF\textsubscript{4}]-based MLS-silica composites as compared to the [TFSA]-based systems. Especially for the [Li(SL)\textsubscript{2}][BF\textsubscript{4}]-silica.
composites, a slight enhancement in conductivity was observed at $V_{\text{silica}} = 0.02$ and 0.04. In the case of [Li(SL)$_2$][BF$_4$]-silica composites at $V_{\text{silica}} = 0.08$, the conductivity loss was only 3% from the neat MLS, in contrast to 21% loss of conductivity in the same composition of the [Li(SL)$_2$][TFS][silica]-composite. This suggests that the [BF$_4$]-based composites, where the silica particles were well dispersed, can provide less obstruction to ion conduction, as compared to the [TFS]-based systems that contain larger silica aggregates. Moreover, the reduction in conductivity is likely affected by the solvent species of the MLSs. In other words, the conductivity loss is less pronounced for the SL-based MLS composites in comparison to the difference in the ionic transport mechanism in these MLSs. Unlike the vehicular ion conduction mechanism observed in glyme-based systems, the ionic conduction through the silica particulate obstacles may be less restricted via the ion hopping conduction mechanism in the SL-based MLSs.$^{22,23}$

Furthermore, we studied the effects of the presence of silica particles on the lithium transference number ($t_{\text{Li}^+}$) via the electrochemical polarization method using a Li/Li symmetric cell.$^{32,33}$ However, there was no significant difference in the $t_{\text{Li}^+}$ values between the MLSs and the composites, as indicated by the $t_{\text{Li}^+}$ of 0.048 and 0.047 for [Li(G3)][TFS][ and the silica composite ($V_{\text{silica}} = 0.025$), respectively. Consequently, the addition of silica particles to the MLSs had only limited effects in the ionic transport properties, and the ionic conductivity was the least affected for the shear thickening [Li(SL)$_2$][BF$_4$]-silica composites.

4. Conclusion

In this work, we successfully prepared MLS-based silica nanocomposite electrolytes with two different rheological responses by changing the values of $V_{\text{silica}}$ of the anions of Li salts, and the solvents without compromising the superior ionic transport properties of the neat MLSs. The anion structures primarily determined the rheological responses of these materials under shear. The shear thickening colloidal gels were formed using the [TFS][-based MLS-silica composites, while the shear thickening response was observed in the [BF$_4$]-based MLS-silica composites. Stronger hydrogen bonding interaction was suggested between the BF$_4$ anion and silica surface to enhance the colloidal stability of silica in the suspensions, which in turn emerged as the shear thickening behavior. The ionic conductivity was found to be slightly reduced by the addition of silica, and the extent of reduction depended on the structures of Li salts and solvents of the MLSs. The impact-resistive nanocomposite electrolytes prepared from less-flammable MLS electrolytes can become a good alternative to conventional liquid electrolytes and other solid electrolytes in high-energy density and large-sized energy storage devices.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00016.

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