Deep Eutectic Solvent Based on Lithium Bis[(trifluoromethyl)sulfonyl] Imide (LiTFSI) and 2,2,2-Trifluoroacetamide (TFA) as a Promising Electrolyte for a High Voltage Lithium-Ion Battery with a LiMn$_2$O$_4$ Cathode

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ABSTRACT: To design safe and electrochemically stable electrolytes for lithium-ion batteries, this study describes the synthesis and the utilization of new deep eutectic solvents (DESs) based on the mixture of 2,2,2-trifluoroacetamide (TFA) with a lithium salt (LiTFSI, lithium bis[(trifluoromethane)sulfonyl]imide). These prepared DESs were characterized in terms of thermal properties, ionic conductivity, viscosity, and electrochemical properties. Based on the appearance of the product and DSC measurements, it appears that this system is liquid at room temperature for LiTFSI mole fraction ranging from 0.25 to 0.5. At $\chi_{\text{LiTFSI}} = 0.25$, DESs exhibited favorable electrolyte properties, such as thermal stability (up to 148 °C), relatively low viscosity (42.2 mPa.s at 30 °C), high ionic conductivity (1.5 mS.cm$^{-1}$ at 30 °C), and a quite large electrochemical stability window up to 4.9−5.3 V. With these interesting properties, selected DES was diluted with slight amount of ethylene carbonate (EC). Different amounts of EC ($x = 0−30$ %wt) were used to form hybrid electrolytes for battery testing with high voltage LiMn$_2$O$_4$ cathode and Li anode. The addition of the EC solvent into DES expectedly aims at enhancing the battery cycling performance at room temperature due to reducing the viscosity. Preliminary results tests clearly show that LiTFSI-based DES can be successfully introduced as an electrolyte in the lithium-ion batteries cell with a LiMn$_2$O$_4$ cathode material. Among all of the studied electrolytes, DES (LiTFSI: TFA = 4:1 + 10 %wt EC) is the most promising. The EC-based system exhibited a good specific capacity of 102 mAh.g$^{-1}$ at C/10 with the theoretical capacity of 148 mAh.g$^{-1}$ and a good cycling behavior maintaining at 84% after 50 cycles.

1. INTRODUCTION

Lithium-ion batteries (LIBs) are one of the most commonly utilized rechargeable batteries, and the cathode materials for lithium-based batteries are embedded compounds formed by lithium and transition metal oxides. At present, LiCoO$_2$ is popular for commercial applications. The less recoverability and low natural reserves of cobalt are, however, barriers to the development of LIBs. Thus, further development of high-quality and low-cost materials is vital. Because of good cyclic operation performance, safety, and non-toxicity, LiMn$_2$O$_4$ (LMO) is a perspective electrode material in the manufacture of LIBs. The conventional electrolyte consists of a lithium salt, typically LiPF$_6$ dissolved in carbonate solvents, i.e., the mixture of ethylene carbonate and ethyl methyl carbonate, usually exhibiting chemical degradation and oxidation reaction at high voltage.

According to prior research, room temperature molten salts (RTMSs) are potentially safer electrolytes for LIBs due to their chemical and physical properties, such as high thermal stability, ionic conductivity, and wide liquid temperature scale.$^5$ Among various types of RTMS, deep eutectic solvents (DESs), which are composed of ammonium salt and metal salt,$^6$ hydrated salt, or hydrogen bond donor (HDB),$^7$ are suitable for the preparation of LIB electrolytes because of their outstanding compatibility with existing electrode materials.$^8$ Moreover, the high conductivity and stability with no
hydrolysis reaction, low-cost, sustainability, and environmental friendliness. are also the reasons why DESs have gain significant research interests in recent years. Nevertheless, a wider application of DESs still requires further development to overcome their drawbacks, in terms of the limitation on applicable reactions and hygroscopicity.

To evaluate DESs as a new generation of solvents for practical battery applications, enough knowledge on the physical, chemical, and thermodynamic properties are required. Hence, there is still quite a large area of research remaining to be explored.

In the last few decades, substantial research has been done to study and ameliorate the characteristics of DESs. Fang studied the effect of different electrode materials on the properties of DESs. Leron et al. and Yadav et al. claimed that the strength of hydrogen bonding changed with the variety of ambient temperatures. Gajardo-Parra et al. indicated that the density and viscosity of DESs with 1:2 ratio of choline chloride and hydrogen bond donors (i.e., levulinic acid, ethylene glycol, and phenol) decreased with the rise of operating temperature.

Specifically, more features of DESs made of lithium bis[(trifluoromethane)sulfonyl]imide (LiTFSI) and acetamide have been found in prior studies. Boisset’s group reported the change of the compatibility between DESs (prepared from LiTFSI and N-methyl acetamide) and cathode materials. Moreover, it has been found that the higher thermal stability and conductivity of the electrolyte with increasing temperatures can make up for the shortcomings of the decrease in LMO conductivity at high temperatures. Due to wide applications such as agricultural pesticide, chemical catalyst, and nucleophilic reagent, DESs made of 2,2,2-trifluoroacetamide (TFA) meet the demand for recycling and environmental friendliness. Hassoun’s group found that the LIBs with electrolyte composed of LiTFSI and TFA had a promising performance in terms of cycle life and rate capability. However, only a few studies on such DESs exist, especially as electrolytes for lithium-ion batteries.

In this study, the physical/chemical properties of DESs based on the binary mixture of LiTFSI and TFA have been investigated at different mole fraction ratios between the two constituents. The thermal behavior, viscosity, conductivity, and oxidation stability of the prepared DESs were analyzed to select the formulation of suitable electrolytes for lithium-ion batteries application. The selected DES was mixed with ethylene carbonate (EC, %wt) aims to reduce the viscosity of the electrolyte. The hybrid electrolyte was tested with the LMO cathode at room temperature for cycling performance.

2. RESULTS AND DISCUSSION

2.1. Physical Properties of DESs and DES-Based Electrolytes. 2.1.1. Infrared Spectra. When a lithium salt, LiTFSI, and TFA are mixed with an appropriate molar ratio range, a homogeneous liquid mixture is obtained. It is interesting to note that the two solids at room temperature (TFA, Tm = 72.5 °C) and LiTFSI, Tm > 200 °C) can form a liquid solution in a specific composition range. The formulating of the DESs is based on different interactions between the TFA and ions in LiTFSI salt. These interactions affect both the physical properties of DESs and their performance as an electrolyte in Li-ion batteries. First, the withdrawing effect of the trifluoromethyl group in TFA makes the H···bond interaction stronger, as shown in Figure 1, through the schematic representation of the expected DES formula. Second, the presence of the functional groups (C=O and NH2 group) of TFA enables the coordination with cations and anions of LiTFSI, respectively. These interactions weaken the Coulombic interaction between the TFSI anion and Li+ ion in the salt and induce the breaking of the hydrogen bonds between TFA molecules. Baoku et al. reported the same interactions with DESs prepared between the TFA and S111TFSI. Similarly, Hu et al. mentioned the same behavior with DES based on LiTFSI-urea or LiTFSI–acetamide mixtures.

The changes of interactions inside the DES mixture could be analyzed in detail by infrared spectroscopy (IR) using the vibration modes of different functional groups. Figure 2 illustrates the IR spectra of synthesized DES, pure LiTFSI, and TFA.

The vibration mode of N−H stretching significantly increases from 3174 (pure TFA) to 3209 cm⁻¹ (for DES 1:4). Additionally, C=O stretching broadband shifted from 1670 (pure TFA) to 1724 cm⁻¹ (for DES 1.4). In this new configuration, the oxygen atom in the C=O group and F atom in the CF3 group of TFA tends to coordinate with the Li+ cations because O and F atoms are negatively charged. As a result, Li+ cations can strongly interact with these atoms to form a 5-ring complex leading to the blue-shift of C=O and N−H vibration modes. Previously, similar studies reported the large blue shift of C−H stretching upon an F,C,CHO···OHCH3 complex presumably to the electronegative effect of fluorine groups (CF3). Meanwhile, the intramolecular (N−H···O) hydrogen bond is weakened or even broken due to the competitive Li+-···O···F interactions in solution. Hence, it could be concluded that DES was formed by the strong interaction between −CO, −NH, and −CF3 group of TFA precursors with Li+ and TFSI− ions of the lithium salt as evidenced by the formation of new polar bonds.

Additionally, SO2 asymmetric stretching mode of TFSI− anion, νSO2, increases from 1322 to 1351 cm⁻¹ (Figure 2a) and decreases its intensity when increasing the content of TFA, also indicating the formation of new hydrogen bonds at the LiTFSI: TFA ratio from 1:2 to 1:4.

As mentioned earlier, even that DESs are less viscous than ionic liquids (imidazolium, pyrrolidinium, etc.); their viscosity is still quite high as an expected electrolyte in Li-ion batteries. Following our reported strategy, in the present cases, the addition of conventional organic aims at reducing the viscosity and enhancing the ion transport in the electrolyte solution without penalization on the oxidation stability. Figure 3 shows the IR spectra of pure DES 1:4 and the mixtures of DES 1:4 +

**Figure 1.** Schematic representation of the hypothetical polar bond formed between LiTFSI and 2,2,2-trifluoroacetamide.
x %wt. EC. In comparison with pure DES 1:4, the wavenumber of the C═O stretching band increases sharply when carbonate solvent (EC) is added. For example, C═O stretching of TFA appears at 1724 cm⁻¹, while the C═O characteristic bond of pure EC shows at higher wavenumbers of 1778–1809 cm⁻¹ (Figure 3a). When the proportion of the organic solvent increases, the C═O stretching mode shows a blue shift, which is nearer to the C═O mode of pure EC and the peak becomes broader. Based on that, it is reasonable to assume that EC may partially join the LiTFSI-TFA coordination complexes. Additionally, these observations indicate that the addition of organic solvents induces a slight effect on the hydrogen bonds in the DES configuration. Since more carbonate solvents are added, more intermolecular hydrogen bonds are broken due to the dilution phenomenon. Furthermore, the competition between the C═O group (EC) and C═O (TFA) might induce a converted interaction with cation Li⁺ (LiTFSI) or even in the formation of the hydrogen bond. However, in our case, the DESs blended with EC do not show any shifting for both C═O and N═H modes. The hybrid electrolyte with different %wt EC has the same wavenumbers of 1729 and 3309 cm⁻¹. Thus, the addition of EC cannot break down the hydrogen bond in the DES structure but could give rise to weaker bonds between C═O of EC and H of NH₂ (in TFA) or Li⁺ in LiTFSI. In addition, the formation of coordination complexes like [(LiTFSI-TFA)]EC could occur in the mixture.

2.1.2. Thermal Properties of DESs and DES-Based Electrolytes. Regarding the DES formation, the mixing of two solids can generate a new liquid phase by self-association via hydrogen bonds. In general, the freezing point of the new phase is lower than that of the initial, individual constituents. Figure 4 shows a typical result for the studied DESs, obtained by DSC between −100 and 100 °C (also shown here for TFA and LiTFSI precursors). As shown in Figure 4, only one endothermic peak in each DSC curve is obtained when the salt mole ratio ranges from 0.25 to 0.5. The freezing point of the eutectic solvents is about 10–11 °C depending on the composition, which is considerably lower than the melting point of initial LiTFSI and TFA. Furthermore, most DSC curves also show an exothermic peak, which is a devitrification temperature between −80 and −60 °C (similar to the intrinsic plastic crystal), as already mentioned in similar systems.29 Boisset et al. reported the typical eutectic character of the LiTFSI-MAc mixture, having a eutectic point localized at a eutectic temperature of −72 °C (201 K) and lithium fraction close to 0.20. Baoku et al. established a solid–liquid equilibrium diagram of the S₁₁₁TFSI/FMD binary system obtained from DSC thermograms for all mass fractions (0 < ω(FMD) < 1) to characterize the eutectic composition and temperature of DESs. However, they mentioned that most of the systems become solid on freezing, and the exact freezing point is difficult to identify. Thermal decomposition temperatures and percentage of weight loss were also analyzed and recapitulated in Table 1.
Generally, all of the prepared DESs showed relatively higher thermal stability, up to 150 °C, compared to the traditional organic solvents (acetonitrile, carbonate, etc.). This property makes DESs potentially suitable to be used for safe and low-cost batteries. As shown in Table 1 and Figure 5, the mixtures underwent two steps of weight loss, corresponding to the decomposition of TFA and LiTFSI, respectively.

Specifically, the weight loss versus temperature in step 1 of the DESs increases with a decrease in the TFA molar ratio. The result could be explained by the increase of extra hydrogen bond, which is much stronger than intermolecular hydrogen bonds (as demonstrated in Figure 1), thus reducing the heat resistance of the whole DES mixtures.

The impact of the EC content on the thermal properties of DES-based electrolytes was also evaluated by thermogravimetric analysis (TGA) as shown in Figure 6. DES-based electrolytes represent two stages of weight loss despite its mixtures DES 1:4 + % wt EC has three main components (LiTFSI, TFA, and EC). Based on the weight reduction at each stage, the first step is related to the evaporation of EC and the decomposition of TFA as well, while phase 2 at ~400 °C is the decomposition of LiTFSI salt. Although pure EC has a much higher boiling point (230 °C) than that of TFA (154 °C from Table 1), it seems that both EC and TFA start to evaporate or decompose at a lower temperature of ~150 °C (Table 2). This result supports that the interaction between C=O groups of EC and NH₂ of TFA could occur in the mixture. As a result, when the TFA decomposes, the interaction becomes weaker, and the “free” EC will begin to evaporate. It is noticeable that EC increases the Td of electrolytic solutions since more EC molecules are added, the more physical interaction is formed between EC and TFA or LiTFSI.

2.1.3. Transport Properties of DESs and DES-Based Electrolytes. The ion transport property is among the key factors to elucidate the effectiveness of the electrolyte in Li-ion batteries. This property relates to the viscosity and ionic conductivity values of the electrolyte. Low viscosity is mostly preferred to obtain a high ionic conductivity because ionic species can move easily in the free volume of a solution. It is important to wisely choose the H−bond donor and acceptor since they generally strongly affect the viscosity of the DESs. 25 That feature is driven by the structures of the DESs, which determine the nature of intermolecular interactions occurring between TFA and LiTFSI molecules.

The viscosity can be affected by several factors such as the anionic species, their alkalinity, size, relative capacity to form hydrogen bonds, van der Waals interaction, and the size of the cation. 26 Typically, the viscosity of DESs with different LiTFSI: TFA ratios ranges from 59 to 134 mPa s at 30 °C.
The DES viscosity values seem to be closer to those reported for imidazolium-based ionic liquids (ILs) with the TFSI\(^-\) anion but higher than pyrrolidinium cation-based ILs.\(^{31,32}\) As expected, the viscosity decreases along with the increase of TFA in the mixtures due to the decrease of hydrogen bond while the strong electrostatic force (Li\(^+\), TFSI\(^-\)) becomes dominant. Indeed, the presence of a TFA molecule enhances the dissociation capability of LiTFSI and allows better ionic mobility. Hence, the facile movement of ions not only increases the free volume or the void’s volume but also limits the packing of the molecule arrangement. Moreover, according to Figure 7, the viscosity ($\eta$) for DESs diminishes logically when the temperature rises from 30 to 60 °C. This strong decreasing effect is due to the higher mobility of ions when the hydrogen bonds are broken. Indeed, the viscosity is mainly attributed to the intermolecular hydrogen bonding (N–H···O), which can be affected by the temperature increase.

The change in viscosity with temperature obeys the Vogel–Tamman–Fulcher equation (VTF, which implies a solvent-assisted viscous flow mechanism, likely in the case of ionic liquid). It may be able to explain the variation in viscosity during the temperature increase by a decrease in the interaction in the mixture between Li\(^+\), TFSI\(^-\) ions, and TFA molecules driven by the hydrogen bonds. Moreover, at high temperatures, this hydrogen bond is preferably replaced by the weaker intra one between TFA molecules.\(^{33}\)

DES-based electrolytes expectedly showed a much lower viscosity than the pure ones. The addition of 10 %wt or 20 % wt EC did not much change the viscosity value of DES 1:4. This observation is coherent with the IR results, which confirm that the presence of EC could not break down the hydrogen bonds between TFA and LiTFSI. Oppositely, the EC addition induces an increase in free volume by a dilution effect of the mixture and somehow weakens the strong hydrogen bonding by the interaction between EC and LiTFSI or C═O (EC) with NH\(_2\) (TFA).

In Figure 8, the ionic conductivity of DES 1:4 at 333 K is 3.71 mS cm\(^{-1}\), which is relatively lower than that of DES formed by LiTFSI-MAc (5.59 mS cm\(^{-1}\)), but quite similar to that of LiNO\(_3\)-M Ac (3.25 mS cm\(^{-1}\)).\(^{2}\) The difference in conductivity between DES (LiTFSI-MAc) and (LiTFSI-TFA) may be due to lower mobility of Li\(^+\) cation in the solution because of the interaction with the fluorine group. At room temperature, our DES 1:4, DES from LiTFSI-acetamide 1:4, and LiTFSI-based ionic liquid demonstrate relatively the same value of ionic conductivity (1.53, 1.07, and 1.91 mS cm\(^{-1}\), respectively)\(^{26,34}\).

Contrary to the viscosity, the ionic conductivity of DESs systematically increases with the increased amount of the “transport solvent” TFA in the mixture. It was reported that the NH\(_2\) group of TFA enables the coordination with cations and anions and acts as a complex agent, which stabilizes both

| Table 3. Density, Ionic Conductivity, and Viscosity of DESs and DES-Based Electrolytes at 30 °C |
|---|
| electrolytes | d (g/cm\(^3\)) | $\sigma$ (mS/cm) | $\eta$ (cP) |
| DES 1:2 | 1.650 | 0.26 | 134.0 |
| DES 1:3 | 1.601 | 0.77 | 120.1 |
| DES 1:4 | 1.539 | 1.53 | 59.2 |
| DES 1:4 + 10 %wt EC | 1.527 | 1.86 | 30.5 |
| DES 1:4 + 20 %wt EC | 1.513 | 2.59 | 28.6 |
| DES 1:4 + 30 %wt EC | 1.509 | 3.49 | |

Figure 7. Evolution of the viscosity, $\eta$, of the DESs and DES-based electrolyte. The curve serves as a guide to the eye.

Figure 8. Arrhenius plots of conductivity versus temperature of (a) DES mixtures and (b) DES-based electrolytes. The curves serve as a guide to the eye.
Li\(^+\) and TFSI\(^-\). In addition to the fact that Li\(^+\) generally solvates 4–6 solvent molecules, the more TFA present, the more easily LiTFSI dissociates and the higher the conductivity due to the formation of a hydrogen bond.\(^{27}\)

Similar to viscosity, the evolution of the conductivity of DESs and DES-based electrolyte in a temperature range from 30 to 60 °C also followed VTF law because the Arrhenius equation fitting (according to eq 1) has a curve profile.

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{R T} \right)
\]

\[
\sigma = \sigma_0 \times \exp \left[ \frac{-E_a}{R(T - T_0)} \right]
\]

\[\Leftrightarrow \ln \sigma = \ln \sigma_0 - \frac{B}{T - T_0}\]

The Vogel–Tamman–Fulcher equation (VTF equation) (eq 2) is proposed to determine the correlation between respected temperature versus conductivity of electrolytes. The regression lines from eq 2 perfectly show a linearity behavior (Figure 9). This implies a solvent-assisted ionic conduction mechanism, which may be originated from the strong interactions between LiTFSI and TFA.

Table 4 shows all VTF equation parameters for the temperature-dependence conductivity \(T_0\) of DESs and DES-based electrolytes. The term \(B\) can be linked to the energy barrier that needs to overcome for the species in DESs to move past each other. The smaller the \(B\) values, the easier it is for the ions to move and past each other. Moreover, this value can be associated with the salt structure and the hydrogen-bond donor molecule. Herein, the opposite trend between the viscosity and ionic conductivity was observed, whereas the \(B\) value slows down increase of the TFA concentration. Therefore, as the same peak as other reports in the literature.\(^2\), \(^4\), \(^35\) TFA combined with LiTFSI is expected to be stable in oxidation due to the trifluoroacetate group in TFA. In Figure 10, the oxidation potential of the as-synthesized DESs was determined by cyclic voltammetry (CV) technique at a scan rate of 1 mV s\(^{-1}\).

As seen in Figure 10, the oxidation current decreases in order: DES 1:4 (75 \(\mu\)A), DES 1:3 (28 \(\mu\)A), and DES 1:2 (15 \(\mu\)A). The oxidation resistance of DESs decreases with the increase of the TFA concentration. Therefore, as the same current density, DES 1:2 has the highest oxidation limit since it has the lowest TFA concentration. Overall, the oxidation stability determined at the current of 10 \(\mu\)A was approximately 5.0 V versus Li/Li\(^+\); which is proven to be more compatible with high voltage cathodes than typical organic solvents, such as EC-DMC (1:1) + 1 M LiTFSI (Table 5).

Regarding DES-based electrolytes, the elevation of the EC content decreases oxidation resistance since the excess “free EC” or EC weakly coordinated other molecules quickly initiates the oxidation under high electric force (high voltage, >4 V vs Li/Li, Figure 10b). Among DES-based electrolytes, the DES 1:4 + 10 \%wt EC with the highest stability oxidation

| Electrolyte | \(T_0\) (K) | \(\sigma_0\) (mS/cm) | \(E_a\) (J/mol) | \(R^2\) |
|-------------|-------------|---------------------|----------------|--------|
| DES 1:2     | 205         | 59.06               | 4418           | 0.990  |
| DES 1:3     | 204         | 24.75               | 2899           | 0.989  |
| DES 1:4     | 200         | 75.26               | 3388           | 0.996  |
| DES 1:4 + 10 \%wt EC | 199\(^a\) | 90.21               | 3230           | 0.996  |
| DES 1:4 + 20 \%wt EC | 198\(^b\) | 82.32               | 2834           | 0.991  |
| DES 1:4 + 30 \%wt EC | 198\(^b\) | 114.33              | 2884           | 0.999  |

\(T_0\) is the glass-phase transition temperature from DSC curve \(E_a\) is calculated from the equation: \(E_a = \frac{B}{T - T_0}\).
(4.932 V vs Li+/Li) was selected for further testing with LMO cathode materials.

2.2.2. Charge/Discharge Performance at Room Temperature in Half Cells with LMO Cathode.

The electrochemical behavior of LiMn$_2$O$_4$ in non-aqueous lithium electrolyte is widely reported. The electrochemical reaction of LMO is represented as Li$_{1-x}$Mn$_2$O$_4$ (s) + xLi$^+$ + xe$^-$ $\rightleftharpoons$ Li$_{1-x}$Mn$_2$O$_4$ (s), which involves the diffusion of lithium-ion and the kinetics of electron transfer, the two key factors determining the performance of the cells. Electrochemical properties of DES-based electrolytes were tested in half-cell configuration of Li/Li$^+$ and LMO cycling between 3.2 and 4.5 V (vs Li+/Li).

Figure 11 visualized the electrochemical kinetics of lithium-ion insertion/extraction during the charge/discharge process through the evaluation of the lithium diffusion coefficient characterized by cyclic voltammetry at various scan rates from 0.015 to 0.1 mV s$^{-1}$. Noting that the non-Faradic current is negligible than the Faradic one, so the background current is very low and smooth. Typical two well-defined redox peaks corresponding to the oxidation/reduction couple of Mn$^{4+}$/Mn$^{3+}$, corresponds to the two processes during which lithium ions were embedded in and removed from the lattice of LMO. As the scan rate is varied, the shifting of the double peak could be observed due to the change in reaction kinetics, whereas the ion-diffusion or charge transfer is dominant. Generally, the higher current of the peak relates to the fast charge transfer reaction at a high scan rate. More specifically, the sharp peak feature and a very smooth current background indicate the good compatibility with the LMO cathode without the background current.

| mixtures                        | $E_{\text{anode}}$ vs Li$^+$/Li (V) |
|---------------------------------|-----------------------------------|
| DES 1:2                         | 5.33                              |
| DES 1:3                         | 5.15                              |
| DES 1:4                         | 4.95                              |
| EC-DMC (1:1) + 1 M LiTFSI       | 4.57                              |
| DES 1:4 + 10 %wt EC             | 4.93                              |
| DES 1:4 + 20 %wt EC             | 4.92                              |
| DES 1:4 + 30 %wt EC             | 4.83                              |

Figure 11. CV curves of LMO cathode in the potential range 3.2–4.5 V (vs Li$^+$/Li) at various scan rates $\nu = 0.015–0.1$ mV/s: (a) DES 1:4 + 10 %wt EC and (b) DES 1:4 + 20 %wt EC.
any side reaction between the electrode—electrolyte within the working potential range.

The diffusion coefficient \( (D_{Li}) \) values were calculated from the slope of \( I_{pa} \) (or \( I_{pc} \)) versus \( v^{1/2} \) plot, using Randles–Sevcik equation

\[
I_p = 0.4463nFAC \left( \frac{nF}{RT} \right)^{1/2} \theta^{1/2}D^{1/2}
\]

(where \( n \) = number of electrons, \( F \) = the Faraday constant, \( A \) = electrode area, \( C \) = concentration, \( R \) = gas constant, \( T \) = temperature, \( \theta \) = scan rate, and \( D \) = diffusion coefficient). The scan rates used were between 0.015−0.1 mV s\(^{-1}\). We also assumed that the lithium concentration in LMO is approximately 2.434×10\(^{-2}\) mol cm\(^{-3}\), and \( D \) values are given in Table 6.

![Figure 12](image)

**Figure 12** (a−d) shows the discharge—charge profile and cycling performance of Li//LMO half-cell in DES 1:4 with 10 %wt EC and 20 %wt EC at room temperature. In Table 7, the first cycle discharge capacity approached 70% of the theoretical value for DES 1:4 + 10 %wt EC, while only 42% of the capacity value was obtained for DES 1:4 + 20 %wt EC. Moreover, the Coulombic efficiency was as high as 84% for DES 1:4 + 10 %wt EC, which is comparable to the conventional electrolyte for the first cycle. Unfortunately, the discharge capacity of DES-based electrolytes shows an unstable trend during cycling. Using a higher EC content leads to a severe decrease in discharge capacity and Coulombic efficiency as well. Electrolyte DES 1:4 + 10 %wt EC exhibited the capacity value of 102 mAh g\(^{-1}\) which is comparable with the value obtained in the case of the ionic liquid-based electrolyte N\(_{1123}\)TFSI + 0.25 M LiTFSI + 20 % wt EC (≈100 mAh g\(^{-1}\)).

This unstable performance might stem from the relatively high viscosity of the electrolytes and the lower ionic conductivity, comparing to the conventional electrolytes. These factors are an obstacle, including a barrier to prevent the smooth and reversible lithium-ion transport, and hence the lithium insertion/extraction process through the DES electrolyte was unfortunately affected. In addition to that, the dilution
of DESs should be considered on the physical nature of the solvent to explain its side effect. In the present case, owning the high dielectric constant ($\varepsilon = 92$ at 298 K), EC can solvate very well lithium ions and stabilizes the solvated ions in competing with other molecules in the DES solution. Interestingly, the solvated ions constitute not only EC-Li+ but also the relatively big ones, such as the complex EC-TFA/Li+ (found in IR spectra), which move slowly under the electromagnetic field. Moreover, it is hard to remove the solvated shell surrounding Li+ ion to activate the intercalation process of Li+ into the LMO cathode. Consequently, the cell resistance and polarization significantly increase after each cycle. Briefly, the Li+ ion mobility determines the stable performance of lithium-ion batteries but extremely depends on the transport properties of ions inside the electrolyte. More precisely, the different types of interactions (hydrogen bond, dipole-ion, or van der Waals interaction) could compete and weaken the electrostatic force between ions, which helps enhance the ion mobility. However, the presence of coordinated complexes (relatively big solvates) must require higher activation energy than the available energy of the electrolyte–electrode interphase to break the physical bonding and release the Li+ ion for insertion/extraction. As a result, it consumes electric energy from the external source, reduces the charge efficiency, and finally decreases the cells’ performance significantly. So far, we could not study the cycling performance of cells consisting of DES-based electrolytes with more than 20 %wt EC at room temperature. Even in the first cycle, the irreversible capacity is so high, thus leading to an incomplete discharge.

Further studies will be focusing on the use of diluent solvent without any solvation phenomena with LiTFSI, such as bis(2,2,2-trifluoroethyl) ether (BTFE) and 1,2,2,3,3-pentafluoropropyl ether (TTE), which were reported for localized high concentrated electrolytes to decrease the viscosity and enhance high rate capability performance.39,40

3. CONCLUSIONS AND PERSPECTIVES

The formulation of DESs was successfully confirmed by IR spectroscopy and DSC, indicating the formation of intermolecular hydrogen. The synthesized DESs with varied constituents’ ratio showed the eutectic point at about 10 °C with only $X_{LiTFSI} = 0.25–0.5$. It was found that DESs exhibited a relatively high electrochemical stability (~5.2 V vs Li+/Li) and high thermal stability (148 °C). However, the higher viscosity of DESs leads to lower conductivity compared to the commercial electrolytes. DES 1:4 with the highest conductivity (1.5 mS cm$^{-1}$ at 30 °C) was selected for further testing as an electrolyte in Li/LiMn$_2$O$_4$ half-cell by mixing with 10–20 %wt of EC to decrease apparent viscosity and increase ionic conductivity.

In comparison with the DES 1:4, DES-based electrolytes demonstrated: (i) a negligible effect in DES configuration at low content of EC from IR spectroscopy; (ii) the relatively lower thermal stability and oxidative strength compared to pure 1:4 DES. However, viscosity and conductivity were improved when increasing the content of EC; (iii) the favorable lithium-ion insertion/extraction in DES-based electrolyte with two well-defined reversible redox peaks; (iv) in terms of electrochemical performance, the peak of DES 1:4 + 10 %wt EC during discharge displays a capacity of around 102 mAh g$^{-1}$ and remains at 84% efficiently after 20 cycles. Our future work will be focusing on different types of diluents to reduce the viscosity without any solvation effect or participation in physical bonding.

4. EXPERIMENTAL SECTION

4.1. Preparation of DESs and DES-Based Electrolytes.

Chemical reagents including lithium bis[(trifluoromethane)-sulfonyl]imide (LiTFSI, 99.9%), 2,2,2-trifluoroacetamide (TFA, ACS reagent, 98%), ethylene carbonate (EC, 99%), and dimethyl carbonate (DMC, 99%) were purchased from Sigma-Aldrich and stored in an argon-filled glovebox (MBraun, USA). The solid reagents, namely, TFA and LiTFSI, were opened and dried in the antechamber of the glovebox overnight at 120 °C before using for DESs synthesis. The preparation of the DESs was performed inside the glovebox with water and oxygen concentration controlled below 5 ppm.

The solid precursors, LiTFSI and TFA (with the respective molar ratios: 1:2, 1:3, 1:4, and 1:5), were mixed and stirred at 80 °C (at a speed of 150 rpm) for at least 8 h to obtain homogeneous and transparent solutions. The DESs prepared in this work are referred to as DES followed by the molar ratio of LiTFSI/TFA. For instance, DES 1:4 was prepared from the molar ratio of LiTFSI: TFA (1:4). The selected DES was then diluted with $x$ %wt EC amount ($x = 10–30$ %wt) to form DES-based electrolytes.

4.2. Preparation of Cathode Material.

The slurry of LiMn$_2$O$_4$ (LMO) cathode was prepared by mixing different components: solid LiMn$_2$O$_4$ (MT1), powder super P carbon (Timcal, Switzerland), and a binder solution of 10 %wt poly(vinylidene fluoride) (PVdF, 99%, Sigma-Aldrich) in the weight ratio of 80:15:5, respectively. The solvent N-methyl-2-pyrrolidone (NMP, Merck, 99%) was used to disperse the mixed powder and was added to obtain 70 %wt solid content. The prepared wet slurry was then directly cast on aluminum foil and vacuum dried at 80 °C for 15 h. The cathode sheet was punched into 14 mm diameter round discs for coin cell assembly. The mass loading is about 2.5 mg/cm$^2$.

4.3. Characterization.

DESs based on the mixture of TFA and LiTFSI is formed by the interaction between a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HAC). Hence, the formation of DESs could be monitored by hydrogen bonding characteristics via infrared spectroscopy (IR) using FT/IR-6600 spectrometer in the wavenumber ranging from 500 to 4000 cm$^{-1}$. The TGS detector was utilized to detect the reflected light. After the triangular apodization, the spectral resolution was 8 cm$^{-1}$, and the scanning speed was 2 mm$^{-1}$.

Electrolyte viscosity measurement was carried out with a Brookfield DV2 ProViscometer using a conical geometry, which was automatically regulated by a thermostat bath for temperature control. The DES-based electrolyte was put directly in the closed sample holder and the temperature was stabilized for 10 min before measuring. The uncertainty of viscosity measurement did not exceed ±1%.

Ionic conductivity of electrolytes was calculated through electronic resistance measured by AC impedance spectroscopy using a multichannel potentiostat instrument (VSP-3, Biologic, France) in the frequency range of 10 Hz−1 MHz. DESs electrolyte was put into the dip-type glass cell with two Pt electrodes fixed at a constant distance. During the experiments, the temperature was monitored to increase gradually from 25 to 60 °C with an accuracy of ±2 °C. The uncertainty for the viscosity did not exceed ±0.02 °C. A precise 0.100 M KCl solution was used as the reference.
solution was utilized to calibrate the cell constant. Collected data and linear regressions were visualized via Kaleida Graph version 4.03 (2006).

Thermal properties of DES-based electrolytes were evaluated by thermogravimetric analysis (TGA) on the LABSYS Evo instrument. All the measurements were performed in the temperature range from 0 to 600 °C with a heating rate of 10 °C·min⁻¹ under the nitrogen atmosphere. Differential scanning calorimetry (DSC) measurement was carried out on a Perkin-Elmer DSC 4000 coupled with an Intercorder SP VLT 100 under a nitrogen atmosphere. Samples for DSC measurements were sealed in Al pans. Each DSC measurement was repeated three times for productivity.

The electrochemical window of DESs and DES-based electrolytes were estimated by cyclic voltammetry (CV) technique on a multichannel potentiostat (MGP2, Biologic, France). A three-electrode cell was used for CV measurement, including a nickel counter electrode, a platinum working electrode, and a silver wire dipped in a solution of AgNO₃ 10 mM in acetonitrile +0.1 M tetrabutylammonium perchlorate (TBAP) which was used as the reference electrode (E = 3.548 vs Li⁺/Li). The voltage range for the CV study is from 3.5 to 6.0 V, which is converted versus Li⁺/Li.

The cycling test was performed by using a 2032-type coin cell assembled in an argon-filled glovebox. Coin cells are consisted of LMO cathodes, Li anodes (14-mm diameter), glass microfiber (Whatman, GF/C, 50 μm) separators, and DES-based electrolytes. Charge/discharge cycling was evaluated by using a constant current in the voltage range of 3.5–4.3 V at the rate of C/10 on a 16-channel MGP2 (Biologic).

Lithium-ion intercalation/deintercalation kinetics was also studied using Swagelok two-electrode cell with an LMO cathode and a Li anode. Cyclic voltammetry was performed at different scan rates: 0.1, 0.08, 0.05, 0.02, and 0.015 mV/s in the potential range of 3.2–4.6 V at room temperature.

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