

Research Article

Carbonate Solvents and Ionic Liquid Mixtures as an Electrolyte to Improve Cell Safety in Sodium-Ion Batteries

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Ionic liquid-based electrolytes proved to be effective in terms of alleviating the safety problems associated with lithium/sodium ion batteries, especially for large-scale applications, due to their superior thermal stability and nonflammability. The main disadvantage of ionic liquids is their relatively high viscosity. Adding a suitable amount of organic “thinning” solvents could be a potential solution for this problem: while the electrolyte viscosity is greatly reduced, the electrochemical properties and thermal stability remain almost as good as those of pure ionic liquid. In this study, electrolyte mixtures based on 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) (EMI-TFSI) and carbonate solvents (EC-PC) were prepared. The electrochemical compatibility in half-cell configuration with respect to sodium metal anode of various electrode materials, including SnS/C, hard carbon (HC), and Na_{0.44}MnO₂, was evaluated. Moreover, the thermal stability, the flammability, and the conduction mechanism of such electrolyte mixtures were also explored and discussed.

1. Introduction

Li-ion batteries (LIBs) have been widely used in portable devices due to their high-voltage and high-energy density characteristics. Although LIBs are considered one of the most potential contenders for automotive application, there are still some limitations regarding lithium battery safety, lifetime, cost, and poor low-temperature performance [1–7]. In fact, the concern about lithium shortage for large-scale applications and the continuously increasing price of lithium carbonate have driven researchers to investigate alternative battery technologies for large-scale application (stationary storage or future electric vehicles). Sodium technology, with the positive attributes of sodium including high abundance, easy recover, and nonalloying toward Al, has recently attracted great attention of scientists. Furthermore, the chemical similarities between Na and Li allow the comprehensive knowledge about LIBs to be applied successfully

to sodium cells, making Na-ion batteries (NIBs) competitive to Li-ion batteries in the cell market [8–10]. Eftekhari [11] also mentioned that the target-specific energy/energy density of future commercial sodium-ion battery (NIB) is only 20% lower than that of LIBs.

However, the performance of NIBs is currently insufficient for commercialization because Na-based chemistry has not been thoroughly explored. In other words, the main challenge of NIB is still the lack of well-rounded electroactive materials for Na⁺ hosting on both sides (anode and cathode) [11]. Additionally, the large size of Na⁺ ion (compared to that of Li⁺) strictly limits both the kinetics of sodium diffusion in electrodes and the formation of an effective solid-electrolyte interphase (SEI film), which are the main reasons for poor high-rate charge-discharge performance of NIBs [10, 12]. Further studies on electrode materials, electrolytes, electrode-electrolyte interface, and in-depth intercalation mechanism, with a

special focus on overall battery safety, are requisite to improve the behavior of NIBs [13–15]. Safety risk typically derived from organic electrolytes with poor thermal stability, high flammability, and low heat capacity [16, 17]. Besides, there are also environmental problems associated with such electrolytes due to their volatility and toxicity [18, 19].

Ionic liquids (ILs) or molten salt liquids contain only ionic species. These salts are liquid below 100°C. In the context of batteries, this term implies room-temperature ionic liquid. The unique combination of favorable properties such as intrinsic ionic conductivity, wide electrochemical window, excellent thermal stability, nonvolatility, and nonflammability renders ionic liquids (ILs) a very attractive and promising candidate to replace the traditional carbonate electrolytes in rechargeable cell [20–22]. However, they also have disadvantages: high cost, low conductivity, high viscosity, and poor wetting characteristics with some electrodes due to high contact angle.

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMI-TFSI) with relatively high ionic conductivity of $1.06 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ and low viscosity at room temperature could be potentially applied to NIBs as earlier reported for lithium-ion cell [23–25]. Furthermore, EMI-TFSI is attractive because of its high oxidation stability limit ($>5.0 \text{ V}$ vs. Na^+/Na); and even though its reductive potential is relatively positive compared to sodium anode (associated with the reduction of EMI^+), so far, this potential value still allows good adaptability with most carbon-based anode materials in NIBs. The interest in ILs for Li-ion batteries is based on the perfluoro anions as counter-ions for lithium salts: BF_4 and TFSI. This finding was extended to the use of mixtures of ILs and organic electrolytes (EC-DEC, PC, DMC, etc.) to take advantage of both the low vapor pressure coupled with nonflammability of ILs and the high conductivity of organic electrolytes [2, 24–30]. A thorough study on ILs using EMI-TFSI ionic liquid/EC-DEC mixtures at different concentration of EMI-TFSI was reported. It was found that at 60% IL, the mixed electrolyte demonstrated optimum performance ability to cycle smoothly in LiFePO_4 half-cell at 2C rate.

Inspired by that work, we investigated the electrochemical properties of different electrode materials: SnS/C, hard carbon, and $\text{Na}_{0.44}\text{MnO}_2$ in ionic liquid-carbonate (EC-PC = 1:1 in vol.) mixed electrolyte. NaTFSI salt and fluoroethylene carbonate (FEC) were added to suppress the ILs reduction and facilitate the SEI stabilization, which greatly enhances the Na^+ transport ability and cycling performance of batteries.

2. Experimental Setup

2.1. Preparation of Cathode Materials and Ionic Liquid Electrolytes. EMI-TFSI (Sigma-Aldrich, 99.8% purity) was purified by column chromatography before being used as an electrolyte in NIBs. After purification, ionic liquids (ILs) were vacuum-dried at 100°C for 12 h and stored in a glove box ($[\text{H}_2\text{O}] < 3 \text{ ppm}$). The water content of all ILs (determined by Karl Fisher titration) is below 20 ppm. The structure of ILs was confirmed by ^1H NMR, ^{13}C NMR, and mass spectroscopy. NMR spectra were measured in DMSO-

d_6 or acetone- d_6 , on a Bruker 500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C). Mass spectra were recorded via GC-MS and LC-HR-MS techniques. GC-MS analyses were performed on an Agilent GC System 7890A, equipped with a mass selective detector Agilent 5973 and a capillary column HP-5MS (30 m \times 0.25 mm \times 0.25 μm). LC-HRMS analyses were performed on a Bruker MICROTOF-Q II (for supporting information details, refer to [22]).

All battery-grade carbonate solvents including ethylene carbonate (EC), propylene carbonate (PC), and fluorinated ethylene carbonate (FEC) were purchased from Sigma Aldrich and used without further purification. EMI-TFSI was mixed with carbonate solvents EC-PC at different weight percentages (10, 20, 30, 40, and 50 wt.%). FEC (2 wt.%) was also used as an additive. These mixtures were prepared in a glove box and used as electrolytes for investigating physicochemical and electrochemical properties of NIBs. NaTFSI salt (99 wt.%, Acros) after dried in a vacuum oven for 15 hours at 80°C was dissolved into the mixed ionic liquids to promote sodium-ion conduction. Upon preparation, all mixtures were continuously stirred with a magnetic paddle for 24 h to ensure uniformity.

2.2. Cell Assembly. Cathode mixture of synthesized $\text{Na}_{0.44}\text{MnO}_2$ (NMO) powder, acetylene black (Timcal, Swiss) and PVdF-HFP binder (Sigma-Aldrich) dissolved in *N*-methyl pyrrolidone (50 mg/ml) with the weight ratio of 80:15:5, respectively, was prepared, coated onto technical Al foil, and dried in vacuum oven at 80°C for 15 hours. Anode mixture of active material, hard carbon (HC) (KUREHA, Japan) or SnS/C (synthesis reported elsewhere [31]), acetylene black, and PVdF-HFP binder (Sigma-Aldrich) with the weight ratio of 90:5:5, respectively, was prepared and then coated onto Cu foil. After drying in a vacuum chamber at 80°C, the thin electrode films were cut into 15 mm diameter round shapes. CR2032-type coin cells using sodium metal foil (Aldrich, battery grade) as anode, Whatman microfiber membrane as separator, and as-prepared thin films (HC, SnS/C or NMO composite) as cathode were assembled in glove box under argon flow.

2.3. Physicochemical and Electrochemical Characterization. Thermogravimetric analysis (TGA) measurements of mixed electrolytes were carried out on a TGA Q500 V20.10 Build. A few milligrams of the sample were heated from room temperature up to 800°C at $10^\circ\text{C}\cdot\text{min}^{-1}$ in nitrogen flow.

Ionic conductivities of the electrolytes were determined by using dip-type glass cell with two Pt electrodes fixed at a constant distance. The conductivity cell was connected to an HP 4192A impedance analyzer, and the electrolyte impedance values in the frequency range of 5 Hz–13 MHz were measured. For equilibrating the temperature, the glass cell was placed in a controlled-temperature chamber and left undisturbed for 180 minutes at each heating step. The cell constant was determined by using 0.01 M KCl solution. The viscosity of IL-based electrolytes was measured by using the Ostwald CANNON viscometer in a temperature-controlled bath.

The temperature dependence of ionic conductivity can be fitted using Vogel–Tammann–Fulcher (VTF) type equation to obtain the pseudo-activation energy. It is common for researchers to utilize the Vogel–Tammann–Fulcher (VTF) equation as a means to separate the effects of charge carrier concentration, often related to the prefactor, A , and of segmental motion, related to the activation energy, E_a , on the overall conductivity, σ , at a given temperature T [32].

$$\sigma = A \cdot \exp\left(-\frac{E_a}{R(T-T_0)}\right), \quad (1)$$

where T_0 is the reference temperature and is usually close to the glass transition T_g in ideal glasses [33] but might be taken as 50°C below the glass transition temperature in several electrolytes.

The flammability of the organic solvents, IL-based electrolytes, and commercial electrolytes was tested under air. Each sample was prepared by soaking glass fiber into a fixed weight of an electrolyte. The distance between the sample and burner is 15 cm. The fire was retained for 5 seconds, and after that, the self-extinguishing time was recorded. All self-extinguishing time values were then normalized against sample mass.

Cyclic voltammetry of pure ILs and ILs-solvent mixtures was recorded at the scan rate of 1 mV·s⁻¹ on MGP2 Biologic Instrument (France) using a three-electrode cell. The counter electrode was a Pt wire and the working electrode was a Pt microelectrode with the diameter of 25 μm. The reference electrode was a silver wire in the solution of 10 mM AgNO₃ + 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile.

Cycling test was done on a 16-channel Biologic MGP2 using CR2032-type coin cell in half-cell configuration with sodium metal as anode. The charge-discharge rate was C/10 at 25°C maintained using a controlled-temperature chamber. The operational potential range is varied for each kind of electrode materials.

3. Results and Discussion

3.1. Thermal Stability. Pure EMI-TFSI has low melting temperature of -18.5°C and excellent thermal stability (the onset decomposition starts at 358°C [34]). Therefore, the introduction of EMI-TFSI as a cosolvent to EC-PC (1:1) mixture are aimed to enhance the thermal stability and oxidation potential limit of carbonate-based electrolytes, and it should not impose any penalty on the ionic conductivity.

Figure 1(a) shows the TGA curves of all as-prepared electrolytes. All mixtures, regardless of their EC content, underwent 2 stages of decomposition. The initial weight loss corresponds to vaporization of carbonate-based solvent molecules, notifying the weak EC-ILs interaction and free EC vaporized under temperature flux. However, compared to pure EC or EC-PC mixture, which starts evaporating at around 120–130°C, the evaporation temperature of EMI-TFSI-EC mixtures shifted to a higher value, more than

170°C. At the highest EMI-TFSI concentration (50 wt.%), the highest evaporation temperature and the lowest weight loss were obtained (Figure 1(b)). The second step is in accordance with the decomposition of ionic liquid, which originates from the reduction in ionic interaction between cation and anion. That being said, EMI-TFSI-based electrolytes show almost no sign of the second weight loss up until 350°C. This confirms the high thermal stability of EMI-TFSI (Figure 1(a)). The presence of EC does not have a negative effect on the thermal stability of the pure ionic liquid phase. Kühnell et al. [35] when studying the mixed electrolyte Py₁₄TFSI-propylene carbonate (PC) + 0.3 M LiTFSI at different amounts of PC also reported similar results.

3.2. Flammability Test. To clarify the safety of ionic liquid-based electrolytes and get more evidence of the thermal stability enhancement induced by ionic liquid, the flammability test was carried out (Figure 2). EMI-TFSI produced only small flare-ups that immediately extinguished after removed from the burner (Figure 2(g)). Table 1 gives an evidence of the flame-inhibition effect induced by the addition of IL. The minimum amount of EMI-TFSI needed to observe the flame-inhibition effect was about 20 wt.%, whereas at 40 wt.% EMI-TFSI, the igniting ability of electrolytes was reduced considerably. In agreement with our results, An et al. [34] reported that while the combustion of organic electrolytes occurred within the first second of the ignition, mixed electrolytes did not catch fire even after more than 10 s of flame exposure. However, the SET values follow the opposite tendency: the greater the IL content in the sample, the greater the time it takes for the flame to self-extinguish. Indeed, the SET value of the sample with 10 wt.% IL (55 s·g⁻¹) is higher than that of pure EC-PC + NaTFSI (51 s·g⁻¹). In brief, although IL-rich mixture is more difficult to ignite, they keep burning for a longer time once they are ignited.

The results can be explained by the fact that the combustion of IL was assisted by igniting EC-PC vapors. The appearance of the glass fiber mats after the flammability tests gave evidence of ILs combustion. The flame completely burned the EC and PC vapors without leaving any carbon vestige on the mat surface, as seen with the EC-P + 1 M NaTFSI sample (Figure 2(a)). By contrast, the samples soaked in the IL-based electrolytes produced apparent carbon traces on the surface due to a slow, oxygen-poor combustion of the IL triggered by the organic electrolyte: the more the IL in the mixture, the more the carbon formed (Figure 2(f)). At these high temperatures, most of the organic electrolyte evaporates and the vapors was burned and continued to burn even after the burner was switched off [31, 36].

3.3. Ionic Conductivity. The evolution of ionic conductivity in the temperature range of 20–80°C for all considered electrolytes is reported in Figure 3. In general, ionic liquids display a relatively high viscosity, which even increases with the addition of the Na-salt. The ionic conductivity of the

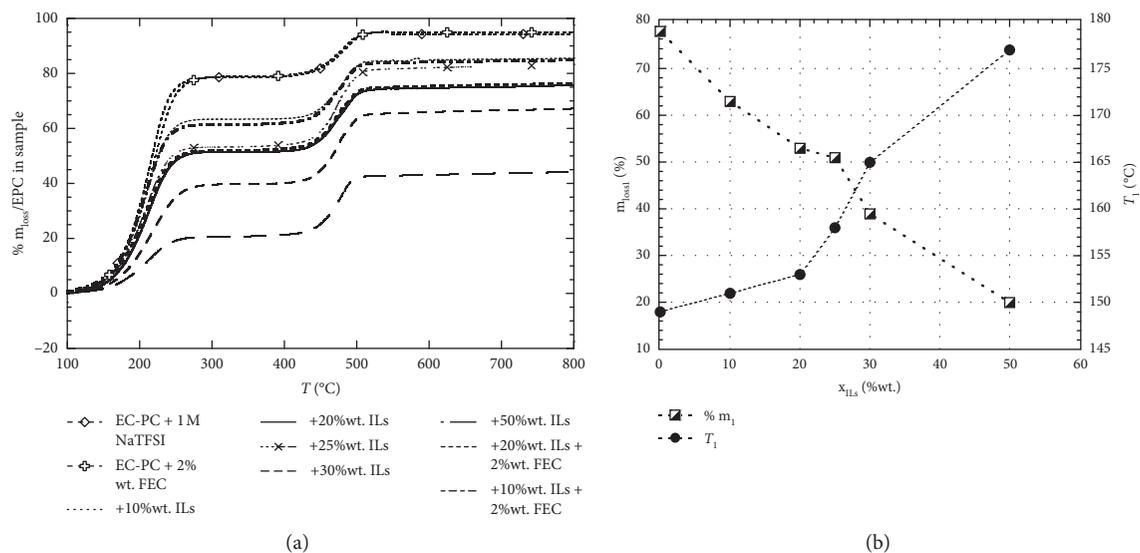


FIGURE 1: TGA diagrams of EC-PC (1 : 1) + x wt.% EMI-TFSI (a) and the evolution of 1st degradation temperature and 1st weight loss of the mixtures (b).

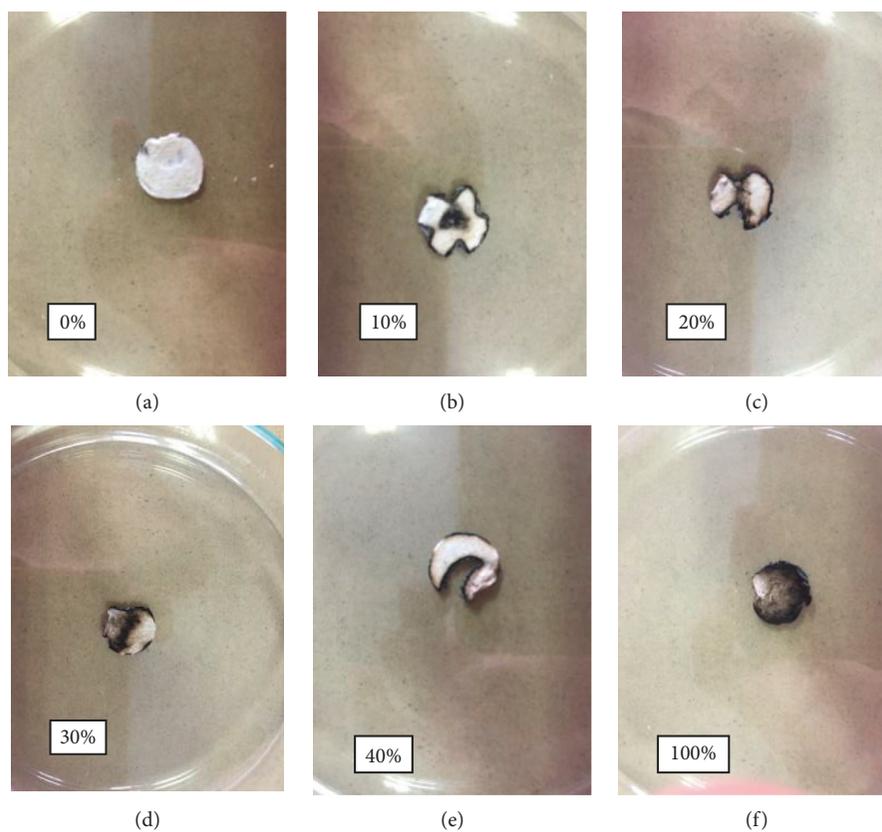


FIGURE 2: Continued.



(g)

FIGURE 2: (a–f) Glass fiber mat after flammability tests of the mixed solutions at wt.% of EMI-TFSI in EC-PC (1 : 1) with 1 M NaTFSI; (g) IL during exposure to flame.

TABLE 1: The mean values of the self-extinguishing time (SET) of several mixtures of IL and EC-PC (1 : 1) with 1 M NaTFSI.

Electrolytes	Self-extinguishing time ($s \cdot g^{-1}$)
EC-PC + 1 M NaTFSI	51
EC-PC (1 : 1) + 10 wt.% IL + 1 M NaTFSI	55
EC-PC (1 : 1) + 20 wt.% IL + 1 M NaTFSI	58
EC-PC (1 : 1) + 30 wt.% IL + 1 M NaTFSI	65
EC-PC (1 : 1) + 40 wt.% IL + 1 M NaTFSI	71
Pure IL	106

complex electrolytes decreased with increasing IL amount due to the dominance of viscosity factor.

Additionally, the excessive increase in the concentration of ionic species in complex electrolytes has raised strong ion-ion interactions instead of weak ion-dipole and dipole-dipole interactions. Thus, a suitable amount of added ionic liquid should be chosen to compromise the ionic conductivity and the thermal stability of mixed electrolyte. Besides, temperature also has considerable contribution to viscosity and conductivity values. The increase in temperature draws the decrease in viscosity and the rise of ionic mobility, thus leading to enhanced conductivity.

The temperature dependence of the conductivity exhibited a typical curvature of Vogel–Tammann–Fulcher (VTF) behavior for supercooled liquids and glasses, rather than a straight-line Arrhenius behavior. The fitting results into Vogel–Tammann–Fulcher (VTF) equation of ionic conductivity (σ) in the range of 25–60°C helps to clarify the conduction mechanism of the complex electrolytes. Table 2 showed that the activation energy of IL used as co-solvent rose up with increasing IL amount. Expectedly, this result is due to the increase in viscosity as well as the presence of significant ionic interactions between anion-cation and ion-dipole molecules. However, the activation energy values deduced for these mixtures are gently lower than that of pure ILs or IL-rich solutions (in which ILs are used as the main solvent and only a small amount of organic co-solvents is added) [2].

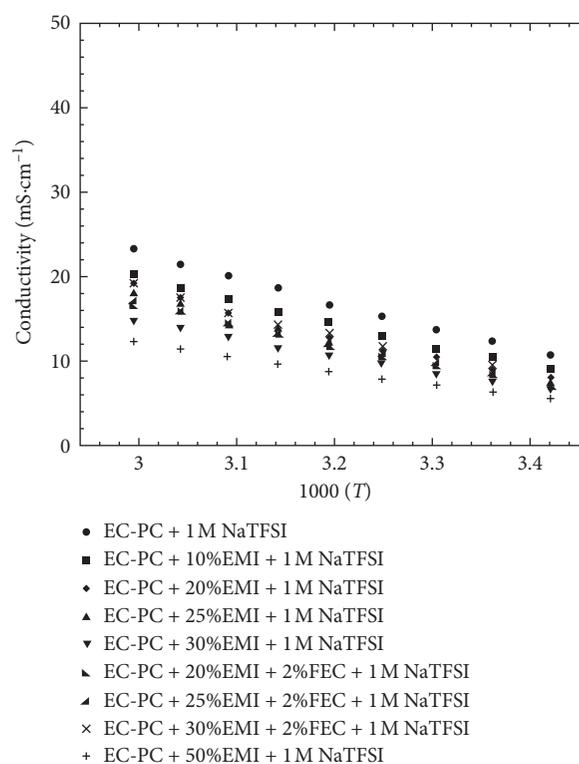


FIGURE 3: Plots of ionic conductivity versus temperature of EC-PC (1 : 1) + x wt.% EMI-TFSI + 1 M NaTFSI.

TABLE 2: The activation energy of the mixed electrolytes EC-PC (1 : 1) + x wt.% EMI-TFSI + 1 M NaTFSI.

Electrolytes (EMI-TSFI as co-solvent)	E_a ($J \cdot mol^{-1}$)
EC-PC + 1 M NaTFSI	1812
EC-PC + 10 wt.% IL + 1 M NaTFSI	1927
EC-PC + 20 wt.% IL + 1 M NaTFSI	2097
EC-PC + 25 wt.% IL + 1 M NaTFSI	2147
EC-PC + 30 wt.% IL + 1 M NaTFSI	2219
EC-PC + 20 wt.% IL + 2 wt.% FEC + 1 M NaTFSI	1832
EC-PC + 25 wt.% IL + 2 wt.% FEC + 1 M NaTFSI	1928
EC-PC + 30 wt.% IL + 2 wt.% FEC + 1 M NaTFSI	2011
EC-PC + 50 wt.% IL + 1 M NaTFSI	2320

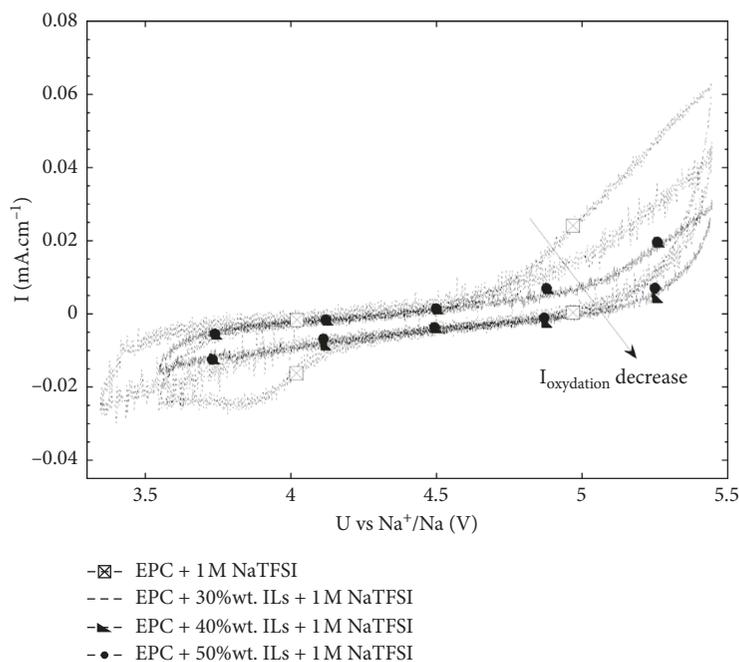


FIGURE 4: Cyclic voltammety profiles of EMI-TFSI used as co-solvent with binary system EC-PC and 1 M NaTFSI added.

3.4. Electrochemical Stability. The electrochemical stability of electrolytes plays an important role in determining the practical performance and operational potential of sodium-ion battery. ILs usually have a wider electrochemical stability window compared to organic solvent-based electrolytes. This feature allows a diverse choice of electrode materials (anode or cathode) for making full-cell prototype. The oxidation stability of mixed electrolytes was studied by cyclic voltammety performed on a platinum microelectrode (Figure 4). Figure 4 shows that with the rising IL content in the mixtures, the oxidation current expectedly decreased as the number of “free-to-be-oxidized” species is limited by the enhanced interaction between ion pairs (cation-anion) as well as between ions and dipole molecules. Additionally, the oxidation potential is also enlarged by more than 50 mV at the arbitrary current ($0.02 \text{ mA}\cdot\text{cm}^{-2}$) with an increase in EMI-TFSI content.

When increasing the amounts of IL in the binary electrolytes, large irreversible capacity is observed in the first cycle of discharge due to the formation of SEI layer on the anode material (SnS/C or HC in Figures 5 and 6). In the following cycles, the discharge capacity will be stabilized. However, if the IL content is too high, the 1st irreversible reduction can be so extreme that the battery will completely lose its performance in a few cycles. This issue becomes pretty obvious at 30 wt.% IL (Figure 5(b)). As earlier reported, the main problem of EMI-TFSI-based electrolytes is their low reduction stability on carbon anodes. In the case of Li-ion batteries, the electrochemical stability of ILs is improved in the negative voltage region with the addition of lithium salts forming an SEI [37–39]. The SEI can be easily formed from ionic species that prevent further electrochemical reduction of cationic species. Contrarily, in case of sodium-ion batteries,

the stabilization of SEI is more of a challenge due to the following two reasons. First, sodium salts can have very different solubility from their lithium analogues in the same solvent. Second, there is some evidence that sodium perchlorate in propylene carbonate systems gives mostly soluble decomposition product [40–42]. Thus, we believe that high concentration of ILs could not be adapted for cycling batteries due to unfavorable effects linking to low cathodic stability, unstable SEI layer, and high viscosity of electrolyte as a barrier for sodium-ion diffusion.

The presence of EC-PC mixed solvent is seen as a disadvantage for anodic stability, typically on the HC or SnS/C surface because the formation of the solid electrolyte interphase layer (SEI) is not enough for the effective passivation of electrode surface. The stable performance coupled with a good value of capacity is only maintained when using a small amount of FEC additive, which can stabilize the SEI layer after the 1st discharge cycle. As previously demonstrated, additives such as vinyl carbonate (VC) or fluoroethylene carbonate (FEC) and complex lithium salts can simultaneously suppress ILs reduction and stabilize the SEI layer, which, in principle, helps to overcome the weakness of EC and PC [43–46]. The best capacity value of about $410 \text{ mAh}\cdot\text{g}^{-1}$ was achieved with EC-PC binary solvents +20 wt.% IL + 2 wt.% FEC + 1 M NaTFSI.

Similarly, half-cell using hard carbon exhibited excellently stable discharge capacity of $300 \text{ mAh}\cdot\text{g}^{-1}$ in EC-PC (1 : 1) + 20 wt.% EMI-TFSI + 2 wt.% FEC (Figure 6(b)). As ILs content increased and without using additive, 1st discharge capacity significantly increased and capacity loss became increasingly severe (Figure 6(a)).

The cycling test was also performed on cathode material $\text{Na}_{0.44}\text{MnO}_2$ to evaluate its oxidation compatibility with

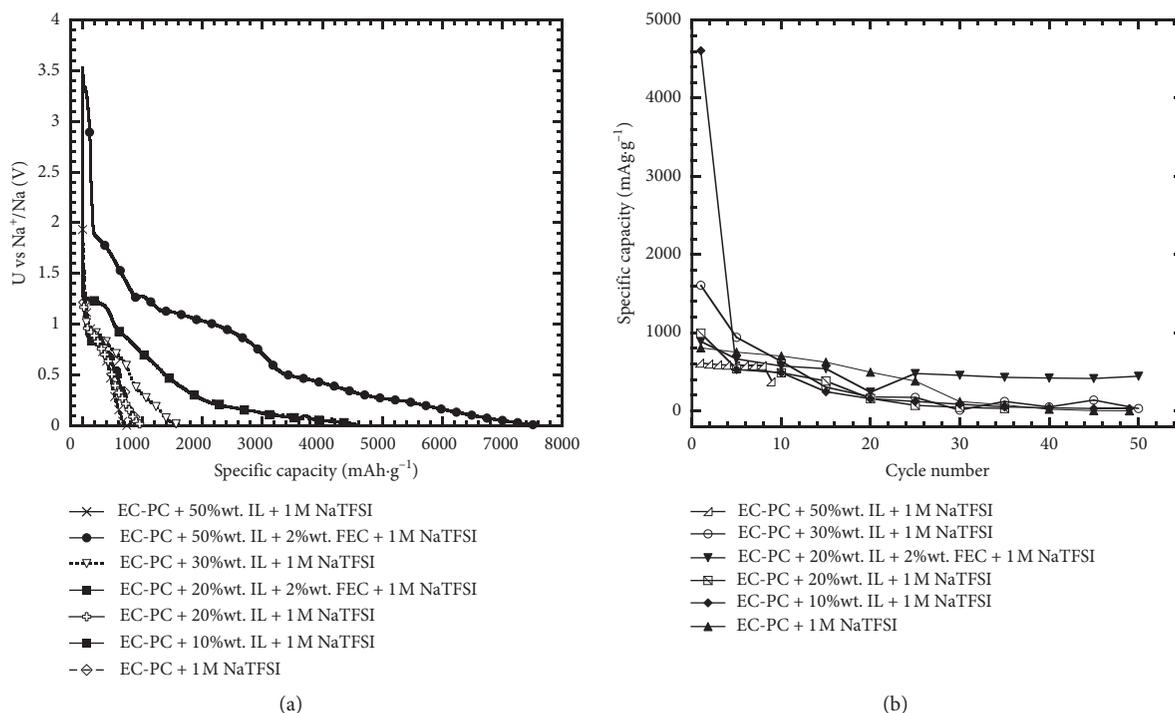


FIGURE 5: (a) 1st discharge curve of half-cell (-) Na | EC-PC (1 : 1) + x wt.% EMI-TFSI + 1 M NaTFSI | SnS/C and (b) cycling discharge capacity as a function of cycle number at C/10 rate.

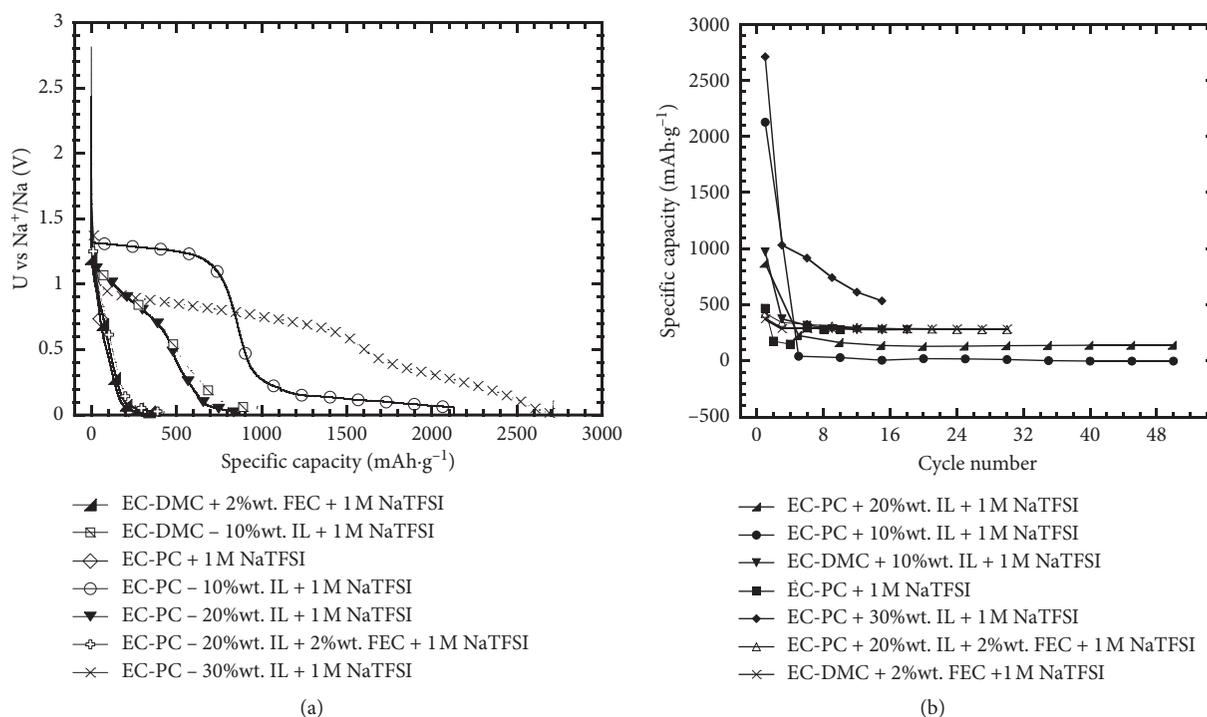
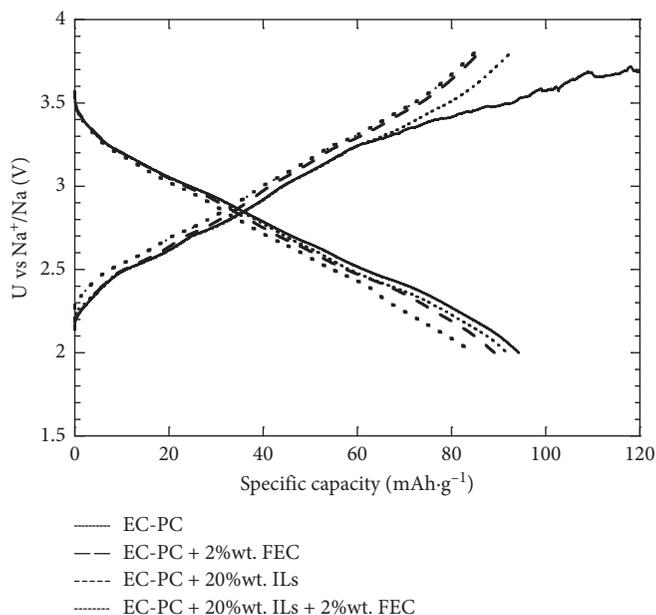


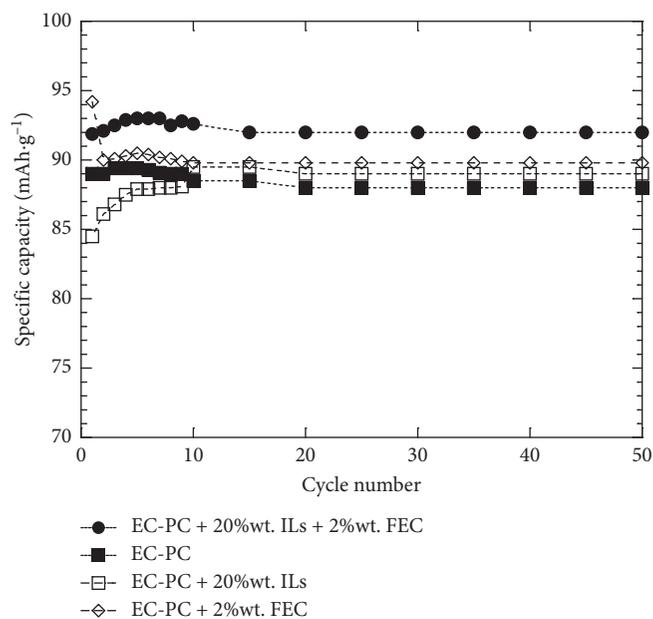
FIGURE 6: (a) 1st discharge capacity of half-cell (-) Na | EC-PC (1 : 1) + x wt.% EMI-TFSI + 1 M NaTFSI | hard carbon and (b) cycling discharge capacity as a function of cycle number at C/10 rate.

mixed electrolyte using 20 wt.% EMI-TFSI as co-solvent. In Figure 7, the half-cell using electrolytes based on EMI-TFSI exhibited as stable performance as carbonate-based

electrolyte (EC-PC). The highest discharge capacity of 92 mAh·g⁻¹ was obtained for the mixed electrolyte EC-PC (1 : 1) + 20 wt.% EMI-TFSI + 2 wt.% FEC + 1 M NaTFSI.



(a)



(b)

FIGURE 7: (a) 1st charge-discharge curve of half-cell (-) Na | EC-PC (1 : 1) + x wt.% EMI-TFSI + 1 M NaTFSI | Na_{0.44}MnO₂ and (b) cycling discharge capacity as a function of cycle number at C/10 rate.

4. Conclusions

We show here the systematic study of ionic liquid EMI-TFSI-based electrolytes for sodium-ion cell. The addition of ILs increased the thermal stability and oxidative limitation potential of electrolytes, but a significant decrease of ionic conductivity was observed at high IL concentration due to the increase of viscosity. Cycling performance was tested for the following electrode materials: hard carbon, SnS/C, and Na_{0.44}MnO₂. The abnormally large 1st discharge

capacity was attributed to the formation of SEI layer, and this value climbed up with increasing ILs content in mixtures as the reductive decomposition of electrolytes became more and more intense. Stable discharge capacity of SnS/C (up to 410 mAh·g⁻¹) and hard carbon (up to 300 mAh·g⁻¹) was obtained when they were cycled in half-cell using EC-PC (1 : 1) + 20 wt.% IL + 2 wt.% FEC. In case of Na_{0.44}MnO₂ cathode material, excellently stable discharge capacity was obtained even without using FEC additive.

Data Availability

The supplement information data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Detailed description about the chemical structure analysis of EMITFSI ionic liquid (after purification, using NMR spectroscopy). (*Supplementary Materials*)

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