Charge–Discharge and Interfacial Properties of Ionic Liquid-Added Hybrid Electrolytes for Lithium–Sulfur Batteries

Shruti Suriyakumar,†‡,‡*,† Murugavel Kathiresan,‡ and A. Manuel Stephan*,†,‡

†CSIR-Central Electrochemical Research Institute, Karaikudi 630 003, India
‡Academy of Scientific and Innovative Research (AcSIR), CSIR-CECRI Campus, Karaikudi 630 003, India

ABSTRACT: Even though lithium–sulfur batteries possess higher theoretical capacity and energy density than conventional lithium-ion batteries, the challenging issues such as poor electronic conductivity of sulfur, dendrite formation and subsequent polysulfide shuttling, and the undesirable interfacial properties of the lithium metal anode with an electrolyte impede this system from commercialization. To circumvent the dissolution of lithium polysulfides and to improve the interfacial properties of the electrolyte with the lithium metal anode, numerous tactics have been employed. Therefore, in this work, hybrid electrolytes composed of room-temperature ionic liquids of different cations with the bis(trifluoromethanesulfonyl)imide (TFSI) anion and a nonaqueous liquid electrolyte [1 M LiTFSI in tetraethylene glycol dimethyl ether/1,3-dioxolane 1:1 (v/v)] have been prepared, and their physicoelectrochemical properties were thoroughly investigated. The lithium surface upon cycling was characterized by Raman, Fourier transform infrared, and X-ray photoelectron spectroscopy analyses. The dendrite and shuttle current measurements also indicated the formation of a stable solid electrolyte interphase and lower polysulfide shuttling between the electrodes. Among the systems examined, the hybrid electrolyte composed of 1-methyl-1-propylpyrrolidinium TFSI exhibited appreciable charge–discharge characteristics, better interfacial properties with the lithium metal anode, and increased ionic conductivity which were attributed to the enhanced ion-pair interaction that is present between the 1-methyl-1-propylpyrrolidinium cation and the TFSI anion in the electrolyte which was substantiated by Raman analysis.

INTRODUCTION

Although the mechanism of the first lithium–sulfur battery system was introduced by Ulam and Herbert in 1962, its technological importance was recognized only two decades ago. The unique properties such as the high theoretical capacity of sulfur (1672 mA h g\(^{-1}\)), environment-friendliness, low cost, and so forth have identified lithium–sulfur batteries as a promising candidate for energy storage and conversion.\(^1\)–\(^4\)

Unfortunately, the low conductivity of sulfur, dissolution and polysulfide shuttling between the electrodes, and the poor electrode/electrolyte interfacial properties of the lithium metal anode with nonaqueous liquid electrolytes impede this system from practical applications.\(^4\) However, enormous attempts have been made to address these challenges around the world.\(^5\)

The conductivity of sulfur was appreciably increased by wrapping elemental sulfur in carbon nanotubes\(^6\) and conducting polymers\(^7\) and incorporating solid additives such as MgAl\(_2\)O\(_4\)\(^8\) metal organic frameworks\(^9\) and so forth. However, the performance of Li–S batteries continues to suffer from low Coulombic efficiency and capacity fade because of the low utilization of elemental sulfur which arises from the dissolution of Li\(_2\)S\(_x\) when the system is in conjunction with a nonaqueous liquid electrolyte. The most commonly used electrolyte is a combination of tetraethylene glycol dimethyl ether (TEGDME) and 1,3-dioxolane (DOL) containing approximately 1 M Li bis(trifluoromethanesulfonyl)imide (TFSI) with LiNO\(_3\) as an additive. To overcome the shuttling of lithium polysulfides as intermediates of the discharged products, attempts have been made to replace the nonaqueous liquid electrolytes with solid\(^10\) and gel polymer electrolytes.\(^11\)

Superionic conductors have also been employed as solid electrolytes for lithium-sulfur\(^12\) and for Li-ion batteries with LiFePO\(_4\) cathode materials.\(^13,14\) Although the migration of Li\(_2\)S\(_x\) was effectively suppressed by the solid electrolytes, the poor solid electrolyte/solid electrode interfacial properties and low diffusion of Li\(^+\) ions restrict the rate capability of the Li–S system.\(^15,16\) Therefore, designing of the liquid electrolyte with a potentially lower solubility of discharge species (S\(_8\) to Li\(_2\)S\(_x\)) is an effective way to enhance the performance of Li–S batteries.

Generally, the ether-based electrolytes selectively coordinate with the Li\(^+\) Lewis acidic cation and have a high donor number. This offers an improved solubility to lithium polysulfide and provides an adequate concentration of redox...
Among the different organic solvents, DOL has a high stability toward lithium anode by passively creating a solid electrolyte interphase (SEI) layer on the surface of lithium and also better polysulfide solubility.\(^\text{15}\) As a result, this mixture (TEGDME + DOL) can provide sufficient specific discharge capacity and longer cycle life at a high C rate. Nevertheless, DOL is easily prone to degradation by small amounts of contaminants in addition to polysulfide shuttling.

Ionic liquids (ILs) made of only ions have been identified as a possible replacement to highly inflammable organic solvents. The advantages of ILs include negligibly low volatility, relatively less flammability, high thermal stability, wide electrochemical stability, and better safety. However, the properties of ILs are mainly determined by their ionic nature. According to Cairns and Shin, ILs for lithium battery applications are employed in different formulations: IL—lithium salt as binary electrolytes,\(^\text{19}\) IL—lithium salt with a polymer as gel electrolytes,\(^\text{20}\) and IL—lithium salt with an organic solvent as ternary mixtures/hybrid electrolytes.\(^\text{21}\)

Earlier reports clearly demonstrated the solubility and mobility of Li\(_2\)S, which can be successfully controlled by PP13TFSI by the weak Lewis acidic/basic coordination of Li\(^+\)-cation.\(^\text{25}\) The same group has identified \(N,N\)-diethyl-N-methyl-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)amide as an alternative electrolyte for the lithium—sulfur batteries in which lithium polysulfide was significantly suppressed.\(^\text{24}\) Earlier reports clearly demonstrated the solubility and mobility of Li\(_2\)S, which can be successfully controlled by PP13TFSI by the weak Lewis acidic/basic coordination of Li\(^+\)-cation.\(^\text{25}\)

Ionic Conductivity and Compatibility Studies. The dependence of ionic conductivity on the inverse of temperature for IL-LiTFSI and their hybrid electrolytes is displayed in Figure 2a–c. It is observed from Figure 2a,b that the conventional nonaqueous electrolyte exhibited the lowest ionic conductivity. Upon the addition of BMP and MPP, the conductivity is increased. Maximum ionic conductivity was achieved when the content of e tare electrolyte/IL was of the ratio of 3:1. Generally, the addition of IL will reduce the values of ionic conductivity because of the increase in viscosity of the hybrid solution. A similar trend was observed by Shin and

**RESULTS AND DISCUSSION**

Figure 1a–f illustrates the molecular/chemical structures of 1-butyl-1-methylpyrroldinium TFSI (BMP), 1-methyl-1-propylpyrroldinium TFSI (MPP), triethylsulfonylmethyl TFSI (TES), LiTFSI, TEGDME, and DOL. Generally, the large sizes of the solvent molecules and the high viscosity of room temperature ILs (RTILs) are considered as favorable properties to avoid polysulfide diffusion.

Cairns.\(^\text{26}\) On the contrary, in the present study, in Figure 2c, there is no increase in conductivity when the composition was changed from TES-3 to TES-4, which is attributed to the different ion aggregation behavior responsible for the discrepancies between the IL solvent conductivity and viscosity, as discussed by Fox et al.\(^\text{27}\) The reduction in conductivity in TES-containing ILs could be attributed to the steric hindrance offered by the branched structure of the cation which leads to a sluggish mass transport.

Generally, the enhanced cycling performance of a Li–S cell with IL is attributed to the low solubility of polysulfide in IL. However, the passivating film formed on the lithium metal also contributes crucially to the determination of the charge–discharge behavior of the lithium—sulfur cells. To evaluate the interface properties of the lithium metal, symmetric cells with different electrolytes were fabricated, and their interface resistance (\(R_i\)) was measured as a function of time and displayed in Figure 3. The value of \(R_i\) can be generally obtained from the Nyquist plots. The parallel combination of resistance (\(R_{\text{film}}\)) and capacitance associated with the passivating film on the Li electrode is represented by large semicircles. The small semicircle is attributed to the double-layer capacitance in parallel with the charge-transfer resistance. Interestingly, the intercept of the large semicircle at high frequency on the real Z-axis is presumably associated with the \(R_i\) value of the lithium surface with the electrolyte system. It can be clearly seen from Figure 3 that for a symmetric cell with BMP and TES, the value of \(R_i\) increases with the increase of time, which is presumably because of the formation of a resistive precipitation layer on the lithium anode.\(^\text{24}\) However, in the case of IL 2, IL
ILs, the value of $R_i$ was found to be lower and is attributed to the cation—TFSI interaction with the electrolyte, which helps to form a dense SEI layer with a thickness of a few micrometers, which prevents the direct contact between the polysulfides and the lithium metal. It is found that the ILs alone exhibited the highest interfacial resistance because of their increased tendency to form a passivation layer compared to that of alkyl carbonates. These results are in accordance with the work by Katayama et al., wherein PEGDME was employed as a solvent to reduce the interfacial resistance compared to pure ILs.

**Surface Morphology.** Figure 4a shows the digital photographs of the lithium surface viewed from an optical microscope, which were exposed to a conventional nonaqueous liquid electrolyte (bare) and electrolytes comprising BMP-4, MPP-4, and TES-4 (as the hybrid electrolyte composed of IL-4 composition exhibited the maximum ionic conductivity, these systems were used for further characterization). Figure 4a shows a rough morphology on the lithium surface when the lithium metal was exposed to a conventional electrolyte and a hybrid electrolyte comprising MPP-4. However, the lithium surface is not much altered by the hybrid electrolytes comprising BMP-4 and TES-4. The scanning electron microscopy images (Figure 4b) show the surface morphology of the lithium metal exposed to a nonaqueous liquid electrolyte and a hybrid electrolyte (IL-4).
comprising BMP, MPP, and TES. The lithium surface shows a rough surface with the formation of island structures, irrespective of the electrolytes used; however, the size of islands varied from 5 to 10 μm and is attributed to the corrosion of the lithium metal anode by IL moieties.29

To further analyze the chemical composition of the passivating film formed on the lithium metal surface, Raman, Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses were employed for the lithium surface exposed to the bare electrolyte and the hybrid electrolytes containing ILs.30

Raman Analysis. Vibrational spectroscopy has been employed in the present study to understand the structural properties and interactions present in ILs, irrespective of their physical characteristics.31 Raman spectra give information on the conformational or structural changes of the chemical structures. In a typical electrolyte system, the anion bands usually dominate because of their vibrations arising from the polarizability fluctuation.32 Raman spectroscopy reveals the coexistence of the cisoid and transoid conformers of [NTf2]− in normal ILs. The lithium metal surface which is in contact with the hybrid electrolyte (IL-4) was studied, as it exhibited the highest ionic conductivity. For all of the modes associated with the TFSI− anion, the intensity relative to the MPP+ cation was found to increase upon the addition of LiTFSI to the MPP IL. The strongest band of the TFSI anion at 742 cm−1 was ascribed to the bending of CF3 in the SCF3 groups.33

Interestingly, the peaks corresponding to the expansion and contraction of the bulky TFSI anion occur, and these vibrational modes induce an adverse change in the polarizability, and the corresponding energy associated with this is intensely affected by the anion coordination.33

In accordance to an earlier report,29 the Raman spectrum of BMP depicted in Figure 5 shows two closely positioned bands which are ascribed to the vibrational motion of TFSI− in the region of 380−450 cm−1. The one strong, sharp line at 740 cm−1 in the fingerprint region is distinctive for the TFSI anion, and the peak corresponds to the S−N and C−F stretching coupled with the SO2 wagging motion. In addition, the fingerprint region also consists of relatively weak peaks observed at 558, 557, 713, 1135, 1237, and 1445 cm−1. The peaks at 1135 and 1237 cm−1 are respectively attributed to the C−F stretching and C−F symmetric bending in the TFSI anion.29 A strong peak at 740 cm−1 is observed in the Raman spectra of TES, indicative of the presence of the TFSI− group.32

Except the bare electrolyte (nonaqueous electrolyte without IL), in all the other cases, a very intense band at 741 cm−1 (indicated with *) is observed which is assigned to the cisoid and transoid conformers of TFSI−. It is noteworthy that this band is very sensitive to small cation coordination (e.g., Li+). In all these cases, typical cation and anion vibrational bands are observed. It is found that among the three hybrid IL-4 electrolytes, MPP-4 exhibits the less intense peak at 741 cm−1, which indicates a strong ion-pair interaction between the MPP cation and the TFSI anion, thereby enhancing the mobility of Li+ ions.

FTIR Analysis. As demonstrated by Fumino and Ludwig,35 infrared spectroscopy is an apt method for analyzing the interaction between cations and anions in ILs. In the present work, the surface of the lithium metal in contact with the bare and hybrid electrolytes (IL-4) is analyzed using FTIR spectroscopy between 4000 and 400 cm−1 in attenuated total reflectance (ATR) mode, and the results are presented in Figure 6.

Figure 6 shows the IR spectra of the mixture of the DOL, TEGDME, and LiTFSI electrolytes with BMP, MPP, and TES ILs.
ILs. It is found that C–E, C–S, and S–O stretching appeared at 939 cm$^{-1}$. Although this band is clearly visible in the IL–electrolyte mixture, its absence in the bare electrolyte indicates a very low concentration of the TFSI anion. Similarly, S=O stretching appeared as a sharp band at 1124–36 cm$^{-1}$ in the IL–electrolyte mixture, whereas the same appeared as a very weak and broad band in the bare nonaqueous electrolyte. The bands between 2800 and 2900 cm$^{-1}$ are assigned to C–H stretching. The distinctive carbonyl absorption appeared at 1732 cm$^{-1}$ approximately, and it corresponds to the carbonyl group present in DOL. In the case of IL–electrolyte mixtures, the N$^+$–C (quaternary N–C) band and the C–H bending band in the cations appeared at 1465 cm$^{-1}$, whereas this is absent in the bare nonaqueous electrolyte, indicating the absence of quaternary structures. The bands at 493 and 615 cm$^{-1}$ (approximately) are assigned to the cis and trans TFSI anions. Upon the addition of IL to the electrolyte, slight changes in the peak shifts were observed accompanied by peak broadening. This clearly indicates the interaction between the IL and the nonaqueous electrolyte.

It is noteworthy that the cis-TFSI conformation exhibits a clear shoulder peak around 520 cm$^{-1}$ and intense absorption lines located at 585, 603, and 654 cm$^{-1}$. Quite the opposite way, trans-TFSI shows two intense vibration modes located around 581 and 625 cm$^{-1}$. The FTIR spectra in Figure 6 show that although the bare electrolyte contains LiTFSI salt, it does not show any such peak, whereas all these modes are detected in the spectra, thus demonstrating the presence of both conformers in the liquid phase of all ILs.

**Dendrite Studies.** The SEI layer, a polycrystalline film, is mainly formed because of the decomposition products arising from the nonaqueous liquid electrolyte, densely packed inorganic compounds, and aggregated organic compounds on reaction with the Li metal. The thickness of the SEI layer varies from a few nanometers to tens of nanometers and is sensitive to chemical conditions; though it is insulating in nature, it is ionically conducting. It also serves as a protective barrier in screening the bulk electrolyte from the strongly reducing lithium metal anode. To get a better insight into the SEI phenomena and dendrite formation, a closer understanding of the lithium dissolution kinetics, which represents the discharge (stripping) and deposition kinetics congruent to the charging process, is required. As this can be quantified by an overpotential, a simple tool to probe the formation of dendrites in a lithium metal anode when in conjugation with a liquid electrolyte under constant current cycling experiments was employed as proposed by Bieker et al.$^{36}$ In the present work, a symmetric cell composed of Li/Li was used to eliminate the effects from a nonlithium electrode.

In Figure 7a, the positive and negative potentials, respectively, denote the dissolution and deposition of the lithium working electrode (WE) against the Li/Li symmetric cells. The positive and negative overpotentials significantly reduce after five cycles of deposition and dissolution of lithium at the WE. As seen from Figure 7a, the apparent initial high overpotentials of lithium dissolution on the lithium surface is attributed to the smooth and less surface area of fresh lithium. Further, the overpotential remains constant even after prolonged cycling, which confirms that the dissolution of lithium is stable in an already roughened lithium surface with a robust SEI.

An initial maximum overpotential of 0.105 mV was observed in a symmetric cell with the MPP-based electrolyte compared to the BMP (0.080 mV)- and TES (0.082 mV)-based electrolytes. This can be attributed to the kinetic hindrance for the deposition of lithium over the electrode surface (smooth and low surface area) as explained in Figure 7a. Apparently, as seen from Figure 7b, after 400 h of continuous stripping and deposition, the positive overpotential was found to be +0.0176 mV for all the three systems, viz., BMP, TES, and MPP. However, MPP was found to have a negative overpotential of −0.0161 mV, whereas the symmetric...
cell with both BMP and TES had −0.0175 mV. The marginal reduction in the negative overpotentials of the cell with MPP indicates a general decrease of the overall resistance toward lithium deposition.

**Charge–Discharge Studies.** Figure 8a illustrates the galvanostatic first charge–discharge profiles of Li–S cells with ILs and hybrid electrolytes of different cations/anions at a rate of 0.1 C at 25 °C. The discharge capacity as a function of cycle number is also displayed in Figure 8b–e. It is apparent from Figure 8 that the anionic structure of an IL has a major influence on the cycling performance. The cells with IL + 1 M LiTFSI show a single voltage plateau at 2.1 V, approximately. However, the discharge capacity was reduced very rapidly within 50 cycles (Figure 8b).

On the other hand, the IL-4 hybrid electrolytes exhibited two voltage plateaus during discharging (2.1 and 2.3 V) and a single plateau (2.3 V) during charging. It is clear from the discharge curves that the first reduction voltage corresponds to the conversion of S8 to longer order Li2S8 (m > 4), whereas the reduction of Li2S8 to Li2S is represented by the lower voltage. It is also apparent from Figure 8a that the first reduction voltage of the Li–S cell containing bare electrolytes is slightly higher than that of IL/IL-4 containing hybrid electrolytes. This is ascribed to the solvent effect associated with the less solubility of Li2Sx.24,37 These insoluble intermediates, Li2Sω, as solids will get deposited inside the composite sulfur cathode. The Li–S cell with the hybrid electrolyte comprising MPP-4 exhibited a high overpotential, and it also delivered a discharge capacity of 300 mA h g−1 on its first cycle which is much lower than that of the Li–S cell with other hybrid electrolytes. Although the solubility of Li2Sx is very low in ILs, the transport properties of the hybrid electrolytes are shown to have an influence on the charge–discharge behavior of these systems. The ionic conductivity of MPP and its hybrid is high compared to TES and BMP. The charge–discharge behavior of ILs is even worse than that of the hybrid electrolytes, and only 50 cycles could be achieved. Among the three hybrid electrolytes, the Li–S cell with MPP-4 exhibited the maximum discharge capacity on its first cycle (1346 mA h g−1) and the 50th cycle (398 mA h g−1). In a similar way, the Li–S cells with BMP-4 and TES-4 exhibited 301 and 1237 mA h g−1 on their first cycles, respectively. However, the discharge capacity reduced rapidly for the Li–S cells with BMP-4 and TES-4 as electrolytes. The IL-4 hybrid electrolyte containing MPP has a balance between the solubility of polysulfides and the diffusion rate. MPP offers a wide electrochemical range,21 and
the weak coordination of the Lewis acid and base pairs in the MPP-containing electrolyte alleviates lithium polysulﬁde solubility. In addition, MPP is less viscous (10.3 cP at 25 °C) compared to the others and has the potential to suppress the lithium polysulﬁde diffusion rate appreciably as evidenced by the shuttle current measurement (as discussed in the following section).

**Shuttle Current Estimation.** One of the crucial parameters for capacity fade in Li–S cells is associated with the shuttle process. The insight into the diﬀerences in the shuttling process observed with various IL-based hybrid electrolytes was determined by shuttle current estimation, as proposed by Moy et al. In general, the open-circuit potential of the anode is relatively constant and depends on the concentration of lithium ions in the electrolyte and the accessibility of metallic lithium on the anode. However, the potential of the cathode steadily decreases because of the arrival of lower order polysulﬁdes continuously at the cathode from the anode by the shuttling phenomenon. In this experiment, the cathode potential is maintained as constant by the application of an external current which is proportional to the diﬀusion ﬂuxes of the polysulﬁdes in the electrolyte across the electrodes. Hence, the shuttle current can be quantiﬁed by forcing the electrode potential to a constant value and measuring the response via the steady-state current through the cell.

The linear region can be ﬁt by a straight line equation of the form (1).

\[ y = mx + C \]  

where the slope of the equation denoted by \( m \) quantitatively represents the rate of decrease of the shuttle current. Here, \( y \) represents the current and \( C \) denotes the \( y \)-intercept. Usually, a linear decay in shuttle current is observed for all lithium–sulfur cells.

As it was shown previously, the decay in shuttle current sheds information on the amount of polysulﬁde reduced to insoluble lower order polysulﬁde at the lithium metal surface. Therefore, prevention of the deposition of lower order species at the anode is expected to decrease the capacity fade in Li–S cells, via its eﬀects on decreasing the slope of the shuttle current. Figure 9 displays the shuttle current versus time plot for the lithium–sulfur cell with the hybrid electrolyte IL-4. It is found that the trend in shuttle current is TES > BMP > MPP, which implies that the electrolyte containing MPP exhibits lesser shuttling current compared to the Li–S cell with BMP and TES in the electrolyte.

**XPS Analysis of Electrode/Electrolyte Interface.** In the present work, lithium metal post contact with the bare and MPP-4 electrolytes was analyzed by XPS, as it shows the highest ionic conductivity and discharge capacity among the systems studied. A detailed investigation of the lithium surface post contact with the nonaqueous electrolyte with and without MPP has been carried out.

Figure 10a,b shows the deconvoluted XPS spectra of the C 1s, F 1s, Li 1s, N 1s, O 1s, and S 2p peaks obtained from the lithium surface when in contact with the bare electrolyte and MPP-containing hybrid electrolyte for 24 h. The F 1s peak at 684.8 and 688.6 eV, respectively, corresponds to LiF and −CF3 of the LiTFSI salt or its decomposition product. The deconvoluted XPS spectrum of S 2p shows S–O bands at 168.5 and 167 eV which are ascribed to −SO2CF3 or Li2SO from the LiTFSI salt or its decomposition product, respectively. The peak between 164 and 165 eV correspond to S–S bonds, and similarly the peaks between 160 and 162.9 eV indicate the presence of Li2S or the Li2S–SO3 complex. The peak at 399.5 eV in the N 1s spectra corresponds to the imide groups of LiTFSI salt. The C 1s peaks at 284.8 eV (peak A) and 286.5 eV (peak B) are respectively assigned to the R3CO−(CH2) and R3CO− groups which is due to the solvent residues and decomposition products (alcoholates) or aliphatic carbons. While quantitatively analyzing the C 1s peaks, peaks A and B cover an area of 15 955 and 7260 (a.u.), respectively, for the lithium metal in contact with the bare electrolyte, whereas in the case of the lithium metal in contact with the hybrid electrolyte, the area is 9809 and 1092 (a.u.). This indicates that the amount of decomposition products deposited on the lithium metal in contact with the bare electrolyte is more than that of the surface in contact with the hybrid electrolyte with MPP-4, which is a direct indication that MPP helps in the formation of a stable and thin SEI on the lithium surface.

**CONCLUSIONS**

Although the nonaqueous electrolyte composed of 1 M LiTFSI in a combination of TEGDME and DOL (1:1 v/v) has been widely used, the polysulﬁde shuttling and SEI on lithium are the challenging issues. In the present work, the role of diﬀerent cations of ILs to overcome these challenges was systematically investigated. A series of hybrid electrolytes composed of the aforementioned liquid electrolyte and ILs of diﬀerent cations, viz., BMP, MPP, and TES were prepared, and their ionic conductivity and compatibility with the lithium metal anode were also analyzed. It is found that the solvent–IL interaction inﬂuences the ionic conductivity and the SEI ﬁlm thickness. The Raman and FTIR studies of the lithium surface in contact with the bare and hybrid electrolytes conﬁrmed the presence of both conformers (cis and trans) in the liquid phase of all hybrid electrolytes (IL-4). Among the three cations investigated, the MPP-4 hybrid electrolyte showed an enhanced cycling performance which was attributed to the suppression of dendrite formation, polysulﬁde shuttling, and SEI growth, as evidenced by the dendrite, shuttle current, and XPS analyses.
EXPERIMENTAL PROCEDURE

Preparation of Hybrid Electrolytes. RTILs, namely, BMP, MPP, and TES (TCI, Japan) were used as received. The conventionally used nonaqueous electrolyte in lithium–sulfur cells composed of 1 M lithium TFSI LiN(CF₃SO₂)₂ in a combination of DOL and TEGDME 1:1 (v/v) was prepared in an argon atmosphere. The hybrid electrolytes were prepared by mixing ILs, namely, BMP, MPP, and TES separately, and the nonaqueous electrolytes for different volume ratios, viz., 1:3, 1:1, and 3:1, as shown in Table 1 are labeled accordingly.

Table 1. Nomenclature of Various Hybrid Electrolytes

| bare electrolyte                  | IL-1 (BMP/MPP/TES) | IL-2 (BMP/MPP/TES) | IL-3 (BMP/MPP/TES) | IL-4 (BMP/MPP/TES) |
|-----------------------------------|--------------------|--------------------|--------------------|--------------------|
| 1:1 v/v TEGDME/DOL in 1 M LiTFSI | IL + 1 M LiTFSI    | 3:1 v/v bare electrolyte/IL | 1:1 v/v bare electrolyte/IL | 1:3 v/v bare electrolyte/IL |
| **BMP, MPP, and TES.**          |                    |                    |                    |                    |

**Figure 10.** (a) XPS spectra of the lithium metal surface in contact with the bare electrolyte for 24 h. (b) XPS spectra of the lithium metal surface in contact with the MPP-4 hybrid electrolyte for 24 h.
All the preparations were made in an argon-filled glovebox (M. Braun, Germany).

**Assembly of 2032-Type Li–S Coin Cell.** Sulfur–graphene–magnesium aluminate (SGM)-based ternary composite cathodes for cycling studies were prepared as reported earlier by us. A 2032-type coin cell was assembled with the SGM electrode with an areal sulfur loading of 0.5 mg/cm² and the lithium metal foil anode (Aldrich) with 0.25 mL of the as-prepared hybrid electrolytes. This amount was found to be optimal for charge–discharge studies. Further, an increase in the electrolyte volume led to leakage of the electrolyte after crimping.

**Electrochemical Characterization.** The surface morphology of the lithium metal–electrolyte interface was examined by a scanning electron microscope (JSM-6301F, Japan) and an optical microscope, and the viscosity of the hybrid electrolyte was measured using a Brookfield DV1 viscometer. To investigate the surface properties of the lithium–electrolyte interface, Raman and FTIR studies were carried out.

The ionic conductivity of the electrolyte was measured by sandwiching a Celgard 2320 separator activated by the hybrid electrolyte by two stainless steel blocking electrodes (1.0 cm in diameter) for various temperatures using an electrochemical impedance analyzer (BioLogic, France) with an alternating current sine wave perturbation of 10 mV between the frequency ranges of 1 MHz and 50 mHz. To investigate the interfacial properties of the lithium metal anode with the as-prepared electrolyte, a symmetric nonblocking cell composed of Li/Celgard 2320 activated by the hybrid electrolyte/Li was assembled, and the time dependence of the impedance was analyzed at RT. The galvanostatic charge–discharge profiles for the assembled 2032-type coin cell were measured between 3 and 1.6 V at ambient temperature by a computer-controlled battery testing unit (Arbin, USA) as reported earlier.

To study the interfacial properties and dendrite growth in a lithium metal anode, symmetrical coin cells of lithium electrodes in different electrolyte solutions were assembled. The lithium metal foil was cut into 10 mm diameter disks as lithium electrodes. A 2320-type Celgard separator was employed to separate both the Li electrodes, and the cycling behavior of the symmetrical cells was evaluated using an electrochemical workstation (VSP3 BioLogic, France) at a current density of 0.10 mA cm⁻². The time for a single charge and discharge process was 1 h each. The shuttle current of the Li−S cell was measured at 2.3 V as proposed by Moy et al. This study sheds more information on the factors which influence the shuttling of polysulfide in a Li−S cell.

To analyze the surface properties by FTIR, XPS, and Raman spectroscopic analyses, the lithium metal was exposed to bare and hybrid electrolytes for 24 h in an argon-filled glovebox. The Raman spectra (HORIBA, model: LabRAM HR Evolution) of the lithium surface was probed by a laser source of 514 nm wavelength. The FTIR spectroscopy data were obtained [Bruker Optik GmbH, Germany (model no: TENSOR 27, OPUS TM)] in ATR mode. The ATR technique used in conjunction with infrared spectroscopy enables samples to be analyzed in the solid or liquid state without further preparation. The lithium/electrolyte interface was analyzed by XPS (Thermo Scientific; model: ESCALAB 250 XI base system). A thin lithium foil of area 10 mm² with a thickness of 2–3 mm was carefully transferred to the XPS sample chamber using a vacuum shuttle for analysis, as reported elsewhere.
Temperature Solid-State Lithium Batteries. ACS Appl. Mater. Interfaces 2018, 10, 13588–13597.
(15) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. Chem. Rev. 1999, 99, 2071–2084.
(16) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-Liquid Materials for the Electrochemical Challenges of the Future. Nat. Mater. 2009, 8, 621–629.
(17) Tachikawa, N.; Yamauchi, K.; Takashima, E.; Park, J.-W.; Dokko, K.; Watanabe, M. Reversibility of Electrochemical Reactions of Sulfur Supported on Inverse Opal Carbon in Glyme–Li Salt Molten Complex Electrolytes. Chem. Commun. 2011, 47, 8157.
(18) Aurbach, D.; Youngman, O.; Dan, P. The Electrochemical Behavior of 1,3-Dioxolane–LiClO4 Solutions—II. Contaminated Solutions. Electrochim. Acta 1990, 35, 639–655.
(19) Shin, J. H.; Cairns, E. J. N-Methyl-(n-butyl)pyrrolidinium bis(trifluoromethanesulfonyl)imide-LiTFSI-poly(ethylene glycol) dimethyl ether mixture as a Li/S cell electrolyte. J. Power Sources 2008, 177, 537–545.
(20) Sato, T.; Marukane, S.; Narutomii, T.; Akao, T. High Rate Performance of a Lithium Polymer Battery Using a Novel Ionic Liquid Polymer Composite. J. Power Sources 2007, 164, 390–396.
(21) Sakaee, H.; Matsumoto, H. N-Methyl-N-Propylpiperidinium Bis(Tri fluoromethanesulfonyl)imide (PP13-TFSI) - Novel Electrolyte Base for Li Battery. Electrochim. Commun. 2003, 5, 594–598.
(22) Ueno, K.; Tokuda, H.; Watanabe, M. Ionicity in Ionic Liquids: Correlation with Ionic Structure and Physicochemical Properties. Phys. Chem. Chem. Phys. 2010, 12, 1649.
(23) Wang, L.; Byon, H. R. N-Methyl-N-Propylpiperidinium Bis(Tri fluoromethanesulfonyl)imide-Based Organic Electrolyte for High Performance Lithium-Sulfur Batteries. J. Power Sources 2013, 236, 207–214.
(24) Park, J.-W.; Yamauchi, K.; Takashima, E.; Tachikawa, N.; Ueno, K.; Dokko, K.; Watanabe, M. Solvent Effect of Room Temperature Ionic Liquids on Electrochemical Reactions in Lithium-Sulfur Batteries. J. Phys. Chem. C 2013, 117, 4431–4440.
(25) Park, J.-W.; Ueno, K.; Takashima, N.; Dokko, K.; Watanabe, M. Ionic Liquid Electrolytes for Lithium-Sulfur Batteries. J. Phys. Chem. C 2013, 117, 20531–20541.
(26) Shin, J. H.; Cairns, E. J. N-Methyl-(n-butyl)Pyrrolidinium Bis(Tri fluoromethanesulfonyl)imide-LiTFSI-Poly(Ethylene Glycol) Dimethyl Ether Mixture as a Li/S Cell Electrolyte. J. Power Sources 2008, 177, 537–545.
(27) Fox, E. T.; Paillard, E.; Borodin, O.; Henderson, W. A. Physicochemical Properties of Binary Ionic Liquid-Aprotic Solvent Electrolyte Mixtures. J. Phys. Chem. C 2012, 117, 78–84.
(28) Fang, S.; Zhang, Z.; Jin, Y.; Yang, L.; Hirano, S.-i.; Tachibana, K.; Katayama, S. New Functionalized Ionic Liquids Based on Pyrrolidinium and Piperidinium Cations with Two Ether Groups as Electrolytes for Lithium Battery. J. Power Sources 2011, 196, 5637–5644.
(29) Budi, A.; Basile, A.; Opletal, G.; Hollenkamp, A. F.; Best, A. S.; Rees, R. J.; Bhatt, A. L.; O’Mullane, A. P.; Russo, S. P. Study of the Initial Stage of Solid Electrolyte Interphase Formation upon Chemical Reaction of Lithium Metal and N-Methyl-N-Propyl-Pyrrolidinium- Bis(Fluorosulfonyl)imide. J. Phys. Chem. C 2012, 116, 19789–19797.
(30) Zheng, J.; Gu, M.; Chen, H.; Meduri, P.; Engelhard, M. H.; Zhang, J.-G.; Liu, J.; Xiao, J. Ionic liquid-enhanced solid state electrolyte interface (SEI) for lithium-sulfur batteries. J. Mater. Chem. A 2013, 1, 8464.
(31) Umebayashi, Y.; Fujimori, T.; Sukizaki, T.; Asada, M.; Fujii, K.; Kanzaki, R.; Ishiguro, S.-i. Evidence of Conformational Equilibrium of 1-Ethyl-3-Methylimidazolium in Its Ionic Liquid Salts: Raman Spectroscopic Study and Quantum Chemical Calculations. J. Phys. Chem. A 2005, 109, 8976–8982.
(32) Paschoal, V. H.; Faria, L. F. O.; Ribeiro, M. C. C. Vibrational Spectroscopy of Ionic Liquids. Chem. Rev. 2017, 117, 7053–7112.
(33) Huang, W.; Frech, R.; Wheeler, R. A. Molecular Structures and Normal Vibrations of Trifluoromethane Sulfonate (CF3SO3−) and Its Lithium Ion Pairs and Aggregates. J. Phys. Chem. 1994, 98, 100–110.