

Research Article

Low-Temperature Conductivity Study of Multiorganic Solvent Electrolyte for Lithium-Sulfur Rechargeable Battery Application

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The conductivity of an electrolyte plays a significant role in deciding the performance of any battery over a wide temperature range from -40°C to 60°C . In this work, the conductivity of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) at a varied salt concentration range from 0.2 M to 2.0 M in a multisolvent organic electrolyte system over a wide temperature range from -40°C to 60°C is reported. The mixed solvents used were 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and tetraethylene glycol dimethyl ether (TEGDME) with an equal ratio of DOL:DME:TEGDME (1:1:1 by volume). The experimental analysis performed over a wide temperature range revealed the maximum conductivity at salt concentrations ranging from 1.0 M to 1.4 M for equal molar solvents. The optimum salt concentration and maximum conductivity in a different solvent composition ratio (i.e., 3:2:1) for all the temperatures is reported herein. The temperature-dependence conductivity of the salt concentration did not fit the Arrhenius plot, but it resembled the Vogel–Tamman–Fulcher plot behavior. The present conductivity study was carried out to evaluate the overall operable temperature limit of the electrolyte used in the lithium-sulfur battery.

1. Introduction

Lithium-sulfur batteries have become an attractive option for new-generation high-performance batteries due to their high theoretical capacity (1,675 mAh/g) and specific energy (2,600 Wh/kg) [1–6], which is up to three times higher than that of the commercially viable Li ion batteries. However, rapid capacity attenuation [7] with poor cycle [8] and rate performance make the batteries far from ideal for real-commercial applications. Extensive literature surveys and previous experimental works reported multisolvent organic-based electrolytes for lithium-sulfur batteries at the ambient temperature, but limited work was reported on subambient temperature behavior of the electrolyte.

The typical operation of lithium-sulfur batteries for telemetry applications requires temperatures from -40°C to 60°C . The conductivity is one of the important factors to consider for the formulation of an electrolyte. In the present study, the

conductivity of lithium bis(trifluoromethanesulfonyl)imide [9] in DOL [10]:DME:TEGDME (1:1:1 by volume) mixture was investigated as a function of increasing concentrations of salt (LiTFSI) over a wide temperature range.

Formulation of electrolytes with a multisolvent system provides higher conductivity in a broader temperature range compared to that with a single electrolyte system. The physicochemical properties of the electrolytes, such as viscosity, conductivity, thermal stability, and wettability, are governed by the composition of the electrolyte (i.e., the salt and solvent) [11].

The electrolyte has been the primary element for the poor performances of a battery at low temperatures. Thus far, the addition of lower melting cosolvents has been the most favorable approach adopted by researchers to develop an electrolyte for subambient applications. As a pioneering attempt to develop a low-temperature electrolyte for lithium-ion chemistry, Ein-Eli et al. used methyl formate (MF,

mp -99°C) and reported that the ion conductivity of 1 M LiMe in an MF/EC (3 : 1) mixture at -40°C was 5.4 mScm^{-1} . The authors concluded that the depression effect of MF rendered the electrolyte liquid at such low temperatures [12].

A consequential contribution to the search for a low-temperature electrolyte was made by Smart et al., in the late 1990s, which was driven by the need of NASA for the application of lithium-ion batteries in space missions [13]. In other words, the reformulation of these low-temperature electrolytes had to consider the surface chemistry of the new cosolvents in addition to their positive effects on ion conductivity, where the conductive electrolyte did not necessarily provide the best improvements at low temperatures [14]. After the initial work done by Smart et al., similar efforts were reported based on various binary and ternary compositions, such as EC/DMC/DEC (2 : 2 : 1) [15], EC/DMC/EMC (1 : 1 : 1), and EC/EMC (1 : 3) series with varying compositions. Unfortunately, the above compositions still failed to function well below -30°C [16].

Organic electrolytes containing salt, lithium bis(trifluoromethanesulfonyl)imide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$), and a mixture of cyclic or linear ethers as solvents, namely, 1,3-dioxolane, 1,2-dimethoxyethane, and tetraethylene glycol dimethyl ether, are commonly reported and used for lithium-sulfur batteries because of their good thermal stability and excellent hydrolytic stability compared to LiPF_6 which is popularly used in lithium-ion batteries [11, 17, 18]. Gao et al. [19] found that the solvents in the electrolyte for the lithium-sulfur battery played an important role in affecting the electrochemical performance, but the lithium salts had no apparent effects. Such ethereal solvents (DOL/DME and TEGDME) with low viscosity could be appropriate solvents because they could lead to the complete reduction of soluble polysulfide during the cycle. Moreover, X-ray absorption spectra revealed that reduced sulfur species could chemically react with carbonate-based solvents, such as EC, PC, and DEC, making them unsuitable for lithium-sulfur batteries. The glyme structure of TEGDME with high donor number and dielectric constant (ϵ_r) of 7.9 helps in the dissociation of lithium salt and active sulfur materials [20]. Barchasz et al. experimented on various ether electrolytes with different structures and found that the electrochemical performance of the TEGDME electrolyte was promising than that of other ether groups. This behavior could be explained by the presence of more solvating oxygen atoms in the glyme structure of TEGDME; therefore, it solubilizes and dissociates Li salts and polysulfide compounds well [21]. Li et al. reported the electrochemical performance of carbonate-based electrolyte systems such as EC : DMC, EC : DEC, and EC : DEC : FEC in LiPF_6 salt for lithium-sulfur batteries across a wide temperature range from -20°C to 55°C , wherein the future applicability of this alucone-coated sulfur cathode was well demonstrated [22].

In the present study, we focused on the development of an optimized salt composition in electrolytes for lithium-sulfur batteries to meet a wide temperature range from -40°C to 60°C . The conductivity behavior at a wide temperature range for various salt concentrations is reported in order to find the maximum conductivity.

2. Materials and Methods

Battery grade solvents, such as DME, DOL, and TEGDME, and salt $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ were purchased from Sigma-Aldrich with high purity ($>99\%$) and used in the experiment without further purification. All the chemicals as received were stored in a chemical storage cabin in a fume hood. Before electrolyte preparation, they were equilibrated into the argon atmosphere with <0.1 ppm moisture and oxygen level.

Electrolyte preparation steps were done inside a four-port inert gas glove box (MBraun) by purging high purity argon gas (99.9995%) to maintain the moisture and oxygen content of <0.1 ppm. The experiments were carried out with different salt (LiTFSI) concentrations from 0.2 M to 2.0 M. Solvents DME, DOL, and TEGDME were mixed in an equal volume ratio DOL : DME : TEGDME. Similarly, to change the solvent composition, DOL : DME : TEGDME mixture was prepared in a 3 : 2 : 1 volume ratio. The conductivity was then measured by using multichannel conductivity spectroscopy (MCS-10) from Biologic Science Instruments, France. The MCS-10 is a fully integrated conductivity measurement system with a working range from 2 mScm^{-1} to 200 mScm^{-1} . MCS-10 is an advanced tool in electrochemical research, specially designed for measuring the conductivity of liquid electrolytes and impedance in a wide temperature range from -40°C to 150°C .

3. Results and Discussion

The conductivity of the electrolyte with varied concentrations at different temperatures is shown in Figure 1. The conductivity of the electrolyte was increasing as salt concentration increased from 1.0 M to 1.4 M. Beyond that, it gradually decreased, which might be attributed to the association of Li^+ ions and N^- ions with the solvent molecules resulting in the formation of solvated complexes of ion pair, which are electrically neutral. The formation of solvated complexes of ion pair might be responsible for the reduction in conductivity. A maximum conductivity value was obtained within the LiTFSI salt concentration range of 1.0 M to 1.4 M over a wide temperature range. This indicates that a minimum salt concentration larger than 1.0 M was required to generate sufficient salt ions to take part in the electrochemical reaction. If we further increased the salt concentration, the conductivity is decreased due to larger steric interaction in the salt-salt ion interaction. From Figure 1, a pattern was observed; at a LiTFSI salt concentration of 1.0 M, the maximum conductivity was achieved within -40°C to 0°C , which was due to the TEGDME melting point of -30°C . Meanwhile, by increasing the temperature from 0°C to 60°C , the maximum conductivity shifted from 1.2 M to 1.4 M, which was due to the decrease in viscosity of the electrolyte. It is clearly shown that the optimum salt concentration was 1.0 M at -40°C to 0°C , whereas it was increased in the range of 1.2 M to 1.4 M at 0°C to 60°C .

To understand the shifting of conductivity maxima and to optimize the solvent composition, a further experiment was conducted to find the optimum salt concentration ranging from 1.0 M to 1.4 M in a different solvent volume ratio (DOL : DME : TEGDME = 3 : 2 : 1), as shown in Figure 2. The

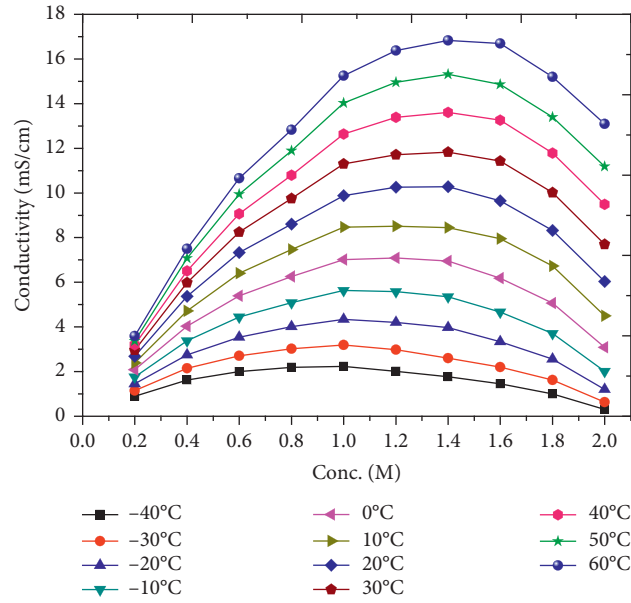


FIGURE 1: Conc. (M) vs. conductivity (mS/cm) ratio of (1:1:1) DOL:DME:TEGDME.

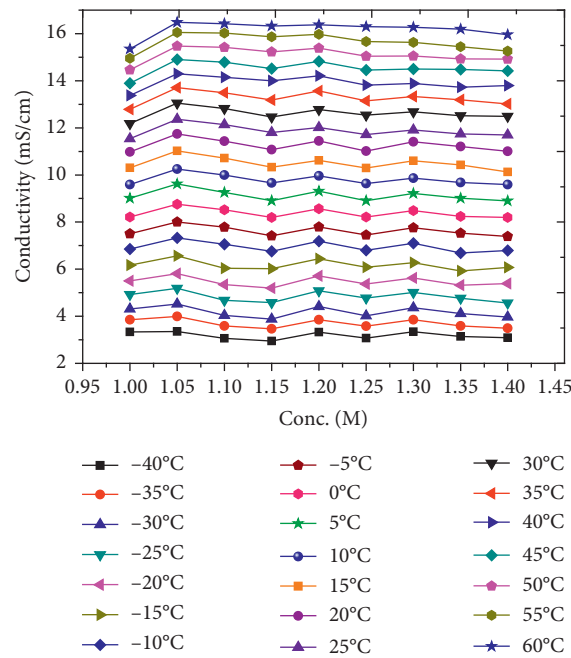


FIGURE 2: Conc. (M) vs. conductivity (mS/cm) ratio of (3:2:1) DOL:DME:TEGDME.

maximum conductivity was observed at an optimum salt concentration of 1.05 M at temperatures ranging from -40°C to 60°C . Different salt concentrations resulted in minute differences in conductivity from the maximum value, which might be contributed by the TEGDME solvent composition. This can be seen by decreasing the TEGDME solvent composition in the electrolyte (i.e., from 1:1:1 to 3:2:1), and the viscosity of the electrolyte solution decreased with the increasing temperature; thus, the optimum salt concentration dropped from 1.4 M to 1.05 M for all the temperatures ranging from -40°C to 60°C .

The present objective of the state-of-the-art electrolyte is to be used at the dynamic temperature range; thus, Arrhenius plots correlating the temperature dependence of the conductivity of the electrolyte over the temperature range of -40°C to 60°C are shown in Figures 3 and 4. The temperature dependence of the conductivity can be seen in the Arrhenius equation as follows:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{RT}\right), \quad (1)$$

where E_a is the activation energy, and in practice, it is taken to be the slope of a natural log of the Arrhenius plot, $\ln \sigma$

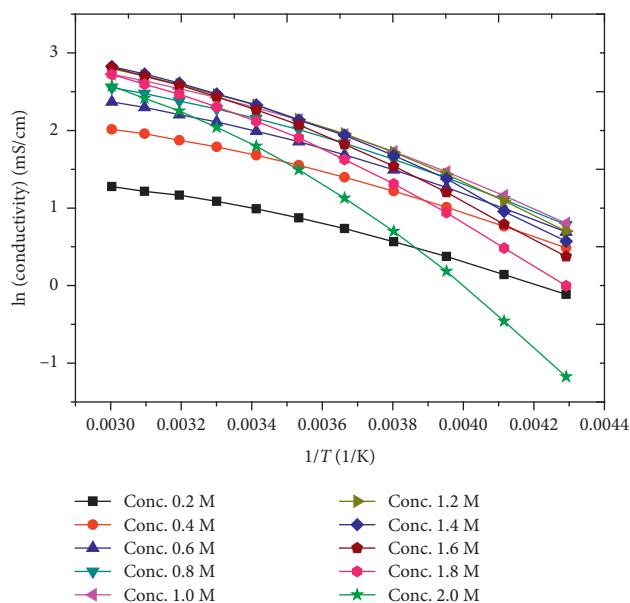


FIGURE 3: Arrhenius plot of (1 : 1 : 1) DOL : DME : TEGDME.

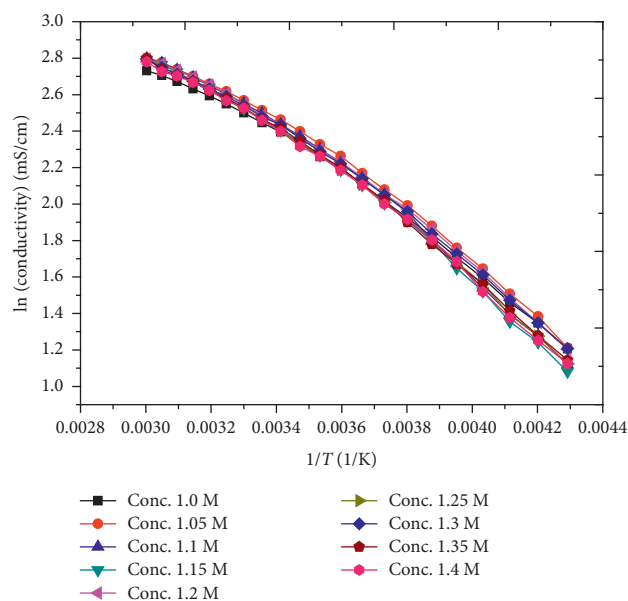


FIGURE 4: Arrhenius plot of (3 : 2 : 1) DOL : DME : TEGDME.

versus an inverse of T (K^{-1}). Consequently, the value of E_a can be computed from the graph of $\ln(\sigma)$ vs. $1/T$ with a negative slope. Figures 3 and 4 are not following the Arrhenius trend as it seems to be following the Vogel–Tamman–Fulcher trend.

The impedance of the organic electrolyte is usually low at a lower salt concentration (<1.0 M) but can vary considerably with many factors. The impedance value was measured at each frequency over a wide range of temperatures. The Nyquist plot was plotted for 1.0 M, 1.05 M, and 1.4 M salt concentration with a solvent composition of DOL : DME : TEGDME (3 : 2 : 1), as shown in Figure 5. Figure 5 shows that the impedance was decreasing as the temperatures increased from -40°C to 60°C with the lowest

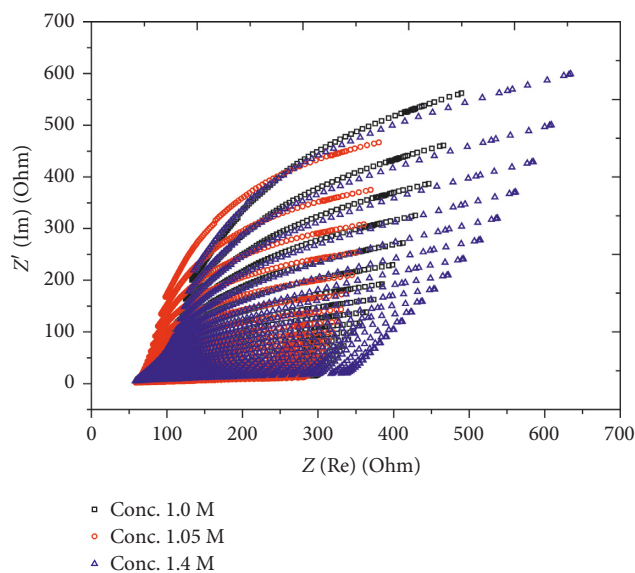


FIGURE 5: Nyquist plot of conc. 1.0 M, 1.05 M, and 1.4 M plotted from temperature ranging from -40°C to 60°C with a ratio of (3 : 2 : 1) DOL : DME : TEGDME.

impedance observed at 1.05 M salt concentration, which confirmed the maximum conductivity noted earlier.

4. Conclusions

A temperature study for the multiorganic solvent-based electrolyte system displaying maximum conductivity at an optimum LiTFSI salt concentration of 1.0 M to 1.4 M over a wide temperature range from -40°C to 60°C was reported. However, during the change in solvent volume ratio, despite the wide temperature range, the reported optimum salt concentration was 1.05 M. The results of the system did not follow the Arrhenius equation for all the temperatures, but it seemed to follow the Vogel–Tamman–Fulcher trend. Overall, in the present investigation, the operating temperature limit of the electrolyte was studied and reported for the corresponding conductivity and optimum salt concentration.

Data Availability

No data were used to support this study.

Conflicts of Interest

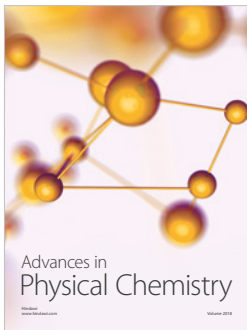
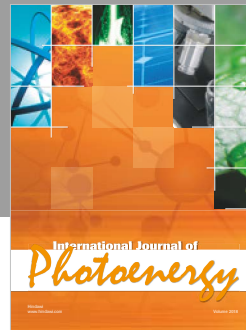
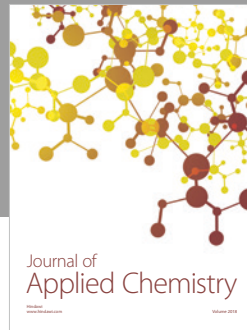
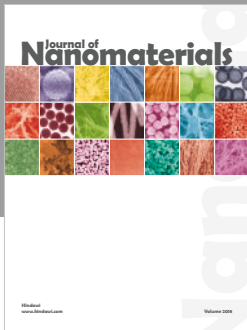
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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