Synthesis and Use of Zwitterion Bearing Sulfonyl(trifluoromethane sulfonyl)imide Anion as Additive for Polymer Electrolytes

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Abstract: In order to improve the electrochemical properties of poly(ethylene oxide), a well-known solid polymer electrolyte, by adding zwitterion molecules, the synthesis of a new zwitterion (ZN) having imidazolium cation and sulfonyl(trifluoromethane sulfonyl)imide anion is investigated. The addition of different amounts of ZN to the mixture of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and poly(ethylene glycol)dimethyl ether (PEGDM) of 1000 g mol\(^{-1}\) does not significantly affect the transition temperature of PEGDM but causes a slight decrease in ionic conductivity of the electrolyte mixtures. However, even with the presence of only 0.05 mole fraction of ZN, the anodic stability of LiTFSI/PEGDM based electrolytes is improved to over 4.5 V vs. Li+/Li at 25 °C. This makes the new synthesized zwitterion a promising electrolyte’s additive for high voltage batteries.

Keywords: zwitterion; sulfonyl(trifluoromethane sulfonyl)imide anion; polymer electrolyte

1. Introduction

Among different ion conductive polymers reported as solid polymer electrolytes for lithium batteries, the mixture of lithium salt and poly(ethylene oxide) (PEO) based polymers was by far the most investigated [1–6]. Indeed, PEO exhibits unique properties, including high polarity and chain mobility, which make it a good candidate to promote the dissociation of lithium salts and the transport of dissociated ions [7,8]. However, the strong interactions between lithium and ether oxygen sites restrict the transport of lithium ions in PEO matrix and the conductivity in such electrolytes is mainly contributed by the fast migration of anion species rather than that of lithium ions. As a consequence, strong concentration gradients occur during Li metal battery operation leading to deleterious effects on battery performance, such as Li dendrites growth and limited power density. In addition, the pristine PEO exhibits an anodic stability lower than 3.8 V vs. Li+/Li at 60 °C, which makes PEO-based electrolytes unstable against high-voltage cathode materials, such as LiCoO\(_2\) (LCO), LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) (NMC) and LiNi\(_{0.80}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) (NCA) [9,10]. In order to overcome these issues, various electrolyte additives have been proposed to increase the mobility of lithium ions and extend the anodic stability window of PEO-based electrolytes including the addition of inorganic fillers, such as TiO\(_2\), Al\(_2\)O\(_3\), SiO\(_2\) and POSS [11–14], ionic liquids [15–17] and zwitterions [18–25]. Addition of nanosized ceramic fillers to PEO matrix forms composites with better mechanical properties and enhanced conductivity due to the disruption of crystallites formation. Ionic liquids plasticize PEO and form an amorphous solid polymer electrolyte. Their incorporation into PEO matrix leads to significant increases in conductivity.
Zwitterions (ZIs) are organic molecules that contain the same number of cations and anions covalently bonded together. They possess unique properties reflecting those of ionic liquids, including non-volatility as well as thermal and electrochemical stabilities. Owning to their dipole structure, zwitterions can enhance the dissociation and mobility of lithium ions and hence increase the ionic conductivities of various lithium-based electrolyte systems. For example, Ohno et al. [18] observed a positive effect in ionic conductivity and lithium ion transference number after the addition of 1-ethylimidazolium-3-n-propane (or butane)sulfonate to a neutral polymer. Tiyapiboonchaiya et al. [19] also reported that the ionic conductivity of a lithium methyl acrylate copolymer, a single-ion conducting electrolyte, was increased from $1.6 \times 10^{-4}$ to $5.6 \times 10^{-4}$ S cm$^{-1}$ at 30 °C after adding 1-ethylimidazolium-3-n-butanesulfonate zwitterion. On the other hand, Fujita and coworkers recently showed that the addition of 5.5 wt% of ZIs improved the oxidation limit of oligoether-based electrolytes as well as the charge/discharge cycle stability of their Li/LCO cells [20,21,26]. These numerous reports show without a doubt the significant improvement of the electrochemical performance of electrolytes by the introduction of ZI structures, although the current understanding of zwitterion interactions with different species of lithium-based electrolytes is quite limited. Narita et al. [27] systematically investigated the effect of cation and anion nature as well as the spacer chain length on the electrochemical properties of ZI-lithium salt mixtures. They showed that the cation’s structure affects the ionic conductivity and the formation of an ionic liquid-like domain, as does the spacer-chain length, whereas the anion structure affects both ionic conductivity and transference number of carrier cations. Based on their studies, imidazolium cation is considered as the most suitable cation while (sulfonyl)imide-type anion has a significant effect on the mobility of carrier cations. Wohde et al. [23] recently reported that the addition of ZIs, bearing a sulfonate group, to ionic liquid/lithium salt mixtures used for battery application did not improve the overall electrochemical properties of the electrolytes. By considering these results, ZIs with negative group should link less strongly to lithium ions for improving the performance of ZIs as ion conductive materials. However, almost all studies on ZIs as conductive materials considered ZI molecules bearing either sulfonate or carboxylate groups. To our knowledge, there is no study reporting the use of ZI molecules possessing both cationic imidazolium and anionic (sulfonyl)imide groups.

The motivation of our work is thus the synthesis of a new ZI molecule bearing both an imidazolium cation and a sulfonyl(trifluoromethane sulfonyl)imide anion site and its use as an electrolyte additive for lithium batteries. In order to improve the oxidation resistance of PEO, the new ZI molecule was added to the electrolyte mixture containing lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and poly(ethylene glycol)dimethyl ether of 1000 g mol$^{-1}$.

2. Materials and Methods

2.1. Materials

Imidazole (99%) and chloroacetonitrile (99%) were purchased from TCI and used as received. Bis(trifluoromethane sulfonyl)imide lithium salt (99,95%) (LiTFSI), poly(ethylene glycol)dimethyl ether (PEGDM, $M_n = 1000$ g mol$^{-1}$) and anhydrous acetonitrile were purchased from Sigma-Aldrich. LiTFSI and PEGDM were dried under vacuum at 90 °C and 60 °C, respectively, before use. All solvents and other reagents were synthesis grade and they were used without further purification. Potassium vinyl sulfonyl(trifluoromethane sulfonyl)imide (vinyl-STFSI) was synthesized according to the published procedure [28].

2.2. Synthesis of potassium ((2-(1H-imidazol-1-yl)ethyl) sulfonyl)-(trifluoromethane sulfonyl)imide (potassium Im-2C-STFSI)

In a round-bottom flask equipped with a condenser, imidazole (1.09 g, 159.0 mmol) and potassium vinyl-STFSI (3.00 g, 10.6 mmol) were dissolved in 40 mL of methanol. The solution was stirred under reflux for 24 h. After the reaction, the solvent was removed by a rotary evaporator and the solid residue was then washed with 50 mL of dichloromethane. The resulting solid was filtered, rinsed with 20 mL of $n$-pentane and dried under vacuum to give the final product as a beige solid.
(mass = 2.8 g, yield = 76%). HRMS analysis of C₇H₇N₃O₄S₂F₃K: calculated m/z = 305.9821 [M-K]⁺, experimental m/z= 305.9813 [M-K]⁺. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 7.64 (s, –N=C–H, 1H); 7.20 (t, =CH–N<, 1H); 6.86 (t, =N–C=–CH, 1H); 4.31 (t, >N–C=–CH₂, 2H); 3.44 (t, CH₂–C=–SO₂, 2H). ¹⁹F NMR (376 MHz, DMSO-d₆, δ ppm): −77.49.

2.3. Synthesis of ((2-(3-(cyanomethyl)-1H-imidazol-3-ium-1-yl)ethyl)sulfonyl)((trifluoromethane sulfonyl)imide (called ZN))

To obtain the zwitterion bearing STFSI anion, potassium Im-2C-STFSI (2.00 g, 5.7 x 10⁻³ mol) and chloroacetonitrile (2.21 g, 28.7 x 10⁻³ mol) dissolved in 10 mL of acetonitrile were loaded in a 50 mL round-bottom flask equipped with a condenser. The solution was stirred under reflux overnight. After the reaction, the solvent was removed by a rotary evaporator and the solid residue was then washed by stirring with 50 mL of dichloromethane for 1 h. The resulting solid was filtered, rinsed with 20 mL of dichloromethane and dried under vacuum to give the final product as a beige solid (mass = 1.3 g, yield = 65%) (Scheme 1). HRMS analysis of C₈H₉N₄O₄S₂F₃: calculated m/z= 347.0090 [M + H⁺]⁺, experimental m/z= 347.0080 [M + H⁺]⁺. ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 9.36 (s, –N=C–N<, 1H); 7.92 (t, =C–N<, 1H); 7.89 (t, =N–C=–CH–, 1H); 5.59 (s, NC–C=–N, 2H); 4.61 (t, >N–C=–CH₂, 2H); 3.61 (t, CH₂–C=–SO₂, 2H). ¹⁹F NMR (376 MHz, DMSO-d₆, δ ppm): −77.54.

Scheme 1. Synthesis pathway of ((2-(3-(cyanomethyl)-1H-imidazol-3-ium-1-yl)ethyl)sulfonyl)((trifluoromethane sulfonyl)imide (ZN)) zwitterion.

2.4. Preparation of Electrolytes

The electrolytes were prepared by dissolving a given quantity of poly(ethylene glycol)dimethyl ether (PEGDM), lithium salt (LiTFSI) and different amounts of ZN zwitterion in anhydrous acetonitrile. These solutions were stirred at room temperature (RT) for 24 h and then the solvent was evaporated by using a rotary evaporator. The electrolytes were dried under vacuum at 60 °C for 6 h. The molar ratio of the ethylene oxide unit to the lithium salt ([EO]/[Li]) was fixed at 15. The molar content of ZN in the electrolytes varies from 0.05 to 0.15 relative to the mole number of LiTFSI salt. Table 1 summarizes the experimental data used for the preparation of electrolytes. Electrolyte mixtures were called ZN-x where x represents the molar ratio of ZN to the lithium salt.

Table 1. Experimental data used for the preparation of electrolytes.

| Sample | Mass of PEGDM (g) | Mass of LiTFSI (g) | Mass of ZN zwitterion (mg) | Volume of acetonitrile (mL) | ZN wt% in electrolyte (%) |
|--------|------------------|-------------------|--------------------------|----------------------------|--------------------------|
| ZN-0   | 3.0              | 1.24              | 0.0                      | 2.0                        | 0                        |
| ZN-0.05| 3.0              | 1.24              | 75.1                     | 2.0                        | 1.74                     |
| ZN-0.10| 3.0              | 1.24              | 150.1                    | 2.0                        | 3.41                     |
2.5. Methods

High resolution mass spectrometry (HRMS) experiments were performed with a Synapt G2 HDMS quadrupole/time-of-flight (Manchester, UK). The samples were introduced at 10 µl min⁻¹ flow rate (capillary voltage +2.8 kV, sampling cone voltage varied between +20 V and +60 V) under a desolvation gas (N₂) flow of 100 L h⁻¹ heated at 35 °C. Accurate mass experiments were performed using reference ions from poly(prolylene glycol) (PPG), poly(ethylene glycol) (PEG) or CH₃COONa internal standards. All the samples were dissolved in methanol doped with 3 mM ammonium acetate prior to analysis. Data analyses were conducted using MassLynx 4.1 programs provided by Waters.

Fourier-transformation infrared (FTIR) spectra were recorded using a Perkin Elmer Spectrum Two FTIR Spectrometer with an attenuated total reflectance (ATR) accessory.

Nuclear magnetic resonance (NMR) spectra of different nuclei were recorded by using Bruker AC 400 MHz. For the 7Li NMR measurements of electrolytes, an internal standard LiCl in D₂O (500 µL; 0.05 mol L⁻¹) was used and the signal related to Li peak was set at 0 ppm. The electrolytes were separated from the LiCl standard by a sealed insert in a 5 mm tube. All NMR experiments were carried out at room temperature.

Differential scanning calorimetry (DSC) experiments were carried out on a TA DSC Q20 using a heat/cool/heat cycle from -80 °C to 80 °C for the electrolyte mixtures and from -80 °C to 220 °C for zwitterion. The heating and cooling rates were fixed at 10 °C min⁻¹ and the measurements were carried out under nitrogen atmosphere. Glass transition temperature (Tg) and melting point (Tm) were determined from the second heating cycle of the DSC thermograms.

Thermogravimetric analysis (TGA) was performed with a TA Instruments Q500 employing an aluminum pan with a small amount of sample (3–5 mg). The experiments were recorded in dynamic conditions under nitrogen atmosphere heating at a rate of 10 °C min⁻¹ from room temperature to 600 °C. Before measurements, all compounds were dried at 60 °C for 18 h and stored in a dry room with dew point below -50 °C.

The ionic conductivity of the glass fiber separator impregnated with the zwitterion-based electrolytes was measured by electrochemical impedance spectroscopy (EIS) technique in symmetrical coin cells (2025, Hohsen) with blocking stainless steel electrodes (SS) and a glass fiber separator (Albet GF52203254) impregnated with 75 µL of the investigated electrolyte, using a 1470E potentiostat coupled with 1455 FRA interface (both from Solatron Analytical, UK). A 20 mV sinusoidal amplitude was applied in the 1 MHz – 1 Hz frequency range at different temperatures from 80 °C to 20 °C every 10 °C. The tests were performed using a dynamic climatic chamber Binder MK53 (Germany) with a temperature control accuracy of ±0.5 °C. The cells were allowed to stabilize for 1 h at each temperature before measurement. The so obtained EIS spectra were fitted using ZView software 3.5 (Scribner). Three parallel cells of each electrolyte were assembled and measured to guarantee a good reproducibility.

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) methods were employed to evaluate the oxidation (anodic) and reduction (cathodic) stability of the investigated electrolytes, respectively. To do this, a three-electrode cell HS-3E (Hohsen) with a stainless steel disc (SS) as the working electrode (area of 1.76 cm²), and lithium foil (50 µm, Albermarle), as the counter and reference electrodes, was assembled in a dry room (dew point -50 °C). The glass fiber separator impregnated with 150 µL of the investigated liquid electrolyte was placed in between the counter and the working electrodes. Then, the cell was kept at 25 °C for about 3 h before measurement to achieve a good internal contact and a stable interface between the electrolyte and electrodes. LSV and CV measurements were performed by 1470E potentiostat (Solatron Analytical) at scan rate 1 mVs⁻¹ and 25 °C. The LSV scan was measured starting from open circuit voltage (OCV) to 6 V vs. Li+/Li reference electrode and CV curve was measured starting from OCV to -0.5 V vs. Li+/Li ending at OCV. The tests were performed using a climatic chamber Binder MK53 (Germany).
3. Results

3.1. Thermal Properties

The thermal stability of the ZN molecule and electrolyte solutions was characterized by using TGA. The zwitterion molecule ZN starts to decompose at around 280 °C with a maximum weight loss above 300 °C where a unique decomposition process causes almost 80% of weight loss. This decomposition temperature is quite similar to those reported in the literature [21,29]. Thus, we can conclude that ZN possesses a good thermal stability, which enable its use as electrolyte additive for battery applications. All prepared electrolytes present a good thermal stability with the maximum weight loss above 390 °C. The electrolytes present two decomposition events; the first one causes almost 60 wt% loss while the second one, recorded as a small shoulder at higher temperature, causes approximately 20 wt% loss (Figure 1, Table 2). This second transition can be attributed to the degradation of LiTFSI salt. Its intensity decreases with the increasing of the zwitterion content in the formulation. While in the zwitterion there is almost no weight loss beside the main decomposition event, all electrolytes suffer a gradual weight loss due to moisture uptake by hygroscopic PEGDM and LiTFSI during the transfer of samples from the dry room to the TGA.

![Figure 1. TGA curves of ZN molecule and the investigated electrolyte solutions with and without ZN.](image)

DSC data show that ZN exhibits a T_g and a T_m at 12 °C and 166 °C, respectively. The T_m of ZN is higher than that of 3-(butyldimethylammonio)propyl sulfonyl-(trifluoromethane sulfonyl)imide, which is 104 °C [27], but lower than that observed for imidazolium-based zwitterions having a sulfonate group [29]. LiTFSI/PEGDM mixture shows a T_g at –56 °C and a small melting peak at around 20 °C. Yamaguchi et al. [21] reported a T_g of –54 °C and no melting point for the same mixture but with a molar ratio of [EO]/[Li] = 8. It is well known that increasing the lithium salt concentration allows it to decrease the crystallization of PEO. All the prepared LiTFSI/PEGDM solutions containing ZN zwitterion show no melting point and have almost the same T_g values as that of LiTFSI/PEGDM (Table 2). In comparison, Yamaguchi et al. [21] noted an increase of T_g of 9 °C for their sample composing of LiTFSI/PEGDM ([EO]/[Li] = 8) and 4.6 wt% of 3-(1-(2-(2-cyanoethoxy)ethyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate zwitterion. The only difference between Yamaguchi’s work and ours is the nature of the zwitterion anion sulfonate group in their study and STFSI anion in the present study. This suggests that the interaction between the STFSI anion and lithium ions is less strong, hence leading to a slight increase in the T_g value of electrolyte mixtures.
Table 2. Summary of TGA and differential scanning calorimetry (DSC) studies of the ZN molecule and investigated electrolytes.

| Sample          | Tg (°C) | Tm (°C) | T at 10 wt% loss (°C) | DTA max (°C) | R600°C (wt%) |
|-----------------|---------|---------|----------------------|--------------|--------------|
| ZN zwitterion   | 12      | 166     | 287                  | 310          | 21           |
| ZN-0            | -56     | 20      | 241                  | 405          | 3            |
| ZN-0.05         | -55     | /       | 238                  | 396          | 4            |
| ZN-0.10         | -53     | /       | 245                  | 397          | 6            |
| ZN-0.15         | -53     | /       | 270                  | 400          | 8            |

1 DTA max is the temperature at which the derivative of loss weight curve reaches the maximum. 2 R600°C is the residual mass at 600 °C.

3.2. Dissociation State of Lithium Salts

ATR-FTIR spectra of different compounds are presented in Figure 2. The dissociation state of LiTFSI salt in the PEGDM matrix can be observed by analyzing the shift of TFSI anion in the wavenumber range between 670 cm⁻¹ and 820 cm⁻¹. For example, the deformation band of CF₃ (δCF₃) in LiTFSI appears at around 746 cm⁻¹ [27], this band is also observed at the same position for ZN zwitterion. After mixing LiTFSI with PEGDM, the δCF₃ peak shifts to 739 cm⁻¹ indicating the dissociation statute of TFSI anion due to the strong solvation of lithium ion by PEGDM. The shift of vibration bands at 799 cm⁻¹ and 772 cm⁻¹ related to νS-N-S and νC-S respectively is also observed. However, the addition of ZN zwitterion to LiTFSI/PEGDM mixtures does not change the position of these bands since the anion site of zwitterion has similar structure as TFSI anion of lithium salt.

Figure 2. ATR-FTIR of ZN zwitterion, lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and poly(ethylen glycol) (PEG)-based electrolytes in a wavenumber range from 670 cm⁻¹ to 820 cm⁻¹.

To further characterize the molecular environment of lithium cations, liquid ⁷Li NMR measurements were performed. Figure 3 shows the ⁷Li NMR spectra of ZN-0 and ZN-0.1 electrolyte mixtures. Broadening of the lithium peak is observed for both electrolyte samples that is caused by an increase of their viscosity in the electrolyte mixtures. Analyzing the chemical shift of these spectra reveals that the coordination of the lithium ion is not changed upon addition of ZN since the anion natures of the lithium salt and zwitterion compound are very similar. Indeed, the Li peak in ZN-0...
and ZN-0.1 electrolytes are observed at −1 ppm and −0.98 ppm, respectively. In contrast, Wohde et al. [23] reported a pronounced change in the lithium ion coordination when the sulfonate based ZI was used.

![Figure 3. ](image)

**Figure 3.** $^7$Li NMR spectra of ZN-0 and ZN-0.1 electrolytes.

### 3.3. Ionic Conductivity

The ionic conductivity of all prepared electrolytes was measured by EIS technique and is reported through the Arrhenius plots from 80 to 20 °C (Figure 4). The curvature of these plots indicates that the temperature dependence of conductivity can be expressed by Vogel–Fulcher–Tamman relation, which also describes the temperature dependence of viscosity in viscous material. The ionic conductivity value of ZN-0 is $2.6 \times 10^{-4}$ S cm$^{-1}$ at 30 °C, whereas the ionic conductivities of ZN-$x$ $(x = 0.05, 0.10$ and $0.15)$ at the same temperature are $2.2 \times 10^{-4}$ S cm$^{-1}$, $1.6 \times 10^{-4}$ S cm$^{-1}$ and $1.4 \times 10^{-4}$ S cm$^{-1}$, respectively. The addition of ZN causes a slight decrease of ionic conductivity as its content increases. This drop in ionic conductivity after adding the zwitterion was already observed for PEG-based electrolytes [20,21] and ionic liquid based electrolytes [23,25]. Indeed, the electrostatic interaction of zwitterion with LiTFSI and PEGDM causes an increase in the viscosity of the electrolytes and, consequently, decreases their ionic conductivity [29]. However, the presented electrolytes possess good ionic conductivity at 30 °C which is higher than those obtained for similar electrolyte systems reported previously using 3-(1-(2-(2-cyanoethoxy)ethyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate zwitterion as electrolyte additive [21].
3.4. Electrochemical Stability

In battery application, the stability of electrolytes in a wide electrochemical window is an important factor. The electrochemical stability of the prepared electrolytes was tested by linear sweep voltammetry (LSV) and cyclic voltammetry (CV). Since the ionic conductivity values of ZN-0.1 and ZN-0.15 are very similar, the electrochemical stability study was only performed for ZN-0.05 and ZN-0.1 electrolytes. Figures 5 and 6 show, respectively, the linear sweep voltammograms and cyclic voltammograms of PEG-based electrolytes containing various amount of ZN zwitterion. As it can be seen, all investigated compounds present quite similar profiles during both electro-oxidation and electro-reduction processes.
Figure 5. Linear sweep voltammograms of three-electrode cells with LiTFSI/PEGDM electrolytes containing various amount of ZN zwitterion. Testing conditions: 25 °C; scan rate 1 mV s⁻¹; counter and reference electrodes—Li metal (50 µm); working electrode—polished stainless steel. The inset is a zoom in between current 0 and 0.2 mA cm⁻².

The oxidative degradation of all compounds presents a unique defined on-set electrode potential. The oxidation limit of LiTFSI/PEGDM was 4.0 V at 25 °C which is consistent with other reported values of PEO based electrolytes [9] but that is lower than that reported by Yamaguchi et al. [21] in the same electrolyte system but with higher lithium salt concentration. The presence of only 0.05 mole fraction of ZN in the electrolytes’ formulations is able to notably improve the electrochemical stability of LiTFSI/PEGDM-based electrolytes. Indeed, the anodic limit of LiTFSI/PEGDM/ZN mixtures shifts to values higher than 4.5 V vs. Li⁺/Li. Several reports showed that the electrochemical stability of oligomer and polymer electrolytes was improved by addition of zwitterions [19–21]. This improvement is the result of the formation of a zwitterion stable layer on electrode surface that prevents the PEGDM and TFSI anion to approach to the electrode.

The CV study of the electrolytes (Figure 6) shows that all compounds go through similar reduction processes. In principle, it can be seen that Li deposition/stripping process is quite reversible for all investigated electrolytes. Generally, organic molecules having a nitrile group, as in ZN, can exhibit reductive reaction at potential above 0 V vs. Li⁺/Li due to the polymerization of the nitrile group. In the present study, the reduction peak of ZN-0.05 and ZN-0.1 is observed at 0.35 V and 0.42 V vs. Li⁺/Li, respectively. In the literature, the reduction of 3-(phenylsulfonyl)propionitrile as the electrolyte additive added to carbonate-based liquid electrolyte was reported at 0.8 V vs. Li⁺/Li [30].
Figure 6. Cyclic voltammograms (first scan) of three-electrode cells with LiTFSI/PEGDM electrolytes containing various amount of ZN zwitterion. Testing conditions: 25 °C; scan rate 1 mV s⁻¹; counter and reference electrodes – Li metal (50 µm); working electrode – polished stainless steel.

4. Conclusion

In conclusion, we demonstrated an easy way to synthesize a new zwitterion (ZN) containing imidazolium cation and sulfonyl(trifluoromethane sulfonyl)imide anion. The addition of ZN to LiTFSI/PEGDM electrolytes does not significantly affect the thermal properties of electrolytes as well as their ionic conductivity. We noted only a slight decrease of conductivity from 2.6 x 10⁻⁴ S cm⁻¹ to 2.2 x 10⁻⁴ S cm⁻¹ at 30 °C after adding 0.05 mole fraction of ZN thanks to the STFSI anion bearing by ZN, allowing a better dissociation of the lithium ion than other anion groups like carboxylate or sulfonate. The electrochemical stability of LiTFSI/PEGDM/ZN exceeds 4.5 V vs. Li⁺/Li, which is higher than that of Li/PEO-based electrolytes (3.8 V vs. Li⁺/Li), even for low ZN content. From these results, we can say that the new ZN zwitterion is an effective candidate for improving the electrochemical stability of PEGDM in particular and PEO in general, hence making it a promising candidate for Li metal and Li ion batteries with conventional high-voltage materials. More electrochemical tests in relevant battery environments (e.g., Li-Li, Li/Cathode and Anode/Cathode coin cells) are definitely required to assess all electrochemical properties of the investigated electrolytes.

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