Asymmetric sulfonium-based molten salts with TFSI⁻ or PF₆⁻ anion as novel electrolytes

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Abstract

A novel series of molten salts based on asymmetric sulfonium cations ($[R_1R_2RS]^+$, wherein R_1, $R_2 = CH_3$, $R = C_2H_5$, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, corresponding to S_{112}^+, S_{114}^+, S_{116}^+, S_{118}^+, respectively) with TFSI⁻ or PF₆⁻ anion as novel electrolytes have been prepared and characterized. Some of the physical and electrochemical properties of the salts, including thermal property, density, solubility in common solvents, conductivity, and electrochemical stability have been investigated. Three types of phase transition behavior and two types of decomposition behavior have been observed for these molten salts on heating. In the case of $[R_1R_2RS]^+$ PF₆⁻, which have much higher solubility in water compared to those with imidazolium cation which have only alkyl groups. In addition, the Arrhenius equation approximately describes the relationship between conductivity and temperature for some of these sulfonium-based molten salts with TFSI⁻ anion in the high temperature region studied. The electrochemical windows are approximately 4.1 V for S_{112}TFSI and S_{114}TFSI, which are liquid at room temperature (25 °C).
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1. Introduction

Room temperature molten salts (RTMS), that is, room temperature ionic liquids, are liquids composed entirely of cations and anions within a wide temperature range (including room temperature). Due to their unique characteristics such as negligible volatility, non-flammability and high thermal stability, they have attracted considerable interest in recent years for applications as promising "green" electrolytes for electrochemical devices, such as lithium-ion batteries, dye-sensitized solar cells and super capacitors [1–6].

Chloroaluminate-type room temperature molten salts are the first generation of room temperature molten salts [7], however, sensitivity of such molten salts to water and air is a principal drawback. Recently, nonchloroaluminate room temperature molten salts have been studied extensively [8–32]. Among these molten salts, there are many species of anions, such as BF₄⁻ [8], PF₆⁻ [9], $[(CF_3SO_2)_2N]^-$ (TFSI⁻) [10],

$[(CF_3SO_2)(CF_3CO)N]^-$ (TSAC⁻) [11], $[F(HF)_{2.3}]^-$ [12], $[N(CN)_2]^-$ [13], $[C(CN)_3]^-$ [14], $[R_fBF_3]^-$ [15], BOB⁻ [16], and so on. On the cationic side, molten salts incorporating imidazolium [17–21], pyrrolidinium [22], tetraalkylammonium [23,24], and quaternary phosphonium (QP) [25,26] cations have undergone extensive investigation. Moreover, it has been pointed out that most of such molten salts have the general structure of an asymmetrical organic cation [27,28]. Relative to them, electrochemical researches involving sulfonium cations-based molten salts are quite rare [29–31], especially nonchloroaluminate molten salts based on asymmetric sulfonium cations. One recent paper [32] reported some asymmetric sulfonium-based room temperature molten salts with TFSI⁻ anion, however, research focused on their temperature dependence of viscosity.

In order to gain further understanding and extend the range of applications of asymmetric sulfonium-based molten salts electrolytes, investigation on preparation method and properties of new class of such molten salts is necessary. In this paper, therefore, we report the preparation and characterization of a new group of molten salts based on asymmetric trialkylsulfonium cation (AS-based molten salts, $[R_1R_2RS]^+$, where R_1, $R_2 = CH_3$, $R = C_2H_5$, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, corresponding to S_{112}^+,

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Table 1
Structures of AS-based molten salts prepared

Salts	Cation	R	Anion
$S_{112}TFSI$	S_{112}^+	Ethyl	$TFSI^-$
$S_{114}TFSI$	S_{114}^+	1-Butyl	$TFSI^-$
$S_{116}TFSI$	S_{116}^+	1-Hexyl	$TFSI^-$
$S_{118}TFSI$	S_{118}^+	1-Octyl	$TFSI^-$
$S_{112}PF_6$	S_{112}^+	Ethyl	PF_6^-
$S_{114}PF_6$	S_{114}^+	1-Butyl	PF_6^-
$S_{116}PF_6$	S_{116}^+	1-Hexyl	PF_6^-

S_{114}^+, S_{116}^+, S_{118}^+, respectively) used as novel electrolytes, as shown in Table 1. Some of these prepared salts are liquid at room temperature (25 °C). At the same time, we investigate the thermal properties, including phase behavior and thermal stability, for these salts, as well as solubility in some common solvents. Additionally, we study the electrochemical stability for the salts having melting points below room temperature (25 °C), and the temperature dependence of conductivity.

2. Experimental

2.1. Reagents and materials

Methyl sulfide (99+%), 1-bromohexane (99+%), 1-bromo-octane (99%) and hexafluorophosphoric acid (60 wt.% solution in water) were purchased from Acros Organics and used without further purification. Bromoethane and *N*-butylbromide were obtained from Shanghai Chemical Reagent Company and redistilled before use. Lithium bis (trifluoromethylsulfonyl) imide (LiTFSI) was kindly provided by Morita Chemical Industries Co., Ltd. and used as received. All the other chemicals used in this work were of A.R. grade.

2.2. Synthesis and characterization of asymmetric sulfonium-based molten salts

A series of dimethylalkylsulfonium bromide were prepared by mixing equimolar amount of methyl sulfide and alkylbromide in dry acetonitrile according to procedures reported previously [33]. The products were washed with excess anhydrous ether, and dried in vacuo at room temperature for 3 days. Ethyldimethylsulfonium bis(trifluoro-methylsulfonyl) imide ($S_{112}TFSI$), ethyldimethylsulfonium hexafluorophosphate ($S_{112}PF_6$), 1-butyldimethylsulfonium bis (trifluoromethylsulfonyl) imide ($S_{114}TFSI$), 1-butyldimethylsulfonium hexafluorophosphate ($S_{114}PF_6$), 1-hexanedimethyl sulfonium bis(trifluoromethylsulfonyl) imide ($S_{116}TFSI$), 1-hexanedimethylsulfonium hexafluorophosphate ($S_{116}PF_6$) and 1-octyldimethylsulfonium bis(trifluoromethylsulfonyl) imide ($S_{118}TFSI$) were synthesized according to procedures described in REFs [9,10]. $S_{112}TFSI$, $S_{114}TFSI$, $S_{116}TFSI$ and $S_{118}TFSI$ were dried under vacuum at 80 °C for 24 h, then dried over activated

4A molecular sieves. On the other hand, $S_{112}PF_6$, $S_{114}PF_6$ and $S_{116}PF_6$ were dried under vacuum at 40 °C for 3 days. Finally, they all were stored in a desiccator. The structures of synthesized salts were identified by ^1H NMR and ^{13}C NMR (Mercury Yplus), and the characterization data are as follows.

Results of ^1H NMR (400 MHz): $S_{112}TFSI$ (neat): δ 2.77 (t, CH₂), 2.31 (s, 2CH₃), 0.89 (t, CH₃); $S_{114}TFSI$ (neat): 2.76 (t, CH₂), 2.35 (s, 2CH₃), 1.23 (m, CH₂), 0.98 (m, CH₂), 0.45 (t, CH₃); $S_{116}TFSI$ (acetone-d₆): 3.19 (t, CH₂), 2.99 (t, 2CH₂), 2.83 (t, CH₃), 1.32 (s, 2CH₃), 0.86 (t, 2CH₂); $S_{118}TFSI$ (acetone-d₆): 3.25 (t, CH₂), 3.09–2.98 (broad, 18H), 2.88 (t, CH₃); $S_{112}PF_6$ (methanol-d₄): 3.31 (t, CH₂), 2.88 (s, 2CH₃), 1.47 (t, CH₃); $S_{114}PF_6$ (methanol-d₄): 2.89 (t, CH₂), 2.89 (s, 2CH₃), 1.79 (m, CH₂), 1.51 (m, CH₂), 1.00 (t, CH₃); $S_{116}PF_6$ (acetone-d₆): 3.19–3.05 (broad, 17H), 2.85 (m, CH₂) ppm. Results of ^{13}C NMR (100 MHz): $S_{112}TFSI$ (neat): δ 124.8–115.4 (s, N(CF₃SO₂)₂), 37.8 (S, CH₂), 23.7 (t, 2CH₃), 7.7 (s, CH₃); $S_{114}TFSI$ (neat): 124.9–117.9 (s, N(CF₃SO₂)₂), 43.0 (s, CH₂), 25.6 (s, CH₂), 24.1 (t, 2CH₃), 21.4 (s, CH₂), 12.8 (s, CH₃); $S_{116}TFSI$ (acetone-d₆): 124.8–116.0 (s, N(CF₃SO₂)₂), 43.2 (s, CH₂), 26.4 (t, 2CH₃), 24.3 (s, CH₂), 24.0 (s, CH₂), 23.6 (s, CH₂), 22.1 (s, CH₂), 13.4 (s, CH₃); $S_{112}PF_6$ (methanol-d₄): 37.5 (s, CH₂), 23.2 (t, 2CH₃), 7.5 (s, CH₃); $S_{114}PF_6$ (methanol-d₄): 42.8 (s, CH₂), 25.5 (s, CH₂), 23.8 (t, 2CH₃), 21.4 (s, CH₂), 12.5 (s, CH₃) ppm.

2.3. Measurement

The water content in the molten salts, of which melting point is below room temperature (25 °C), that is, $S_{112}TFSI$ and $S_{114}TFSI$, were detected by a moisture titrator (Metrohm 73KF Coulometer) according to Karl–Fischer method, and the values are about 130 and 190 ppm, respectively. The density was approximately determined by weighting a measured volume of the prepared salts. The solubility was estimated by gradual addition of deionized water or other solvents in salts. Thermal measurements were performed using sealed aluminum pans containing a small amount of samples (10–20 mg) with a differential scanning calorimeter (DSC, Perkin-Elmer Pyris 1). The samples were cooled at 10 °C min⁻¹ from room temperature to ~−70 °C and then heated at a same rate to a predetermined temperature. Thermogravimetric analysis data were obtained by TGA (Perkin-Elmer, 7 series thermal analysis system) from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The aluminium pans were used in all experiments. Ionic conductivities were measured by using a DDS-11A conductivity meter with a DJS-1C conductivity cell having a nominal cell constant of 0.95/298 K under Ar atmosphere. The electrochemical measurement was carried out by cyclic voltammetry (scan rate 10 mV s⁻¹) using a HSV-100 electrochemical working station (Hokuto Denko) with three-electrode cell in an argon-filled UNILAB glove box ([O₂] < 1 ppm, [H₂O] < 1 ppm). Platinum disk (geometric area = 3.14 × 10⁻² cm²) was used as working electrode, and lithium metal was used as both counter electrode and reference electrode.

Table 2
Physical properties of AS-based salts prepared (25 °C)

Salt	M_W[a] (g mol^{-1})	d[b] (g cm^{-3})	T_c[c] (°C)	T_{s-s}[d] (°C)	T_m[e] (°C)	T_d[f] (°C)	ΔS_m[g] (J mol^{-1} K^{-1})
S_{111}TFSI[h]	357.32	1.58[h]	nm[i]	nm	44.5[h]	nm	nm
S_{112}TFSI	371.34	1.56	no[j]	no	19.1	290.2	80.7
S_{114}TFSI	399.40	1.55	−45.0	no	−3.6	278.4	49.3
S_{116}TFSI	427.45	∼1.60[k]	no	no	43.5	293.5	50.1
S_{118}TFSI	455.50	nm	no	no	44.0	296.6	68.6
S_{112}PF$_6$	236.16	nm	no	no	>200[l]	289.1	no
S_{114}PF$_6$	264.21	nm	no	no	84.3	289.4	35.8
S_{116}PF$_6$	292.27	nm	no	−26.4, 9.6	133.0	407.1	7.3

[a] Molecular weight.
[b] Density.
[c] Crystallization temperature (onset of the crystallization peak).
[d] Solid–solid transition temperature (onset of the solid–solid peak).
[e] Melting point (onset of the endothermic peak).
[f] Decomposition temperature (onset of decomposition peak).
[g] Entropy of melting ($\Delta S_m = \Delta H_m / T_m$, where ΔH_m is melting enthalpy at T_m).
[h] From Ref. [29], measured at 45 °C.
[i] Not measured.
[j] Not obtained.
[k] Measured at 55 °C.
[l] Measured by a microscope melting point apparatus.

3. Results and discussion

3.1. Thermal properties of AS-based molten salts prepared

Thermal properties of the salts including crystallization temperature (T_c), solid–solid transition (T_{s-s}), melting point (T_m) and decomposition temperature (T_d), if appropriate, are obtained and summarized in Table 2. The glass transition does not occur within experiment temperature range due to limitation of cool treatment to a minimum temperature of ∼ −70 °C. In addition, the DSC curve of S_{112}PF$_6$ does not exhibit transition behavior in experimental condition.

These AS-based salts exhibit three types of phase transition behavior. Fig. 1 shows the DSC curves of three molten salts (S_{114}TFSI, S_{116}TFSI and S_{116}PF$_6$) as examples. S_{114}TFSI shows a crystallization transition and melting transition. Unlike S_{114}TFSI, S_{112}TFSI, S_{116}TFSI, S_{118}TFSI and S_{114}PF$_6$ exhibit
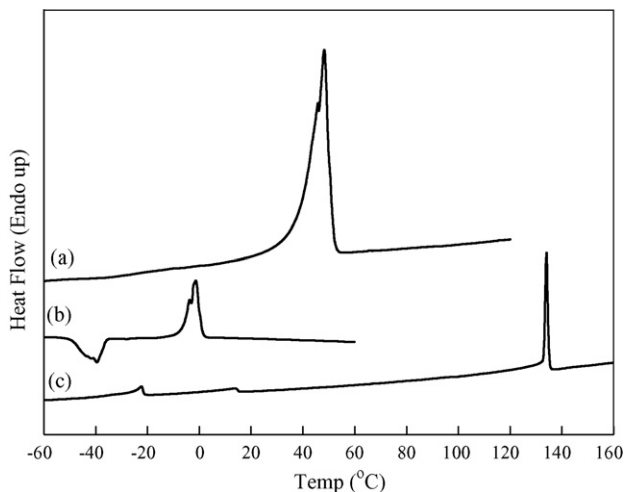
Fig. 1. DSC curves of (a) S_{116}TFSI; (b) S_{114}TFSI; (c) S_{116}PF6.

that there are only a melting transition. In addition, S_{116}PF$_6$ exhibits multiple solid–solid transitions before melting, like some pyrrolidinium and morpholinium molten salts [22,34–37].

The melting entropies (ΔS_m) of the above salts are also listed in Table 2. Timmermans [38] firstly described in detail plastic crystals and indicated that ΔS_m of molecular compounds showing plastic phases was less than 20 J K^{-1} mol^{-1}. Recently, MacFarlane, et al. [22,35] modified this criterion and pointed out that ΔS_m of ionic plastic crystal phases was approximately 40 J K^{-1} mol^{-1} for ionic materials having relatively flexible anions such as TFSI$^-$ anion. In the case of prepared salts containing PF$_6$$^-$ anion, S_{116}PF$_6$ exhibits solid–solid transition characteristics with $\Delta S_m = 7.2$ J K^{-1} mol^{-1}, suggesting that S_{116}PF$_6$ may show ionic plastic behavior, however, S_{114}PF$_6$ with $\Delta S_m = 35.8$ J K^{-1} mol^{-1} did not show this transition, which indicates that AS-PF$_6$$^-$ salts prepared obey Timmermans criterion due to low degree of freedom of PF$_6$$^-$ [34]. On the other hand, all AS-TFSI$^-$ salts studied in this work do not exhibit solid–solid transition because ΔS_m of these salts are higher than 40 J K^{-1} mol^{-1}.

Fig. 2 shows the melting point (T_m) of AS-based salts. The melting point of the salt with TFSI$^-$ decreased initially as carbon number in R group in AS cation increased, and reached a minimum value, and then tended to increase when further increasing of carbon number in the R group. At the same time, the relationship between the melting points of AS-PF$_6$$^-$ salts and carbon number in the R group has the same tendency as that of AS-TFSI$^-$ salts. In addition, AS-TFSI$^-$ salts prepared had melting points below 50 °C and could be used as reaction solvents in synthetic reactions run above 50 °C. Moreover, it is apparent that S_{112}TFSI and S_{114}TFSI are liquids at room temperature (25 °C).

The AS-based salts prepared exhibit different decomposition behavior, as shown in Fig. 3. S_{112}PF$_6$ and S_{114}PF$_6$ showed a distinct two-stage decomposition behavior, and their behavior was almost same. Taking S_{114}PF$_6$ as an example, it was stable
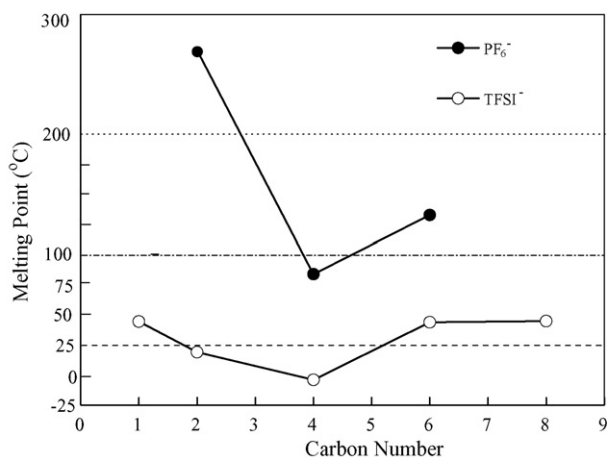
Fig. 2. The relationship between melting points and the carbon number of R group in AS cation. The melting point of S_{111}TFSI (carbon number = 1) is taken from Ref. [29].
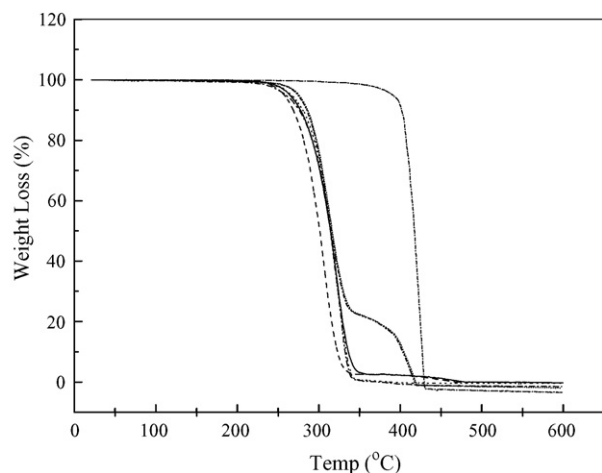

Fig. 3. TGA traces of prepared salts (solid: S_{112}TFSI; dash: S_{114}TFSI; dot: S_{116}TFSI; dash dot: S_{118}TFSI; dash dot dot: S_{112}PF$_6$; short dot: S_{114}PF$_6$; short dash dot: S_{116}PF$_6$).

until approximately 270 °C and decomposed between 290 and 340 °C. The weight loss percentage was about 77.14%. Subsequently, it started to decompose again at about 390 °C. On the other hand, all remained salts containing TFSI$^-$ were stable until 270–280 °C and decomposed rapidly between 290 and 340 °C. Particularly, S_{116}PF$_6$ showed the thermal stable property until about 390 °C.
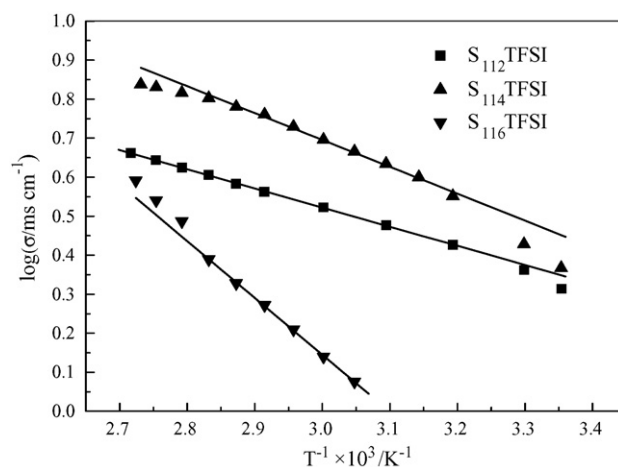

Fig. 4. Arrhenius plot of conductivity (log σ vs. 1/*T*) for the molten salts.

3.2. Solubility of AS-based salts in organic solvents

Table 3 shows the solubility of AS-based salts prepared in some common solvents at room temperature (25 °C). It can be observed that all the salts were immiscible in diethyl ether, and miscible in dichloromethane and in methanol and in acetone. In 99.7% ethanol (w/w), the salts containing TFSI$^-$ anion were miscible while the remained salts were partially miscible. Additionally, the salts with PF$_6^-$ anion had much higher solubility in water when compared to those with TFSI$^-$ anion. Moreover, it was interesting that compared with molten salts based on PF$_6^-$ anion combined with imidazolium cation in which there have only alkyl groups and do not have hydroxyl or ether functional groups [39,40], solubility in water of the prepared salts with PF$_6^-$ anion increased obviously, which can also confirmed by the remarkable decrease in the yields of AS-PF$_6^-$ salts after the addition of deionized water to remove excess HPF$_6$, demonstrating the species of the cation also influence the solubility in water of molten salts. At the same time, with the elongation of cation alkyl chain, the solubility in water of molten salts incorporating PF$_6^-$ anion decreased initially, and then increased. This phenomenon will be further investigated.

3.3. Electrochemical properties of prepared salts

The Arrhenius plot of conductivity for prepared salts containing TFSI$^-$ anion except for S_{118}TFSI is shown in Fig. 4. Generally, the Arrhenius equation was valid in describ-

Table 3
Solubility of prepared salts in some solvents

Salt	H$_2$O (g L^{-1})	CH$_2$Cl$_2$	(CH$_3$CH$_2$)$_2$O	CH$_3$CH$_2$OH	CH$_3$OH	CH$_3$COCH$_3$
S_{112}TFSI	sm	misc	immisc	misc	misc	misc
S_{114}TFSI	sm	misc	immisc	misc	misc	misc
S_{116}TFSI	sm	misc	immisc	misc	misc	misc
S_{118}TFSI	sm	misc	immisc	misc	misc	misc
S_{112}PF$_6$	33.3	misc	immisc	pm	misc	misc
S_{114}PF$_6$	17.6	misc	immisc	pm	misc	misc
S_{116}PF$_6$	22.7	misc	immisc	pm	misc	misc

misc: miscible; immisc: immiscible; sm: slightly miscible; pm: partially miscible.

Table 4
Ionic conductivities σ (ms cm^{-1}) of the prepared salts containing TFSI$^-$ anion except for S$_{118}$TFSI at 40 °C and Arrhenius activation energies E_a (kJ mol^{-1}), unless otherwise noted

Salt	σ (ms cm^{-1})	E_a (kJ mol^{-1})	R^2
S$_{112}$TFSI	2.67	9.39	0.999
S$_{114}$TFSI	3.56	13.18	0.995
S$_{116}$TFSI	1.19[a]	27.85[a]	0.999

[a] 55 °C
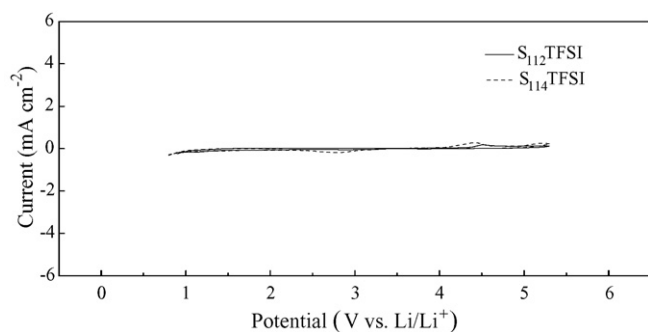
Fig. 5. Cyclic voltammograms of S$_{112}$TFSI and S$_{114}$TFSI at 25 °C. Scan rate: 10 mV s^{-1}; working electrode: Pt, counter electrode; reference electrode: Li.

ing conductivity temperature relationship for molten salts containing imidazolium cation in the low temperature region [21,28,41]. As shown in Fig. 4, the temperature dependences of the conductivity of S$_{112}$TFSI and S$_{114}$TFSI follow the Arrhenius relation in the high temperature region studied, not including room temperature. For S$_{116}$TFSI, the Arrhenius plot was approximately fit for the relationship between conductivity and temperature over temperature range above melting point. The ionic conductivities and activation energies calculated from the slope of the linear Arrhenius region around 40 °C, unless otherwise noted, are listed in Table 4.

Cyclic voltammograms are shown in Fig. 5 for S$_{112}$TFSI and S$_{114}$TFSI cycled on a platinum disk working electrode at 25 °C. The cathodic limit potentials (E_{cl}) of S$_{112}$TFSI and S$_{114}$TFSI are about 1.0 and 0.9 V versus Li/Li$^+$, respectively, and the anodic limit potential (E_{al}) of the above two salts is about 5.1 V versus Li/Li$^+$, which indicates their electrochemical window values are approximately 4.1 V at 25 °C.

4. Conclusions

A new family of molten salts electrolytes containing asymmetric sulfonium cations and TFSI$^-$ or PF$_6^-$ anion have been synthesized and characterized, at the same time, some physical and electrochemical properties have been determined. These prepared salts exhibit three types of phase transition behavior on heating. S$_{114}$TFSI exhibit a crystallization transition and melting transition while S$_{112}$TFSI, S$_{116}$TFSI, S$_{118}$TFSI and S$_{114}$PF$_6$ only show melting transitions. Additionally, S$_{116}$PF$_6$ shows multiple solid–solid transitions. Moreover, such salts exhibit two types of decomposition behavior. S$_{112}$PF$_6$ and S$_{114}$PF$_6$ show a distinct two-stage decomposition behavior while the

others exhibit one stage behavior. Those salts with PF$_6^-$ anion show much higher solubility in water compared with PF$_6^-$-type molten salts containing imidazolium cation in which there have only alkyl groups, revealing the type of the cation also influences the solubility in water of molten salts. The relationship between conductivity and temperature of some of prepared salts containing TFSI$^-$ anion is fitted to Arrhenius equation in the high temperature region studied, not including room temperature. The potential windows are approximately 4.1 V for S$_{112}$TFSI and S$_{114}$TFSI.

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