Stabilisation of the superoxide anion in bis(fluorosulfonyl)imide (FSI) ionic liquid by small chain length phosphonium cations: Voltammetric, DFT modelling and spectroscopic perspectives

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ABSTRACT
Ionic liquids (ILs) containing the bis(fluorosulfonyl)imide anion, FSI, have been investigated as electrolytes for metal-air batteries. Full chemical reversibility is found for the reduction of oxygen to superoxide at 60 °C under short time scale conditions of cyclic voltammetry at a glassy carbon electrode when the IL contains the small chain length triisobutyl(methyl)phosphonium rather than a pyrrolidinium cation. DFT calculations suggest that this is a consequence of the higher ion pair association energy and shorter intermolecular distance associated with the interaction of the superoxide anion with the phosphonium cation. Stabilization on longer timescales was also established by spectroscopic techniques when the phosphonium based ILs were exposed to KO2. Studies on superoxide stability in related ionic liquids containing the triisobutyl(methyl)phosphonium cation with the fluorosulfonyl(trifluoromethanesulfonyl)imide, FTFSI, or bis(trifluoromethanesulfonyl)imide, TFSI, anions are also reported.

1. Introduction

The increase in demand for high energy density, fast charging and long lifetime batteries is driving alternatives to Li-ion batteries. In this context, the use of lithium and sodium as metal anodes has attracted a great deal of attention due to their high theoretical energy density [1–5]. However, the use of reactive metals introduces new issues such as dendrite formation, organic liquid electrolyte decomposition and unstable passivation layers, which can lead to battery failure [2,4–7]. The formation of a solid electrolyte interphase (SEI) can limit the formation and growth of dendrites on the surface of the metallic anode and hence improve the lifetime of the battery [5]. Clearly, since the SEI is formed as a result of partial electrolyte decomposition by reaction with the metallic anode, the electrolyte composition has a crucial effect on its properties [8]. Bis(fluorosulfonyl)imide (FSI)-based ionic liquids (ILs) have become of interest for Na and Li metal-based energy storage as they provide high Na (and Li) solubility and mobility, and a more stable, conductive and uniform SEI rich in inorganic fluorinated compounds [5,9,10]. This exciting property has triggered the use of FSI-based ILs in metal-air batteries [1]. Metal-air batteries have emerged as a clear substitute for Li-ion batteries due to their high energy density (e.g. 1108 Wh kg−1 for Na-air vs 548 Wh kg−1 for Li-ion) [11]. Since lithium and sodium metal are the anodes in metal-air technologies, they will also benefit from a stable and uniform SEI. Unfortunately, despite the advantages of the FSI anion from the anodic perspective, FSI-based electrolytes, such as N-methyl-N-propyl pyrrolidinium ([C3mpyr]+) [12] and N-butyl-N-methyl pyrrolidinium ([C4mpyr]+) [13], perform poorly from the cathodic perspective because of the chemical irreversibility of the oxygen reduction reaction (ORR), and therefore unsuitable in this context.

A family of ionic liquids based on the combination of FSI anion and a short alkyl chain phosphonium cation provides promising electrolytes for Na and Li batteries [4,14–16]. For instance, triisobutyl(methyl) phosphonium based ionic liquids, [P14i4i4i4]+, have been studied as...
electrolytes for Na-metal batteries and exhibit good cyclability and a stable SEI [4,17]. This family of ILs have not been investigated in regard to their oxygen reduction stability and hence their potential as electrolytes for metal-air batteries is unknown. Interestingly, ILs with the larger tris(n-hexyl)tetradecyl phosphonium ([P_{66614}]\(^+\)) cation and anions such as bis(trifluoromethanesulfonylimide) (TFSI), tris(perfluoroalkyl)trifluorophosphate (FAP) or chloride, commonly have chemical processes accompanying the ORR under conditions of cyclic voltammetry consistent with only short term stability of superoxide [18–24]. Thus, a major aim of this study is to establish whether in fact a high level of superoxide stability may be a desirable property more readily achieved with ILs containing smaller chain length phosphonium cations.

Here, we report a comparison of the electrochemical performance, in the presence of oxygen, of a series of neat [P_{114444}]\(^+\)-based ILs containing the FSI anion, TFSI anion, and a recently introduced asymmetric fluorosulfonyl(trifluoromethanesulfonylimide), FTFSI, anion. A comprehensive study of the chemical and electrochemical reversibility of the oxygen reduction reaction is presented using cyclic voltammetry in combination with data provided by density functional theory (DFT) and spectroscopic techniques (NMR, Raman and FTIR). Via these studies, we establish that the chemical reversibility of ORR strongly depends on the nature of the cation in FSI-based ILs. The

Fig. 1. Cyclic voltammograms obtained in O\(_2\)-saturated for a) [P_{114444}]\(^+\)-ILs at a GC electrode (inset: electrochemical window for [P_{114444}][FSI]), b) experimental and simulated data for [P_{114444}][FSI] IL, c) [P_{114444}]\(^+\)-based ILs at a Au electrode, d) normalised cyclic voltammograms and e) scan rate dependence in [C\(_3\)mpyr][FSI] at a GC electrode. Temperature: 60 °C, Scan rate: 100 mV s\(^{-1}\).

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enhanced chemical reversibility of the ORR in the newly investigated ILs is attributed to the shorter intermolecular distance between the $[P_{144644}]^{+}$ cation and the electrogenerated superoxide anion compared to the $[C_{3}mpyr]+$ cation, as determined by computational studies. This generic study therefore establishes a new family of ILs of interest for metal-air battery technologies.

2. Results and discussion

Fig. 1a displays cyclic voltammograms (CVs) obtained with a glassy carbon (GC) electrode at 60 °C for the ILs with a $[P_{144644}]^{+}$ cation and FSI, TFSI and the asymmetric FTFSI anions (Fig. 2) under oxygen saturated conditions. This elevated temperature is required to achieve a liquid state due to the plastic crystal nature of the FSI and TFSI-based $[P_{144644}]^{+}$ materials at lower temperatures [25]. However, this also could be of advantage, as usually a lower overpotential is obtained at higher temperatures due to the enhanced mobility of the ions, leading to longer and more efficient cycling of the batteries [4,26]. Within the electrochemical window available (Fig. 1a inset), one cathodic (C) and one anodic (A) process is observed in the potential region of −1.2 to −1.4 V vs Fe$^{3+}$/Fe$^{2+}$, which is associated with the O$_{2}$/O$_{2}^{-}$ couple. This process is followed by a second (Fig. S1b) chemically irreversible reduction process at more negative potentials analogous to that described in reference [23] in other ILs. Thus, in the short alkyl chain phosphonium materials at lower temperatures [25] . However, this also means due to overlap of second reduction process with ORR one.

Due to the highly nucleophilic character and hence reactive nature of O$_{2}^{-}$ with protons, the chemical reversibility of the O$_{2}$/O$_{2}^{-}$ couple can be strongly affected by adventitious moisture, which can facilitate a disproportionation reaction to generate an overall irreversible two electron oxygen reduction process [21,28,29]. However, a chemically reversible one electron ORR is observed in this study in the presence of a small concentration of residual water (below 50 ppm). Insensitivity to the relative current densities. On the basis of their structures, a current density for the IL with the FTFSI anion midway between FSI and TFSI, the relative current densities in determining the theory describing the transient peak current for reduction of O$_{2}$ from cyclic voltammograms obtained at a GC macrodisk electrode and the steady state limiting current obtained at a Pt microdisk electrode as described in the SI.

A higher C$_{O_{2}}$ (7.7 mM) in the TFSI-based IL in comparison with the FSI and FTFSI analogues, that have lower oxygen solubilities of about 4 mM (Table 1), accompanies the higher fluorine content of this anion. This is consistent with reports for pyrrolidinium-based ILs with highly fluorinated anions such as nonafluorobutylsulfonyl(trifluoromethanesulfonyl)imide and bis(pentafluoroethanesulfonyl)imide [30]. Oxygen diffusivity (D$_{O_{2}}$) is slightly higher for the FSI anion (13.5 *10$^{-10}$ m$^{2}$ s$^{-1}$) than other anions. This and indeed the diffusion coefficients for oxygen with other anions are higher than those reported in other ILs (Table S1) which is predominantly attributed to the use of significantly higher temperatures in this work (60 °C). The value obtained with the FSI and FTFSI anions is in fact similar to that for ferrocene and other species in molecular solvents such as acetonitrile (17 *10$^{-10}$ m$^{2}$ s$^{-1}$ at RT) [31]. According to the Randles-Sevcik equation, the current density is proportional to D$_{O_{2}}$*$C_{O_{2}}$, so differences in C$_{O_{2}}$ impact more than do those for D$_{O_{2}}$ in determining the relative current densities. On the basis of their structures, a current density for the IL with the FTFSI anion midway between FSI and TFSI could be expected, whereas it is closer to that for the FSI anion because of their similar oxygen solubilities. The Randles-Sevcik equation has been previously used in ILs [32,33].

In principle, the electrode kinetics for the ORR process are reflected by the peak-to-peak potential separations ($\Delta$E$_{p}$) in cyclic voltammograms [34]. All $\Delta$E$_{p}$ values (Table 1) at a GC electrode for the ORR reaction in $[P_{144644}]^{+}$-based ILs lie in the range of 0.09 to 0.13 V, which is in the electrochemically quasi-reversible, rather than reversible, regime at a scan rate of 100 mV s$^{-1}$. The fact that the FSI-based IL has the smallest $\Delta$E$_{p}$ implies slightly faster electrode kinetics than in the other ILs.

The heterogeneous charge transfer rate constant ($k_{0}$) for the O$_{2}$/O$_{2}^{-}$ process at a GC electrode is more accurately calculated from comparison of the experimental and simulated data (Fig. 1b and S4) than from $\Delta$E$_{p}$ values. For the determination of $k_{0}$, the reversible potential ($E^{0}$, Table 1) was approximated as the mid-point potential (E$_{mp}$). This approximation assumes that D$_{O_{2}}$ and D$_{O_{2}^{-}}$ are equal, which is certainly not true [35-38]. The $k_{0}$ values at a GC electrode estimated by reference to

Table 1

<table>
<thead>
<tr>
<th>Conductivity/10$^{-3}$ (S cm$^{-1}$)</th>
<th>$E_{mp}$ (V)</th>
<th>$\Delta$E$_{p}$ (V)</th>
<th>D$<em>{O</em>{2}}$/10$^{-10}$ (m$^{2}$ s$^{-1}$)</th>
<th>C$<em>{O</em>{2}}$(mM)</th>
<th>$k_{0}$/10$^{-2}$ (m s$^{-1}$)</th>
<th>$[P_{144644}][FSI]$</th>
<th>$[P_{144644}][TFSI]$</th>
<th>$[P_{144644}][FTFSI]$</th>
<th>$[C_{3}mpyr][FSI]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6 ± 0.5</td>
<td>$-1.24$</td>
<td>0.09</td>
<td>13.5 ± 1.5</td>
<td>3.7 ± 0.6</td>
<td>$10 \pm 2.2$</td>
<td>6.6 ± 0.5</td>
<td>3.7 ± 0.5</td>
<td>2.8 ± 0.5</td>
<td>18.3 ± 0.5</td>
</tr>
<tr>
<td>$E_{mp}$ (V)</td>
<td>$-1.25$</td>
<td>0.13</td>
<td>6.5 ± 1.9</td>
<td>7.7 ± 0.8</td>
<td>5 ± 1.1</td>
<td>$-1.22$</td>
<td>$-1.19$</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>$\Delta$E$_{p}$ (V)</td>
<td></td>
<td></td>
<td>12.0 ± 1.2</td>
<td>4.2 ± 0.4</td>
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<td>$a$</td>
<td>$a$</td>
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<td>$a$</td>
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<tr>
<td>D$<em>{O</em>{2}}$/10$^{-10}$ (m$^{2}$ s$^{-1}$)</td>
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<td></td>
<td>$a$</td>
<td>$a$</td>
<td>$a$</td>
<td>$a$</td>
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<tr>
<td>C$<em>{O</em>{2}}$(mM)</td>
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<td>$a$</td>
<td>$a$</td>
<td>$a$</td>
<td>$a$</td>
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<tr>
<td>$k_{0}$/10$^{-2}$ (m s$^{-1}$)</td>
<td></td>
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<td></td>
<td></td>
<td>$a$</td>
<td>$a$</td>
<td>$a$</td>
<td>$a$</td>
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</table>

*Not measurable due to overlap of second reduction process with ORR one.

Fig. 2. Structures of the ILs used in this study.
simulated data vary from 5 to 10 $\times 10^{-5}$ m s$^{-1}$ for the TFSI derivative respectively (with $k^{0} = 8 \times 10^{-5}$ m s$^{-1}$ for the FTFSI IL), which correlates with the trend of the $\Delta E_{p}$ values. Errors present in $E^{0}$ and $k^{0}$ values by assuming $D_{O_{2}}$ and $D_{O_{3}^{•}}$ are equal are considered in some detail in the SI section and are believed to be small.

The ORR voltammetry is also dependent on the identity of the working electrode. Fig. 1c provides cyclic voltammograms for the series of [P141444][FSI] ILS with a gold working electrode. In comparison to the GC data, $\Delta E_{p}$ is increased from just over 0.10 V to about 0.20 V, implying slower electrode kinetics on the Au electrode, as reported for a family of imidazolium and ammonium-based ILS at room temperature [28,36,39]. Comparisons of $k^{0}$ values with literature data are difficult because of variability in experimental conditions. Nevertheless, $k^{0}$ values for the O$_{2}$/O$_{3}^{•}$ process in the same range have been reported for hexyltriethylammonium-TFSI ILS at Au and Pt electrodes (e.g. $k^{0} = 5 \times 10^{-5}$ and 3$\times 10^{-5}$ m s$^{-1}$, respectively), although these apply at the lower temperature, 35 °C [35]. The identity of the anion has also been reported to influence the $k^{0}$ value in the case of [P66644][IL], with respect to the TFSI and trifluorotris(pentfluoroethyl)phosphinate anions (i.e. 1.77 vs 0.11 $\times 10^{-3}$ cm s$^{-1}$, respectively at an Au electrode) [35]. Different cation and anion domains exist within the IL [37,38] and the structural change that accompanies electron transfer when converting O$_{3}^{•}$ (most strongly dependent) to O$_{2}$ (resides in cation domain) is expected to be IL dependent. Within experimental uncertainty, the $k^{0}$ values for the ILS with the FSI and FTFSI anions are indistinguishable, but slightly higher than that obtained for the TFSI derivative. In a thermodynamic context it can also be noted (Table 1) that $E_{p}$ values are also not strongly dependent on the identity of the anion. In summary, with respect to the electrode kinetics at a GC electrode it is concluded that in all the phosphonium-based ILS studied the ORR process is quasi-reversible in the electrochemical sense and reversible in the chemical sense.

The higher chemical ORR reversibility in the [P141444][FSI] IL, as opposed to pyrrolidinium-based ones, such as [Cmpyr][FSI] [13] and [Cmpyr][FSI] [12], was examined in greater depth by undertaking new studies at a GC electrode with [Cmpyr][FSI] at 60 °C with a scan rate of 100 mV s$^{-1}$. Under the now experimentally equivalent conditions used in the phosphonium-based IL, the cyclic voltammetry in O$_{2}$-saturated [Cmpyr][FSI] exhibits a smaller oxidation than reduction peak current (Fig. 1a) which is attributed to a lack of full chemical reversibility. The peak current ratio departure from unity and the comparison with the phosphonium analogue is more clearly visualised in the normalised version of the cyclic voltammograms (Fig. 1d). Increasing the scan rate for the ORR in [Cmpyr][FSI] leads to full chemical reversibility, but also increases the peak-to-peak potential separation, as expected for an electrochemically quasi-reversible system (Fig. 1e) [34].

The cyclic voltammetric data reveal that the stability of O$_{3}^{•}$ in FSI based ILSs of interest in battery development is dependent on the identity of the IL cation. DFT calculations were therefore undertaken to probe the origin of this cation dependent enhanced stability. In this theoretical study, a series of ion pairs were constructed to determine possible sources for stabilisation of O$_{2}$ derived from interaction of the IL cation ([P141444]$^{+}$ and [Cmpyr]$^{+}$) with O$_{2}$$. For comparison, Cl$^{-}$ and O$_{3}^{•}$ were paired with the cations to probe the influence of having a charged species and establish the oxygen affinity of the cation. The ion pair association energy shows that the interaction with O$_{3}^{•}$ is very weak and similar with both cations (Table 2). This is expected since uncharged O$_{2}$ will not specifically reside in the cationic domain of the IL. Both ionic liquid interaction values are regarded as equal within the DFT intrinsic error. In contrast, with the Cl$^{-}$ and O$_{2}$--cation ion pairs that are expected to reside in the cationic domain, differences in the association energy values are statistically significant, with values being larger for [P141444]$^{+}$ than for [Cmpyr]$^{+}$ (61.9 vs 26.1 kJ mol$^{-1}$), as expected if the IL cation nature is to have an impact on the stability of the O$_{3}^{•}$ anion. It is also noted that the intermolecular distance from the central heterocatom of the IL cation and oxygen, superoxide and chloride exhibit the same trend as for the ion pair association energies (Table 2). The DFT calculations also suggest that higher stabilization of superoxide is achieved with [P141444]+ than with [Cmpyr]$^{+}$.

According to DFT theory, a weaker cation-O$_{2}$ interaction translates into a larger intermolecular distance. Thus, the fact that the [Cmpyr]$^{+}$ + Cl$^{-}$ and [Cmpyr]$^{+}$ + O$_{3}^{•}$ distances are similar, implies a lack of anion dependence. In contrast, the intermolecular distance in the [P141444]+ IL does depend on the anion nature, with the highest association energy correlated with the shortest intermolecular [P141444]+ -O$_{2}$ distance. Additionally, it is noted that the [P141444]+ distance to the two superoxide O atoms (2.21 and 3.03 Å) are smaller than that for [Cmpyr]+ -O$_{2}$ (3.25 and 3.52 Å) (Fig. 3a and b). The shorter distance again suggests a stronger interaction for P-O$_{2}$ than N-O$_{2}$, which implies higher stability of the O$_{2}$ in the presence of the P-cation. However, if the interaction is too strong, the superoxide could be hindered when undergoing oxidation back to O$_{2}$, giving rise to slow electrode kinetics. Thus, it is concluded that the N-O$_{2}$ distance is not short enough to prevent O$_{2}$ reacting with other species in the electrolyte, whereas the distance P-O$_{2}$ is short enough to inhibit side reactions, but not short enough to appreciably hinder superoxide oxidation back to O$_{2}$. Similar behaviour has been observed in our previous studies when comparing phosphonium and tetraethylammonium cations having the same chain length [23].

In order to provide information relevant to the long term degradation of the ILSs by superoxide, as reported with ILSs containing longer chain phosphonium cations [18–20,35,40], the [P141444]+ and [Cmpyr][FSI] ILSs mixed with excess K$_{2}$O$_{2}$ were maintained with stirring at 60 °C for at least a month. Samples both exposed and non-exposed to K$_{2}$O$_{2}$ were then examined by FTIR, NMR and Raman spectroscopy (Fig. 3c and Figs. S5 and S6b). Due to the nucleophilic character of O$_{2}$, electron-deficient groups in the anions such as S=O, are prone to degradation [41]. In the case of [P141444][FTFSI], only a new shoulder at 1042 cm$^{-1}$ was observed in the presence of K$_{2}$O$_{2}$ (Fig. S5a). The origin of this band has not been identified. No spectroscopic changes were observed in the anion regions of the other two [P141444]+ ILSs on addition of K$_{2}$O$_{2}$. In contrast, the FTIR spectra for [Cmpyr][FSI] show a well-defined new band at 1024 cm$^{-1}$ in the [Cmpyr]$^{+}$ ring mode region (1100–900 cm$^{-1}$), implying degradation of this cation (Fig. 3c). In the NMR spectra, the $^{1}$H and $^{19}$F resonances shift and broaden in the presence of K$_{2}$O$_{2}$, attributed to the paramagnetic effect of the superoxide, but no new resonances are detected (Fig. S5b and c).

Raman spectra showed a broadening of the band corresponding to the C–H vibration in the cation region for [Cmpyr][FSI], in the presence of O$_{2}$ as depicted in Fig. S6a, probably to degradation, with no change detected in the phosphonium-based ILSs (Fig. S6b–d).

### Table 2

<table>
<thead>
<tr>
<th>Ion pairs</th>
<th>Association energy/kJ mol$^{-1}$</th>
<th>Distance/Å</th>
<th>r$_{1}$</th>
<th>r$_{2}$</th>
<th>r$_{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cmpyr]$^{+}$ - O$_{2}$</td>
<td>-2.6</td>
<td>4.39; 5.59</td>
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<td></td>
</tr>
<tr>
<td>[P141444]$^{+}$ - O$_{2}$</td>
<td>-1.8</td>
<td>4.74; 5.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cmpyr]$^{+}$ - O$_{3}^{•}$</td>
<td>-431.6</td>
<td>3.25; 3.52</td>
<td></td>
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<tr>
<td>[P141444]$^{+}$ - O$_{3}^{•}$</td>
<td>-450.0</td>
<td>2.21; 3.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cmpyr]$^{+}$ - Cl$^{-}$</td>
<td>-405.5</td>
<td>3.58</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>[P141444]$^{+}$ - Cl$^{-}$</td>
<td>-388.1</td>
<td>3.80</td>
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</tbody>
</table>
3. Conclusions

The oxygen reduction reaction, ORR, has been studied in a series of short alkyl chain \([P_{11444}\] \(^-\) based ILs containing bis(fluorosulfonyl) imide, FSI, bis(trifluoromethanesulfonyl)imide, TFSI, and fluorosulfonyl (trifluoromethanesulfonyl)imide, FTFSI as anions. All the ILs in this family display high chemical reversibility for the ORR under cyclic voltammetric conditions at a GC electrode using a scan rate of 100 mV s\(^{-1}\) at 60 °C. The IL with the TFSI anion displays the highest current density, predominantly attributable to the higher solubility of O\(_2\). However, the electrode kinetics are not strongly dependent on the IL anion when comparing the FSI vs FTFSI anions, respectively, despite the significant differences in ionic conductivity.

When comparing the cyclic voltammetry of FSI-based phosphonium and pyrrolidinium ILs, the ORR is not fully chemically reversible in the latter, demonstrating that superoxide stability is impacted by the nature of the cation. The higher ORR reversibility in the phosphonium-FSI IL is attributed to enhanced stabilization of the superoxide anion by the cation as supported by computational DFT calculations. This stabilization is reflected in higher association energy and shorter intermolecular distances between the \([P_{11444}\] \(^-\)O\(_2\)• ion pair. Experimental studies on the degradation of the ionic liquids and ORR non-reversibility have been undertaken by addition of KO\(_2\). Raman, NMR and FTIR spectra for the anions with a phosphonium cation essentially remain unaltered, consistent with high stability of O\(_2\)•, whereas differences in the IR and Raman spectra with the pyrrolidinium cation-based IL are observed as a consequence of chemical degradation.

The findings reported in this paper suggest pathways for conducting further research to establish the viability of non-volatile and safe IL electrolytes for use in metal-air batteries that employ the FSI anion, with the recognised advantages for operation with alkali metal anodes. In particular, further electrochemical investigations of these ionic liquids in the presence of alkali salts are required to establish their potential for specific metal-air chemistries.

CRediT authorship contribution statement

Laura Garcia-Quintana, cyclic voltammetry and spectroscopic experiments, experiment design, data analysis, results discussion, manuscript preparation. Erlendur Jónsson, MD simulations experiments, data analysis, revised manuscript. Ruhamah Yunis, materials synthesis, data analysis, revised manuscript. Douglas R. MacFarlane, discussion and revised manuscript. Maria Forsyth, discussion and revised manuscript. Alan M. Bond, supervision, project conception, discussion and revised manuscript. Patrick C. Howlett, discussion and revised manuscript. Cristina Pozo-Gonzalo supervision, project conception, discussion and revised manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2021.107029.

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