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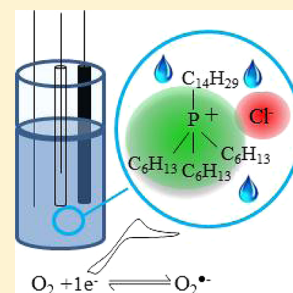
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S Supporting Information

ABSTRACT: Stable electrogenerated superoxide ion has been observed for the first time in a phosphonium-based ionic liquid in the presence of water, leading to a chemically reversible $O_2/O_2^{\bullet-}$ redox couple instead of the disproportionation reaction that is usually observed. It appears that the cation solvates the superoxide anion, stabilizing it against the disproportionation reaction. The electrogeneration is studied at various levels of water or other diluents including toluene to explore the limits of stability of the superoxide ion under these conditions.



SECTION: Energy Conversion and Storage; Energy and Charge Transport

The chemistry of the superoxide anion has been studied for decades in different aprotic solvents such as acetonitrile and *N,N*-dimethylformamide dimethyl sulfoxide and more recently in room-temperature ionic liquids (RTILs), where a stable superoxide anion is observed.^{1–3} Unfortunately, the presence of small quantities of water, which can be expected to be present in many contexts both pure and applied, affects the stability of the superoxide anion through a disproportionation reaction (eq 1).⁴ This is a major drawback for the performance of energy-storage devices because the superoxide ion ($O_2^{\bullet-}$) cannot participate in subsequent reduction reactions,⁵ thereby reducing the specific capacity of the device.



However, the chemistry of dioxygen and related electrochemical species has proved to be somewhat different in ionic liquids compared with conventional solvents, due to the specific interactions between the electrogenerated $O_2^{\bullet-}$ and the ionic liquid cation.^{6,7} Furthermore, it has recently been reported that the nature of the ionic liquid and additional additives plays an important role in the performance of energy-storage devices. For instance, ionic liquid electrolytes based on phosphonium chloride and with the addition of up to 8 wt % water have shown promising results in terms of efficient discharge of a magnesium electrode, apparently due to the formation of a protective and ionically conductive interface on the anode.^{8,9} However, understanding of the impact of this electrolyte composition on the cathodic reaction has not been elucidated thus far.

Therefore, the role of water on the oxygen reduction reaction (ORR) in electrolytes based on the ionic liquid trihexyl-

(tetradecyl)phosphonium chloride, $[P_{66614}][Cl]$, has been studied here. Surprisingly, to the best of our knowledge, we are able to report for the first time the chemical reversibility of the superoxide ion in the presence of water. This is attributed to the stabilizing of the electrogenerated $O_2^{\bullet-}$ in these electrolytes and may have significant implications for practical metal-air battery devices.

The cyclic voltammetry experiments of an oxygen-saturated trihexyl(tetradecyl)phosphonium chloride ionic liquid, $[P_{6,6,6,14}][Cl]$, solution containing 1.5% v/v of water using glassy carbon (GC) as the working electrode and scanning the potential from 0.8 to -1.9 V versus Ag/Ag^+ is depicted in Figure 1.

Two cathodic processes, E_{Red1} at -0.8 V and E_{Red2} at -1.3 V, and two anodic processes, E_{Ox1} at -0.13 V and E_{Ox2} at -0.23 V, were observed when the potential was scanned up to -1.9 V. However, when the potential was scanned only up to -1 V, only a single cathodic process, E_{Red1} , and one corresponding anodic process, E_{Ox1} , were observed. This implies that the second oxidation process depends on the formation of species Red_2 in the cathodic sweep.

Another feature notable in Figure 1 is the current density of the anodic process, E_{Ox1} , which is lower when the potential is scanned up to -1.9 V in comparison with scanning the potential up to -1 V. This is consistent with a further reduction

Received: April 2, 2013

Accepted: May 15, 2013

Published: May 15, 2013

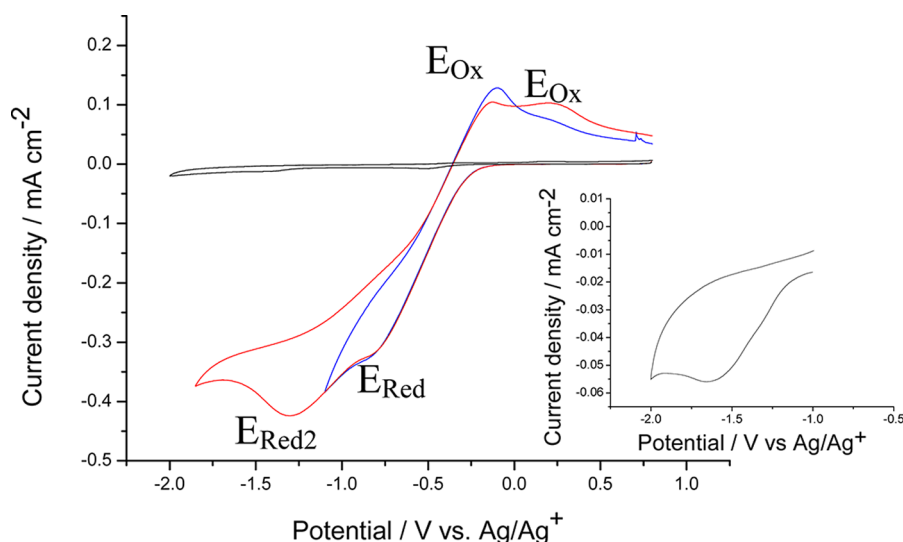


Figure 1. Cyclic voltammograms corresponding to the ORR in O_2 -saturated $[\text{P}_{6,6,6,14}][\text{Cl}]$ containing 1.5% v/v H_2O using a GC working electrode and (—) N_2 -saturated $[\text{P}_{6,6,6,14}][\text{Cl}]$ solution. Inset: Cyclic voltammogram corresponding to 0.79 mmol of H_2O_2 /gram of IL under nitrogen. Scan rate: 20 mV s^{-1} .

process of the reduced species (Red_1) which makes it unavailable for oxidation.

Additionally, the intensity of the second oxidation process, $E_{\text{Ox}2}$, increases when the potential is scanned to more negative potentials than -1 V , and this is probably due to a greater concentration of Red_2 that would be present near the working electrode at more negative potentials.

To confirm the nature of the electrochemical processes observed, we added 0.79 mmol of H_2O_2 per gram of IL was to the system and the cyclic voltammetry was determined. This can provide an indication of the generation of H_2O_2 or H_2O after the reduction process $E_{\text{Red}2}$ in the experiment in Figure 1 through either a two- or a four-electron pathway.¹⁰ The inset of Figure 1 shows for this situation an irreversible reduction process at -1.64 V , which is more negative than the two processes observed for the ORR in the $[\text{P}_{6,6,6,14}][\text{Cl}]$ solution in the absence of H_2O_2 (i.e., Red_1 and Red_2). Therefore these two cathodic processes may be ascribed to the reduction of O_2 and $\text{O}_2^{\bullet-}$, respectively (rather than to further reduction of H_2O_2).

When scanning the potential to -1 V , the peak potential separation (ΔE_p) corresponding to $\text{O}_2/\text{O}_2^{\bullet-}$ is 0.66 V . Such a large peak separation between the reduction process and the corresponding oxidation process, $E_{\text{Ox}1}$, may be due to an abnormally small heterogeneous electron-transfer rate constant leading to slow kinetics of the reduction process $E_{\text{Red}1}$ in the phosphonium based ionic liquid. René et al.⁶ have reported similar behavior for the $\text{O}_2/\text{O}_2^{\bullet-}$ couple in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

Also, a strong interaction between the superoxide anion, $\text{O}_2^{\bullet-}$, and the phosphonium cation could lead to a more hindered species in comparison with the neutral dioxygen, which may affect the mass transport and the diffusion coefficient of the superoxide anion ($D_{\text{O}_2^{\bullet-}}$). In fact $D_{\text{O}_2^{\bullet-}}$ tends to be between 1/30 to 1/50 smaller in comparison with the diffusion coefficient corresponding to O_2 .⁶ This can also explain the differences observed in the peak current corresponding to the cathodic process $E_{\text{Red}1}$ compared with the anodic process, $E_{\text{Ox}1}$.

The apparent stability of the superoxide $\text{O}_2^{\bullet-}$ in the case of the phosphonium-based ionic liquid containing a significant

quantity of water is quite surprising and has not previously been observed. Prior work has shown that in the presence of water in an ionic liquid the well-known disproportionation reaction⁴ will occur. The behavior observed here may be attributed to the stabilization of the superoxide anion due to a strong ion-pairing phenomenon between it and the phosphonium cation, as has been previously observed for this cation.¹¹ It is also important to note that the nucleophilic nature of the chloride anion and its strong tendency for hydration is likely to influence the balance of these interactions. Further investigations are required to determine the breadth of this behavior in phosphonium ILs with a range of anions. Furthermore, we should also consider that the nature of the working electrode can play a key role in the ORR mechanism, as already reported for GC in aqueous media.^{12,13} Nevertheless, in ionic liquid electrolytes the reversibility of the superoxide anion has not been observed in the presence of water using a GC working electrode. Several consecutive scans from 0.8 to -1 V stopping for 30 s prior to starting the next scan were performed showing reproducible voltammograms (Figure S1b in the Supporting Information), indicating the absence of any significant decomposition process or side reaction during each cycle. In addition, the potential was kept at -0.75 V versus Ag/Ag^+ for 30 min without any visual color change in the ionic liquid solution (Figure S1a in the Supporting Information). This is in contrast with the observation of Evans et al.,¹⁴ in a dry phosphonium IL, where the formation of a phosphorus ylide has been proposed involving α -proton abstraction from $[\text{P}_{6,6,6,14}]^+$ by superoxide.

Control experiments were performed in 0.1 M KOH aqueous solution to mimic basic media normally used in metal-air batteries.¹⁵ The ORR in 0.1 M KOH aqueous solution was performed (Figure S2 in the Supporting Information) using the same GC working electrode and by scanning the potential from 0.1 to -0.55 V versus Ag/AgCl (3 M NaCl). As expected, this showed one irreversible reduction process with similar values of current density as for the IL electrolytes. This may be related to the superior solubility of oxygen in the phosphonium-based ionic liquid (ca. 7.8 mM), as reported in the literature¹⁴ in

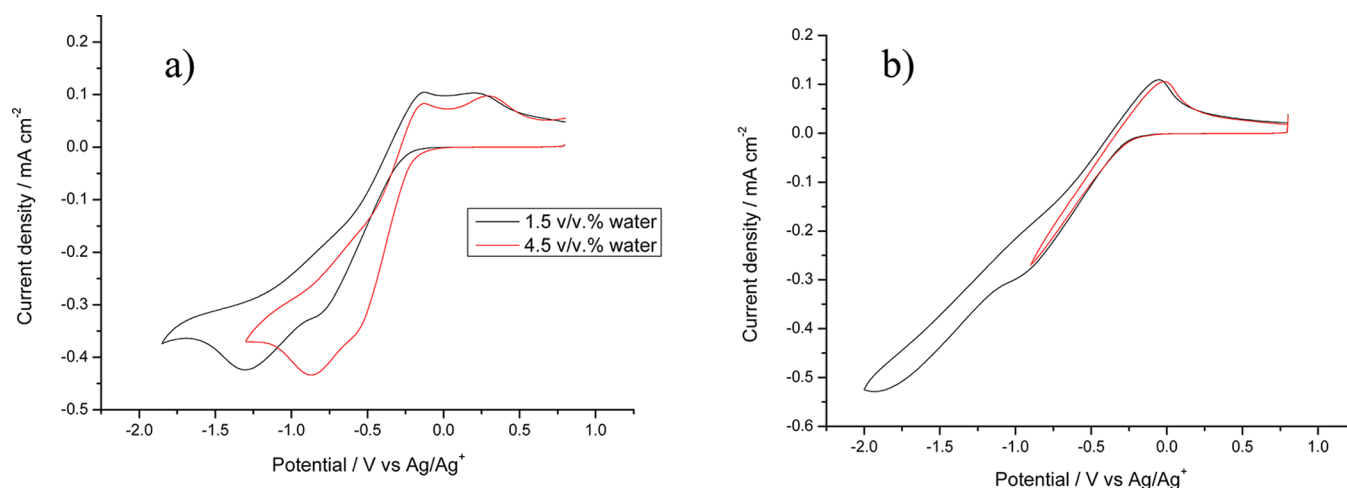


Figure 2. (a) Cyclic voltammograms for the ORR in ionic liquid [P_{6,6,6,14}][Cl] with water content of 1.5 and 4.5% v/v using GC as working electrode and (b) O₂-saturated [P_{6,6,6,14}][Cl] solution in the presence of 4.5% v/v toluene. Scan rate: 20 mV s⁻¹.

comparison with the 0.1 M KOH aqueous solution (ca. 1.2 mM).¹⁶

The effect of water content was then studied (Figure 2a). The cathodic processes corresponding to the reduction of O₂ and O₂^{•-} were observed to shift to less negative values. The shift in the *E*^{0'} value for a redox couple, as reported in the literature in aprotic solvents and anhydrous ionic liquids, can be due to the polarity of the solvent, nature of the electrolyte or the presence of acidic additives.¹⁷ For instance, Ohsaka et al.⁷ reported a positive shift in the ORR potential in a O₂-saturated DMSO solution upon increasing addition of 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMI][BF₄], using Au as the working electrode. In that work, the shift was ascribed as an ion-pairing phenomenon, which was more dominant than the solvation and protonation processes.⁷

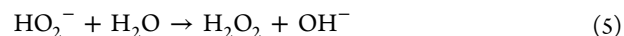
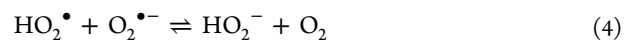
A further effect arising from the increase in water in the ionic liquid is a significant reduction of the viscosity of the electrolyte, which affects the mass transport of the dioxygen and electrogenerated species such as O₂^{•-} and O₂²⁻ and therefore the corresponding diffusion coefficient. Additionally, an increase in protons present in the solution due to the presence of water may lead to the protonated superoxide and peroxide ions, (HO₂[•] and HO₂⁻), which are prone to be reduced at lower potentials due to strong solvation, as already reported for the superoxide anion in the presence of water and dimethylformamide.¹⁸ In addition, because of the low conductivity of the systems being measured (i.e., 3.31 × 10⁻⁶ S cm⁻¹ without additional water content, 7.64 × 10⁻⁶ S cm⁻¹ for 2 wt %, and 3.56 × 10⁻⁵ S cm⁻¹ 4 wt % of water),¹⁹ some residual uncompensated resistance is also expected.

To establish which parameter has the most influence in the merging of the cathodic processes, we added a solvent with no acidic protons, such as toluene, instead of water. The cyclic voltammogram for the ORR in the presence of toluene is depicted in Figure 2b. The first difference observed is the onset potential for the ORR in this system, which is more negative than that corresponding to the water containing [P_{6,6,6,14}][Cl] solution (ca. 70 mV).

Furthermore, there are two major differences in comparison with the water experiment (Figure 2a): (i) two well-separated reduction waves are observed and (ii) the absence of the second oxidation process (*E*_{ox2}) in the reversible scan of the dioxygen reduction.

The viscosity of both samples was measured at 20 °C showing 423 and 1188 mPa s for the water and toluene IL electrolytes, respectively. To confirm that the differences in electrochemical behavior were not simply an effect of this viscosity difference, we prepared another IL/toluene sample with an equivalent molar concentration of toluene (i.e., 2.5 mmol/gram of IL) that has a viscosity of 121.6 mPa s. Interestingly, the same major electrochemical features were observed in this more fluid IL/toluene electrolyte as for the lower toluene concentration. These results confirm that the increase in proton concentration, due to the presence of water in the phosphonium IL electrolyte solution, plays a significant role in the behavior of the ORR.

As already discussed, a tentative mechanism (eqs 2–5) can therefore be established for the ORR in the presence of water after studying the role of protons in the process.



The ORR mechanism starts with the generation of the superoxide anion through a reduction reaction (eq 2). This is followed by the protonation of the superoxide anion to generate HO₂[•] (eq 3), as evidenced by the reduction potential *E*_{red2} in the presence or absence of acidic protons. As already mentioned, the protonated superoxide will be reduced at a more positive value than the nonprotonated species due to the strong solvation.¹⁸ Figure 2a shows that *E*_{red2} occurs at -1.3 V, a more positive potential as opposed to the ORR experiments undergone in the IL/toluene electrolyte solution, where a lack of acidic protons prevents the superoxide anion from protonation, and thus it is reduced at -1.9 V. The resulting HO₂[•] in eq 3 may undergo various reactions, as reported by Andrieux et al.,²⁰ in conventional organic solvents: (i) reduction at the electrode surface, (ii) reduction by O₂^{•-} in the solution, (iii) H-atom abstraction from the solvent, or (iv) H-atom disproportionation.

More recently, Hapiot et al.⁶ reported the protonation of superoxide in imidazolium-based ionic liquids by a family of weak acids (4-chlorophenol, phenol, *p*-cresol, and 2,4-

dimethylphenol). In that work, comparison of the voltammograms recorded in DMF and in [BMIm][TFSI] strongly suggests that HO_2^\bullet is immediately reduced in solution by another $\text{O}_2^{\bullet-}$, leading to HO_2^- and O_2 (eq 4), followed by the protonation of HO_2^- (eq 5).

This mechanism is also plausible in the case of the phosphonium-based ionic liquid with water as an additive due to the weak acidic nature of the water protons.²¹

Establishing the ORR mechanism enables the identification of the reactions that are active in the reverse scan as being the oxidation of $\text{O}_2^{\bullet-}$ for E_{Ox1} , while the second process E_{Ox2} may be due to the oxidation of HO_2^- .

In conclusion, we have shown that in a trihexyl(tetradecyl)-phosphonium chloride ionic liquid, when the ORR is investigated on a GC working electrode, the superoxide anion can be generated in the presence of large quantities of water, most likely due to a strong ion-pairing phenomenon between the superoxide anion and the phosphonium cation. As a result, reversibility of this redox reaction is observed for the first time in the presence of water. Furthermore, the increased presence of reactive protons from the water in the $[\text{P}_{6,6,6,14}][\text{Cl}]$ solution further improved the kinetics of the ORR, mainly due to the subsequent generation of the protonated superoxide and peroxide ions, HO_2^\bullet and HO_2^- . Finally a tentative mechanism for the ORR in the phosphonium-based ionic liquid has been established, highlighting the protonation step due to presence of water. This mechanism may also be the origin of the fact that the $[\text{P}_{6,6,6,14}][\text{Cl}]$ ionic liquid-based electrolyte can support the cathodic reaction in a metal-air battery, as previously seen for a primary Mg-air device.⁸

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental procedures and additional cyclic voltammograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the Australian Research Council (ARC) through the ARC Centre of Excellence for Electromaterials Science (ACES). M.F. and D.R.M. are grateful to the Australian Research Council for support under the Australian Laureate and Federation Fellowship schemes, respectively.

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