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Short communication

# Enhanced performance of phosphonium based ionic liquids towards 4 electrons oxygen reduction reaction upon addition of a weak proton source

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## ABSTRACT

The oxygen reduction reaction (ORR) in the presence of proton donors of similar proton activities (water, methanol and ethylene glycol), as well as weak and strong acids has been studied in a phosphonium-based IL, $[P_{66614}][Cl]$.

$[P_{66614}][Cl]$/ethylene glycol mixtures showed better ORR performance than mixtures containing water or methanol in terms of onset potential and current density. This enhancement in performance similar to that produced by weak acids, is attributed to the self-stabilization of ethylene glycol after proton removal; this has been corroborated by calculation of the hydrogen-bond donating ability. Interestingly under these conditions, the oxygen reduction reaction on a glassy carbon electrode follows an overall 4-electron pathway (i.e., two 2-electron processes) which is of importance in the performance of air cathodes in electrochemical devices.

## 1. Introduction

Aprotic ionic liquids (ILs) of interest in electrochemical applications typically have high chemical and electrochemical stability, good conductivity, negligible volatility and low flammability, making them candidates to replace aqueous and nonaqueous organic electrolytes [1,2]. IL electrolytes have been successfully demonstrated in a number of energy storage applications including metal–air batteries [3,4]. In the latter context the oxygen reduction reaction (ORR) either results in the production of an unprotonated species if a proton source is not available (such as may be the case in some Li–air concepts [1,5,6]) or a proton donor is required.

In IL electrolytes, where the proton availability is low, the mechanism of the oxygen reduction reaction (ORR) appears to be limited to a 2-electron process [7–10], typically resulting in $O_2^{2-}$ as the final product, which is not optimum with respect to maximizing the efficiency of energy storage/generating devices.

The effect of different protic additives (such as water or weak acids) in ILs on the superoxide ($O_2^{\bullet-}$) and peroxide anion ($O_2^{2-}$) electrochemistry has also shown 2 electrons per molecule of oxygen are typically obtained [7–10]. We have also recently reported that the phosphonium cation, $[P_{66614}]^+$, which has been shown to react with the superoxide anion, [11] is stabilized in the presence of water [8]. On the other hand, a 4-electron ORR process has recently been reported on glassy carbon (GC) in an imidazolium-based ionic liquid containing strong acid [12]. However, in the context of a metal–air battery, strong acids are not useful additives, because they corrode the metallic anode.

Here we show that oxygen reduction via a four-electron pathway can be induced on GC in trihexyl(tetradecyl)phosphonium chloride, $[P_{66614}][Cl]$, when ethylene glycol (EG) is added as a weak proton source, but not when water or methanol is used as proton sources. This apparent superior proton activity (or increased acidity) of EG is attributable to a self-stabilization of the EG anion after deprotonation. We compare the ORR in the presence of EG to that with different protic additives having $pK_a^{aq}$ values from 15 to −8.

## 2. Experimental

Trihexyl(tetradecyl)phosphonium chloride, $[P_{66614}][Cl]$, was received from Cytec and purified as previously reported [8]. The content of water, less than 800 ppm, was determined by Karl–Fischer titration. Anhydrous ethylene glycol (Sigma–Adrich, 99.8%), acetic acid glacial (Sigma–Aldrich), methanol (Merck), hydrochloric acid (Ajax finechem, 32%) and deionised water (Millipore SuperQ system, resistivity 18.2 MΩ/cm) were used as additives.

Voltammetric experiments were performed with a Biologic VMP3/Z multi-channel potentiostat in a standard 3 electrodes set-up, using Pt

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wire as counter electrode, glassy carbon (GC) (1 mm diameter, ALS Co., Ltd. Japan) as working electrode and a Ag/Ag$^+$ reference electrode consisting of a silver wire in a 5 mM AgCl [$P_{66614}$][Cl] solution separated from the bulk solution with a porous frit. The measurements were carried out with an IR drop compensation prior to the cyclic voltammetry experiments compensating approximately 85% of the total internal resistance. The scan rate was 10 mV s$^{-1}$.

The ionic liquid was bubbled either with oxygen (ultrahigh purity grade, Air Liquide) for 15 min prior to voltammetry measurements, or with nitrogen (ultrahigh purity grade, Air Liquide) for 30 min prior to control experiments. Viscosity measurements were performed using Microviscometer Lovis 2000 M (Anton Paar).

Stock solutions of Kamlet Taft dyes, Reichhardts dye 4-Nitroaniline (Sigma) and *N,N*-diethyl-4-nitroaniline (Sigma) at 1.2 mol/L were prepared in methanol and sonicated prior to use. Then, 10 μL of the stock solution was transferred to the ionic liquid solution and allowed to evaporate under vacuum. The $\lambda_{max}$ of each sample was measured at 298 K in a quartz cuvette by UV–visible spectrophotometry (Shimadzu). The hydrogen bond acceptor value (α) is calculated according to the following equation:

$$\alpha = \frac{\left(E_T(30)/\left(\mathrm{kcal\ mol^{-1}}\right) - 14.6(\pi^* - 0.23) - 30.31\right)}{16.5}$$

Where the solvent polarity $E_T(30)$ is determined by Reichardt's dye (1), and calculated according to

$$E_T30/\left(\mathrm{kcal\ mol^{-1}}\right) = 28591\ \lambda(\mathbf{1})_{max}/\mathrm{nm}$$

## 3. Results and discussion

### 3.1. Effect of ethylene glycol

Fig. 1a shows cyclic voltammograms in $O_2$ saturated-[$P_{66614}$][Cl] containing 0.83 mmol of ethylene glycol (EG) per gram of IL on a GC electrode. Two reduction processes, at −0.67 V (C1) and at −0.99 V (C2), followed by two subsequent oxidation processes, at −0.13 V

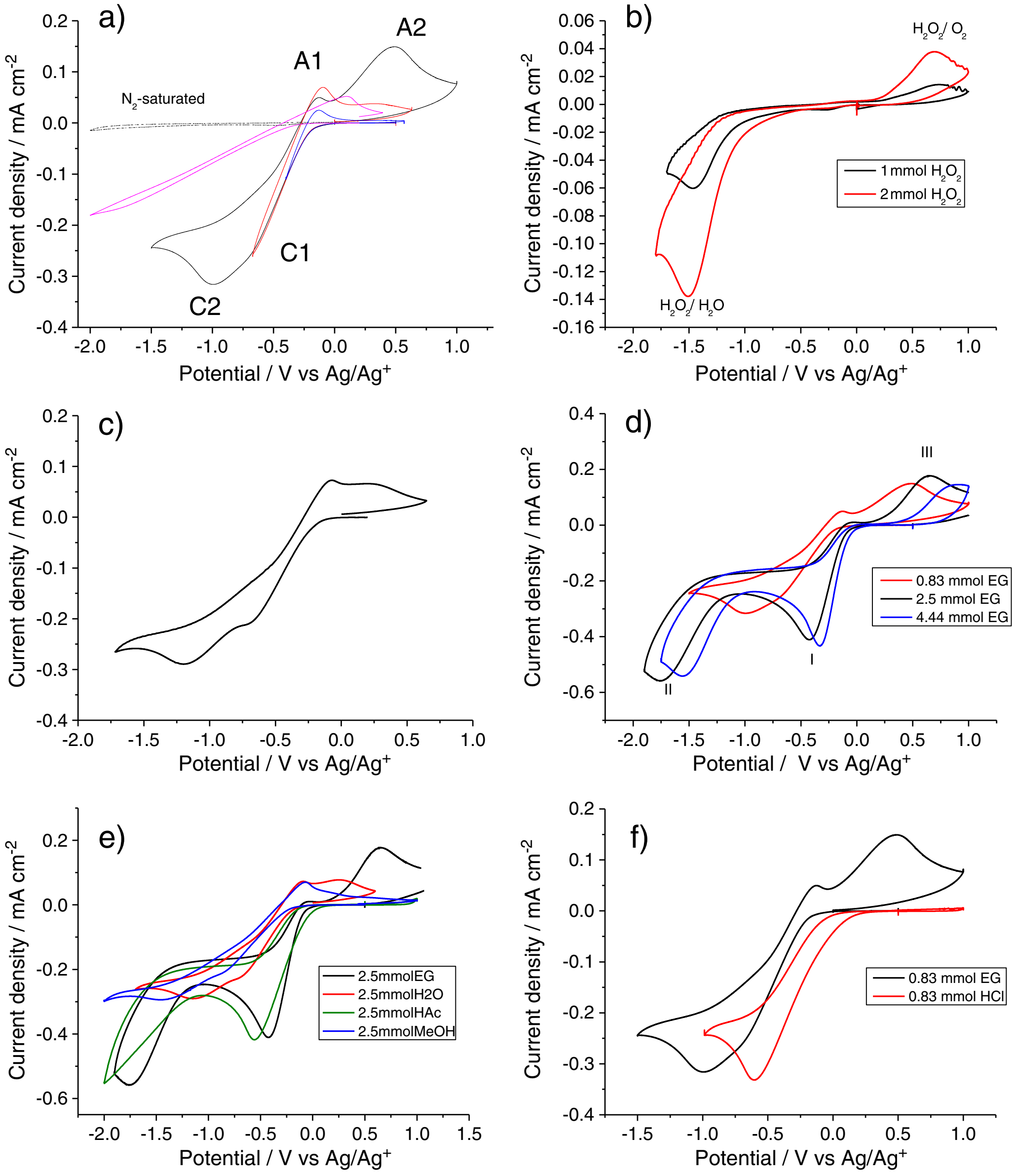

**Fig. 1.** a) Cyclic voltammograms of $N_2$ and $O_2$-saturated [$P_{66614}$][Cl] with 0.83 mmol EG/g IL scanned up to −1.5 V (—), −0.67 (—) and −0.4 V (—); and neat [$P_{66614}$][Cl] (—) on GC b) cyclic voltammograms containing 1 mmol and 2 mmol $H_2O_2$/g IL in $N_2$-saturated [$P_{66614}$][Cl], Cyclic voltammograms for ORR on GC in $O_2$-saturated [$P_{66614}$][Cl] c) with 0.83 mmol $H_2O$/g IL, d) with different concentrations of EG/g IL, e) containing 2.5 mmol additive/g IL, f) comparing the effects of EG or HCl. Scan rate: 10 mV s$^{-1}$.