



Electrode Reactions Coupled with Chemical Reactions of Oxygen, Water and Acetaldehyde in an Ionic Liquid: New Approaches for Sensing Volatile Organic Compounds



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ABSTRACT

Water and oxygen are ubiquitous present in ambient conditions. This work studies the unique oxygen, trace water and a volatile organic compound (VOC) acetaldehyde redox chemistry in a hydrophobic and aprotic ionic liquid (IL), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([Bmpy][NTf₂]) by cyclic voltammetry and potential step methods. One electron oxygen reduction leads to superoxide radical formation in the IL. Trace water in the IL acts as a protic species that reacts with the superoxide radical. Acetaldehyde is a stronger protic species than water for reacting with the superoxide radical. The presence of trace water in the IL was also demonstrated to facilitate the electro-oxidation of acetaldehyde, with similar mechanism to that in the aqueous solutions. A multiple-step coupling reaction mechanism between water, superoxide radical and acetaldehyde has been described. The unique characteristics of redox chemistry of acetaldehyde in [Bmpy][NTf₂] in the presence of oxygen and trace water can be controlled by electrochemical potentials. By controlling the electrode potential windows, several methods including cyclic voltammetry, potential step methods (single-potential, double-potential and triple-potential step methods) were established for the quantification of acetaldehyde. Instead of treating water and oxygen as frustrating interferences to ILs, we found that oxygen and trace water chemistry in [Bmpy][NTf₂] can be utilized to develop innovative electrochemical methods for electroanalysis of acetaldehyde.

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1. Introduction

Room-temperature ionic liquids (ILs) are organic salts that are liquid at room temperature [1,2]. Due to their high ion concentration, negligible volatility, high heat capacity and good electrochemical stability, they have been demonstrated as highly efficient heat transfer fluids [3] as well as electrolytes for electrochemical applications such as super capacitors, fuel cells, lithium batteries, photovoltaic cells, electrochemical mechanical actuators and electroplating [2,4–6]. In the past decade, our lab has systematically characterized the redox chemistry of a broad range of gaseous species (e.g. oxygen [7], methane [8], TDI [9]) in ILs for developing IL-based electrochemical gas sensors. We and others have discovered new electrochemical reactions in the IL that are not feasible in conventional solvents [10–12]. For example, in traditional aqueous based electrochemical systems, oxygen is

removed by purging with inert gas such as nitrogen or argon to avoid interference from oxygen reduction reactions (i.e. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ or $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) [13]. However, in the anhydrous aprotic IL, oxygen reduction reaction (ORR) is a simple one electron reduction process ($O_2 + e^- \rightarrow O_2^{\cdot-}$) [14,15] instead of a complicated four electron reduction process shown in aqueous electrolyte. Rather than acting as an interferent as in aqueous systems, oxygen reduction in an IL is able to be quantified and utilized, which beneficially allows calibration of the quasi-reference electrode potential [16], and serving as an internal standard for quantification of other gaseous analytes [8]. Because the simple one electron reduction of oxygen forms the superoxide radical that is stable in the IL (i.e. [Bmpy][NTf₂]), this reaction has been successfully utilized for an amperometric oxygen sensor [7,17–21]. However, ILs for electrochemical gas sensor applications are challenged by the varying ambient conditions particularly humidity. Many literature reports have shown that water can strongly affect the physical and chemical properties of ILs such as viscosity, electrical conductivity, and reactivity, as well as solvation and solubility properties [22–24]. The effects of water depend on

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the amount of water present in the IL system. Water is a proton source. The oxygen reduction product superoxide radical is very reactive with water [25]. In the presence of some volatile organic compounds (VOCs), the protonation reaction between superoxide radicals and VOCs have also been observed [26]. Thus, fundamental understanding of the redox reactions of gaseous analytes in the IL in conditions closely related to real world ambient situations where oxygen and water co-exist is essential for the design and development of the IL based electrochemical sensors.

In this report, rather than treating water and oxygen as frustrating interferents in the IL electrochemical systems, we systematically studied the unique oxygen, trace water and their coupling chemistry in an ionic liquid in the presence of volatile organic compound (VOC). Since water is shown to have a much more dramatic acceleration effect on the diffusion of the ionic compounds compared to its effect on neutral species in the ILs, we select a neutral analyte, “acetaldehyde”. We also select aprotic 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([Bmpy][NTf₂]) IL since it is stable in the presence of superoxide

radical. Thus, it will be inert and do not act as a proton source [14,27–29]. [Bmpy][NTf₂] is also hydrophobic which keeps the level of the water in the system at trace level. So the special ‘[Bmpy][NTf₂]-trace water’ system, which behaves as both non-aqueous solvent, where one electron reduction of oxygen [14,15] is dominant, and aqueous solvent, where water can be treated as a proton source [30–32] can be utilized to our advantages. By utilizing cyclic voltammetry or potential step methods, we could explore the water and oxygen coupling electrochemistry in the IL system so that the overall electrochemical reactions are balanced, i.e. the total amount of water and oxygen initially present at the IL system will be equal to the total amount of water produced as a product. This will ensure the ‘IL-trace water’ system remain constant during the quantitative analysis. We studied the electrode reactions coupled with chemical reactions of oxygen, water and acetaldehyde at two conditions by cyclic voltammetry and potential step methods. In one, the redox reactions of the acetaldehyde as well as water and oxygen could allow a mass balance of water and oxygen to be maintained by using cyclic

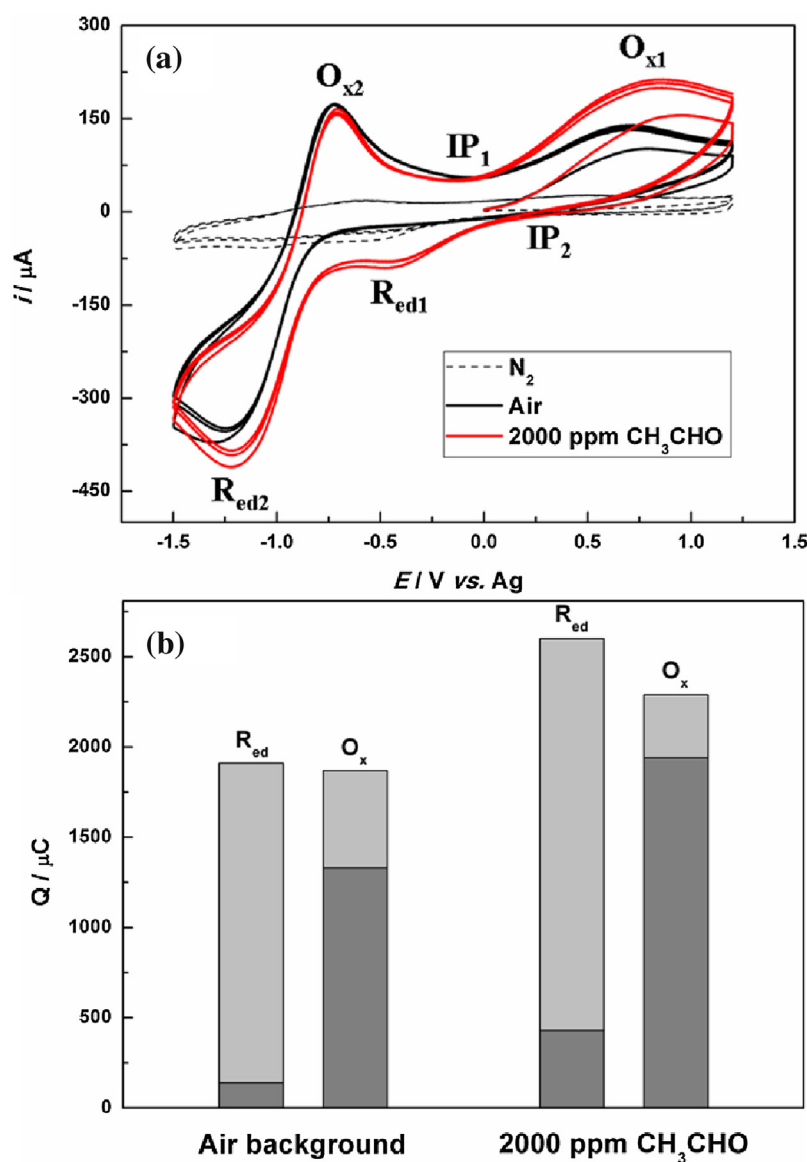


Fig. 1. (a) Cyclic voltammograms (multiple cycles) of Pt gauze working electrode in pure nitrogen, air and 2000 ppm (v/v) acetaldehyde in air (scan rate: 100 mV/s), conditioning potential is at zero volt; (b) Integrated charges of the redox peaks in the 3rd cycle of the cyclic voltammograms in air and 2000 ppm CH_3CHO (O_x : oxidation process; R_{ed} : reduction process; dark gray: $\text{R}_{\text{ed}1}$ or $\text{O}_{\text{x}1}$; gray: $\text{R}_{\text{ed}2}$ or $\text{O}_{\text{x}2}$) (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.).

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