# Water electrolysis: an excellent approach for the removal of water from ionic liquids

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**An electrochemical system based on platinum cathode and glassy carbon anode was assembled for a successful removal of water from ionic liquids *via* the water electrolysis strategy.**

Ionic liquids (ILs) have attracted a great deal of attention as the excellent media used in synthesis, fundamental electrochemical studies, batteries, electrosynthesis, electrodeposition, electrochromic device, solar cells, fuel cells and capacitors and so on.[1,2] In general, a low vapour pressure, reasonable thermal stability and large electrochemical potential window (2–6 V) largely grant them superiority over the conventional media for practical purposes. The ILs supplied commercially often contain a trace amount of water and continuously absorb moisture from the ambient environment. Water may be produced as a bi-product in a particular reaction in ILs that are expected to be recycled. In contrast, a trace amount of water dramatically changes the viscosity, conductivity, capacitance and electrochemical potential window of ILs.[1,2] Moreover, some reactions, *e.g.*, the generation of superoxide ion ($O_2^{\bullet -}$) used as a reagent in many applications including pollutant management,[3a] may be affected by a trace amount of water in ILs.[2,3] These facts obviously demand a complete and on-site removal of water from ILs. Moreover, Clare *et al.*[4] have recently proven that alumina and silica used commonly for the purification of ILs contaminate ILs, resulting in a non-negligible impact on the electrochemical, spectroscopic and physical properties of an IL.

$$\text{Anodic reaction: } 2H_2O \rightarrow O_2 + 4H^+ + 4\,e^- \quad (1)$$

$$\text{Cathodic reaction: } 4H_2O + 4\,e^- \rightarrow 2H_2 + 4OH^- \quad (2)$$

In this study, removal of water from ILs was carried out for the first time using the water electrolysis strategy. Electrolysis of water where the cathodic and anodic reactions are recognized as the $H_2$ and $O_2$ evolution reactions (HER and OER), respectively (eqns (1) and (2)), has focused a lot of interest from the viewpoints of electrochemical science and technology.[5,6] Schroder *et al.* have reported that the potential window of IL narrows by the addition of water.[6a] Suzoa *et al.* have developed an electrochemical system for the production of pure $H_2$ gas *via* the electrolysis of water in IL.[6b] Here, we explore the OER and HER as smart, simple and economical tools for the on-site removal of water from IL. We studied OER and HER at gold (Au), platinum (Pt) and glassy carbon (GC) electrodes in *N*,*N*-diethyl-*N*-methy(2-methoxyethyl)ammonium tetrafluoroborate (**1**) and *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide (**2**) ILs (Kanto Chemicals, Japan). In a specially-designed, two-compartment electrochemical cell comprised of a GC plate (1.5 × 1.5 cm) cathode and a cylindrical Pt mesh # 80 (diameter: 0.5 cm; height: 1.2 cm) anode placed in one compartment and an IL-based $Ag/Ag^+$ reference electrode in the other compartment, the water added purposely into IL could be removed with a potentiostatic bulk electrolysis method. The removal of water was examined by the redox reaction of the $O_2/O_2^{\bullet -}$ couple,[2,3] the surface oxidation–reduction reactions of Au electrode,[7] the measurement of conductivity and Karl Fisher titration.

The typical results concerning the OER and HER are shown in Fig. 1, where the potential window of **1** was found to be about 4 V (Fig. 1(a,a′)). The cyclic voltammograms (CVs) obtained at Pt electrode (Fig. 1A) show no well-defined peak in the potential range of 0 → −2.0 → 0 V in **1** (Fig. 1A(a′)), while a cathodic shoulder at −1.2 V and an anodic peak were obtained by the addition of water (Milli-Q) (Fig. 1A(b′)). No such peak was found in the CV measured at the GC electrode (Fig. 1B(a′,b′)). The observed peaks at the Pt electrode may be considered as the so-called HER (eqn (2)) that favorably takes place at the Pt electrode (Fig. 2), but less favorably at the GC electrode in aqueous solution.[7] At the Au electrode, the HER occurred at −1.8 V (not shown).

Similarly no well-defined peaks were observed in the potential range of 0 → 1.4 → 0 V at the Pt electrode (Fig. 1A(a)) and 0 → 1.8 → 0 V at the GC electrode (Fig. 1B(a)). On the contrary, when water was added to **1**, an anodic shoulder starting from 0.6 V and a cathodic peak at 0.2 V were obtained at the Pt electrode (Fig. 1A(b)), while an anodic shoulder starting from *ca.* 0.8 V was obtained at the GC electrode (Fig. 1B(b)). Similar anodic shoulder (and cathodic peak at Pt and Au electrodes) was obtained in **2** (Fig. 3A). In analogy to aqueous solution,[7] the observed anodic shoulder may be assigned to OER (Fig. 2) that is generally found at Pt and Au electrodes to occur in succession to the oxidation of the corresponding metal surface. Thus, the cathodic peak observed at the Pt and Au electrodes is associated with the reduction of thus-formed surface oxides.[7]

Based on the mechanisms reported for HER and OER in aqueous solution,[5] the reactions expressed by eqns (1) and (2)

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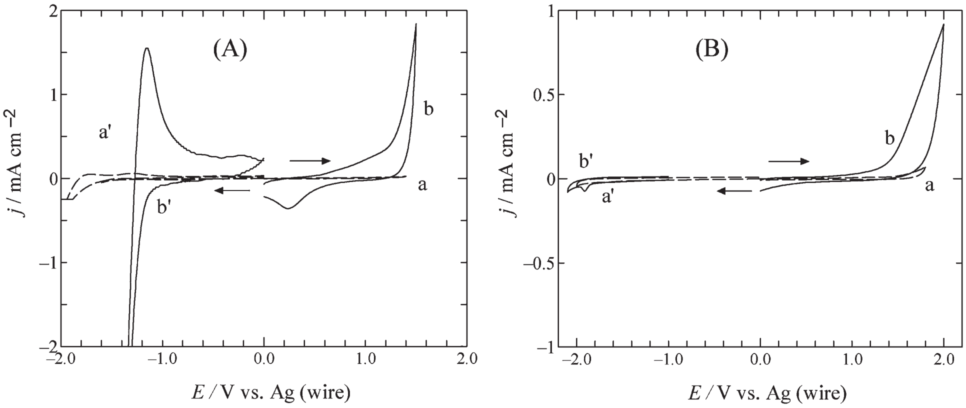

**Fig. 1** CVs measured at (A) Pt and (B) GC electrodes in $N_2$-saturated **1** without (a,a′) and with (b,b′) 1.8 M $H_2O$. Potential scan rate: 0.05 V $s^{-1}$.

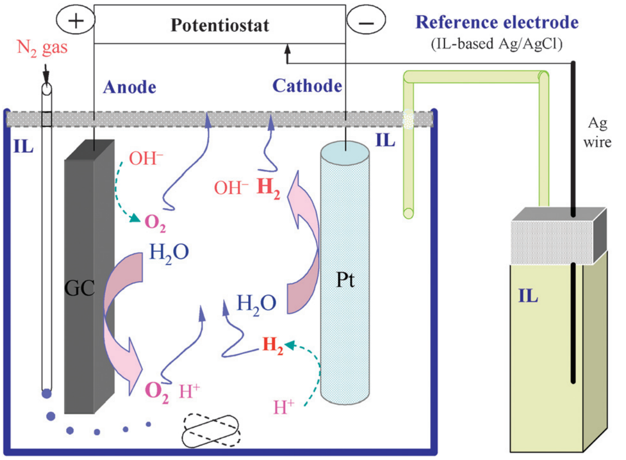

**Fig. 2** Schematic presentation of water removal from IL *via* the so-called OER and HER.

may be proposed to be associated with the anodic and cathodic shoulders observed in **1** containing water, respectively, *i.e.*, the anodic shoulder is due to $O_2$ evolution and the cathodic one is ascribed to the production of $H_2$ gas (Fig. 2) that may evidently be seen by considering the anodic peak at −1.1 V at the Pt electrode (Fig. 1A(b′)) as $H_2$ oxidation.[7]

As mentioned above, we found that HER and OER took place in ILs and their starting potentials largely depend on the electrode material. Based on the CV measurements (*e.g.*, Fig. 1), we chose GC and Pt electrodes as the anode and cathode materials, respectively, at which the OER and HER occurred favourably, to construct the cell used for water removal (Fig. 2). Typically, 2 ml of **2** containing 1.8 M water was charged into the cell and the electrolysis of water was performed by applying a constant potential of 1.2 V *vs.* Ag/$Ag^+$ (IL-based) (*i.e.*, 1.7 *vs.* Ag wire) at the GC electrode while stirring the solution. During this electrolysis, it was found that the potential of the Pt cathode is −1.9 V *vs.* Ag/$Ag^+$ (IL-based) and decreases continuously with the progress of the electrolysis and eventually becomes −0.5 V.[8] During the electrolysis, $N_2$ gas (99.9%) was purged into the solution. The water content in the IL solution was monitored from time to time and the typical results are shown in Fig. 3.

In Fig. 3A, the anodic shoulder at potential >1.0 V and the cathodic peak that may be considered as the sign of the presence of water were observed in the supplied **2** (Fig. 3A(a)). By the addition of water, these peaks shifted to more negative potentials with an increase in the peak current (Fig. 3A(b)). Interestingly, when the CV measurement was followed by the water electrolysis for 1 h, the observed peaks shifted to more positive potentials with a concurrent minimization of the peak current (Fig. 3A(c)), indicating that the added water could be removed from **2**. Such

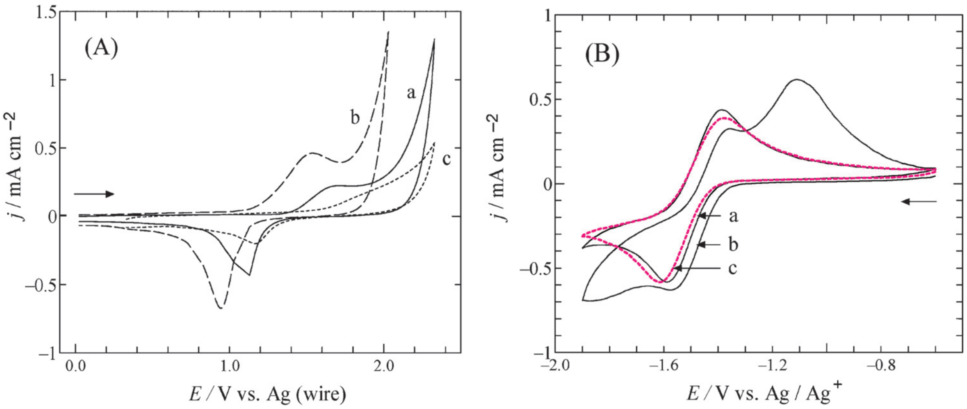

**Fig. 3** CVs obtained at the Au (A) and GC (B) electrodes in $N_2$- (A) and $O_2$-saturated (B) **2** as supplied (a), containing 1.8 M $H_2O$ (b) and after electrolysis of the added $H_2O$ (c). Potential scan rate: 0.1 V$s^{-1}$.

removal of water was further justified by probing the redox reaction of $O_2/O_2^{\bullet -}$ couple (Fig. 3B), where $O_2^{\bullet -}$ is known to react with $H_2O$ *via* a concerted proton transfer mechanism[2b] to form $HO_2^-$ species. When water was added into **2**, the redox peaks of the $O_2/O_2^{\bullet -}$ couple were found to deform[9] and a new anodic peak was observed (Fig. 3B(c)). These observations necessarily reflect the presence of water in **2**.[2,3c] Interestingly, the shape of the CV measured in the **2** after 1 h electrolysis (Fig. 3B(c)) was almost the same[9] as obtained in **2** supplied commercially (Fig. 3B(a)). The ILs may not be contaminated by the unknown product by the water electrolysis since the potential window of IL is sufficiently larger than that determined by the so-called OER and HER. In addition, any other products[8] (*e.g.*, $OH^-$ and $H^+$ (eqns (1) and (2))) generated during the electrolysis of water[4] may be essentially oxidized or reduced to $O_2$ or $H_2$ under the applied potential (Fig. 2). Most remarkably, we minimized the formation of water in IL *via* the back reactions expressed by eqns (1) and (2) (due to the reduction and oxidation of the formed $O_2$ and $H_2$, respectively) by stirring the IL solution together with $N_2$ gas bubbling to efficiently remove the $H_2$ and $O_2$ gases from the solution. Here, the conductivity of **2** measured before (2.45 mS $cm^{-1}$) and after (2.55 mS $cm^{-1}$) water electrolysis using electrochemical impedance technique was found to be almost the same, but a higher value (2.92 mS $cm^{-1}$) was obtained for **2** containing 1.8 M (2.2% w/w) water. Furthermore, the amounts of water in **2** measured as supplied and after the water electrolysis by Karl Fisher titration were found to be 0.035 ± 003 and 0.060 ± 0.005%,[9] respectively (note: in a dried system with purging of dried $N_2$ gas and vigorous agitation of ILs solution, the complete removal of water would be possible). Thus, the water could be successfully removed from **1** and **2** using the present water electrolysis strategy which can be essentially applied for any ILs.

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9 The small negative shift (0.02 V) of the midpoint potential of the CV measured in **2** after the water electrolysis compared with that observed in the commercially supplied **2** may also indicate the presence of water in the latter.[2] All measurements were performed in ordinary laboratory conditions, and thus the water content (20–30 ppm) in the supplied **2** would not be entirely inherent, but it may be enriched by the absorption of moisture from the environment.