

Electrochemistry of water in 1-butyl-3-methylimidazolium tetrafluoroborate at nickel electrode: application to hydrogen peroxide production and water sensing

Guan-Ping Jin · Juan Li · Yaling Lu · Fanli Meng ·
Tao Luo · Jinhuai Liu

Received: 11 November 2009 / Accepted: 16 January 2010 / Published online: 9 February 2010
© Springer-Verlag 2010

Abstract The electrochemistry of water dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$) was studied by cyclic voltammetry and electrochemical impedance spectroscopy using a nickel electrode. Hydrogen peroxide is being produced by direct electrolysis of water in a cooperative process between the nickel electrode and $[\text{C}_4\text{mim}][\text{BF}_4]$. There is linear response between the concentration of water and the oxidation peak current at 1.60 V. Impedance decreases significantly with increasing concentration of water. The findings resulted in two promising applications: The first is the production of hydrogen peroxide, and the second is in water sensing. Both methods are environmentally friendly and convenient.

Keywords 1-Butyl-3-methylimidazolium tetrafluoroborate · Hydrogen peroxide production · Water sensing

Introduction

Hydrogen peroxide, an important chemical material, can be produced from peroxygenated compounds and electrolysis of water [1]. Actually the electrolysis of water has attracted an increase attention due to high purity, economy and simple procedure. Various electrolysis systems have been reported to produce hydrogen peroxide, such as anodic oxidation of water in sulphuric acid or sulphates [2], cathodic reduction of oxygen in potassium hydroxide [3] and peroxide electrolysis in Fenton reagent [1]. However, in our opinion, the studies have not been achieved so far. The challenge still consists in producing hydrogen peroxide in terms of convenient and economical way.

Room-temperature ionic liquids (RTILs) are composed of ions and exist in the liquid state at 298 K. They have many interesting properties including negligible vapor pressures, low combustibility, high thermal and chemical stability [4], specially wide electrochemical windows [5, 6]. There is no supporting electrolyte required because of abundant charge carriers when RTILs are used as solvents for electrochemical experiments [7]. Since the diffusion coefficients of electroactive species in RTILs are generally orders of magnitude lower than in common organic solvents, and the intermediate products are easier to be observed during the electrochemical process, the mechanism of electrochemical reaction in RTILs can be better understood compared with in conventional solvents [3]. Meanwhile it has been proved that a raise in water content in an RTILs can lead to an increase in the mass transport of analyte to the electrode surface with the decrease of viscosity and electrochemical window [3, 8, 9]. Among various RTILs, 1-n-butyl-3-methylimidazolium ($[\text{C}_4\text{mim}][\text{BF}_4]$) has been found to be liquid with unique properties in terms of electrical conductance, soluble in water at

G.-P. Jin (✉) · J. Li · Y. Lu
Department of Application Chemistry of School of Chemical Engineering, Hefei University of Technology,
Hefei 230009, People's Republic of China
e-mail: jgp@hfut.edu.cn

G.-P. Jin · F. Meng · T. Luo · J. Liu (✉)
Key laboratory of Biomimetic Sensing and Advanced Robot Technology, Institute of Intelligent Machines,
Chinese Academy of Sciences,
Hefei 230031, China
e-mail: jhliu@iim.ac.cn

G.-P. Jin · J. Li
Anhui Key Laboratory of Controllable Chemistry Reaction and Material Chemical Engineering,
Hefei, Anhui 230009, People's Republic of China

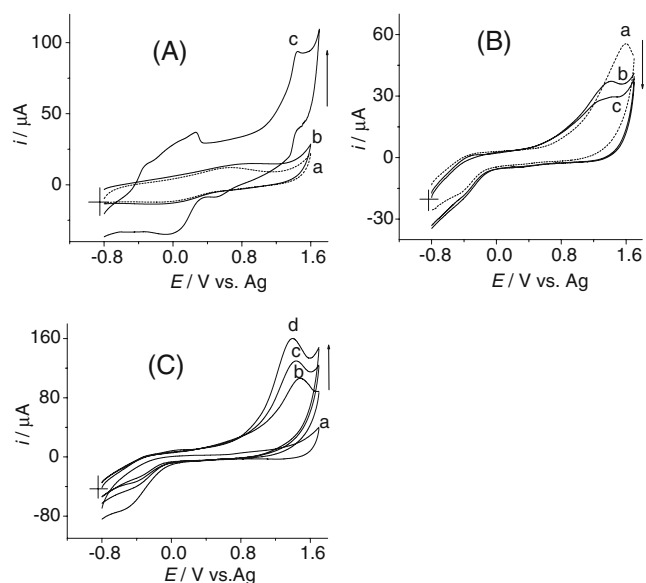


Fig. 1 **a** CVs of water (0.0 (a), 0.01 (b) and 0.5 mM (c)) at Ni electrode. **b** CVs of water (0.0 (a), 0.35 (b) and 3.88 (c)M) at WGE. **c** CVs of hydrogen peroxide (0.000 (a), 0.001 (b), 0.006 (c) and 0.01 (d) M) at Ni electrode. Quiet time: 200 s; Scan rate: 50 mV s⁻¹; Solution: [C₄mim][BF₄]

temperatures higher than 6 °C, chemical and electrochemical stability [8, 10–15]. Souza RFD successfully used [C₄mim][BF₄] as an electrolyte for hydrogen production by water electrolysis at room temperature and atmospheric pressure [15]. The scheme is relative to a cathodic reaction of 2H₂O + 2e⁻ → H₂ + 2OH⁻. The catalytic activity of the electrode surface was not affected during the electrolysis mainly due to the chemical stability of the RTILs. But the hydrogen

peroxide production has not been reported for water electrolysis in [C₄mim][BF₄] up to now.

The previous studies have illustrated that [C₄mim][BF₄] is advantageous for water electrolysis. As we know that water is hardly to sensing through electrochemical methods because most of the solvents often contain water. In the present work, we proposed a novel method to produce hydrogen peroxide and to detect water using [C₄mim][BF₄] as an electrolyte. As a comparison, the electrochemistry of hydrogen peroxide was also investigated.

Experimental section

Chemical reagents

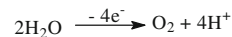
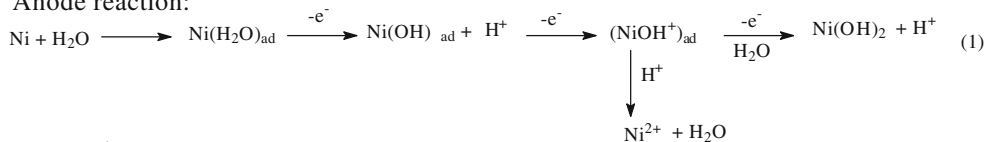
All chemicals of the highest qualities are commercially available: 1-Butyl-3-methylimidazolium tetrafluoroborate (Chenjie Chemical Reagents Company of Shanghai, China); hydrogen peroxide (H₂O₂), NaCl, HCl, KI, starch and alumina powder (Yuanda Company of Shanghai, China). The [C₄mim][BF₄] was dried thoroughly before being used at room temperature in a vacuum drying oven. After drying, the [C₄mim][BF₄] was stored in a nitrogen atmosphere. Doubly distilled water (prepared in a quartz apparatus) was used in the experiments. High purity nitrogen gas was used for deaeration.

Experiment instruments and electrode preparation

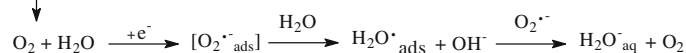
All electrochemical experiments were performed using a model CHI 660B electrochemical analyzer (Cheng-Hua,

Scheme 1 The scheme of electrolysis of water at Ni electrode in [C₄mim][BF₄]

Anode reaction:



Cathode reaction:



Shanghai, China). The electrochemical experiments were performed in a homemade cell, using a platinum wire as the auxiliary electrode and an Ag wire as the reference electrode. A nickel electrode (2 mm diameter) and a paraffin-impregnated graphite electrode (WGE, 2 mm diameter) were used as working electrodes, respectively. The nickel working electrode was polished on self lapping pads using alumina powder of size 5.0, 1.0, and 0.3 μm , and followed by ultrasonic in ethanol and purified water for 15 min, respectively. UV-spectrophotometry experiment was performed at 401PC spectrophotometer (Shimadzu, Japan).

Results and discussion

The electrochemical behaviors of water in $[\text{C}_{4\text{mim}}][\text{BF}_4]$

$[\text{C}_{4\text{mim}}][\text{BF}_4]$ was chosen as the solvent due to its hydrophilic property and wide electrochemical window [3, 15]. The dissociation of $[\text{C}_{4\text{mim}}][\text{BF}_4]$ yields an organic cation with strong electrochemistry stability in a large potential range [8]. To remove residual atmospheric water vapor initially present in the ionic liquid, the cell was purged with pure nitrogen prior to the experiments. The level of the impurities was monitored by running background cyclic voltammograms (CV), and 30 min of purging was found to be sufficient to obtain a constant response. These procedures were adopted for the collection of all the data reported below.

Figure 1 displays the electrolysis of the water in $[\text{C}_{4\text{mim}}][\text{BF}_4]$. The Scheme 1 was suggested to describing the characteristics. A pair of peaks (0.65/−0.08 V) can be observed matching to redox of the nickel ($\text{Ni} \leftrightarrow \text{Ni}^{2+}$) (Fig. 1a, curve a). The anode current (no peak) are obviously increase with the addition of 0.01 mM water

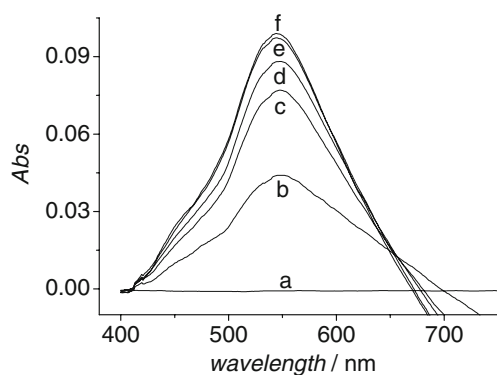


Fig. 2 The UV-spectra of 6.67 M water depending on the delay of electrolysis time in 0 (a), 400 (b), 800 (c), 1,200 (d), 2,000 (e) and 2,400 (f). Indicator: starch. Color solution: mixing four stock solutions of NaCl (200 $\text{g}\cdot\text{L}^{-1}$), HCl (18.2 $\cdot\text{L}^{-1}$), KI (5 $\text{g}\cdot\text{L}^{-1}$) and starch (10 $\text{g}\cdot\text{L}^{-1}$) with a volume rate of 10: 1: 1: 1 diluting to 25 mL

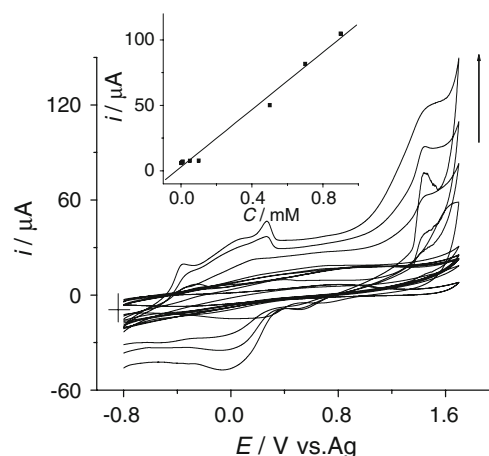


Fig. 3 CVs of water (2.0–9.0, 10.0 to 90.0 and 100.0 to 900.0 μM ; every 2, 20, 200 μM) at Ni electrode; Inset: Oxidation peak currents of water depend on the concentration at Ni electrode. Quiet time: 200 s; Solution: $[\text{C}_{4\text{mim}}][\text{BF}_4]$; Scan rate: 50 $\text{mV}\cdot\text{s}^{-1}$

(Fig. 1a, curve b) due to the oxidation of water (reaction (2)). The acidity of the solution is gradually increasing with the delay of reaction and the increase of water content, which induced nickel dissolution to form two oxidative peaks at −0.33 and 0.28 V matching to the display of $\text{NiOH}^+/\text{Ni}(\text{OH})_2$ (reaction (1)) (Fig. 1a, curve c) [16]. It is noticeable that the oxidative peak currents (1.43 V) become significant in higher water content at Ni electrode (Fig. 1a, curve c), it is attributed to the oxidation of hydrogen peroxide, the time taken of water diffusion and the generation of O_2 at Ni electrode [1]. The peak current is linearly increasing not only depending on the square root of scan rate from 5 to 400 $\text{mV}\cdot\text{s}^{-1}$, implying a diffusion controlled process; but also with the increase of water concentration (reaction (3)). The result was proved by following experiments in Fig. 1c. A similar oxidation peak at 1.43 V can be readily seen after hydrogen

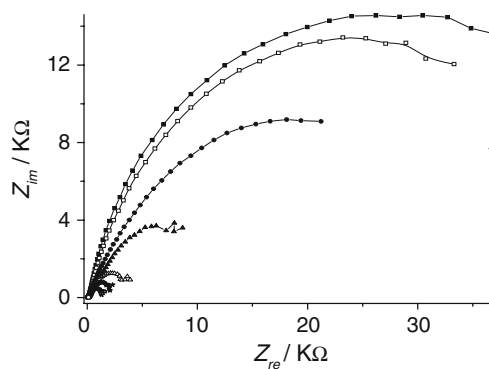


Fig. 4 Electrochemical impedance spectroscopy of water (0, 0.01, 0.1, 0.3, 0.5, 0.7, 0.9, 1 mM and 9 mM at Ni electrode. Init 1.6 V; Frequency: 962 (Hz); Amplitude: 10 V; Quiet time: 200 s. Solution: $[\text{C}_{4\text{mim}}][\text{BF}_4]$

peroxide followed the same processes with different concentration. For the cathode reaction, two successive waves of dissolved oxygen reduction are observed at 0.52 and 0.00 V with a two-step process matching to reaction (4) and (5). Moreover, the CVs of water also were investigated at WGE to prove the effect of Ni electrode, it is observed that the response is irregular and small while the WGE followed the same processes (Fig. 1b). It illustrates that Ni electrode plays an important role towards the electrolysis of the water and in line with the literatures [16–19].

Hydrogen peroxide production

Hydrogen peroxide production can be further proved by UV- spectrophotometric method based on a color reaction of $2\text{I}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + \text{H}_2\text{O}$ using starch as indicator [20, 21], and the max adsorption peak displays at about 550 nm [21]. Figure 2 shows the spectra of 6.67 M water depending on electrolysis time in 0 (a), 400 (b), 800 (c), 1200 (d), 2000 (e) and 2400 (f). An obvious adsorption peak at about 550 can be seen matching to the formation of hydrogen peroxide and in line with the literature [20]. The peak is significantly increased with the delay of electrolysis time from 0 to 2,000 s; it reaches a flat at 2,400 s, suggesting the end of reaction. Moreover, under the same conditions, the adsorption peak is raising with the increasing of water concentrations (no show).

Analysis characteristics

The accumulation time towards oxidation of the water was investigated (no show). The response is increasing with the delay of quiet time. It reaches a peak value at 200 s, then, evenness. Figure 3 shows the CVs of water depending on the concentration at Ni electrode in $[\text{C}_{4\text{mim}}][\text{BF}_4]$. The response at 1.43 V are linearly increasing in a concentration range of 2.0 μM to 9.0 mM ($i (\mu\text{A}) = 2.94 \times 10^{-6} + 0.11 C_x$ (mM), $R=0.994$, determination limit: 1 μM (3σ)).

Electrochemical impedance spectroscopy (EIS) was investigated for water electrolysis at 1.43 V in a frequency range from 50 mHz to 10 kHz. The EIS curves depending on the water content are shown in Fig. 4. The larger semicircle corresponds to the charge-transfer resistance. Since $[\text{BF}_4]^-$ anions can form much more viscous ionic liquids with strong H...F interactions, and make the mass transport and charge-transfer of analyte to the electrode surface difficulty. The origin impedances in pure $[\text{C}_{4\text{mim}}][\text{BF}_4]$ is large. However, the impedances are observed to be decrease with the increase of water content compared with that in pure $[\text{C}_{4\text{mim}}][\text{BF}_4]$, it illustrates that the mass transport and charge-transfer of analyte to the electrode surface become easy. It is attributed to that water added causes a decrease in the density and viscosity of the

solution. Thus the present result is advantageous of developing a water sensor and in line with the Fig. 3b.

Conclusion

A novel way of hydrogen peroxide production was established using $[\text{C}_{4\text{mim}}][\text{BF}_4]$ as a solvent (electrolyte) in the electrolysis of water at Ni electrode. Both $[\text{C}_{4\text{mim}}][\text{BF}_4]$ and Ni electrode play cooperative role in this process. The present result suggests that the method is an environmentally friendly and convenient. A water sensor also was developed according to a liner increase in oxidation peak response or the liner decrease in impedances. The data obtained also aid the use of $[\text{C}_{4\text{mim}}][\text{BF}_4]$ as a solvent in other electrochemical application.

Acknowledgements The authors gratefully acknowledge financial support from the Nation Basic research Program of China (No. 2007CB936603), the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (The Project-sponsored by SRF for ROCS, SEM, 2009), the Undergraduate innovation experiment program (2009CXSY135) of Hefei University of Technology, the Student innovation fund (200924) of Hefei University of Technology.

References

1. Drogui P, Elmaleh S, Rumeau M et al (2001) Oxidising and disinfecting by hydrogen peroxide produced in a two-electrode cell. *Wat Res* 35:3235–3241
2. Campos MJM, Blanco BG, Fierro JL (2006) Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process. *Angew Chem Int Ed* 45:6962–6984
3. Chatenet M, Micoud F, Roche I et al (2006) Kinetics of sodium borohydride direct oxidation and oxygen reduction in sodium hydroxide electrolyte: Part II. O_2 reduction. *Electrochim Acta* 51:5452–5458
4. Topal SZ, Ertekin K, Topkaya D et al (2008) Emission based oxygen sensing approach with tris(2, 2'-bipyridyl)ruthenium(II) chloride in green chemistry reagents: room temperature ionic liquids. *Microchim Acta* 161:209–216
5. Buzzeo MC, Evan RG, Compton RG (2004) Non-haloaluminate room-temperature ionic liquids in electrochemistry—a review. *Chem Phys Chem* 5:1106–1120
6. Rogers EI, Silvester DS, Poole DL et al (2008) Voltammetric characterization of the ferrocene/ferrocenium and cobaltocenium/cobaltocene redox couples in RTILs. *J Phys Chem C* 112:2729–2735
7. O'Mahony AM, Silvester DS, Aldous L et al (2008) Effect of water on the electrochemical window and potential limits of room-temperature ionic liquids. *J Chem Eng* 53:2884–2891
8. Widegren JA, Saurer EM, Marshc KN et al (2005) Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity. *J Chem Thermodyn* 37:569–575
9. Kelkar MS, Maginn EJ (2007) Effect of temperature and water content on the shear viscosity of the ionic liquid 1-ethyl-3-

- methylimidazolium bis(trifluoromethanesulfonyl)imide as studied by atomistic simulations. *J Phys Chem B* 111:4867–4876
- Wadhawan JD, Schröder U, Neudeck A et al (2000) Ionic liquid modified electrodes. Unusual partitioning and diffusion effects of $\text{Fe}(\text{CN})_6^{4-}/3-$ in droplet and thin layer deposits of 1-methyl-3-(2,6-(S)-dimethylocten-2-yl)-imidazolium tetrafluoroborate. *J Electroanal Chem* 493:75–83
 - Schroder U, Wadhawan JD, Compton RG et al (2004) Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl] imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids. *New J Chem* 24:1009–1015
 - Zhang J, Wu W, Jiang T et al (2003) Conductivities and viscosities of the ionic liquid [bmim][PF₆] + water + ethanol and [bmim][PF₆] + water + acetone ternary mixtures. *J Chem Eng* 48:1315–1317
 - Ding J, Zhou D, Spinks G et al (2003) Use of ionic liquids as electrolytes in electromechanical actuator systems based on inherently conducting polymers. *Chem Mater* 15:2392–2398
 - Evans RG, Klymenko OV, Price PD et al (2006) A comparative electrochemical study of diffusion in room temperature ionic liquid solvents versus acetonitrile. *Chem Phys Chem* 6:526–533
 - Souza RFd, Loget G, Padilha JC et al (2008) Molybdenum electrodes for hydrogen production by water electrolysis using ionic liquid electrolytes. *Electrochem Commun* 10:1673–1675
 - Barbosa MR, Bastos JA, García-Jareño JJ et al (1998) Chloride role in the surface of nickel electrode. *Electrochim Acta* 44:957–965
 - Real SG, Vilche JR, Arvia AJ (1980) The characteristics of the potentiodynamic potential/current profiles obtained with the Ni/0.5N H₂SO₄ interface. A contribution to the mechanism of the electrode process. *Corros Sci* 20:563–586
 - Barbosa MR, Real SG, Vilche JR et al (1998) Comparative potentiodynamic study of nickel in still and stirred sulfuric acid-potassium sulfate solutions in the 0.4–5.7 pH range. *J Electrochem Soc* 135:1077–1085
 - Real SG, Barbosa MR, Vilche JR et al (1990) Influence of chloride concentration on the active dissolution and passivation of nickel electrodes in acid sulfate solutions. *J Electrochem Soc* 137:1696–1702
 - Wong GTF, Zhang LS (2008) The kinetics of the reactions between iodide and hydrogen peroxide in seawater. *Mar Chem* 111:22–29
 - Yayan Z, li l (2001) Determination of trace H₂O₂ by KI iodine-blue spectrophotometry. *Chinses J Analysis Laboratory* 20:41–42