

— Communication —

# Accelerated Electron-Transfer Reaction of the $O_2/O_2^-$ Redox Couple on Multi-Walled Carbon Nanotubes — Modified Edge-Plane Pyrolytic Graphite Electrode in Room-Temperature Ionic Liquids

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An electrocatalysis of the multi-walled carbon nanotubes (MWCNTs)/Nafion-modified edge-plane pyrolytic graphite (EPPG) electrode for the one-electron reduction-oxidation reaction of the  $O_2/O_2^-$  (superoxide ion) redox couple in three 1-*n*-alkyl-3-methylimidazolium tetrafluoroborate room temperature ionic liquids (RTILs), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), 1-*n*-propyl-3-methylimidazolium tetrafluoroborate (PMIBF<sub>4</sub>) and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>) has been found. We have observed that in all the RTILs both the cathodic and anodic peak currents and the peak potential separations ( $\Delta E_p$ ) between the anodic and cathodic peak potentials at the MWCNTs/Nafion-modified electrode are increased and decreased, respectively, compared with those at the bare electrode. The values of the standard rate constant ( $k^0$ ) were estimated from the  $\Delta E_p$  values, *i.e.*, the  $k^0$  values at the MWCNTs/Nafion-modified electrode are  $(8.3 \pm 0.1) \times 10^{-3}$ ,  $(10.4 \pm 0.1) \times 10^{-3}$  and  $(4.2 \pm 0.1) \times 10^{-3}$  cm s<sup>-1</sup> in EMIBF<sub>4</sub>, PMIBF<sub>4</sub> and BMIBF<sub>4</sub>, respectively, while the corresponding values at the bare electrode are  $(4.3 \pm 0.1) \times 10^{-3}$ ,  $(2.9 \pm 0.1) \times 10^{-3}$  and  $(2.3 \pm 0.1) \times 10^{-3}$  cm s<sup>-1</sup>, respectively. The observed enhancement of the  $O_2/O_2^-$  redox reaction is discussed briefly based on the catalytic effects and physicochemical properties of carbon nanotubes.

**Key Words :** Multi-walled Carbon Nanotubes (MWCNTs), Room-Temperature Ionic Liquids, Oxygen Reduction Reaction, Edge-Plane Pyrolytic Graphite Electrode

## 1 Introduction

The one-electron reduction-oxidation reaction of the oxygen/superoxide ion ( $O_2/O_2^-$ ) redox couple is one of the most fundamental electrode processes and also of a great importance in biological phenomena such as respiration and aging.<sup>1-4)</sup> This redox reaction has been well realized at the conventional electrodes such as carbon, Pt and Au in aprotic organic solvents such as dimethyl sulfoxide, dimethyl formamide, acetonitrile, pyridine, quinoline and its derivatives.<sup>1,5-11)</sup> Also, this reaction has been found to occur at a hanging mercury drop electrode in aqueous media containing quinoline or its methyl or phenyl derivatives as surfactants.<sup>12)</sup> Recently, several research groups have reported the  $O_2/O_2^-$  redox reaction in room-temperature ionic liquids (RTILs) in which this reaction is electrochemically quasi-reversible (*i.e.*, not so fast).<sup>13-17)</sup>

In this paper the significantly accelerated redox reaction of the  $O_2/O_2^-$  couple at the multi-walled carbon nanotubes (MWCNTs)/Nafion-modified edge-plane pyrolytic graphite electrode in 1-*n*-alkyl-3-methylimidazolium tetrafluoroborate RTILs will be reported for the first time. To the best of our knowledge, there is no report regarding the electrocatalysis of MWCNTs towards the  $O_2/O_2^-$  redox reaction in RTILs, although a great deal of attention has been recently devoted to the electrocatalysis of carbon nanotubes (CNTs)<sup>18-24)</sup> and the use of CNTs in conjunction with RTILs as electrolytes.<sup>25)</sup>

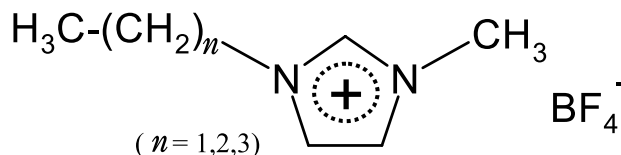
## 2 Experimental

### 2.1 Reagents and materials

Multi-walled carbon nanotubes (MWCNTs, outer diameter: 60-100 nm, inner diameter: 5-10 nm, length: 0.5-500 μm) were purchased from Aldrich and used as received. Ferrocene (Fc) was provided by Kanto Chemical Co. Inc. (Japan). RTILs of EMIBF<sub>4</sub>, PMIBF<sub>4</sub>, and BMIBF<sub>4</sub> with a purity of more than 99% and water content of less than 30 ppm (*i.e.*, *ca.* 2.1 mM) were obtained from Stella Chemifa Co. (Japan). The molecular structures of the RTILs are shown in Scheme 1.  $O_2$  (99.98%) gases were supplied from Nippon Sanso Co., Inc. (Japan). The edge-plane pyrolytic graphite (EPPG)(3 mm in diameter) electrode purchased from BAS (Japan) was used as the working electrode.

### 2.2 Apparatus and procedures

Cyclic voltammetry was performed using a computer-controlled electrochemical system (ALS/CHI 600) with a home-made three-electrode one-compartment electrochemical cell. A Pt spiral wire was employed as the aux-



Scheme 1

iliary electrode and a home-made silver chloride coated-Ag wire (denoted as Ag/AgCl) or Ag/AgCl (KCl-saturated) electrode as the reference electrode.

The EPPG electrode was successively polished with 1 and 0.06  $\mu\text{m}$  alumina powder on micro-cloth wetted with Milli-Q water before use. And then the electrode was carefully sonicated in Milli-Q water for 10 min and rinsed with Milli-Q water. After that, the electrode was electrochemically cleaned by repeating the potential scan between -0.9 and 1.6 V vs. Ag/AgCl(KCl-saturated) reference electrode at a scan rate of 0.1  $\text{V s}^{-1}$  in 0.05 M  $\text{H}_2\text{SO}_4$  solution until the steady-state cyclic voltammetric response was obtained. The thus-pretreated electrode was well dried with hot air to avoid bringing any water into the ionic liquid system. For deaeration,  $\text{N}_2$  gas was bubbled into the ionic liquid for 30 min, while  $\text{O}_2$  gas was bubbled directly into the electrochemical cell at least for 30 min to gain an  $\text{O}_2$ -saturated ionic liquid. All the electrochemical experiments were conducted at ambient temperature ( $25 \pm 1$ ) $^\circ\text{C}$ .

To quote the formal potential ( $E^0$ ) of the  $\text{O}_2/\text{O}_2^-$  redox couple with respect to that of the ferrocene/ferricenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple, CVs for the  $\text{Fc}/\text{Fc}^+$  redox couple in the RTILs containing 0.5 mM ferrocene were measured. The values of  $E^0$  the  $\text{Fc}/\text{Fc}^+$  couple in EMIBF<sub>4</sub>, PMIBF<sub>4</sub> and BMIBF<sub>4</sub> were estimated to be 0.23, 0.23 and 0.26 V vs. the Ag/AgCl reference electrode, respectively.

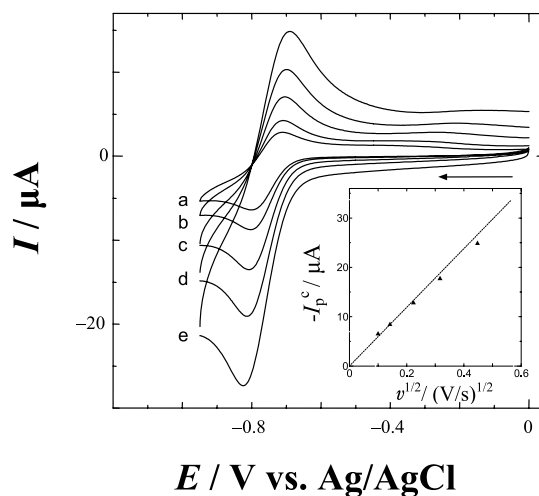
### 2.3 Preparation of MWCNTs/Nafion-modified electrode

The MWCNTs-Nafion suspension was prepared by dispersing MWCNTs into alcohol solution containing 0.05% Nafion by ultrasonication agitation for about 15 min to form a solution in which the content of MWCNTs is about 1 mg/mL. The EPPG electrode was modified with 5  $\mu\text{L}$  of the MWCNTs-Nafion suspension by droplet and allowed to evaporate the solvent at room temperature for 30 min.<sup>26)</sup> The thus-prepared electrode was denoted as MWCNTs/Nafion-modified EPPG electrode. The Nafion film-modified EPPG electrode was prepared by the same procedure using 0.05% Nafion alcohol solution containing no MWCNTs.

## 3 Results and Discussion

### 3.1 Cyclic voltammetry of the $\text{O}_2/\text{O}_2^-$ redox couple on bare EPPG electrode

Figure 1 shows the typical cyclic voltammograms (CVs) obtained for the oxygen reduction reaction (ORR) on the bare EPPG electrode in EMIBF<sub>4</sub>. The peak potential separation  $\Delta E_p$  between the anodic and cathodic peak potentials ( $E_p^a$  and  $E_p^c$ ) was *ca.* 64-120 mV at  $v = 10 - 200$   $\text{mV s}^{-1}$  and the ratio of the anodic peak current to the cathodic one was less than 1 (*ca.* 0.5-0.75), indicating that the  $\text{O}_2/\text{O}_2^-$  redox reaction is quasi-reversible under the present experimental condition in agreement with the results obtained at the glassy carbon (GC), Pt and Au electrodes in EMIBF<sub>4</sub>.<sup>15)</sup> The cathodic peak current ( $I_p^c$ ) was found to be almost proportional to  $v^{1/2}$  with a slight deviation from the linearity at higher scan rates (see the inset in Fig. 1). This also indicates the electrode reaction is quasi-reversible. Similar results were also obtained in



**Fig. 1** CVs obtained at bare EPPG electrode in  $\text{O}_2$ -saturated EMIBF<sub>4</sub>. Scan rates: (a) 10, (b) 20, (c) 50, (d) 100 and (e) 200  $\text{mV s}^{-1}$ . Inset shows the plot of  $-I_p^c$  vs.  $v^{1/2}$ .

PMIBF<sub>4</sub> and BMIBF<sub>4</sub>.

The standard rate constants ( $k^0$ ) were estimated from the  $\Delta E_p$  values obtained at various  $v$ 's using the Nicholson's procedure with the assumption that the diffusion coefficients of  $\text{O}_2$  and  $\text{O}_2^-$  are equal,<sup>27)</sup> and the results are given in Table 1. The  $k^0$  values at the EPPG electrode are  $4.3 \times 10^{-3}$ ,  $2.9 \times 10^{-3}$  and  $2.3 \times 10^{-3}$   $\text{cm s}^{-1}$  in EMIBF<sub>4</sub>, PMIBF<sub>4</sub> and BMIBF<sub>4</sub>, respectively and are about two-three times smaller than those at the GC electrode.<sup>15)</sup>

### 3.2 Cyclic voltammetry of the $\text{O}_2/\text{O}_2^-$ redox couple on MWCNTs/Nafion-modified EPPG electrode

Figure 2 shows the typical CVs obtained for the  $\text{O}_2/\text{O}_2^-$  redox reaction at the bare, Nafion-modified and MWCNTs/Nafion-modified EPPG electrodes in EMIBF<sub>4</sub>. At first glance we can see that both the cathodic and anodic peak currents are increased at the MWCNTs/Nafion-modified electrode, compared with those at the bare and Nafion-modified electrodes, and also the peak potential separation  $\Delta E_p$  value is decreased, that is, at 0.1  $\text{V s}^{-1}$ , from *ca.* 0.20 V at the bare and Nafion-modified electrodes to 0.10 V at the MWCNTs/Nafion-modified electrode. The similar results were also obtained in other ionic liquids used in this study, *i.e.*, PMIBF<sub>4</sub> and BMIBF<sub>4</sub>. These facts demonstrate an essential enhancement of the  $\text{O}_2/\text{O}_2^-$  redox reaction by the modification of the EPPG electrode surface with MWCNTs. Here it should be noted that the modification of the electrode surface by the Nafion film without MWCNTs slightly decreased the anodic and cathodic peak currents, probably due to the increased resistance for the diffusion of  $\text{O}_2$  and  $\text{O}_2^-$  through the Nafion film.

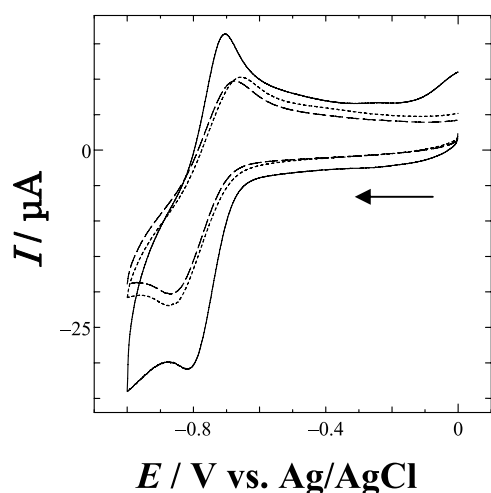
To clarify the observed acceleration of the  $\text{O}_2/\text{O}_2^-$  electrode reaction quantitatively, we estimated the  $k^0$  values at the MWCNTs/Nafion-modified electrodes using the same procedure as mentioned above. The obtained results are summarized in Table 1 together with those obtained at the bare electrode for comparison. The  $k^0$

**Table 1** Electrochemical data obtained for the redox reaction of the  $O_2/O_2^-$  couple at bare and MWCNTs/Nafion-modified EPPG electrodes in RTILs.

Ionic liquid	EPPG electrode	$E^0/V^a)$	$10^3 k^0/cm s^{-1}$
EMIBF <sub>4</sub>	bare	$-(0.99 \pm 0.01)$	$4.3 \pm 0.1 (6.4 \pm 0.1)^b)$
EMIBF <sub>4</sub>	MWCNTs-modified	$-(0.99 \pm 0.01)$	$8.3 \pm 0.1$
PMIBF <sub>4</sub>	bare	$-(0.99 \pm 0.01)$	$2.9 \pm 0.1 (7.3 \pm 1.6)^b)$
PMIBF <sub>4</sub>	MWCNTs-modified	$-(0.99 \pm 0.01)$	$10.4 \pm 0.1$
BMIBF <sub>4</sub>	bare	$-(1.00 \pm 0.01)$	$2.3 \pm 0.1 (7.5 \pm 0.1)^b)$
BMIBF <sub>4</sub>	MWCNTs-modified	$-(1.01 \pm 0.01)$	$4.2 \pm 0.1$

<sup>a)</sup> The values are presented with respect to the formal potential of the Fc/Fc<sup>+</sup> redox couple.

<sup>b)</sup> The values of  $k^0$  obtained at GC electrode. <sup>15)</sup>



**Fig. 2** CVs obtained at (···) bare, (- - -) Nafion film-modified and (-) MWCNTs/Nafion-modified EPPG electrodes in  $O_2$ -saturated EMIBF<sub>4</sub>. Scan rate: 100 mV s<sup>-1</sup>.

values at the MWCNTs/Nafion-modified EPPG electrode are by about 1.9, 3.6 and 1.8 times larger than those at the bare EPPG electrode in EMIBF<sub>4</sub>, PMIBF<sub>4</sub> and BMIBF<sub>4</sub>, respectively. The values of the formal potential ( $E^0$ ) of the  $O_2/O_2^-$  redox couple with respect to that of the Fc/Fc<sup>+</sup> redox couple were estimated to be  $-(1.00 \pm 0.01)$  V at both the bare and MWCNTs/Nafion-modified electrodes irrespective of the kind of ionic liquids used.

The observed enhancement of the  $O_2/O_2^-$  redox reaction at the MWCNTs/Nafion-modified electrode, *i.e.*, the increased peak currents and  $k^0$  values, may be considered to be due to the increases of the electrode/electrolyte interfacial area and the Nafion film porosity as suggested by Hu *et al.*<sup>26)</sup> They have examined in detail the electrochemical properties of MWCNTs-Nafion composite films on GC electrode based on the redox behavior of incorporated Eu<sup>3+</sup> by voltammetry and electrochemical impedance spectroscopy and have considered that the improved redox response of the Eu<sup>3+/2+</sup> couple originates from the increased electrode/electrolyte interfacial area and the enlarged porosity of the Nafion coatings as a result of the incorporation of MWCNTs. Depending on their atomic arrangements, carbon nanotubes (CNTs) behave electrically as a metal.<sup>28,29)</sup> Further it has been demonstrated that because of their electronic properties,

excellent conductivity and large specific area, CNTs-modified electrodes can effectively promote the electrooxidation of some biomolecules such as DNA,<sup>30,40)</sup> protein,<sup>31)</sup> H<sub>2</sub>O<sub>2</sub>,<sup>32)</sup> glucose<sup>18)</sup> and catecholamines<sup>19,33)</sup> and the electroreduction of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in aqueous media.<sup>23,34,35)</sup> CNTs also accelerate the redox reaction of Fe(CN)<sub>6</sub><sup>3-/4-</sup> couple.<sup>19,20)</sup> Recently, Britto *et al.*<sup>24)</sup> have explained the improved reduction of O<sub>2</sub> at CNTs-electrodes in aqueous acidic (H<sub>2</sub>SO<sub>4</sub>, pH = 2) and neutral (1 M KNO<sub>3</sub>) media based on the so-called defects on the carbon nanotube surface which are considered to be suitable sites for the favorable adsorption of O<sub>2</sub> molecule, resulting in the accelerated reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. This idea is considered to be also applicable for the present case.

In summary, we have found, for the first time, the electrocatalysis of the MWCNTs/Nafion-modified EPPG electrode for the  $O_2/O_2^-$  redox reaction in 1-*n*-alkyl-3-methylimidazolium tetrafluoroborate RTILs. The observed enhancement of the electron transfer kinetics, *i.e.*, the increase of both the cathodic and anodic peak currents as well as the  $k^0$  values has been explained based on the idea recently proposed for the electrocatalysis of CNTs in aqueous media. The present study suggests the promising use of CNTs as electrocatalysts in conjunction with RTILs with various advantages as electrolytes such as relatively high conductivity, wide potential window, chemical stability and nonvolatile nature.<sup>36-39)</sup>

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