

Cyclic Voltammetric Investigation on the Catalysis of Electrodeposited Manganese Oxide on the Electrochemical Reduction of Oxygen (ORR) in Room Temperature Ionic Liquids (RTILs) of 1-Ethyl-3-Methylimidazolium Tetrafluoroborate (EMIBF₄) on Glass Carbon (GC) Electrode

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Abstract

In this preliminary work, for the first time, the electrochemical oxygen reduction reaction (ORR) was investigated using cyclic voltammetry (CV) on the electrodeposited manganese oxide (MnO_x)-modified glass carbon electrode (MnO_x-GC) at room temperature ionic liquids (RTILs) of EMIBF₄, i.e., 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄). The results demonstrated that, after being modified by MnO_x on GC, the reduction peak current of oxygen was increased to some extent, while the oxidation peak current, corresponding to the oxidation of superoxide anion, O₂⁻, was attenuated in some degree, suggesting that MnO_x catalyzed ORR in RTILs of EMIBF₄, which is consistent with the results obtained in aqueous solution. To accelerate the electron transfer rate, multi-walled carbon nanotubes (MWCNTs) were modified on GC, and then MnO_x was electrodeposited onto the MWCNTs-modified GC electrode to give rise to the MnO_x/MWCNTs-modified GC electrode; consequently, the improved standard rate constant, κ_s, originated from the modified MWCNTs, along with the modification of electrodeposited MnO_x, showed us a satisfactory electrocatalysis for ORR in RTILs of EMIBF₄. In addition, not only for the MnO_x-modified GC but also for the MnO_x/MWCNTs-modified GC, there is a novel small oxidation peak appearing at -0.2 V vs. solid Ag/AgCl, implying that the catalysis of MnO_x for ORR in EMIBF₄ is somewhat different from that observed in aqueous solution, though the exact interpretation is not achieved in this preliminary work. Initiating the catalysis of MnO_x on ORR in RTILs is the main contribution of this work. Further discussions are in progress.

Keywords: manganese oxide (MnO_x), multi-walled carbon nanotubes (MWCNTs), room temperature ionic liquids (RTILs), electrochemical oxygen reduction reaction (ORR), glass carbon (GC) electrode.

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Introduction

As far as 1973, manganese oxide used for oxygen reduction reaction (ORR) has been found by Zoltowski [1], and in 1979, Brenet proposed that catalysis for ORR by manganese oxide was accomplished by the redox couple of $\text{Mn}^{4+} / \text{Mn}^{3+}$ existing in manganese oxide [2]. Matsuki and Kamada probed ORR on some crystal manganese oxides in alkaline solutions using a rotating ring-disk electrode (RRDE) and Teflon-bonded electrode, and found that much higher electrocatalytic activity of $\gamma\text{-MnOOH}$ was observed when compared to $\gamma\text{-MnO}_2$ [3]. Recently, Mao et al. [4], comparing catalysis of many kinds of manganese oxides, also pointed out that $\gamma\text{-MnOOH}$ exhibited the best catalysis for ORR among the employed manganese oxides, e.g., Mn_2O_3 , Mn_3O_4 , Mn_5O_8 , but, due to being lacking of direct proof, also owing to complicated valence states of manganese oxides; still now, unfortunately, the exact catalysis mechanism of manganese oxide for ORR was not reached. Therefore, researching the catalysis mechanism of manganese oxides for ORR, and extending the application of catalysis of manganese oxides for ORR is still the focused area for researchers who are mainly investigating ORR.

As we know, recently, due to their significant potential applications, room temperature ionic liquids (RTILs) have attracted much more attentions [5,6]. Although existing a plenty of papers concerning RTILs published every year, to the best of our knowledge, the application of RTILs in large scale was seldom reported, i.e., the magnificent application of RTILs still remains unrevealed. Additionally, due to lacking of protons, RTILs was selected as a benign electrolyte where the electrochemical oxygen reduction reaction (ORR) was well explored by Osteryoung and Alnashef [7,8]; they proved the existence of superoxide anion, O_2^- , reductively produced by molecular oxygen. Ohsaka group has also discussed the effect of both electrode and kinds of RTILs on ORR systematically [9].

As we know, the catalysis of manganese oxide on the electrochemical reduction of oxygen in alkaline solutions has been well discussed by Mao [10], where manganese oxide was directly physically immobilized on the gold electrode. In addition, the electrodeposition of manganese oxide has been well developed by Wu [11], where the amount of manganese oxide could be easily controlled by the electrodeposition conditions.

Carbon nanotubes (CNTs), classified as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs), have cylindrical graphite sheets with nanometer diameter and behave like metallic or semi-conducting wires. Carbon nanotubes have been utilized as an attractive material in biochemical sensing system for immobilizing biomolecules (proteins or enzymes) and facilitating the electron transfer reaction occurring between huge biomolecules and the electrode [12,13]. Besides, CNTs has been used as a novel ideal support for the electrochemically generated catalysis particle [14,15]. Lemay's group successfully achieved the electrodeposition of noble metal nanoparticle on carbon nanotubes, where the direct potentiostatic method was employed [16]. Lee's group has utilized the imidazolium-based ionic liquid to

covalently modify the MWCNTs, with an intention to enhance the dissolubility of CNTs [17].

Except for these merits exhibited by RTILs, higher viscosity is the main flaw of RTILs; higher viscosity could result in the lowered diffusion coefficient of the substance in RTILs [18], limiting the application of RTILs not only in organic synthesis, but also in the electrochemical field. To overcome these flaws, in this preliminary work, we introduced MWCNTs onto GC to acquire the promoted electrochemical response of ORR.

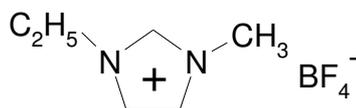
Investigating ORR at least has two widely accepted meanings. On one hand, as one half reaction happens at the cathode in fuel battery, clarifying the mechanism of ORR is helpful to improve the ability of fuel battery [19]. The other one is that as one of the reduction products of oxygen, i.e., superoxide anion O_2^- , was reported to be closely involved in the etiology of aging, cancer, and progressive neurodegenerative diseases such as Parkinson's disease [20,21], thus, comprehending the behavior of superoxide anion, O_2^- , is benefit for revealing the mechanism of molecular oxygen cycle in human body.

To the best of our knowledge, there is no paper discussing the catalysis of manganese oxide on ORR in RTILs. In this work, electro-catalysis of MnO_x for ORR in RTILs of $EMIBF_4$ was directly testified by the enhanced reduction peak current of oxygen. The increased value of standard rate constant, κ_s , corresponding to ORR, was achieved by the modification of MWCNTs, hence, the MnO_x /MWCNTs-modified GC electrode exhibited the satisfactory catalysis for ORR in RTILs of $EMIBF_4$. The possible catalysis mechanism of MnO_x for ORR in RTILs was also discussed. More detailed discussion is under progress.

Experimental

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. RTILs of $EMIBF_4$ with a purity of more than 99% and water content less than 30 ppm (i.e., ca. 2.1 mM) were obtained from Stella Chemifa Co. (Japan). The molecular structures of RTILs are shown in Scheme 1. O_2 (99.98%) gases were supplied from Nippon Sanso Co., Inc. (Japan). GC ($\varnothing = 3$ mm) electrode purchased from Nikko Keisoku Co (Japan) was used as the working electrode for our experiment.



Scheme 1

Apparatus

Cyclic voltammetry (CV) 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 auxiliary electrode and solid potassium chloride saturated silver/silver chloride

(solid Ag/AgCl) as the reference electrode. SEM was measured using FE-SEM (S-4700) supported by HITACH.

Preparation of solid Ag/AgCl reference electrode

The reference electrode of solid Ag/AgCl was prepared using bulk electrolysis technique, in which silver wire was utilized as working electrode, Ag/AgCl (KCl saturated) as reference electrode, platinum wire as counter electrode and a saturated potassium chloride solution was employed as electrolyte. Prior to electrolysis, silver wire was polished with sand paper to obtain a mirror-like surface. Pre-electrolysis potential was set at 0.35 V, electrolysis time was set to 180 s, and electrolysis potential was kept at 0.3 V. Then, electrolysis was stopped until a brown film appeared on the surface of silver wire, which will take about 2 min. The silver wire was rinsed with water and noted as solid Ag/AgCl electrode. All the potential values in this report were respect to the reference electrode of solid Ag/AgCl otherwise specified.

The working electrode, i.e., glass carbon electrode (GC), was successively polished with 1 and 0.06 μm alumina powder on micro-cloth wetted with Milli-Q water before use. The electrodes were carefully sonicated in Milli-Q water for 10min and rinsed with Milli-Q water. And then the electrode was cleaned by repeating the potential scan between -0.9 V and 1.6 V vs. Ag/AgCl, KCl-sat at a scan rate of 0.1 V/s in 0.05 M H_2SO_4 until stable CVs plots were obtained. The pretreated electrodes were well dried with hot air to avoid bringing any water into ionic liquid system. For degassing oxygen, N_2 was bubbled into the used ionic liquid, and O_2 gas was bubbled directly into the cell at least for 30 min to gain the O_2 -saturated ionic liquid. All the electrochemical experiments were conducted at ambient temperature (25 ± 1) $^\circ\text{C}$.

Preparation of MWCNTs-modified electrode

The MWCNTs-Nafion suspension was achieved 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. Prior to modification, the GC (3 mm in diameter) was carefully polished as stated above to obtain a mirror-like surface, and then rinsed and sonicated in distilled water for 10 min. The surface of GC was modified by 5 μL of the MWCNTs-Nafion suspension by droplet and treated to evaporate the solvent at room temperature for 30 min [22]; before transferring into RTILs, the MWCNTs-modified GC was dried again to guarantee free of water, which was noted as MWCNTs-modified GC, while the Nafion film-modified GC was prepared by the same process with only 0.05% Nafion alcohol solution.

Electrodeposition of manganese oxide on GC electrode

As reported before [23], the electro-deposition solution was 0.1 M Na_2SO_4 containing 0.05 mM manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2$). The applied potential on the well-pretreated GC was scanned at the scan rate of 20 mV s^{-1} from 0 V to 0.4 V vs. Ag/AgCl, KCl-sat for 20 circles. And then, the MnO_x -modified GC was carefully rinsed with doubly distilled water, prior to

transferring into EMIBF₄, the MnO_x-modified electrode must be blown dry. The electrodeposition of MnO_x on MWCNTs-modified GC electrode was accomplished by the same process as described for the MnO_x-modified GC electrode.

Results and discussion

SEM of the electrodeposited MnO_x

As we know, manganese oxide is a kind of complex oxide that contains many types, for example, MnO₂, Mn₂O₃, Mn₂O₅. To confirm the type of oxide we electrodeposited under our used condition, SEM was employed to obtain a direct photograph of MnO_x, as shown in Fig. 1. Fig. 1A is the image of the bare GC, where no evident substance was observed, Fig. 1B was obtained with 20 scan circles at the potential scan rate of 20 mV s⁻¹ within the potential region from 0 to 0.4 V versus Ag/AgCl, KCl-sat, where needle-like morphology was observed, consistent with the former report [24]. So we confirm the manganese oxide we electrodeposited was mainly composed of MnO₂ [24], allowing us to continue further work concerning MnO_x.

The electrochemical redox of oxygen on the MnO_x-modified GC electrode in EMIBF₄

Fig. 2 is the comparison of cyclic voltammograms (CVs) of electrochemical redox of oxygen on glass carbon electrode (GC) in the oxygen-saturated EMIBF₄ at the scan rate of 100 mV s⁻¹, where the dotted line was recorded on the bare GC electrode, and the solid line was plotted on the MnO_x-modified GCE. As we can see, after being electrodeposited by MnO_x, at the same condition, the reduction peak current of oxygen was increased to some extent, which accorded with the former report obtained alkaline solution [10]. Meanwhile, the oxidation peak current of superoxide anion, O₂⁻, was also somewhat suppressed, suggesting that the well defined quasi-reversible electrochemical redox of oxygen occurring in EMIBF₄ [9] was varied in some degree. This phenomenon was not observed in the case of alkaline solution, since only the reduction peak of oxygen occurred in alkaline solution [10]. In the nitrogen-saturated EMIBF₄ as shown by line a and line b, no reduction peaks were found, implying that in the employed potential range no electrochemical reduction of MnO_x was detected, i.e., the electrodeposited MnO_x was stable in our employed potential.

Interestingly, there was an obvious small oxidation peak appearing at about -0.2 V vs. solid Ag/AgCl when the scan rate is as low as 10 mV s⁻¹, as shown in Fig. 3. Through comparing the dotted line and solid line in fig. 3, we can conclude that the small peak appearing at around -0.2 V was resulted from MnO_x, though its exact electrochemical reaction mechanism could not be achieved by the present method. To our knowledge, till now, no report involving this small oxidation peak in RTILs was published.

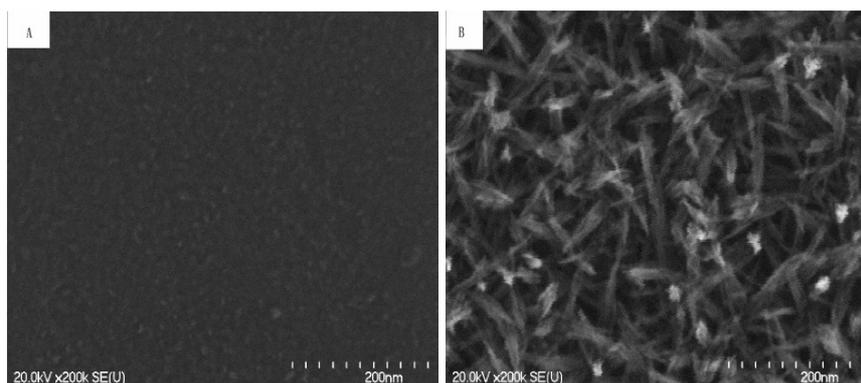


Figure 1. SEM images of electrodeposited MnO_x . A: bare GC electrode, B: MnO_x – modified GC electrode.

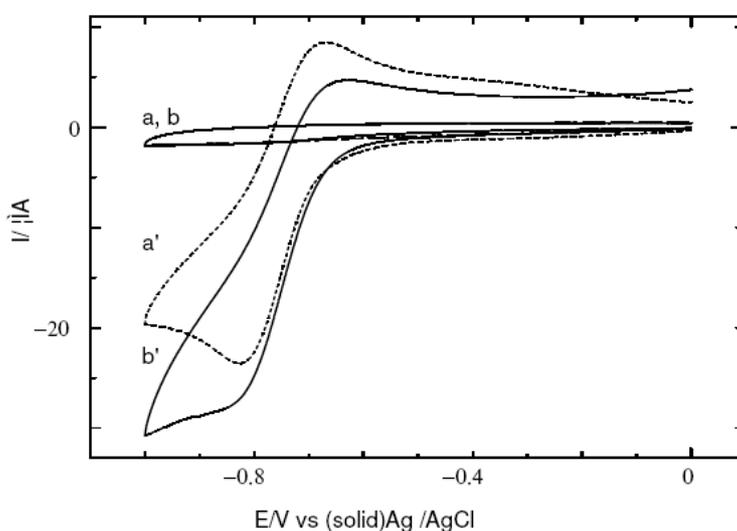


Figure 2. CVs of oxygen reduction reaction (ORR) in EMIBF_4 ; a, b: saturated with N_2 , a', b': saturated with oxygen; a, a': measured on bare GC electrode; b, b': measured on the MnO_x -modified GC. Scan rate: 100 mV s^{-1} .

The catalysis of MnO_x for the electrochemical reduction of oxygen was well addressed by Mao [10], in which the reduction process of oxygen was thought to be a two-electron process, i.e., $\text{O}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HO}_2^-$, and then with the presence of MnO_x , HO_2^- was easily chemically decomposed to yield OH^- and O_2 ; as a result, the regenerated molecular oxygen was electrochemically reduced repeatedly, leading to the enlarged reduction peak current. Mao [10] also pointed out that MnO_x catalyzed not only the disproportionation of the produced HO_2^- into O_2 and OH^- , but also for disproportionation of O_2^- into O_2 and HO_2^- ; unfortunately, the exact mechanism of MnO_x was not proposed. While in our used EMIBF_4 , the electrochemical redox of oxygen only involved a one-electron quasi-reversible process due to the absence of protons [8,9], Sawyer [25] has investigated the redox of oxygen in organic solvent of acetonitrile, and proposed that the produced superoxide anion, O_2^- , can react with platinum oxide to yield

platinum peroxide, $\text{PtO} + \text{O}_2^- \rightarrow \text{Pt-O-O-Pt}$, and then the peroxide could be oxidized to release molecular oxygen again, $\text{Pt-O-O-Pt} - 2e \rightarrow \text{PtO} + \text{O}_2 + \text{H}_2\text{O}$, but in his proposition, direct proof was not presented. Here, the appearing of a small oxidation peak at about -0.2 V strongly suggested that in our used potential range, there was an oxidation reaction for the employed MnO_x . More direct proofs about our results are really required in further discussion.

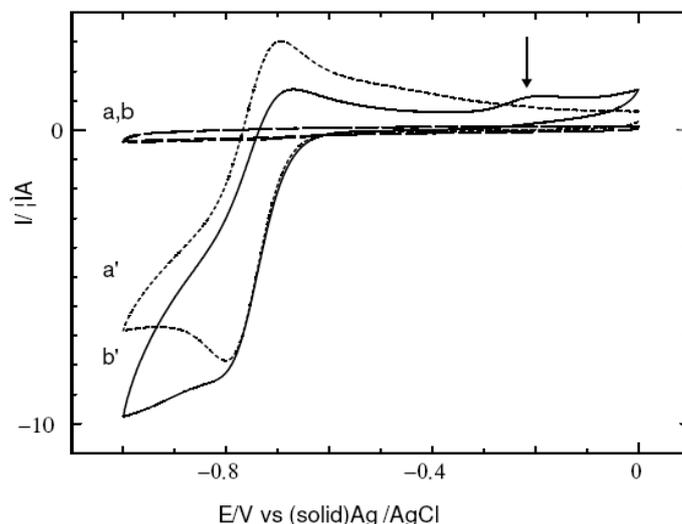


Figure 3. CVs of ORR in EMIBF₄. a, b: saturated with N₂; a', b': saturated with oxygen; a, a': measured on bare GC; b, b': measured on the MnO_x-modified GC. Scan rate: 10 mV s⁻¹.

Usually, the standard rate constant, κ_s , is the main parameter to describe the electron transfer rate happening at the electrode. To obtain the value of κ_s , the effect of scan rate on the electrochemical redox of oxygen was carried out, in which from the relationship between potential separation, ΔE_p , i.e., ($E_{pa} - E_{pc}$), and scan rate, the value of κ_s could be estimated [26].

The cyclic voltammograms of electrochemical redox of oxygen on the bare GC electrode has been presented in Fig. 4, where the value of κ_s was evaluated to be about $2.6 \times 10^{-3} \text{ cm s}^{-1}$, smaller than the reported data of $6.4 \times 10^{-3} \text{ cm s}^{-1}$ [9]. The difference between our measured data and the reported data probably resulted from the measuring conditions: the former reported data was evaluated by the method of normal pulse voltammograms (NPVs). The value of κ_s for the electrochemical redox of oxygen on the MnO_x-modified GC was found to be about $1.5 \times 10^{-3} \text{ cm s}^{-1}$, as shown in Fig. 5. That is to say, the introduction of MnO_x on GC electrode did not facilitate the electron transfer rate of redox of oxygen, though the improved reduction peak current of oxygen was observed in the presence of the electrodeposited MnO_x on GC electrode.

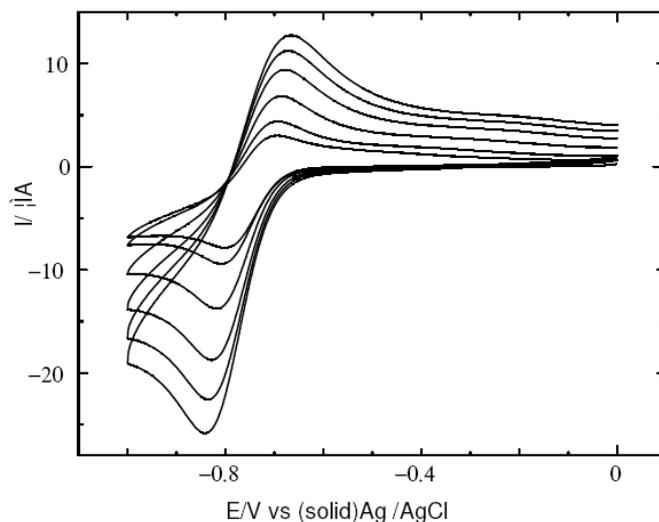


Figure 4. CVs of ORR in O_2 -saturated EMIBF $_4$ on bare GC electrode. Scan rate: 10, 20, 50, 100, 150, 200 $mV s^{-1}$.

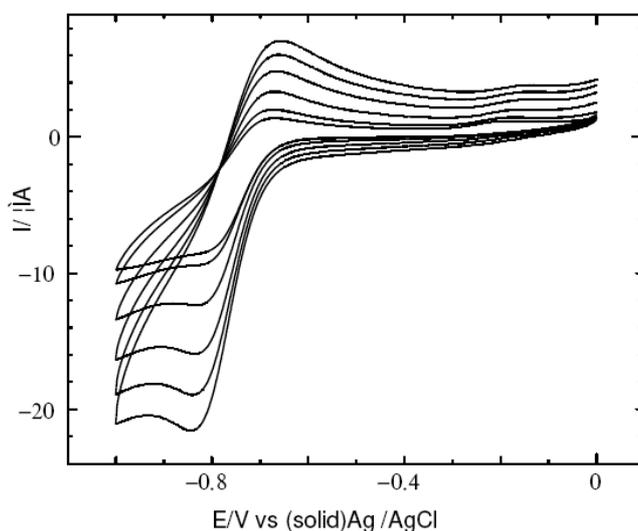


Figure 5. CVs of ORR in O_2 -saturated EMIBF $_4$ on the MnO_x -modified GC electrode. Scan rate: 10, 20, 50, 100, 150, 200 $mV s^{-1}$.

To interpret the small oxidation peak happening at $-0.2 V$ on the MnO_x -modified GC, the CVs of redox of oxygen in water-contained EMIBF $_4$ (content of distilled water is 0.56 M), was also detected as shown in Fig. 6. In Fig. 6, a novel oxidation peak was observed at about $-0.4 V$; moreover, this oxidation peak potential shifted for the positive direction as the scan rate was increased, indicating that the products generated by this oxidation process were not stable [27]. Generally, it was proposed that, in the presence of protons, $O_2^- + H^+ \leftrightarrow HO_2^\cdot$, and $HO_2^\cdot + O_2^- \rightarrow HO_2^- + O_2$ or $HO_2^- + H^+ \rightarrow H_2O_2$, the oxidation of HO_2^\cdot or HO_2^- or H_2O_2 , generated the broad oxidation peak appearing at about $-0.4 V$ [27]. While for the oxidation peak at $-0.2 V$, the peak potential was almost unchangeable as the scan rate was increased, indicating that the substance that was oxidized at $-0.2 V$ was a kind of stable substance. In addition, CVs

measured at the nitrogen saturated EMIBF₄ presented in Fig. 5 by line a and line b, have showed us that in the absence of oxygen, no oxidation peak at -0.2 V was observed for the MnO_x-modified GC electrode, suggesting that the oxidation peak at -0.2 V was not stemmed from the oxidation of the deposited MnO_x. Thus, basing on the above analysis, the small peak appearing at -0.2 V probably should be originated from the compound substance composed by MnO_x and superoxide anion, O₂⁻ rather than the compound substance generated by the interaction of MnO_x with the contained water in EMIBF₄. More direct proofs are required in further work.

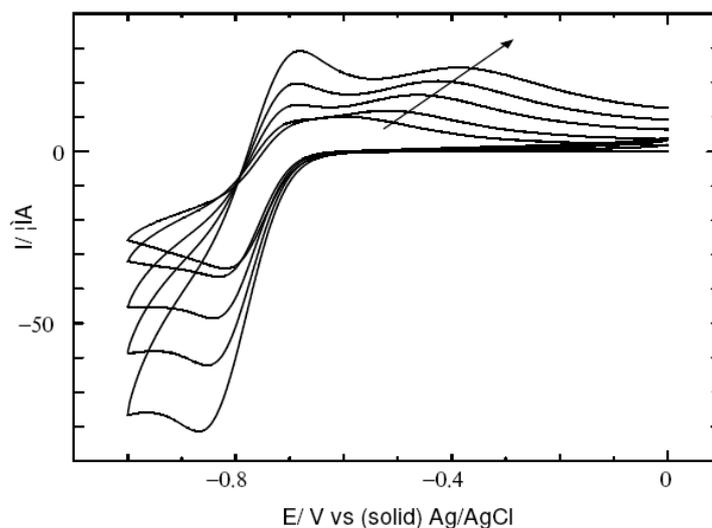


Figure 6. CVs of ORR in O₂- saturated EMIBF₄ containing 0.56 M H₂O on bare GC electrode. Scan rate: 10, 20, 50, 100, 200 mV s⁻¹.

The electrochemical redox of oxygen on the MnO_x/MWCNTs--modified glass carbon electrode in EMIBF₄

As reported, carbon nanotubes (CNTs) have been regarded as a kind of potential nano-materials not only for generating nano-scale device, but also for accelerating the electron transfer rate happening at the interface between electrolyte and the electrode [12,13]. The electrodeposition of metal particles on the single-walled carbon nanotubes(SWCNTs) has been developed by Lemay group [16], where the electrodeposition process was simply completed by the direct potential controlling. In this work, MnO_x was electrodeposited on MWCNTs by the potential scanning basing on the former paper [23], where MWCNTs was used after the pretreatment by strong acid on MWCNTs, i.e., many polar groups were created at the surface of MWCNTs, for example, groups of -OH or -COOH, and ORR were measured in alkaline solution. In this work, MWCNTs was used directly without the strong acid pretreatment. To the best of our knowledge, this is the first report concerning the electrochemical redox of oxygen on MWCNTs modified GC electrode in RTILs.

As shown in Fig. 7, where the dotted line corresponds to the CVs obtained on the bare GC, the dashed line stands for the case on the MWCNTs-modified GC, while the solid line is the CVs obtained on the MnO_x/MWCNTs-modified GC

electrode. The first change originated from the modification of MWCNTs is the increased peak current compared to the bare GC; for example, as shown in Fig. 7, at scan rate of 100 mV s^{-1} , the reduction peak current was increased from $23 \mu\text{A}$ for the bare GC to around $33 \mu\text{A}$ for the MWCNTs-modified GC; after being electrodeposited by MnO_x , the reduction peak current was also increased to about $40 \mu\text{A}$, while the oxidative peak current was attenuated from $25 \mu\text{A}$ for the MWCNTs-modified GC to $20 \mu\text{A}$ at the scan rate of 100 mV s^{-1} , suggesting that there is an evident catalysis of MnO_x for the electrochemical redox of oxygen even in RTILs. Meanwhile, the formal potential, $E^{0'}$, i.e., $(E_{\text{pa}} + E_{\text{pc}})/2$, was shifted for the positive direction from -0.752 V for the bare GC to -0.730 V for the MWCNTs-modified GC at the scan rate of 100 mV s^{-1} , indicating that MWCNTs have an evident electrocatalysis for the electrochemical redox of oxygen in RTILs. After being electrodeposited by MnO_x , the formal potential was changed to -0.735 V , suggesting that there is no obvious influence of the electrodeposited MnO_x on the formal potential of redox of oxygen on the MWCNTs-modified GC electrode under our employed conditions. Interestingly, the value of potential separation, ΔE_p , i.e., $(E_{\text{pa}} - E_{\text{pc}})$, was remarkably reduced by the introduction of MWCNTs; for an instance as shown in Fig. 7, for the bare GC, the value of ΔE_p is about 134 mV , while after being modified by MWCNTs, the value of ΔE_p was reduced to about 60 mV at the scan rate of 100 mV s^{-1} , leading to the dramatically increased value of κ_s [26].

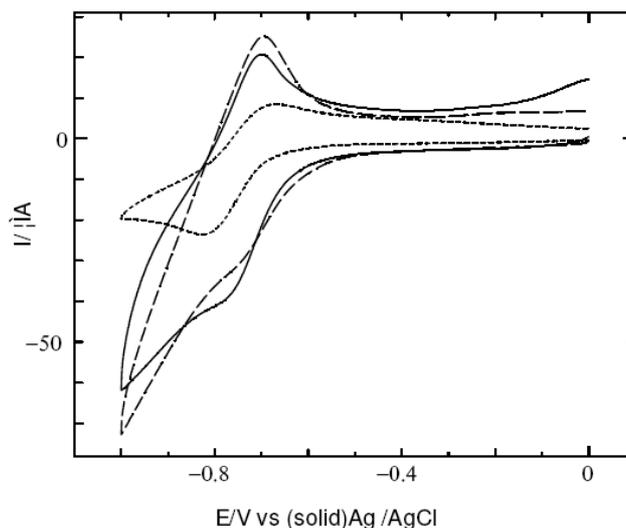


Figure 7. CVs of ORR in O_2 -saturated EMIBF_4 . Dotted line: on the bare GC; dashed line: on the MWCNTs-modified GC; solid line: on the MnO_x /MWCNTs-modified GC. Scan rate: 100 mV s^{-1} .

Besides, the linear relationship between scan rate and square root of scan rate, as shown by the inset in Fig. 8a, in which to exclude the influence of capacitance current, the scan rate was initiated at 20 mV s^{-1} , allowed us to estimate the value of κ_s for the electrochemical redox of oxygen according to the former derived formula [27], where κ_s was estimated to be about $45 \times 10^{-3} \text{ cm s}^{-1}$, implying that MWCNTs really acted as a promoter for the electron transfer process of redox of oxygen in our investigated RTILs of EMIBF_4 , being consistent with the

conclusion obtained in aqueous solution [25]. Unfortunately, for the $\text{MnO}_x/\text{MWCNTs}$ -modified GC, the value of κ_s was calculated to be about $11.5 \times 10^{-3} \text{ cm s}^{-1}$, as shown in Fig. 8b, some smaller than in the case of MWCNTs-modified GC. But for the $\text{MnO}_x/\text{MWCNTs}$ -modified GC, the increased reduction peak current and the attenuated oxidation peak current also strongly testified that MnO_x exhibited catalysis for the electrochemical redox of oxygen even on MWCNTs-modified GC in RTILs of EMIBF₄.

In addition, even for the MWCNTs-modified GC, after being modified by the electrodeposited MnO_x , there is an evident oxidation peak appearing at about -0.2 V , as shown in Fig. 9, the exact process were not very clear.

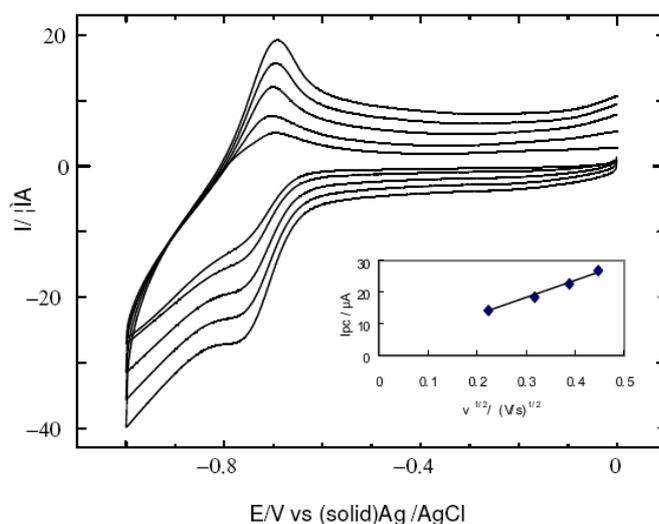


Figure 8a. CVs of ORR in O_2 -saturated EMIBF₄ on the MWCNTs-modified GC. Scan rate: 20, 50, 100, 150, 200 mV s^{-1} .

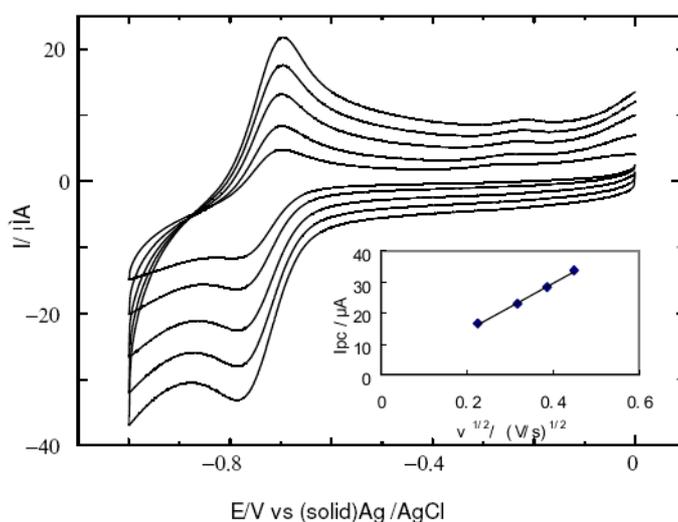


Figure 8b. CVs of ORR in O_2 -saturated EMIBF₄ on the $\text{MnO}_x/\text{MWCNTs}$ -modified GC electrode. Scan rate: 20, 50, 100, 150, 200 mV s^{-1} .

As one kind of supercapacitor materials, manganese oxide was widely investigated [24]. According to previous paper, MnO_x obtained by

electrodeposition under similar conditions was MnO_2 [24], and charge-discharge process was completed according to the process, i.e., $\text{MnO}_2 + \text{H}^+ + \text{e} \rightarrow \text{MnOOH}$ [28]; combining with our results, we think, because there is no direct electron transfer between MnO_2 and electrode of GC, as verified by Fig. 2, the catalysis of MnO_2 for ORR should be originated from the chemical reaction between MnO_2 and the produced superoxide anion, O_2^- , i.e., $\text{MnO}_2 + \text{H}^+ + \text{e} (\text{O}_2^-) \rightarrow \text{MnOOH} + \text{O}_2$, leading to the attenuation of the oxidation peak current and the regenerated molecular oxygen could participate the electrochemical reduction repeatedly, presenting the increased of reduction peak current of oxygen. At the same time, the produced MnOOH could also catalyze the reduction of O_2 to yield HO_2^- [10], leading to the enhanced reduction peak current of oxygen. Here, RTILs of EMIBF_4 , compared to the alkaline solution, due to lacking of protons and OH^- , should be favorable to the exiting of MnOOH , which probably was oxidized at around -0.2 V, leading to a small oxidation peak.

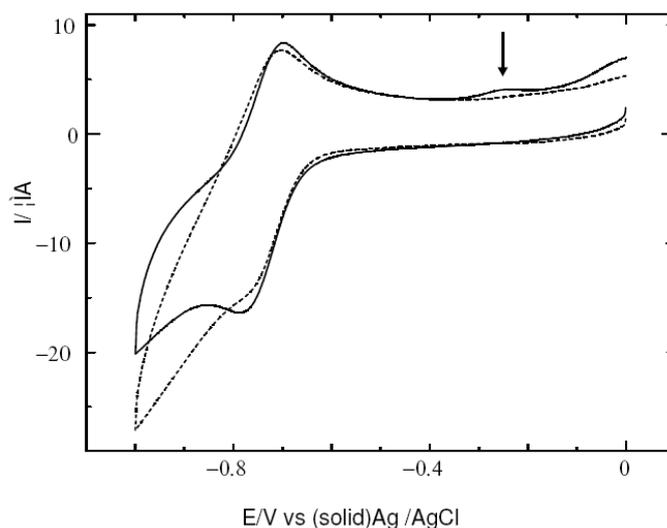


Figure 9. Comparison of CVs for ORR in O_2 -saturated EMIBF_4 . Dotted line: on the MWCNTs-modified GC; solid line: on the $\text{MnO}_x/\text{MWCNTs}$ - modified GC. Scan rate: 50 mV s^{-1} .

Also, the electrocatalysis exhibited by MnO_x depended on many factors: for example, its powder morphology, crystal structure, and so on. As for the MnO_x produced by electrodeposition, the electrodeposition condition, for instance, employed potential range, used potential scan rate, potential scanning cycles, etc., also directly affect catalysis of MnO_x on ORR [10].

As reported before, for the catalysis of MWCNTs, there were also several available reasons, for example, MWCNTs has increased the electrode surface, improving the conductivity between the electrolyte and electrode [29,30]. Among these proposed reasons, we think the existing of “defect pairs in the lattice of MWCNTs” [31,32] should be responsible for our observed results. That is to say, MWCNTs has numerous “defects”, consequently, MWCNTs could create many “active points” on the electrode of GC. In addition, we think, the introduction of EMIBF_4 has greatly altered the ion-atmosphere of molecular oxygen, i.e., the ion-atmosphere of molecular oxygen in EMIBF_4 is different from that in aqueous

solution, probably, the environment owned by RTILs of EMIBF₄ is favorable for molecular oxygen to interact with these “defects” on MWCNTs. The above reasons may be taken into account for our obtained results.

Final comments

In this preliminary work, for the first time, the catalysis of manganese oxide MnO_x, electrodeposited on GC and on the MWCNTs-modified GC electrode, for the electrochemical oxygen reduction reaction (ORR) was clearly observed by CVs in the RTILs of EMIBF₄. After being modified by MnO_x, not only for the bare GC but also for the MWCNTs-modified GC, the reduction peak current of oxygen was increased, along with the attenuated oxidation peak current of superoxide anion, suggesting that the electrodeposited MnO_x has an obvious catalysis for ORR in our used RTILs of EMIBF₄. Basing on a former report, combining with our results, the generation of MnOOH, produced by the chemical reaction of MnO_x with the superoxide anion, O₂⁻, was thought to be mainly responsible for catalyzed electrochemical response of ORR. Additionally, the reasons for the catalysis of MWCNTs for ORR was also discussed, proposing that these “defects” on the surface of MWCNTs and the novel “ion-atmosphere” created by EMIBF₄ should account for the catalysis of MWCNTs for ORR in RTILs of EMIBF₄. Initiating the electrocatalysis of MnO_x, and MWCNTs as well, for ORR in RTILs is the main contribution of this work, which is helpful to the research of ORR, as well as the application of MWCNTs, and to the application of RTILs in the field of supercapacitor.

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