ChemComm



View Article Online

COMMUNICATION



Cite this: DOI: 10.1039/c4cc08410a

Received 24th October 2014, Accepted 12th January 2015

DOI: 10.1039/c4cc08410a

www.rsc.org/chemcomm

A novel fabrication of a polymeric ionic liquid hybrid film modified electrode and its successful application to the electrogeneration of a superoxide anion in aqueous media[†]

Dilani Nilushika,^a Mohamed I. Awad,^b Mahmoud M. Saleh,^b Takeyoshi Okajima,^a Lanqun Mao^c and Takeo Ohsaka*^a

A novel polymeric ionic liquid hybrid film-modified electrode, in which the electrode surface is coated with a hydrophobic hybrid material composed of an ionene polymer with quaternary ammonium sites in its polymeric backbone and ionic liquids, was fabricated by electropolymerization of N,N-dimethylaniline in a hydrophobic ionic liquid, which can be applied for the electrogeneration of a superoxide anion *via* one-electron reduction of O_2 in aqueous media.

Room Temperature Ionic Liquids (RTILs), being entirely composed of cations and anions, have been receiving intense attention as a new class of solvents¹ that offer alternatives to conventional molecular solvents for numerous applications in the general field of chemistry, because of their unique physicochemical properties (such as low volatility, nonflammability, electrochemical and thermal stability and high ionic conductivity) which could be arbitrarily tailored by appropriately choosing cations and anions.²

Since the late 1990s, RTILs have been also deliberately used for electrode modifications by covering electrode surfaces typically with free-standing IL films, IL droplets, adsorbed ILs, mixtures of ILs and other components (such as organic or inorganic polymers, nanoparticles, nanotubes and other micro- or nano-objects) and polymeric ILs.³ By careful and appropriate choice of the cation and anions, we can introduce, for example, a hydrophobic IL domain on electrode surfaces and the resulting IL-modified electrodes are expected to allow for electrochemical experiments in aqueous media with fundamental and practical prospective

applications for ion transfer across the IL/aqueous solution interface, concentration of redox active anions from the aqueous phase, electrochemical sensing, electrocatalysis, stable immobilization of enzyme for biosensing, fuel cells, *etc.*^{3,4}

In this communication, we report a novel, simple fabrication of a polymeric ionic liquid hybrid (PILH)-modified electrode, in which the electrode surface is coated with an ionene polymer with quaternary ammonium sites in its polymeric backbone and ILs are embedded into its matrix, via electropolymerization of N,N-dimethylaniline in ILs. This PILH-modified electrode is applied successfully for electrogeneration of a superoxide anion $(O_2^{-\bullet})$ via 1e-reduction of O_2 in aqueous media in contrast to the conventional O₂ reduction (*i.e.*, 2e- and 4e-reductions of O₂ to H₂O₂ and H₂O, respectively, depending on the electrocatalyst used).⁵ The present idea for preparing the PILH film with a polymeric ionene structure in which $O_2^{-\bullet}$ is chemically stable is developed originally from our previous studies⁶ on the preparation of such polymeric ionone films by electropolymerization of dialkylanilines, which was carried out in acidic aqueous media, and recent studies⁷ on the electrochemistry of the $O_2/O_2^{-\bullet}$ redox couple in ILs.

The PILH film-modified electrode was prepared by an oxidative electropolymerization of *N*,*N*-dimethylaniline (DMA) in hydrophobic IL, typically *N*-methyl-*N*-propyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide ($[MPP]^+$ [N(Tf)₂]⁻, Kanto Chemicals Co. Japan) with a purity of >99% and less than 0.005% water (Scheme 1). The anodic peak corresponding to



 $\label{eq:scheme1} \begin{array}{l} \mbox{Electro-oxidative polymerization of DMA in [MPP]^+ $[N(Tf)_2]^-$,} \\ \mbox{resulting in a PILH film impregnated with [MPP]^+ $[N(Tf)_2]^-$.} \end{array}$

^a Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259-G1-5 Nagatsuta, Midori-Ku, Yokohama 226-8502, Japan. E-mail: ohsaka@echem.titech.ac.jp;

Fax: + 81-45-924-5489; Tel: + 81-45-924-5404

^b Chemistry Department, Faculty of Science, Cairo University, Cairo 12613, Egypt

^c Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Science, 2 Zhongguancum North First Street, Beijing 100190, P. R. China

 $[\]dagger$ Electronic supplementary information (ESI) available: Preparation of PDMA from aqueous solution, surface image, surface profiles. See DOI: 10.1039/ c4cc08410a



Fig. 1 Consecutive CVs (100 cycles) at GC electrode in IL $[MPP]^+ [N(Tf)_2]^-$ containing 0.2 M DMA at 50 mV s⁻¹ under Ar atmosphere. The inset shows an LSM image of the PILH-modified GC electrode.

the formation of the monocation radical (DMA^{+•}) of DMA was observed at ca. 0.8 V and on successive potential cycling this anodic peak current continuously decreased and actually completely disappeared after the 100th scan (Fig. 1), suggesting the formation of an electroinactive polymer film (poly(N,Ndimethylaniline), PDMA) through the polymerization of DMA^{+•} on the electrode surface and that new DMA monomers from the bulk of the $[MPP]^+$ $[N(Tf)_2]^-$ must diffuse through this film to reach the electrode surface and then they are oxidized to DMA^{+•}, *i.e.*, the film becomes more compact as the electrolysis proceeds and the diffusion of DMA and DMA^{+•} through the formed film is retarded accordingly and thus a limiting film thickness is finally reached. Actually, the thickness of the PDMA film obtained by the potential scan for 100 times was ca. 16 µm and further scan did not increase it (Fig. S3, ESI[†]). This maximum thickness is much larger than that (*ca.* $1 \mu m$) of the PDMA film prepared in aqueous media (Fig. S1-S3, ESI⁺).⁶ The obtained cyclic voltammetric behaviour (Fig. 1) is essentially almost the same as that obtained for the electropolymerization of N,N-dialkylanilines in acidic aqueous media (Fig. S1, ESI⁺), but formation of the dimer, tetramethylbenzidine (TMB), the redox response of which is faintly observed at ca. 0.4 V only in the initial several scans, by a tail-tail coupling of DMA^{+•} is considerably less and the decrement in the main anodic peak current upon the potential cycling is larger. These facts indicate that the electropolymerization of DMA is more feasible under the present IL condition compared with that in aqueous media.^{6,8} The PILH film exhibits a uniform microporous structure (inset in Fig. 1) being different from the PDMA films (prepared in aqueous media) with slightly compact microstructure and poor porosity (Fig. S2, ESI⁺) and the films of aniline and its derivatives, which have irregular grains, slice or rod-like structures.⁹

The obtained PDMA film is a composite impregnated with the IL used, as can be seen from the deconvoluted N1s XPS spectra (Fig. 2).¹⁰ That is, three different peaks were obtained; the peak at 403.5 eV corresponds to the quaternary ammonium sites in the PDMA backbone and the remaining two peaks at 399.6 and 402.7 eV, which were also observed for the IL used itself (Fig. S4, ESI[†]), correspond to the $-N^-$ -group of $[N(Tf)_2]^-$ and





the quaternary ammonium sites of $[MPP]^+$, respectively. The comparison of each area of these three peaks indicates that the ratio of the total area of two cationic N moieties to the peak area of the anionic N moiety is almost close to unity and at the same time confirms that the obtained PILH film is composed of a cationic ionene polymer, PDMA with $[N(Tf)_2]^-$ as a counter anion and the neat IL, $[MPP]^+[N(Tf)_2]^-$ (Scheme 1).

Immobilization of $[Fe(CN)_6]^{3-}$ into the PILH film of PDMA was used to confirm its polycationic ionene property and further to examine the anion-exchange capability. Incorporation of the $[Fe(CN)_6]^{3-/4-}$ redox couple into the PDMA film was examined by consecutively recording a series of cyclic voltammograms (CVs) obtained with the PDMA film-modified GC electrode in 0.1 M phosphate buffer solution (PBS) containing 0.1 mM $[Fe(CN)_6]^{3-}$ (Fig. 3A). At a glance, we can see that the redox response corresponding to the redox reaction of the $[Fe(CN)_6]^{3-/4-}$ couple increases with increasing potential scan duration and the response reaches a constant after a potential scan of ca. 90 min and the peak height is about 20 times larger than that (the dashed line in Fig. 3A) at the bare GC electrode in the same solution, indicating the incorporation of $[Fe(CN)_6]^{3-1}$ into the PDMA film *via* anion exchange. The thus $[Fe(CN)_6]^{3-/4-}$ incorporated PDMA modified electrode was transferred into the $[Fe(CN)_6]^{3-}$ -free supporting electrolyte (0.1 M PBS) and the CV



Fig. 3 (A) Continuous potential cycling at the PILH film-modified GC electrode (solid line) and the bare GC electrode (dashed line) in 0.1 M PBS solution (pH 7) containing 0.1 mM [Fe(CN)₆]^{3-.} (B) CV response of [Fe(CN)₆]^{3-/4-} immobilized PILH film-modified GC electrode in [Fe(CN)₆]³⁻⁻ free 0.1 M PBS. (C) Variation of Γ ([Fe(CN)₆]³⁻) with pH. Potential scan rate: 10 mV s⁻¹.

response was examined (Fig. 3B). A small decrease in the current response was observed only for the initial few scans and after that, a stable response was obtained. In addition, we found that the surface coverage $(\Gamma([Fe(CN)_6]^{3-}))$ of the incorporated $[Fe(CN)_6]^{3-}$ does not change with pH when the $[Fe(CN)_6]^{3-}$ incorporated PDMA electrode was transferred into the $[Fe(CN)_6]^{3-}$ free electrolyte solutions of various pHs (Fig. 3C). In this case, $\Gamma([Fe(CN)_6]^{3-}) = 2.0 \times 10^{-9} \text{ mol cm}^{-2}$, corresponding to *ca.* 1.3 mM (based on the thickness of 16 µm) which is 13 times the concentration (0.1 mM) of the $[Fe(CN)_6]^{3-}$ solution into which the PDMAmodified electrode was soaked. These facts demonstrate that the $[Fe(CN)_6]^{3-/4-}$ couple is electrostatically incorporated, concentrated highly and immobilized stably in the PDMA film. In other words, the present PDMA is a polycationic ionene polymer with positively charged ammonium sites in its backbone and thus has a pHindependent anion-exchange property (eqn (1)).



Fig. 4A(b) shows a typical CV obtained at the PILH filmmodified GC electrode in O₂-saturated 0.1 M PBS (pH 10.0). A couple of well-defined redox peaks were obtained at around -0.6 V vs. Ag/AgCl/KCl (sat.) and the redox behaviour (eqn (2)) is almost the same as those (Fig. 4B(b) and (c)) for the O₂/O₂^{-•} couple in a hydrophobic IL, *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide ([TMPA]⁺[N(Tf)₂]⁻) in which is [TMPA]⁺ has a quaternary ammonium group similar to the *N*,*N*-dimethyl ammonium moieties of PDMA and [MPP]⁺[N(Tf)₂]⁻.¹¹

$$O_2 + e \rightleftharpoons O_2^{-\bullet} \tag{2}$$

The cathodic peak can be assigned to the one-electron reduction of O_2 to $O_2^{-\bullet}$, while the anodic one corresponds to the oxidation of $O_2^{-\bullet}$ to O_2 . The ratio of the anodic peak current (I_p^a) to the cathodic one (I_p^c) is close to unity and the peak separation (ΔE_p) is about 350 mV, too large compared with the ΔE_p of 59 mV theoretically expected for a one-electron reversible redox reaction¹² and the ΔE_p values obtained in conventional aprotic media



Fig. 4 (A) CVs at the PILH film-modified GC electrode in the absence (a, b) and the presence (c) of 12 μ M SOD in 0.1 M PBS (pH 10.0) under (a) Ar and (b, c) O₂ atmosphere and (B) CVs at the bare GC electrode in (b) [TMPA]⁺[N(Tf)₂]⁻ and (c) [MPP]⁺[N(Tf)₂]⁻ under O₂ atmosphere and in (a) [TMPA]⁺[N(Tf)₂]⁻ under Ar atmosphere at 100 mV s⁻¹.



Scheme 2 (A) $O_2^{-\bullet}$ electrogeneration *via* one-electron reduction of O_2 at the PILH modified electrode in aqueous media and (B) $O_2^{-\bullet}$ dismutation catalyzed by SOD enzyme at the PILH film/aqueous interface.

such as DMSO, DMF, and AN^{13} as well as those (*ca.* 115 and 170 mV, respectively) obtained at the bare GC electrode in $[MPP]^+[N(Tf)_2]^-$ and $[TMPA]^+[N(Tf)_2]^-$ (Fig. 4B(b) and (c)). The large ΔE_p in Fig. 4A(b) may be due to the retarded diffusion of O_2 and $O_2^{-\bullet}$ and the electrolyte ions ($[MPP]^+$ and $[N(Tf)_2]^-$) through the coating of insulating PDMA. The results in Fig. 4 demonstrate that the present PILH modified electrode can be successfully applied for the electrogeneration of $O_2^{-\bullet}$ *via* 1e-reduction of O_2 in aqueous media (Scheme 2(A)), in which the PILH film is only an electrolyte layer, while the electrochemical reaction takes place on the GC substrate surface, in contrast to the conventional O_2 reductions, ⁵ *i.e.*, 2e- and 4e-reductions of O_2 to H_2O_2 and H_2O , respectively, depending on the electrode used.

The formation of $O_2^{-\bullet}$ in aqueous media was also confirmed by examining the $O_2/O_2^{-\bullet}$ redox reaction in the presence of superoxide dismutase (SOD), which effectively catalyzes the dismutation of $O_2^{-\bullet}$ to O_2 and H_2O_2 (Fig. 4A(c)¹⁴ Scheme 2(B)). Interestingly, the anodic peak for the oxidation of $O_2^{-\bullet}$ disappears completely, while the cathodic one corresponding to the reduction of O_2 is almost doubled as expected for a fast dismutation of O_2^{-} . The overall O_2 reduction is expressed by eqn (3).

$$O_{2} + e \longrightarrow O_{2}^{-}$$

$$2O_{2}^{-} \longrightarrow O_{2} + H_{2}O_{2}$$

$$H_{2}O(H^{+}) \longrightarrow O_{2} + H_{2}O_{2}$$

$$(3)$$

Again, such a fact confirms the $O_2^{-\bullet}$ generation *via* the 1ereduction of O_2 at the present PILH-modified electrode in aqueous solution and at the same time demonstrates that this modified electrode could be applied for electrochemically clarifying various chemical and biochemical reactions of unstable $O_2^{-\bullet}$, typically at a hydrophilic/hydrophobic interface similar to biological circumstances where $O_2^{-\bullet}$ plays various physiological roles.¹⁵

In conclusion, we have fabricated a novel polymeric ionic liquid composite film-modified electrode by electro-oxidative polymerization of DMA in a hydrophobic ionic liquid, typically $[MPP]^+[N(Tf)_2]^-$. The electrode surface is coated with a hydrophobic composite composed of an ionene polymer, PDMA, with quaternary ammonium sites in its polymeric backbone and ionic liquids $[MPP]^+[N(Tf)_2]^-$ and thus its use in aqueous media inevitably establishes a hydrophobic ionic liquid layer/hydrophilic water interface on the electrode surface. This modified electrode actually allowed us to electrogenerate a superoxide anion in aqueous media

via 1e-reduction of O₂ (which is usually possible in conventional aprotic organic media¹³ and some ILs,⁷ but not in protic media (*e.g.*, water)⁵), opening a new avenue for electrochemically studying various chemical and biochemical reactions and reactivities of O₂^{-•} at a hydrophobic layer/hydrophilic liquid interface, similar to biological circumstances where O₂^{-•} plays various physiological roles.

The present work was financially supported by Grant-in-Aid for Scientific Research (A) to T. O. from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan and to D. N. from Tokyo Institute of Technology Global COE program for Energy Science.

Notes and references

- 1 (a) Ionic Liquids in Synthesis, ed. P. Wassersheid and T. Welton, Wiley-VCH, Weinheim, 2003; (b) Ionic Liquids: Industrial Applications for Green Chemistry, ed. R. Rogers and K. R. Seddon, ACS Symp.Ser., 2002, p. 818; (c) Electrochemical Aspects of Ionic Liquids, ed. H. Ohno, John Wiley and Sons, New Jersey, 2005; (d) B. Kirchner, Ionic Liquids, Topics in Current Chemistry, Springer, 2009.
- 2 (a) T. Welton, Chem. Rev., 1999, 99, 2071; (b) P. Wassercheid and W. Keim, Angew. Chem., Int. Ed., 2009, 39, 3772.
- 3 M. Opallo and A. Lesniewski, *J. Electroanal. Chem.*, 2011, **656**, 2 and references therein.
- 4 (a) J. D. Wadhawan, U. Schroder, A. Neudeck, S. J. Wilkins, R. G. compton, F. Marken, C. S. Consorti, R. F. de Souza and J. Dupont, J. Electroanal. Chem., 2000, 493, 75; (b) V. A. Hernandez and F. Scholz, Electrochem. Commun., 2006, 8, 967; (c) Y. Shen, Y. Zhang, X. Qiu, H. Guo, L. Niu and A. Ivaska, Green Chem., 2007, 9, 746; (d) Y. Liu, L. Huang and S. Dong, Biosens. Bioelectron., 2007, 23, 35.
- 5 K. Kinoshita, *Electrochemical Oxygen Technology*, John Wiley & Sons, Inc, New Jersey, 1992.

- 6 (a) N. Oyama, T. Ohsaka and T. Shimizu, Anal. Chem., 1985,
 57, 1526; (b) T. Oshaka, T. Okajima and N. Oyama, J. Electroanal. Chem., 1986, 200, 159.
- 7 (a) X. J. Huang, E. I. Rogers, C. Hardacre and R. G. Compton, J. Phys. Chem. B, 2009, 113, 8953; (b) M. Hayyan, F. S. Mjalli, M. A. Hashim, I. M. AlNashef, S. M. Alzahrani and K. L. Chooi, J. Electroanal. Chem., 2012, 664, 26; (c) M. M. Islam and T. Ohsaka, J. Phys. Chem. C, 2008, 112, 1269; (d) C. Pozo-Gonzalo, P. C. Howlett, J. L. Hodgson, L. A. Madsen, D. R. MacFarlane and M. Forsyth, Phys. Chem. Chem. Phys., 2014, 16, 25062; (e) S. K. Praneshwar, J. R. Monnier, M. A. Matthews and J. W. Weidner, Anal. Bioanal. Electrochem., 2013, 5, 711; (f) T. Nakagawa, Y. Katayama and T. Miura, ECS Trans., 2012, 50, 159; (g) A. Rene, D. Hauchard, C. Lagrost and P. Hapiot, J. Phys. Chem. B, 2009, 113, 2826.
- 8 O. Ocon and P. Herrasti, J. Mater. Sci., 1991, 26, 6487.
- 9 (a) S. Golczak, A. Kanciurzewaks, M. Faheman, K. Langer and S. S. Langer, *Solid State Ionics*, 2008, **179**, 2234; (b) M. H. Pournaghi-Aazar and B. Habibi, *Electrochim. Acta*, 2007, **52**, 4222; (c) M. C. Li, C. A. Ma, B. Y. Liu and Z. M. Jim, *Electrochem. Commun.*, 2005, **7**, 209.
- 10 M. Shigeyasu, H. Murayama and H. Tanaka, *Chem. Phys. Lett.*, 2008, 463, 373.
- 11 Here note that, in Fig. 4B, Ag, wire was used as quasi-reference electrode to avoid any contamination of water to which $O_2^{-\bullet}$ is very sensitive chemically. The difference in the formal potentials of the $O_2/O_2^{-\bullet}$ couple in $[TMPA]^{H}N(Tf)_2]^-$ and $[MPP]^{H}N(Tf)_2]^-$ reflects the difference in the solvation energies of O_2 and/or $O_2^{-\bullet}$ in both ionic liquids.
- 12 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals* and Applications, John Wiley and Sons, inc., New York, 2nd edn, 2001.
- 13 T. D. T. Sawyer, Oxygen Chemistry, Oxford Univ. Press, New York, 1991.
- 14 (a) T. Ohsaka, Y. Tian, M. Shioda, S. Kasahara and T. Okajima, *Chem. Commun.*, 2002, 990; (b) Y. Tian, L. Mao, T. Okajima and T. Ohsaka, *Anal. Chem.*, 2002, 74, 2428; (c) Y. Tian, T. Ariga, N. Takashima, T. Okajima, L. Mao and T. Ohsaka, *Electrochem. Commun.*, 2004, 6, 609; (d) Y. Tian, L. Mao, T. Okajima and T. Ohsaka, *Anal. Chem.*, 2004, 76, 4162.
- 15 Reactive Oxygen Species in Biological Systems: An Interdisciplinary Approach, ed. D. L. Gilbert and C. A. Colton, Kluwer Academic/ Plenum Publishers, New York, 1999.