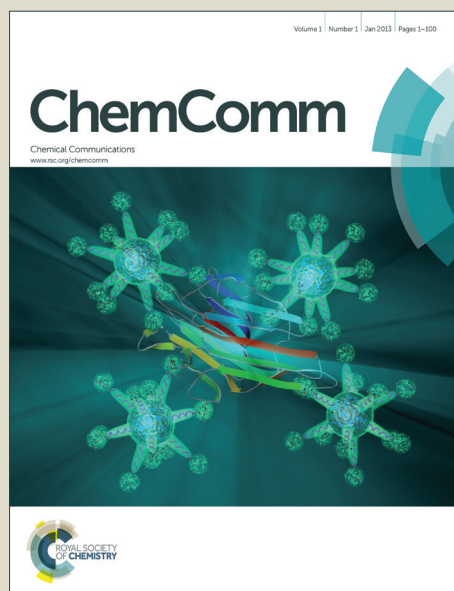


# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

## Catalysis at room temperature ionic liquid|water interface: H<sub>2</sub>O<sub>2</sub> generation

Justyna Jedraszko,<sup>a</sup> Wojciech Nogala,<sup>a</sup> Wojciech Adamiak,<sup>a</sup> Saustin Dongmo,<sup>b</sup> Gunther Wittstock,<sup>b</sup> Hubert H. Girault<sup>c</sup> and Marcin Opallo<sup>\*a</sup>

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

H<sub>2</sub>O<sub>2</sub> is produced at the interface between a room-temperature ionic liquid with decamethylferrocene as electron donor and an acidic aqueous solution. The electron donor can be regenerated electrochemically.

Room temperature ionic liquids (RTILs) are exploited for various chemical and industrial processes and are considered environmentally friendly in many cases.<sup>1,2,3</sup> They are also components of an increasing number of physicochemical systems including advanced materials.<sup>4,5,6</sup> Biphasic systems with RTIL|water interfaces as crucial constituent represent important examples in this respect. Extraction and liquid-liquid phase separation of RTIL and aqueous solution are intensively studied,<sup>7,8,9,10,11,12</sup> whereas the application of RTIL–water systems in synthesis has been limited so far.<sup>13,14,15,16</sup>

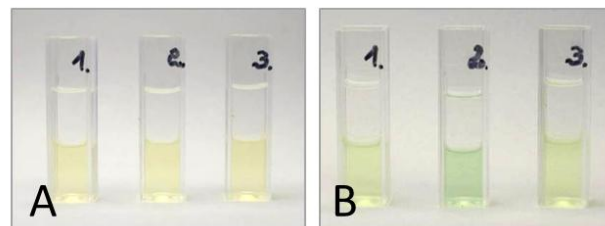
When the aqueous phase containing ionic species is in direct contact with a RTIL, the efficiency and pathway of interfacial processes involving charged reactants depends on the Galvani potential difference across the interface. The latter can be controlled externally by means of a potentiostat or by the composition and concentration of supporting electrolytes in the aqueous and RTIL phases. Recently, this aspect of ion transfer across RTIL|water interface has been studied.<sup>17,18,19</sup> Polarisation control of the liquid|liquid interface may provide favourable conditions for chemical reactions generating important fuels like hydrogen or hydrogen peroxide.<sup>20</sup> It has been shown that H<sub>2</sub>O<sub>2</sub> can be obtained from dissolved dioxygen at the interface between water and an organic solvent immiscible with water using a strong electron donor such as decamethylferrocene (DMFc) dissolved in the organic phase.<sup>21</sup> So far, these studies were restricted to interfaces formed by aqueous solutions of acids and salt solutions in nonaqueous polar solvents such as 1,2-dichloroethane<sup>21</sup>, 1,2-dichlorobenzene<sup>22</sup> or trifluorotoluene.<sup>23</sup>

Here, we demonstrate that a simple chemical compound, namely hydrogen peroxide, can be generated at a RTIL|water interface with a sufficiently strong electron donor in the RTIL phase. Indeed, when DMFc is dissolved in the hydrophobic RTILs i.e. 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide (C<sub>4</sub>mimN(Tf)<sub>2</sub>) or 1-decyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (C<sub>10</sub>mimN(Tf)<sub>2</sub>) and left in contact with aqueous perchloric acid, the color of the DMFc solution changes from yellow to green near the interface (Fig. 1, Figs. S1, S2 ESI†) indicating the oxidation of DMFc to the decamethylferrocenium (DMFc<sup>+</sup>) cation.<sup>21,23,24</sup> The colour change is more intensive for longer experiment (Fig. 1, Figs. S1C, S2A ESI†). This effect is not observed in low concentration of hydrated protons in the aqueous

phase (Fig. 1, Figs. S1,S2 ESI†). Upon addition of KI and starch to the aqueous phase after the reaction produces a violet coloration (Figs. S1D, S2B ESI†) due to the oxidation of I<sup>-</sup> to I<sub>3</sub><sup>-</sup> by H<sub>2</sub>O<sub>2</sub>.<sup>21</sup> Therefore, the interfacial reaction can be written as follows:



The solubility of dioxygen in C<sub>4</sub>mimN(Tf)<sub>2</sub> in equilibrium with air, calculated from Henry constant<sup>25,26</sup> is equal 0.42 mM, almost two times higher than in water. Therefore both phases are the sources of O<sub>2</sub>.

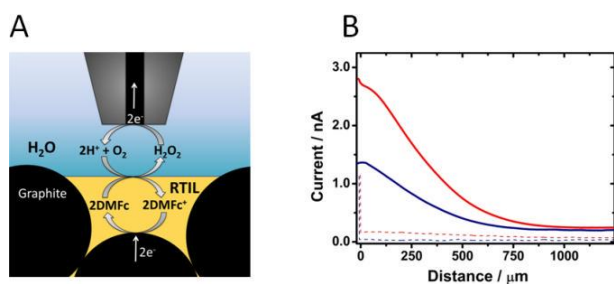


**Fig. 1** Results of shake flask experiments (details in ESI†). Cuvette 1, and 2 contain 0.1 M aqueous HClO<sub>4</sub> (upper phase) and 5 mM DMFc solution in C<sub>4</sub>mim N(Tf)<sub>2</sub> (bottom phase). Cuvette 3 contains 0.1 M aqueous NaClO<sub>4</sub> (upper phase) and 5 mM DMFc solution in C<sub>4</sub>mim N(Tf)<sub>2</sub> (bottom phase). Photographs were taken before (A) and after (B) 30 min of reaction. Cuvette 1 was not shaken, cuvettes 2 and 3 were shaken.

No significant effect of the alkyl chain length of the alkyylimidazolium cation was observed except when the flask was not shaken during the experiment. In this case the colour change from yellow to green is less clear (Fig S1 ESI†) and a colour gradient near the C<sub>10</sub>mim N(Tf)<sub>2</sub>|acidic aqueous solution interface is still visible after 24 h (Fig S1C ESI†). This is due to the slower diffusion of the DMFc<sup>+</sup> cation as compared to less viscous C<sub>4</sub>mim N(Tf)<sub>2</sub>.<sup>27</sup>

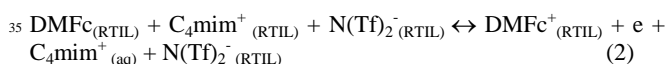
To provide further evidence of H<sub>2</sub>O<sub>2</sub> generation at RTIL|water interface, scanning electrochemical microscopy (SECM) experiments were performed. For this purpose and also to explore the possibility of electrochemical regeneration of the electron donor, a carbon paste electrode<sup>28</sup> (CPE) was prepared from DMFc solution in RTIL mixed with carbon microparticles (ESI†). The CPE was fixed as substrate electrodes at the bottom of the cell filled with aqueous 0.1 M HClO<sub>4</sub> (Fig. 2A). A Pt disk microelectrode (25 μm diameter) was applied as SECM probe - (ESI†) and was placed above the CPE surface. Then the probe was biased at 0.6 V vs. Hg|Hg<sub>2</sub>SO<sub>4</sub>|K<sub>2</sub>SO<sub>4</sub> and moved towards the

CPE surface at  $10 \mu\text{m s}^{-1}$  velocity. The recorded anodic current is expected to result from oxidation of  $\text{H}_2\text{O}_2$  generated at liquid-liquid interface.<sup>23,29,30</sup> Indeed the increase of the anodic current is seen when the tip-CPE distance decreases (Fig. 2B, and Fig S3 ESI†) and CPE is not biased. This is not the case, when DMFc is absent in RTIL, confirming its role as electron donor (reaction (1)). Larger anodic current was recorded when the CPE was biased at  $-0.85 \text{ V}$  vs.  $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4$  (Fig. 2, Fig S3 ESI†). In this situation  $\text{DMFc}^+$  produced during  $\text{H}_2\text{O}_2$  generation (reaction (1)) at the RTIL-water interface is electrochemically regenerated at the carbon particles (Fig. 2A). The magnitude of the current depends on the type of RTIL and is ca. two times higher for  $\text{C}_4\text{mim N(Tf)}_2$  than for  $\text{C}_{10}\text{mim N(Tf)}_2$  (Fig S3 ESI†). This is probably due to faster diffusion of  $\text{DMFc}/\text{DMFc}^+$  in the less viscous  $\text{C}_4\text{mim N(Tf)}_2$  as compared to  $\text{C}_{10}\text{mim N(Tf)}_2$ .



**Fig. 2** (A) The scheme of SECM experiment. (B) The approach curves to CPE prepared from 5 mM DMFc solution in  $\text{C}_4\text{mim N(Tf)}_2$  immersed in 0.1 M aqueous  $\text{HClO}_4$ . Probe potential: 0.6 V. CPE unbiased (blue solid), and CPE potential  $-0.85 \text{ V}$  (red solid). Dotted curves correspond to analogous experiments in the absence of DMFc in  $\text{C}_4\text{mim N(Tf)}_2$ .

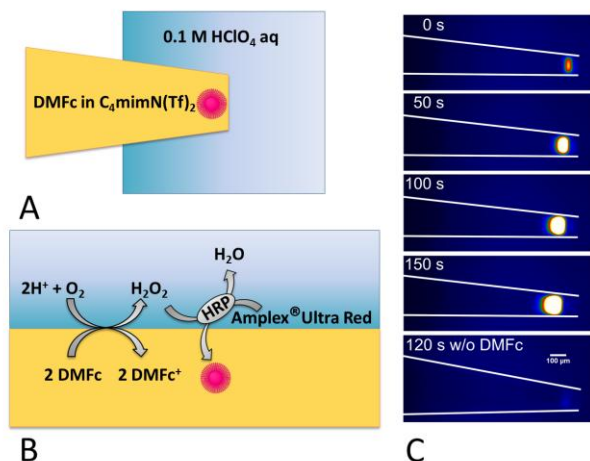
The stability of the voltammetric signal corresponding to DMFc reduction and reoxidation during continuous scanning (Fig. S4, ESI†) indicates that oxidised form of electron donor  $\text{DMFc}^+$  remains in the RTIL phase, where it can be continuously regenerated. The potential of voltammetric signal of  $\text{DMFc}/\text{DMFc}^+$  redox couple (Fig. S5 ESI†) is independent of the anion present in the aqueous phase pointing out that the cation of the RTIL is transferred across RTIL|water interface during the DMFc oxidation to maintain electroneutrality<sup>31,32</sup>.



The generation of  $\text{H}_2\text{O}_2$  at RTIL|water interface was also confirmed by an optical readout using the fluorogenic substrate<sup>33</sup> Amplex UltraRed®. This experiment was performed with a pipette (ca.  $100 \mu\text{m}$  diameter) with hydrophobised interior<sup>34</sup> filled with DMFc solution in RTIL. This pipette was immersed into the acidic aqueous solution containing horseradish peroxidase (HRP) and Amplex UltraRed® (Fig. 3A, ESI†). It was observed that in these conditions the liquid|liquid interface is fixed at the pipette orifice (Fig S6 ESI†).

Only in the presence of DMFc in RTIL and  $\text{O}_2$  in acidic aqueous solution of HRP and Amplex UltraRed®, a strong fluorescence appears near the pipette tip (Fig. 3C, Fig S7 ESI†). The fluorescence intensity increases with time. This is due to HRP catalysed oxidation of Amplex UltraRed® by  $\text{H}_2\text{O}_2$  (Fig. 3B). The oxidation product emits strong red fluorescence monitored by a fluorescence microscope.<sup>23</sup> Most of the light is emitted close to the pipette orifice within RTIL phase. This may be because of partial extraction of the fluorophore to the organic phase and the fact that fluorescence emission of the oxidised form of Amplex UltraRed®, remaining in acidic aqueous phase is

deteriorated due to its protonation. The size of the emitting zone is larger for experiment performed with the less viscous  $\text{C}_4\text{mim N(Tf)}_2$  (compare Fig. 3C and Fig S7 ESI†). Both fluorescence intensity and expansion rate of fluorescent zone towards the pipette bulk is larger than for the more viscous  $\text{C}_{10}\text{mim N(Tf)}_2$ . This is in accordance with results of flask and SECM experiments showing a larger  $\text{H}_2\text{O}_2$  flux with  $\text{C}_4\text{mim N(Tf)}_2$ . A slow (ca.  $0.5 \mu\text{m s}^{-1}$ ) movement of the RTIL|aqueous solution interface towards the pipette bulk is probably caused by hydrophilisation of the pipette interior by  $\text{H}_2\text{O}_2$  produced at the interface favouring wetting of the pipette inner wall by the aqueous solution.



**Fig. 3** (A) The scheme of  $\text{H}_2\text{O}_2$  detection system; (B) enlarged scheme detailing the reactions at RTIL|aqueous solution interface; (C) fluorescence micrographs of the area close to the pipette tip. The light intensity scale runs from blue to white. The pipette containing 5 mM DMFc (except lowest image) solution in  $\text{C}_4\text{mim N(Tf)}_2$  was immersed in  $0.1 \text{ mg ml}^{-1}$  HRP and  $30 \mu\text{M}$  Amplex UltraRed® in 0.1 M aqueous  $\text{HClO}_4$ . Time elapsed after pipette immersion in the aqueous phase is marked on every image. Scale bar:  $100 \mu\text{m}$ . The pipette contour is marked by white lines.

## Conclusions

In conclusion, we have shown that  $\text{O}_2$  can be reduced by an electron donor, here DMFc, dissolved in a room temperature ionic liquid to produce  $\text{H}_2\text{O}_2$ . This work demonstrates that simple fuels can be generated at the RTIL| $\text{H}_2\text{O}$  interface and that hydrophobic RTILs can be considered as a component of such a biphasic systems. It seems that the reduction power of  $\text{DMFc}^+$  in RTILs is large enough for the reaction to occur. We also demonstrated that the electron donor can be regenerated electrochemically if the RTIL phase is mixed with electronically conductive microparticles.

This work was supported by a grant from Switzerland through the Swiss Contribution to the enlarged European Union within the project "PSPB-035/2010: Electrocatalysis at Droplets". Justyna Jedraszko acknowledges support for her research stay in Oldenburg from Nanotechnology Biomaterials and Alternative Energy Source for ERA Integration Project [FP7-REGPOT-CT-2011-285949-NOBLESSE] from the European Union.

## Notes and references

- <sup>100</sup> *Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224, Warszawa, Poland. Fax: +48 22 343 3333; Tel: +48 22 343 3375; E-mail: mopallo@ichf.edu.pl*

<sup>b</sup>Department of Chemistry, Center of Interface Science, School of Mathematics and Science, Carl von Ossietzky University of Oldenburg, D-26111 Oldenburg, Germany. Fax: +49 441 798 3979; Tel: +49 441 798 3971; E-mail: gunther.wittstock@uni-oldenburg.de

<sup>c</sup>Switzerland LEPA, Ecole Polytechnique Federale de Lausanne, CH B2 401 (Bâtiment CH) Station 6 CH-1015 Lausanne, Switzerland. Fax: +41 21 693 3667; Tel: +41 21 693 3145; E-mail: hubert.girault@epfl.ch

34 Y. Shao and M.V. Mirkin, *Anal. Chem.*, 1998, **70**, 3155.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- 1 M. Smiglak, J.M. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D.R. MacFarlane, R.D. Rodgers, *Chem. Commun.*, 2014, **50**, 9228
- 2 N.V. Plechkova, K.R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
- 3 S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao, J. Wang, *Chem. Soc. Rev.*, 2014, **43**, 7838.
- 4 M.V. Fedorov, A.M. Kornyshev, *Chem. Rev.*, 2014, **114**, 2978.
- 5 M. Opallo, A. Lesniewski, *J. Electroanal. Chem.*, 2011, **656**, 2
- 6 P. Hapiot, C. Lagrost M.V. Fedorov, A.M. Kornyshev, *Chem. Rev.*, 2008, **108**, 2238.
- 7 X. Sun, H. Luo, S. Dai, *Chem. Rev.*, 2012, **112**, 2100.
- 8 X. Q. Sun, B. Peng, Y. Ji, J. Chen, D.Q Li, D. Q. *AIChE J.* 2009, **55**, 2062.
- 9 A. Ouadi, B. Gadenne, P. Hesemann, J.J. E. Moreau, I. Billard, I.; C. Gaillard,; S. Mekki, G. Moutiers, *Chem.-Eur. J.*, 2006, **12**, 3074.
- 10 L. C. Branco, J. G. Crespo and C. A. M. Alfonso, *Angew. Chem., Int. Ed.*, 2002, **41**, 2771.
- 11 J. Liu, G. Jiang, Y. Chi, Y. Cai, Q. Zhu and J. Hu, *Anal. Chem.*, 2003, **75**, 5870.
- 12 J.H. Zhang, H. Gao, Y.B. Li, Z.Q. Zhou, *J. Separation Sci.*, 2011, **34**, 3178.
- 13 V. Ladnak, N. Hofmann, N. Brausch, *Adv. Synth. & Cat.*, 2007, **349**, 719.
- 14 J.H. Zhang, Z. Liang, S.Q. Li, Y.B. Li, B. Peng, W.F. Zhou, H.X. Gao, *Talanta*, 2012, **98**, 154.
- 15 M. Petkovich, K.R. Seddon, *Chem. Soc. Rev.*, 2011, **40**, 1383.
- 16 S. Sunitha, S. Kanjilal, P.S. Reddy, R.B.N. Prasad, *Tetrahedron Lett.*, 2007, **48**, 6962.
- 17 Z. Samec, J. Langmaier, T Kakiuchi, *Pure Appl. Chem.*, 2009, **81**, 1473.
- 18 Y. Wang, T. Kakiuchi, Y. Yasui, M.V. Mirkin, *J. Am. Chem. Soc.*, 2010, **132**, 16945.
- 19 T. Kakiuchi, *Anal. Chem.*, 2007, **79**, 6442
- 20 M. A. Mendez, R. Partovi-Nia, I. Hatay, B. Su, P. Ge, A. Olaya, N. Younan, M. Hojeij and H. H. Girault, *Phys. Chem. Chem. Phys.*, 2010, **12**, 15163.
- 21 B. Su, R. NiaPartovi, F. Li, M. Hojeij, M. Prudent, C. Corminboeuf, Z. Samec, H.H. Girault, *Angew. Chem. Int. Ed.*, 2008, **47**, 4675.
- 22 P. Peljo, L. Murtomaki, T. Kallio, H.J. Xu, M. Meyer, C.P. Gros, J.M. Barbe, H. H. Girault, K. Laasonen, K. Kontturi, *J. Am. Chem. Soc.*, 2012, **134**, 5974.
- 23 W. Adamiak, J. Jedraszko, O. Krysiak, W. Nogala, J. Hidalgo-Acosta, H.H. Girault, M. Opallo, *J. Phys. Chem. C*, 2014, **118**, 23154.
- 24 B. Su, I. Hatay, P. Y. Ge, M. Mendez, C. Corminboeuf, Z. Samec, M. Ersoz, H.H. Girault *Chem. Commun.*, 2010, **46**, 2918.
- 25 J.L. Anthony, J.L. Anderson, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B*, 2005, **109**, 6369
- 26 K.R. Harris, M. Kanakubo, L.A. Woolf, *J. Chem. Eng. Data*, 2007, **52**, 1080.
- 27 S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, X. *J. Phys. Chem. Ref. Data*, 2006, **35**, 1475.
- 28 G. Shul, J. Sirieix-Plenet, L. Gaillon, M. Opallo, *Electrochem. Commun.*, 2006, **9**, 1111.
- 29 C.M. Sanchez-Sanchez, J. Rodriguez-Lopez, A.J. Bard, *Anal. Chem.*, 2008, **80**, 3254.
- 30 Y. Shen, M. Trauble, G. Wittstock, *Anal. Chem.*, 2008, **80**, 750.
- 31 S. Komorsky-Lovric, M. Lovric, F. Scholz, *J. Electroanal. Chem.*, 2001, **508**, 129.
- 32 J. Niedziolka, E. Rozniecka, J. Stafiej, J. Sirieix-Plenet, L. Gallion, D. Di Caprio, M. Opallo, *Chem. Comm.*, 2005, 2954.
- 33 M. Burchardt and G. Wittstock, *Langmuir*, 2013, **29**, 15090.