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Catalysis at the room temperature ionic liquid|water interface: H₂O₂ generation†

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H₂O₂ is produced at the interface between a room-temperature ionic liquid with decamethylferrocene as an 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 to be environmentally friendly in many cases.^{1–3} They are also components of an increasing number of physicochemical systems including advanced materials.^{4–6} Biphasic systems with RTIL|water interfaces as the crucial constituent represent important examples in this respect. Extraction and liquid–liquid phase separation of RTIL and aqueous solution are intensively studied,^{7–12} whereas the application of RTIL–water systems in synthesis has been limited so far.^{13–16}

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 using a potentiostat or by the composition and concentration of supporting electrolytes in the aqueous and RTIL phases. Recently, this aspect of ion transfer across the RTIL|water interface has been studied.^{17–19} Polarisation control of the liquid|liquid interface may provide favourable conditions for chemical reactions generating important fuels like hydrogen or hydrogen peroxide.²⁰ It has been shown that H₂O₂ 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.²¹ 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,²¹ 1,2-dichlorobenzene²² or trifluorotoluene.²³

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(trifluoro-methylsulfonyl)imide (C₄mimN(Tf)₂) or 1-decyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (C₁₀mimN(Tf)₂) and left in contact with aqueous perchloric acid, the color of the DMFc solution changes from yellow to green near the interface (Fig. 1, Fig. S1 and S2, ESI†) indicating the oxidation of DMFc to the decamethylferrocenium (DMFc⁺) cation.^{21,23,24} The colour change is more intensive for a longer experiment (Fig. 1, Fig. S1C and S2A, ESI†). This effect is not observed at low concentration of hydrated protons in the aqueous phase (Fig. 1, Fig. S1 and S2, ESI†). Addition of KI and starch to the aqueous phase after the reaction produces a violet coloration (Fig. S1D and S2B, ESI†) due

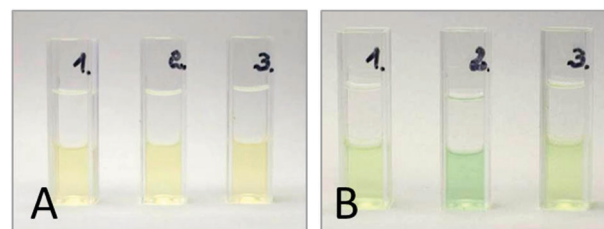


Fig. 1 Results of shake flask experiments (details in ESI†). Cuvettes 1 and 2 contain 0.1 M aqueous HClO₄ (upper phase) and 5 mM DMFc solution in C₄mim N(Tf)₂ (bottom phase). Cuvette 3 contains 0.1 M aqueous NaClO₄ (upper phase) and 5 mM DMFc solution in C₄mim N(Tf)₂ (bottom phase). Photographs were taken before (A) and after (B) 30 min of reaction. Cuvette 1 was not shaken, cuvettes 2 and 3 were shaken.

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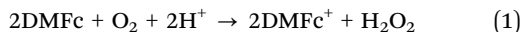
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to the oxidation of I^- to I_3^- by H_2O_2 .²¹ Therefore, the interfacial reaction can be written as follows:



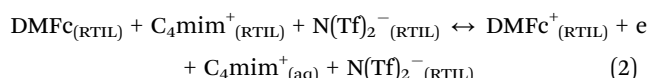
The solubility of dioxygen in $\text{C}_4\text{mimN}(\text{Tf})_2$ in equilibrium with air, calculated from the Henry constant^{25,26} is equal 0.42 mM, almost two times higher than in water. Therefore both phases are the sources of O_2 .

No significant effect of the alkyl chain length of the alkyl-imidazolium 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 $\text{C}_{10}\text{mim N}(\text{Tf})_2$ /acidic aqueous solution interface is still visible after 24 h (Fig. S1C, ESI†). This is due to the slower diffusion of the DMFc^+ cation as compared to less viscous $\text{C}_4\text{mim N}(\text{Tf})_2$.²⁷

To provide further evidence of H_2O_2 generation at the 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 electrode²⁸ (CPE) was prepared using a DMFc solution in RTIL mixed with carbon microparticles (ESI†). The CPE was fixed as the substrate electrode at the bottom of the cell filled with aqueous 0.1 M HClO_4 (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. $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4$ 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 H_2O_2 generated at the liquid|liquid interface.^{23,29,30} 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 an electron donor (reaction (1)). A larger anodic current was recorded when the CPE was biased at -0.85 V vs. $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4$ (Fig. 2 and Fig. S3, ESI†). In this situation DMFc^+ produced during H_2O_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 $\text{C}_4\text{mim N}(\text{Tf})_2$ than for $\text{C}_{10}\text{mim N}(\text{Tf})_2$ (Fig. S3, ESI†). This is

probably due to the faster diffusion of $\text{DMFc}/\text{DMFc}^+$ in the less viscous $\text{C}_4\text{mim N}(\text{Tf})_2$ as compared to $\text{C}_{10}\text{mim N}(\text{Tf})_2$.²⁷

The stability of the voltammetric signal corresponding to DMFc reduction and reoxidation during continuous scanning (Fig. S4, ESI†) indicates that the oxidised form of electron donor DMFc^+ remains in the RTIL phase, where it can be continuously regenerated. The potential of the voltammetric signal of the $\text{DMFc}/\text{DMFc}^+$ 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 the RTIL|water interface during the DMFc oxidation to maintain electroneutrality.^{31,32}



The generation of H_2O_2 at the RTIL|water interface was also confirmed by an optical readout using the fluorogenic substrate³³ Amplex UltraRed®. This experiment was performed using a pipette (*ca.* 100 μm diameter) with a hydrophobised interior³⁴ filled with a 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 under these conditions the liquid|liquid interface is fixed at the pipette orifice (Fig. S6, ESI†).

Only in the presence of DMFc in RTIL and O_2 in an acidic aqueous solution of HRP and Amplex UltraRed®, a strong fluorescence appears near the pipette tip (Fig. 3C and Fig. S7, ESI†). The fluorescence intensity increases with time. This is due to HRP catalysed oxidation of Amplex UltraRed® by H_2O_2 (Fig. 3B). The oxidation product emits strong red fluorescence which was monitored using a fluorescence microscope.²³ Most of the light is emitted close to the pipette orifice within the RTIL phase. This may be because of partial extraction of the fluorophore to the organic

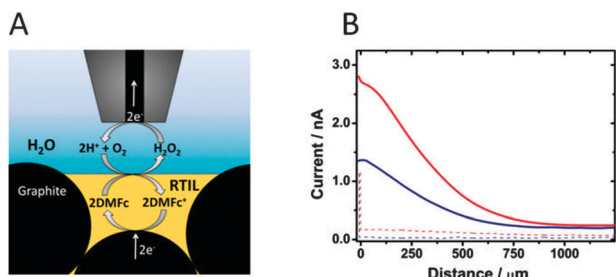


Fig. 2 (A) The scheme of the SECM experiment. (B) The approach curves to CPE prepared from 5 mM DMFc solution in $\text{C}_4\text{mim N}(\text{Tf})_2$ immersed in 0.1 M aqueous HClO_4 . Probe potential: 0.6 V. CPE unbiased (blue solid), and CPE potential -0.85 V (red solid). Dotted curves correspond to analogous experiments in the absence of DMFc in $\text{C}_4\text{mim N}(\text{Tf})_2$.

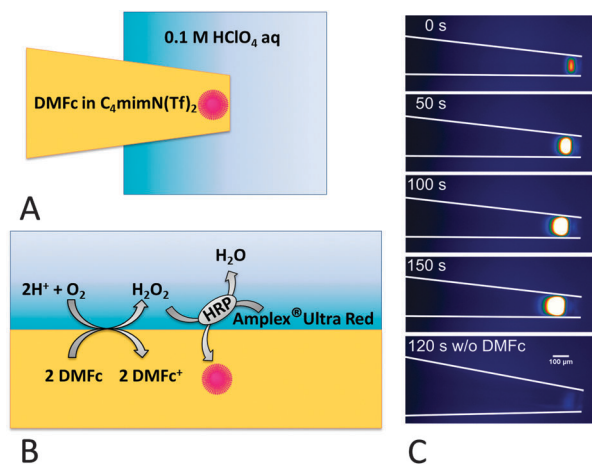


Fig. 3 (A) The scheme of the H_2O_2 detection system; (B) enlarged scheme detailing the reactions at the RTIL|aqueous solution interface; (C) fluorescence micrographs of the area close to the pipette tip. The light intensity scale runs from blue to white. The pipette containing 5 mM DMFc (except lowest image) solution in $\text{C}_4\text{mim N}(\text{Tf})_2$ was immersed in 0.1 mg mL^{-1} HRP and 30 μM Amplex UltraRed® in 0.1 M aqueous HClO_4 . Time elapsed after pipette immersion in the aqueous phase is marked on every image. Scale bar: 100 μm . The pipette contour is marked by white lines.



phase and the fact that fluorescence emission of the oxidised form of Amplex UltraRed[®], remaining in the acidic aqueous phase, is deteriorated due to its protonation. The size of the emitting zone is found to be larger in the case of the experiment performed with the less viscous C₄mim N(Tf)₂ (compare Fig. 3C and Fig. S7, ESI†). Both the fluorescence intensity and expansion rate of the fluorescent zone towards the pipette bulk is larger than that for the more viscous C₁₀mim N(Tf)₂. This is in accordance with results of flask and SECM experiments showing a larger H₂O₂ flux with C₄mim N(Tf)₂. A slow (*ca.* 0.5 μm s⁻¹) movement of the RTIL/aqueous solution interface towards the pipette bulk is probably caused by hydrophilization of the pipette interior by H₂O₂ produced at the interface favouring wetting of the pipette inner wall by the aqueous solution.

In conclusion, we have shown that O₂ can be reduced by an electron donor, here DMFc, dissolved in a room temperature ionic liquid to produce H₂O₂. This work demonstrates that simple fuels can be generated at the RTIL/H₂O interface and that hydrophobic RTILs can be considered as a component of such biphasic systems. It seems that the reduction power of 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.

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