Catalysis at the room temperature ionic liquid|water interface: H$_2$O$_2$ generation†

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H$_2$O$_2$ 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. They are also components of an increasing number of physicochemical systems including advanced materials. 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, whereas the application of RTIL–water systems in synthesis has been limited so far.

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.†

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 (C$_{4mim}$N(Tf)$_2$) or 1-decyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (C$_{10mim}$N(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†). This effect is not observed at low concentration of hydrated protons in the aqueous phase (Fig. 1, Fig. S1C and S2A, ESI†). The colour change is more intensive for a longer experiment (Fig. 1, Fig. S1 and S2, ESI†) indicating the oxidation of DMFc to the decamethylferrocenium (DMFc$^+$) cation. The colour change is more intensive for a longer experiment (Fig. 1, Fig. S1C and S2A, ESI†).

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Fig. 1 Results of shake flask experiments (details in ESI†). Cuvettes 1 and 2 contain 0.1 M aqueous HClO$_4$ (upper phase) and 5 mM DMFc solution in C$_{4mim}$N(Tf)$_2$ (bottom phase). Cuvette 3 contains 0.1 M aqueous NaClO$_4$ (upper phase) and 5 mM DMFc solution in C$_{4mim}$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.
to the oxidation of $I^{-}$ to $I_{3}^{-}$ by $H_{2}O_{2}$. Therefore, the interfacial reaction can be written as follows:

$$2DMFc + O_2 + 2H^+ \rightarrow 2DMFc^+ + H_2O_2 \quad (1)$$

The solubility of dioxygen in $C_{4}mimN(Tf)_{2}$ 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 $C_{10}mimN(Tf)_{2}$|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 $C_{4}mimN(Tf)_{2}$. $^{27}$

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 electrode$^{28}$ (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. $Hg|Hg_2SO_4|K_2SO_4$ (Fig. 2A). The CPE was biased at 0.85 V vs. $Hg|Hg_2SO_4|K_2SO_4$. The oxidation product emits strong red fluorescence which was monitored using a fluorescence microscope. $^{23}$ Moreover, the fluorescence emission spectrum of $H_2O_2$ (Fig. 2B) was compared to that of the $Amplex UltraRed$ (Fig. 3B). The excitation peak was at 560 nm and the emission maximum was at 588 nm.

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 $DMFc/DMFc^+$ 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.$^{31,32}$

$$DMFc_{(RTIL)} + C_{10}mim^+(RTIL) + N(Tf)_{2}^-(RTIL) \leftrightarrow DMFc^+(RTIL) + e^- + C_{10}mim^-(aq) + N(Tf)_{2}^-(RTIL) \quad (2)$$

The generation of $H_2O_2$ at the RTIL|water interface was also confirmed by an optical readout using the fluorogenic substrate$^{33}$ $Amplex UltraRed$. This experiment was performed using a pipette (ca. 100 µm diameter) with a hydrophobised interior$^{34}$ 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 from the organic phase.
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 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.

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 hydrophilization of the pipette interior by H₂O₂ produced at the interface favouring wetting of the pipette inner wall by the aqueous solution.

Notes and references