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Hydrogen Peroxide Production

H_2O_2 Generation by Decamethylferrocene at a Liquid | Liquid Interface**

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The reduction of molecular oxygen (O_2) is a technologically important research topic, particularly in the context of a hydrogen economy. The O_2 reduction reaction (ORR) can proceed by a direct four-electron reduction to produce water or a two-electron reduction to give hydrogen peroxide, with the former pathway being highly desirable for fuel cell applications. The development of fuel cells for the combined production of electricity and hydrogen peroxide (H_2O_2) has been proposed recently.[1] H_2O_2 is an industrially important product that is used on a scale of about three million metric tons per year worldwide. Its production is currently based almost exclusively on the anthraquinone hydrogenation and oxidation process.[2] Many alternative routes have also been developed, one of which is the electrochemical cathodic reduction of O_2[2–4] in the presence of molecular electrocatalysts such as metalloporphyrins[5] and anthraquinones.[6]

Herein we present an electrochemical method for producing H_2O_2 at a soft molecular interface rather than at a solid electrode. This approach relies on controlling the interfacial Galvani potential difference between two immiscible phases, in other words the polarization at the liquid | liquid interface, to allow the reduction of O_2 to H_2O_2. We chose the ORR by ferrocene derivatives, a reaction that has been known for many years, to illustrate this principle.[7,8] Specifically, we studied the reduction of O_2 by decamethylferrocene (DMFc) in 1,2-dichloroethane (DCE)[9] in contact with an aqueous solution of sulfuric acid. As described below, the polarization of the interface can be controlled by the distribution of different salts. The main advantage of the present biphasic system is that the ORR can be stopped at the formation of H_2O_2, which can be directly extracted into the aqueous phase during the reaction. H_2O_2 is a strong oxidant that readily oxidizes ferrocene derivatives, which usually leads to the absence of H_2O_2 in the final products of the homogeneous oxidation of ferrocene derivatives by O_2.[8,10]

When an interface is formed between an aqueous electrolyte containing hydrophilic ions and an organic solution containing lipophilic ions, this interface becomes polarizable. This leads to a polarization potential window, the width of which is defined by the transfer reactions of the electrolyte ions across the interface. The potential dependence for ion transfer across the interface follows a Nernst equation:

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi_i^{\mathrm{O}} + \frac{RT}{z_i F}\ln\left(\frac{a_i^{\mathrm{O}}}{a_i^{\mathrm{W}}}\right) \qquad (1)$$

where $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi_i^{\mathrm{O}}$ represents the standard transfer potential, in other words the Gibbs energy of transfer expressed in a voltage scale. For example, using Li_2SO_4 and bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB) as the hydrophilic and lipophilic electrolytes, respectively, in water and DCE results in a potential window from -0.5 to 0.4 V, as shown by the dotted line in Figure 1. This window is determined by the transfer of Li^+ and SO_4^{2-} ions from water to DCE at positive and negative potentials respectively, since $BTPPA^+$ and $TPFB^-$ ions are too lipophilic to transfer first. If an ion having a medium lipophilicity, for example decamethylferrocenium ($DMFc^+$) in DCE, is present it will transfer within the above potential window, and this transfer can be monitored by cyclic voltammetry, as shown by the full line in Figure 1.

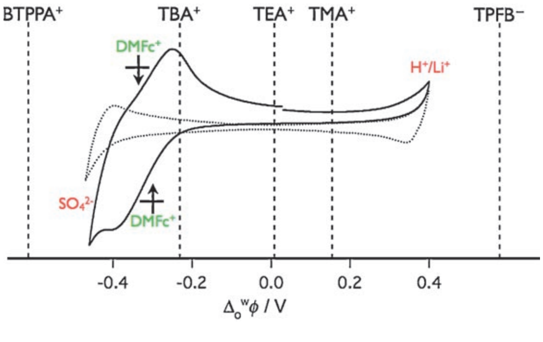

Figure 1. Polarization of a water | DCE interface by various common ions. The dotted and full lines show the potential window and transfer of $DMFc^+$ due to polarization by external voltages, respectively.

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Alternatively, the interface polarization can be controlled by the distribution of ions, for example by dissolving a hydrophilic and a lipophilic salt featuring a common ion (either cation or anion) in water and in the organic solution, respectively. In this way, the Galvani potential difference across the interface is given by the Nernst equation for the distribution of this common ion. As illustrated in Figure 1, the Galvani potential difference across the interface can be varied by employing different common ions. This method allows a chemical control of the Galvani potential difference without supplying an external voltage.

Figure 2a illustrates an equal-volume (2:2 mL), two-phase reaction under static conditions using $TPFB^-$ as the common ion. The Galvani potential difference across the water|DCE interface is fixed at potentials greater than 0.59 V. Although the standard ion-transfer potential of the $TPFB^-$ ion is unknown, it is known to be more positive than the Li^+ cation, whose standard transfer potential is 0.59 V.[11] A fresh solution of 5 mM DMFc in DCE is yellow. After 4 h in contact with 5 mM Li_2SO_4, the DCE phase turns green, thus indicating the oxidation of DMFc to $DMFc^+$, whereas the aqueous phase remains colorless. The two phases were then separated and the UV/Vis spectrum of the DCE solution measured. As can be seen in Figure 2b, this solution shows an absorption band due to the $DMFc^+$ cation ($\lambda_{max} = 779$ nm) whereas the absorption peak for DMFc ($\lambda_{max} = 425$ nm) has disappeared and has been replaced by a very large absorbance in the UV range. Formation of the $DMFc^+$ ion was also confirmed by the cyclic voltammetric response of a platinum microdisc electrode (diameter: 25 μm) in the organic phase, as illustrated in Figure 2c. After 4 h of reaction, a steady-state current wave, which consists of a larger cathodic steady-state current (I_{SC}) and a smaller anodic steady-state current (I_{SA}), is observed at the same potential as for DMFc in DCE. As DMFc and $DMFc^+$ ion have about the same diffusion coefficient, the percentage of DMFc oxidized can be calculated from the ratio I_{SC}/I_{SS} to be 74%, that is, a resulting concentration of 3.7 mM. Furthermore, the sum of the magnitudes of I_{SC} and I_{SA} is very close to that of freshly prepared 5 mM DMFc in DCE (I_{SS}), as can be seen from Figure 2c. This voltammetric result provides two indications. First, DMFc is oxidized to the $DMFc^+$ cation, which stays in the DCE phase. This coincides with the full line shown in Figure 1 in that the transfer of $DMFc^+$ ion from DCE to water only occurs at negative Galvani potential differences. Second, it indicates that both DMFc and the $DMFc^+$ cation are stable over the course of the two-phase reaction and that no decomposition takes place. This was also confirmed by mass spectrometric measurements as the mass spectra do not display any peaks for iron ions or a free cyclopentadienyl ring (see Figures S1.1–1.5 in the Supporting Information).

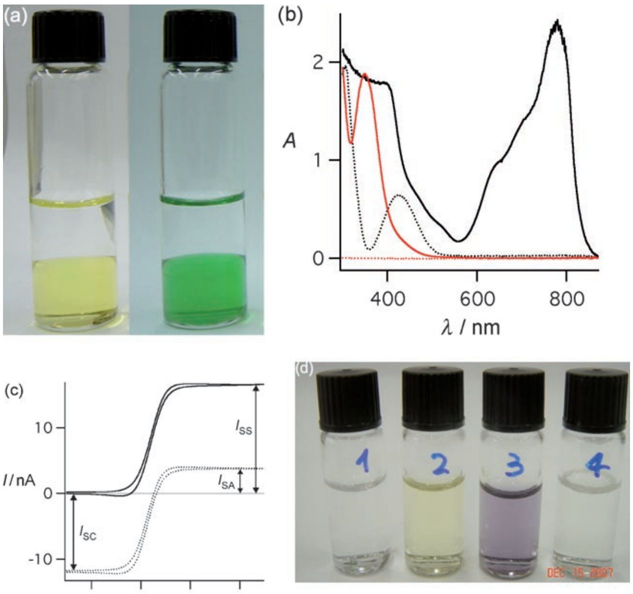

Figure 2. a) Two-phase reaction controlled by $TPFB^-$ ions at the beginning (left) and after 4 h (right). b) UV/Vis spectra of the DCE phase (full black) and the water phase before (dotted red) and after (full red) treatment with 0.1 M NaI after 4 h of the two-phase reaction; the spectrum of freshly prepared 5 mM DMFc (dotted black) is also included for comparison. c) CVs obtained with a 25-μm Pt microelectrode of freshly prepared 5 mM DMFc (full line) and the DCE phase after 4 h of the two-phase reaction (dotted line). d) Flask 1: water phase after 4 h of the two-phase reaction in (a); flask 2: flask 1 + 0.1 M NaI; flask 3: flask 2 + starch; flask 4: 5 mM LiTPFB + 5 mM H_2SO_4 + 0.1 M NaI + starch.

The isolated aqueous solution was titrated with NaI to detect the formation of H_2O_2. Thus, 29.98 mg (corresponding to 0.1 M, a large excess) of NaI was added to 2 mL of the solution and, as shown in Figure 2d, the solution changed from colorless to pale yellow (flask 2). Adding NaI to an aqueous solution containing 5 mM LiTPFB and 5 mM H_2SO_4 in a controlled titration did not lead to any color change within the present experimental time scale, thus confirming the presence of H_2O_2 in the aqueous solution. H_2O_2 is a strong oxidant that can oxidize I^- to I_3^-, which can be visualized by adding starch to give a red-brown color (flask 3). I_3^- can be also detected by UV/Vis spectroscopy, as shown in Figure 2b (sharp absorption band at $\lambda_{max} = 352$ nm). Taking a ε_{max} value of $2.76 \times 10^4\ M^{-1}cm^{-1}$,[12] the concentration of I_3^- can be calculated to be 0.070 ± 0.003 mM, which corresponds to that of H_2O_2 formed.

Thus far, it can be concluded that a two-electron reduction of O_2 to H_2O_2 by DMFc occurs in the two-phase reaction:

$$2\,DMFc + O_2 + 2\,H^+ \rightarrow 2\,DMFc^+ + H_2O_2 \qquad (2)$$

Two reaction mechanisms can be considered: either DMFc reduces O_2 heterogeneously to produce H_2O_2 in water, or DMFc reduces O_2 homogeneously in DCE to H_2O_2, which is then extracted into the aqueous phase. Fomin has proposed a mechanism for the reduction of O_2 by ferrocene derivatives in the presence of an acid based on the form of the experimental rate equation and on some computed thermodynamic data. This mechanism involves protonation of the ferrocene derivative followed by the reduction of O_2 by two protonated ferrocene derivatives to give H_2O_2.[10] A similar mechanism can be proposed in this biphasic system: the first step consists of the protonation of DMFc to form the $DMFc\text{-}H^+$ cation. Once $DMFc\text{-}H^+$ is formed in DCE, it can react homogeneously with O_2 in DCE to produce H_2O_2 and also heterogeneously with O_2 in water to produce H_2O_2 directly. However, these two reaction pathways are difficult to discriminate in this biphasic system.

Figure 3 illustrates the influence of the Galvani potential difference on this two-phase reaction when employing different common ions. The Galvani potential difference at the water | DCE interface is set at >0.59, 0.160, 0.019, -0.225, and <-0.53 V by the ions $TPFB^-$, TMA^+, TEA^+, TBA^+, and $BTPPA^+$,[11] respectively, as shown in Figure 1. It is clear from the color change in Figure 3, as well as the UV/Vis spectra (Figure S2.1 in the Supporting Information), that the reaction rate follows the order $TPFB^- > TMA^+ > TEA^+ > TBA^+ > BTPPA^+$. The reaction is very fast when $TPFB^-$ is used as the common ion. The color change of the DCE solution from yellow to green starts immediately at the interfacial region upon contact of the aqueous solution with the DCE solution, thereby indicating that the O_2 reduction by DMFc occurs at the interface. When TMA^+ and TEA^+ are used as the common ion, however, the green color of the DCE phase can only be seen after more than 10 h, and in the case of TBA^+ the DCE phase remains yellow after 102 h and only a weak absorption band at $\lambda_{max} = 779$ nm can be seen in the UV/Vis spectrum. In contrast, the DCE phase remains yellow after 102 h with $BTPPA^+$ as the common ion but the aqueous phase is slightly green. Absorption measurements show that the appearance of an absorption band at $\lambda_{max} = 779$ nm in the UV/Vis spectrum of the aqueous phase is concomitant with a decrease of the absorbance of DMFc in the DCE phase ($\lambda_{max} = 425$ nm); only a negligible absorbance is observed for the $DMFc^+$ ion in the DCE phase. This suggests that the $DMFc^+$ ion formed in the $BTPPA^+$-controlled experiment is transferred from DCE to water, which coincides with the illustration shown in Figure 1. Figure 3 clearly shows the influence of the Galvani potential difference on this biphasic reaction, which reflects the potential dependence of either the proton partition or the heterogeneous O_2 reduction, or both.

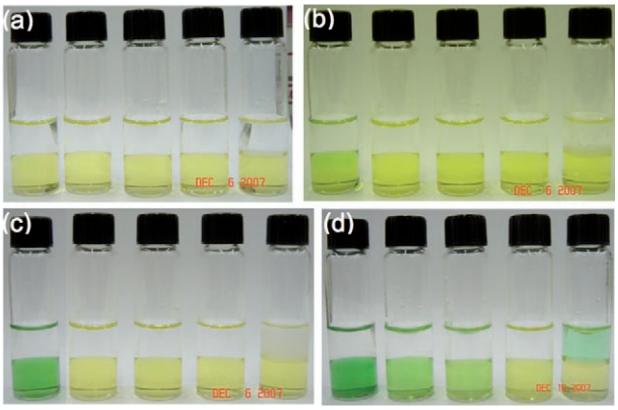

Figure 3. Two-phase reaction controlled by different common ions ($TPFB^-$, TMA^+, TEA^+, TBA^+, and $BTPPA^+$ from left to right; 5 mM in both phases) after a) 0 min, b) 62 min, c) 17.5 h, and d) 102 h.

A control experiment using 5 mM H_2SO_4 and 5 mM LiTPFB in water with 0.5 mM DMFc and 5 mM BTPPATPFB in DCE was carried out to elucidate the stoichiometry of the reaction. Figure 4, which displays the UV/Vis spectra of the two separated phases, shows that about 95 % of the DMFc is oxidized and 0.090 ± 0.004 mM H_2O_2 is detected in water. Considering that the stoichiometric ratio given by Equation (2) is 2:1, the above ratio of 5:1 indicates that either the partition coefficient for the extraction of H_2O_2 into water is less than unity or that part of the H_2O_2 formed is reduced by DMFc and/or decomposes. The former possibility was examined by performing a titration measurement of the H_2O_2 partition between water and DCE using NaI. This experiment reveals that partition of the H_2O_2 initially present in water into DCE is negligible (see Figure S3.1 in the Supporting Information). Reduction of H_2O_2 by DMFc and/or decomposition must therefore account for the low quantities observed. H_2O_2 is a strong oxidant in acidic solution and it can readily oxidize DMFc to $DMFc^+$.[10] H_2O_2 can also decompose in a reaction that is catalyzed by most transition metals and their compounds.[3]

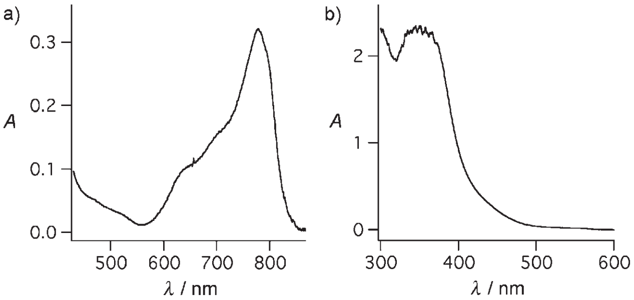

Figure 4. UV/Vis spectra of the DCE (a) and water phases (b) after an equal-volume two-phase reaction. Conditions: 5 mM H_2SO_4 and 5 mM LiTPFB in water and 0.5 mM DMFc and 5 mM BTPPATPFB in DCE; the two-phase system was first stirred for 10 min then left for 30 min for phase separation. The separated aqueous solution was treated with excess NaI.

In summary, we have shown that O_2 reduction by DMFc occurs in the absence of any noble metal catalysts at a polarized water | DCE interface. The rate of reaction is controlled by the Galvani potential difference across the interface, which has been determined chemically using various salts with a common ion. The resulting concentration of H_2O_2 has been measured and shows a yield of 20 % with respect to the concentration of the reducing agent (DMFc). This work illustrates how a biphasic system can be used to simultaneously supply electrons from nonaqueous donors and protons from an aqueous phase to drive interfacial reactions.

Experimental Section

All chemicals were used as received. DMFc (97 %) and H_2SO_4 (5 M) were purchased from Sigma–Aldrich. Li_2SO_4 (> 98.0 %), NaI (> 99.5 %), tetramethylammonium chloride (TMACl, > 98.0 %), tetraethylammonium chloride (TEACl, ≥ 98 %), tetraethylammonium perchlorate ($TEAClO_4$, ≥ 99 %), tetrabutylammonium chloride

(TBACl, ≥97%), tetrabutylammonium perchlorate ($TBAClO_4$, ≥99%), bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl, ≥98%), potassium tetrakis(4-chlorophenyl)borate (KTPBCl, ≥98%), DCE (≥99.8%), and starch (from potatoes) were obtained from Fluka. Lithium tetrakis(pentafluorophenyl)borate (LiTPFB) diethyl etherate was provided by Boulder Scientific Company. TMATPBCl and BTPPATPFB were prepared by metathesis of 1:1 mixtures of TMACl and KTPBCl and BTPPACl and LiTPFB, respectively, in a methanol/water mixture (2/1, v/v), followed by recrystallization from acetone. All the aqueous solutions were prepared with ultrapure water (18.2 MΩ cm).

The two-phase reactions were performed in a small flask under static conditions unless specified otherwise. A DCE solution (2 mL) containing 5 mM DMFc was added first, followed by the addition of 2 mL of an aqueous solution containing 5 mM H_2SO_4. The aqueous and organic common ion salt solutions were added at the same concentration (5 mM).

The microelectrode cyclic voltammetric measurements were performed with a CHI-900 potentiostat (CH Instrument, USA) with a platinum electrode (diameter: 25 μm), a platinum wire, and a silver wire as the working, counter, and reference electrodes, respectively. A scan rate of 0.02 $V s^{-1}$ was employed. The potential scale was referred to the Fc^+/Fc ($E_{Fc^+/Fc}$ vs. SHE = 0.64 V[13]) couple.

The UV/Vis spectra were measured with an Ocean Optical CHEM2000 spectrophotometer with a quartz cuvette (path length: 10 mm).

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