Angewandte Chemie

Hydrogen Evolution

DOI: 10.1002/anie.200901757

Hydrogen Evolution at Liquid–Liquid Interfaces**

*Imren Hatay, Bin Su, Fei Li, Raheleh Partovi-Nia, Heron Vrubel, Xile Hu, Mustafa Ersoz, and Hubert H. Girault**

Hydrogen (H_2) production by proton reduction is a technologically important research topic, in particular in the context of a hydrogen economy.[1] Most approaches are electrochemical (based on electrocatalytic cathodes) or photoelectrochemical, with the ultimate goal of using sunlight for water splitting.[2] Molecular electrocatalysis is an active research area, and the catalysts proposed are often transition-metal complexes, such as synthetic biomimetic hydrogenase compounds[3] or metallamacrocyclic complexes,[4,5] with the goal of H_2 evolution at low overpotentials. Hydrogen evolution in bulk solutions has also been observed, in particular with metallocene compounds and their derivatives.[6] Ferrocenophanes, for example, were found to be oxidized by tetrafluoroboric acid with concomitant hydrogen evolution in dichloromethane.[7] Similarly, cobaltocene phosphine complexes,[8] cobaltocene,[9] decamethylferrocene (DMFc),[6] permethyltungstenocene,[10] molybdocene,[11] and osmocene[12] have been shown to react with acids, which in most cases are organic, and thus the H_2 evolution yield was largely dependent on the acid strength.

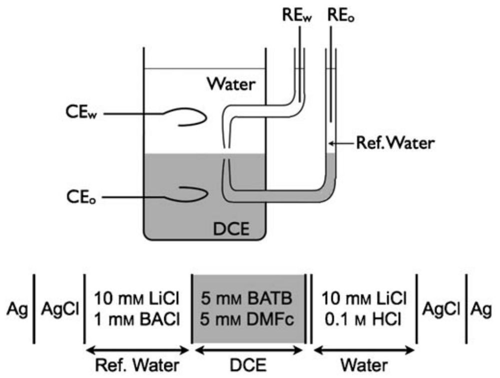


Figure 1. Illustration of the four-electrode cell configuration (top) and the electrochemical cell composition (bottom). RE = reference electrode, CE = counter electrode, BA^+ = bis(triphenylphosphoranylidene)ammonium, TB^- = tetrakis(pentafluorophenyl)borate, subscript o indicates organic phase, subscript w indicates water phase.

Herein, we present a heterogeneous hydrogen evolution reaction at a soft interface, formed between an aqueous acidic solution and an immiscible organic solvent, 1,2-dichloroethane (DCE), containing DMFc as an electron donor. Such an interface is usually referred to as an interface between two immiscible electrolyte solutions (ITIES), which can be polarized like the conventional electrode–electrolyte interface using a four-electrode potentiostat as shown in Figure 1. The extent of the interfacial polarization is defined by the transfer of supporting electrolyte ions, which follows the Nernst equation for ion partition [Eq. (1)]:[13]

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi = \Delta_{\mathrm{O}}^{\mathrm{W}}\phi_i^\circ + \frac{RT}{z_iF}\ln\left(\frac{a_i^{\mathrm{O}}}{a_i^{\mathrm{W}}}\right) \tag{1}$$

where $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi_i^\circ$ represents the standard ion transfer potential, that is, the Gibbs energy of transfer expressed in a voltage scale ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi_i^\circ = \Delta G_{\mathrm{tr},i}^{\circ,\mathrm{W}\to\mathrm{O}}/z_iF$). That is so say, we can apply a potential difference across a liquid–liquid interface and polarize it up to a point where one of the ions of the supporting electrolytes will transfer from one phase to another. For example, when using LiCl/HCl and bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) as the hydrophilic and lipophilic electrolytes in water and DCE, respectively (Figure 1), a polarization potential window from −0.2 to 0.3 V is obtained during cyclic voltammetry (Figure 2). This window is limited by the transfer of H^+ and Cl^- from water to DCE at positive and negative potentials (water vs. organic), respectively, as the Gibbs transfer energies of the very lipophilic BA^+ and TB^- are too high for them to be transferred within this potential range.

Upon addition of 5 mM DMFc to DCE, an irreversible positive current wave was observed at positive potentials (Figure 2), indicating the transfer of a positive charge from the aqueous to the organic phase. We have shown previously that under aerobic conditions a similar current wave precedes the production of H_2O_2 in DCE that transfers back to the aqueous phase.[14,15] In this case as well, under anaerobic

---

[*] I. Hatay, Dr. B. Su, Dr. F. Li, R. Partovi-Nia, Prof. H. H. Girault
Laboratoire d'Electrochimie Physique et Analytique
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Station 6, 1015 Lausanne (Switzerland)
Fax: (+41) 21-693-3667
E-mail: hubert.girault@epfl.ch

I. Hatay, Prof. M. Ersoz
Department of Chemistry, Selcuk University
42031 Konya (Turkey)

H. Vrubel, Prof. X. Hu
Laboratory of Inorganic Synthesis and Catalysis, EPFL, BCH 3305
1015 Lausanne (Switzerland)

[**] This work was supported by EPFL, the Swiss Natural Science Foundation (FNRS 200020-116588) and European Cost Action D36/007/06. I.H. and M.E. also gratefully acknowledge the Scientific and Technological Research Council of Turkey (TUBITAK) under the 2212-PhD Scholarship Program. We also thank Profs. Cleménce Corminboeuf and Christian Amatore for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901757.

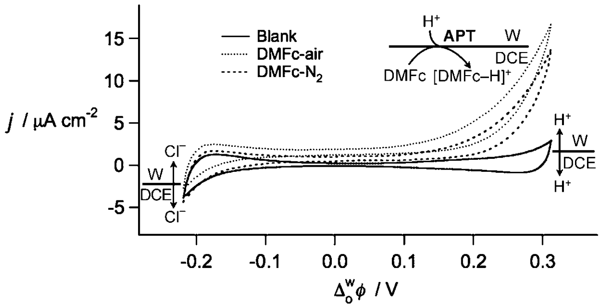


Figure 2. Cyclic voltammograms obtained with the electrochemical cell shown in Figure 1 in the absence of DMFc (——, aerobic) and in the presence of DMFc (•••••, aerobic; -----, anaerobic); scan rate 0.05 V s^{-1}. APT = assisted proton transfer.

conditions the onset potential of this wave becomes about 60 mV more negative per pH unit (see the Supporting Information, Figure S-1), thus indicating that the observed current is associated with an assisted proton transfer (APT) reaction by DMFc, which acts as a lipophilic base under both aerobic and anaerobic conditions. The corresponding pK_a value of DMFcH$^+$ in DCE is estimated to be around 6.6. Under aerobic conditions, the APT step is followed by reduction of oxygen by DMFc in DCE. To investigate a possible subsequent reaction in DCE in the anaerobic case, two-phase reactions were performed with the Galvani potential difference across the interface fixed at a value greater than 0.55 V by the distribution of a common ion (TB$^-$) using LiTB (5 mM) and HCl (100 mM) in water and BATB (5 mM) in DCE. With such a chemically controlled polarization of the interface, the protons are driven from water to DCE assisted by DMFc, and the water–DCE interface essentially functions as a proton pump.

Figure 3 shows the results of a two-phase reaction performed under anaerobic conditions. A fresh solution of DMFc in DCE appears yellow (Figure 3a) and displays an absorption band in the UV/Vis spectrum at $\lambda_{max} = 425$ nm (Figure 3b). After the two-phase reaction, the DCE phase turned very green, and a strong absorption band at $\lambda_{max} = 779$ nm was observed in its UV/Vis spectrum, which is the signature of DMFc$^+$.[14] Moreover, during stirring small gas bubbles were generated continuously at the water–DCE interface and moved up into the headspace above the liquids. A large gas bubble can be clearly seen in Figure 3a. The head gas above the liquids was then sampled and analyzed by gas chromatography (Figure 3c). Hydrogen generation from the two-phase reaction was confirmed by comparison of the chromatogram of the head gas with those of pure nitrogen and of mixtures of nitrogen and hydrogen (see the Supporting Information, Figure S-2). Furthermore, the amount of hydrogen gas dissolved in DCE was determined by amperometry using a platinum microelectrode. The anodic current for the oxidation of 5 mM DMFc in DCE with BATB before the addition of the aqueous phase has a steady-state current value of 18.4 nA (Figure 3d). After 4 h of two-phase reaction, we can observe a large cathodic wave and a double anodic wave. The first anodic wave ($I_{ss} = 2$–3 nA, indicated by the dashed line in Figure 3d) corresponds to the oxidation of unreacted DMFc, and the second one corresponds to the oxidation of H$_2$. Assuming a diffusion coefficient of H$_2$ in DCE of roughly 10^{-5} cm^2 s^{-1},[16] the concentration of H$_2$ in DCE is in the millimolar range. The magnitude of the cathodic wave suggests that it corresponds to the reduction of DMFc$^+$ formed during hydrogen evolution. In another two-phase reaction using an aqueous phase with an initial pH value of 2, the pH value increased to around 2.3 after reaction with the organic phase, thus showing that protons are consumed during the biphasic reaction.

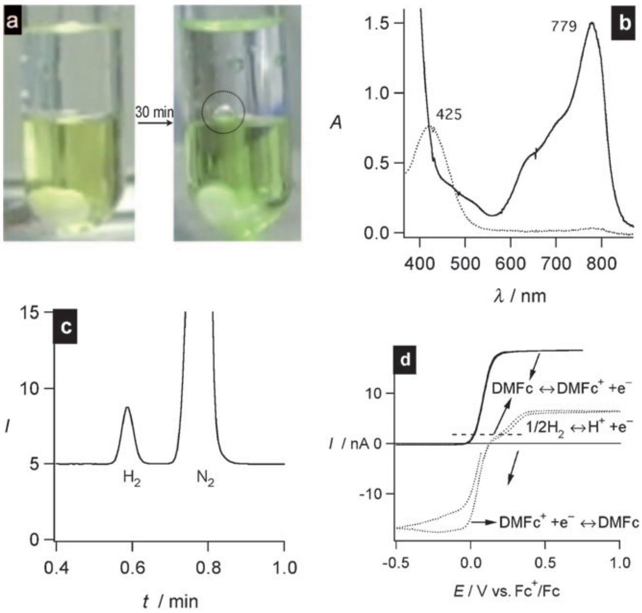
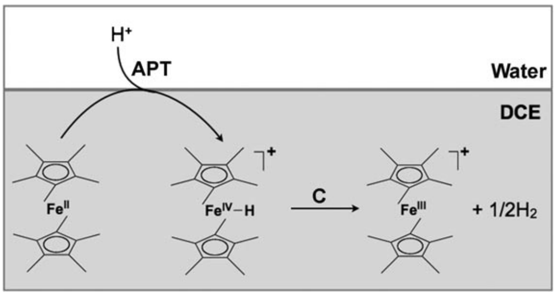


Figure 3. a) Photographs of the anaerobic two-phase reaction controlled by TB$^-$ at the beginning (left) and after 30 min (right). b) UV/Vis absorption spectra of DCE solution before reaction (•••••) and of DCE solution diluted twice after 4 h of anaerobic two-phase reaction (——). c) GC chromatograms of the head gas above the liquids (4 h reaction). d) Microelectrode voltammograms of the DCE phase after 4 h of two-phase reaction (•••••) and of a fresh DCE solution containing 5 mM DMFc under anaerobic condition (——).

It can therefore be undoubtedly concluded that proton reduction by DMFc occurs in the two-phase reaction, and the overall reaction can be written as in Equation (2):

$$\mathrm{DMFc}_{(\mathrm{DCE})} + \mathrm{H}^+_{(\mathrm{W})} \rightarrow \mathrm{DMFc}^+_{(\mathrm{DCE})} + \tfrac{1}{2}\,\mathrm{H}_{2(\mathrm{g})} \qquad (2)$$

The corresponding reaction scheme (Scheme 1) shows that the reaction proceeds basically in two steps. APT denotes the



Scheme 1. General reaction scheme of H$_2$ evolution by proton reduction with DMFc. Only protonation of Fe^{II} is shown.

assisted proton transfer by DMFc [Eq. (3)]:

$$\mathrm{DMFc_{(DCE)} + H^{+}{}_{(W)} \rightarrow DMFcH^{+}{}_{(DCE)}} \quad (3)$$

The subsequent reaction involving DMFcH$^+$ can be simply considered as a chemical step (C), which finally results in the production of DMFc$^+$ and H$_2$ [Eq. (4)]:

$$\mathrm{DMFcH^{+}{}_{(DCE)} \rightarrow DMFc^{+}{}_{(DCE)} + {}^{1}\!/\!_{2}\, H_{2(g)}} \quad (4)$$

Note that only the APT step gives rise to the positive current signal shown in Figure 2, while the subsequent H$_2$ evolution by DMFc occurs in the organic phase and does not involve any charge transfer across the interface. We know that the standard redox potentials of DMFc and H$^+$ in DCE are 0.07[17] and 0.55 V, respectively (see Table 1 and the Supporting Information). Therefore, proton reduction by DMFc in DCE is exergonic with a standard Gibbs energy of $\Delta G^\circ = -46.3\ \mathrm{kJ\,mol^{-1}}$. Of course, in the present biphasic system, the transfer of protons to the organic phase must be paid for energetically. The Gibbs energy of this process is pH-dependent and equal to 19.3 kJ mol^{-1} at pH 2 in the presence of DMFc as base.

Table 1: Standard redox potentials of DMFc oxidation in DCE and proton reduction in DCE and in water.

Reaction	E° vs. SHE [V]
$\mathrm{H^{+}{}_{(W)} + e^{-} \rightarrow {}^{1}\!/\!_{2}\, H_{2(g)}}$	0[13]
$\mathrm{H^{+}{}_{(DCE)} + e^{-} \rightarrow {}^{1}\!/\!_{2}\, H_{2(g)}}$	0.55[a]
$\mathrm{DMFc^{+}{}_{(DCE)} + e^{-} \rightarrow DMFc_{(DCE)}}$	0.07[17]

[a] Calculated as in the Supporting Information.

DMFc can be protonated either on the metal (Fe^{II}) or on the pentamethylcyclopentadienyl ring (Cp*) or on both through an agostic position bridging Cp* and Fe^{II},[18] thus hydrogen evolution in DCE may proceed along different pathways. In the case of protonation on the Cp* ring, the formed [Cp*Fe^{II}Cp*H]$^+$ ion can be reduced by DMFc to form [Cp*Fe^{I}Cp*H], which can be attacked by a proton to form DMFc$^+$ with concomitant evolution of H$_2$. The protonation on the Fe^{II} center corresponds to a metal hydride pathway that starts with [Cp*(Fe^{IV}H)Cp*]$^+$ and can proceed along several plausible routes. The first is a bimolecular reaction between two [Cp*(Fe^{IV}H)Cp*]$^+$ ions leading to H$_2$ elimination and DMFc$^+$ formation. The second is proton attack to produce H$_2$ and [Cp*Fe^{IV}Cp*]$^{2+}$, which is subsequently reduced by DMFc to DMFc$^+$. The third proceeds by reduction of [Cp*(Fe^{IV}H)Cp*]$^+$ by DMFc to yield [Cp*(Fe^{III}H)Cp*], which either follows a bimolecular disproportionation pathway or is subject to proton attack to finally yield H$_2$. Note also that in the present biphasic system, in which the aqueous proton concentration is much higher than that of DMFc and TB$^-$, the organic phase will contain both the conjugate acid DMFcH$^+$ and the strong acid H$^+$TB$^-$, thus favoring reaction pathways involving proton attack.

In conclusion, we report herein hydrogen evolution by direct proton reduction with DMFc at a soft interface between water and DCE. The reaction proceeds by assisted proton transfer by DMFc across the water–DCE interface with subsequent proton reduction in DCE. The interface essentially acts a proton pump, allowing hydrogen evolution by directly using the aqueous proton. Most previous investigations on hydrogen evolution by transition-metal complexes used an organic acid as the proton source; in those cases, H$_2$ evolution is largely dependent on the acid strength.[19]

Experimental Section

All chemicals were used as received. DMFc (99%) was purchased from ABCR. Bis(triphenylphosphoranylidene)ammonium chloride (BACl, ≥98%), tetraethylammonium chloride (TEACl, >98.0%), lithium chloride (≥99%), and 1,2-dichloroethane (DCE, >99.8%) were ordered from Fluka. Lithium tetrakis(pentafluorophenyl)borate (LiTB) diethyl etherate was provided by Sigma–Aldrich. Hydrochloric acid (HCl$_{(aq)}$, 37%) was bought from Merck. BATB was prepared by metathesis of a 1:1 mixture of BACl with LiTB in a methanol/water mixture (2:1 v/v) and subsequent recrystallization in acetone. All the aqueous solutions were prepared with ultrapure water (18.2 MΩ cm^{-1}). The two-phase reactions were performed in a small flask with stirring. A DCE solution (2 mL) containing 5 mM DMFc was added first, followed by the addition of 2 mL of an aqueous solution containing 100 mM HCl. The aqueous and organic common ion salts, LiTB and BATB, were added at the same concentration (5 mM). The electrochemical measurements at the water–DCE interface were performed on a PGSTAT 30 potentiostat (Eco-Chemie). The Galvanic potential difference across the interface ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi$) was estimated by assuming the formal ion transfer potential of TEA$^+$ to be 0.019 V.[20] The microelectrode voltammetric measurements were carried out on a Ivium Compact potentiostat with a platinum disk electrode (diameter 25 μm) and a silver wire as the working and quasi-reference electrodes, respectively. A scan rate of 0.02 V s^{-1} was employed, and the potential was converted to the ferrocene/ferrocenium scale.[17] The UV/Vis spectra were measured on an Ocean Optical CHEM2000 spectrophotometer. The gas chromatograms were obtained on a Perkin–Elmer gas chromatograph (Clarus 400) using a TCD detector and argon as the carrier gas. The experiments under anaerobic conditions were performed in a glovebox purged by nitrogen gas.

Received: April 1, 2009

Keywords: hydrogen evolution · proton transfer · liquid–liquid interfaces · metallocenes · reduction

---

[1] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729.
[2] A. J. Bard, M. A. Fox, *Acc. Chem. Res.* **1995**, *28*, 141.
[3] F. Gloaguen, T. B. Rauchfuss, *Chem. Soc. Rev.* **2009**, *38*, 100.
[4] V. Artero, M. Fontecave, *Coord. Chem. Rev.* **2005**, *249*, 1518.
[5] X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis, J. C. Peters, *Chem. Commun.* **2005**, 4723.
[6] U. Koelle, *New J. Chem.* **1992**, *16*, 157.
[7] U. T. Mueller-Westerhoff, A. Nazzal, *J. Am. Chem. Soc.* **1984**, *106*, 5381.
[8] U. Koelle, S. Paul, *Inorg. Chem.* **1986**, *25*, 2689.
[9] U. Koelle, P. P. Infelta, M. Graetzel, *Inorg. Chem.* **1988**, *27*, 879.
[10] M. Yoon, D. R. Tyler, *Chem. Commun.* **1997**, 639.
[11] G. T. Baxley, A. A. Avey, T. M. Aukett, D. R. Tyler, *Inorg. Chim. Acta* **2000**, *300–302*, 102.

[12] H. Kunkely, A. Vogler, *Angew. Chem. Int. Ed.* **2009**, *48*, 1685.

[13] H. H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, Lausanne, **2004**.

[14] B. Su, R. P. Nia, F. Li, M. Hojeij, M. Prudent, C. Corminboeuf, Z. Samec, H. H. Girault, *Angew. Chem.* **2008**, *120*, 4753; *Angew. Chem. Int. Ed.* **2008**, *47*, 4675.

[15] F. Li, B. Su, F. Cortes-Salazar, R. Partovi-Nia, H. H. Girault, *Electrochem. Commun.* **2009**, *11*, 473.

[16] J. V. Macpherson, P. R. Unwin, *Anal. Chem.* **1997**, *69*, 2063.

[17] N. Eugster, D. J. Fermin, H. H. Girault, *J. Phys. Chem. B* **2002**, *106*, 3428.

[18] M. L. McKee, *J. Am. Chem. Soc.* **1993**, *115*, 2818.

[19] X. Hu, B. S. Brunschwig, J. C. Peters, *J. Am. Chem. Soc.* **2007**, *129*, 8988.

[20] T. Wandlowski, V. Marecek, Z. Samec, *Electrochim. Acta* **1990**, *35*, 1173.