Supporting Information

© Wiley-VCH 2009

69451 Weinheim, Germany

Supporting Information

Hydrogen Evolution at Liquid-Liquid Interfaces**

Imren Hatay,^{a,b} Bin Su,^a Fei Li,^a Raheleh Partovi-Nia,^a H. Vrubel,^c Xile Hu,^c Mustafa Ersoz^b and Hubert H. Girault^{a*}

^a *Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland*

Fax: (+)41 21 6933667

E-mail: hubert.girault@epfl.ch

Homepage: <http://lepa.epfl.ch>

^b *Department of Chemistry, Selcuk University, 42031 Konya, Turkey*

^c *Laboratory of Inorganic Synthesis and Catalysis, Ecole Polytechnique Fédérale de Lausanne, BCH 3305, CH-1015 Lausanne, Switzerland*

1. pH dependence of assisted proton transfer by DMFc

Figure S-1. (a) pH dependence of assisted proton transfer by DMFc. The electrochemical cell shown in Scheme 1 was used except the pH was varied by HCl; (b) pH dependence of $\Delta_o^w \phi_{\text{DMFcH}^+}^{1/2}$ at $7 \mu\text{A cm}^{-2}$.

Figure S-1a illustrates the pH dependence of the current signal, which positively shifts with increasing the aqueous pH. Taking approximately the intersection point of the slope of the current and the current baseline as the formal potential, we can estimate the $\text{p}K_a$ of DMFcH^+ according to the following Nernst equation for assisted ion transfer at the liquid-liquid interface:^[s1]

$$\Delta_o^w \phi_{\text{DMFcH}^+}^{1/2} = \Delta_o^w \phi_{\text{H}^+}^{\circ'} + \frac{RT}{2F} \ln \left(\frac{D_{\text{DMFc}}}{D_{\text{DMFcH}^+}} \right) - \frac{2.303RT}{F} \text{p}K_a + \frac{2.303RT}{F} \text{pH}^w \quad (\text{s1.1})$$

where $\Delta_o^w \phi_{\text{H}^+}^{\circ'}$ is the formal transfer potential for the transfer of H^+ that is 0.55 V.^[s1]

D_{DMFc} and D_{DMFcH^+} represent the diffusion coefficients of DMFc and DMFcH^+ in DCE, and for simplicity they are assumed to be equal. pH^w is the aqueous pH. As shown in **Figure S-1b**, the relationship between $\Delta_o^w \phi_{\text{DMFcH}^+}^{1/2}$ and the pH (from 1 to 3) is found to be linear with a slope of 56.4 mV, which coincides with the assisted single proton transfer across the interface. From the intercept, the $\text{p}K_a$ value of DMFcH^+ was determined to be equal to 6.58.

2. Gas chromatograms under different conditions

Figure S-2. Gas chromatograms of: (a) the gas from the head space of the reaction flask shown in Figure 2a; (b) pure hydrogen + pure nitrogen; (c) the gas in the glovebox chamber purged with nitrogen; (d) pure nitrogen.

3. Absolute standard redox potential of proton reduction in DCE

The absolute standard redox potential of proton reduction in water is well known to be 0 as the classical reference in electrochemistry, namely the Standard Hydrogen Electrode

(SHE) with $\left[E_{\text{H}^+/\frac{1}{2}\text{H}_2}^\oplus \right]_{\text{SHE}}^{\text{w}} = 0 \text{ V}$, while that of in organic media is not. Since the proton

reduction by DMFc occurs in DCE in the present biphasic system (Scheme 1 in paper), the absolute standard redox potentials of proton reduction reaction in DCE with respect to SHE was estimated on the basis of thermodynamic principle. First, a general redox reaction is considered:

The standard redox potentials for the redox couple O/R in the aqueous phase and organic phase with respect to SHE are defined as:^[s2]

$$\left[E_{\text{O/R}}^\oplus \right]_{\text{SHE}}^{\text{w}} = \left[\left(\mu_{\text{O}}^{\oplus, \text{w}} - \mu_{\text{R}}^{\oplus, \text{w}} \right) - n \left(\mu_{\text{H}^+}^{\oplus, \text{w}} - \frac{1}{2} \mu_{\text{H}_2}^{\oplus} \right) \right] / nF \quad (\text{s3.2})$$

$$\left[E_{\text{O/R}}^\oplus \right]_{\text{SHE}}^{\text{o}} = \left[\left(\mu_{\text{O}}^{\oplus, \text{o}} - \mu_{\text{R}}^{\oplus, \text{o}} \right) - n \left(\mu_{\text{H}^+}^{\oplus, \text{w}} - \frac{1}{2} \mu_{\text{H}_2}^{\oplus} \right) \right] / nF \quad (\text{s3.3})$$

where $\mu_{\text{O}}^{\oplus, \text{s}}$ (s = o or w) and $\mu_{\text{R}}^{\oplus, \text{s}}$ (s = o or w) denote the standard chemical potentials of O and R, respectively. $\mu_{\text{H}^+}^{\oplus, \text{w}}$ and $\mu_{\text{H}_2}^{\oplus}$ represent the standard chemical potentials of proton in water and of hydrogen in gas phase. From eqs. s3.2 and s3.3 we can get:

$$\left[E_{\text{O/R}}^\oplus \right]_{\text{SHE}}^{\text{o}} = \left[E_{\text{O/R}}^\oplus \right]_{\text{SHE}}^{\text{w}} + \left[\left(\mu_{\text{O}}^{\oplus, \text{o}} - \mu_{\text{O}}^{\oplus, \text{w}} \right) - \left(\mu_{\text{R}}^{\oplus, \text{o}} - \mu_{\text{R}}^{\oplus, \text{w}} \right) \right] / nF \quad (\text{s3.4})$$

or

$$\left[E_{O/R}^{\oplus} \right]_{SHE}^o = \left[E_{O/R}^{\oplus} \right]_{SHE}^w + \left(\Delta G_{tr,O}^{\oplus,w \rightarrow o} - \Delta G_{tr,R}^{\oplus,w \rightarrow o} \right) / nF \quad (s3.5)$$

where $\Delta G_{tr,O}^{\oplus,w \rightarrow o}$ and $\Delta G_{tr,R}^{\oplus,w \rightarrow o}$ denote the standard Gibbs energy of transferring O and R from water to organic phase, respectively. Eq. s3.5 tells that the work needed to reduce O to R in an organic phase can be equivalent to the sum of the work needed to reduce O to R in water and the work needed to transfer both O and R from water to the organic phase. As reported previously, a series of redox potentials of ferrocene derivatives, such as

$\left[E_{DMFc^+/DMFc}^{\oplus} \right]_{SHE}^o = 0.07 \text{ V}$ in DCE, have been estimated with respect to that of ferrocene.^[s3]

Thus in the case of proton reduction reaction:

According to the definition, the standard redox potentials for the redox couple $H^+/\frac{1}{2}H_2$ in the aqueous ($s = w$) and organic ($s = o$) phase with respect to SHE are:

$$\left[E_{H^+/\frac{1}{2}H_2}^{\oplus} \right]_{SHE}^w = \left(\mu_{H^+}^{\oplus,w} - \frac{1}{2} \mu_{H_2}^{\oplus} \right) / F = 0 \quad (s3.7)$$

$$\left[E_{H^+/\frac{1}{2}H_2}^{\oplus} \right]_{SHE}^o = \left(\mu_{H^+}^{\oplus,o} - \frac{1}{2} \mu_{H_2}^{\oplus} \right) / F \quad (s3.8)$$

where $\mu_{H^+}^{\oplus,s}$ ($s = o$ or w) and $\mu_{H_2}^{\oplus}$ represent the standard chemical potential of proton in solutions and of hydrogen in the gas phase. Combining eqs. s3.7 and s3.8, one obtain:

$$\left[E_{H^+/\frac{1}{2}H_2}^{\oplus} \right]_{SHE}^o = \left(\mu_{H^+}^{\oplus,o} - \mu_{H^+}^{\oplus,w} \right) / F = \Delta G_{tr,H^+}^{\oplus,w \rightarrow o} / F \quad (s3.9)$$

where $\Delta G_{\text{tr}, \text{H}^+}^{\oplus, \text{w} \rightarrow \text{o}}$ is the standard Gibbs energy transfer of proton from water to the organic

phase, being 53 kJ mol^{-1} at the water/DCE interface.^[s1] Therefore, $\left[E_{\text{H}^+ / \frac{1}{2}\text{H}_2}^{\oplus} \right]_{\text{SHE}}^{\text{DCE}} = 0.55 \text{ V}$

in DCE can be estimated, which suggests that hydrogen evolution is easier in the organic medium. Of course, one needs to pay the transfer of proton to the organic medium.

Nevertheless, if a base that is able to lower the Gibbs energy of proton-transfer (that is a facilitated proton transfer) it is then advantageous.

References:

- [s1] A. Sabela, V. Marecek, Z. Samec, R. Fuoco, *Electrochim. Acta* **1992**, 37, 231.
- [s2] H. H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, **2004**.
- [s3] N. Eugster, D. J. Fermin, H. H. Girault, *J. Phys. Chem. B* **2002**, 106, 3428.