

Supplementary material

## **Heterogeneous versus Homogeneous electron transfer reactions at liquid-liquid interfaces: The wrong question?**

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## S1. Model for the heterogeneous and homogeneous electron transfer

The model of the electron transfer across the liquid-liquid interface was built in 1D utilizing COMSOL Multiphysics 4.4 and 5.2. Effects of migration were assumed negligible, so two “Transport of Diluted Species–physics” were utilized for diffusion of all the species, one in aqueous phase and the other in oil phase. The potential ramp was done using a triangle –function with 5 mV transition zone and two continuous derivatives. The general diffusion equation for a species  $i$  is:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = R_i \quad (\text{S1})$$

where  $c$  is concentration,  $t$  is time,  $D$  is the diffusion coefficient and  $R$  is the reaction term for the species  $i$ . The species in the model are Fc,  $\text{Fc}^+$ , (present in both phases) and  $[\text{Fe}(\text{CN})_6^{3-}]$  and  $[\text{Fe}(\text{CN})_6^{4-}]$  present only in the aqueous phase. Additionally, we have the potassium cation  $\text{K}^+$  in both phases. There are no reactions in the organic phase. Fc can partition into the aqueous phase, where it will react homogeneously by the following reaction:



This reaction is described as a bimolecular reaction

$$R_{\text{Fc}} = -R_{\text{Fc}^+} = -R_{[\text{Fe}(\text{CN})_6^{4-}]} = +R_{[\text{Fe}(\text{CN})_6^{3-}]} = \frac{\partial c_{\text{Fc}}}{\partial t} = -k_1 [\text{Fc}][\text{Fe}(\text{CN})_6^{3-}] + k_{-1} [\text{Fc}^+][\text{Fe}(\text{CN})_6^{4-}] \quad (\text{S3})$$

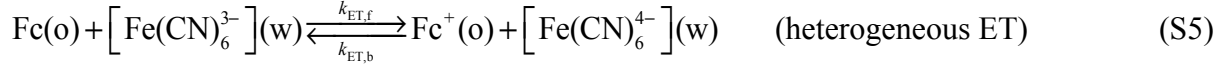
The equilibrium constant  $K_{\text{hom}} = k_1/k_{-1}$  can be evaluated when the redox potentials of both redox couples are known.  $[E_{\text{Fc}^+/\text{Fc}}^{0'}]_{\text{w}} = 0.381 \text{ V vs. SHE}$  [1] and the formal potential for ferro-ferricyanide  $[E_{\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}}^{0'}]_{\text{w}}$  was evaluated as  $0.467 \text{ V vs. SHE}$  in 100 mM LiCl [2] and as  $0.4445 \text{ V vs. SHE}$  in 10 mM  $\text{Li}_2\text{SO}_4$  in this work. The equilibrium constant for the reaction (S2) can be calculated as

$$K_{\text{hom}} = \exp\left(\frac{-\Delta G}{RT}\right) = \exp\left(\frac{F}{RT}\left(\left[E_{\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}}^{0'}\right]_{\text{w}} - \left[E_{\text{Fc}^+/\text{Fc}}^{0'}\right]_{\text{w}}\right)\right) = 30.1 \text{ (LiCl)}$$

or 12.4 (Li<sub>2</sub>SO<sub>4</sub>) (S4)

$k_1$  was varied to match the simulations and experimental data

The concentration boundary conditions were used at outer boundaries of the phases ( $c_i$  = bulk concentration). The boundary conditions at the liquid-liquid interface were set as inward fluxes ( $N_i$ ) according to the following reactions:



In the aqueous phase, the inward fluxes are

$$N_{\text{w, Fe(CN)}_6^{4-}} = -N_{\text{w, Fe(CN)}_6^{3-}} = k_{\text{ET,f}} [\text{Fc(o)}] [\text{Fe(CN)}_6^{3-}(\text{w})] - k_{\text{ET,b}} [\text{Fc}^+(\text{o})] [\text{Fe(CN)}_6^{4-}(\text{w})] \quad (\text{S9})$$

$$N_{\text{w, Fc}^+} = -k_{\text{IT,f}} [\text{Fc}^+(\text{w})] + k_{\text{IT,b}} [\text{Fc}^+(\text{o})] \quad (\text{S10})$$

$$N_{\text{w, K}^+} = -k_{\text{IT2,f}} [\text{K}^+(\text{w})] + k_{\text{IT2,b}} [\text{K}^+(\text{o})] \quad (\text{S11})$$

$$N_{\text{w, Fc}} = -k_{\text{p,f}} [\text{Fc(w)}] + k_{\text{p,b}} [\text{Fc(o)}] \quad (\text{S12})$$

In the TFT phase, the inward fluxes include both contributions from reactions (S5) and (S6) or (S7):

$$\begin{aligned} N_{\text{o, Fc}} = & -k_{\text{ET,f}} [\text{Fc(o)}] [\text{Fe(CN)}_6^{3-}(\text{w})] + k_{\text{ET,b}} [\text{Fc}^+(\text{o})] [\text{Fe(CN)}_6^{4-}(\text{w})] \\ & + k_{\text{p,f}} [\text{Fc(w)}] - k_{\text{p,b}} [\text{Fc(o)}] \end{aligned} \quad (\text{S13})$$

$$N_{o, \text{Fc}^+} = k_{\text{ET},f} [\text{Fc}(o)] [\text{Fe}(\text{CN})_6^{3-}(w)] - k_{\text{ET},b} [\text{Fc}^+(o)] [\text{Fe}(\text{CN})_6^{4-}(w)] + k_{\text{IT},f} [\text{Fc}^+(w)] - k_{\text{IT},b} [\text{Fc}^+(o)] \quad (\text{S14})$$

$$N_{o, \text{K}^+} = k_{\text{IT2},f} [\text{K}^+(w)] - k_{\text{IT2},b} [\text{M}^+(o)] \quad (\text{S15})$$

Here the bimolecular rate constants  $k_{\text{ET},f}$  and  $k_{\text{ET},b}$  and unimolecular rate constants for ion transfer reactions ( $k_{\text{IT}}$  and  $k_{\text{IT2}}$ ) are Butler-Volmer type rate constants depending on the Galvani potential difference  $\Delta_o^w \phi$  with the expressions:

$$\begin{aligned} k_{\text{ET},b} &= k_{\text{ET}}^0 \exp\left((\alpha - 1) f \left(\Delta_o^w \phi - \Delta_o^w \phi_{\text{ET}}^{0'}\right)\right) \\ k_{\text{ET},f} &= k_{\text{ET}}^0 \exp\left(\alpha f \left(\Delta_o^w \phi - \Delta_o^w \phi_{\text{ET}}^{0'}\right)\right) \\ k_{\text{IT},b} &= k_{\text{IT}}^0 \exp\left((\alpha - 1) f \left(\Delta_o^w \phi - \Delta_o^w \phi_{\text{Fc}^+}^{0'}\right)\right) \\ k_{\text{IT},f} &= k_{\text{IT}}^0 \exp\left(\alpha f \left(\Delta_o^w \phi - \Delta_o^w \phi_{\text{Fc}^+}^{0'}\right)\right) \\ k_{\text{IT2},b} &= k_{\text{IT2}}^0 \exp\left((\alpha - 1) f \left(\Delta_o^w \phi - \Delta_o^w \phi_{\text{K}^+}^{0'}\right)\right) \\ k_{\text{IT2},f} &= k_{\text{IT2}}^0 \exp\left(\alpha f \left(\Delta_o^w \phi - \Delta_o^w \phi_{\text{K}^+}^{0'}\right)\right) \end{aligned} \quad (\text{S16})$$

where  $f = F/RT$ . The  $\alpha$  for all the ion transfer reactions was set to 0.5, and was varied between 0 and 1 for electron transfer reactions. The unimolecular standard rate constants for ion transfer ( $k_{\text{IT}}^0$  and  $k_{\text{IT2}}^0$ ) were set to  $0.1 \text{ cm} \cdot \text{s}^{-1}$ , as the ion transfer across the liquid-liquid interface is fast and reversible. Similar values for normal ion transfer reactions have been reported in the literature, [3], and the bimolecular standard rate coefficient for the ET reaction  $k_{\text{ET}}^0$  was varied in the simulations. The kinetics for partition of neutral ferrocene were employed by calculating the partition coefficient of Fc,  $K_p$ , setting  $k_{p,b}$  as  $0.1 \text{ cm} \cdot \text{s}^{-1}$  and calculating the forward rate constant  $k_{p,f} = K_p k_{p,b}$ . Partition coefficient of Fc between TFT and water was calculated from the thermodynamic cycle as described by Fermin and Lahtinen [4]. Standard potential of a redox couple in organic solvent can be expressed with the help as the redox potential in water and the Gibbs energies of transfer of reduced and oxidized species from water to oil:

$$\left[ E_{\text{ox/red}}^{0'} \right]_o = \left[ E_{\text{ox/red}}^{0'} \right]_w + \frac{\Delta G_{\text{ox}}^{0,w \rightarrow o} - \Delta G_{\text{red}}^{0,w \rightarrow o}}{F} \quad (\text{S17})$$

Hence, the redox potential of Fc in TFT can be expressed as

$$\left[ E_{\text{Fc}^+/ \text{Fc}}^{0'} \right]_o = \left[ E_{\text{Fc}^+/ \text{Fc}}^{0'} \right]_w + \Delta_o^w \phi_{\text{Fc}^+}^{0'} - \frac{\Delta G_{\text{Fc}}^{0,w \rightarrow o}}{F} \quad (\text{S18})$$

This equation can be used to calculate the transfer energy and also partition coefficient of Fc from water to TFT (standard redox potentials of Fc in water ( $\left[ E_{\text{Fc}^+/ \text{Fc}}^{0'} \right]_w = 0.381 \text{ V vs. SHE}$  [1]) and TFT ( $\left[ E_{\text{Fc}^+/ \text{Fc}}^{0'} \right]_o = 0.736 \text{ V vs. SHE}$  as obtained in this work) are known, and  $\Delta_o^w \phi_{\text{Fc}^+}^{0'}$  was taken as the half-wave potential of  $\Delta_o^w \phi_{1/2, \text{Fc}^+} = 0.115 \text{ V}$  [2]) as

$$K_{p, \text{Fc}} = \exp\left(-\frac{\Delta G_{\text{Fc}}^{0,w \rightarrow o}}{RT}\right) = 13373 \quad (\text{S19})$$

The standard electron transfer potential was evaluated by

$$\Delta_o^w \phi_{\text{ET}}^{0'} = \left[ E_{\text{Fc}^+/ \text{Fc}}^{0'} \right]_o - \left[ E_{\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}}^{0'} \right]_w \quad (\text{S20})$$

## S2. Model for the NP catalyzed interfacial electron transfer

Another approach was used to consider the metal particle as a bipolar electrode in between the two phases. In this case, the model was constructed with two “Transport of Diluted Species–physics” and “Electric Currents–physics” to account for the current through the bipolar electrode. For simplicity, only electron transfer was considered (Reaction S5). Now, the oxidation of Fc was considered to take place at the oil side of AuNP, and reduction of Fe(III) in the aqueous phase.





Now, the inward fluxes at the aqueous and oil side are

$$N_{\text{w, Fe}(\text{CN})_6^{4-}} = -N_{\text{w, Fe}(\text{CN})_6^{3-}} = k_{\text{w,ox}} \left[ \text{Fe}(\text{CN})_6^{4-} (\text{w}) \right] - k_{\text{w,red}} \left[ \text{Fe}(\text{CN})_6^{3-} (\text{w}) \right] \quad (\text{S23})$$

$$N_{\text{o, Fe}} = -N_{\text{o, Fe}^+} = -k_{\text{o,ox}} \left[ \text{Fe}(\text{o}) \right] + k_{\text{o,red}} \left[ \text{Fe}^+ (\text{o}) \right] \quad (\text{S24})$$

where the rate constants for oxidation and reduction are expressed as

$$\begin{aligned} k_{\text{w,red}} &= k_{\text{aq}}^0 \exp \left( (\alpha - 1) f \left( E_{\text{NP}} - \left[ E_{\text{FeCN}_6^{3-}/\text{FeCN}_6^{4-}}^{0'} \right]_{\text{w}} - \Delta_o^{\text{w}} \phi \right) \right) \\ k_{\text{w,ox}} &= k_{\text{aq}}^0 \exp \left( \alpha f \left( E_{\text{NP}} - \left[ E_{\text{FeCN}_6^{3-}/\text{FeCN}_6^{4-}}^{0'} \right]_{\text{w}} - \Delta_o^{\text{w}} \phi \right) \right) \\ k_{\text{o,red}} &= k_{\text{o}}^0 \exp \left( (\alpha - 1) f \left( E_{\text{NP}} - \left[ E_{\text{Fe}^+/\text{Fe}}^{0'} \right]_{\text{o}} \right) \right) \\ k_{\text{o,ox}} &= k_{\text{o}}^0 \exp \left( \alpha f \left( E_{\text{NP}} - \left[ E_{\text{Fe}^+/\text{Fe}}^{0'} \right]_{\text{o}} \right) \right) \end{aligned} \quad (\text{S25})$$

Note that in Eq. (S23) the direction of flux is reversed, as in reactions (S21-22) the electrons are flowing from oil to metal to aqueous phase, and current is flowing the opposite way (oxidative current is positive as defined by IUPAC). The effect of the Galvani potential difference included in the exponents of the rate constants of the aqueous phase.  $k_{\text{w}}^0$  was set as  $0.04 \text{ cm s}^{-1}$  [5], and all values of  $\alpha$  were set to 0.5.  $k_{\text{o}}^0$  was varied to obtain satisfactory correspondence with the experimental CVs.

The governing equations of the ‘‘Electric Currents –physics’’ in the metal phase are:

$$\mathbf{J} = \sigma \mathbf{E} = -\sigma \nabla E_{\text{NP}} \quad (\text{S26})$$

where  $\mathbf{J}$  and  $\mathbf{E}$  are current density and electric field (both are vector variables),  $\sigma$  is conductivity and  $E_{\text{NP}}$  is the nanoparticle potential. This equation is Ohm’s law for the current and the potential. The boundary conditions were set utilizing the inward current density:

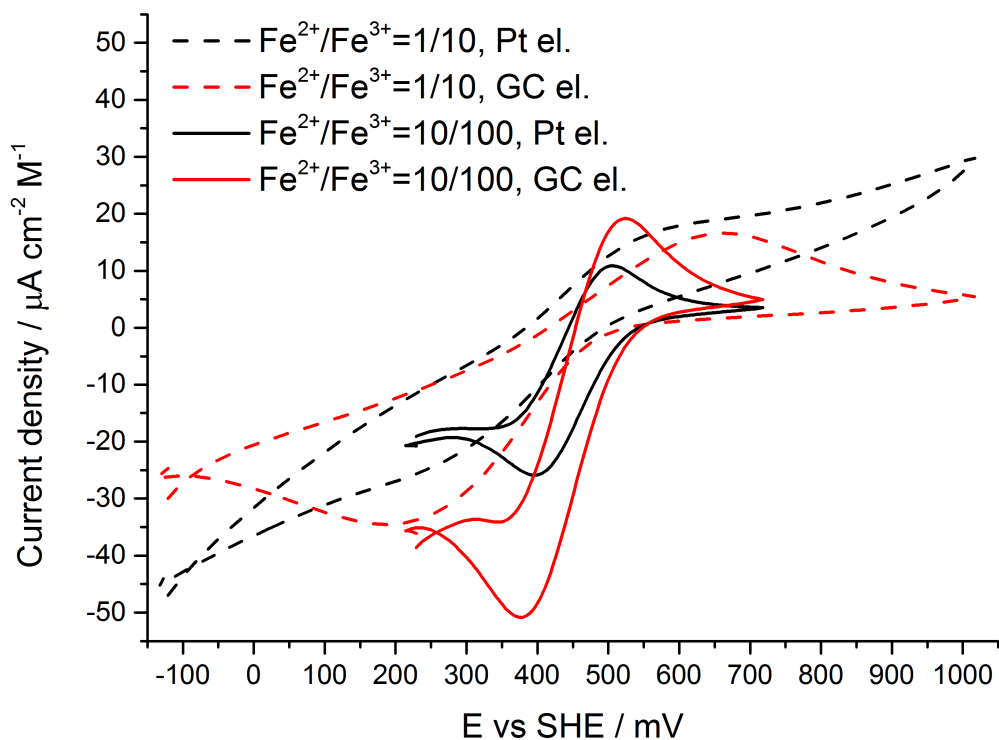
$$J_{\text{w}} = FN_{\text{w, Fe}(\text{CN})_6^{4-}} \quad (\text{S27})$$

$$J_o = -FN_{o, \text{Fc}} \quad (\text{S28})$$

When solving the system, the NP potential  $E_{\text{NP}}$  is floating so that both  $J_w$  and  $J_o$  have the same magnitude. In this case, simulations were performed in conditions where aqueous redox couple was always in hundred-fold excess. Hence the Fermi level of the NP was fixed by the ferro-ferricyanide redox couple ( $E_{\text{NP}} \approx \left[ E_{\text{FeCN}_6^{3-}/\text{FeCN}_6^{4-}}^{0'} \right] + \phi_w$ ), and the over potential was mostly on the oil side. For example, the over-potential with the Fe(II)/Fe(III) ratio of 1/10 in the aqueous phase was only 0.4 mV at the positive potential limit of the scan.

### S3. Cyclic voltammetry of ferro/ferricyanide couple

Figure S-1 shows the concentration normalized CVs obtained with Pt and Gc disk electrodes, showing decreased reversibility for 1/10 mM  $\text{Fe}^{2+}/\text{Fe}^{3+}$  concentration in 10 mM  $\text{Li}_2\text{SO}_4$  electrolyte.

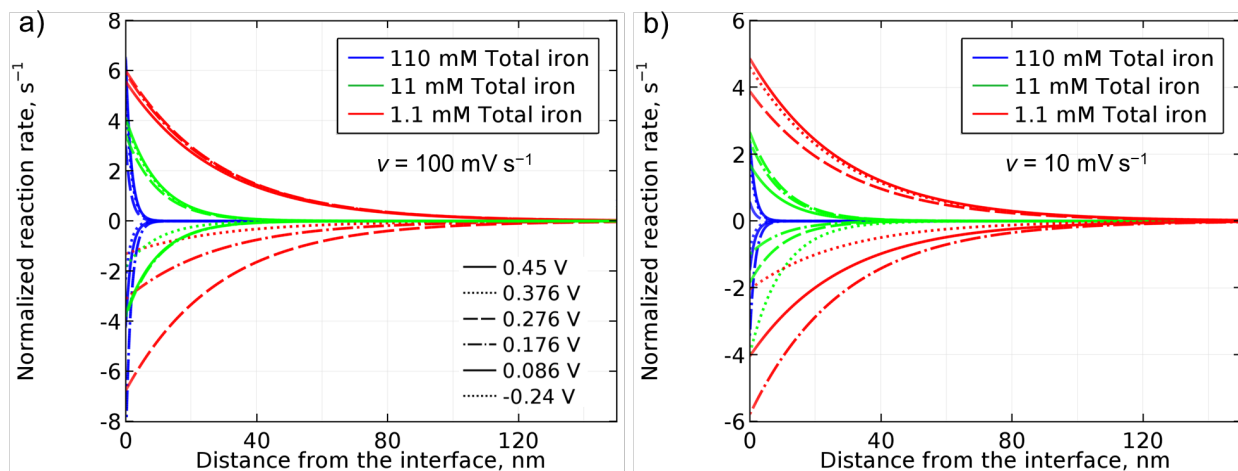


**Figure S-1. CVs of the ferro/ferricyanide couple obtained with Pt and Gc disk electrodes.** The current density was normalized by the total iron concentration, 10 mM  $\text{Li}_2\text{SO}_4$  electrolyte, scan rate  $10 \text{ mV} \cdot \text{s}^{-1}$ .

#### S4. Reaction layer thickness in the pre-partitioning mechanisms

Figure S-2 shows the reaction rate of oxidation of Fc (  $R_{\text{Fc}^+} = k_1[\text{Fc}][\text{Fe}(\text{CN})_6^{3-}] - k_{-1}[\text{Fc}^+][\text{Fe}(\text{CN})_6^{4-}]$  from Eq. S3, oxidation reaction shown as positive) in the aqueous side of the interface, normalized by the initial concentration of total iron in the aqueous phase, as a function of distance from the liquid-liquid interface, for different amount of total iron at the scan rates of 100 (S-2a) and  $10 \text{ mV} \cdot \text{s}^{-1}$  (S-2b) at different Galvani potential differences. The results shown that the reaction layer thickness increases from 10 to 100 nm with decreasing initial total iron concentration in the aqueous phase.





**Figure S-2. Reaction layer thicknesses with different ferro/ferricyanide concentrations.** The normalized homogeneous reaction rate in the aqueous phase as a function of distance from the interface, scan rate  $100 \text{ mV} \cdot \text{s}^{-1}$  (a) and  $10 \text{ mV} \cdot \text{s}^{-1}$ . Fe(II)/Fe(III) ratio of 1:10. Simulations done as in Figure 3 a-c).

### Supplementary References

- [1] S. Daniele, M.A. Baldo, C. Bragato, A steady-state voltammetric investigation on the oxidation of ferrocene in ethanol–water mixtures, *Electrochem. Commun.* 1 (1999) 37–41. doi:10.1016/S1388-2481(98)00011-3.
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