

## A Novel Micro-hole Electrode Used to Investigate Electron Transfer Reactions at ITIES

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**Abstract:** A novel micro-hole electrode was fabricated to investigate the electron transfer reaction at the interface between two immiscible electrolyte solutions (ITIES). The electron transfer reaction between ferro/ferricyanide in aqueous phase (W) and ferrocene in 1, 2-dichloroethane (O) phase was studied as a test experiment. The results showed that the diffusion coefficient obtained from the micro-hole electrode was consistent with that obtained at macro-interface. Due to its simplicity and the very small IR drop it will be a useful tool for the study of ITIES systems.

**Keywords:** Micro-hole electrode, electron transfer, ITIES.

The charge transfer phenomena at ITIES are very important theoretically and practically in many fields, such as electrochemical sensors, phase transfer catalysis, solar energy conversion, pharmacokinetics *etc.*. Similar to the utility of ultramicroelectrode (UME) in solid/liquid electrochemistry, adopting micro-ITIES would minimize the problems caused by the charging current and ohmic drop. The micropipette and the micro-hole supported ITIES have been adopted by several research groups since 1986<sup>1</sup>. In 1995 V. J. Cunnane *et al.* reported a micro-ITIES in a microcavity created by chemical dissolution of a glass-encapsulated silver microwire<sup>2</sup>. This was used to investigate ion transfer at ITIES. But no further reports can be obtained since then. Here we reported a novel micro-hole electrode used in study electron transfer reaction at ITIES.

Fabrication of the micro-hole electrode: A 1 cm-long clean gold or platinum thread was sealed in a 5 cm-long neat borosilicate glass tube. The electrode was checked carefully with a 40× microscope to ensure that there were no bubbles in the tip part. The electrode tip was polished until the mirror surface was formed. After it was washed with acetone and water, the electrode was immersed into the 10% silanizing agent WD-10 (Chemical Factory of Wuhan University)/ethanol solution for 10 minutes. Then the electrode was taken out and aired. The silanizing operation was repeated for several times and the electrode surface would be well silanized. The tip of the silanizing electrode was dipped into aqua regia and heated to form the micro-hole until the depth was a little longer than the radius. Thus an inner hydrophilic and outer hydrophobic micro-hole electrode was fabricated. Before experiment the micro-hole electrode was sonicated in aqueous solution and then immersed in organic solution to

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form the micro-ITIES. The experiments showed that the WD-10 was either stable in aqua regia or possessed a good restore function. **Figure 1** shows the configuration of the micro-ITIES supported by the micro-hole electrode introduced above. The tetrabutylammonium tetrphenylborate (TBATPB) was used as supporting electrolyte in 1, 2-dichloroethane (DCE). The electrolyte of the aqueous solution in the reference electrode was tetrabutylammonium chloride (TBACl). The concentrations of TBACl in reference solution and TBATPB in DCE solution were the same for establishing the Donan equilibrium between the two phases.

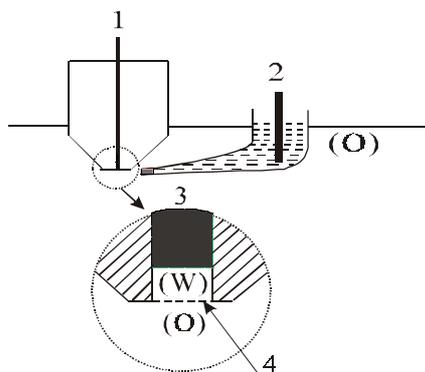
Three cells were designed as follows:

**Cell 1:** Ag | AgCl | 10 mmol/L TBACl (W) | 10 mmol/L TBATPB + 1 mmol/L Ferrocene (DCE) |  $\delta$  | 1.5 mol/L K<sub>2</sub>SO<sub>4</sub> (W) | Au;

**Cell 2:** Ag | AgCl | 10 mmol/L TBACl(W) | 10 mmol/L TBATPB (DCE) |  $\delta$  | 0.1 mol /L K<sub>3</sub>Fe(CN)<sub>6</sub> + 0.02 mol/L K<sub>4</sub>Fe(CN)<sub>6</sub> + 1.5 mol /L K<sub>2</sub>SO<sub>4</sub> (W) | Au;

**Cell 3:** Ag | AgCl | 10 mmol/L TBACl (W) | 10 mmol/L TBATPB + 1 mmol/L Ferrocene (DCE) |  $\delta$  | 0.1 mol/L K<sub>3</sub>Fe(CN)<sub>6</sub> + 0.02 mol/L K<sub>4</sub>Fe(CN)<sub>6</sub> + 1.5 mol/L K<sub>2</sub>SO<sub>4</sub> (W) | Au;  $\delta$  is the micro-ITIES studied.

**Figure 1** Configuration of the electrochemical cell



1. micro-hole electrode; 2. Ag/AgCl reference electrode; 3. Au microwire; 4. micro-ITIES constructed by the micro-hole.

Both **Cell 1** and **Cell 2** (**Figure 2**) were in ideal polarizing state. Only the charging current of the double layer capacitance but not faradic current was observed. Above results showed that no electron transfer reaction would occur if there were no electroactive reactants either in aqueous phase or in organic phase. Curve 3 is the steady-state polarizing curve of **Cell 3**. Obviously the faradic current was observed and the curves for the forward and backward scan were basically identical. The following reaction would occur in such a case:

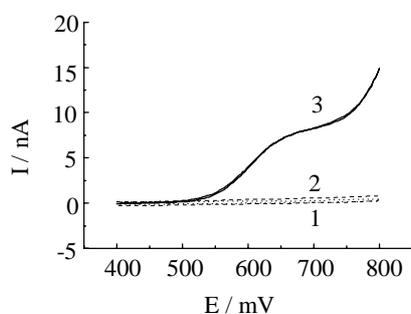


In the system of **Cell 3**, the concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub> and K<sub>4</sub>Fe(CN)<sub>6</sub> in aqueous solution are very much higher than that of ferrocene in DCE solution, and both

exchange current densities ( $i^0$ ) of the two redoxes are very high, so the rate-limiting step must be the diffusion of ferrocene in DCE solution. In this case, the electrochemical response of the system will be just like to that of a metal microdisc electrode/electrolyte interface. Thus, the limiting diffusion current can be calculated by using the formula as follows:

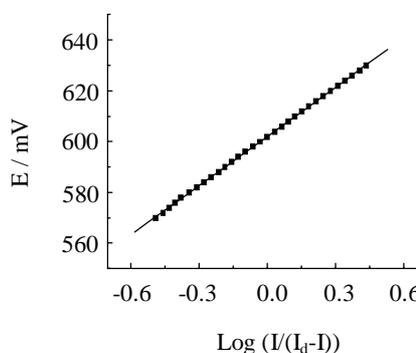
$$I_d = 4nFDC^0r \quad (2)$$

**Figure 2** Voltammograms of Cell 1, Cell 2 and Cell 3



Curve 1, Curve 2 for Cell 1 and Cell 2, scan rate: 10 mV/s; Curve3 for Cell 3, scan rate: 1 mV/s.

**Figure 3** The semi-logarithmic plot of E and  $\log ((I_d-I)/I)$  with the slope of 64 mV/decade



In the equation (2),  $I_d$  is the limiting diffusion current,  $n$  is the reactive electron number,  $F$  is the Faraday constant,  $D$  is the diffusion coefficient,  $C^0$  is the bulk concentration of ferrocene,  $r$  is the radius of the micro-hole. So the average diffusion coefficient of  $Fc/Fc^+$  could be obtained as  $7.2 \times 10^{-6} \text{ cm}^2/\text{s}$ . The semi-logarithmic plot of  $E$  and  $\log [(I_d-I)/I]$  was linear with the slope of 64 mV/decade as showed in **Figure 3**. It appeared that the reaction was a reversible single electron transfer process.

**Figure 4** depicts the voltammograms of **Cell 3** at different scan rates. As described above, we can quote the equation for microdisk electrode proposed by K. Aoki *et al.*<sup>3</sup> to derive the diffusion coefficient of  $Fc/Fc^+$ :

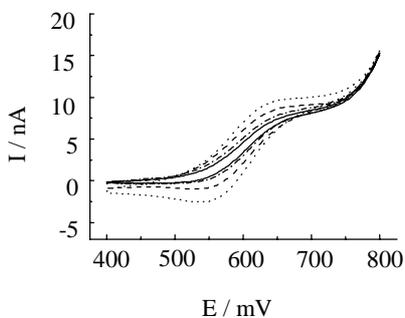
$$NF (E_{m/2}-E^0)/RT = -0.694 \tan^{-1} (0.85 P) \quad (3)$$

In the equation (3),  $E_{m/2}$  is the potential of half maximum current obtained from the voltammograms,  $E^0$  is the equilibrium potential of the studied redox,  $R$  is the gas constant,  $T$  is the absolute temperature,  $n$  and  $F$  are the same as above.  $P$  is a parameter defined as follows:

$$P^2 = nFr^2v/RTD \quad (4)$$

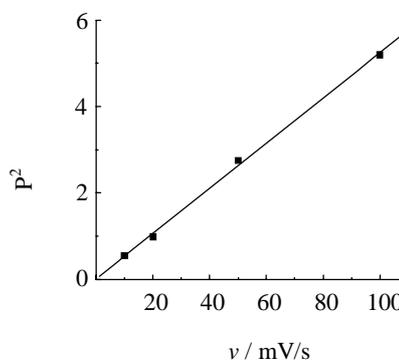
In the equation (4),  $\nu$  is the scanning rate. According to Curve 3 in **Figure 2**,  $E^0 = (E_{1/4} + E_{3/4})/2 = 606\text{mV}$ .  $E_{1/4}$  and  $E_{3/4}$  are the potentials at  $1/4I_d$  and  $3/4I_d$ . The plot of  $P^2$  and  $\nu$  was linear as showed in **Figure 5**. According to the slope we could calculate the average diffusion coefficient of  $\text{Fc}/\text{Fc}^+$  was  $6.8 \times 10^{-6} \text{ cm}^2/\text{s}$ . The average diffusion coefficient of  $\text{Fc}/\text{Fc}^+$  derived from the both experimental methods were in accordance with the literature value obtained at macro-ITIES<sup>4</sup>.

**Figure 4** Cyclic voltammograms of Cell3



Scan rates: 10, 20, 50, 100 mV/s.

**Figure 5** The linear relationship between the parameter  $P^2$  and sweep rates  $\nu$



The further investigation of this special micro-hole based micro-ITIES and its application to indirect organic electro-synthesis are in progress and will be reported elsewhere.

## References

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