



Influence of supporting electrolytes on the electron transfer and ion transfer coupling processes at a liquid/liquid interface



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ABSTRACT

In this work, the reduction and oxidation capacities of organic supporting electrolytes for ferricenium (Fc⁺) and ferrocene (Fc) were investigated by micro and nano hybrid electrodes in this work. The Fc⁺ can be produced in situ at the carbon electrode and collected simultaneously at the liquid/liquid (L/L) interface. The experiments were based on the generation/collection (G/C) technique and the redox capability of the supporting electrolytes was defined by the collection efficiency. Five common employed supporting electrolytes in the organic phase (TBADCC, TBATPB, TBATPBCl, TBATPBF and TBATPBF₅) were discussed and the experimental results indicated that the reduction power of these supporting electrolytes was weakened successively. The oxidation ability of cations of some supporting electrolytes (TPAsTPBF₅, TBATPBF₅ and BTPPATPBF₅) were also tested using the same methodology, showing that TBA⁺ and BTPPA⁺ have little influence on this system in comparison with oxidation of Fc to Fc⁺ by TPAs⁺. Besides, the different concentration of supporting electrolyte versus Fc was also studied to further prove the redox effect of supporting electrolytes on Fc⁺.

1. Introduction

The electron transfer (ET) and ion transfer (IT) coupling processes at a liquid/liquid (L/L) interface have attracted much attention in the past few decades since it is significantly related to mimicking the function of biological membranes, understanding the mechanism of phase-transfer catalysis and studying proton-coupled electron transfer (PCET) reactions [1–7]. For the system between Fe(CN)₆³⁻ in the aqueous phase (W) and ferrocene (Fc) in 1,2-dichloroethane (DCE), although there have been a large number of studies about this ET-IT coupling system, there are still some debates regarding of its mechanisms [8–13]. For example, it is essential to understand the redox property of the supporting electrolyte to avoid unwanted reactions in the system. Previously, Quinn et al. [14] compared the redox potentials of anions of supporting electrolyte, that is, TPB⁻, TPBCl⁻ and TPBF₅⁻ with Fc, and proposed that ferricenium (Fc⁺) would decompose to Fc by the TPB⁻ or TPBCl⁻, but this reduction in the presence of TPBF₅⁻ was almost impossible because of the great difference in redox potentials. Beside, Hanzlík et al. [15] have reported that there is a possibility that the oxidation of Fc with the supporting electrolyte cation of TPAs⁺. However, there has not been thoroughly studied of this matter.

Electrochemical generation/collection (G/C) techniques have been widely used in time-of-flight measurements [16], rotating ring-disk electrode [17] and scanning electrochemical microscopy (SECM)

[18,19]. They are also useful tools for studying the mechanisms and kinetics of IT-IT and IT-ET coupling reactions at L/L interfaces. A novel G/C technique for the study of ionic reactions based on dual micro-pipettes was first introduced by Shao et al. [20]. And using this method, Chen et al. [21] investigated IT-ET coupling reactions and distinguished IT-IT coupling processes occurring simultaneously at a L/L interface. Meng et al. [22] further studied the transfer behavior of protonated pyridine at the L/L interface and discussed the dependence of collection efficiency upon potential and pH.

Carbon-filled micro and nanopipette electrodes can be produced by the pyrolysis decomposition. It was first proposed by Ewing and coworkers to produce carbon-ring microelectrodes [23]. In recent report, Takahashi et al. [24] fabricated nano-sized electrodes by depositing pyrolytic carbon into glass pipettes used in nanoscale imaging of living cell in SECM. By using dual pipettes, Zhang et al. [9] blocked off one channel while carbon was deposited inside another one to fabricate hybrid electrode to study the ET-IT coupling processes. In the same way, Unwin's group [25] produced nanoscale dual function pH-scanning ion conductance microscopy (SICM) probes. And by depositing carbon into both barrels, dual carbon electrodes as probes for SECM were also fabricated [26].

In this work, we utilize the micro and nano hybrid electrodes made by the quartz dual pipettes as the working electrode. One of the barrels is a carbon electrode, and another is an empty channel, which can

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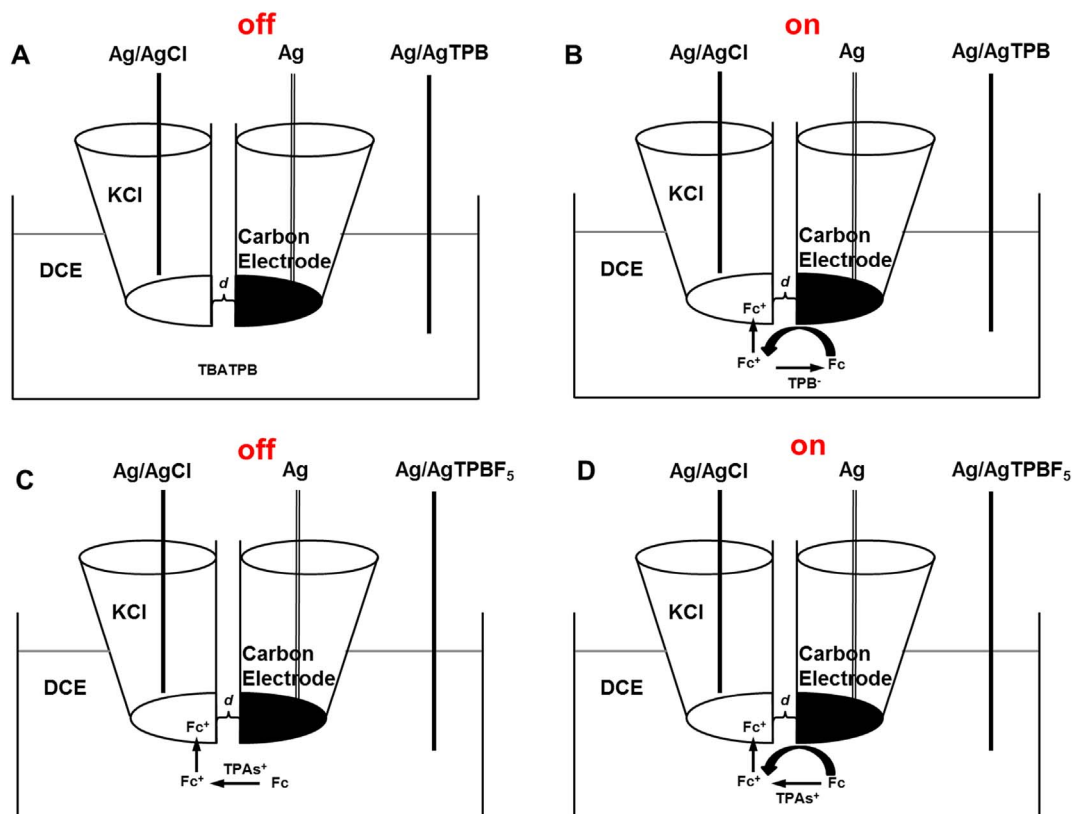


Fig. 1. Schematic illustration of the experimental setup based on the hybrid electrodes. (A) In cell 1 ($X = \text{TPB}$), when the carbon electrode is off, no Fc^+ is in the organic phase. (B) In cell 1 ($X = \text{TPB}$), when the carbon electrode is on, Fc^+ is generated at the carbon electrode and collected at the L/L interface, which meanwhile is reduced by the TPB^- . (C) In cell 2, there is a transfer of Fc^+ at the L/L interface despite no potential is applied at carbon electrode. (D) In cell 2, when the carbon electrode is on, the Fc^+ in the organic phase comes from two ways, in other words, oxidized either by carbon electrode or by TPAs^+ .

support a liquid/liquid interface. The Fc^+ is produced during the oxidation of the Fc by the carbon electrode, which is then collected by the liquid/liquid interface. The advantage is that the IT can be measured without additional ferrocene salt which is normally unstable in the organic phase [15]. The collection efficiency is defined as the ratio of collection current to generation current. Based on this G/C technique, the effect of seven different organic supporting electrolytes, including TBADCC, TBATPB, TBATPBCl, TBATPBF, TBATPBF₅, BTTPATPBF₅ and TPAsTPBF₅, on the ET-IT coupling process was investigated.

2. Experimental

2.1. Chemicals

Potassium chloride (KCl, $\geq 99.5\%$), ferrocene (Fc, 98%), and 1,2-dichloroethane (DCE, $\geq 99\%$) were purchased from Beijing Chemical Co. Tetrabutylammonium chloride (TBACl, $\geq 99.0\%$), potassium tetrakis(4-chlorophenyl)borate (KTPBCl, $\geq 98\%$), sodium tetrakis(4-fluorophenyl)borate (NaTPBF, $\geq 98\%$), lithium tetra (pentafluorophenyl)borate (LiTPBF₅) were purchased from Fluka. Tetraphenylarsonium chloride hydrate (TPAsCl, 97%), bis(triphenylphosphoranylidene)ammonium chloride (BTTPACl, 98.0%), sodium tetraphenylborate (NaTPB, $\geq 99.5\%$) were purchased from Sigma-Aldrich. All these reagents were used as received without purification. Tetrabutylammonium tetrakis(pentafluorophenyl)borate (TBATPB), tetrabutylammonium 3,3'-comobis(undecahydro-1,2-dicarba-3-cobaltocloso-dodecaborate) (TBADCC), tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl), tetrabutylammonium tetrakis(4-fluorophenyl)borate (TBATPBF), tetrabutylammonium tetrakis(pentafluorophenyl)borate (TBATPBF₅), tetraphenylarsonium tetrakis(pentafluorophenyl)borate (TPAsTPBF₅) and bis(triphe-

nylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BTTPATPBF₅) were prepared using the methods as described previously [27,28]. All aqueous solutions were prepared from triply distilled water.

2.2. Fabrication of hybrid electrodes

The hybrid electrodes were fabricated using the similar method previously described by Takahashi et al. and Zhang et al. [9,29]. Dual pipettes were made from quartz theta capillaries (0.90 mm inner diameter, 1.2 mm outer diameter, Sutter Instrument Co.) using a P-2000 CO₂-laser-based puller (Sutter Instrument Co.). Although the pulling programs are dependent upon each laser puller, the parameters in our study for fabrication of dual micropipettes are listed below:

Line 1, H: 760, F: 4, V: 45, D: 140, P: 25;

Line 2, H: 680, F: 3, V: 40, D: 130, P: 120.

To obtain hybrid electrodes, one of the barrels was blocked by clay and the butane would pass through the other barrel. Then the tip of the dual pipette was heated by alcohol lamp under the protection of nitrogen, during which the butane would pyrolytically deposit onto the wall of one channel to form carbon electrode at one tip of the pipettes [9]. Details of the characterization of the hybrid electrodes are shown in the supporting information of Fig. S1.

2.3. Electrochemical measurements

Carbon electrode setup was formed by inserting a 0.125 mm silver wire through the end of the pipette to make contact with the carbon layers. The other barrel was backfilled with the aqueous solution using a 10 μL syringe. A 0.125 mm silver wire coated with AgCl was inserted into it from the back and employed as the aqueous reference electrode.

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