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Electrochemical behaviors in closed bipolar system with three-electrode driving mode

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ABSTRACT

Here we report the studies on the electrochemical behaviors at a closed bipolar cell which is composed of two separated reaction cells containing a closed bipolar electrode (c-BPE) and its driving electrodes. The influence factors such as the concentration of the reagents, the size and material of the electrodes are studied experimentally and theoretically. And the experimental results fit with the theoretic calculation very well. Significantly, unlike the previous studies focusing on the coupling of the two c-BPE poles, this work also considers the effect of the reaction on the driving electrode on the electrochemical behavior. We believe that this research could deepen our understanding of bipolar chemistry and be useful for the future c-BPE-based applications.

1. Introduction

Bipolar electrode (BPE) has demonstrated its great potential for chemical and biological analysis [1–4], synthesis and screening of materials [5–8], and also industrial processes [9,10], etc. As an electronic conductor without any direct electrical connections, BPE has two styles: open BPE (o-BPE) and closed BPE (c-BPE) [11]. The o-BPE, which is located in one channel and transfers current by electrons and ions between the two poles, has been well-documented in numerous reports in theory by Crooks et al. [11–14] and widely used over the past years [1,15–17]. Recently, c-BPE, whose two poles are located in two separated solutions and bridged by c-BPE itself [11,18], has also attracted increasing attentions. Compared with the o-BPE, c-BPE has its own advantages, especially in the detection fields. For example, it can separate the reagents for generating detection signals, such as electrochemiluminescence (ECL) [19,20], fluorescence [21], etc. from the detection targets, which is conducive to deduce the background signals and interferences. And also because the driving voltage of the c-BPE is mainly distributed in the electrode interface and the potentials on the BPE poles is basically uniform, it means that a smaller driving voltage is needed to drive the reactions on the BPE poles and uniform detection signals could be obtained [22,23]. Our group combined c-BPE with electrochemiluminescence (ECL) to achieve quantitative detection of cancer biomarkers, peroxide, etc. [24–26]. Lin et al. constructed a closed bipolar platform for high-throughput screening of electrocatalysts used in fuel cells [6]. Zhang's group reported the use of c-BPEs array combining with fluorescence microscopy to reveal electrochemical and electrocatalytic activity [21]. Wang's group also reported a series of closed bipolar systems based on a variety of detection technologies for the detection of electroactive substances, screening of materials, etc. [18,20,27].

Several specialized theoretical studies about electrochemical properties of the c-BPE were performed for in-depth study of c-BPE [22,28–30]. Dryfe and co-workers studied the voltammetric response of a bipolar cell, formed by making electrical connection between two half cells with two three-electrode systems, respectively [28,29]. Zhang and co-workers reported the theory and experimental study of the electrochemical behaviors of c-BPEs with Ag/AgCl as driving electrodes and systematically investigated the effects of electroactive species concentration and relative size of the two c-BPE poles to the electrochemical behaviors [22,23,30]. Takano et al. developed a liquid-junction-free electrochemical system (c-BPE) for substitutional stripping voltammetry [31]. However, most of the above studies did not consider the impact of the driving electrode on the electrochemical behaviors of the bipolar system. But in many really application, the impact of the driving electrode was usually an important factor that have to be taken into account.

Herein, a closed bipolar cell containing a c-BPE and its driving electrodes is constructed and then its electrochemical behaviors are studied extensively. Unlike the reported studies just confined to the study at the two c-BPE poles, this work further discussed the impacts of the driving electrodes on the system behaviors. As shown in Scheme 1, this closed bipolar cell is composed of two half-cell (i.e., cell 1 and cell 2) and bridged by the c-BPE with two separated poles (i.e., pole 1 and pole 2), and driven by a common three-electrode system with working electrode (WE, electrode 1) in cell 1, reference electrode (RE, electrode 2) and counter electrode (CE, electrode 3) in cell 2. E_1, $E_{pole\ 1}$, $E_{pole\ 2}$ are

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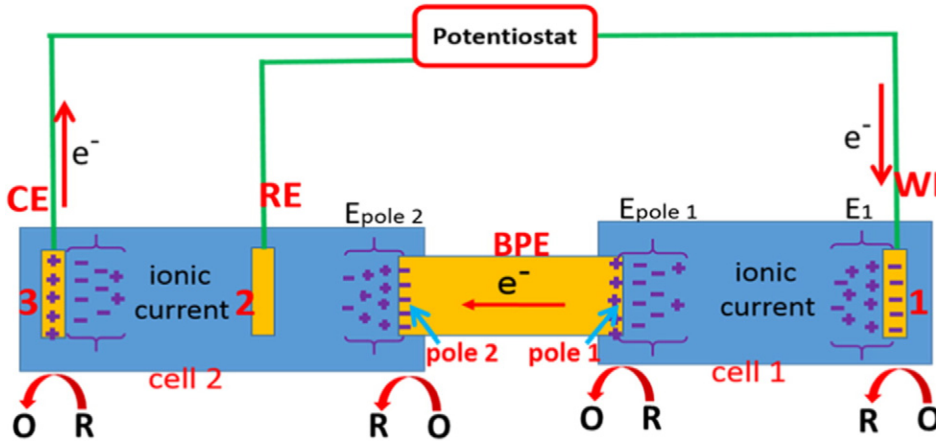

Scheme 1. The sketch map of the closed bipolar cell containing a c-BPE and its driving system. E_1, $E_{pole\ 1}$, $E_{pole\ 2}$ are the redox potentials on electrode 1, pole 1 and pole 2. Note that the situation of the electrode interface when oxidation reaction occurs on driving electrode 1 is opposite to the above sketch.

the redox potentials on electrode 1, pole 1 and pole 2 when reactions occurred on the above electrodes driven by a potentiostat. The effects of various influence factors on the system's electrochemical behaviors, such as the concentration of the reagents in cell 1, the size and material of the driving electrode 1, are investigated detailedly through the cyclic voltammetry (CV) and the theoretical calculation. And both the results of the voltammogram and the calculation have assured that the special potential on driving electrode (i.e. E_1 in this work) has great influence on the behaviors of the closed bipolar cell. We believe this work essentially deepens our understanding of the c-BPE and its driving system, and is very promising to expand its application. For example, in some special situations showed in the work, the c-BPE system just performed the electrochemical behavior of the half bipolar cell. It will be very helpful to study the interface situation of single c-BPE pole and do some special processing such as electrodeposition on the pole.

2. Experimental

2.1. Reagents, materials, apparatus

Refer to the Supporting Information 1 (S1).

2.2. Fabrication of the closed bipolar cell

The closed bipolar cell was fabricated by microchip manufacturing technology. The fabrication process was similar to our previous work [25]. Scheme 2 is the fabrication process of the closed bipolar cell (A) and its diagrammatic sketch (B). Briefly, it is made up of three layers: a polydimethylsiloxane (PDMS) top layer with two equal rectangular cell (12 mm in length, 4.5 mm in width, 3 mm in depth, Scheme 2A (b)), a PDMS sandwich film (0.2 mm in thickness, Scheme 2A (c)) and a patterned Indium Tin Oxide (ITO) glass ground layer (Scheme 2A (f)). They were bonded with each other by plasma bonding technology. The holes' sizes on the sandwich film covering the ground patterned ITO bands controlled the sizes of c-BPE poles and driving electrodes (Scheme 2A (g), Scheme 2B).

The diameters of the driving electrode 2 (counter electrode, CE) and electrode 3 (reference electrode, RE) in cell 2 are 3.0 mm and that of pole 2 is 1.5 mm (Scheme 2B). The size of pole 1, the material and size of driving electrode 1 (working electrode, WE) depends on the needs of the experiment (Scheme 2B). The two poles of c-BPE are in two separated cells and bridged by the c-BPE itself. Scheme 2C is the sketch map of the closed bipolar cell when an external voltage is supplied by a potentiostat. And Scheme 1 is the more detailed sketch map of Scheme 2C involving the reactions on the electrodes of the closed bipolar cell. Scheme 2D is the sketch map of a conventional three-electrode system in cell 2 with pole 2 as working electrode, electrode 2 as reference electrode, electrode 3 as counter electrode. The connections to the potentiostat for the closed bipolar cell and the conventional three-electrode system are realized by the exposed ITO bands on the glass ground layer outside of closed bipolar cell (Scheme 2C and D).

3. Results and discussion

3.1. Electrochemical behavior of the closed bipolar cell with reversible redox couple in cell 1

As shown in Scheme 1, the c-BPE performed a similar function to a salt bridge, but the current through the two poles of the c-BPE was electrochemical instead of ionic. Firstly, to fully study the impacts of the driving electrodes on the system behaviors, conventional electrode material (i.e. ITO for electrodes 1 and 3) rather than unpolarized electrode material in the reported work were employed as driving electrodes of the c-BPE. An additional electrode 2 was added as independent quasireference electrode to maintain the system's potential stability. This structure is very similar to the work of Takano et al. [31], while it is different from those of Zhang's group [23] and Dryfe's group [28] which mainly focus on the reactions on the c-BPEs by using unpolarized electrodes as driving electrode or dual three-electrode systems.

As illustrated in Fig. 1A, we first discuss the electrochemical behaviors of the closed bipolar cell as electrode 1, pole 1 and pole 2 with the same electrode size (1.5 mm) and the same electrode material (ITO). Various concentrations of $Fe(CN)_6^{3-/4-}$, as reversible redox couples, were added in cell 1 while fixed concentration of $Fe(CN)_6^{3-/4-}$ (2.0 mM) was in cell 2. 1.0 M KCl was added as electrolyte to the above solution to eliminate solution resistance. As shown in the cyclic voltammogram (CV) curves 1–7 of Fig. 1A, with the increased concentration in cell 1 (2.0 mM–200 mM), the peak separations of the redox peak potentials are becoming smaller (curves 1–4), and at last nearly invariable (curves 5–7). Meanwhile, the redox peak currents increase gradually and then are close to specific values in the end.

For comparison, the conventional three-electrode system with pole 2 as WE, electrode 2 as RE and electrode 3 as CE was then constructed as demonstrated in Scheme 2D, in which the electric circuit was irrelevant to cell 1 and the construction just was same to the cell 2 of the closed bipolar cell. With 2.0 mM $Fe(CN)_6^{3-/4-}$ in cell 2, the CV was obtained as shown in curve 8 of Fig. 1A. And we find that it is nearly the same as that of curves 6–7 in Fig. 1A. That is to say, as the concentration of $Fe(CN)_6^{3-/4-}$ in cell 1 is high enough, the closed bipolar cell just