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Rotating minidisk–disk electrodes

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Abstract

Rotating minidisk–disk electrode (RMDDE) was developed by replacing ring electrode of rotating ring–disk electrode (RRDE) with a minidisk electrode. Its applications were demonstrated by studying electrochemical reactions of ferricyanide and divalent copper. The replacement of ring electrode by minidisk electrode results in following advantages. First, the fabrication of RMDDE is easier than that of RRDE with the same electrode material. Second, there is more freedom in choosing electrode materials and sizes, since it is difficult to make thin ring electrodes of RRDE with fragile materials. Third, the replacement of ring electrode by minidisk electrode saves electrode materials, especially rare materials. Finally, the substitution of minidisk electrode for ring electrode allows using multiple minidisks for simultaneous monitoring of multiple components. Therefore, RMDDE is a promising generator–collector system, especially when special generator–collector systems are not commercially available, such as corrosion study and electrocatalysis study of new electrode materials.

Keywords: Rotating minidisk–disk electrode; Rotating ring–disk electrode; Generator–collector systems; Collection efficiency; Hydrodynamics; Double-electrode systems

1. Introduction

The generator–collector systems are very powerful and popular electrochemical techniques that involve in generator electrodes and collector electrodes [1–20]. In these systems, a species generated at the generator electrodes can move to collector electrodes, and can thus be monitored at the collector electrodes. Consequently, the generator–collector systems have found widespread application for the elucidation of electrode mechanisms, the study of coupled homogeneous reaction, measurement of kinetic parameters, and analytical determinations [1–20].

The generator–collector systems can be roughly divided into two categories: (a) hydrodynamic double-electrode systems, and (b) double-electrode systems consisting of at least one microelectrode [1–20]. The former systems include rotating ring–disk electrode (RRDE) [1–23], double channel electrode [24,25], double tubular hydrodynamic electrode [26], the rotating ring–ring electrode [27], double rotating cylinder electrode [28], and so on [29,30]. The latter systems include interdigitated microelectrode [31,32], ring–disk microelectrode [33–35], dual microband electrodes [36–41], dual-disk microelectrodes [42–45], a microdisk electrode coupled with a larger collecting electrode [46,47], and so on [48–52]. In comparison with the latter systems, hydrodynamic double-electrode systems are far more popular for the elucidation of electrode mechanisms, the study of coupled homogeneous reaction, and the measurement of kinetic parameters. These hydrodynamic double-electrode systems can be subdivided into two categories [53]: (1) those in which the electrode induces flow in the cell via its motion, such as rotating ring–disk electrode [1–12], and (2) those in which the electrode is stationary and flow

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is forced over the electrode surface, such as double channel electrode and double tubular electrode [24–26].

Among various generator–collector systems, RRDE first described almost 40 years ago by Frumkin and Nekrasov is the most popular generator–collector system [54]. Its popularity results from the following facts [55]. First, an adequate theory has been available for a long time [1–12]. Second, the RRDE has the advantage of well-controlled hydrodynamics and the rate of mass transport can be varied easily by varying the rotation rate. Third, the electrodes can be easily polished. Fourth, the RRDE is placed in a recipient that can easily be deaerated and thermostated. Finally, there is no need for a pumping system. In spite of the above advantages of RRDE, the fabrication of RRDE is rather difficult, especially to make a closely spaced concentric thin ring electrode or a thin ring electrode with fragile materials [1–3]. Meanwhile, limited kinds of RRDE are commercially available, and in many cases one needs to make generator–collector systems by oneself especially for electrochemical studies of special electrode materials, such as in corrosion studies and electrocatalytic studies. It is desirable to develop a simple generator–collector system.

Because the fabrication of disk electrode is much easier than that of thin ring electrode, we develop here rotating minidisk–disk electrode (RMDDE) by replacing ring electrode of RRDE with a minidisk electrode (Fig. 1). The RMDDE consists of two electrodes in a cylindrical holder: a centric disk electrode accompanied with an acentric disk electrode. The area between the centric disk electrode and the acentric disk electrode is electrochemically inactive. Previous studies have shown that rotating ring–disk microelectrode experiments are rendered impossible by changes in the diffusional regime caused by small deviations from the axis of rotation, and a rigorous theoretical description of diffusional-convective transport to a rotating microelectrode is not yet established [56–58]. To avoid the problems, both the centric disk electrode and the acentric disk electrode used were conventional-size disk electrodes, instead of microelectrodes, and the diameter of the centric disk electrode was comparatively large. The as-prepared RMDDE was characterized by studying electrochemical reactions of ferricyanide, oxygen, and divalent copper [1–3,59,60].

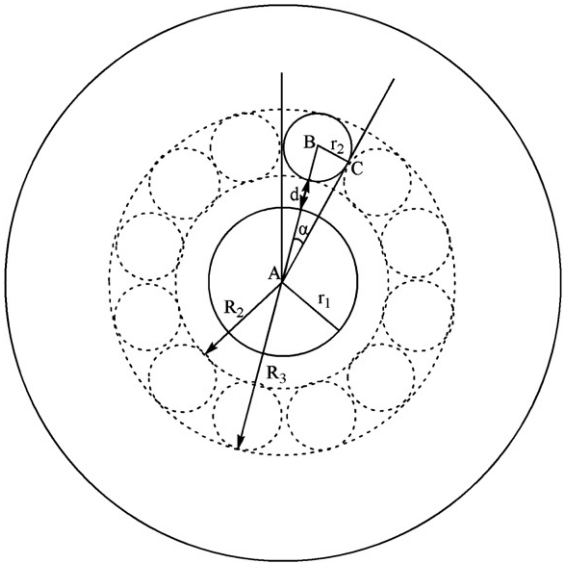

Fig. 1. Schematic representation of RMDDE. $r_1 = 1500$ μm, $r_2 = 262.5$ μm, $d = 120$ μm.

2. Experimental

2.1. Reagents

Potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium chloride, sodium hydroxide and copper nitrate were of reagent grade, and used as received. All solutions were prepared with doubly distilled water.

2.2. Apparatus

Electrochemical experiments were carried out in a four-electrode cell with a CHI 832B bipotentiostat (CH Instruments, Shanghai). The working electrodes, the counter electrode, and the reference electrode are a home-made RMDDE, a platinum slice, and an Ag/AgCl (saturated KCl) electrode, respectively. As shown in Fig. 1, the RMDDE comprised a centric glass carbon disk electrode (GC-D, 3.0 mm in diameter) and an acentric platinum minidisk electrode (Pt-MD, 0.525 mm in diameter). The distance between the GC-D and the Pt-MD is 0.120 mm. Prior to each electrochemical experiment, the RMDDE was regularly polished with an aqueous slurry of 0.05 μm alumina particles on a Microcloth polishing cloth, sonicated in water, and then rinsed thoroughly with water. The RMDDE was driven by an EG and PARC model 636 rotating ring–disk electrode system. All experiments were performed in the cell at room temperature. To minimize the interference of oxygen during electrochemical investigation of ferricyanide and divalent copper, the solution were purged with high-purity nitrogen at least 20 min before this measurement and a nitrogen atmosphere was maintained above the solution during the electrochemical measurements.

3. Results and discussion

3.1. Collection efficiency coefficient of RMDDE

The collection efficiency coefficient (N) is an important parameter for quantitative analysis in RRDE [59–62]. Similar to N of RRDE, N of RMDDE (N_{RMDDE}) is defined as the proportion of material produced electrochemically at the centric disk electrode, which reaches the acentric minidisk electrode. If all the material reaching the acentric minidisk electrode is electrochemically converted back into its precursor, then