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Research Paper

Generator–collector electrochemical sensor configurations based on track-Etch membrane separated platinum leaves

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ABSTRACT

We report a novel, simple and cheap generator–collector electrode system, employing platinum leaves, with micron-sized pores and typically 100–300 nm thickness, sandwiched with a porous track etch membrane spacer with typically 30 nm diameter pores. The electrode assembly is sealed into a polymer lamination pouch with one side 2 mm diameter exposed to electrolyte solution. The generator electrode with sweeping potential (top or bottom electrode) shows transient current with high capacitive current component. The collector electrode with fixed potential shows well-defined steady state current response at low potential sweep rates. The fabricated device shows good performance in monitoring both 1,1′-ferrocenedimethanol oxidation and proton reduction redox processes. Oxygen sensor signals are assigned to a lowering of the steady state proton reduction current.

1. Introduction

Generator–collector systems contain two working electrodes and provide powerful tools in electroanalytical studies [1]. Over the years these systems have been developed and studied in different geometries such as rotating ring-disk electrode [2], interdigitated electrodes [3,4], thin-layer cells [5,6] and nanoscale-recessed ring-disk electrodes [7]. Biasing proper potentials of these two closely spaced electrodes, allows repetitive oxidation and reduction of redox species between them and this leads to a strong amplification effects in sensing (known as redox cycling). This property then causes Faradaic current amplification to enhance the detection limit for analytical detection, also provides features such as suppressing irreversible interferences and enhancing the selectivity for reversible redox couples in electrochemical measurements [8,9]. Furthermore, by fixing the potential on the "monitor" electrode and scanning the potential only for the second electrode, voltammograms can be recorded free of capacitive currents with improved analytical detection of the Faradaic current.

One of the key and challenging features of these devices is the gap between the electrodes. Reducing the gap size to the nanometer range can enhanced the sensitivity toward single molecule detection [10,11]. However, in most cases fabrication of such a nanogap device needs access to the cleanroom facilities and requires following multiple sophisticated nanofabrication steps [10,12–14].

Hence, in recent years there is a great interest for developing simple low cost methods to fabricate the micro/nano junctions between two electrodes that work under redox cycling conditions. Wang et al. fabricated a generator–collector system by growing a silicon nanochannel membrane on electrodes to fabricate a nanogap [15], Park et al. employed spherical beads as spacer between the electrodes [16] and Adly et al. fabricated nanoporous redox cycling devices employing multilayer inkjet printing [17]. However in these methods several steps of substrate treating or preparing the inks and access to inkjet printing facilities are needed. Previously, we developed simple low cost methods to develop the micro-junctions between two electrodes that work under redox cycling conditions. Electro-deposition and employing an epoxy spacer layer can be a feasible way for creating dual electrodes with analytical applications [18–22]. Often, the dual electrode configuration was based on a "microtrench" with one side open to the electrolyte solution.

In this work we introduce a novel generator–collector electrode system using track-etch membrane and "platinum leaf" electrodes. Porous platinum leaf electrodes are employed and the two electrodes are mounted with one of the platinum leaves facing "outward" into the solution phase (Fig. 1). Using a porous track-etch

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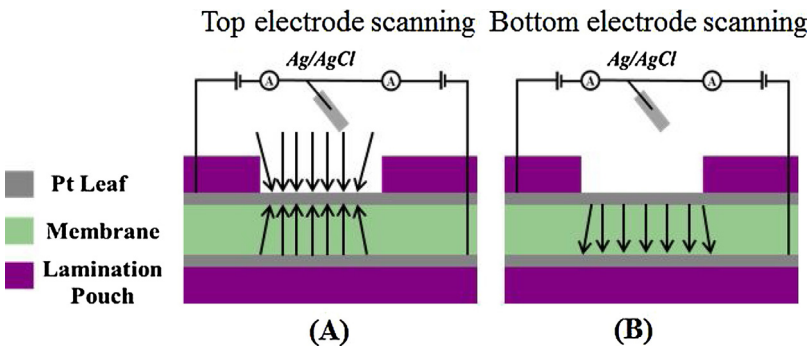

Fig. 1. Schematic drawing of a dual-platinum leaf sensor with (A) the outward facing electrode scanning and (B) the inward facing electrode scanning. Arrows are shown to indicate diffusional transport towards the "actively scanning" electrode.

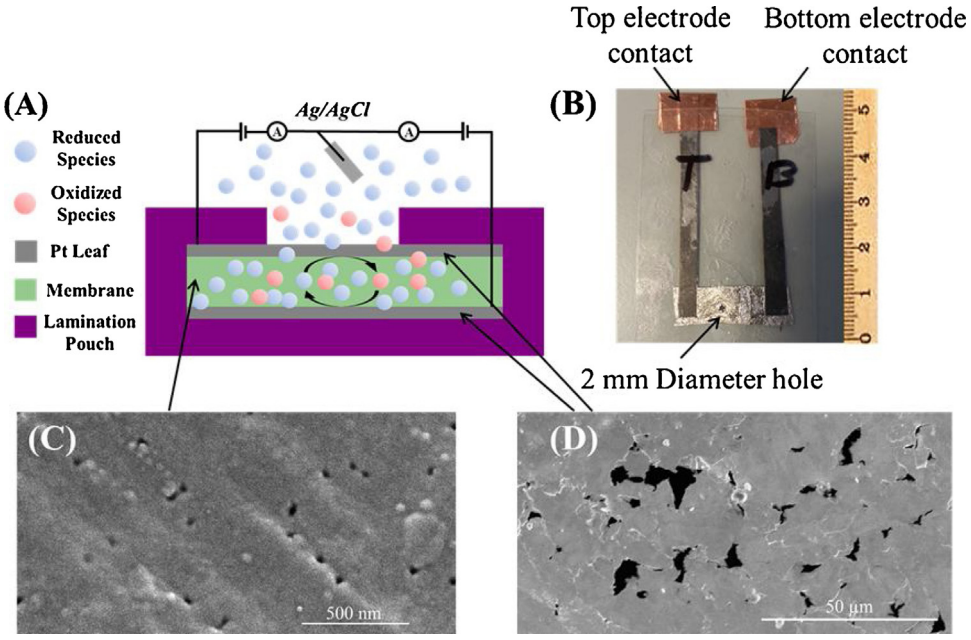

Fig. 2. (A) Scheme of the device. (B) Fabricated device. (C) SEM image of the track etch membrane. (D) SEM image of the platinum leaf.

membrane layer between the two platinum leaf electrodes helps to prevent short–circuits while providing the diffusion path for redox species in the redox cycling process.

It is shown that the two electrodes can be employed in generator–collector mode, although significant differences are observed when using (A) the outward facing electrode as the scanning electrode or (B) the inward facing electrode as the scanning electrode. Processes based on the 1,1′-ferrocenedimethanol redox systems are demonstrated. Next, the reduction of protons is investigated and it is shown that oxygen concentration in solution is detected indirectly by lowering the local proton concentration within the dual-electrode generator–collector sensor. A wider range of applications is envisaged.

2. Experimental

2.1. Chemical reagents

1,1′-Ferrocene dimethanol, $Fc(MeOH)_2$, potassium nitrate, KNO_3 and nitric acid, HNO_3 were purchased from Sigma-Aldrich. Genuine platinum leaves (Wrights of Lymm Ltd) were purchased. Scanning electron micrographs suggest approximately 100–300 nm thick platinum (*vide infra*) with 1–10 μm diameter holes. Osmonics Inc. (Catalog No.KN3CP02500) polycarbonate track etch membrane with 30 nanometer diameter pore size was employed. Goodfellow Cambridge Ltd graphitic carbon foil was used to assemble the device (see Fig. 2).

2.2. Instrumentation

Electrochemical experiments were carried out using an Autolab PGSTAT302N bipotentiostat system. A commercial Ag/AgCl (3 M KCl) reference electrode (BASi Inc.) and a platinum counter electrode were used in electrochemical measurements. Generator–collector voltammetry was performed with one electrode potential fixed and one electrode potential scanning. Scanning electron microscopy images (SEM) were obtained using FEI NovaNano SEM.

2.3. Device fabrication

Porous platinum leaves were cut into two small pieces (10 mm × 30 mm) and a track etch membrane was placed as a separating layer between two platinum leaves. Strips of carbon foil were connected to each platinum piece as connection conductors to the top (T) and the bottom (B) electrode. Then the structure was laminated into a lamination pouch with a 2 mm diameter hole on top of the Pt/membrane/Pt sandwich exposing one of the electrodes to the electrolyte solution (Fig. 2).

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