Available online at www.sciencedirect.com
SCIENCE DIRECT®
Electrochemistry Communications 8 (2006) 571–576
electrochemistry communications
www.elsevier.com/locate/elecom

Fabrication of disposable ultramicroelectrodes: Characterization and applications

Jen-Lin Chang, Jyh-Myng Zen *

Department of Chemistry, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung 402, Taiwan

Received 17 January 2006; received in revised form 31 January 2006; accepted 31 January 2006
Available online 28 February 2006

Abstract

We report an easy method for fabricating disposable screen-printed edge band ultramicroelectrodes (designated as SPUMEs) with a built-in three-electrode pattern of alternating printed-layer of carbon, silver, and insulator on a non-conducting polypropylene substrate. Central idea is that the edge of the carbon and/or metal-sandwiched films between the insulator layers can serve as a band type ultramicroelectrode. Simply by slicing the edge of working window, the SPUME dimension can be easily varied (e.g., in the range of 0.18–1.35 mm length with a width of 20 μm in this study). Cyclic voltammograms of ferricyanide in aqueous media displayed low-noise, low-background, sigmoidal responses with virtually no current hysteresis similar to that of a hemicylindrical electrode. The proposed SPUMEs exhibit very low electrical noise and can be reproduced multiple times by repetitively cutting the strip. Since they are cheap and easy for mass production, the disposable nature further offers to application in diverse field of electroanalytical chemistry.

Keywords: Ultramicroelectrode; Disposable; Screen printed; Iodide; Nitrite

1. Introduction

Electrodes of dimensions lower than millimeter size with diffusion-limited process have attracted considerable interest to electrochemist. Their unique electrochemical properties have been used in many applications preferable to electrodes of conventional size [1–5]. The advantages include minimizing of *iR* drop even in the absence of supporting electrolyte or in highly resistive media, reducing of the double layer capacitance, enhancing of flux and thus current sensitivity, facilitating fast response with a steady state current–potential curve, etc. [6,7]. Indeed these properties can be exploited to many useful research fields, especially in sensor applications [8–18], electron transfer kinetics measurements [2,19–25], and scanning electrochemical microscope (SECM) [26], etc. Nevertheless the fabrication of many types of ultramicroelectrodes (UMEs) normally requires tedious and time-consuming instrumental procedures. The as-prepared UMEs are in general expensive and are thus not designed for single-use purpose.

In this report, we have utilized the screen printed technique for the fabrication of screen-printed ultramicroelectrodes (SPUMEs). Screen-printed electrode (SPE), in which thin film of metal or carbon ink is printed on a polymeric non-conductive substance, have attracted analytical chemists due to its easy and simple preparation procedures [27,28]. Important advantages of SPEs include low-cost (thus disposable), easy for mass production, and flexible in design. The idea behind our proposed fabrication method is that the edge of the carbon and/or metal-sandwiched film between insulator screen-printed layers can serve as a band type ultramicroelectrode (BUME).

Our proposed fabrication method possesses two major advantages. Firstly, the same three-electrode SPUME pattern can be arranged as either: (1) carbon-working, silver-quasi reference, silver-counter electrodes (designated as SPUME-1); or (2) silver-working, silver-quasi reference,

* Corresponding author. Fax: +886 4 22854007.
E-mail address: jmzen@dragon.nchu.edu.tw (J.-M. Zen).

1388-2481/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2006.01.028

carbon-counter electrodes (designated as SPUME-2) for different electroanalytical applications. Note that a trend in the development of sensors for decentralized analysis is to integrate together with the working electrode both reference and counter electrodes on one strip in order to miniaturize and to simplify the instrumentation. In this study, cyclic voltammograms of nitrite and iodide in aqueous media were applied to validate the electrochemical behavior of SPUME-1 and SPUME-2, respectively. Secondly, the dimension, i.e., width (w) and length (l), of the SPUME can be tunable simply by adjusting the screen printed film thickness and breadth, respectively. As reported earlier, band geometry can provide larger currents than disk UME, while maintaining the properties of non-linear diffusion [2,7]. Overall, new design and fabrication of ultramicroelectrodes is a significant and demanding research work in electroanalytical chemistry. Screen printed methods are useful because they provide the ability to reproducibly design multiple-layered electrode systems for a particular UME application. The disposable in nature of the SPUME makes it especially attractive for electroanalysis.

2. Experimental section

2.1. Reagents and chemicals

Sodium nitrite, potassium iodide, and potassium ferricyanide were obtained from Sigma (St. Louis, MO, USA). Carbon and silver inks were purchased from Acheson (Tokyo, Japan). Conventional SPEs (3 mm in diameter) in three-electrode configuration were obtained from Zensor R&D (Taichung, Taiwan). All the other compounds (ACS-certified reagent grade) were used without further purification. Aqueous solutions were prepared with deionized water purified using Millipore-Q purification system.

2.2. Apparatus

All electrochemical experiments were performed either on a CHI 832 or CHI 8021 electrochemical workstation (Austin, TX, USA). The SPUME in three-electrode configuration consisted of either SPUME-1 (i.e., carbon-working, silver-quasi reference, silver-counter electrodes) or SPUME-2 (i.e., silver-working, silver-quasi reference, carbon-counter electrodes). The physical features, such as electrode topography and edges, were characterized by scanning electron microscopy (SEM).

2.3. Electrode fabrication

Different stencil assemblies were first prepared properly to making the multi-layer SPE on a 50 mm × 15 mm polypropylene (PP) base. Fig. 1A shows typical layer-by-layer assembly of the built-in three-electrode system using stencil format in the order of carbon ink → insulating polymer → silver ink → insulating polymer → silver ink → insulating polymer. The methodology is similar to the classical SPE preparation method using a semi-automatic screen-printing machine [28]. The as-prepared SPUMEs were then cured in an UV radiation source at an intensity of 1.85 mW/cm^2 for 2 h. The tip edge window was suitably sliced to expose the SPUME with a built-in three-electrode pattern, as illustrated in Fig. 1B. The procedures can allow for preparing versatile three-electrode SPUME suitably in-between the insulating polymeric layers. Since the working electrode possesses a triangle-shaped end portion, different cut distance (S_E) represents for different SPUME dimensions.

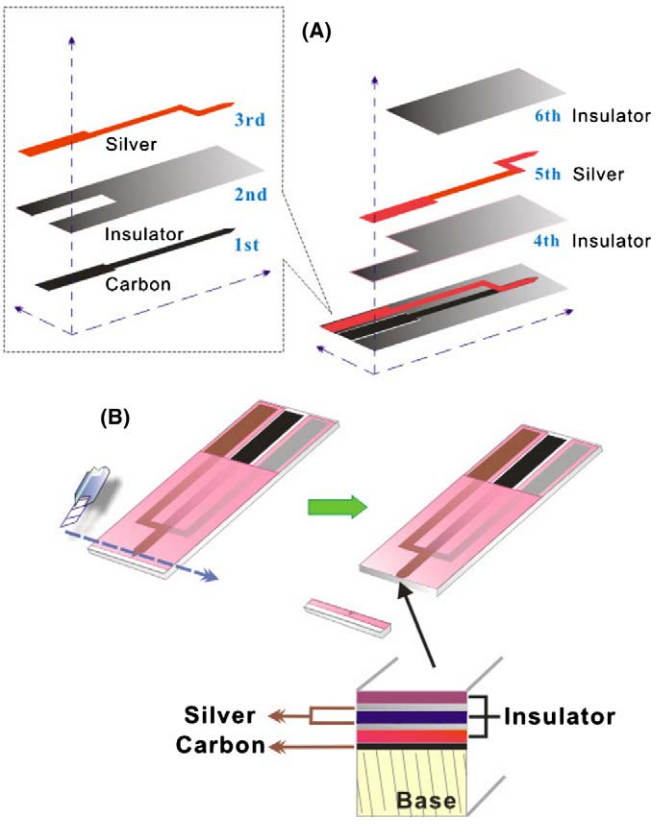

Fig. 1. (A) An alternating layer-by-layer pattern structure of the SPUME assembly. (B) Cross-sectional diagram of a typical SPUME with a built-in three-electrode configuration.

2.4. Electrochemical studies

Measurements were all carried out with the SPUME in a three-electrode configuration. The working electrode of the SPUME in three-electrode configuration was electrochemically pretreated in respective pH with the potential window between oxygen and hydrogen gas evolution reaction until the current become constant. It normally took 20 continuous cycles at $v = 50$ mV/s. Experiments with ferricyanide were studied in pH 2 KCl/HCl using an SPUME-1. Trace analyses with nitrite (in 10 μM H_2SO_4) and iodide (in pure water) were carried out with SPUME-1 and SPUME-2, respectively.