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Electrochemical properties of porous bismuth electrodes

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ABSTRACT

The properties of Bi surfaces with different roughnesses were characterized by electron microscopy, cyclic voltammetry, and impedance spectroscopy. Two different strategies were used for preparation of porous bismuth layers onto Bi microelectrode surface in aqueous 0.1 M $LiClO_4$ solution. Firstly, treatment at potential $E < -2$ V (vs. Ag|AgCl in sat. KCl) has been applied, resulting in bismuth hydride formation and decomposition into Bi nanoparticles which deposit at the electrode surface. Secondly, porous Bi layer was prepared by anodic dissolution ($E = 1$ V) of bismuth electrode followed by fast electroreduction of formed Bi^{3+} ions at cathodic potentials $E = -2$ V. The nanostructured porous bismuth electrode, with surface roughness factor up to 220, has negligible frequency dispersion of capacitance and higher hydrogen evolution overvoltage than observed for smooth Bi electrodes.

1. Introduction

Deposition of porous bismuth by fast electroreduction of the Bi^{3+} ions has been described in different studies [1–3]. The electrode surface roughening has been detected during anodic oxide layer formation and reduction of Bi_2O_3 to a metallic Bi [4–7]. Bi surface roughening has also been established at high cathodic current densities under intensive hydrogen evolution conditions [6–10], explained as a result of decomposition of volatile bismuth hydride BiH_3, formed together with hydrogen, and deposition of Bi nanoclusters [10]. The differential capacitance and chronocoulonometry measurements can be used to determine the surface area formed [6,11–14].

The ideally polarizable electrode behaves as an ideal capacitor because there is no faradaic charge transfer across the solution|electrode phase boundary. In this case, the equivalent electrical circuit (EC) consists only of the solution resistance, R_s, in series with the double-layer capacitance, C_{dl} [14]. The electropolished Bi single crystal electrode has been found to behave as a nearly ideally polarizable electrode [12]. Frequency dispersion of capacitance is often observed in the case of solid electrodes, which have been attributed to the atomic scale roughness, crystallographic heterogeneity, and chemical inhomogeneities on the solid surface [13–21]. Frequency dispersion can be represented with a constant phase element CPE with an impedance $Z_{CPE} = A^{-1}(j\omega)^{-\alpha}$, where A is a CPE coefficient, $j = (-1)^{1/2}$, ω is angular frequency of the ac signal, and α is fractional exponent, equal to 1 for an ideal capacitor, 0.5 for Warburg semi-infinite diffusion and 0 for an ideal resistor [13,14].

Porous systems usually show larger frequency dispersion than smooth ones [14,15]. Surprisingly, it was found that porous pure metal or nanoporous carbon electrodes may have only small frequency dispersion effect in the absence of specific adsorption [15–18]. Frequency dispersion occurs for the Au and Pt electrodes in halide solutions within the potential region, where adsorption and superficial species rearrangement take place [22–24].

The properties of a solid substance depend on its size, and the quantum confinement effects occur when the dimensions of a solid reach a level of molecular dimensions. The electrical properties of semimetallic Bi demonstrate strong dependence on the nanowire diameter or nanofilm thickness, and the semimetal-to-semiconductor transition is expected to take place at the film with thicknesses from 23 to 32 nm [25,26]. Oscillating dependence of resistivity on the film thickness, and large magnetoresistance effects appear for the Bi nanostructures [26]. The nanoporous Bi thin films exhibit an order-of-magnitude reduction in thermal conductivity, compared to that of solid films, due to the reduction in the phonon mean free path [27].

The main aim of this work is to compare the electrochemical properties of the smooth and porous Bi electrodes prepared using 50 μm diameter bismuth cleaved capillary electrode (BiCCE) and simple in situ roughening techniques.

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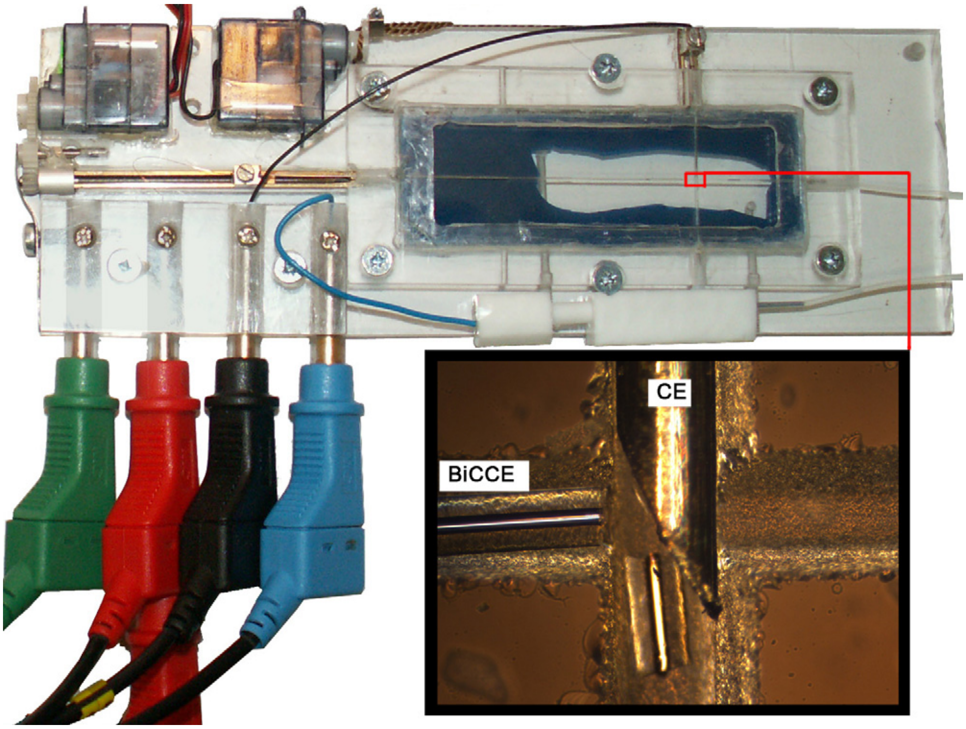

Fig. 1. Photograph (18 cm × 9 cm) of the BiCCE measurement system. Inset: BiCCE cleaving procedure (1.6 mm × 1.2 mm) under optical microscope.

2. Experimental

2.1. Preparation of Bi macro- and microelectrodes and construction of measurement cells

The Bi(0 0 1) and Bi(1 1 1) (purity 99.9999%) single crystal electrodes (rhombohedral symmetry indices are used throughout this paper) of 4 mm in diameter were glued into a glass tube with transparent epoxy glue, polished to a mirror finish by 50 nm alumina suspension, and purified in an ultrasound bath filled with pure water [12]. Additionally, the Bi electrodes were electrochemically polished in a HCl + KI solution immediately before each experiment [12,28]. Electrochemical measurements with Bi macroelectrodes were carried out in a single-compartment glass cell including large platinum gauze as a counter electrode and Luggin capillary for the reference electrode connection. Ag|AgCl in saturated KCl aqueous solution was used as a reference electrode in all experiments, and temperature was kept at 25 ± 1 °C.

The Bi microelectrodes of 50 ± 10 μm diameter were prepared by filling the soda-lime glass capillaries with bismuth (Mateck; purity > 99.9999%) in vacuum according to the procedure described in our previous work [11]. The cleaved surface of BiCCE can be repeatedly prepared in situ under an electrolyte solution by breaking the small cylinders from the top of the electrode (inset in Fig. 1). It has been found that the BiCCE surface is mainly atomically flat with (1 1 1) orientation, however, sometimes there are also some (0 0 1) steps [11]. The solution flow cell (Fig. 1) has four connections: the working electrode (BiCCE) moves to the right before each cleavage; the counter electrode (CE) moves downward, breaking the electrode, and thereafter it moves back; the right channel is for incoming the fresh solution; the downward channel is an outlet for the solution and broken cylinders, also accommodating the Ag|AgCl reference electrode. The BiCCE glass cell was filled with 0.1 M $LiClO_4$ aqueous solution with the help of the syringe pump Aladdin-1000. A small flow rate of 0.1 mL h^{-1} of the electrolyte solution (saturated with hydrogen) was maintained during the electrochemical measurements in order to keep dissolved oxygen, diffusing slowly through the connections of the measurement cell, away from the electrode surface. The BiCCE with in situ renewable surface in a combination with the solution flow cell enable to prepare repeatedly the new cleaved electrode surface, and thereafter dissolve and deposit a new porous electrode and, after rinsing the measurement compartment with clean electrolyte, to study the electrochemical properties of the deposited Bi in the Bi^{3+} cation free solution. Due to spherical diffusion for the small electrode, the *iR*-drop is small even at the high current densities applied. It was found by optical microscope that the hydrogen bubbles do not adsorb onto the Bi microelectrode surface.

2.2. Reagents and other apparatus

The solutions for electrochemical measurements were prepared from ultra pure water (MilliQ+), $LiClO_4$ (Sigma Aldrich 99.99%), and were saturated with electrolytic hydrogen (Barken BALSTON hydrogen generator, purity > 99.9999%) for 30 min prior to the measurements in order to remove dissolved oxygen. Electrochemical measurements were carried out using Autolab PGSTAT 30 potentiostat with a FRA 2 impedance measurement system. Frequency range was varied from 10 mHz to 1 MHz with 5 mV ac amplitude. The BiCCE|electrolyte interface was monitored through the glass cell using a Meiji optical reflectance microscope MX8530. The scanning electron microscope (SEM) images were taken with the Leo 1430 apparatus.

3. Results and discussion

3.1. Single crystal Bi macroelectrodes

Cyclic voltammetry measurements in 0.1 M $LiClO_4$ aqueous solution indicate low-current density (*j*) within the potential