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Single tungsten nanowires as pH sensitive electrodes

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ABSTRACT

The electrochemical potentials of tungsten nanowire samples, covered with their own oxide, were measured in dependence of the pH value. The samples were prepared by selective etching of a directionally solidified eutectic NiAl–W alloy. Directional solidification in a Bridgman-type crystal growth furnace yields nanostructured two-phase materials. Electrochemical processing allows selective etching of the phases exposing the nanoscale structures. In this work, pointed samples with a single wire 200 nm in diameter protruding from the tip were produced. Subsequently the tungsten oxide layer on these single nanowires was electrochemically modified to optimize their pH sensing capabilities. The method has a potential for further downsizing since the wire diameter and exposed length can be controlled by the process parameters during solidification and during electrochemical processing. The advantages of these nanowire pH probes along with possible applications such as the pH measurement in ultra small cavities and other small systems of interest such as corrosion pits and biological cells are discussed.

1. Introduction

The measurement of the pH values has a long tradition in science and was initially performed by visualising the colour change of indicators [1]. Today pH measurements are usually performed electrochemically by using an electrode of the 2nd type [2]. Sensing of the proton concentration becomes possible if either the electrochemical equilibrium involves protons in the reaction or if a separation of the electrolyte is achieved by a proton specific ionophore. In this way micro capillaries have been used for pH sensing [3,4].

It is much simpler if the electrode itself is pH sensitive as it is the case for tungsten covered by its oxide. Tungsten oxide was consequently used to construct pH probes [5]. In the 1950s the first experiments were performed to investigate the intercellular pH value of a crab muscle using a tungsten wire with a diameter of 10–15 μm [6,7]. There is a small number of other metals with pH sensitive oxides that can be used to prepare pH sensors, e.g., Pd and PdAg [8]. Nanowire sensors are potentially smaller, faster and more sensitive and an attempt was made towards pH sensing by means of silicon nanowires, in which the silicon oxide was modified by a covalently linked amine that is sensitive to protonation and deprotonation in the range from pH 2 to pH 9 [9].

Recently, a new technique to produce tungsten nanowires by selective dissolution of a directionally solidified eutectic NiAl–W alloy was reported [10]. Depending on the growth parameters the wire diameter and the spacing can be controlled [11] and by controlling the dissolution conditions, namely the dissolution time, the length of the released wires can be intentionally varied [12].

This type of tungsten nanowires with a diameter of 100–200 nm were manufactured and employed for pH sensing.

2. Experimental

2.1. Chemicals and electrodes

A Ag|AgCl|3 M KCl reference electrode from Deutsche Metrohm, Germany was used. All chemicals and the metals for fabricating the employed alloy were acquired from various sources in Germany: chemicals VWR International, Ni (99.97%) GfE Gesellschaft für Elektrometallurgie; Al (99.99%) VAW Aluminium; W (99.9%) Goodfellow.

2.2. Electronics

Electrochemistry was conducted with an IviumStat Potentiostat (Ivium Technologies, The Netherlands). Scanning electron microscopy was performed using a Leo 1550 VP apparatus (Leo Elektronenmikroskopie, Germany).

2.3. Preparation of macroscopic tungsten wires

A tungsten wire (diameter: 1 mm, length: 2 cm) was ground with 4000 grit emery paper and ultrasonicated. The electrode was oxidized between +1.00 V and +2.00 V (SHE) in 2.0 M H_2SO_4

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at a scan rate of 20 mV s^{-1} for 20 cycles with a Pt-wire as counter electrode. Each cycle showed a small anodic current reaching approximately 50 μA at 2.00 V (SHE) [13].

2.4. Preparation of tungsten nanowire samples

The tungsten nanowire probes used in this work were prepared from a *ds*-NiAl–W (*ds* = directionally solidified) eutectic alloy. This method was described in detail in [10,11]. It consists of preparing a ternary pre-alloy with quasi binary eutectic composition which is then processed in a Bridgman-type crystal growth oven. The sample is slowly moved from a hot into a cold zone facilitating unidirectional heat extraction and the crystallisation of nanostructured, self organized arrays of tungsten nanowires embedded in the NiAl matrix. Varying the process parameters allows precise control of the tungsten wires diameters down to 100 nm [9,10] at a growth rate of 200 mm h^{-1} and temperature gradient of 40 K cm^{-1}.

Fig. 1. SEM picture of the tungsten nano wire protruding from the NiAl matrix.

The samples are cut into sticks with the dimensions 0.5 mm × 0.5 mm × 20 mm and the tips of the sticks are immersed in 1 M HCl and etched by applying the potential mentioned below. During the etching process the samples are slowly lifted up and out of the solution, yielding a cone shaped tip with protruding wires. Subsequent to the tapering of the sticks the samples were electrochemically processed in order to partially release the tungsten nanowires. By applying appropriate chemical and electrochemical conditions it is possible to selectively dissolve the matrix elements while simultaneously passivating the tungsten. The conditions chosen for this were 1 M hydrochloric acid (pH 0.1) at a potential of 200 mV SHE for 10 min [10]. Applying a moderate anodic potential accelerates the matrix dissolution while at the same time covering the wires with a thin oxide layer. It is also possible to produce nanowire probes with a single tungsten nanowire protruding from the tip, as shown in Fig. 1. The nanowire tips were treated in the same manner as the macroscopic tungsten samples. When dipping the tip into liquids, capillary forces caused the entire sample to be wetted. This was not desired; therefore a capillary cell was constructed (Fig. 2) that prevented the liquid from wetting the matrix through counter capillary forces. For electrochemical experiments the capillary was equipped with a μ-Ag|AgCl|sat. KCl RE [14] and a 200 μm Pt-wire CE.

2.5. pH dependent potential measurements

The pH dependence of the samples potential was determined by monitoring the open circuit potential (ocp) while immersed in solutions of various pH values. All potentials given in this work refer to the standard hydrogen electrode (SHE). The pH values investigated were 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 [15]. The ocp was monitored for 20 min to ensure that the equilibrium potential had stabilized. These measurements were performed on tungsten wires with a diameter of 1 mm and the single nanowire tips described in Section 2.4.

3. Results and discussion

The ocp of WO_3 can be used to measure the pH [16]. It was stated that the pH dependence is an effect of the intercalation and deintercalation of H^+ ions into the oxide layer, accompanied by a

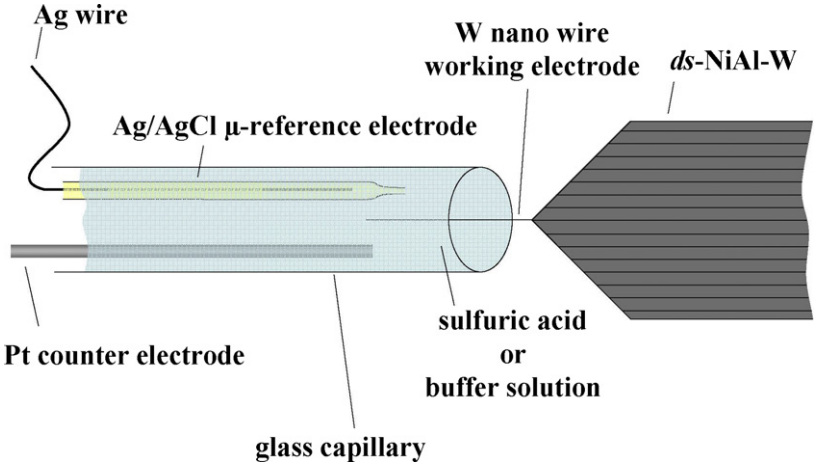

Fig. 2. Capillary cell for electrochemical measurements on single nano wires.