



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.

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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 $50 \mu\text{A}$ 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



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

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} .

The samples are cut into sticks with the dimensions $0.5 \text{ mm} \times 0.5 \text{ mm} \times 20 \text{ mm}$ 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 $1 \text{ M hydrochloric acid}$ ($\text{pH } 0.1$) 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 $\mu\text{-Ag|AgCl|sat. KCl RE}$ [14] and a $200 \mu\text{m Pt-wire CE}$.

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

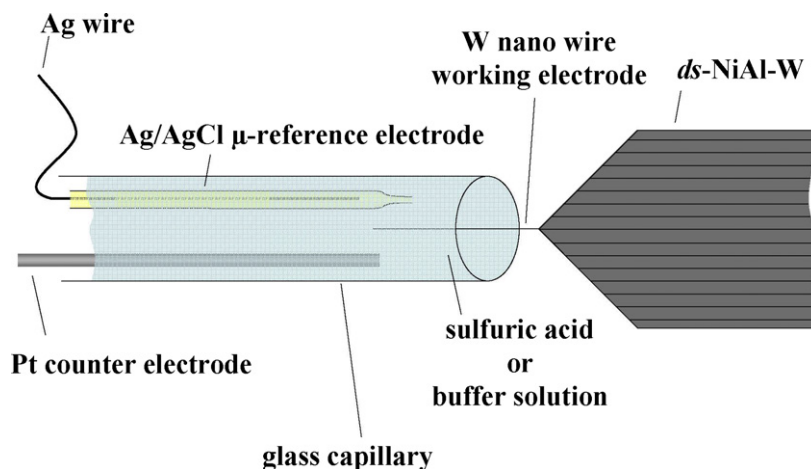
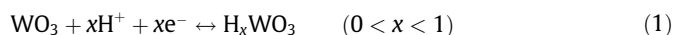


Fig. 2. Capillary cell for electrochemical measurements on single nano wires.

change in the oxidation state of the tungsten oxide [17]. The pH dependent reaction of WO_3 can be written as [18]:



For $x = 1$ the chemical formula is HWO_3 with a perovskite structure, which is responsible for the electrochromism of tungsten oxide [19]. For smaller x a defect perovskite structure will result that exhibits proton conductivity in the relatively open structure. For $x = 0$ when each H atom is removed, a structure results that is of the ReO_3 -type even though it is distorted [20]. According to the Nernst-equation for the equilibrium between H^+ ions and H_2 the following can be stated:

$$\begin{aligned} E &= E_0 + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{c_{\text{ox}}}{c_{\text{red}}} = E_0 + \frac{2.303 \cdot R \cdot T}{z \cdot F} \cdot \lg \frac{c_{\text{ox}}}{c_{\text{red}}} \\ &= E_0 + \frac{2.303 \cdot R \cdot T}{z \cdot F} \cdot \lg \frac{c_{\text{H}^+}}{\sqrt{p_{\text{H}_2}/p_0}} \end{aligned} \quad (2)$$

with $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the gas constant, $F = 96487.3415 \text{ C mol}^{-1}$ is the Faraday constant, T is the absolute temperature and p_{H_2} is the hydrogen partial pressure.

By definition $E_0 = 0$ for the SHE; using $\text{pH} = -\lg c_{\text{H}^+}$ it follows that:

$$\begin{aligned} E &= \frac{2.303 \cdot R \cdot T}{z \cdot F} \cdot \lg \frac{c_{\text{H}^+}}{\sqrt{p_{\text{H}_2}/p_0}} = -\frac{2.303 \cdot R \cdot T}{z \cdot F} \cdot \text{pH} \\ \Rightarrow E &= -m \cdot \text{pH} \end{aligned} \quad (3)$$

Under standard conditions $p = 1013.25 \text{ hPa}$, $T = 298 \text{ K}$ the slope m should be

$$m = 59.1 \text{ mV} \cdot \text{pH}^{-1} \quad (4)$$

As shown in Fig. 3a, the potential of a macroscopic $\text{W}|\text{WO}_3$ sample is linearly dependent on the pH. However, the slope was determined to be -61.1 mV pH^{-1} . This discrepancy is assumed to be due to the mixed potential at the $\text{W}|\text{WO}_3$ surface which behaves in accordance to both the anodic and cathodic reactions of tungsten oxidation and proton reduction – which is not necessarily in equilibrium [16].

From a thermodynamic point of view, tungsten oxide is not stable at pH values higher than 6. This can be seen by viewing the Pourbaix-diagram of tungsten which shows a transition from solid WO_3 to the ionic species WO_4^{2-} at a wide potential range and at pH values that are above neutral values [21] neglecting kinetic aspects.

The nanowire tip sample shown in Fig. 1 has a tungsten wire with a diameter of 200 nm which protrudes from the matrix with a length of approximately 50 μm . Fig. 3b shows a potential transient measured with such a nanowire tip. Initially, the potential is at -0.092 V . The large peak in the transient results from intentionally removing the wire from the solution and reinserting it a few seconds later. This shows the excellent response time of the nano pH probe. After approximately 40 s the potential reaches its final value of -0.104 V .

Fig. 3a also shows the ocp values measured on a nanoscopic tungsten wire at different pH values. Both wires show approximately the same linear dependency of the pH. The ocp values for the nanoscopic wire are shifted by -550 mV . This discrepancy may be due to the high resistance of the oxide layer covering the nanowire. Considering the nanowires' extremely small surface area, the total sample resistance is in the range of 10^{11} Ohms . Since this value is in the range of the input impedance of the operation amplifier a non negligible potential shift can result. A possibility to overcome this problem may be a different metrology based on a periodic current interruption. Once the nanowire is calibrated

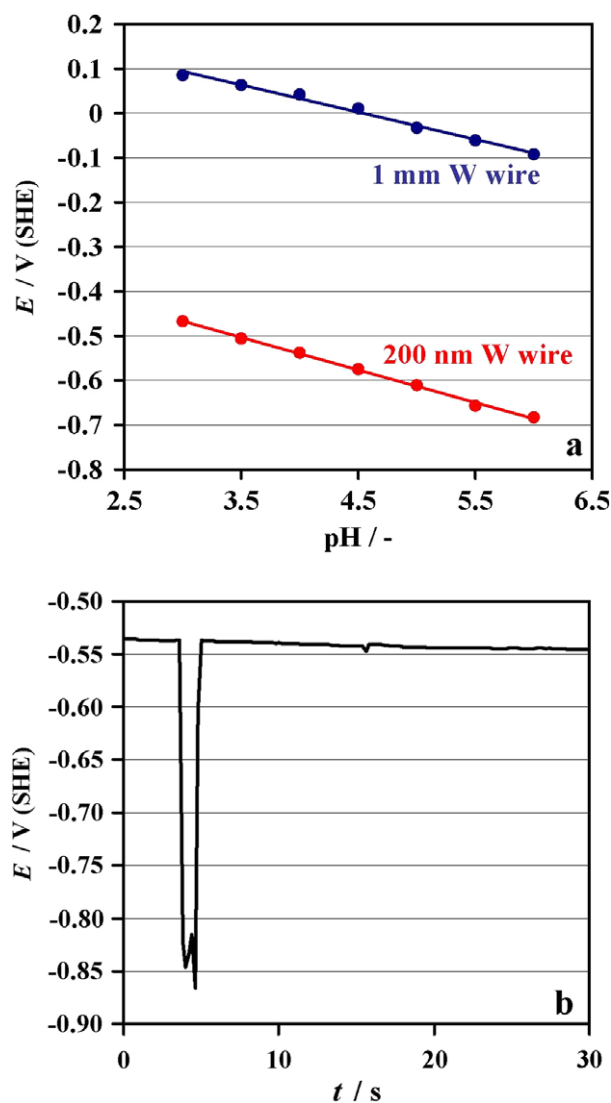


Fig. 3. (a) pH-potential dependence of the tungsten wire and the tungsten nano wire array (including the line of best fit). (b) Excerpt of the ocp transient of a tungsten nano wire immersed in a buffer solution of pH 6.0.

against the reference electrode, it can be employed. These first trials yielded one functioning wire out of four. This is attributed to the principle difficulty in handling such small objects like nanowires and depends decisively on the experimenter's skill.

These results clearly demonstrate that tungsten nanowires can be used to measure pH values. Single wires can be obtained by complete dissolution of the NiAl matrix and manipulated using piezo driven tweezers. Fig. 4 shows a schematic of a suggested nano-pH-probe setup. First, a single tungsten nanowire is attached to a macroscopic Cu wire using a sputter deposition or ion-lithography technique. The wire surface can then be electrochemically tailored as described above. Next, a theta-capillary with two separated, parallel channels is pulled in order to obtain a very small tip. Subsequently, it is ground using a micro-grinder (Narishige EG-400) to adjust the tip geometry to a flat 1 μm tip. One channel of this capillary could be filled with a μ -RE, e.g., $\text{Ag}|\text{AgCl}$ or $\text{Hg}|\text{Hg}_2\text{SO}_4$ [14,22]. The other channel could be fitted with the prepared tungsten nanowire, embedded in a resin. This probe could then be used to investigate ultra small cavities such as corrosion pits or other small systems of interest such as biological cells, etc [23].

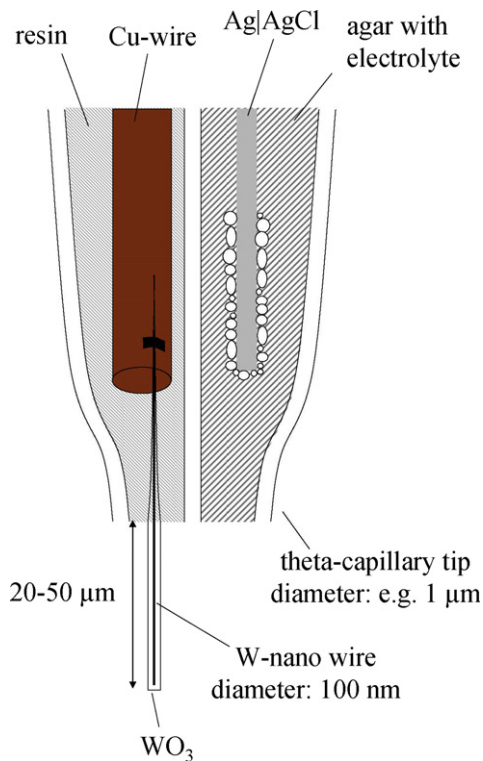


Fig. 4. Schematic of the suggested nano pH probe.

4. Conclusion

It could be shown that the use of tungsten oxide as a pH sensitive electrode could be applied to the nanoregime. This was achieved by preparing a tungsten nanowire tip from a directionally solidified eutectic alloy and covering it with a well defined oxide layer. Subsequently, this oxide layer was characterized in solutions of various pH values and the performance was compared to the behaviour of a macroscopic tungsten oxide sample. In particular

the extreme aspect ratio of the wires, that can easily reach 1000 or more, makes this material very interesting. It is noteworthy to say that the production of these nanowires is no longer on the prototype level. The production in the gram range is already possible which would equal some 10^9 wires with a diameter of 100 nm and a length of 300 μm .

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