



Short communication

Decreasing the time response of calibration-free pH sensors based on tungsten bronze nanocrystals

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ABSTRACT

A considerable improvement of time constants of tungsten bronze pH sensors was achieved by decreasing the crystal size of the tungsten bronze previously reported by the authors. Experiments have been performed on the basis of a previously developed calibration-free pH tungsten bronze electrode. The nano-sizing of the tungsten bronze was realized by addition of sodium chloride to the Na₂WO₄/WO₃ melt in which tungsten wires were oxidized. With increasing NaCl concentration, the crystals size decreased.

1. Introduction

In a previous study, a new tungsten bronze electrode has been developed which operates as direct-contact calibration free pH-sensor [1]. The working mechanism of this electrode allowed for the first time to separate the free energies of ion and electron transfer in case of an insertion electrochemical system, which made this electrode also interesting to gain information about the thermodynamics of insertion electrochemistry [2]. These insights have been corroborated by Doménech-Carbó et al. in a recent study using solid gold complexes [3].

The synthesis of the tungsten bronze is very simple: a tungsten wire is oxidized in a stoichiometric melt of Na₂WO₄ and WO₃ for 5 to 30 s. Under these conditions the resulting stoichiometry of the tungsten bronze layer on the surface of the metallic tungsten wire is constant and the electrode response is constant and highly reproducible. The sensors had rather short response times depending on the film thickness and pH. The time constants τ decreased depending on the layer thickness: for thinner films τ is 41 s and for thicker is 145 s at pH = 1. Moreover, the time constants decreased when the pH was increased due to the dissolution process in alkaline solutions [4].

From literature its known that nanostructures may have higher sensitivities and shorter response times compared to bulk material [5,6,7,8,9]. For example, Pd and Pd/Cr nanowires [10,11] which respond to H₂, respond faster when the thickness of the network is reduced due to the kinetics of hydrogen absorption, the absorption energy, and the hydrogen diffusion coefficient in palladium [12]. Also in case of tungsten oxide pH sensors a similar trend has been found [13,14,15].

In this paper, we demonstrate that the crystal size of the tungsten bronze coating of tungsten wires can be considerably decreased by adding sodium chloride to the Na₂WO₄/WO₃ melt, and this result in a very desirable decrease of response times. M. Mann et al. [16] have previously reported this effect of NaCl in the synthesis of tungsten bronze powders. We can show in this paper, that the decrease of crystal size of the tungsten bronze coating of tungsten wires leads to considerably decreased response times (time constants).

2. Experimental

2.1. Chemicals

Coiled tungsten wires (0.25 mm coil diameter, 0.08 mm wire diameter, 9.3 cm length) produced for incandescent lamps (NARVA Berlin, former GDR), Na₂WO₄ × 2H₂O (Merck, Germany), WO₃ (Sigma-Aldrich, USA) and NaCl (> 99%, Sigma-Aldrich, USA) were used for electrode preparation. Standard buffer solutions (pH between 2.00 ± 0.02 and 10.00 ± 0.02) were purchased from Merck, Germany. HCl, NaCl, KCl, CaCl₂ and MgCl₂ (Merck, Germany) were used to determine the selectivity coefficients under the same procedure reported previously [2].

2.2. Electrode preparation

The preparation of the electrodes is described in [1,2]. 1.0 cm of the tungsten wires were immersed in a melt of Na₂WO₄ and WO₃

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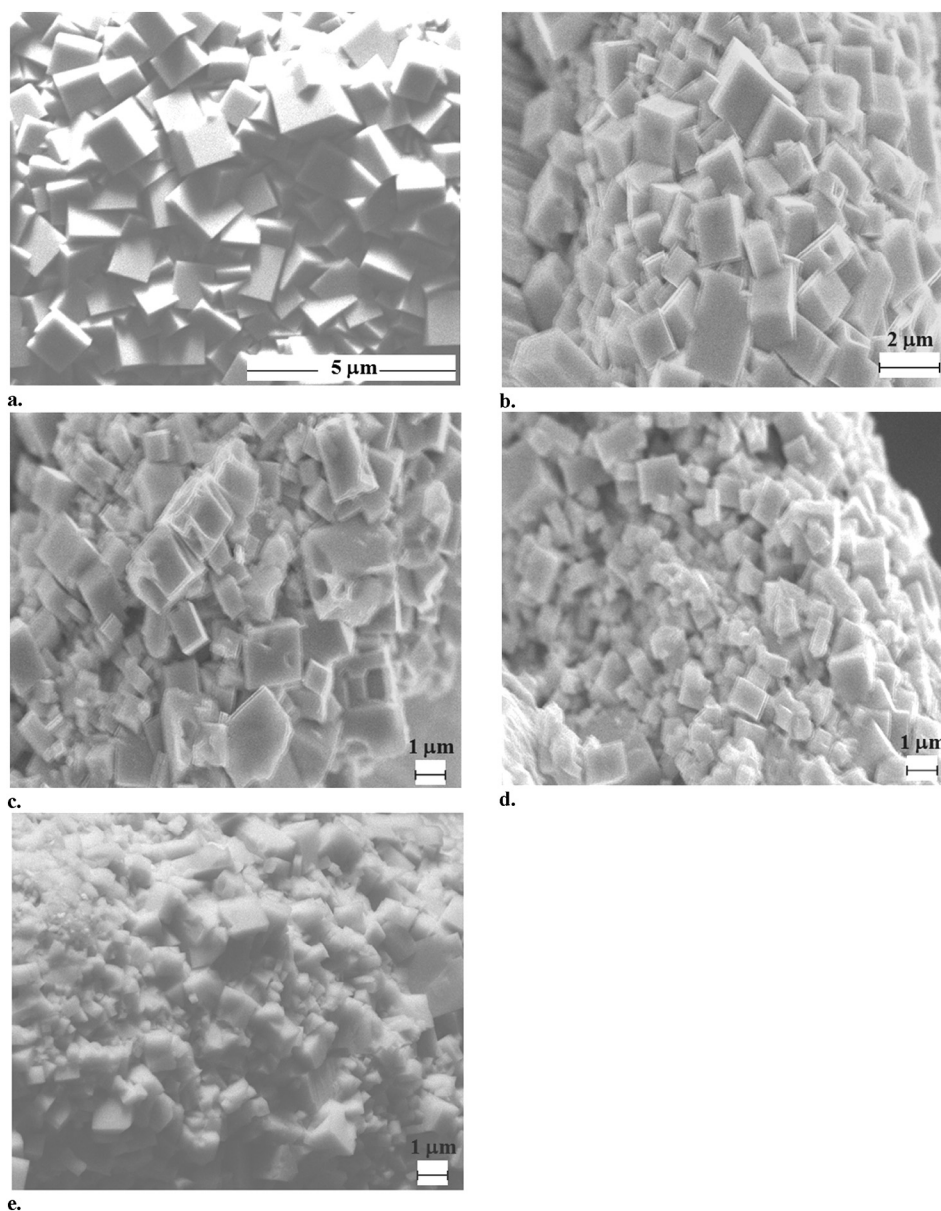
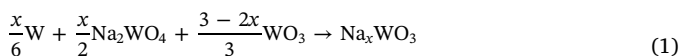


Fig. 1. SEM micrographs of W/Na_xWO_3 : a. WB1 (0% NaCl in melt), b. WB_a (10% NaCl in melt), c. WB_b (20% NaCl in melt), d. WB_c (30% NaCl in melt), and e. WB_d (40% NaCl in melt).

(1:1 molar ratio, 690 °C). The oxidation follows the reaction:



The melt contained 10 (WB_a), 20 (WB_b), 30 (WB_c), 40% (WB_d) of NaCl. The immersion time was 5 s. This time was chosen because a thinner film was obtained with shorter response times with respect to a higher immersion times [2]. After oxidation, the wires were cooled down, washed with diluted hydrochloric acid and deionized water and finally cleaned in an ultrasonic bath for 10 min in deionized water. The wires were fitted into micropipette tips so that only the bronze covered part of the wire was exposed to the solutions. The experimental results were compared with a tungsten/tungsten bronze electrode without NaCl added in the melt (WB1).

2.3. Measurement equipment

Forty modified W/Na_xWO_3 electrodes were glued as close as possible to each other onto a glass plate (1 cm²) for XRD diffractometry (normal Bragg-Brentano geometry) regarding crystallographic phases and preferential orientations. XRD was performed on a Bruker D8

Advance diffractometer (Cu K α radiation (40 kV, 30 mA)) equipped with Göbel mirror. Image analysis of tungsten bronzes was performed using a SEM (EVO/MA10 Karl Zeiss, Germany) at magnifications of 30,000–50,000.

Potentiometry was performed using a CHI 620D workstation (CH Instruments Inc., USA). A Saturated Calomel Electrode ($E = 0.242$ V vs. SHE) was used as reference electrode (Bas Inc., Japan).

3. Results and discussions

3.1. XRD

XRD has shown that the composition of the tungsten bronze was the same as published previously. We assume that the addition of NaCl only affected the surface tension, density and viscosity of the melt, as mentioned in Ref. [16].

3.2. SEM

The scanning electron microscopy (SEM) micrographs of the tungsten bronzes WB_a, WB_b, WB_c and WB_d deposited onto W electrodes are

Table 1
Crystal size for tungsten bronze samples.

% NaCl in the Na ₂ WO ₄ /WO ₃ melt	Electrode	Crystal size (average)/nm
0	WB1	1238
10	WB _a	1101
20	WB _b	560.8
30	WB _c	469.1
40	WB _d	389.0

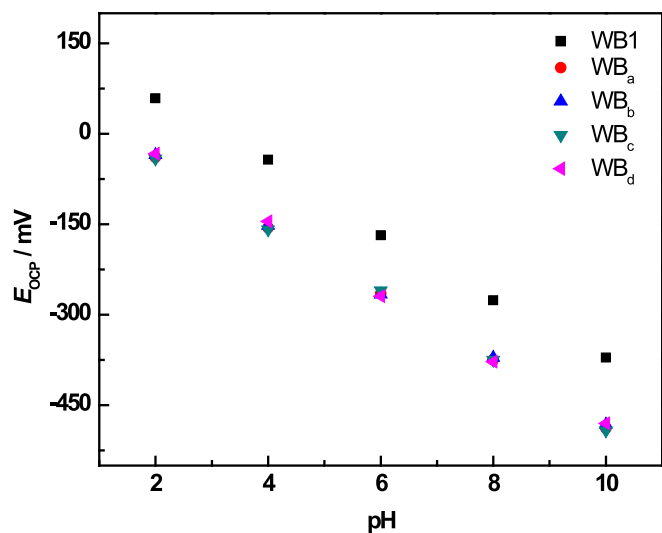


Fig. 2. Dependence of E_{OCP} of WB_{a-d} and WB1 on pH of the solution. 25 °C.

shown in Fig. 1. Crystal cubes of various sizes are visible in all the images. Fig. 1a shows the morphology of WB1 electrode (without NaCl) with a crystal size range between 0.9 and 1.6 μm with an average of 1.2 μm . Fig. 1b, c, d, e and Table 1 show clearly that the crystal size decrease when the NaCl concentration increases in the Na₂WO₄/WO₃ melt. The crystals still exhibit a distribution of sizes. The experiments demonstrate the possibility to synthesize nanocrystals of tungsten bronze Na_{0.75}WO₃: at 40% NaCl the smaller fractions of crystals have an average size of 125 nm.

The images analyses showed that the presence of NaCl in the melt modified only the crystal size of the bronze crystals. Similar results have been obtained in another conventional solid-state reaction [17].

3.3. pH measurements

The open circuit potentials (E_{OCP}) of the electrodes (WB_{a-d}) were measured in different commercial buffer solutions (between 2 and 10). The potentials were read when the final drift was less than 0.1 mV min⁻¹. Fig. 2 shows that all the electrodes exhibit a linear response in the pH range 2 to 10. The potentials and the slopes of the tungsten bronze electrodes are highly reproducible (no significant difference at $p = 0.05$) due to the reproducibility of their composition,

Table 2

E_{OCP} of WB_{a-d} and WB1 vs. Ag/AgCl (3 M KCl) at different pH values, and resulting slopes of the E_{OCP} -pH curves at 25 °C. Three electrodes were prepared and tested for each W/Na_xWO₃ sample.

pH	$E_{OCP,WB1}$ in mV	E_{OCP,WB_a} in mV	E_{OCP,WB_b} in mV	E_{OCP,WB_c} in mV	E_{OCP,WB_d} in mV
2	59 ± 1	-39 ± 1	-35 ± 2	-41 ± 1	-33 ± 2
4	-43 ± 1	-156 ± 1	-152 ± 1	-159 ± 1	-145 ± 1
6	-168 ± 2	-265 ± 2	-266 ± 2	-260 ± 1	-269 ± 2
8	-276 ± 4	-375 ± 1	-371 ± 2	-375 ± 2	-378 ± 3
10	-371 ± 7	-488 ± 3	-482 ± 1	-492 ± 3	-480 ± 4
Slope in mV (pH-unit) ⁻¹	-54.7 ± 0.4	-55.9 ± 0.1	-55.7 ± 0.1	-55.9 ± 0.1	-56.4 ± 0.1

Table 3

Dependence of the experimentally determined time constants τ on pH for the different tungsten bronze electrodes (three electrodes were tested for each W/Na_xWO₃ sample).

Electrode	$\tau_{pH=2/s}$	$\tau_{pH=4/s}$	$\tau_{pH=6/s}$	$\tau_{pH=8/s}$	$\tau_{pH=10/s}$
WB1	38 ± 2	32 ± 3	31 ± 2	27 ± 3	26 ± 1
WB _a	36 ± 3	37 ± 2	34 ± 4	31 ± 2	26 ± 3
WB _b	28 ± 4	30 ± 3	25 ± 5	20 ± 3	19 ± 2
WB _c	21 ± 1	24 ± 5	22 ± 2	20 ± 5	17 ± 4
WB _d	15 ± 3	18 ± 2	15 ± 1	14 ± 2	13 ± 2

Table 4

Selectivity coefficients ($k_{A,B^{POI}}$) determined by fixed interference method.

Ion	Selectivity coefficient WB1	Selectivity coefficient WB _d
Na ⁺	6 × 10 ⁹	1 × 10 ⁸
K ⁺	2 × 10 ⁹	7 × 10 ⁹
Ca ²⁺	2 × 10 ⁹	6 × 10 ⁹
Mg ²⁺	7 × 10 ⁹	9 × 10 ⁹

with a near-Nernstian slope (cf. Table 2). In more alkaline solutions (pH above 10) tungsten bronze dissolve and the electrode potentials are unstable.

E_{OCP} of electrodes WB_{a-d} are 100 mV more negative respect to WB1 (without NaCl in the synthesis procedure). This is attributed to changes in acid-base properties of nanostructures as such properties are known to change markedly with the domain size [18]. All electrodes exhibited a linear response in the pH range studied.

3.4. Time response

The aim of this study was to decrease the time response of tungsten bronze electrodes by synthesis of smaller tungsten bronze crystals, which was achieved by adding different amounts of NaCl to the synthesis melt. The time constants of the electrodes were determined according to IUPAC recommendations [19]. Table 3 shows the dependence of experimentally determined time constants τ on pH for the different tungsten bronze electrodes WB_a to WB_d.

The data in Table 3 clearly show that the time constants decrease with decreasing size of the tungsten bronze crystals, i.e., with increasing sodium chloride concentration in the melt for syntheses. Shorter time constants may be caused by smaller crystal size. However, since the kinetic model of response is not known, yet, we do not want to speculate about the underlying reasons. Additionally, one sees, that the time constants decrease with increasing pH, which may be due to thinner reaction layers for solutions with lower proton activity.

Long term stability of WB_d electrodes were performed under air storing over 6 months. The potential responses of the electrodes (pH range 2–10) were reproducible over the time studied and no aging effects were observed (slope -56.1 ± 0.3, three electrodes were tested). Comparing with long term stability of WB1 reported previously, when the crystal size decreases, the long term stability increases. Potential responses of WB_d were also measured in the same pH range in order to study the repeatability of the measurements every day for one

week. The electrode responses are repeatable over the time (slope -56.4 ± 0.6 , three electrodes were tested).

The selectivity coefficients $k_{A,B}^{\text{pot}}$ for Na^+ , Li^+ , Mg^{2+} , Ca^{2+} were determined with WB_4 electrodes by the fixed interference method [20] and then compared with those reported previously [2]. As is shown in Table 4, the interference of common cations in the pH range 2 to 10 is similar to the reported for WB_1 .

4. Conclusions

The results reported in this paper demonstrate, that a tungsten bronze layer synthesized on the surface of tungsten metal wires can consist of nano size crystals, provided that NaCl is added to the $\text{Na}_2\text{WO}_4/\text{WO}_3$ melt. The considerable decrease of time constants of response is obviously due to the decrease of crystal size. No convincing explanation of the reasons for the decreased time constants can yet be offered, because the response is due to a surface equilibrium, and the crystal volume is not involved.

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