



# The electrode responses of a tungsten bronze electrode differ in potentiometry and voltammetry and give access to the individual contributions of electron and proton transfer



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## ABSTRACT

A tungsten wire covered with  $\text{Na}_{0.75}\text{WO}_3$  acts in potentiometry as a reversible pH electrode having a pH dependent open-circuit potential  $E_{\text{ocp}}$  with Nernstian slope. The mid-peak potential  $E_{\text{mp}}$  of cyclic voltammograms also depends on pH. At low pH (e.g., pH 2) and slow scan rates (e.g.,  $2 \text{ mV s}^{-1}$ ) the voltammetric response is almost completely reversible. At higher pH and faster scan rates, the voltammetric systems exhibit features of increasing irreversibility. Under the conditions of reversibility, the  $E_{\text{ocp}}$  and  $E_{\text{mp}}$  differ significantly.  $E_{\text{ocp}}$  is determined by the proton transfer at the electrode surface; whereas  $E_{\text{mp}}$  is determined by the electron transfer equilibrium tungsten(VI)/tungsten(V) and the proton transfer at the electrode surface. The difference between  $E_{\text{ocp}}$  and  $E_{\text{mp}}$  provides the individual thermodynamic contributions of electron and proton transfer to the overall pH dependent redox electrode. This is the first time that both contributions can be separated for an insertion electrochemical system (thin surface layer). It is also shown for the first time that the mechanism of an ion-sensitive electrode can differ in potentiometry and voltammetry.

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## 1. Introduction

Tungsten metal behaves as a pH electrode [1–3]. Also various tungsten bronzes act as pH electrodes, different response mechanisms have been discussed [4–6]. Here we show that a tungsten wire can be covered by a layer of tungsten bronze of very reproducible composition ( $\text{Na}_{0.75}\text{WO}_3$ ) when the tungsten wire is oxidized in a  $\text{Na}_2\text{WO}_4/\text{WO}_3$  melt. Surprisingly, the surface oxidation of the tungsten wire always resulted in pure well-ordered crystal layers of  $\text{Na}_{0.75}\text{WO}_3$  with cubic perovskite structure. These electrodes exhibit a pH dependent open-circuit potential  $E_{\text{ocp}}$  in potentiometry, and a pH dependent mid-peak potential  $E_{\text{mp}}$  in cyclic voltammetry (CV).  $E_{\text{ocp}}$  is determined by the proton transfer equilibrium between the electrode surface and the solution, whereas  $E_{\text{mp}}$  is determined by the electron and proton transfer equilibria. This offers the unique opportunity to separate the thermodynamic contribution of electron and ion transfer in case of a solid insertion electrochemical system, for which that has never been described before. So far, such separation was only possible for three-phase systems, where two phases were liquid [7–9].

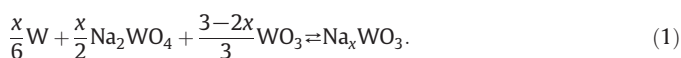
## 2. Experimental

### 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),  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (Fluka, Germany) and  $\text{WO}_3$  (Reachim, former USSR) were used for electrode preparation. The pH response of the electrodes was monitored in buffer solutions (pH between  $2.00 \pm 0.02$  and  $10.00 \pm 0.02$  (Merck, Germany)). Buffer pH = 1.04 was prepared by dissolving 0.1863 g KCl (Merck, Germany) in 98 mL deionized water, and adjusting the pH by addition of concentrated hydrochloric acid (Merck, Germany).

### 2.2. Electrode preparation

1.0 cm of the tungsten wires was immersed in a melt of  $\text{Na}_2\text{WO}_4$  and  $\text{WO}_3$  (1:1 molar ratio, 690 °C). The oxidation follows the reaction:



The immersion time was varied between 5 and 30 s. 5 s oxidation gave the fastest responding electrodes. After oxidation, they were cooled down, washed with diluted hydrochloric acid and deionized

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water and finally cleaned in an ultrasonic bath for 10 min in deionized water. The electrodes were fitted into micropipette tips or glued into glass capillaries so that only the bronze covered part of the wire was exposed to the solutions.

### 2.3. X-ray diffractometry

Forty modified  $W/Na_xWO_3$  electrodes were glued as close as possible to each other onto a glass plate (area =  $1\text{ cm}^2$ ) for X-ray diffractometry (normal Bragg–Brentano geometry) regarding crystallographic phases and preferential orientations. XRD was performed on a Seifert XRD 3000  $\theta$ – $\theta$  diffractometer (Cu  $K\alpha$  radiation (40 kV, 40 mA)) equipped with Goebel mirror.

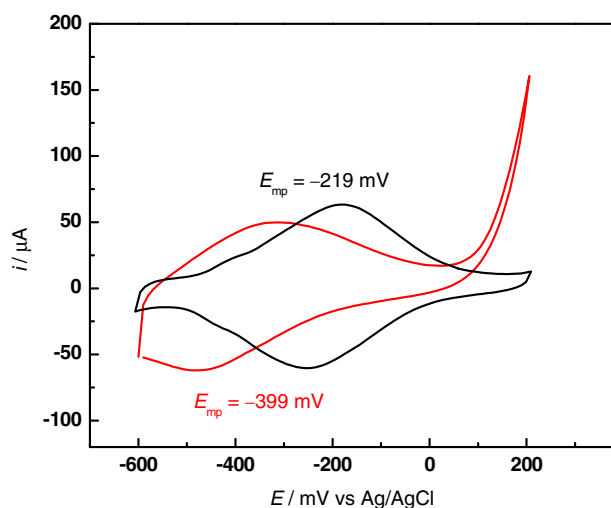
### 2.4. Electrochemical measurements

$E_{ocp}$  was measured against a Ag/AgCl (3 M KCl) ( $E = 0.208\text{ V}$  vs. SHE) reference electrode (Metrohm, Switzerland) using a  $\mu$ AUTOLAB Potentiostat/Galvanostat (Eco Chemie, The Netherlands) in unstirred solution. Solutions were thermostated (GFL 1022, Germany). The same instrumentation was used for CV where a platinum sheet served as counter electrode. For CV, solutions were deaerated 20 min with pure nitrogen, if necessary.

## 3. Results and discussion

### 3.1. The electrode response

The tungsten bronze on the tungsten wires showed in all experiments the same composition, i.e.,  $Na_{0.75}WO_3$  (XRD). The  $E_{ocp}$  approached rather quickly constant values (response times 20–40 s), and the slope of  $E_{ocp}$  versus pH was  $-58.3\text{ mV}$  at  $25^\circ\text{C}$ , when the electrodes were pre-conditioned by (a) cyclic voltammetry (2 cycles between  $-600$  and  $200\text{ mV}$ , scan rate  $20\text{ mV s}^{-1}$ ) and (b) performing a potentiostatic pretreatment at  $E_{mp}$  for 2 min. Without that pretreatment, the slope was  $-54.8\text{ mV}$ . The properties of the electrode for analytical pH determinations will be published in a separate paper. The individual tungsten bronze electrodes exhibit highly reproducible potentials, which is certainly a result of the reproducibility of their composition, and a resulting high reproducible potential drop at the interface between tungsten metal and tungsten bronze.



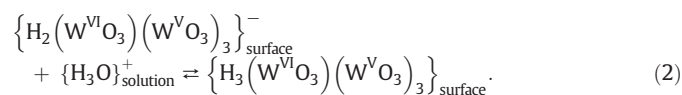
**Fig. 1.** Cyclic voltammograms of tungsten bronze electrode (W oxidized for 5 s in melt). pH = 2 (black line) and pH = 4 (red line) at  $25^\circ\text{C}$ . Scan rate =  $20\text{ mV s}^{-1}$ , deaerated solutions. Electrolyte: buffer solutions given in Experimental.

The tungsten bronze electrodes showed an almost reversible redox system in cyclic voltammetry (Fig. 1). The peak separation was a function of pH and scan rate: at pH 2 and  $2\text{ mV s}^{-1}$  the peak separation was below  $40\text{ mV}$  (approaching thin-layer behavior), with  $20\text{ mV s}^{-1}$  it was  $75\text{ mV}$ , with  $100\text{ mV s}^{-1}$  it was  $77\text{ mV}$ , and at pH 4 ( $100\text{ mV s}^{-1}$ ) it was  $165\text{ mV}$ , and  $121\text{ mV}$  at pH 8 ( $100\text{ mV s}^{-1}$ ). Fig. 2 shows a plot of  $E_{ocp}$  and  $E_{mp}$  as a function of pH. The  $E_{ocp}$  was measured with the as-such prepared electrodes (not shown), and also after the before mentioned voltammetric and potentiostatic pretreatment. The latter was made to condition the electrode surface so that it will have equal activities of W(V) and W(VI), to make the measurement comparable with the  $E_{mp}$  data. Without pretreatment the  $E_{ocp}$  at pH 2 to 8 were 52 to  $85\text{ mV}$  more positive and the slope versus pH was  $-54.8\text{ mV}$  per pH unit.

### 3.2. The electrode response in potentiometry

The composition of the tungsten bronze was  $Na_{0.75}WO_3$  ( $= Na_3(W^{VI}O_3)(W^VO_3)_3$ ). Since all measurements (potentiometric and voltammetric) have been performed with electrodes conditioned in aqueous electrolytes, it is highly probable that sodium ions of the most upper layer of the bronze were substituted by protons yielding  $H_3(W^{VI}O_3)(W^VO_3)_3$  ( $= (W^{VI}O_3)(W^VO_2OH)_3$ ). This layer possesses W(V)OH surface moieties (cf. Fig. 3).

At that surface an interfacial potential difference establishes according to:

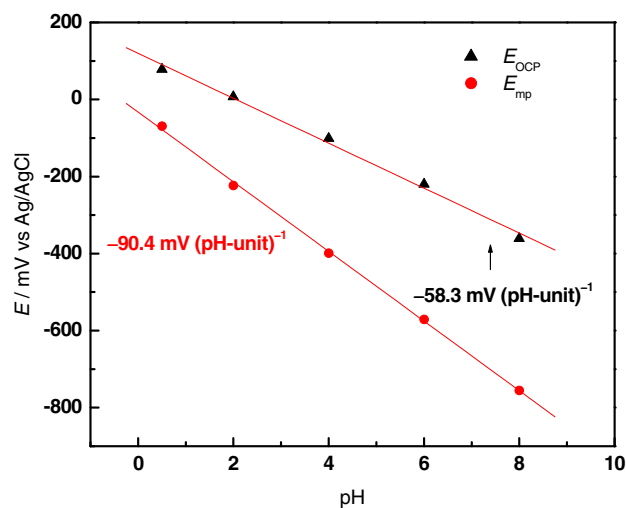


This is completely analogous to the equilibrium at a glass electrode [10,11]. The resulting  $E_{ocp}$  can be described by the following equation:

$$\begin{aligned} E_{ocp} &= E_{PT}^{\ominus} + \frac{RT}{F} \ln \frac{a_{\{H_2(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}}{a_{\{H_3(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}} \frac{a_{H_3O^+}}{a_{\{H_2(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}} \\ &= E_{PT}^{\ominus} + \frac{RT}{F} \ln \frac{a_{\{H_2(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}}{a_{\{H_3(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}} + \frac{RT}{F} \ln a_{H_3O^+} \end{aligned} \quad (3)$$

A formal potential of the systems can be defined as follows:

$$E_{c, PT}^{\ominus} = E_{PT}^{\ominus} + \frac{RT}{F} \ln \frac{a_{\{H_2(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}}{a_{\{H_3(W^{VI}O_3)(W^VO_3)_3\}_{\text{surface}}}} \quad (4)$$



**Fig. 2.** Dependence of  $E_{ocp}$  and  $E_{mp}$  on pH. (W oxidized for 5 s in melt). Temperature  $25^\circ\text{C}$ , CV: scan rate  $100\text{ mV s}^{-1}$ , deaerated solutions.

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