

Scientific paper

Tungsten – Tungsten Trioxide Electrodes for the Long-term Monitoring of Corrosion Processes in Highly Alkaline Media and Concrete-based Materials

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Abstract

The determination of pH in highly alkaline solutions and concrete materials is extremely important for monitoring or predicting the corrosion processes of reinforced concrete structures and to follow the hydration process of Portland cement, fly-ash, micro silica and other materials used in concrete manufacturing. The corrosion of reinforced concrete structures and the hydration of pozzolanic materials are long-term processes, which means, that appropriate durable, and resilient pH electrodes are needed, for direct implantation regarding solid concrete bodies.

The purpose of this work was to characterise the potentiometric and surface properties of tungsten electrodes after exposure to extreme alkaline solutions. The tungsten wire surface was activated at 800 °C for 30 min within an oxygen flow. The formation of homogenous and compact multiple layers of WO₃ crystals was observed using X-ray diffraction and scanning electron microscopy. X-ray diffraction of those tungsten electrodes exposed to saturated calcium hydroxide solution or the pore-water of cement-based materials during 10 months, indicated partly dissolved WO₃. Two new compounds appeared on the electrodes surfaces; pure tungsten and CaWO₄. The presence of tungsten was affecting any potentiometric response in acidic pH region (2–5) but in pH 5–12 region the response still remained linear with a slope of 42 ± 2 mV/pH unit.

The W/WO₃ electrode was suitable for the long-term monitoring of corrosion processes in concrete-based materials according to the pH changes as it has stable and repeatable responses to alkaline solutions (pH > 12). All the tested interfering ions had no significant influence on electrode potential. The W/WO₃ electrode is simple, robust, inexpensive, and temperature resistant and can be applied in potentiometric titrations as well as in batch and flow-injection analysis. The prepared electrode is a highly promising pH sensor for the monitoring of pH changes in highly alkaline capillary water of concrete.

Keywords: Potentiometry, pH, tungsten – tungsten trioxide, pore water, concrete, flow-injection analysis.

1. Introduction

Tungsten trioxide (WO₃) has been used in several applications since Meixner et al.¹ and Shuk et al.² introduced semiconducting metal oxides as promising gas and pH sensors. Over the last few years, the development of tungsten oxides nanostructures has improved further pro-

perties of gas sensors for the detection of H₂S, NO₂, and O₃.^{3–5} In potentiometry, WO₃-electrodes are mainly used in flow-injection systems as pH sensors⁶ or for indirect determination of carboxylic acids^{7,8}, of total inorganic carbon in water⁹, of trimethylamine¹⁰, and of volatile basic nitrogen in seafood.¹¹ In batch potentiometry pure-tungsten wire electrodes are used for measuring pH during mining and sugar industry processes under more extreme

conditions (strongly alkaline media, high and oscillating temperatures, the presence of suspended particles).¹² The WO_3 electrode surface is also used for monitoring hydrogen ion activity within a latex polymerization system.¹³ The properties of this electrode were studied at different temperatures and the response explained as a mixed potential resulting from two processes: an anodic ($\text{W} + 3\text{H}_2\text{O} \rightleftharpoons \text{WO}_3 + 6\text{H}^+ + 6\text{e}^-$) and a cathodic ($2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$). Ultramicrosensors based on the electrodeposition of WO_3 on tungsten wires were used within a wide pH range (from pH 2 to pH 12) with a super-Nernstian slope of 53.5 mV/pH unit.¹⁴ The response of the electrode was described by a proton-dependent redox reaction ($\text{WO}_3 + n\text{H}^+ + n\text{e}^- \rightleftharpoons \text{H}_n\text{WO}_3$). Fenster et al.¹⁵ recently published nanoscale structures of tungsten oxide, which were successfully introduced as pH sensors in small systems. The electrochemical behaviour of tungsten in alkaline media was already been discussed in detail.^{16,17} In NaOH solutions tungsten is electro-oxidised producing species with different oxidation states:

- below -0.9 V ($\text{WO}_3 + n\text{H}^+ + n\text{e}^- \rightleftharpoons \text{H}_n\text{WO}_3$) “tungsten bronze (H_nWO_3)” is formed,
- from -0.7 V to $+0.3$ V the oxidation state W^{6+} is favored ($\text{W} + 8\text{OH}^- \rightleftharpoons \text{WO}_4^{2-} + 4\text{H}_2\text{O} + 6\text{e}^-$),
- from the 0.3 V to 1.0 V electro-formations of different tungsten oxides (stoichiometric WO_2 , WO_3 and non-stoichiometric $\text{WO}_{2.72}$, $\text{WO}_{2.90}$, $\text{WO}_{2.96}$) has been reported but mainly WO_3 is formed.¹⁶ In Na_2CO_3 solutions, tungsten is electro-oxidised similarly to that in NaOH solutions. The main difference is within the potential range from $+0.1$ V to $+0.3$ V, where the concentration of OH^- is affected by the equilibrium between CO_3^{2-} and HCO_3^- . Here soluble tungstate species are formed by the electro-oxidation of tungsten and the participation of carbonate ions through hydrolysis affects the equilibrium.¹⁷ To our knowledge, the surface properties and application of W/ WO_3 electrodes in the highly alkaline or pore-water of cement based materials have, as yet been unreported. The determination of pH in this type of solution is extremely important for monitoring or predicting the corrosion processes of reinforced concrete structures. The main purpose of this work was, therefore, to study long-time the potentiometric response of W/ WO_3 electrode surfaces after their exposure to extreme alkaline solutions.

2. Experimental

2.1. Chemicals and Solutions

All the chemicals used were of analytical grade purity. All solutions were prepared with deionised water. The following stock solutions were prepared for pH study: $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 mol/L, pH = 4.44). Na_2HPO_4 (0.1 mol/L, pH = 9.16) and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (0.1 mol/L, pH = 12.26) (Kemika Zagreb). Buffer solutions from pH 2 to 12

were fresh prepared daily by mixing the basic solutions with H_3PO_4 (0.1 mol/L), and NaOH, (0.1 mol/L) until the desired pH was reached. The pH measurements were controlled using CRM NIST buffers from Mettler (pH 4.00, 7.01 and 9.21).

2.2. Preparation of W/ WO_3 Electrodes

Pure tungsten wires (Aldrich) (99.99%) of 0.6 mm in diameter and 12 mm length were thoroughly rinsed in deionised water and ethanol. The wires were heat-treated in an oven at 800 °C for 30 min under an oxygen stream. The colour of the tungsten wires became yellow-green, which indicated oxidation of the surface layer. After preparation, the electrodes were connected to a coaxial cable and adhered with epoxy resin in a stainless-steel electrode holder. The electrodes were stored in dark and dry place before use.

2.3. Apparatus

W/ WO_3 wires were analysed by an X-ray diffractometer (AXS Bruker/Siemens® D5005) with $\text{CuK}_{\alpha 1}$ radiation ($\lambda = .54060$ Å) at 20 °C, for structural properties. A positionally-sensitive detector was used (potential 40 kV, current 30 mA) with a rotation of 30 RPM within the range $10^\circ < 2\theta < 70^\circ$ with a step of 0.0358° and a scanning speed of 1s/step, for detection. A pure (99.999%) aluminium holder was selected when fixing and positioning the electrodes.

The surface morphology of the electrodes was studied by a scanning electron microscope (FE-SEM SUPRA 35 VP Carl Zeiss). All pictures were recorded using a 30 µm scan window and 1 kV potential.

A pH/ion-meter (MA235 Mettler) with a combined glass (InLab Micro Pro) electrode was used for pH measurements (buffer solutions and potentiometric titrations).

All other potentiometric data were recorded using a mV/pH-meter (type 301, Hanna Instruments) and transferred to a personal computer via a RS232 interface using corresponding software (HI9200 – 2.8 Hanna Instruments).

All potentiometric measurements were carried out at 25 ± 1 °C. The saturated calomel electrode (SCE) with a salt bridge (0.5 M KNO_3) was used as a reference electrode.

The flow-injection analysis (FIA) system consisted of a peristaltic pump (MCP CA-4, Ismatec) connected to a 100 µL injection valve (model 5020 Rheodyne) through Teflon tubing of 0.5 mm i.d. The W/ WO_3 wire electrode was positioned 80 cm behind the injection valve in an extended Teflon tube (1.0 mm i.d.). The SCE was positioned next to the W/ WO_3 wire electrode in an 0.5 mL Teflon funnel. FIA parameters were optimised by changing the flow rate and the composition of the flow-stream.

3. Results and Discussion

3.1. Surface analysis of W/WO₃ electrodes

Three different preparation procedures of tungsten wires coated with tungsten oxides are reported in the literature.^{18,19} A dark brown–blue colouration was observed after conditioning tungsten in alkaline solutions (KOH).⁶ A mixture of brown tungsten dioxide (WO₂) and blue ditungsten pentoxide (W₂O₅) formed on the surface of the tungsten wire, suggesting where the electrode's surface was activated in hydrogen at high temperatures.¹⁸ Macdonald et al. prepared black films of tungsten oxide by oxidation of tungsten wires in a CH₄ stream¹³. In most studies tungsten wires were typically heated at 500 °C for 1 h.^{7–11} Yellow-green surface was formed and was ascribed to the formation of pure tungsten trioxide. The size of the crystallites and their specific surface area were affected by the temperature when tungsten trioxide was prepared from the precipitation method.²⁰ It was demonstrated that higher temperatures of calcination (800 °C) caused evident crystal growth compared to the experiment at 600 °C (prolonged exposure up to 12 h at 800 °C did not affect the crystal growth). Temperature is important and affects the crystal size that is approximately 0.3 μm at 500 °C and up to 3 μm at 800 °C. When WO₃ thin-films for the detection of NO_x were tested, structural changes of WO₃ were observed – the triclinic phase of WO₃ was transformed into a tetragonal phase when the temperature was increased to 800 °C.²¹

According to the described advantages in the formation of WO₃^{20,21} the tungsten wires were treated at 800 °C for 30 min in the work presented here. In order to ensure an oxidizing environment and to stimulate the formation of a single phase of tungsten oxide on the electrode surface an oxygen stream was additionally applied du-

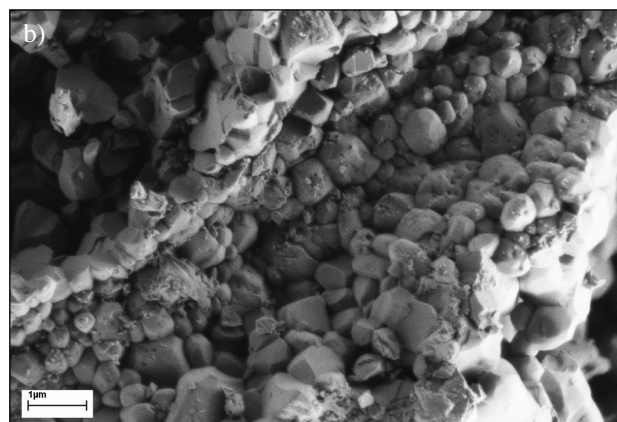
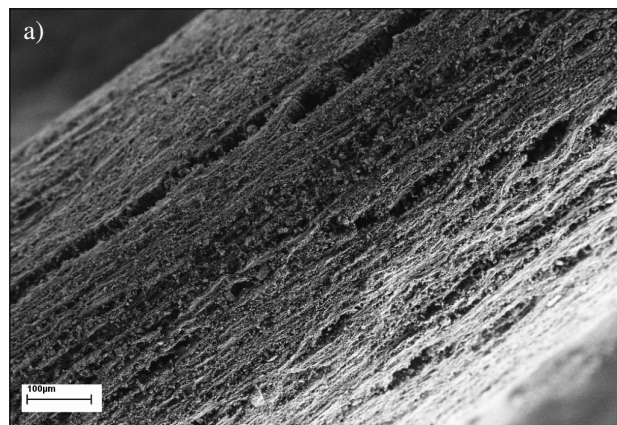


Figure 1: a.) SEM of freshly-prepared W/WO₃ electrode's surface at 300X, b.) at 7500X.

ring the heating. The surface became yellow to light yellow-green after electrode treatment. Figure 1a presents the SEM of the freshly prepared electrode surface with a

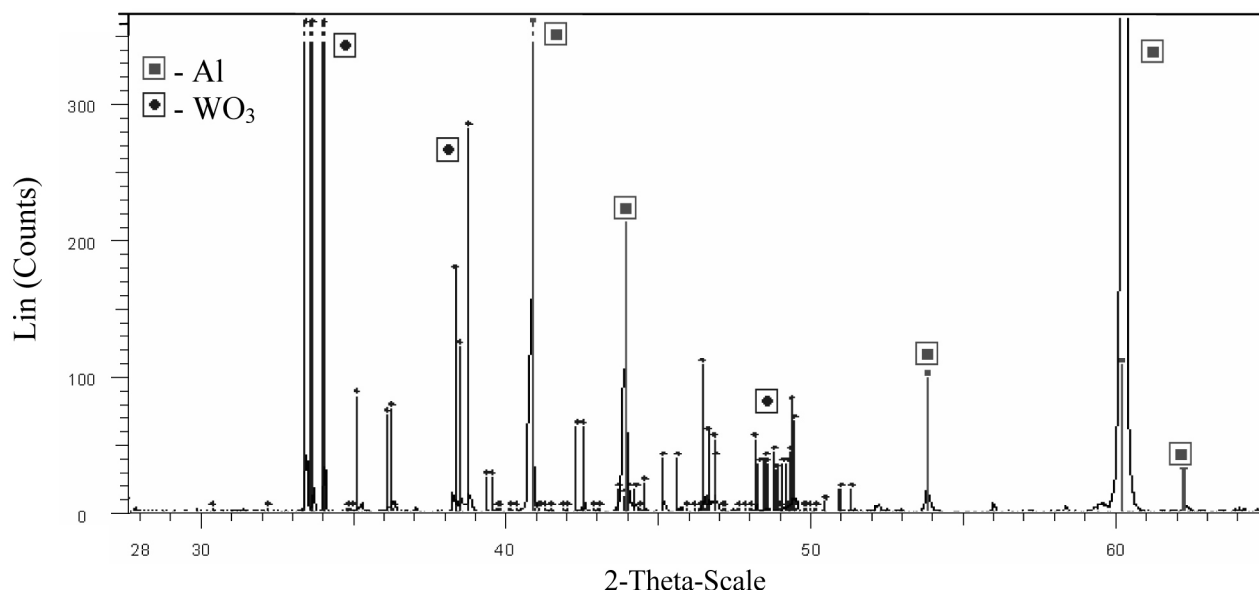


Figure 2: XRD of freshly-prepared W/WO₃ electrode's surface.

magnification of 300 times. The detail of the electrode surface is shown in Figure 1b (magnification 7500 times) and presents a homogenous and compact formation of multiple layers of crystals (the crystal sizes vary from approximately 0.3 μm to 1.5 μm). A XRD was used (an aluminium holder was chosen for positioning the electrode) for characterization of these crystals. The XRD scan in Figure 2 presents two peaks, the background peak of the aluminium, and a peak characterized as pure WO_3 . For potentiometric applications, it is important that a stoichiometric and thick uniform layer of WO_3 forms on the electrode's surface. This was confirmed by XRD, since no other peaks were presented (for example peaks of pure tungsten or non-stoichiometric tungsten oxides). Our observations are comparable with nanoelectrodes based on WO_3 where it was discovered that the thickness of the WO_3 film on the tungsten is crucial for stable properties of the electrodes.¹⁴

Figure 3 shows the XRD scan of W/ WO_3 electrode after storage for 10 months in a saturated $\text{Ca}(\text{OH})_2$ solution. More complex and structural changes can be observed on the surface. WO_3 is still present but the peak is less intensive and two new peaks appear; one is caused by pure tungsten, and the other by CaWO_4 (the background peak of aluminium was filtered out).

The electrode's surface became pale yellow-grey to grey on the visual scale. The dissolution of WO_3 was also confirmed by SEM (Figures 4a and 4b). The SEM in Figure 4a shows that the electrode's surface became rough, turgid, and wrinkled. The SEM picture at a magnification of 7500 times (Figure 4b) uncovers crystals that are non-homogenous and different in shape and size (the crystal size varies at approximately 0.5 μm to 3.5 μm) compared to crystals of pure WO_3 , which are of the same size (Figure 1b).

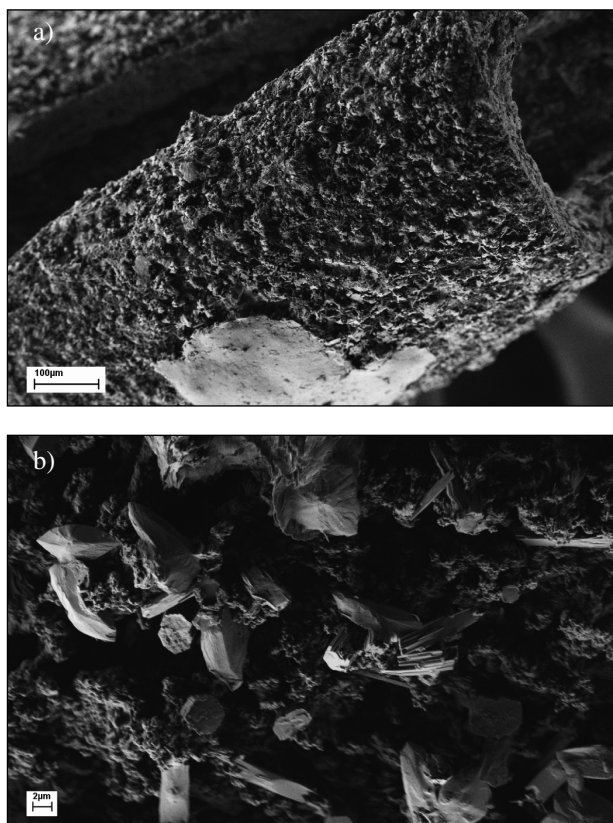


Figure 4: a.) The SEM of the W/ WO_3 electrode's surface stored 10 months in a saturated $\text{Ca}(\text{OH})_2$ solution at 300X, b.) at 7500X.

3. 2. Potentiometric Properties of W/ WO_3 Electrodes

The response of the electrodes to pH changes was studied during potentiometric titrations and in batch and

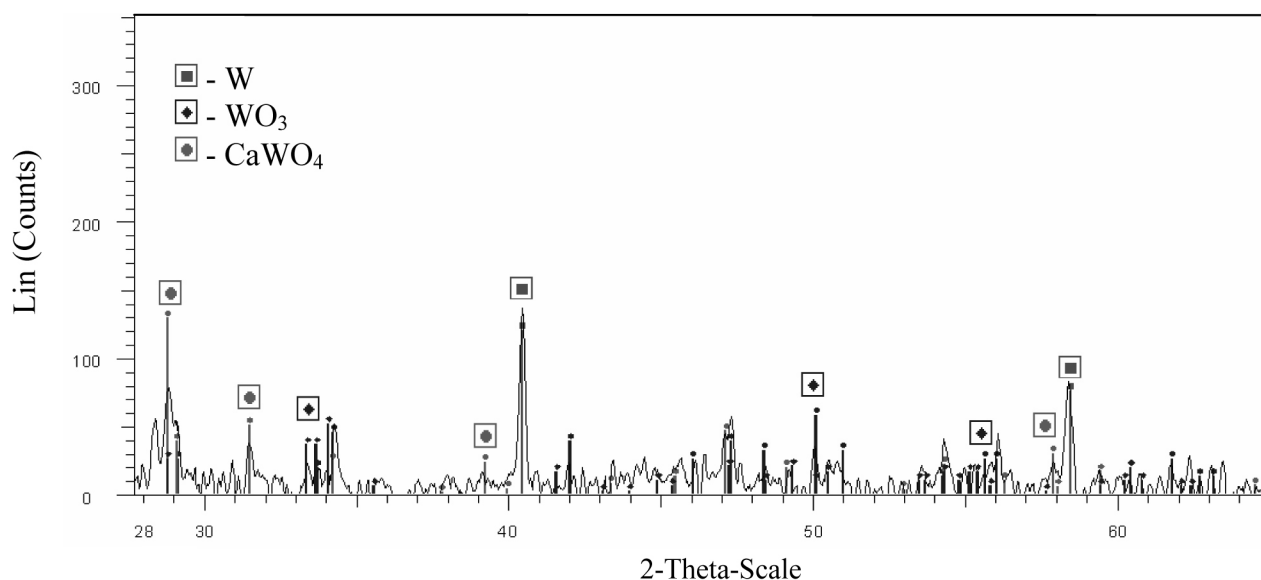


Figure 3: XRD of a W/ WO_3 electrode surface stored for 10 months in saturated $\text{Ca}(\text{OH})_2$ solution.

flow potentiometry. The electrode was used as a pH sensor in different acid-base and base-acid titrations. Figure 5 presents the response of a W/WO₃ electrode when solutions of HCl were titrated with NaOH, and vice versa. In the same picture the response of a commercially-combined glass electrode (InLab Micro Pro) is also displayed. The shape of the titration curve – the start-point, the end-point and the equivalence-point, as indicated by both electrodes are practically identical. The response times of the electrodes are also comparable. The average response time was under 10 s for W/WO₃ electrode.

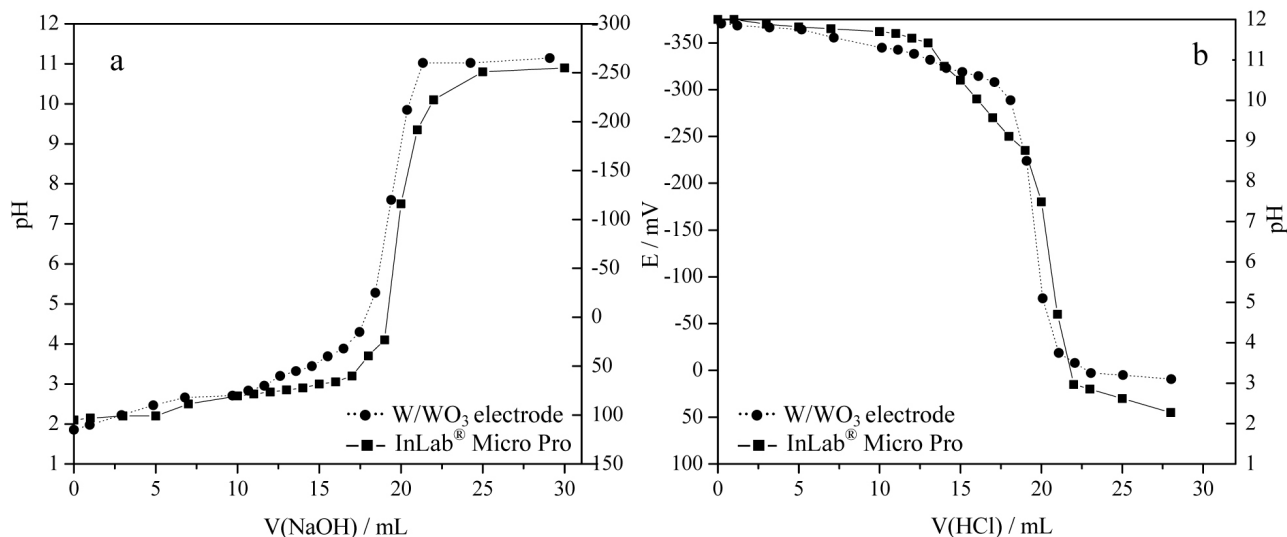


Figure 5: The response of the W/WO₃ electrode used in titrations; a.) titration of 20 mL 0.01M HCl with 0.01M NaOH and b.) titration of 20 mL 0.01M NaOH with 0.01M HCl.

Phosphate buffer solutions (from pH 2 to pH 12) were prepared in order to study the potentiometric properties of the W/WO₃ electrodes during batch analysis. In the literature, the reduction of WO₃ to tungsten according to reaction ($\text{WO}_3 + 6\text{H}^+ + 6e^- \rightleftharpoons \text{W} + 3\text{H}_2\text{O}$) is usually suggested^{7,13} when its response to pH is discussed. Nevertheless, in buffer solution WO₃ can also undergo reversible, proton-dependent redox reaction as follows: ($\text{WO}_3 + n\text{H}^+ + ne^- \rightleftharpoons \text{H}_n\text{WO}_3$).¹⁴ This reversible reaction changes the ratio of the oxide in the film on the surface of the electrode, resulting in membrane potential changes.

Figure 6a displays the response of a freshly prepared W/WO₃ electrode versus pH. In the pH range from 2 to 10 the electrodes ($n = 3$) respond linear with a slope 46 ± 2 mV/pH unit. In the pH region from 10 to 12, the electrodes showed super-Nernstian response. Whenever W/WO₃ electrodes were stored for more than one day in a saturated Ca(OH)₂ solution a decrease of the slope within the pH range from 10 to 12 was observed (Figure 6b), and the electrode response became linear within the whole measured region (slope 45 ± 2 mV/pH unit). The presence of Ca(OH)₂ affected the potentiometric response through the formation of CaWO₄ on the electrode's surfa-

ce. The oxide surface itself became structurally-stable, and a mixed potential WO₃/CaWO₄/W is responsible for a linear response to pH. The electrodes stored in saturated Ca(OH)₂ solutions showed stable and linear responses to pH for several months. Only after a 10 month exposure of electrodes to saturated Ca(OH)₂ solution did the potentiometric response change noticeable (Figure 6c). A slight decrease of the slope (42 ± 2 mV/pH unit from pH 5 to pH 12) and sub-Nernstian response within the range pH 2 to pH 5 were observed. The formation of measurable amounts of tungsten affects those potentiometric proper-

ties that coincide with structural changes, as were discussed previously.

The response of the W/WO₃ electrode to various injected buffer solutions pH (2–12) was studied during flow injection analysis. Using 100 μL of injection volume and a carrier of 0.5 M KNO₃ the optimum flow-rate was 3.5 mL/min (Figure 7). When electrodes had been stored in saturated Ca(OH)₂ solutions, their potentiometric properties (slope, intercept, response time) were comparable to those presented in batch experiments (Figure 6b). The decrease in peak height was only caused by dispersion of the injected samples in FIA. The orientation of peaks changed at -125 mV vs. SCE after injecting neutral or alkaline buffer solutions. When the buffer capacities and pH of the current stream were varied, the peak intensity decreased (the decrease in peak high was observed when injecting solutions from pH 3 to 10). Within this region, the buffer capacity of the current stream is enormous compared to 100 μL of the injected sample and the peak decrease is therefore acceptable. Similar effects were reported previously when carboxylic acids were studied in FIA.^{7,8}

Finally, FIA was used to study sulphate and chloride ions as potential interfering ions when measuring the pH

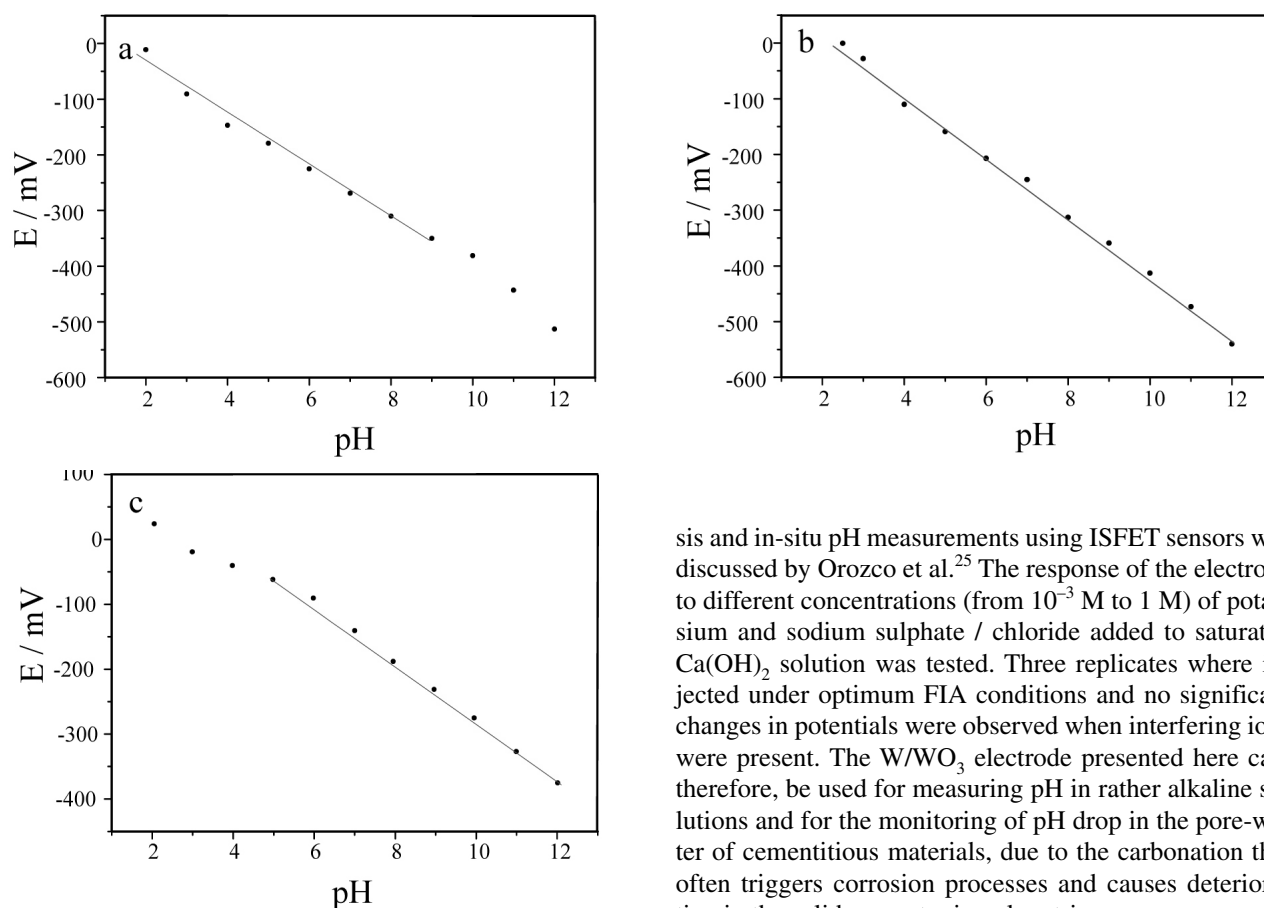


Figure 6: Potentiometric response of W/WO₃ electrode vs. buffer solutions pH (2–12): a.) freshly-prepared electrode, b.) stored one week in saturated Ca(OH)₂ solution, c.) stored 10 months in saturated Ca(OH)₂ solution.

of a pore-water solution. High concentrations of these two anions, together with potassium and sodium cations, are the main constituents of the pore-water of most cement-based materials.^{22–24} The importance of pore-water analy-

sis and in-situ pH measurements using ISFET sensors was discussed by Orozco et al.²⁵ The response of the electrode to different concentrations (from 10⁻³ M to 1 M) of potassium and sodium sulphate / chloride added to saturated Ca(OH)₂ solution was tested. Three replicates were injected under optimum FIA conditions and no significant changes in potentials were observed when interfering ions were present. The W/WO₃ electrode presented here can, therefore, be used for measuring pH in rather alkaline solutions and for the monitoring of pH drop in the pore-water of cementitious materials, due to the carbonation that often triggers corrosion processes and causes deterioration in the solid cement mineral matrix.

4. Conclusions

Tungsten wire electrodes were prepared at 800 °C for 30 min in an oxygen flow. After heat treatment, the electrode's surface became yellow to light yellow-green. The electrode's surface was homogeneously covered by

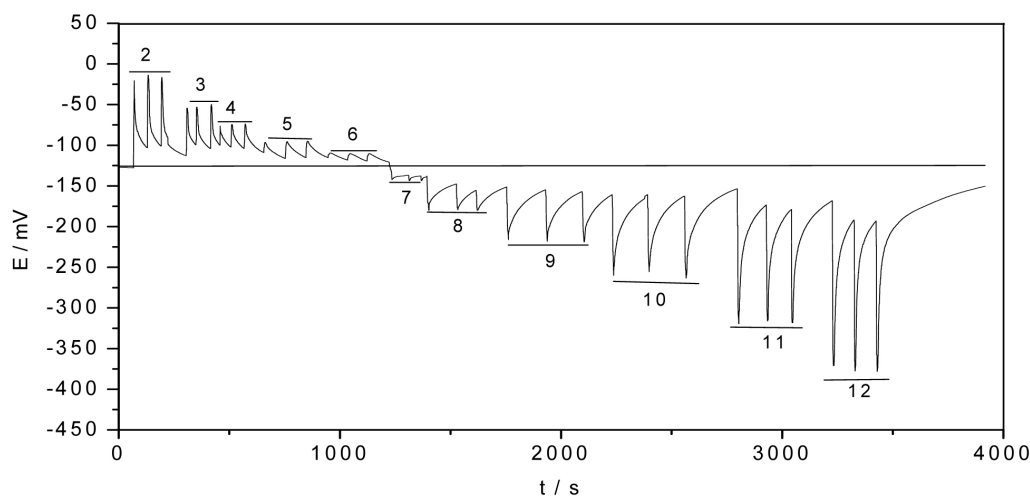


Figure 7: FIA response of the W/WO₃ electrode to 100 µL of injected buffer solutions pH (2–12) at flow rate 3.5 mL/min, current stream 0.5 M KNO₃.

multiple layers of WO_3 crystals. The electrodes were exposed to highly alkaline solutions (saturated calcium hydroxide and the pore-water of cement-based materials) over different time periods. Short-time exposure to $\text{Ca}(\text{OH})_2$ affected the potentiometric response by the formation of CaWO_4 on the electrode's surface. The surface itself became structurally very stable, $\text{WO}_3/\text{CaWO}_4/\text{W}$ being responsible for a linear pH response (from pH 2 to 12 with slope 45 ± 2 mV/pH unit). Electrodes stored in saturated $\text{Ca}(\text{OH})_2$ solutions could be used for pH measurements with repeatable potentiometric properties, for several months. The electrodes showed partial dissolution of WO_3 layer after 10 months of storage in saturated $\text{Ca}(\text{OH})_2$. In addition to WO_3 , pure tungsten and CaWO_4 phases were determined on the electrode's surface by XRD analysis. Slight decreases in sensitivity were observed within the range from pH 5 to pH 12 and the sub-Nernstian response within the range from pH 2 to pH 5. The presence of tungsten was probably affecting the potentiometric response within the acidic pH region (2–5) since, in the pH region (5–12), the response still remains linear with a slope of 42 ± 2 mV/pH unit. The W/WO_3 electrode gives a repeatable and long-term stable response in highly alkaline solutions (pH > 12) and can, therefore, be used as a reliable pH sensor during batch and flow-injection analysis of highly alkaline solutions. This study shows that tungsten wire electrodes are highly promising sensors for the long-term monitoring of pH in highly alkaline media. Concerning the measurements in concrete materials we believe that the importance of having a tungsten trioxide electrode present will grow in the future since there have been few similar studies reported.

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Povzetek

Merjenje pH v močno alkalnih raztopinah in v betonskih vzorcih je zelo pomembno za napoved korozije armature, kakor tudi za spremljanje drugih hidratacijskih procesov materialov, ki se uporabljajo pri proizvodnji betona. Tovrstni procesi so dolgotrajni in zahtevajo robustne, vzdržljive in enostavne pH senzorje, ki omogočajo tudi neposredno namestitve v betonsko matriko.

V delu so predstavljene W/WO₃ elektrode, ki so bile aktivirane pri 800 °C za 30 minut, pri čemer je na površini nastala homogena in stabilna plast WO₃. Tudi dolgotrajna, 10 mesečna izpostavitve v nasičeni raztopini Ca(OH)₂, kaže na nespremenjene potenciometrične lastnosti elektrod v območju med pH 5 in 12 z naklonom 42 ± 2 mV/pH. Preizkušeni interferenčni ioni niso imeli signifikantnega vpliva na elektrodni potencial.

W/WO₃ elektrode so se izkazale kot enostaven, dostopen, temperaturno obstojen in obetaven pH senzor, ki ga lahko uporabljamo tako za klasične potenciometrične titracije kot meritve v pretoku. Še posebej W/WO₃ elektrode odlikuje dobro ponovljiv odziv v močno alkalnih raztopinah (pH > 12), kar nakazuje uporabo pri določanju pH vrednosti kapilarne vode ter in-situ meritvah v betonu.