pH Sensitivity of Screen-Printed Sensors based Onamorphous and Crystalline RuO₂ and the Impact of Conducting and Inert Binders

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Abstract: Whereas crystalline RuO₂ is well-known in thermally prepared layers, the superior sensitivity dE/dpH of the amorphous oxide prepared by a sol-gel process has not been considered in detail so far. RuO₂ pastes, bound with ethyl cellulose, nafion, acrylic resin, and carbon black show Nernstian behavior both in standard pH buffer solutions and in corrosive media. Sintered layers appear to be less sensitive and tend to age. A residual content of chloride influences the properties of the electrode. The impact of the solution resistance on the pH response is obvious during acid-base titrations, which differ considerably from measurements in standard buffer solutions.

Keywords: amorphous ruthenium dioxide, pH sensor, water quality monitoring, binder

1. Introduction

With respect to the protection of humans and the environment, both experts and broad levels of the population wish to monitor the pH value of tap water, food, beverages [1], urine (pH 4.5–8), saliva (pH ≃7), and blood (pH 7.4 ± 0.05) [2, 3]. Since the 1970s the pH glass electrode has been the method of choice in aqueous solutions providing more or less easy handling, sufficient accuracy and response times. However, for consumer applications, the glass electrode appears to be too complicated, too expensive, too fragile, and too corrosive in strong acids and bases. pH-dependent metal oxides allow disposable, miniaturized low-cost sensors.

Platinum group metal oxides [4] have been developed for technical DSA electrodes since the 1970s. pH sensorshave been fabricated by thermal decomposition of salt precursors [5], sol-gel processes [6, 7, 8], sputtering [9, 10], electrodeposition [11], and carbon melt oxidation [12]. Screen printing [13, 14] appears to be the most preferred coating technology for small and flexible sensors. PtO₂, Ta₂O₅, TiO₂, PdO, OsO₂, and RhO₂ exhibit good pH sensitivity, although mainly RuO₂ and IrO₂ [15, 16] have been stressed in the literature because of their high conductivity, chemical stability, redox chemistry [17, 26] and ion-exchanging surface [18]. Iridium dioxide can even be used in solutions containing hydrofluoric acid [19].

Ruthenium dioxides is known for its oxygen defect stoichiometry. Due to the “hydrogen intercalation” into the oxide lattice, the electrode potential (equation 2) depends on the proton activity \( a_{H^+}^{aq} \) in the liquid phase and the oxygen activity \( a_{O_2}^{ss} \) in the solid phase [20].

\[
\text{MO}_x + 2z \text{H}^+ + 2z \text{e}^- \rightleftharpoons \text{MO}_{x-z} + z \text{H}_2\text{O}(1) \\
E = \frac{RT}{F} \ln a_{H^+}^{aq} + \frac{RT}{F} \ln a_{O_2}^{ss} + \text{const} \tag{2}
\]

Once the electrode is immersed in an aqueous electrolyte, protons from the solution penetrate into the porous electrode, diffuse through the defect sites of the rutile lattice, take part in redox reactions and form hydroxide sites (Figure 1).

\[
\begin{align*}
\text{RuO}_2(\text{OH})_y + ze^- + z\text{H}^+ & \rightleftharpoons \text{RuO}_{x-y}^{z+} \text{OH}^{y+z} \\
\text{Simplified:} \quad \text{Ru}^{IV}\text{O}_2 + e^- + \text{H}^+ & \rightleftharpoons \text{Ru}^{III}\text{O}(\text{OH})
\end{align*}
\tag{3}
\]

According to NERNST’s equation, and by neglecting the activity of Ru(III) and Ru(IV) in the solid material, the redox potential of the RuO₂ electrode depends directly on the pH value (equation 4) [22].

\[
E = E^0 - \frac{RT}{F} \ln \frac{a(\text{Ru}^{III})}{a(\text{Ru}^{IV})} = -\frac{RT}{F} \ln 10 \cdot \text{pH} + \ln a(\text{Ru}^{III})^2
\tag{4}
\]

At 25 °C: 

\[
E = E^0 - 0.059 \text{V} \cdot \text{pH}
\]

**Figure 1**: Model of the RuO₂|solution interface: a,b dissociative adsorption of water, c proton displacement during anodic charging, d redox reaction involving hydrogen-ions. Ru: ruthenium, \( O_{br} \): bridged oxygen, \( O_{at} \): on-top oxygen, H: hydrogen. Modified from [23, 24].

The thermodynamically calculated standard potential of the Ru(III)/Ru(IV) couple amounts to \( E^0 = 0.94 \text{ V SHE} \) [25]. The water content of the RuO₂ powder plays an essential role, because a GROETHUSS-like hopping mechanism of the protons is assumed [26].

This work considers the impact of the crystal structure, the water content, and the binder system on the pH sensitivity of screen-printed ruthenium dioxide sensors. The goal of this
study was to increase the oxygen defect structure of RuO₂ by an increased amount of Ru(III), for example by means of insufficient thermal decomposition of the precursors, or the precipitation of metal oxide hydroxides, respectively.

2. Experimental

We compared RuO₂ sensors made by three different fabrication processes.

**Screen printing:** The hydrous active material was made by sol-gel synthesis. A 0.5-molar solution of RuCl₃·xH₂O in ethanol was precipitated with 1.5-molar KOH solution at least until the mixture reached pH 8. After stirring for one hour at 80 °C, the amorphous RuO₂-gel was purified by repeated washing with deionized water and centrifugation until the pH of the waste water remained constant. The dried oxide was used for paste preparation. The mixing ratios of the binders, ethyl cellulose in terpineol (ET200, Kremer Pigmente), alkyl resin varnish (RAL 3000), thick oil (80014, Wolbring GmbH), epoxy resin (Epoxonic ex 2986), carbon primer (EB-012, Henkel), and Nafion (Ion Power; D520) are given in Table 1. According to Figure 2b, the current collector was printed on soda-lime glass (Ag-Pd paste ESL 9695-G, ElectroScience), dried at 125 °C (15 min), and finally annealed at 600 °C (2 h). The screen-printed active layers (Figure 2c) were dried at 150 °C in order to preserve the amorphous structure of hydrous RuO₂. Finally, the silver tracks were sealed with epoxy resin (Figure 2d).

**Spray pyrolysis:** Titanium foil (Ti) of 0.05 mm thickness (Ankuro Int.) was pretreated with abrasive paper and then degreased with acetone to ensure good adhesion of the oxide layer. A mixture of RuCl₃·xH₂O (Sigma-Aldrich) dissolved in acetone was decomposed on the substrate at 500 °C (air) for 2 h. Previous investigations revealed the transition temperature of the oxide formation at about 370 °C (Figure 3). Crystalline RuO₂ is formed at 500 °C. The active layer (area 1 cm² and 8.0 mg/cm²) was about 2 μm thick.

**Electroplating:** Titanium cathodes were coated with ruthenium layers from a 0.04-molar RuCl₃·H₂O solution at a current of 5 mA cm⁻² for 40 and 120 min, and then annealed at 600 °C. Standard buffer solutions were pH 4.01 (phthalate), 7.00 (phosphate), and 10.0 (borate). Titration employed the drop-wise addition of NaOH into 0.5-molar H₂SO₄. The pH was checked using a commercial glass electrode (BlueLine 23 pH). RuO₂ layers were characterized by X-ray diffraction (XRD, RigakuMiniflex 600), electron microscopy (SEM/EDX, Stereoscan LEO 440), and thermogravimetric analysis (TGA, Netzsch 209 F1 Libra) in a platinum-rhodium crucible under oxygen atmosphere. The thermal decomposition of the binders was analyzed by thermogravimetric analysis coupled with an FTIR-spectrometer (Bruker Tensor 27) in an aluminum oxide crucible under oxygen atmosphere.

3. Results and Discussion

In the following, the electrochemical properties and the pH sensitivity of amorphous and crystalline RuO₂ layers (prepared by alkaline precipitation, spray pyrolysis, and electroplating) are critically compared.

3.1 Surface properties

The thermogravimetric analysis (Figure 3a) shows the RuCl₃→RuO₂ transition at about 370 °C. Absorbed and bound water is released below 150–180 °C. Sintering of the particles can be observed above 580 °C. Amorphous RuO₂·xH₂O, which was won from RuCl₃ solution by alkaline precipitation with NaOH, loses most of its water content below 300 to 350 °C. The early water loss below 150 °C corresponds to the formula RuO₂·0.43H₂O. Above 390 °C, more or less water-free RuO₂ is formed.

Crystalline RuO₂ shows defined X-ray diffraction peaks in contrast to the amorphous material (Figure 3b). The ruthenium and oxygen atoms in the bulk material prefer the (110) and (101) planes, whereas (101), (111) and (100) mainly exist on the surface [27]. With the help of the Debye-Scherrer equation, the average crystallite size of 46.0 nm was calculated for powders prepared at 600 °C; the Bragg angle 2θ = 28° belongs to the crystal orientation (110). 2θ = 35° corresponds to 36.7 nm (101).

The SEM images (Figure 4) show the microporous morphology of crystalline and amorphous RuO₂ powders. With heat treatment, bound water is lost, and the apparent ruthenium content increases. The EDX analysis reveals some percent of residual chlorine from the RuCl₃ precursor both in the amorphous powder and in the crystalline sample.

Despite repeated washing of the precipitated RuO₂ powder, chloride is still bound in the material. Residual chloride might be of interest for the pH sensitivity. It seems quite conceivable, that some chloride is exchanged by hydroxide in alkaline solutions. Our previous TOF-SIMS studies suggest the formation of Ru-O-Cl-I clusters [20].

![Figure 2: Screen-printing process](image)

**Figure 2:** Screen-printing process: a) degreased substrate, b)AgPd conductor, c) metal oxide layer (1 cm², 8 mg cm⁻²), d) insulating layer.
Figure 3: a Thermogravimetry analysis and b X-ray diffractograms of crystalline RuO₂ (prepared by decomposition of RuCl₃ at 600 °C) and amorphous RuO₂ (by alkaline precipitation, dried at 150 °C).

3.2 Binders

Amorphous RuO₂, won by alkaline precipitation, exhibits a nanoporous structure and includes bound water, which is lost at high temperatures (> 390 °C). In order to maintain the amorphous structure and to guarantee adhesion on the support material, appropriate binders are required, which do not affect the pH sensitivity of RuO₂. Selected binders are allowed to remain in the amorphous layer as long as they improve the mechanical and chemical stability of the sensor. For this reason, several binders were investigated in detail with respect to the thermal decomposition properties.

The thermal behavior of ethyl cellulose and its decomposition products was characterized by TGA-FTIR-coupling in a gas cell (Figure 5a). Ethyl cellulose shows three decomposition steps around 210 °C, 326 °C and 400 °C. At 210 °C, the decomposition products consist mainly of carboxylic acids or esters, such as propanoic acid fragments. Around 326 °C, long-chained ketones and alcohols occur. As well, small amounts of water and carbon dioxide are released. At temperatures above 400 °C, carbon dioxide is the principal decomposition product of the binder (Figure 6). Above 425 °C, the binder is completely decomposed (mass loss 100%).
In contrast, the carbon binder loses its solvent at about 125 °C. The carbon particles remain in the active material and improve the conductivity of the electrode. Heated at 500 °C, the carbon binder still contains 19 wt% of its initial mass.

We conclude that 150 °C is an adequate drying temperature for amorphous RuO₂. Some residual amount of binder improves the mechanical stability of the active layer.

### 3.3 Sensitivity in buffer solutions

The binder plays an important role for the practical sensitivity of the sensor. Table 1 compiles the slopes dE/dpH of RuO₂ electrodes measured in standard buffer solutions. Preferably, the amorphous RuO₂/ethyl cellulose sensor (20:80) exhibits a linear Nernstian response (59 mV/pH). This sensitivity is confirmed by the data of MANJAKKAL et al. for screen printed sensors based on crystalline RuO₂ (Table 2). The organic binder decomposes at around 300 to 400 °C. Heat treatment of RuCl₃ at 500 °C generates a crystalline RuO₂ layer of low active surface area showing a sensitivity of 52 mV/pH. During aging, the sensitivity of such a thermal Ti/RuO₂ electrode may increase up to 76 mV/pH; and the electrode standard potential drifts.

**Acrylic resin** appears to be useful for sensors; we found NERNSTian behavior. In contrast to that, epoxy resin appears to be inappropriate for flat sensors, because it peels off. ‘Thick oil’ evaporates and decomposes between 100 to 250 °C, so that small amounts are still present in the active layer dried at 150 °C. This explains the undesired sensitivity of 64 mV/pH. Unfortunately, the sensor is not long-term stable, and the layer dissolves visibly after a few measurements.

**Nafion** [28] seems to be a useful binder for metal oxide powders because of its good proton conductivity. Its sensitivity is low compared with ethyl cellulose. Unfortunately, Nafion tends to increase the sheet resistance (Figure 7). Despite long response times, Nafion improves the selectivity against interfering ions, although chloride ions can penetrate the membrane [29, 30].
Carbon. With investigating different compositions of porous carbon and RuO$_2$, surprisingly, the pH response drops with increasing amount of RuO$_2$(Table 1). In order to exclude interfering effects, the sensitivities of the bare substrates and binders were tested separately (Table 3).

Indeed, the substrate plays a minor role for the pH response, because the sensor is coated sufficiently thick with RuO$_2$.

The electroplated sensors(without binder) suggest that chemisorbed and bound water is incorporated in the active layer [31]. The sensitivity $\frac{dE}{dpH}$ amounts to just half the value of the amorphous RuO$_2$ hydrate, because the electrodeposited layers were annealed at 600 $^\circ$C, whereby crystalline RuO$_2$ is generated. The loss of sensitivity corresponds to the mass increase around 576 $^\circ$C in the thermogravimetric analysis. This oxidation of electrodeposited ruthenium between 430 and 480 $^\circ$C was observed by MARIAN et al. [32] as well.

We conclude that the sensitivity of a RuO$_2$ sensor can be improved by amorphous oxide. Binders, except ethyl cellulose and acrylic varnish, reduce the sensitivity (see Table 1). The response of the metal oxide (RuO$_2$:C = 20:80) comes close to the optimum pH-response known from the glass electrode. The sensitivity of the electrodeposited layers suggest that two electrons ($z = E/59$ mV $= 2$) are involved in the potential determining step, whereas the amorphous oxide perfectly utilizes the RuO(OH)/RuO$_2$ couple ($z = 1$). Virgin electrodes prepared by thermolysis show sensitivities around 52 mV/pH ($z = 1$). However, insulating binders such as epoxy resin cause low sensitivity (18 mV/pH). An increase in sensitivity was achieved by the addition of activated carbon [33].

Table 1: RuO$_2$ electrodes manufactured with different binders in pH standard buffer solutions at 20 $^\circ$C.

<table>
<thead>
<tr>
<th>Type</th>
<th>Amorphous oxide (from precipitation and dried at 150 $^\circ$C)</th>
<th>Crystalline oxide (thermolysis at 500 $^\circ$C)</th>
<th>Electrodeposited oxide (annealed at 600 $^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>RuO$_2$ / ethyl cellulose</td>
<td>RuO$_2$ / TiO$_2$</td>
<td>RuO$_2$ / TiO$_2$</td>
</tr>
<tr>
<td></td>
<td>RuO$_2$ / carbon</td>
<td>RuO$_2$ / SnO$_2$</td>
<td>RuO$_2$ / Ta$_2$O$_5$</td>
</tr>
<tr>
<td></td>
<td>RuO$_2$ / carbon / carbon</td>
<td>RuO$_2$ / carbon / carbon / nafion</td>
<td>RuO$_2$ / carbon / nafion</td>
</tr>
<tr>
<td>Sensitivity mV/pH</td>
<td>−59.0 −56.5 −64.6 −17.8 −48.8 −41.5 −36.1 −40.7 −41.5 −15.7 −35.9</td>
<td>−52.0 −23.7 −27.3</td>
<td>−52.0 −23.7 −27.3</td>
</tr>
<tr>
<td>Linearity R$^2$</td>
<td>0.996 0.999 0.906 0.904 0.981 0.992 0.986 0.995 0.954 0.999 0.981</td>
<td>0.974 0.988</td>
<td>0.974 0.988</td>
</tr>
<tr>
<td>E$^e$ / mV vs. Ag/AgCl</td>
<td>670 661 810 710 524 592 623 642 592 882 605</td>
<td>348 400</td>
<td>348 400</td>
</tr>
</tbody>
</table>


Table 3: pH-response of bare substrates and binders vs. Ag/AgCl/KCl in buffer solutions (pH 4, 7, and 10) at 20 $^\circ$C.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Ag/Pd current collector</th>
<th>Ag/Pd + nafion</th>
<th>Ag/Pd + carbon</th>
<th>Ti (500 $^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mV/pH</td>
<td>−13.3</td>
<td>−13.9</td>
<td>−15.0</td>
<td>−46.4</td>
</tr>
<tr>
<td>R$^2$</td>
<td>0.981</td>
<td>0.881</td>
<td>0.999</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Literature data:pH response of crystalline RuO$_2$ composites with ethyl cellulose in terpineol.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>w / %</th>
<th>T / $^\circ$C</th>
<th>pH-range</th>
<th>mV/pH</th>
<th>[a]</th>
<th>[b]</th>
<th>[c]</th>
<th>[d]</th>
<th>[e]</th>
<th>[f]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a]</td>
<td>−</td>
<td>850</td>
<td>2-10</td>
<td>−57</td>
<td>70.30</td>
<td>−</td>
<td>70.30</td>
<td>70.30</td>
<td>30.70</td>
<td></td>
</tr>
<tr>
<td>[b]</td>
<td>70.30</td>
<td>900</td>
<td>2-10</td>
<td>−56.1</td>
<td>−60.7</td>
<td>−65.5</td>
<td>−65.1</td>
<td>−35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[c]</td>
<td>−</td>
<td>700</td>
<td>2-10</td>
<td>−57</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12</td>
<td>−12</td>
<td>−12</td>
</tr>
<tr>
<td>[d]</td>
<td>−</td>
<td>900</td>
<td>2-10</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12</td>
<td>−12</td>
<td>−12</td>
</tr>
<tr>
<td>[e]</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12</td>
<td>−12</td>
<td>−12</td>
</tr>
<tr>
<td>[f]</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12.1</td>
<td>−12</td>
<td>−12</td>
<td>−12</td>
</tr>
</tbody>
</table>

3.4 Hysteresis and drift

Known problems of RuO$_2$ electrodes are (i) hysteresis, i.e., divergent potentials in the same solution after measurements in differently concentrated solutions, and (ii) potential drift, i.e., the slow nonrandom change of the output voltage in time. Table 4 demonstrates the superior stability of the carbon-based binder in contrast to ethyl cellulose. Depending on the preparation procedure, hysteresis and drift values of RuO$_2$ sensors range between 3 and 30 mV (Figure 8). In acid solution, hysteresis is lower than in alkaline solution.
This may be due to the fact that the equilibrium potential is reached faster in acid solution, whereas in alkaline solution higher oxidation states and soluble species are stabilized.

Hysteresis and potential drift directly influence the sensitivity of the electrodes. At pH changes of 4→7→10, the sensitivity of the ethyl cellulose sensor was −54 mV/pH ($R^2 = 0.996$), whereas at pH 7→4→10 it dropped to −52 mV/pH ($R^2 = 0.996$). Carbon-bound RuO$_2$ electrodes decrease from −49 mV/pH ($R^2 = 0.972$) to −48 mV/pH ($R^2 = 0.992$). Unfortunately, the pH response lies not far above the range of thermal noise, $RT/F = 25$ mV.

The sensitivity lies at an average value of −32 ± 4 mV/pH, and is thus lower than in buffer solutions. A drastic loss of the sensitivity is observed in tap water. Originally, we assumed that the low sensitivity was caused by conductivity alterations during the neutralization reaction. However, the electrolyte resistance of the reaction $\text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ is greatest at pH 7. Measurements in diluted acids (1, 0.1, 0.01, and 0.001-molar $\text{H}_2\text{SO}_4$ versus 0.001, and 0.01-molar NaOH) rendered almost the same OCP (Table 5).

The same observations we made with carbon-based electrodes. Since the titration curve is not a straight line, we determined the sensitivity in individual pH ranges. In strongly acid and strongly alkaline solution, qualitatively the same pH responses were observed as in buffer solutions. However, the sensitivity reaches a minimum in the neutral range at pH 6 to 9, especially in tap water. Similar to the electrodes with binders, the sensitivity of the binder-less electrodes decreases by 10 to 25 mV/pH, when the pH was not measured in standard buffer solutions, but during a neutralization reaction.

We conclude that the conductivity of the solution is of importance for the slope $dE/dpH$. Since tap water has a high resistance compared with the neutralized mixture of $\text{H}_2\text{SO}_4$ and NaOH, the sensitivity in water is considerably lower. The binder resistance seems to play a minor role for the loss of sensitivity in “real solutions”. RuO$_2$ bound with ethyl cellulose is usable in a pH range between 0 and 14.

Screen-printed sensors do not show any additional activity in strong acids (pH < 0). The rest potential (OCP) equals 520 mV in 5-molar $\text{H}_2\text{SO}_4$ (negative pH −1.5), about 535 mV in 3-molar $\text{H}_2\text{SO}_4$, and about 534 mV in 1-molar $\text{H}_2\text{SO}_4$ (pH −0.48) vs. Ag[AgCl]KCl.

3.5 Sensitivity during acid-base titration

In practical use, metal oxide electrodes must show the same sensitivity in different media. For this reason, we investigated RuO$_2$ electrodes bound with (i) ethyl cellulose and (ii) carbon during the titration of 0.5-molar sulfuric acid by dropwise addition of sodium hydroxide solution (Table 5). Between each pH measurement, the solution was mixed using a magnetic stirrer for about 2 minutes (300 min$^{-1}$). The pH values were checked by a conventional glass electrode. The open-circuit potential (OCP) in Figure 9 was measured by the help of a galvanostat at the regulated current $I = 0$ for at least 5 min.

The same observations we made with carbon during the titration of 0.5-molar sulfuric acid by dropwise addition of sodium hydroxide solution (Table 5). Between each pH measurement, the solution was mixed using a magnetic stirrer for about 2 minutes (300 min$^{-1}$). The pH values were checked by a conventional glass electrode. The open-circuit potential (OCP) in Figure 9 was measured by the help of a galvanostat at the regulated current $I = 0$ for at least 5 min.

![Figure 8: a) Hysteresis and b) potential drift of a RuO$_2$ sensor (amorphous RuO$_2$:C = 20:80) in buffer solutions.](image-url)

![Figure 9: Rest potential (OCP) of a RuO$_2$ sensor (20 % amorphous RuO$_2$, 80 % ethyl cellulose) in standard buffers.](image-url)

<table>
<thead>
<tr>
<th>pH</th>
<th>Ethyl cellulose</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>18.3</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>18.6</td>
<td>546</td>
</tr>
<tr>
<td>10</td>
<td>9.7</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 4: Hysteresis and potential drift (during 180 s) of RuO$_2$ sensors measured in buffer solutions.
and real aqueous solutions during acid-base titration at 20 °C. pH controlled by a commercial glass electrode.

Table 5: Sensitivity of RuO₂ electrodes during titration of sulfuric acid with NaOH, and in tap water, versus Ag/AgCl at 20 °C. Standard solutions were prepared by dilution: 1. 0.1, 0.01, 0.001, 0.0001-molar H₂SO₄ and 0.001, 0.01-molar NaOH.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Ethyl cellulose (RuO₂:ethyl cellulose = 20:80)</th>
<th>Carbon (RuO₂:C = 20:80)</th>
<th>No binder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>buffer</td>
<td>1st titration</td>
<td>2nd titration</td>
</tr>
<tr>
<td>pH-range</td>
<td>4 to 10</td>
<td>4 to 10</td>
<td>3 to 10</td>
</tr>
<tr>
<td>mV/pH</td>
<td>~76...−52</td>
<td>~50.4</td>
<td>−40.8</td>
</tr>
<tr>
<td>E (mV)</td>
<td>605...882</td>
<td>612</td>
<td>540</td>
</tr>
</tbody>
</table>

3.6 Response time

We define the response time as the time to reach 90 % of the equilibrium potential according to HUANG et al. [34]. The response of amorphous RuO₂:ethyl cellulose (20:80) and RuO₂:carbon (20:80) was measured in buffer solutions in the order: pH 4→7→10→7→4→10. In contrast to sintered layers, we expected extended response times due to the incompletely decomposed binders. On the other hand, binders improve the adhesion and thus the lifetime of the RuO₂ layers. Ethyl cellulose required less than 2 min in acidic and less than 3 min in alkaline solutions, whereas the carbon-based sensor exhibits an average response time of less than 4 min.

During acid-base titration, the sensors bound with ethyl cellulose and carbon work faster than in buffer solutions. RuO₂:ethyl cellulose reaches its open-circuit potential within less than 1 min in acid and alkaline solutions, whereas the carbon-based electrode needs <10 s (acid) and <2 min (alkaline), respectively. The fast response during titration may be due to the higher number of surface charges, and the better conductivity of the solution (~65 mS/cm for buffer solutions and about 40 to 380 mS/cm during titration). In acid solutions, the drift behavior is more pronounced for both sensors: 230 mV/h (ethyl cellulose) and 210 mV/h (carbon) at pH 1. The drift in alkaline solutions is about 32 mV/h (ethyl cellulose) and 46 mV/h (carbon primer) at pH = 10.

4. Conclusions

Until, one day, miniaturized low cost pH sensors based on metal oxides might be able to replace the glass electrode in any solution, some obstacles considered in this paper have to be overcome. In pH buffer solutions, RuO₂ electrodes respond in nearly the same ideal way as the glass electrode does. Challenges arise in real solutions with undefined ionic strength.

1) Amorphous RuO₂ bound with ethyl cellulose shows ideal sensitivity (~59 mV/pH, 25 °C). At drying temperatures below 150 °C, enough Ru(III) in the material provides sufficient redox activity for pH sensitivity. Amorphous RuO₂ was won from RuCl₃by alkaline precipitation with NaOH.

2) The sensitivity dE/dpH of carbon-bound electrodes drops with increasing RuO₂ content. Obviously, a higher number of charge carriers is involved in the conversion of Ru(III) to Ru(IV), when RuO₂ is finely dispersed at the electrode surface, whereas the bulk material behaves inactive. The potential determining step of the amorphous oxide perfectly utilizes the RuO(OH)/RuO₂ couple (z = 1).

3) With sintering RuO₂ electrodes up to 800 °C, the particles agglomerate and lose water, so that electrodes prepared by thermolysis show the low sensitivity of crystalline RuO₂(compared with the amorphous hydrate). Virgin electrodes prepared by thermolysis show sensitivities around 52 mV/pH (z = 1).

4) Both the mechanical stability and the sensitivity dE/dpH of RuO₂ layers can be improved by using a Nafion binder. A bare Nafion layer (e. g. on a Ag/Pd current collector) does not create any pH sensitivity. RuO₂ works as the proton-selective component in the polymer-composite electrode.

5) RuO₂ electrodes respond more quickly during acid-base titrations than in buffer solutions. Unfortunately, sensitivity deviates from 59 mV/pH because the solution resistance changes continuously (maximum at pH 7). This surprising difference between real solutions and “ideal” pH buffers requires further studies with respect to
the ionic strength of the solution. We suggest that RuO$_2$ indicates the real proton activity (H$^+$, aq) at the metal oxide/electrolyte interface.

Up to now, pH values can only be compared in media of the same ionic strength and the same solvent. Absolute pH measurements in any medium have not been feasible so far. Present pH meters must be calibrated against at least two buffer solutions. The primary method for pH measurement, the so-called HARNED cell [35, 36], employing a hydrogen electrode (platinum aerated by dry hydrogen at atmospheric pressure) and a silver-silver chloride electrode, requires the knowledge of activity coefficients that usually are completely unknown for technical media. The future will show whether platinum metal oxide might open up novel ways of pH measurement.

References


