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Hydrogel-based flexible micro-reference electrodes for use in alkaline and neutral pH solutions

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Abstract Two types of nonbreakable, flexible micro-reference electrodes filled with gel-electrolytes were prepared for use in solutions with alkaline and neutral pH. The electrodes are intended for electrochemical measurements, in which chloride-free conditions are important. Due to the flexible, bendable construction of the electrodes, electrochemical experiments at locations difficult to access with common reference electrodes are enabled. $Hg|HgO$-type electrodes were prepared from amalgamated Au wires, followed by oxidation of the amalgam, which is mounted in a PTFE tube filled with 0.1M NaOH solution immobilized in a PAA-g-PEO gel. The potential of this type of electrode was found to be 0.162 ± 0.002 V (SHE) at room temperature. $Cu|CuSO_4$ electrodes, consisting of a Cu wire immersed in a saturated $CuSO_4$ solution jellied with gelatin, showed a stable open-circuit potential of 0.312 ± 0.001 V (SHE). Further characterization of the electrodes was performed in terms of electrochemical impedance spectroscopy and micro-polarization measurements. As an alternative to the flexible electrodes, rigid electrodes in glass enclosure were fabricated in analogy to the flexible-type electrodes.

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Introduction

Providing chloride-free conditions for sensitive electrochemical measurements represent a crucial factor for the choice of the right instrumentation. The two reference electrodes most commonly used in a standard electrochemistry lab are the $Ag|AgCl$ and the $Hg|Hg_2Cl_2$ electrode, both operating in contact with a highly concentrated or saturated aqueous chloride solution as liquid phase. If a simple diaphragm is used for separation, the diffusion of chloride ions is far too high. Even if a salt bridge is used to separate the chloride solution inside the reference electrode from the electrolyte solution in which the measurement takes place, diffusion of chloride ions out of the reference electrode cannot entirely be excluded. In this regard, reference electrodes without chloride like the $Cu|CuSO_4$ or, especially for alkaline media, the $Hg|HgO$ are highly favorable. Moreover, microelectrochemical techniques require miniaturized equipment comprising stability, accuracy, and flexible design [1, 2].

Most often, $Ag|AgCl$ μ-reference electrodes are used due to their stable potential and simple fabrication. Pedrotti et al. [3] described the fabrication of a mini-$Ag|AgCl$ reference electrode using a polypropylene pipette tip and microporous high-density polyethylene junction to keep the saturated NaCl solution inside. A μ-$Ag|AgCl$ electrode mounted in a glass capillary was reported by Hassel et al. [4]. Here, the saturated KCl electrolyte was immobilized by adding agar to the solution, providing the option to further integrate an agar-solidified KNO_3 salt bridge. Another method of fabricating a solid state μ-reference electrode was shown by Nolan et al. [5] by dip-coating a $Ag|AgCl$ wire in poly(vinyl chloride) containing immobilized NaCl electrolyte and protecting the electrodes with polyurethane or Nafion. Various studies focus on the optimization, miniaturization, and adaptation to specific requirements of the $Ag|AgCl$ reference electrode [6–11], due to its nature as an electrode of

the second kind. These electrodes are characterized by precipitation of a poorly soluble metal salt or oxide as soon as dissolving metal ions react with the anions in the electrolyte solution. The potential is determined by the activity of metal ions in the electrolyte and thus by the solubility product of the precipitate. Consequently, for a metal salt with poor solubility, saturation is reached easily and the potential of the electrode depends on the anion activity in the electrolyte [12]. Other examples for electrodes of the second kind are the $Hg|Hg_2Cl_2|Cl^-$ electrode [13], the $Hg|Hg_2SO_4|SO_4^{2-}$ electrode [13], and the $Hg|Hg_2(CH_3COO)_2|CH_3COO^-$ electrode [14]. Both, the mercury sulfate and the mercury acetate reference electrodes, have been prepared as μ-reference electrodes in glass capillaries using agar for electrolyte solidification [15]. A reference electrode especially suitable for alkaline solutions and higher temperatures is the $Hg|HgO|OH^-$ electrode [16]. For solidification of the alkaline electrolyte, usually NaOH or KOH solution, agar and gelatin are not stable. Nevertheless, hydrogel polymers can be used for electrolyte immobilization under alkaline conditions. Hydrogels are cross-linked polymeric materials with hydrophilic functional groups enabling absorption of relatively large amounts of water or aqueous solution for high ionic conductivity. They comprise a wide range of applications like for example hygiene products, pharmaceuticals, food additives, sensors, and biosensors [17, 18]. For alkaline solutions, hydrogel electrolytes like cross-linked sodium polyacrylate [19–21], acidic polyvinyl alcohol/polyacrylic acid blend cross-linked with glutaraldehyde [22], or poly(acrylate-co-acrylamide) [23] have been studied. In this work, a flexible $Hg|HgO|OH^-$ reference electrode with poly(acrylic acid) partial Na-salt graft-poly(ethylene oxide) hydrogel immobilized electrolyte is presented. Very recently, this type of reference electrode has been employed successfully in several studies [24, 25]. The aim of this paper is to give a profound description and characterization of these electrodes.

Furthermore, this paper discusses a flexible $Cu|CuSO_4$ electrode. Although the $Cu|CuSO_4$ system is classified as an electrode of the first kind, as $CuSO_4$ is well soluble in water, a stable potential can be maintained by using a saturated $CuSO_4$ solution as electrolyte. With an excess of solid $CuSO_4$ crystals in the electrolyte solution, a higher resistance against chloride contamination has been reported [26]. Chloride has also been found to form adsorbates on the copper surface [27]. The applications of $Cu|CuSO_4$ reference electrodes lie particularly in the field of corrosion studies, where robustness is crucial, for example, investigation of the corrosion behavior of steel in reinforced concrete [28, 29] or direct corrosion measurements of pipelines and storage tanks in soil [30].

Flexible designs of miniaturized and μ-reference electrodes extend the possibilities of their applications for electrochemical examinations. Furthermore, these reference electrodes show higher mechanical resilience, by bending that they can be brought closer toward the working electrode and therefore dispense with the need for Luggin capillaries.

Experimental

Preparation of Hg|HgO-μ-reference electrodes

For use in alkaline solution, Hg|HgO-reference electrodes were prepared. An Au wire (purity 99.999 %) with 200 μm diameter was ultrasonically cleaned in ethanol and afterwards in water. Amalgamation of the wire was conducted electrochemically by applying a potential of 0.2 V versus standard hydrogen electrode (SHE) for a duration of 180 s in 0.1M $Hg_2(NO_3)_2$ solution. A dimensionally stable anode served as counter electrode and a commercially available Ag|AgCl|3 M KCl electrode (Metrohm) as reference electrode. As next step, two-thirds of the amalgamated part of the wire were dipped in a 0.002 wt% $KMnO_4$ solution for 10 min in order to form HgO. Alternatively, oxidation can be achieved thermally by heating the amalgamated wire for 10 s at 350 °C in air. The latter method however may decrease surface concentration of mercury on the gold wire by fostering the inward diffusion. For the thermal oxidation, it is advisable to not rinse the wire with water after the amalgamation step. For electrochemical oxidation of the amalgam, a potential of 0.5 V (SHE) was applied for 180 s in 0.1M NaOH solution. Characterization of the oxidized surface was performed with a field emission Zeiss Gemini 1540 XB scanning electron microscope (SEM) with 5-kV acceleration voltage and secondary electron (SE2) detector. Chemical composition was studied in terms of energy dispersive X-ray spectrometer (EDX) from INCA X-Sight Oxford Instruments.

The amalgamated and oxidized wire was then inserted into a PTFE tube (VWR) with an outer diameter of 1 mm and an inner diameter of 0.5 mm. The electrolyte was prepared by adding 0.14 g of PAA-g-PEO powder (poly(acrylic acid) partial Na-salt graft-poly(ethylene oxide), Sigma-Aldrich) to 10 cm^3 water resulting in a 1.4 wt% PAA-g-PEO gel. Stirring is performed carefully to avoid introduction of gas inclusions into the gel. After dropwise addition of 2 cm^3 0.6M NaOH solution, resulting in an overall NaOH concentration of 0.1 mol l^{-1}, viscosity of the gel decreases and allowed filling of the wire containing PTFE tube. For this purpose, a syringe is connected to one end of the tube, which is used for sucking the gel electrolyte into the tube. Care should be taken to avoid gas inclusions within the tube. Finally, the electrode is closed on one end by application of a two-component resin glue. This is not only sealing but also acts as pulling relief. As alternative to the PTFE tube, a glass capillary (borosilicate glass, WPI) with the same dimensions can be used to obtain a rigid reference electrode. The produced reference electrodes can be either stored with the tip immersed in 0.1M NaOH

solution or directly in the PAA-g-PEO gel in humid atmosphere (>90 % relative humidity, in desiccator, over saturated K_2SO_4 solution).

Preparation of Cu|CuSO$_4$-μ-reference electrodes

Analogously to the preparation of reference electrodes for usage in alkaline solution, Cu|CuSO$_4$-type electrodes were prepared for measurements in neutral electrolytes. A Cu wire with 200 μm diameter was cleaned by etching with diluted nitric acid. The wire can then be inserted in either a PTFE tube or a glass capillary. The electrolyte is prepared by adding 0.5 g (5 wt%) gelatin powder (Merck) to 10 cm^3 saturated aqueous $CuSO_4$ solution. The mixture was continuously stirred and heated up to 50 °C until the gelatin dissolved. The tube or capillary containing the Cu wire is then filled with the hot gelatin mixture and allowed to cool and solidify inside the tube. After solidification, the gelatin-filled tube was closed with epoxy resin glue. The finished reference electrodes were stored with the tip immersed in saturated $CuSO_4$ solution.

Electrochemical measurements

For all electrochemical experiments, an IVIUM CompactStat potentiostat was used. Electrochemical impedance spectroscopy (EIS) measurements were performed in a frequency range from 10 kHz to 10 mHz with 10 measurement points per decade and a sinusoidal voltage signal amplitude of 10 mV. As DC bias potential, the open-circuit potential (E_{OCP}) was used, which was recorded for 600 s before each EIS measurement. Micro-polarization curves were obtained by potentiodynamic scanning of a potential range of ±10 mV versus E_{OCP} with a scan rate of 2 mV s^{-1}. All electrochemical measurements were performed at room temperature, using a reversible hydrogen electrode (RHE, HydroFlex, Gaskatel) as reference electrode and a Pt wire as counter electrode.

Results and discussion

Preparation of μ-reference electrodes

The fabrication procedures of the two kinds of reference electrodes—Cu|CuSO$_4$ and Hg|HgO—are schematically presented in Fig. 1.

The production of the Hg|HgO-μ-reference electrodes is characterized by additional steps compared to the production of Cu|CuSO$_4$-type electrodes, needed for amalgamation of the starting material, which is in this case a gold wire, and the subsequent oxidation of the amalgam. The proceeding of the reaction steps can be easily visually tracked. The gold amalgam is of silvery appearance and can be clearly distinguished from the original gold color of the wire. During the next step,
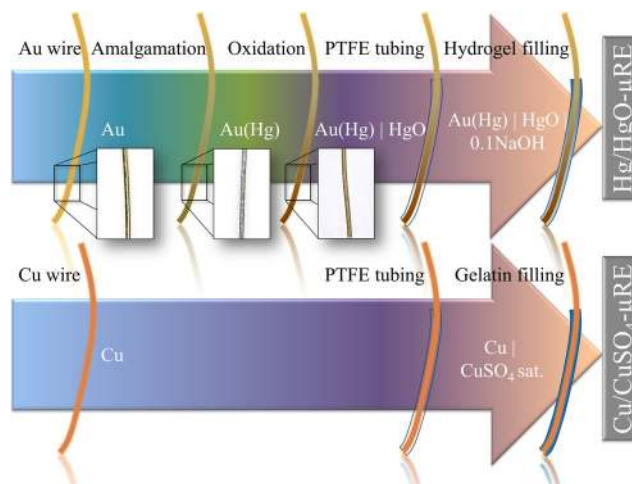

Fig. 1 Schematic presentation of the fabrication procedure of flexible Hg/HgO- and Cu/CuSO$_4$-micro-reference electrodes including light microscopic images showing the original gold wire surface (diameter = 200 μm) as well as the amalgamated and oxidized surface

the silver color vanishes as the formed oxide is characterized by a matt yellow to orange color. HgO can appear in two different colors (yellow or red) depending on its particle size [31]. The influence of the particle size on the electrode potential was reported to be negligible [32].

The oxidation process itself can be carried out in different ways. The oxide can be produced by heating up the amalgam in air. In this case, formation of HgO proceeds as follows:

$$Hg + \frac{1}{2}O_2 \rightleftarrows HgO \quad (1)$$

In the case of electrochemical oxidation of mercury, Hg^{2+} ions react with water resulting in the formation of HgO on the amalgam surface:

$$Hg \rightleftarrows Hg^{2+} + 2e^- \quad (2)$$

$$Hg^{2+} + H_2O \rightleftarrows HgO + 2H^+ \quad (3)$$
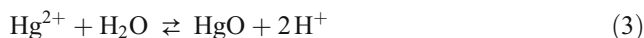
For the chemical formation of HgO, an oxidizing agent, strong enough to oxidize Hg, is needed [33]. For this purpose, permanganate was employed, which is reduced to manganese dioxide according to following reaction equation:

$$3\ Hg + 2MnO_4^- + H_2O \rightleftarrows 3\ HgO + 2MnO_2 + 2OH^- \quad (4)$$
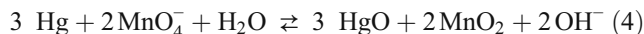
Manganese dioxide is insoluble in water and precipitates during this reaction. The oxidized amalgam wire should be rinsed thoroughly with water after this reaction in order to remove manganese adherences from the wire surface.

The resulting amalgamated and oxidized wire surface was studied using SEM. Corresponding images are presented in Fig. 2. The surface of the thermally oxidized amalgam is free from visible precipitates, in contrast to
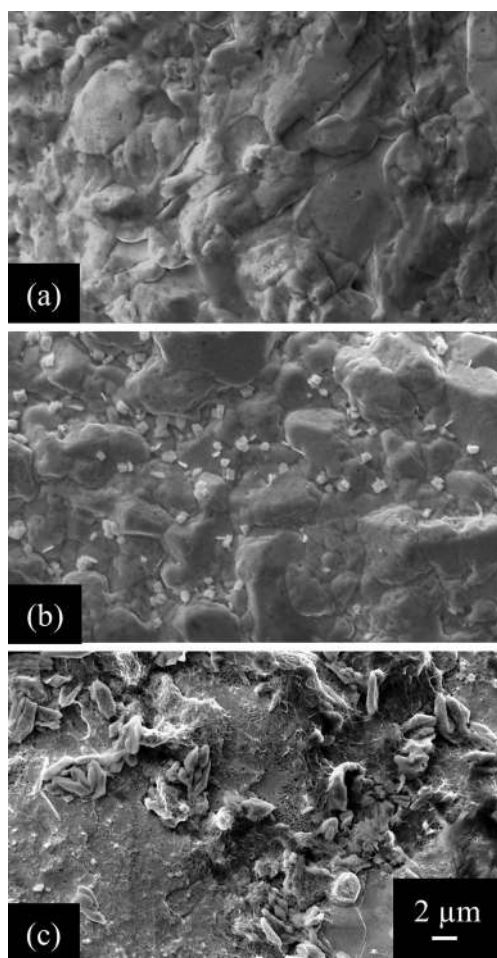
Fig. 2 SEM images from **a** thermally oxidized HgO surface as well as from **b** electrochemically and **c** chemically oxidized HgO, produced on amalgamated gold wire

Table 1 Composition determined by EDX for thermally, electrochemically, and chemically oxidized Au-amalgam as well as atomic ratio n of Hg/O and Hg/Au

Composition/at%	Thermal	Electrochemical	Chemical
Au	38.9	45.3	33.8
Hg	33.3	37.3	33.6
O	27.8	17.4	32.6
n (Hg/O)	1.20	2.14	1.03
n (Hg/Au)	0.46	0.45	0.50

the three different fabrication routes studied, chemical oxidation shows the highest level of Hg oxidation.

Taking into account the simplicity of the chemical oxidation process using permanganate, combined with the high degree of Hg oxidation and the short process duration, it represents the most suitable method to produce HgO on the amalgamated wire surface. Therefore, Au(Hg)/HgO wires fabricated by this method are further used for production of microreference electrodes.

The maximum solubility of Hg in Au was determined as 19.5 at.% [34]. As the measured values based on EDX results show higher concentrations of Hg, it can be assumed that only part of the Hg is used for amalgamation, whereas the residual part is present in unalloyed form at the wire surface, which is in accordance with the SEM interpretation discussed before. Another explanation is the formation of Hg-based reaction products, which are removing Hg from the Au, while the subsequent EDX investigation is probing both, the metallic Hg in the amalgam and the Hg present as precipitates on the surface.

Potential stability of the reference electrodes

For verification of potential stability of the fabricated reference electrodes, open-circuit potential (E_{OCP}) transients were measured for all types of reference electrodes versus a commercially available RHE. Potential values were converted to potentials versus SHE for better comparability. Recorded potential transients, which were measured for almost 14 h, are presented in Fig. 3. Average potential values are 0.319 V (SHE)±1 mV and 0.312 V (SHE)±1 mV for Cu|CuSO$_4$ electrodes in glass and PTFE enclosure, respectively. For Hg|HgO-type reference electrodes, average E_{OCP} values of 0.173 V (SHE)±1 mV (glass enclosure) and 0.162 V (SHE)±2 mV (flexible) were measured. For both reference electrode types, the flexible electrode shows slightly lower E_{OCP} compared to the glass-type electrodes. The difference in potential is 7 mV in the case of Cu|CuSO$_4$ electrodes and 11 mV for Hg|HgO electrodes. The glass capillaries used, consisting of borosilicate glass, are characterized by a higher ionic conductivity compared to PTFE [35, 36]. Moreover,
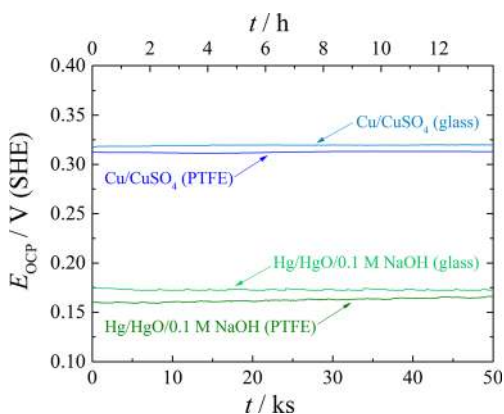
the surface of the electrochemically and chemically oxidized amalgam. Care should be taken in the case of thermal treatment to avoid decomposition of the amalgam followed by evaporation of Hg. The smooth surface of the heat-treated sample results from thermally induced surface restructuring processes combined with homogeneous oxidation. The electrochemically oxidized surface is covered with below 1-μm sized precipitates. The surface of the chemically treated surface exhibits the largest roughness with larger precipitates of 1–2-μm size. Precipitates could be identified as HgO. The basic morphological characteristics of the surface result from the amalgamation process with the formation of Hg droplets on the Au surface. This observation is in accordance with earlier studies [15].

The composition of the oxidized surfaces was analyzed with EDX. The determined compositions are summarized in Table 1. In the case of a complete oxidation of Hg, the atomic ratio n of Hg and O should be 1. In the direct comparison of

Fig. 3 Open-circuit potential measurements of the prepared μ-reference electrodes measured in saturated CuSO₄ solution versus Ag/AgCl-macro RE for Cu/CuSO₄-type electrodes and in 0.1 M NaOH solution versus RHE for Hg/HgO-type electrodes

intercalation of protons into the glass influences the pH value close to the electrode tip [37]. Combined with the hydrophobicity of PTFE, potential shifts resulting from the electrode enclosure material can be explained.

Theoretical values for electrode potentials can be calculated for both types of reference electrodes using the Nernst equation:
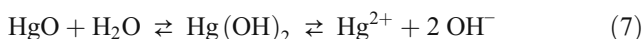
$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{Ox}}{a_{Red}} \qquad (5)$$

Activities of the oxidized and reduced species (a_{Ox}, a_{Red}) can deviate from the concentrations in the case of amalgam formation, leading to values below 1 for the activity of a_{Hg}.

The electrode potential of the Hg|HgO-reference electrode is based on:

$$HgO + H_2O + 2\,e^- \rightleftarrows Hg + 2\,OH^- \qquad (6)$$
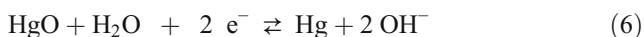
With HgO undergoing following equilibrium reaction

$$HgO + H_2O \rightleftarrows Hg(OH)_2 \rightleftarrows Hg^{2+} + 2\,OH^- \qquad (7)$$

the electrode potential of the Hg|HgO|OH⁻ electrode can be calculated as [8]:

$$E_{Hg|HgO|OH^-} = E^0_{Hg|Hg^{2+}}$$
$$+ \frac{RT}{2F} \ln K_{Hg(OH)_2} - \frac{RT}{F} \ln \left(C_{OH^-} \; \gamma_{OH^-} \right) \qquad (8)$$

Assuming an OH⁻ concentration c_{OH^-} of 0.1 and an activity coefficient γ_{OH^-} of 0.7820 [38] and a standard electrode potential $E^0_{Hg|Hg^{2+}}$ of 0.85 V [39], the electrode potential is theoretically 0.163 V, which is in good agreement with the measured electrode potential of the flexible reference electrode.

In the case of Cu|CuSO₄, electrode following equilibrium determines the electrode potential:

$$Cu \rightleftarrows Cu^{2+} + 2\,e^- \qquad (9)$$

The electrode potential can be described as:

$$E_{Cu|Cu^{2+}} = E^0_{Cu|Cu^{2+}} + \frac{RT}{2F} \ln \left(c_{Cu^{2+}} \; \gamma_{Cu^{2+}} \right) \qquad (10)$$

With $E^0_{Cu|Cu^{2+}} = 0.340$ V [40] and $\gamma_{Cu^{2+}} = 0.039$ for a saturated CuSO₄ solution being 1.41 molal at 25 °C [41], an electrode potential of 0.303 V can be calculated. However, a potential value of 0.317 V (SHE) was determined by Stern et al. [42]. The potential difference compared to the measured values of 0.319 and 0.312 V, respectively, can be due to deviations of the activity coefficient valid for saturated liquid CuSO₄ solution, which is not necessarily equal to the activity coefficient valid for the CuSO₄-gelatin mixture. This would not be surprising as the chemical environment for the Cu ion is different in water as compared with gelatin. As the measured values exceed the theoretical value, an increased activity coefficient can be assumed for the gelatin-immobilized saturated CuSO₄ electrolyte.

Further characterization of the μ-reference electrodes was performed in terms of electrochemical impedance spectroscopy, which was repeatedly shown to be a suitable method of analyzing reference electrode stability [4, 15]. The prepared μ-electrodes were measured in combination with a commercially available reference electrode. Figure 4 presents the EIS spectra obtained for the flexible and rigid type of Hg/HgO-μ-reference electrodes. The phase shift φ is almost completely frequency independent with values between −23° and 0° over the entire frequency range. The impedance of the reference electrodes increases slightly with decreasing frequency. Generally, the impedance of μ-reference electrodes tends to be higher compared to commercially available reference electrodes. The overall change of impedance for a variation of frequency of seven orders of magnitude is a factor of 10 for the flexible and 6 for the rigid type of Hg|HgO-reference electrode, respectively.

The characterization in the frequency domain was performed in a similar way for the Cu|CuSO₄-reference electrodes. The resulting impedance spectra are presented in Fig. 5 revealing a similarly frequency-independent behavior of impedance and phase shift as observed for Hg|HgO electrodes. Changing the frequency over seven orders of magnitude leads to alternation of impedance of factor 2 for flexible and 10 for glass-type electrodes, respectively. The minimum observed phase shift was −21° and −26° for these two types of Cu|CuSO₄ electrodes.
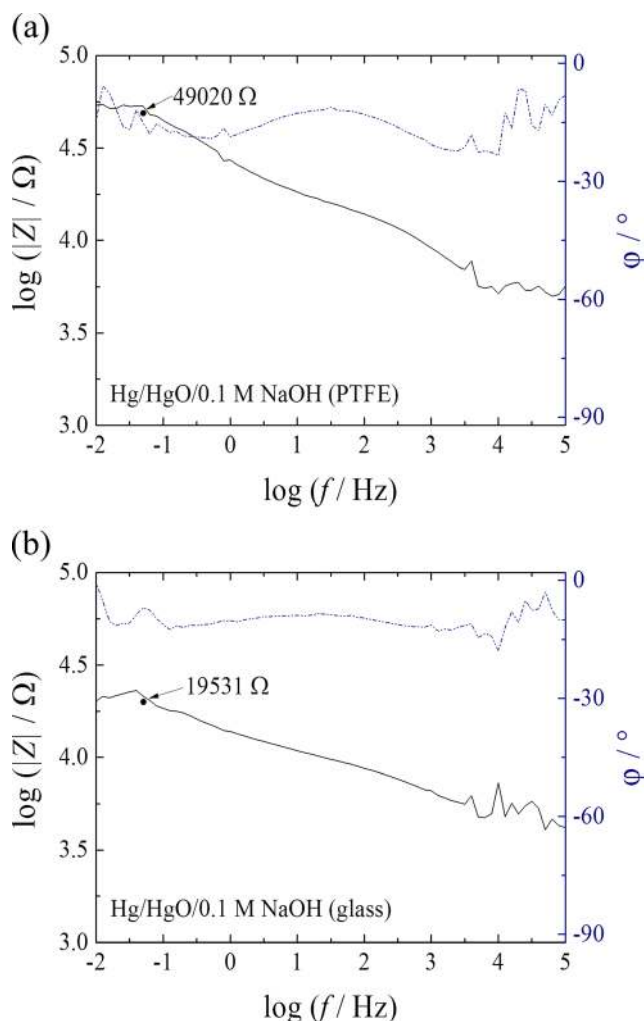
Fig. 4 Impedance spectra presented as Bode plot with phase shift ϕ (*dotted line*) and impedance |Z| (*solid line*) of **a** Hg/HgO-μ-electrodes embedded in PTFE tube and **b** for electrodes embedded in glass capillary. Impedance calculated from micro-polarization curves (Fig. 6) is included (*circle*) for comparison

Fig. 5 Impedance spectra presented as Bode plot with phase shift ϕ (*dotted line*) and impedance |Z| (*solid line*) of **a** Cu/CuSO₄-μ-electrodes embedded in PTFE tube and **b** for electrodes embedded in glass capillary. For comparison, impedance calculated from micro-polarization curves (Fig. 7) is included (*circle*)

For the determination of the electrode's inner resistance and reversibility of its potential when current is forced through the electrode, micro-polarization curves were recorded by applying a triangular potential waveform with $E_{OCP} + 10$ mV and $E_{OCP} - 10$ mV as vertex potentials and a potential scan rate of 2 mV s^{-1}. By evaluating the slope of the line connecting the current values at the potential limits (Fig. 6), the inner resistance of the electrode can be calculated as reciprocal value of the slope. For the flexible Hg|HgO-reference electrode, a value of 49.0 kΩ can be obtained, whereas the resistance of the rigid-type Hg|HgO is lower with 19.5 kΩ. This resistance can be used for comparison with EIS data before. As a potential range of 20 mV was periodically scanned with 2 mV s^{-1}, it can be interpreted as frequency of 0.05 Hz. Strictly speaking, one would need to represent the triangular waveform by the sum of different sinusoidal signals—an approach
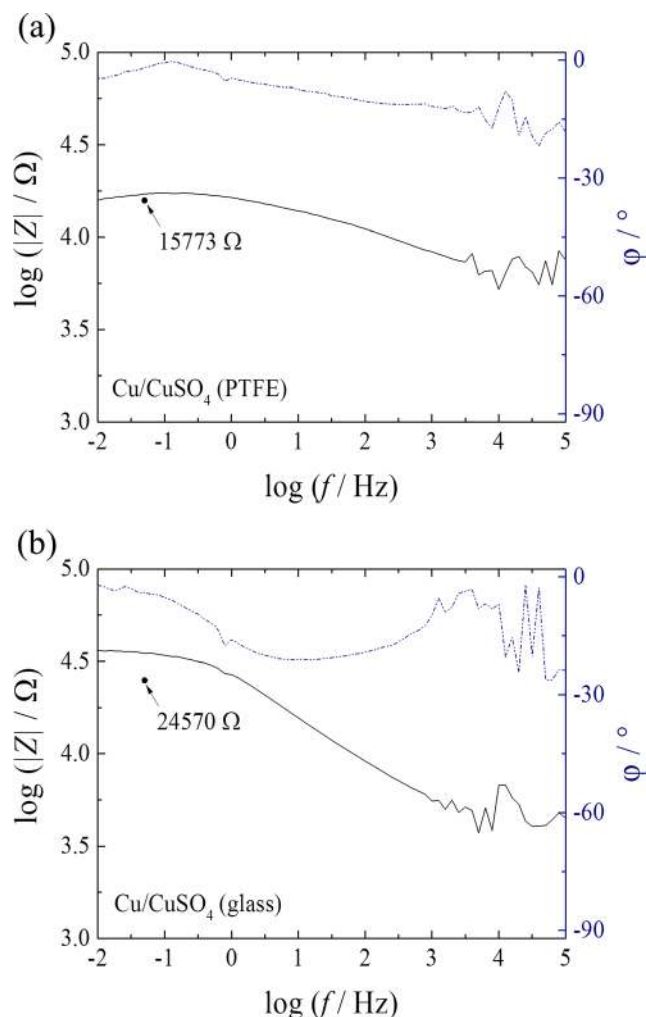
that is called Fourier synthesis. In any case for such a conversion, it is clear that lowest sinusoidal frequency is the triangular frequency of 0.05 Hz and all other higher frequencies are odd orders with a significantly lowered amplitude [43]. The corresponding impedance values calculated from the polarization curves are plotted in the EIS spectra (Figs. 4 and 5). Additionally to the impedance value, the exchange current I_0 can be calculated from the determined slope ($\delta I / \delta E$) [44]:

$$I_0 = \frac{RT}{F} \frac{\delta I}{\delta E} \tag{11}$$

From Eq. 11, values of 524 nA and 1.315 μA are obtained for the flexible and the rigid Hg|HgO-reference electrodes, respectively.

Ideally, the micro-polarization curves should not reveal any kind of hysteresis. However, a small hysteresis can be
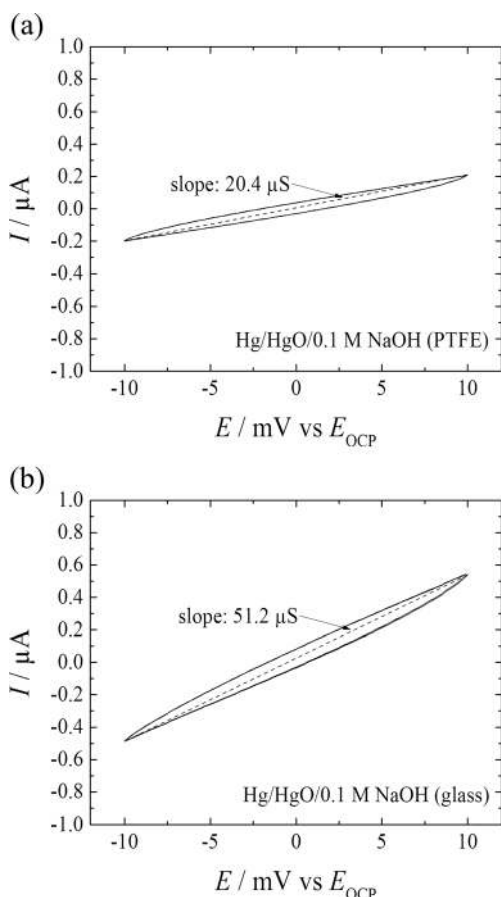
Fig. 6 Micro-polarization curves obtained with a potential scan rate of 2 mV s^{-1} for **a** Hg/HgO-μ-electrodes embedded in PTFE tube and **b** for electrodes embedded in glass capillary. Evaluation of the inner resistance of the electrodes is depicted as *dotted line* between the points of inflection resulting in a slope of **a** 20.4 and **b** 51.2 μS

Fig. 7 Micro-polarization curves obtained with a potential scan rate of 2 mV s^{-1} for **a** Cu/CuSO$_4$-μ-electrodes embedded in PTFE tube and **b** for electrodes embedded in glass capillary. Evaluation of the inner resistance of the electrodes is depicted as *dotted line* between the points of inflection resulting in a slope of **a** 63.4 and **b** 40.7 μS

observed for the Hg|HgO-reference electrodes. The maximum deviation between the scan toward positive and toward negative potential values, with reference to E_{OCP}, is 67 and 115 nA for both studied electrode types. These values correspond to 18 and 11 % deviation referred to overall maximum polarization. After the polarization experiment, fast potential relaxation (<1 min) back to the initial E_{OCP} could be observed, proving the usability of the reference electrodes even in the case of polarization.

In contrast to the Hg|HgO electrodes, Cu|CuSO$_4$-type reference electrodes demonstrate a higher grade of reversibility when current is passed through them. Figures 6 and 7 shows the micro-polarization curves obtained for both flexible and rigid-type electrodes with negligible hysteresis. The inner resistance was determined as described before, resulting in 15.8 kΩ for the electrode in PTFE-enclosure and 24.6 kΩ for the glass-type electrode. The values are also indicated in Fig. 5 at a frequency of 0.05 Hz. Furthermore, exchange currents of 1.628 and 1.045 μA were calculated for PTFE- and glass-type electrode.
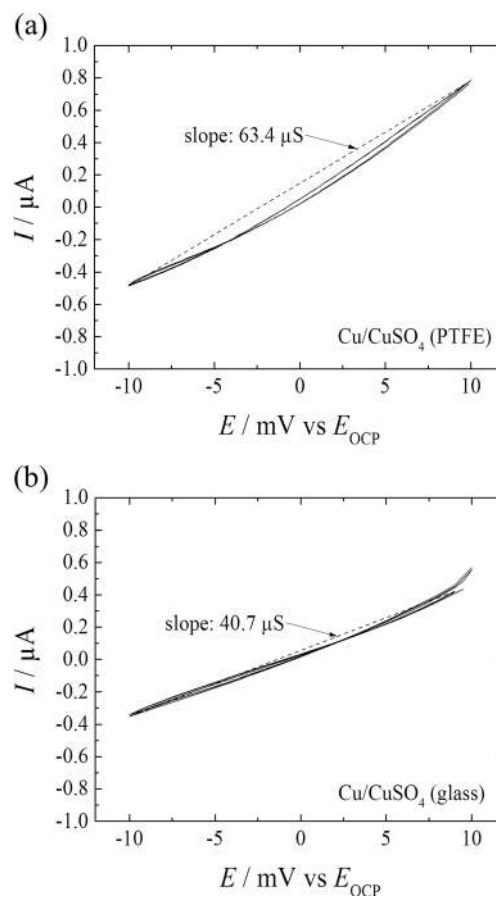
Temperature stability of gel electrolytes and electrode recycling

Use of gel-type reference electrode with respect to temperature is limited to the stability of the gel. Gelatin-based electrolyte gels can be used up to the temperature, at which the gelatin mixture is liquefied, which was determined as 45 to 50 °C for the CuSO$_4$-gelatin gel. In the case of PAA-g-PEO-based electrolyte, the gel is stable up to higher temperatures. When heated above 90 °C boiling and accompanying, gas bubble formation can be observed.

Suitable storage conditions, as described in the Experimental section, ensure electrode potential stability for several months. In the case of drying up of the gel electrolyte or potential instability due to impurities within the gel, the flexible reference electrodes can be reused. For this purpose, the Au(Hg)|HgO-wire can be removed after carefully cutting the PTFE tube at the glued end. The obtained wire can be inserted into a clean PTFE tube, which is then refilled with gel electrolyte.

Conclusion

Hydrogel-based flexible Hg|HgO- and Cu|CuSO$_4$-type micro-reference electrodes were fabricated. HgO formation on amalgamated gold wire was most conveniently achieved by oxidation with a permanganate solution. PTFE enclosure of the electrodes ensures chemical and temperature stability. Potential stability was investigated in terms of long-term open-circuit potential measurements, impedance spectroscopy, and micro-polarization experiments. The two fabricated types of electrodes are intended for use in alkaline solutions in the case of Hg|HgO electrodes and as reference electrodes in neutral electrolytes in the case of Cu|CuSO$_4$ electrodes.

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