

# A combined $\mu$ -mercury reference electrode/Au counter-electrode system for microelectrochemical applications

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**Abstract** Different types of mercury-based  $\mu$ -reference electrodes ( $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ ,  $\text{Hg}/\text{Hg}_2(\text{CH}_3\text{COO})_2/\text{NaCOOCH}_3$ ) have been developed following the concept of agar-based  $\mu$ -reference electrodes. Mercury was electrochemically deposited onto a gold wire to form an amalgam. The corresponding mercury salt was formed electrochemically at the surface. This electrode can be inserted into a capillary that is filled with the electrolyte of interest. To simplify the handling of this  $\mu$ -reference electrode, to reduce diffusion and to avoid leakage, the electrolyte was immobilised with agar. A 250-nm-thick gold layer on the outer surface of the capillary of the reference electrode served as counter-electrode. The electrochemical behaviour of reference electrodes and counter-electrodes were proven by micro-polarisation curves, electrochemical impedance spectroscopy, potential transients and cyclic voltammetry.

**Keywords** Microelectrodes · Reference electrodes · Scanning droplet cell

## Introduction

An agar-based silver/silver chloride reference electrode for use in micro-electrochemistry was introduced by Hassel, Fushimi and Seo in 1999 [1]. Due to the use of electrolyte-containing agar, they developed a simple production way for small Ag/AgCl reference electrodes. They also men-

tioned that the principle used could be adapted to other types of reference electrodes.

Lots of corrosion phenomena are localised in nature and require investigation methods of high spatial resolution. As chloride, which is used in Ag/AgCl, may initiate or accelerate corrosion such as pitting, salt bridges are required. More elegant, however, is the use of a corresponding reference electrode of second type in which the electrolyte is directly determining the concentration of the anions via their solubility product. The concentration of the potential determining cation results from the solubility product  $K_a$ . As mercury and particularly the  $\text{Hg}_2^{2+}$  ion form insoluble salts with most anions, there is a wide selection of systems.

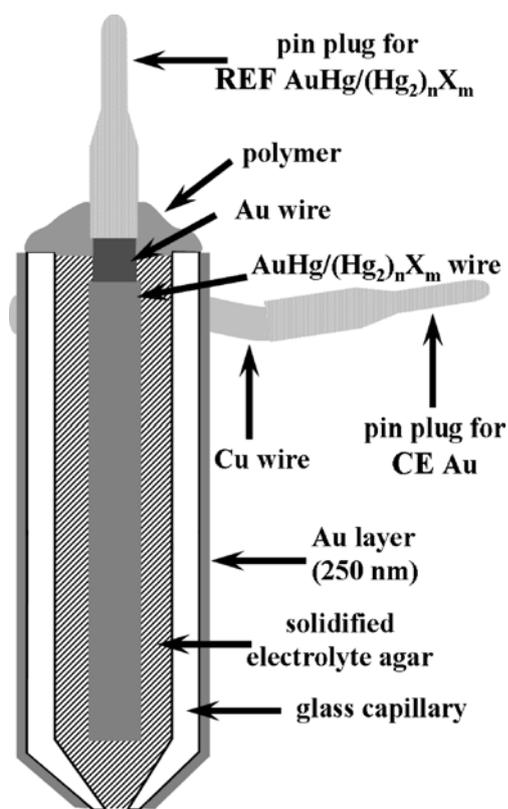
In the work presented here, different types of mercury-based  $\mu$ -reference electrodes based on the concept of solidified electrolyte were realised. Furthermore, the concept of solidified mercury for easy manageability of the metal has been introduced. To achieve this, an amalgamated gold wire was used as mercury reservoir. In this paper, the preparation path and proof of the electrochemical behaviour are presented.

## Experimental

### Chemicals

All solutions were prepared from reagent-grade chemicals and deionised water (USF Elga, Purelab Plus). The gold wire had a diameter of 200  $\mu\text{m}$  and the purity was 99.999 %. A commercial Ag/AgCl/3 M KCl reference electrode (Radiometer) was used to confirm the potentials of the macroscopic reference electrodes used for the comparative studies.

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**Fig. 1** Schematic of the combined  $\mu$ -( $\text{Hg}_2$ ) $_n$ ( $X$ ) $_m$  reference electrode/Au counter-electrode system

## Preparation

### Preparation of the Au counter-electrode

The commercially available capillaries used here had an outer diameter of 1,000  $\mu\text{m}$  and an inner diameter of 800  $\mu\text{m}$ . The glass capillary was cleaned in acetone and ethanol in an ultrasonic bath for 5 min in each case. A thin gold layer of approximately 250 nm was deposited on one side of the capillary by electron beam vapor deposition. After the deposition process, the capillary was formed to the desired shape and size using a capillary puller (PC-10, Narishige, Japan) and a micro-grinder (EG-400, Narishige, Japan). After the melting and the grinding of the capillary, the deposited gold layer covered the glass wall even on the tapered end of the capillary. The tip diameter used in the electrochemical characterisation was 100  $\mu\text{m}$ . To get a contact to the counter-electrode, a thin copper wire which was connected to a pin plug was wrapped around the upper part of the capillary. In addition, to ensure good conductivity, conductive silver paste was applied. The wire was then fixed by using two-component epoxy resin glue. Finally, the copper wire was isolated with a heat shrink tube to avoid contact to the pin plug of the reference electrode.

### Preparation of Au wires and deposition of mercury on Au wire

The Au wires were cut to the required length by a ceramics shear (Kyocera) to avoid rubdown of metal to the Au. Then they were soldered at one end to a pin plug to guarantee an easy connection. Afterwards, they were cleaned in acetone and ethanol in an ultrasonic bath for 5 min in each case.

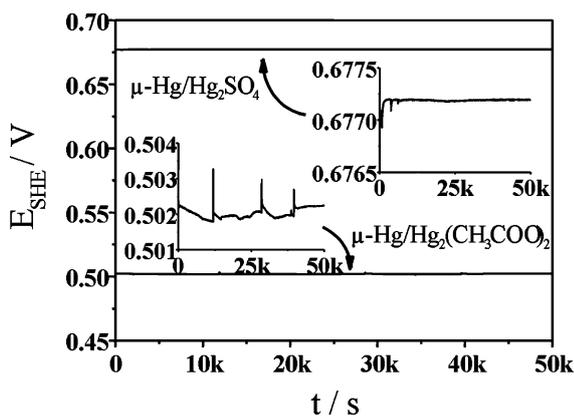
Mercury was deposited electrochemically on gold wire (diameter 200  $\mu\text{m}$ , purity 99.999 %) in aqueous 0.1 M  $\text{Hg}_2(\text{NO}_3)_2$  solution. The mercury was deposited by polarising to 0.2 V (SHE) for 180 s. The partially amalgamated gold wire was then rinsed with water to clean it from residual  $\text{Hg}_2(\text{NO}_3)_2$ .

### Preparation of $\mu$ -AuHg/ $\text{Hg}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ and $\mu$ -AuHg/ $\text{Hg}_2(\text{CH}_3\text{COO})_2/\text{NaCH}_3\text{COO}$ reference electrodes

$\text{Hg}_2\text{SO}_4$  ( $\text{Hg}_2(\text{CH}_3\text{COO})_2$ ) was deposited electrochemically on the gold mercury wire in 1 M  $\text{H}_2\text{SO}_4$  ( $\text{NaCH}_3\text{COO}$ ). The AuHg wire was polarised to 0.7 V (0.58 V) for 180 s (600 s). After polarisation, the wire was rinsed with water to clean it from  $\text{H}_2\text{SO}_4$  ( $\text{NaCH}_3\text{COO}$ ) solution. The wire was inserted into a capillary. Then the capillary was connected to a vacuum pump. A mixture of 0.5 M  $\text{Na}_2\text{SO}_4$  (saturated  $\text{NaCH}_3\text{COO}$ ) solution and 3 wt % agar was boiled until the agar was dissolved. The solution was left until a bubble-free region appeared. The hot solution was drawn into the capillary promptly to prevent further cooling down which would lead to unrequested solidification. After the solution was cooled down, the capillary containing the solidified agar and the AuHg/ $\text{Hg}_2\text{SO}_4$  (AuHg/ $\text{Hg}_2(\text{CH}_3\text{COO})_2$ ) wire was taken out of the agar and the wire was fixed to the glass capillary with two-component epoxy resin glue.

## Electronics

A digital multimeter MXD-4660A (voltcraft), connected to a personal computer, was used to capture the data of the potential transients. For data acquisition, a program based on VEE 6.0 was utilised. The preparation of the electrodes and the investigation on the stability of the  $\mu$ -electrodes, micro-polarisation curves and impedance spectra were recorded by a setup including a Princeton Applied Research Potentiostat/Galvanostat Model 283 and a Solartron SI 1260 Impedance Gain/Phase Analyser. All electronic devices were connected to a personal computer through the GPIB bus. The perturbation signal used in the impedance measurements was 1 mV rms.



**Fig. 2** Potential transients recorded immediately after preparation of the  $\mu$ -reference electrodes. The electrolytes used for  $\mu$ -Hg/Hg<sub>2</sub>SO<sub>4</sub> was 0.5 M H<sub>2</sub>SO<sub>4</sub>; for  $\mu$ -Hg/Hg<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>, 1 M NaCH<sub>3</sub>COO was used

**Results and discussion**

Potential of mercury based  $\mu$ -reference electrodes

Figure 1 shows a schematic of the  $\mu$ -Hg/(Hg<sub>2</sub>)<sub>n</sub>X<sub>m</sub> reference electrode/Au counter-electrode system. The diameter of the electrode is given by the capillary. To characterise the reference electrodes, the potential transients were measured vs. a common macroscopic Hg/Hg<sub>2</sub>SO<sub>4</sub> or Hg/Hg<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> reference electrode, respectively. Both electrodes were calibrated against a commercial macroscopic Ag/AgCl/3M KCl reference electrode previously to confirm the exact potential.

Figure 2 shows the potential transients for both  $\mu$ -reference electrodes. The electrodes were immersed in solution directly after the preparation and the potential recording was started immediately. The stability of the potential is excellent for both types of reference electrodes. Long time measurements showed that the potential deviation was never more than 2 mV from this early average for 4 weeks after preparation.

It should be considered that the activity of the reduced species is less than 1 due to the formation of gold amalgam. The solubility of Hg in Au is max. 19 at.%. Phases like Hg<sub>2</sub>Au are not present in the Au–Hg phase diagram [2].

**Table 1** Literature values for the reference potential  $E_0$  of macroscopic reference electrodes and the solubility constants  $K_a$  for the mercury salts [3, 4]

|   |   |
|---|---|
| Mercury–mercuric X couple                   | $E_0$ SHE/V                                       |
| $2Hg + SO_4^{2-} = Hg_2SO_4 + 2e^-$         | 0.615   |
| $2Hg + 2CH_3COO^- = Hg_2(CH_3COO)_2 + 2e^-$ | 0.51  |
| Mercury–mercuric X couple                   | $K_a$   |
| $Hg_2 + SO_4 = Hg_2^{2+} + SO_4^{2-}$       | $1 \cdot 10^{-6} \text{ mol}^2 \text{ l}^{-2}$    |
| $Hg_2(CH_3COO)_2 = Hg_2^{2+} + 2CH_3COO^-$  | $3.6 \cdot 10^{-10} \text{ mol}^3 \text{ l}^{-3}$ |

In this study, 10 at.% Hg have been deposited onto the Au wire.

Using the Nernst equation

$$E = E_0 + \frac{RT}{zF} \ln \frac{[Ox]}{[Red]} \tag{1}$$

and the chemical equation



the equation for the mercury ion electrode is given by:

$$E^{Hg/Hg_2^{2+}} = E_0^{Hg/Hg_2^{2+}} + \frac{RT}{2F} \ln \frac{[Hg_2^{2+}]}{[Hg]^2} \tag{3}$$

By using the equation for the solubility product of mercury salt:

$$K_a^{mercurysalt} = [Hg_2^{2+}]^n [A^{m-}]^{\frac{2n}{m}} \tag{4}$$

the potential of the mercury/mercury salt electrode can be calculated by the equation given below:

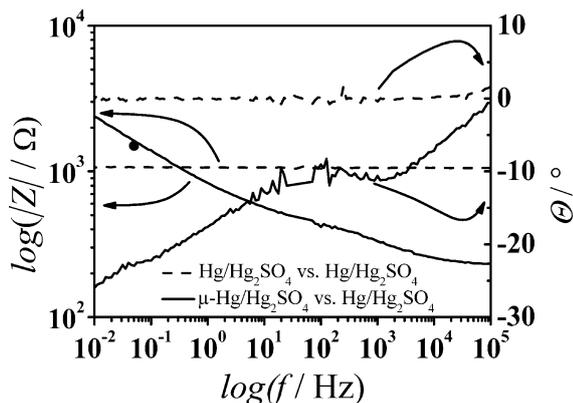
$$E^{Hg/(Hg_2)_n A_{\frac{2n}{m}}/A^{m-}} = E_0^{Hg/(Hg_2)_n A_{\frac{2n}{m}}/A^{m-}} - \frac{RT}{mF} \ln [A^{m-}] - \frac{RT}{F} \ln [Hg] \tag{5}$$

It can be seen that a decreased activity of the reduced species would result in a shift to a more anodic potential. However, the measured potentials are more negative. Therefore, the activity of the deposited mercury can be assumed as 1.

This corresponds to the observation that, after mercury deposition, small Hg droplets were formed on the gold wire surface, which remained visible for weeks. It indicates that, for some reason, the forming of the gold amalgam takes place just in the outer part of the gold wire. Even though it is known that heavy metals such as lead or mercury can easily penetrate gold, the observations made here do not give any hint on a complete absorption of the adsorbed mercury droplets within a time frame of 4 weeks. The literature values of  $E_0$  and  $K_a$  for the reference electrodes are given in Table 1 [3, 4].

Stability of mercury-based  $\mu$ -reference electrodes

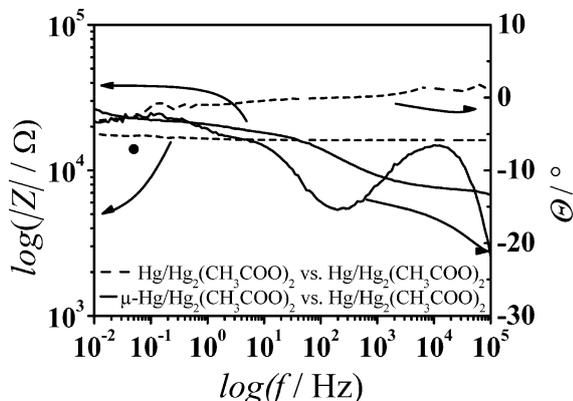
The characterisation of the electrode systems in the frequency domain was performed by electrochemical impedance spectroscopy. The procedure was similar to that described in [1]. In the first step, the impedance behaviour of two macroscopic reference electrodes of similar type was measured. In the second step, a combination of a  $\mu$ -reference electrode with the corresponding macroscopic



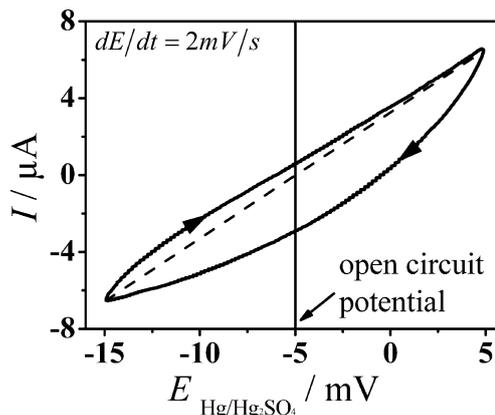
**Fig. 3** Impedance spectra of two different reference electrode combinations. The *dashed lines* (—) present the results for the combination of two macroscopic electrodes. The *bold lines* (—) show the results for the combination of a  $\mu$ -reference electrode with a macroscopic electrode. The *black dot* (•) represents the impedance calculated from the micro-polarisation (Fig. 5)

reference electrodes was investigated in the same way. The results are presented in Figs. 3 and 4.

Figure 3 shows the results performed on Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode combinations. The measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The impedance of the combination of two macroscopic reference electrodes is nearly perfectly frequency independent. The value of the impedance is constantly  $1.06 \cdot 10^3 \Omega$  over the whole frequency range investigated here. The phase shift is near to 0°. The combination of a  $\mu$ -Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode with one of the macroscopic electrodes shows just a weak frequency dependance. In the frequency range  $10^5$ – $10^0$  Hz, the impedance value is lower than for the pre-described combination. The phase shift did not exceed |26°. The



**Fig. 4** Impedance spectra of two different reference electrode combinations. The *dashed lines* (—) present the results for the combination of two macroscopic electrodes. The *bold lines* (—) show the results for the combination of a  $\mu$ -reference electrode with a macroscopic electrode. The *black dot* (•) represents the impedance calculated from the micro-polarisation (Fig. 6)

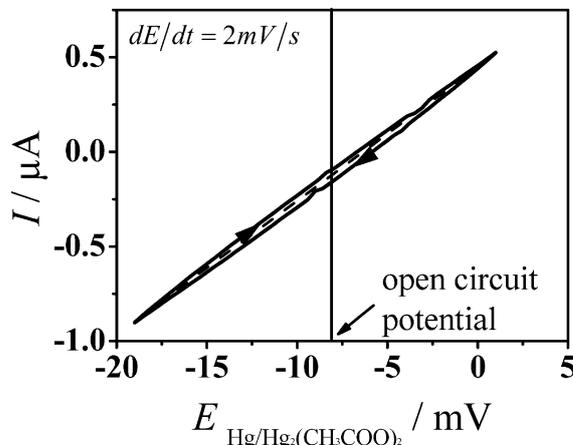


**Fig. 5** Micro-polarisation curve of a  $\mu$ -reference electrode combined with a macroscopic reference electrode. The open-circuit potential was  $E_{OCP} = -5$  mV. Cycling was done with  $dE/dt = 2$  mV/s between  $E_{OCP} - 10$  mV and  $E_{OCP} + 10$  mV. The *dashed line* between the points of inflection has a slope of  $652 \mu S$

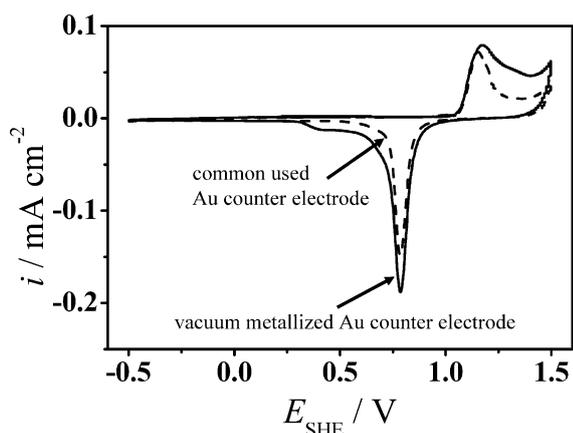
overall change of the impedance is a factor of 10 for a change in frequency of seven orders in magnitude.

Figure 4 shows the results for the measurements performed on the Hg/Hg<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> electrode combinations. The electrolyte was 1 M NaCH<sub>3</sub>COO. The result of the impedance measurement performed on a combination of two macroscopic electrodes is plotted in dashed lines. The behaviour is almost frequency independent. The impedance has a constant value of  $1.6 \cdot 10^4 \Omega$  and the phase shift is nearly 0° over the whole frequency range investigated.

The microscopic/macroscopic combined arrangement shows just a weak dependance in frequency. This phase shift did not exceed |21°. It is notable that the frequency dependance for the phase shift is stronger in the lower



**Fig. 6** Micro-polarisation curve of a  $\mu$ -reference electrode combined with a macroscopic reference electrode. The open-circuit potential was  $E_{OCP} = -7$  mV. Cycling was done with  $dE/dt = 2$  mV/s between  $E_{OCP} - 10$  mV and  $E_{OCP} + 10$  mV. The *dashed line* between the points of inflection has a slope of  $71.35 \mu S$



**Fig. 7** Cyclic voltammograms performed on vacuum-metallised Au electrode (*bold line*) and on a commonly used (bulk) Au electrode (*dashed line*). The scan rate was 20 mV/s. The electrolyte was deaerated acetate buffer solution with pH=6.0

frequency range than in the higher region as for the  $\mu\text{-Hg}/\text{Hg}_2\text{SO}_4$  reference electrode. The overall change is a factor of 4 for a change in frequency of seven orders in magnitude.

The ability to recover and the independence on frequency are important features. Figures 5 and 6 show the micro-polarisation curves obtained from the  $\mu$ -reference electrodes in combination with their corresponding macroscopic electrodes. These combinations enabled a direct comparison with the impedance data discussed before.

The open circuit potential (OCP) was monitored over 600 s. Then,  $E_{\text{OCP}} - 10$  mV and  $E_{\text{OCP}} + 10$  mV were chosen as limits for cycling the potential with a scan rate of 2 mV/s. The micro-polarisation curve of the  $\mu\text{-Hg}/\text{Hg}_2\text{SO}_4$  reference electrode is presented in Fig. 5. The dashed line between the chosen potential limits has a slope  $\delta I/\delta E$  of 652  $\mu\text{S}$ . The slope yields the inner resistance of the electrode. The inner resistance has a value of 1.5 k $\Omega$ . As described in [1], the micro-polarisation curve can be interpreted in terms of an impedance measurement. The triangular instead of a sinusoidal perturbation signal is the main difference. The frequency corresponding to the resistance can be calculated from the perturbation amplitude and the sweep rate. The value is 0.05 Hz. The impedance as calculated from the micro-polarisation curve is plotted in Fig. 3 as black dot.

Figure 6 shows the micro-polarisation curve measured for the  $\mu\text{-Hg}/\text{Hg}_2(\text{CH}_3\text{COO})_2$  reference electrode. The value for the slope  $\delta I/\delta E$  is 71.35  $\mu\text{S}$ . The inner resistance of the electrode has been calculated to be 14 k $\Omega$ . The value for the impedance is shown as black dot in Fig. 4.

Using Eq. (6) [5],

$$I_0 = \frac{RT}{F} \frac{\delta I}{\delta E} \quad (6)$$

the exchange current  $I_0$  can be calculated.  $R$  is the gas constant ( $R=8.3144$  VAs/K mol),  $F$  is the Faraday constant ( $F=9.64846 \cdot 10^4$  As/mol),  $T$  is the temperature (in Kelvin) and  $\delta I/\delta E$  is the slope described before. For the  $\mu\text{-Hg}/\text{Hg}_2\text{SO}_4$  reference electrode, the value is 16.7  $\mu\text{A}$ . The exchange current for the  $\mu\text{-Hg}/\text{Hg}_2(\text{CH}_3\text{COO})_2$  reference electrode is  $I_0=1.83$   $\mu\text{A}$ .

The micro-polarisation curve for the  $\mu\text{-Hg}/\text{Hg}_2\text{SO}_4$  reference electrode shows a hysteresis. The maximum deviation is  $\delta E=9.12$  mV. The  $\mu\text{-Hg}/\text{Hg}_2(\text{CH}_3\text{COO})_2$  reference electrode shows in the micro-polarisation curve just a small hysteresis with a maximum value of  $\delta E=0.99$  mV. The results of the micro-polarisation curves prove the stability and reversibility of the  $\mu$ -reference electrodes presented here. It is hereby demonstrated that tailored reference electrodes are useful for integrated technical solutions not only in microelectrochemistry but also in silicon chip technology [6].

#### Characterisation of the gold counter-electrode

Figure 7 shows the cyclic voltammograms of a gold counter-electrode prepared by electron beam deposition with a surface area of 0.3 cm<sup>2</sup> (solid line —) and bulk material with a surface area of 5 cm<sup>2</sup> (dashed line ---) performed in deaerated acetate buffer solution with pH=6.0. The scan rate was  $\frac{dE}{dt} = 20\text{mV/s}$ . The reference electrode was Ag/AgCl; the counter-electrode was an Au foil counter-electrode. The voltammograms are normalised to the electrode area. Both electrodes show a similar electrochemical behaviour.

As mentioned above, the  $\mu$ -electrode system can be used among others in a scanning droplet cell [7, 8]. The working area in these setups depends on the diameter of the electrolyte droplet attached to the sample surface, which is in turn defined by the capillary diameter. The commonly used capillary diameters are 500  $\mu\text{m}$  or less. In case of a working area diameter of 500  $\mu\text{m}$ , the area ratio of counter-electrode to working area is 153:1 and increases further with decreasing working area diameter.

#### Conclusions

In this work, different types of combined  $\mu\text{-Hg}_2(\text{X})_n$  reference electrode/Au counter-electrode systems for the use in scanning droplet cells and other local techniques have been presented. The electrolyte solidified by agar has been combined with the use of partially amalgamated gold mercury wire, which guarantees easy handling. The  $\mu$ -reference electrodes show a long lifetime and an excellent potential stability.

## References

1. Hassel AW, Fushimi K, Seo M (1999) *Electrochem Commun* 1:180
2. Okamoto H, Massalski TB (1986) In: Massalski TB (ed) *Binary alloy phase diagrams*, vol 1, Au–Hg (gold–mercury). American Society for Metals, Ohio, pp 265–267
3. Janz GJ (1961) In: Ives DJG, Janz DJ (eds) *Silver–silver halide electrodes in reference electrodes, theory and practice*. Academic, New York, pp 179–230
4. Latimer WM (1953) *Oxidation potentials*, second. Edition, zinc, cadmium, and mercury. Prentice-Hall, New York, pp 168–182
5. Brossia CS, Kelly RG (1996) *Electrochim Acta* 41:2579
6. Simonis A, Dawgul M, Lüth H, Schöning MJ (2005) *Electrochim Acta* 51:930
7. Hassel AW, Lohrengel MM (1997) *Electrochim Acta* 42:3327
8. Lohrengel MM, Moehring A (2002) In: Schultze J, Walter, Osaka Tetsuya, Datta Madhav (eds) *Electrochemical micro-system technologies*. Taylor and Francis, New York, ISBN 0-415-27355-2