Generator-collector electrochemical sensor configurations based on track-Etch membrane separated platinum leaves

Zafarani, Hamid Reza; Rassaei, Liza; Sudhölter, Ernst J.R.; Aaronson, Barak D.B.; Marken, Frank

Citation (APA)
Zafarani, H. R., Rassaei, L., Sudhölter, E. J. R., Aaronson, B. D. B., & Marken, F. (2018). Generator-collector electrochemical sensor configurations based on track-Etch membrane separated platinum leaves. *Sensors and Actuators B: Chemical: international journal devoted to research and development of physical and chemical transducers*, *255*(3), 2904-2909. https://doi.org/10.1016/j.snb.2017.09.110

Important note
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Research Paper

Generator–collector electrochemical sensor configurations based on track-Etch membrane separated platinum leaves

Hamid Reza Zafarani [a,b,*], Liza Rassaei [a], Ernst J.R. Sudhölter [a], Barak D.B. Aaronson [b], Frank Marken [b]

[a] Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands
[b] Department of Chemistry, University of Bath, Bath, UK

ABSTRACT

We report a novel, simple and cheap generator–collector electrode system, employing platinum leaves, with micron-sized pores and typically 100–300 nm thickness, sandwiched with a porous track etch membrane spacer with typically 30 nm diameter pores. The electrode assembly is sealed into a polymer lamination pouch with one side 2 mm diameter exposed to electrolyte solution. The generator electrode with sweeping potential (top or bottom electrode) shows transient current with high capacitive current component. The collector electrode with fixed potential shows well-defined steady state current response at low potential sweep rates. The fabricated device shows good performance in monitoring both 1,1′-ferrocenedimethanol oxidation and proton reduction redox processes. Oxygen sensor signals are assigned to a lowering of the steady state proton reduction current.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Generator–collector systems contain two working electrodes and provide powerful tools in electroanalytical studies [1]. Over the years these systems have been developed and studied in different geometries such as rotating ring-disk electrode [2], interdigitated electrodes [3,4], thin-layer cells [5,6] and nanoscale-recessed ring-disk electrodes [7]. Biasing proper potentials of these two closely spaced electrodes, allows repetitive oxidation and reduction of redox species between them and this leads to a strong amplification effects in sensing (known as redox cycling). This property then causes Faradaic current amplification to enhance the detection limit for analytical detection, also provides features such as suppressing irreversible interferences and enhancing the selectivity for reversible redox couples in electrochemical measurements [8,9]. Furthermore, by fixing the potential on the "monitor" electrode and scanning the potential only for the second electrode, voltammograms can be recorded free of capacitive currents with improved analytical detection of the Faradaic current.

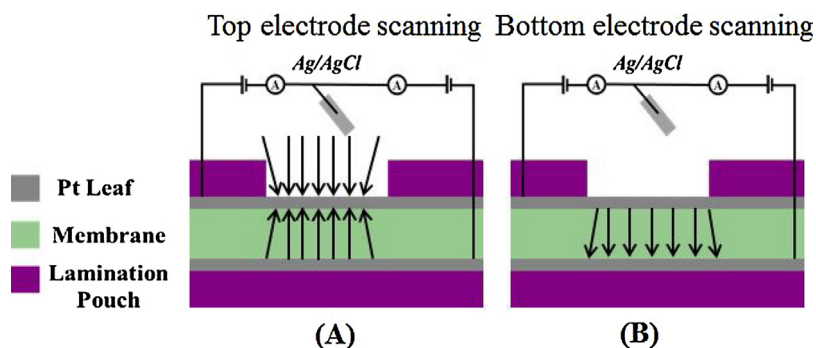One of the key and challenging features of these devices is the gap between the electrodes. Reducing the gap size to the nanometer range can enhanced the sensitivity toward single molecule detection [10,11]. However, in most cases fabrication of such a nanogap device needs access to the cleanroom facilities and requires following multiple sophisticated nanofabrication steps [10,12–14].

Hence, in recent years there is a great interest for developing simple low cost methods to fabricate the micro/nano junctions between two electrodes that work under redox cycling conditions. Wang et al. fabricated a generator–collector system by growing a silicon nanochannel membrane on electrodes to fabricate a nanogap [15], Park et al. employed spherical beads as spacer between the electrodes [16] and Adly et al. fabricated nanoporous redox cycling devices employing multilayer inkjet printing [17]. However in these methods several steps of substrate treating or preparing the inks and access to inkjet printing facilities are needed. Previously, we developed simple low cost methods to develop the micro-junctions between two electrodes that work under redox cycling conditions. Electro-deposition and employing an epoxy spacer layer can be a feasible way for creating dual electrodes with analytical applications [18–22]. Often, the dual electrode configuration was based on a "microtrench" with one side open to the electrolyte solution.
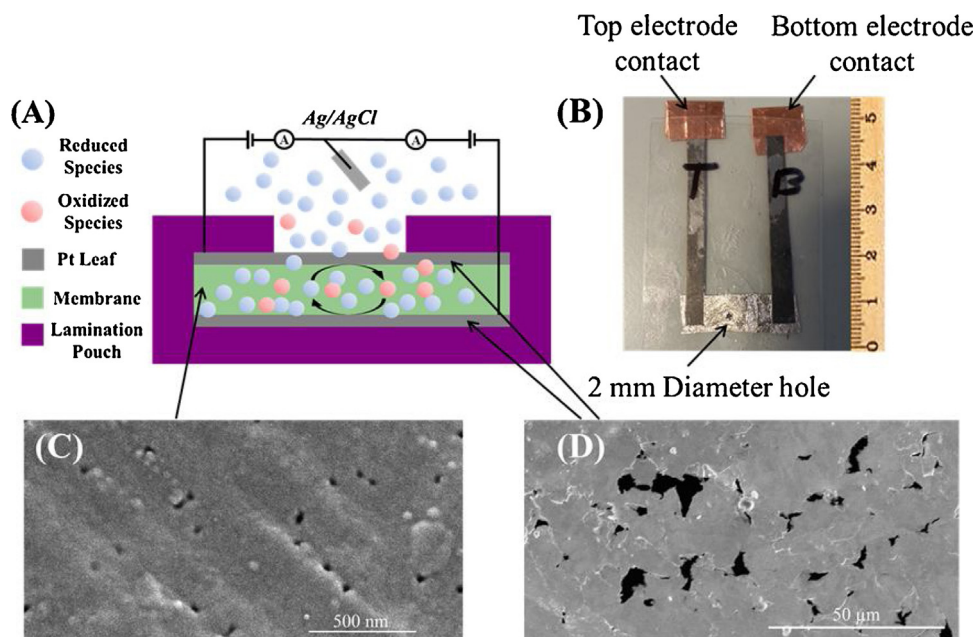
In this work we introduce a novel generator–collector electrode system using track-etch membrane and "platinum leaf" electrodes. Porous platinum leaf electrodes are employed and the two electrodes are mounted with one of the platinum leaves facing "outward" into the solution phase (Fig. 1). Using a porous track-etch

Fig. 1. Schematic drawing of a dual-platinum leaf sensor with (A) the outward facing electrode scanning and (B) the inward facing electrode scanning. Arrows are shown to indicate diffusional transport towards the "actively scanning" electrode.

Fig. 2. (A) Scheme of the device. (B) Fabricated device. (C) SEM image of the track etch membrane. (D) SEM image of the platinum leaf.

membrane layer between the two platinum leaf electrodes helps to prevent short–circuits while providing the diffusion path for redox species in the redox cycling process.

It is shown that the two electrodes can be employed in generator–collector mode, although significant differences are observed when using (A) the outward facing electrode as the scanning electrode or (B) the inward facing electrode as the scanning electrode. Processes based on the 1,1′-ferrocenedimethanol redox systems are demonstrated. Next, the reduction of protons is investigated and it is shown that oxygen concentration in solution is detected indirectly by lowering the local proton concentration within the dual-electrode generator–collector sensor. A wider range of applications is envisaged.

2. Experimental

2.1. Chemical reagents

1,1′-Ferrocene dimethanol, $Fc(MeOH)_2$, potassium nitrate, KNO_3 and nitric acid, HNO_3 were purchased from Sigma-Aldrich. Genuine platinum leaves (Wrights of Lymm Ltd) were purchased. Scanning electron micrographs suggest approximately 100–300 nm thick platinum (*vide infra*) with 1–10 μm diameter holes. Osmonics Inc. (Catalog No.KN3CP02500) polycarbonate track etch membrane with 30 nanometer diameter pore size was
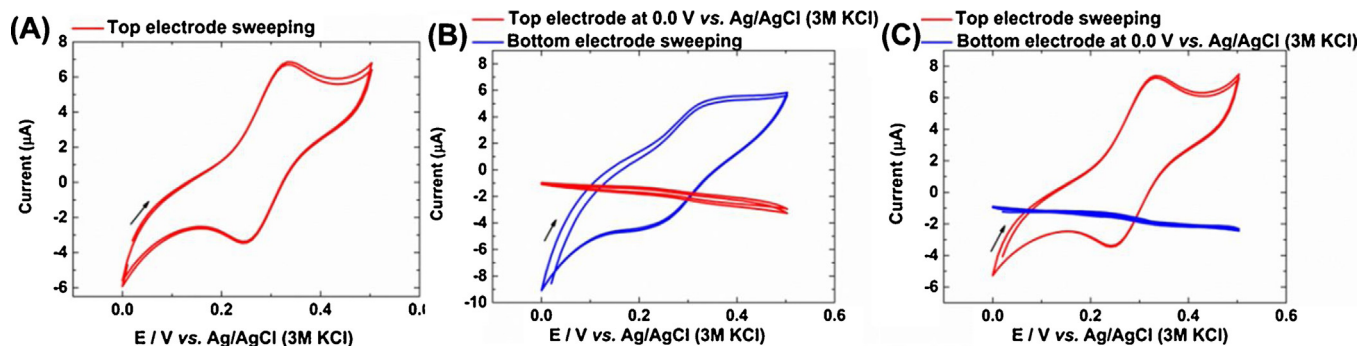
employed. Goodfellow Cambridge Ltd graphitic carbon foil was used to assemble the device (see Fig. 2).
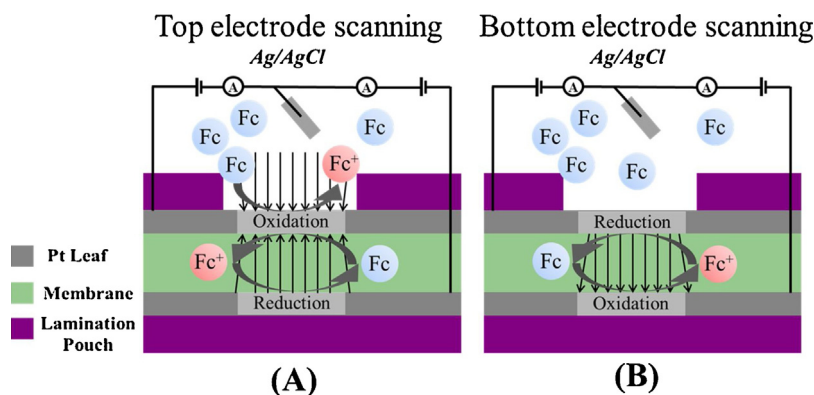
2.2. Instrumentation

Electrochemical experiments were carried out using an Autolab PGSTAT302N bipotentiostat system. A commercial Ag/AgCl (3 M KCl) reference electrode (BASi Inc.) and a platinum counter electrode were used in electrochemical measurements. Generator–collector voltammetry was performed with one electrode potential fixed and one electrode potential scanning. Scanning electron microscopy images (SEM) were obtained using FEI NovaNano SEM.

2.3. Device fabrication

Porous platinum leaves were cut into two small pieces (10 mm × 30 mm) and a track etch membrane was placed as a separating layer between two platinum leaves. Strips of carbon foil were connected to each platinum piece as connection conductors to the top (T) and the bottom (B) electrode. Then the structure was laminated into a lamination pouch with a 2 mm diameter hole on top of the Pt/membrane/Pt sandwich exposing one of the electrodes to the electrolyte solution (Fig. 2).

Fig. 3. Cyclic voltammograms (two potential cycles; scan rate 10 mV s^{-1}) for oxidation of 0.25 mM 1,1'-ferrocenedimethanol in aqueous 0.1 M KNO$_3$. (A) Top electrode scanning and bottom electrode floating (disconnected). (B) Bottom electrode scanning and top electrode at 0.0 V vs. Ag/AgCl. (C) Top electrode scanning and bottom electrode at 0.0 V vs. Ag/AgCl.
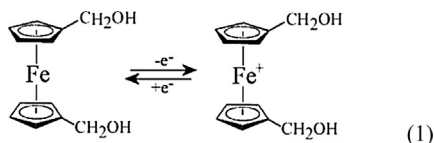

Fig. 4. Schematic drawing of (A) the top electrode scanning and (B) the bottom electrode scanning.

3. Results and discussion

3.1. Generator–collector voltammetry I.: calibration with 1,1'-ferrocenedimethanol

Initially voltammetric experiments were performed with 1,1'-ferrocenedimethanol, Fc(MeOH)$_2$, as a model redox system, in an aqueous 0.1 M KNO$_3$ solution to characterize the generator–collector device (Eq. (1)).

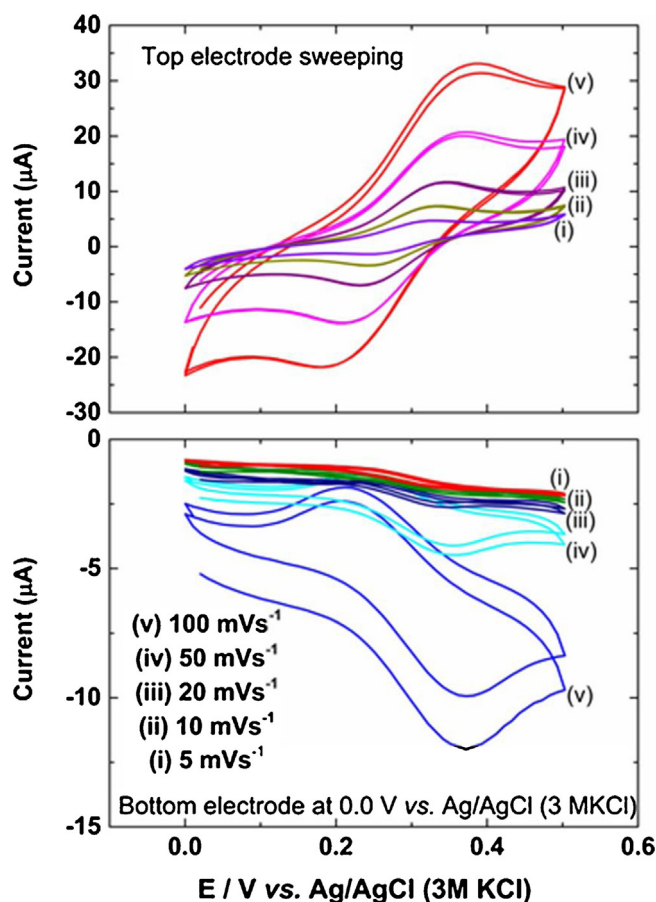Fig. 3 shows a cyclic voltammogram for the oxidation of 0.25 mM 1,1'-ferrocenedimethanol Fc(MeOH)$_2$ in solution. Oxidation of 1,1-ferrocenedimethanol at the top electrode is clearly observed (Fig. 3A). The top electrode is scanning and the bottom electrode is disconnected. In this case the voltammetric response is almost identical with that observed when a fixed potential (0.0 V vs. Ag/AgCl) is applied to the bottom electrode (Fig. 3C). It is most likely that the feedback current is relatively small compared to diffusional flux of 1,1'-ferrocenedimethanol from the bulk phase to the electrode surface.

When the generator–collector currents are recorded due to the feedback effect, an additional current is observed with a sigmoidal shape (limiting current ca. 2 μA) and without any contribution from capacitive charging currents at the collector electrode (with fixed potential). Fig. 3B and C demonstrate that this is possible for both the top electrode scanning and the bottom electrode scanning. The voltammetric signal from the scanning electrode is transient in

nature and more complicated due to the superposition of capacitive currents and diffusional currents for processes in the open solution and in the generator–collector gap. When changing the role of the two electrodes, a complementary data set is obtained (Fig. 3B and C). Fig. 4A and B shows schematic drawings for the case of the top electrode scanning and the bottom electrode scanning. One would anticipate for the case of the bottom electrode scanning that only the feedback current is observed without diffusional peaks. Experimentally, the shape for the voltammetric response at the scanning bottom electrode (Fig. 3B) is indeed more sigmoidal, but there is also a substantial background current, which may be associated with lateral transport in the sandwich electrode configuration. Data for the collector currents obtained for the top electrode scanning appears to be most well-defined with the collector current response reflecting the 1,1'-ferriceniumdimethanol solution concentration. Next, the effect of scan rate is investigated.

Fig. 5 shows data for the top electrodes scanning and the bottom electrode at fixed potential. Perhaps surprisingly, with an increase in potential scan rate peak-shaped current responses are observed also for the collector electrode. A transition appears to occur at approximately 10 mV s^{-1} where the sigmoidal steady state responses changes into a more peak-shaped transient current response.

The change in diffusion characteristics can be attributed to diffusional delay in the track-etch nano-pore membrane. For the configuration with the top electrode scanning and the bottom electrode fixed at 0.0 V vs. Ag/AgCl and at sufficiently slow scan rates a fully developed diffusion layer is established across the membrane. However, for a faster scan rate the steady state current response changes toward peak shaped curves. This transition happens owing to the (A) mass transport delay and (B) the device functioning as capacitor with symmetric charge transfer in the short time domain.

Fig. 5. Cyclic voltammograms as a function of scan rate for the oxidation of 0.25 mM 1,1′-ferrocenedimethanol in aqueous 0.1 M KNO₃ solution. The top electrode as generator was sweeping the potential and the bottom electrode as collector (potential fixed at 0.0 V vs. Ag/AgCl).

From the transition scan rate estimated as $v_{trans} = 10\,mV\,s^{-1}$ the realistic gap size, δ, is estimated as 40 μm, using Eq. (2) [21].

$$\delta = \sqrt{DRT/Fv_{trans}} \qquad (2)$$

In this expression the diffusion coefficient of 1,1′-ferrocenedimethanol is $D = 0.67 \times 10^{-9}\ m^2 s^{-1}$ [6], the estimated transition scan rate is $10\,mV\,s^{-1}$ (for scan rates faster than $10\,mV\,s^{-1}$ peak features appear for the collector electrode), F is the Faraday constant, R is the gas constant and T denotes the absolute temperature. The value $\delta = 40\,\mu m$ is in excellent agreement with the nominal thickness of the track-etch membrane.

3.2. Generator– collector voltammetry II.: separation of oxygen reduction and proton reduction responses

Generator–collector electrode systems can be employed to distinguish between redox processes that allow feedback via redox cycling (e.g. hydrogen evolution, see Eq. (3)) and redox processes that are irreversible (e.g. oxygen reduction to water, see Eq. (4)).

$$H^+ + e^- \rightleftarrows 1/2H_2 \qquad (3)$$

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (4)$$

Here, an indirect but quantitative oxygen determination is investigated based on the proton–hydrogen redox cycle by using the Pt–Pt generator–collector electrode in a solution containing 2 mM HNO₃ and 0.1 M KNO₃. For these measurements the top electrode (solution facing) was kept at a fixed potential of 0.2 V vs. Ag/AgCl and the bottom electrode (inward facing) was scanning (at a $10\,mV\,s^{-1}$ scan rate). Fig. 6A shows data for a solution exposed to ambient air

(approximately 20% oxygen content). In this case, the bottom electrode can be employed to reduce protons to molecular hydrogen (Eq. (3)). The reduced species then diffuses through the track-etch membrane and are oxidised back to protons at the top electrode (Figs. 6A and 7A). A schematic drawing is shown in Fig. 7B to explain proton diffusion towards the top electrode which is accompanied by an anodic current response at the bottom collector electrode. In this configuration there could be some loss of hydrogen into the solution phase. If the configuration is changed (Fig. 7A), hydrogen would be oxidised at the top electrode, which would lead to less loss of hydrogen into the solution and therefore a better defined current response.

Finally, in the presence of oxygen (Fig. 7C) both proton reduction (Eq. (3)) and oxygen reduction (Eq. (4)) occur simultaneously at the bottom electrode. Oxygen reduction consumes protons and this lowers the production of hydrogen and therefore the associated top collector oxidation current. In order to clarify the current responses at the generator and collector electrodes, measurements were performed in different solutions containing varying oxygen concentrations. Solutions were prepared by purging N₂, or pure O₂ gas in 20 mL portion of the electrolyte solution for 20 min. Cyclic voltammetry measurements were then performed immediately under the ambient conditions. Fig. 6B and C present the results from these measurements. As can be seen purging with nitrogen increases the local hydrogen and proton concentration leading to an increased sensor signal (Fig. 6B). In contrast enriching the solution with pure oxygen lowered the local concentration of protons and hydrogen within the sandwich sensor, which leads to a lower collector current response (Fig. 6C). The same trend is visible in the generator current response, but this is partially obscured by other
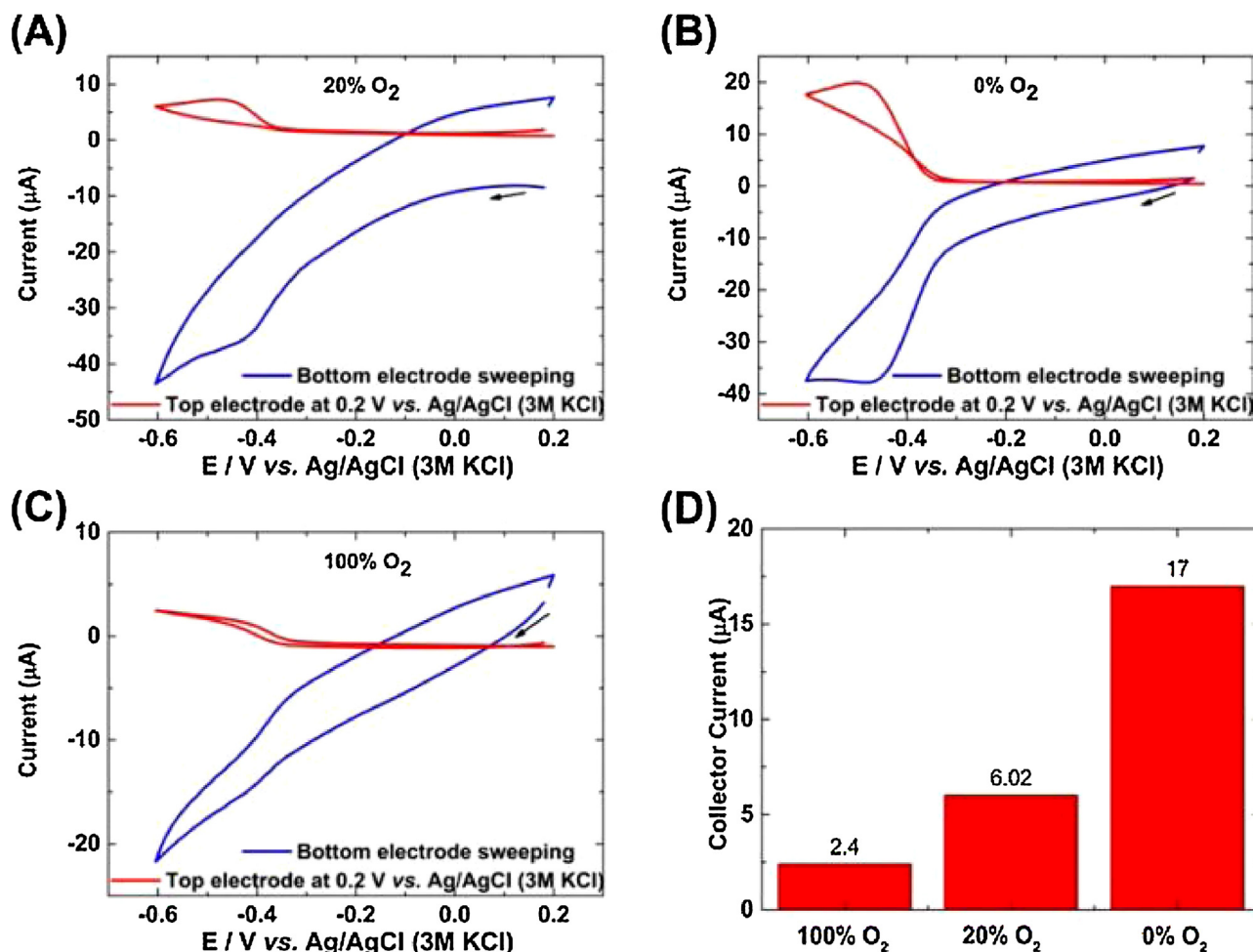
Fig. 6. Cyclic voltammograms for top and bottom electrode for an electrolyte containing 2 mM HNO$_3$ in 0.1 M KNO$_3$ (at a 10 mV s^{-1} scan rate) (A) in ambient air, (B) de-aerated with nitrogen, and (C) saturated with pure oxygen. (D) Bar graph showing the collector current response for hydrogen oxidation diminishing in the presence of oxygen in the electrolyte solution.
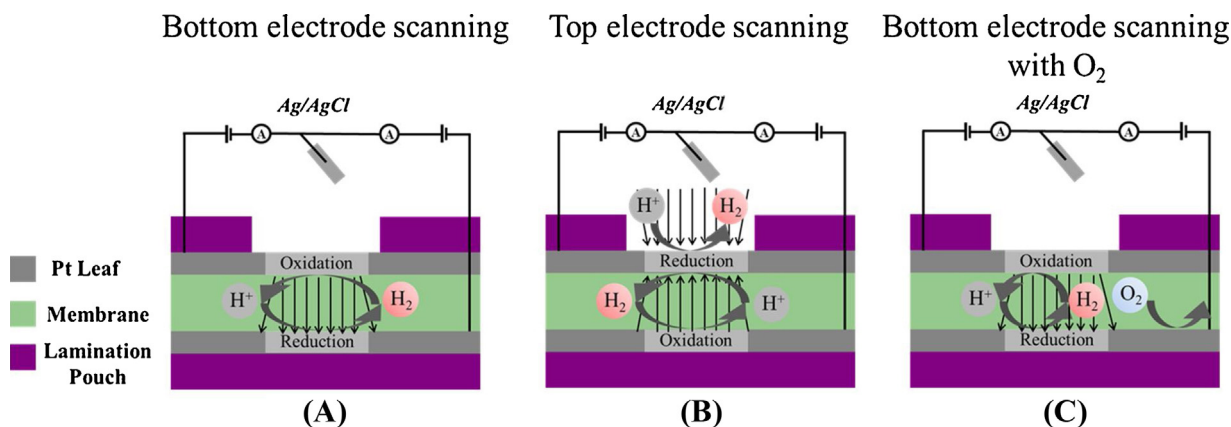

Fig. 7. Schematic drawing for (A) proton-hydrogen redox cycling with the bottom electrode scanning, (B) proton-hydrogen redox cycling with the top electrode scanning, and (C) the effect of oxygen diffusion from the solution and reduction changing local proton and hydrogen concentration within the sandwich sensor.

current contributions. The plot in Fig. 6D clearly demonstrates the correlation of collector current response with oxygen concentration in solution. The choice of 2 mM proton concentration clearly is crucial in optimising the sensor signal for oxygen but the methodology could be improved by employing gel media to fix the proton concentration within the sandwich sensor relative to the outside proton concentration. The detection principle could be useful also for other types of analytes such as sulphide. Finally, redox systems

which require removal of oxygen from the solution phase could be detected at the top electrode whilst in situ removing oxygen at the bottom electrode.

4. Conclusions

It has been shown that platinum leaf materials can be assembled into a sandwich structure with a porous track etch membrane

as a spacer. The resulting sandwich structure can be operated as a novel, simple and cheap generator-collector electrode with reference and counter electrode separately immersed into electrolyte solution. At sufficiently slow scan rates a steady state current without capacitive current contribution is registered at the collector electrode. The limiting current is proportional to the analyte solution concentration. Indirect oxygen sensing is possible based on the proton-hydrogen redox system and based on the fact that oxygen reduction is accompanied by removal of protons localised at the electrode surface. In future the design of the platinum–platinum sandwich sensor can be further improved (by changing the lamination pouch to more professional packaging, exploring solid substrates, optimising the membrane thickness and porosity, and by adding a top layer to protect the open platinum leaf) and adapted for a wider range of electroanalytical application.

References

[1] E.O. Barnes, G.E. Lewis, S.E. Dale, F. Marken, R.G. Compton, Generator-collector double electrode systems: a review, Analyst 137 (2012) 1068–1081.

[2] A. Frumkin, L. Nekrasov, B. Levich, J. Ivanov, Die anwendung der rotierenden scheibenelektrode mit einem ringe zur untersuchung von zwischenprodukten elektrochemischer reaktionen, J. Electroanal. Chem. 1 (1959) 84–90.

[3] M. Čerňanská, P. Tomčík, Z. Jánošíková, M. Rievaj, D. Bustin, Indirect voltammetric detection of fluoride ions in toothpaste on a comb-shaped interdigitated microelectrode array, Talanta 83 (2011) 1472–1475.

[4] D. Bustin, Š. Mesároš, P. Tomčík, M. Rievaj, V. Tvarožek, Application of redox cycling enhanced current at an interdigitated array electrode for iron-trace determination in ultrapure spectral carbon, Anal. Chim. Acta 305 (1995) 121–125.

[5] M.A. Zevenbergen, B.L. Wolfrum, E.D. Goluch, P.S. Singh, S.G. Lemay, Fast electron-transfer kinetics probed in nanofluidic channels, J. Am. Chem. Soc. 131 (2009) 11471–11477.

[6] H.R. Zafarani, K. Mathwig, E.J.R. Sudhölter, L. Rassaei, Electrochemical redox cycling in a new nanogap sensor: design and simulation, J. Electroanal. Chem. 760 (2016) 42–47.

[7] C. Ma, N.M. Contento, L.R. Gibson, P.W. Bohn, Redox cycling in nanoscale-recessed ring-disk electrode arrays for enhanced electrochemical sensitivity, ACS. Nano. 7 (2013) 5483–5490.

[8] B. Wolfrum, M. Zevenbergen, S. Lemay, Nanofluidic redox cycling amplification for the selective detection of catechol, Anal. Chem. 80 (2008) 972–977.

[9] H.R. Zafarani, K. Mathwig, S.G. Lemay, E.J.R. Sudhölter, L. Rassaei, Modulating selectivity in nanogap sensors, ACS Sensors 1 (2016) 1439–1444.

[10] M.A. Zevenbergen, P.S. Singh, E.D. Goluch, B.L. Wolfrum, S.G. Lemay, Stochastic sensing of single molecules in a nanofluidic electrochemical device, Nano Lett. 11 (2011) 2881–2886.

[11] S.G. Lemay, S. Kang, K. Mathwig, P.S. Singh, Single-molecule electrochemistry: present status and outlook, Acc. Chem. Res. 46 (2012) 369–377.

[12] L. Rassaei, P.S. Singh, S.G. Lemay, Lithography-based nanoelectrochemistry, Anal. Chem. (2011) 3974–3980.

[13] H.R. Zafarani, K. Mathwig, E.J.R. Sudhölter, L. Rassaei, Electrochemical amplification in side-by-Side attoliter nanogap transducers, ACS Sens. (2017), http://dx.doi.org/10.1021/acssensors.7b00180.

[14] B. Wolfrum, E. Kätelhön, A. Yakushenko, K.J. Krause, N. Adly, M. Hüske, et al., Nanoscale electrochemical sensor arrays: redox cycling amplification In dual-electrode systems, Acc. Chem. Res. 49 (2016) 2031–2040.

[15] Y. Wang, X. Lin, B. Su, Redox cycling with ITO electrodes separated by an ultrathin silica nanochannel membrane, Electrochem. Commun. 72 (2016) 1–4.

[16] S. Park, J.H. Park, S. Hwang, J. Kwak, Bench-top fabrication and electrochemical applications of a micro-gap electrode using a microbead spacer, Electrochem. 68 (2016) 76–80.

[17] N. Adly, B. Bachmann, K. Krause, A. Offenhäusser, B. Wolfrum, A. Yakushenko, Three-dimensional inkjet-printed redox cycling sensor, RSC Adv. 7 (2017) 5473–5479.

[18] R.W. French, S.N. Gordeev, P.R. Raithby, F. Marken, Paired gold junction electrodes with submicrometer gap, J. Electroanal. Chem. 632 (2009) 206–210.

[19] M.A. Hasnat, A.J. Gross, S.E. Dale, E.O. Barnes, R.G. Compton, F. Marken, A dual-plate ITO–ITO generator–collector microtrench sensor: surface activation, spatial separation and suppression of irreversible oxygen and ascorbate interference, Analyst 139 (2014) 569–575.

[20] A.J. Gross, F. Marken, Boron-doped diamond dual-plate microtrench electrode for generator–collector chloride/chlorine sensing, Electrochem. Commun. 46 (2014) 120–123.

[21] R.W. French, A.M. Collins, F. Marken, Growth and application of paired gold electrode junctions: evidence for nitrosonium phosphate during nitric oxide oxidation, Electroanalysis 20 (2008) 2403–2409.

[22] S.E. Dale, C.E. Hotchen, F. Marken, Generator–collector electroanalysis at tin-doped indium oxide–epoxy–tin-doped indium oxide junction electrodes, Electrochim. Acta 101 (2013) 196–200.

Biographies

Hamid Reza Zafarani received his M.Sc. in Materials Science and Engineering, Shiraz University, Iran. In 2014, He started his Ph.D. at the Department of Chemical Engineering at Delft University of Technology, Netherlands. His current research interests lie in developing and fabrication new nano/micro gap electrochemical sensors working based on redox cycling amplification.

Dr. Liza Rassaei received her PhD in Chemistry in 2008 from the University of Eastern Finland with research on nanomaterials assembly into thin films. Afterwards, she explored the nanothermal effects of microwave radiation on electrochemical processes at the University of Bath (UK). In 2010, she joined the Nanoionics group at the University of Twente (Netherlands) and developed electrochemical bio-nanofluidic devices. In 2012, she moved to the BIOS Lab-on-a-Chip group in Twente and engaged in a project with industry on advanced diagnostic devices for non-invasive skin lactate sensing. Since 2013, she has been an Assistant Professor at Delft University of Technology (Netherlands). She has a multidisciplinary background and a broad interest in advancing electrochemical systems. Recently, she was awarded Delft Global Fellowship with the aim to develop a tuberculosis diagnostic device.

Ernst Sudhölter obtained his PhD degree (cum laude) from the University of Groningen (1981). He was research chemist at the Royal/Dutch Shell in Amsterdam before he was appointed as assistant/associate professor at Twente University (1984–1990). In the period of 1990–2006 he was full professor of physical-organic chemistry at Wageningen University. Since 2007 he is appointed as professor of organic materials & interfaces at Delft University of Technology and he was until 2014 also Chairman of the department of Chemical engineering. His interests are in chemical surface modifications, chemical sensors and membrane separations.

Barak Aaronson completed his PhD degree at Warwick University (2015) under the supervision of Prof. Patrick Unwin. His PhD studies focused on the development of nanoscale imaging techniques (mainly scanning electrochemical cell microscopy (SECCM)) and realizing its application to photoelectrochemistry. He then took a postdoctoral position in Prof. Frank Marken's group at the University of Bath investigating novel materials and mechanisms for ionic diode applications. His research interests lie in the understanding of multi-interfacial processes and the development of novel electrochemical technologies for energy and environmental applications.

Frank Marken obtained a Dr. rer. Nat. degree at RWTH Aachen (1992) and has in September 2004 been appointed to a Senior Lecturer position and in 2011 promoted to a personal chair at the Department of Chemistry, University of Bath. Research focuses on the fundamental mechanistic understanding of multi-interfacial processes and the development of novel electrochemical technologies based on nano-structures, three phase junctions, ultrasound and microwave-activation, paired and self-supported electro-organic syntheses, and analytically relevant electrode reactions.