Electrochimica Acta 55 (2010) 4234–4239

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Flow-injection amperometry at microfabricated silicon-based μ-liquid–liquid interface arrays

Micheál D. Scanlon, Alfonso Berduque, Jörg Strutwolf, Damien W.M. Arrigan*[,1,2]

Tyndall National Institute, Lee Maltings, University College Cork, Cork, Ireland

ARTICLE INFO

Article history:
Received 25 July 2008
Received in revised form
24 November 2008
Accepted 8 December 2008
Available online 13 December 2008

Keywords:
Flow-injection analysis
Amperometry
Micropores
Liquid–liquid interface
Oligopeptides
Hydrodynamic voltammogram

ABSTRACT

Geometrically regular silicon membrane-based micropore arrays were employed for defined arrays of micrometer-sized interfaces between two immiscible electrolyte solutions (μITIES). These were incorporated into a poly(tetrafluoroethylene) (PTFE) hydrodynamic cell. Electrochemistry at the μITIES array was undertaken following gellification of the organic phase using polyvinyl chloride (PVC) and flowing an aqueous phase over the array surface. Cyclic voltammetric characterization of asymmetric diffusion profiles on either side of the μITIES was accomplished under flowing conditions using positively and negatively charged (TEA^+ and $4\text{-}OBSA^-$, respectively) model analyte species. Incorporation of an ionophore (dibenzo-18-crown-6 ether) into the organogel allowed the ion-transfer detection of two oligopeptides (phenylalanine dipeptide and lysine dipeptide) within the available potential window under stationary and flowing conditions. Flow rate studies with TEA^+ indicated that the amperometric peak currents do not obey the Levich equation, due to diffusion dominating the mass transport, as opposed to convection. The influence of the applied potential ($\Delta_o^W\phi$) on the amperometric response of the oligopeptides was studied and hydrodynamic voltammograms (HDVs) for the individual oligopeptides were subsequently constructed. The data presented provide a basis for the use of silicon membrane-based μITIES arrays in flow analytical methods.

1. Introduction

Inducing the transfer of ions across the interface between two immiscible electrolyte solutions (ITIES) by generating a potential difference between the two phases provides a powerful avenue for the detection of non-redox active species [1–11]. Flow-injection analysis (FIA) of numerous charged species using a variety of electrochemical detection techniques (e.g. amperometric, voltammetric or chronocoulometric methods) has been reported at the liquid–liquid interface [12–33].

For analytical applications of such flow systems, the mechanical instability of the liquid–liquid interface was a problem addressed in a variety of ways. On the whole, this problem was circumvented by the gellification of organic phase with poly(vinyl) chloride (PVC) [12,14,18,20,24,28–33] or insertion of solid porous membrane materials between the two immiscible solutions [13,15–17,21,23,25–27]. Inevitable reductions in diffusion coefficients of the analyte ions, associated with gellification of the organic phase, have not proven problematic when monitoring ion-transfer by amperometric and voltammetric methods. Increases in uncompensated resistance in the cell due to gellification have been off-set by incorporating micropore or microhole arrays into the experimental setup [11,19,22]. Micrometre-sized ITIES (μITIES) play the dual role of integrating the advantages associated with solid-state microelectrode arrays (reduced ohmic resistance, increased mass transport and sensitivities) into the system while also serving to provide mechanical stability. Recently we discussed the influence of the number of pores and the pore radius on the trans-membrane resistance of the solid-state membranes used in the present paper [34]. The iR-drop has a negligible effect on the transient currents at the gellified organic–aqueous interface as long as low potential scan rates ($\nu < 20\,mV\,s^{-1}$) are used. The minor influence of the iR-drop is due to the low currents, in the nanoampere range, associated with ion-transfer across the μITIES arrays.

As noted previously [15,21,29], amperometric sensors are more suitable for incorporation into FIA systems than potentiometric sensors. Amperometric sensors have the ability to alter the selectivity of ion-transfer across the interface by controlling the Galvani potential difference ($\Delta_o^W\varphi = \varphi^W - \varphi^O$) using a potentiostat. Essentially, this allows selective transfer (or extraction) of ions from one phase to the other by applying a potential that corresponds to the characteristic Gibbs energy of transfer for that particular species. Thus, in this manner, a mixture of ions in solution may be selectively

* Corresponding author. Fax: +61-(0)8-92664699.
E-mail address: d.arrigan@curtin.edu.au (D.W.M. Arrigan).
[1] Member of ISE.
[2] Present Address: Nanochemistry Research Institute, Department of Chemistry, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia.

0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2008.12.014

detected or separated. In contrast, potentiometric sensors lack the same degree of discrimination.

The potential window at the ITIES is limited by the Gibbs energy of transfer of the aqueous and organic phase electrolyte salts. Using an approach pioneered by Koryta [35], incorporation of ionophores into the organic phase allows the detection of analyte ions (by lowering their Gibbs energy of transfer on binding with the ionophore) that would otherwise be incapable of transferring within the available potential window.

In this paper, we present the characterization of microfabricated silicon micropore arrays via voltammetry and amperometry under hydrodynamic conditions by their incorporation into a poly(tetrafluoroethylene) (PTFE) flow cell. Cyclic voltammetry of the direct ion-transfer of positively and negatively charged model analytes under flowing conditions reveals the different diffusion regimes (radial and linear) on either side of the μITIES. Flow rate studies in the presence of tetraethylammonium chloride at the μITIES are carried out. The ability to construct hydrodynamic voltammograms of two oligopeptides, phenylalanine dipeptide (Phe-Phe) and lysine dipeptide (Lys-Lys), at the μITIES by the incorporation of an ionophore (dibenzo-18-crown-6 (DB18C6) ether) into the organogel and controlling the applied potential at the μITIES is presented.

2. Experimental

2.1. Reagents

All reagents were purchased from Sigma–Aldrich Ireland Ltd. and used without further purification, with the exception of 1,6-dichlorohexane (1,6-DCH) which was purified according to the published procedure [3]. The aqueous phase electrolytes of 10 mM LiCl and 10 mM HCl were prepared in ultrapure water (with a resistivity of 18 MΩ cm) from an Elgastat maxima-HPLC (Elga, UK). The model analyte species studied, i.e. the sodium salt of 4-octylbenzenesulfonate (4-OBSA$^-$) and the chloride salt of tetraethylammonium (TEA$^+$), were prepared in 10 mM LiCl aqueous phase. The oligopeptides studied were dilysine (Lys-Lys) and diphenylalanine (Phe-Phe). The oligopeptides were prepared in an aqueous electrolyte solution of 10 mM HCl, a pH at which they are positively charged. The ionophore used to facilitate the transfer of the oligopeptides was dibenzo-18-crown-6 ether (DB18C6). The organic electrolyte salt was prepared by metathesis of bis-(triphenylphosphoranylidene) ammonium chloride (BTPPA$^+$ Cl$^-$) and potassium tetrakis(4-chlorophenyl)borate (K$^+$ TPBCl$^-$) to obtain BTPPATPBCl, following the published experimental procedure [18].

2.2. Apparatus

Voltammetric and amperometric experiments at the μITIES array were performed using a CH Instruments 620B potentiostat (Texas). The electrochemical cell used in these studies is fabricated from PTFE and is based on that employed by Berduque et al. [29,31] to electrochemically modulate the liquid–liquid extraction of ions at a macroITIES. The present design, detailed in Fig. 1a, incorporates a borosilicate glass cylinder (6 mm external diameter, 3 mm inner diameter) with the microporous silicon membrane sealed onto the lower orifice using silicone rubber (RS Components, stock number 555–588). This design allows the aqueous phase to flow under the organogel supported in the silicon microporous membrane. The cell consists of two pieces that are held together using Teflon nuts and bolts and an O-ring (Viton O-ring, 25 mm approximate internal diameter and 1.8 mm of thickness) to prevent leakage of the aqueous phase. The aqueous phase electrodes consist of a platinum mesh counter electrode and a Ag–AgCl reference electrode. A Ag–AgCl electrode in the organic reference solution acts as both the organic reference electrode and the organic counter electrode. The Ag–AgCl electrodes were prepared by the potentiostatic oxidation of silver wires in a solution of 3 M KCl.

The aqueous phase was introduced into the Teflon cell by means of a syringe pump (KD Scientific KDS200 series syringe pump) with controllable flow rates. A six-port valve (C22-3186 valve, Carl Stuart Ltd.) was used to inject samples via a 100-μL injection loop.

2.3. Preparation of the organogels

The necessity of an ionophore (DB18C6 ether) in the organic phase to facilitate the transfer of the oligopeptides across the ITIES required the preparation of two distinct organogels. The first organogel, detailed in cell 1 (Fig. 1b), did not contain the ionophore and was used as the organic phase in the model analyte studies, while the second organogel, detailed in cell 2 (Fig. 1b), contained the ionophore and was used in the oligopeptide studies. The remaining components of the organogel consisted of an organic solvent (1,6-DCH), an organic electrolyte (BTPPATPBCl) and the low molecular weight PVC. A detailed description of organogel preparation is given elsewhere [11].

2.4. Micropore array designs and fabrication

The micropore arrays were fabricated from 525 μm thick silicon wafers using a combination of wet and dry silicon etching to thin the wafers and etch pores through the thinned portions, as described elsewhere [9]. The fabrication procedure produced pores with hydrophobic walls, facilitating the filling of the pores with organic phase [9]. Two micropore array designs are used in the course of these studies. Design 1 consists of 23 micropores in a hexagonal close packed arrangement. Each individual pore measures 52 μm in diameter and the pore-to-pore (center-to-center) distance is 250 μm. Design 2 consists of eight micropores in a hexagonal close packed arrangement. Each individual pore measures 52 μm in diameter and the pore-to-pore (center-to-center) distance is 500 μm. The organogel was inserted into the glass cylinder as a liquid at ∼60 °C using a glass pipette. In this manner the hydrophobic pores of the micropore array are completely filled rendering an inlaid interfacial geometry on the aqueous side of the ITIES [9,11,34].

2.5. Methodology

By convention [4], positive currents are caused by the transfer of cations from the aqueous phase (w) to the organic phase (o) (or by anions from o to w). On the contrary, negative currents arise as a result of anions transferring from w to o (or by the cations transferring from o to w). The pore-to-pore (center-to-center) spacing of both micropore array designs is sufficiently large (≥10 radius of the pore) to prevent interactions between the individual diffusion fields. As a result steady-state voltammetric responses are expected on transfer of an analyte from w to o due to spherical diffusion at the mouth of the micropore. Conversely, peak-shaped responses are expected on transfer of an analyte from o to w due to the recessed geometry creating a linear diffusion field on the organic side of the ITIES [9].

Once the experimental setup is complete the electrochemical cell is filled with the desired aqueous phase by flowing the liquid at the relatively quick volumetric flow rate of 1 mL min^{-1} using the syringe pump. The cell can be deemed full once drops of aqueous phase begin to fill the waste receptacle placed under the exit tube. At this point the flow of the solution is halted, and a stationary cyclic voltammogram (CV) of the solution is run. In this manner the cell setup and parameters used can be verified prior to each