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Amperometric tape ion sensors for cadmium(II) ion analysis

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ABSTRACT

This paper describes a novel tape platform ion sensing methodology specific to the detection of cadmium(II) ions in aqueous solution based on assisted ion transfer reactions across a polarized water | organic gel micro-interface. The tape ion sensors were constructed to incorporate the micro-water | polyvinylchloride-2-nitrophenylethyl ether (PVC–NPOE) gel interfaces referred to as *ionodes*. The sensors have overall thicknesses less than 300 μm, allowing their packaging in a disposable tape format. The detection methodology is based on the selective assisted transfer of the cadmium ion in aqueous phase by ETH 1062 present in the PVC–NPOE gel layer and was first investigated using cyclic voltammetry. Quantitative analysis of cadmium(II) ions in aqueous solution using the tape sensors was then conducted under stop-flow conditions. Detection limits as low as 20 ppb (178 nM) for Cd(II) ions in very small volumes as low as a single 20 μl droplet without any sample preconcentration was achieved in an analysis time of approximately 20 s, which could be easily employed for the direct measurement of Cd(II) ion levels in various field applications. The tape ion sensor can also be used in a flow-cell geometry to preconcentrate Cd(II) ions from aqueous samples and further improve the detection limit.

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1. Introduction

Amperometric ion selective electrodes (ISE) have been powerfully employed in the sensing of a wide range of ionic species [1–6]. The most common approach is to utilize solidified polymeric membranes composed of a plasticizer and an ion carrier (ionophore or ligand), which selectively complexes to a target ion [7–9]. The same design principle can be applied to construct an amperometric ion sensor to monitor ion transfer reactions at the interface between two immiscible liquids where one of the phases, typically being the organic phase, is gelified [10–17]. This approach has been successfully demonstrated by several authors during the last decade, mainly using a nitrobenzene gel as the organic phase for the direct and assisted ion transfer, in a stagnant aqueous solution or combined with flow systems [18–22]. Due to the increasing concern with environmental issues, the organic phase must have a reduced toxicity and a long-term stability as well as maintaining good electrochemical characteristics. *O*-Nitrophenyloctylether (NPOE) together with polyvinylchloride (PVC) as a gelifying agent fulfils these criteria and can be printed at a temperature above its sol–gel transition (hot casting method) [23,24]. This water | PVC–NPOE gel interface has been implemented into an array of microholes using a standard cell arrangement for studying the selective transfer of alkali metal ions and anions from the aqueous to the organic phase via direct and assisted transfer reactions [25–27].

The ion transfer reaction across the polarized water | organic gel interface can ideally be employed for the selective and sensitive detection of heavy metal ionic species. For example, Katano and Senda [28] have shown that the low ppb detection limit can be attained by stripping voltammetry of heavy-metal ions across a water | gel interface. Electrochemical extraction of large ionic concentrations with the use of micro-machined supported liquid membranes has also been reported, particularly for lead extraction from a lead/zinc solution [29]. In this paper, we demonstrate a novel disposable tape ion sensor utilizing the assisted transfer reaction of Cd^{2+} ions by ETH 1062 across the micro-interface of water | PVC–NPOE gel. The thin strip tape ion sensor was fabricated using a combination of laser micro-machining and screen-printing techniques. A cyclic voltammetry was used to characterize the electrochemical response of Cd^{2+} ion transfer by ETH 1062 at the interfaces. As a first demonstration, the quantitative analysis of cadmium(II) ions using the tape sensors was conducted under stop-flow condition with a small aqueous sample volume (about 20 μl) as well as under continuous flow conditions for achieving a higher preconcentration effect.

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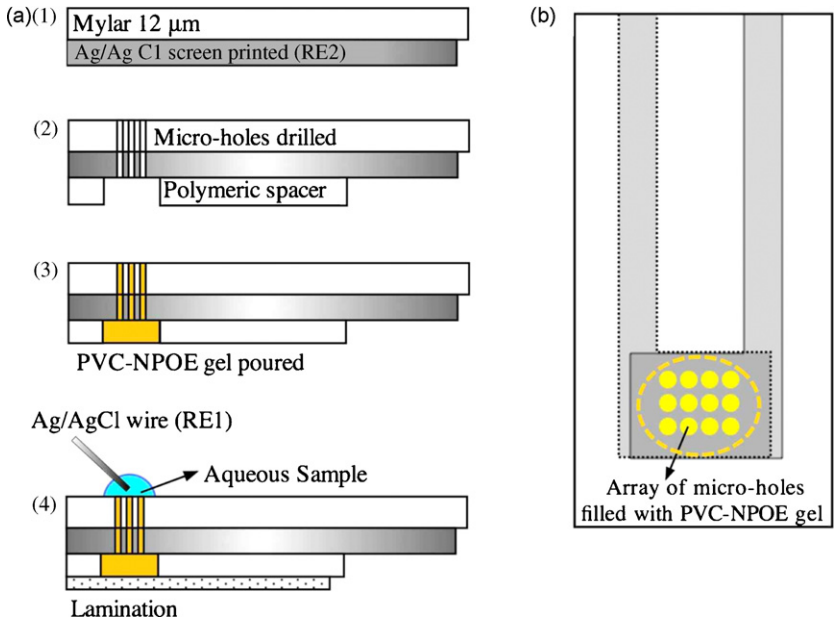

Fig. 1. (a) Schematic showing a four-step fabrication method for creating disposable tape sensors based on metal ion transfer reactions at the water | PVC–NPOE gel micro-interface. The overall thickness of the strip is about 300 μm. (b) A top view of the interface featuring the array of micro-holes containing the PVC–NPOE gel.

2. Experimental

2.1. Chemicals

ETH 1062 (Fluka), polyvinylchloride (PVC, high molecular weight, Sigma), *o*-nitrophenyloctylether (NPOE, Fluka), $CdCl_2$ (Fluka >96%) and LiCl (Fluka >99%) were all used as received. The supporting electrolytes for the organic phase was bis(triphenylphosphoranylidene) ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) or tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl) prepared as described in a previous paper [23,30]. Most of the cases, 10 mM BTPPATPBCl were used unless otherwise specified. Millipore-filtered water was used for preparing all aqueous solutions.

2.2. Fabrication of thin tape sensor

To fabricate the tape sensors, a supporting film of polyethylene terephthalate (12 μm thick, Melinex type "S", ICI Films) supplied on a reel was first cut into strips (30 cm long). After cleaning with ethanol, a silver/silver chloride ink (RE 2) was screen-printed as illustrated in Fig. 1a and cured at 80 °C for 24 h. In a second step, an array of 66 microholes (11 × 6) was drilled through the film using a UV Excimer laser (ArF, 193 nm, Spectra-Physics). The process of laser micro-machining of the polyester film was performed as described previously [24], but the differences here were the number of laser pulses used to drill through the metallised film and the silver layer being placed at the bottom. The entrance diameter of the microholes is 20 μm and the exit 13 μm due to the optics used to focus the laser beam so as to drill through the metallic ink layer. After drilling, an adhesive tape that had been punched with a circular aperture was placed on the silver/silver chloride layer. This microfabricated structure acts as a supporting film to deposit the gelified NPOE phase containing PVC. The gel layer was prepared by dissolving PVC (2.8% m/m) in a solution of 10 mM BTPPATPBCl or TBATPBCl and ETH 1062 in NPOE, at a temperature of approximately 120 °C. Five microliters of the hot PVC–NPOE liquid at around 80 °C was manually casted on the arrays via the aperture in the adhesive film. Finally, the casted PVC–NPOE solution was allowed to cool for a minimum of 6 h to form the gel followed by laminating the underside of the tape with a polyethylene (PE)–polyethylene terephthalate (PET) film (35 μm thick). In the present work, the screen-printing of Ag/AgCl ink was carried out after cutting the tape into sections adapted to the size of the screen used (30 cm × 30 cm). The strip sensor was employed in two different ways for the amperometric measurements of small volumes of Cd^{2+} ions; (i) simply placing a drop of aqueous solution containing Cd^{2+} ions onto the sensing part, with the aqueous reference electrode dipped in the drop (see Fig. 1a), and (ii) placing the sensor in the flow cell prototype (see also Fig. 5). All the processes used here *i.e.* screen printing of Ag/AgCl ink, laser ablation, adhesion of a spacer film and lamination could be mounted in a continuous reel-to-reel assembly line for high-throughput industrial production of the tape.

2.3. Electrochemical measurements

The electrochemical experiments were performed using a computer controlled potentiostat (Sycopel Scientific Ltd.) with the data acquired without IR drop compensation. Half-wave potential measurements for ion transfer reactions are referred to Ag/AgCl (c_{Cl^-} = 0.01 M) unless otherwise stated. The interfacial ion transfer and ion-ligand complexation processes across the water | PVC–NPOE fabricated in a tape platform sensor were studied by cyclic voltammetry using Cell I.

Cell I:

$$\underset{\text{Pseudo RE2}}{\text{AgCl|Ag}} \quad \underset{\text{Polymer membrane}}{\begin{matrix}2.8\%\text{PVC} - \text{NPOE} \\ 10\text{ mM BTPPATPBCl} \\ +\ 10\text{ mM ETH 1062}\end{matrix}} \quad \underset{\text{Water}}{\begin{matrix}y\text{ mM } CdCl_2 \\ 10\text{ mM LiCl}\end{matrix}} \quad \underset{\text{RE1}}{\text{AgCl|Ag}}$$

Ion transfer reactions across micro-interfaces which involve small currents (in all cases here, lower than 100 nA), only two reference electrodes are necessary, each one acting as both the reference and counter for the aqueous and organic phase. The aqueous phase reference electrode was made of silver/silver chloride in equilibrium with a chloride aqueous solution (RE 1). For the organic phase reference system, a pseudo-reference electrode (screen printed Ag/AgCl, RE 2) was utilized where the Ag/AgCl was

directly in contact with PVC–NPOE gel in the absence of organic supporting electrolyte. This was essential to conveniently assemble it to the tape sensing platform. On the other hand, for the case of Fig. 3 where we used a conventional micro-water/PVC–NPOE gel configuration, the cyclic voltammogram for the Cd(II) ion transfer was obtained using the TBA^+ISE organic reference system and Cell II. TBA^+Ion selective electrodes (TBA^+ISE) were composed of a Ag/AgCl reference electrode in contact with the organic supporting electrolyte solution (e.g. 10 mM TBACl).

Cell II:

Ag|AgCl	10 mM TBACl in water	2.8%PVC − NPOE 10 mM TBATPBCl + 10 mM ETH 1062	y mM $CdCl_2$ 10 mM LiCl	AgCl|Ag
	TBA^+ISE	Polymer membrane	Water	RE1

The electrochemical set-up used here was similar to that for the study of alkali metal ion transfer reactions across micro-water | PVC–NPOE gel interface as described previously [23]. Briefly, two reference electrodes for both the aqueous and organic phases were made of silver/silver chloride in equilibrium with a chloride aqueous solution; for the organic phase, a TBA^+ISE reference system was used. The water | organic gel interface was formed by water phase containing $CdCl_2$ in contact with micro-fabricated membranes featuring 66 microholes in a 12 μm thick PET film filled up with PVC–NPOE gel as described above.

3. Results and discussion

Measurements of Cd^{2+} ion concentrations are very important since overexposure is extremely dangerous to public health and our ecology. Consequently, all countries in the world have established regulations on permissible concentrations of Cd^{2+} ions. For example, guidelines supplied world health organization [31], suggest an upper cadmium ion concentration of 3 ppb (26.7 nM) in drinking water. Also, the US Environmental Protection Agency set the permissible Cd ion concentrations in water as 10 ppb (89 nM) [32]. More details on allowed levels of cadmium in various environments can also be found from [33]. A disposable sensor that is easy to use, reliable, free of toxic elements as well as inexpensive to fabricate can be powerfully used for trace cadmium metal ion analysis. We have designed a disposable thin strip type ion sensor featuring micro-water | gel interfaces (see Fig. 1a) that utilizes very small sample volumes below 20 μl. Additional advantages of this sensor include: (i) the sensor packaging can be promptly achieved using a simple printing procedure, and (ii) the sensor strips can be placed on a dispenser such as a tape and consequently used under a flow system.

The electrochemical response of the thin strip sensor associated with the interfacial transfer of cadmium(II) ions facilitated by the ligand, ETH 1062, present in the PVC–NPOE gel layer was first characterized. A series of cyclic voltammograms obtained using Cell I for various cadmium ion concentrations are displayed in Fig. 2a. A small aqueous solution with a volume of about 20 μl containing various concentrations of cadmium(II) ions ranging from 1 to 100 μM and 10 mM of ETH 1062 were used. The transfer of Cd^{2+} ions can be clearly seen within the potential window limited by the transfer of Cl^- ion at the negative end potential and the transfer of Li^+ ion at the positive end potential. The steady-state current observed on the forward scan linearly increased as the cadmium concentration increased when the ligand concentration (10 mM) is in excess (see Fig. 2b). This indicates that the sensing method involving excess ligand concentrations compared to the metal analytes can be usefully employed for the quantitative analysis of Cd^{2+} ions in aqueous samples. However, above 40 μM concentrations of Cd^{2+} ions, the steady state current no longer increases and the top

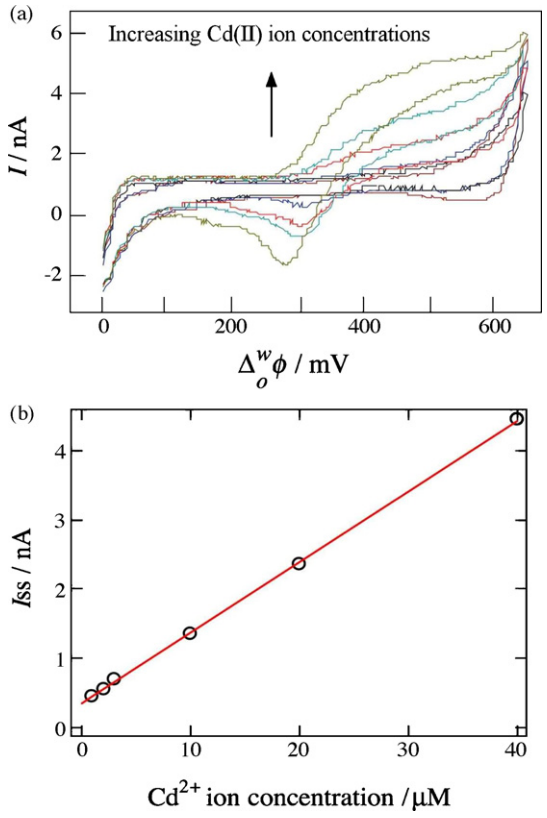

Fig. 2. (a) A series of cyclic voltammograms obtained for the assisted transfer of various concentrations of Cd^{2+} ions by 10 mM ETH 1062 in the PVC–NPOE gel across the water | gel interface using the strip sensor. The aqueous phase contains 10 mM LiCl and the PVC–NPOE gel phase contains 10 mM BTPPATPBCl as a supporting electrolyte respectively. Cell I was used and Cd^{2+} ion concentrations were 1, 2, 5, 20, 40 and 100 μM. Scan rate was 10 mV s^{-1}. (b) Plot of steady-state currents for the assisted transfer of Cd^{2+} by ETH 1062 (10 mM) as a function of Cd^{2+} ion concentrations (calibration curve in the excess ligand case). Some of the data are taken from (a).

curve in Fig. 2a shows two transferring waves for a 100 μM concentration of Cd^{2+} ions on the forward scan. In this region where no clear excess is present from any of the species due to the slow diffusion of the ligand in the gel, a second peak at a more positive potential occurs which can be assigned as the formation of the 1:1 complex $[Cd\text{-}ETH\ 1062]^{2+}$. On the reverse scan, a peak shape of signal was observed mainly due to the fact that the [Cd-ETH 1062] complex formed during the forward scan is diffusing along the hole, up to the interface where the ion is released. When using the hole length is 12 μm (thickness of the PET film), a major part of the complex previously formed is diffusing towards the bulk of the gel even when the potential across the interface allows the transfer back of the metal ion in the aqueous phase [34]. This has the main effect of limiting the possibility of ionic preconcentration in the gel. In an analytical point of view, a compromise must be found between small micro-holes with smaller IR drop and larger ones with higher preconcentration effect but also increased IR drop [24]. It should be noted that the data presented in Fig. 2 appears to be slightly noisy mainly due to the fact that the measured current associated with both the low concentration of Cd^{2+} ions and the small interface is as low as below ~1 nA. In addition, some instability issues may arise from the use of the pseudo-organic reference electrode where the Ag/AgCl layer is directly in contact with the PVC–NPOE gel. Nevertheless, the pseudo-electrode behaves similarly to the organic Ag/AgCl reference electrode which is referenced with the organic supporting electrolyte such as TBACl solution (TBA^+ISE) (see also Fig. 3). The successful application with the pseudo-electrode also

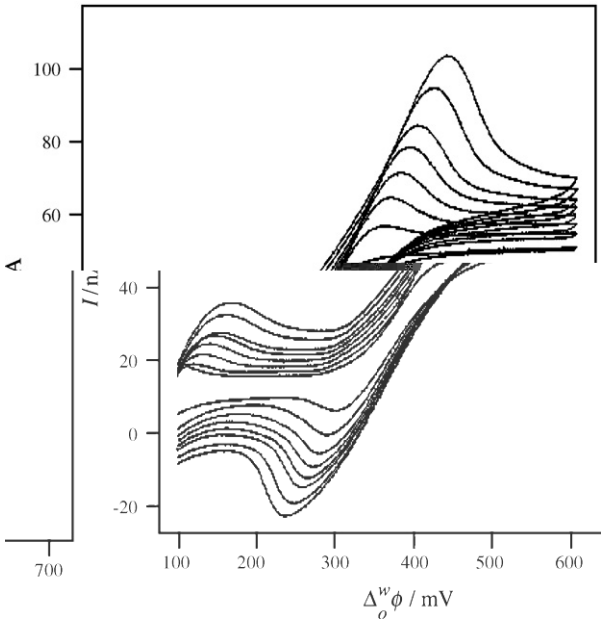

Fig. 3. Cyclic voltammograms obtained for the assisted transfer reaction of Cd^{2+} ions by the ligand ETH 1062 at various scan rates using Cell II. The concentrations used for Cd^{2+} ions and ETH 1062 were 120 mM and 10 mM, respectively. Scan rates were 5, 10, 15, 20, 25, 30, 40 and 50 mV s^{-1}. 10 mM TBATPBCl was used as an organic supporting electrolyte. The IR drop is estimated here to be 200 MΩ.

makes the tape sensor more convenient to fabricate and easy to utilize in field applications.

Further studies elucidating the peak shape of the ion transfer reaction were performed when the Cd^{2+} ion concentration is in excess compared to the ligand ETH 1062 concentration. Fig. 3 shows a series of cyclic voltammograms obtained at different scan rates using the organic reference electrode with Ag/AgCl in contact with the organic supporting electrolyte such as TBACl solution and 10 mM TBATPBCl in the PVC–NPOE gel. For short periods of time (higher scan rates above 50 mV s^{-1}), a strong peak shape voltammogram on the forward scan was observed because the ligand depletion region stays within the hole owing to much lower diffusion coefficients of the ligand in the gel compared to that of the metal ions in the aqueous phase. When the scan rate is of the order of 50 mV s^{-1} or lower, the two successive regimes of ligand diffusion are visible in the peak shapes (peak, then steady-state). At very low scan rates (below 10 mV s^{-1}), the linear diffusion behavior is becoming insignificant and the diffusion is mainly spherical over the forward scan period. At the potential of the transition point between linear and spherical diffusions, it is possible to estimate the diffusion coefficient of the ligand in the gel, knowing the micro-hole length (12 μm long in this experiment), which is calculated to be 3×10^{-11} m^2 s^{-1}. This diffusion coefficient is in relatively good agreement with the values estimated for similar systems in a previous paper [23].

Following the well-defined electrochemical behaviour of Cd^{2+} ion transfer process at the interface of thin strip sensor platforms, we have further employed the strip sensor for the quantitative analysis of Cd^{2+} ion concentration in aqueous sample. Differential pulse stripping voltammetry was applied for Cd^{2+} concentrations ranging from 0 to 391 nM (44 ppb) when the ligand ETH 1062 (10 mM) is in excess. Fig. 4 demonstrates a series of differential pulse stripping voltammograms acquired for aqueous drops (20 μl) in the absence of Cd^{2+} ions, and also Cd^{2+} ions at concentrations of 196 nM and 391 nM. These were obtained without any preconcentration (plating) of Cd^{2+} ions. For comparison, the very top voltammogram in Fig. 4 was obtained at a Cd^{2+} ion concentration of 391 nM after a preconcentration step by applying a potential of 600 mV for 30 s prior to analysis. It can be clearly seen that the preconcentration process enhances the detection signal by approximately a factor of two compared to that obtained without any preconcentration step. All these signals represent the extraction of the Cd^{2+} ions from the organic gel (where they are complexed by the ligand), back to the aqueous phase. The detection limit was found to be about 178 nM (20 ppb) of Cd^{2+} ions in a 20 μl volume assay (about 4 pmol), allowing the direct application of the sensor to determine Cd^{2+} ion levels in various environmental samples. The sensitivity of the ion tape sensor is better than commercially available ion-selective electrodes (e.g. 890 nM (100 ppb) of Cd^{2+} ions) [35] and comparable to conventional atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) atomic emission spectrometry [36]. Nevertheless, the ion sensor has a distinct advantage in requiring smaller sample volumes with additional possibilities for multiplexed and selective sensing as well as portability. Typically, AAS or ICP requires a minimum sample loading volume of over 50 μl. In principle, even smaller volumes of sample drops (below 5 μl) could be applied in the tape sensor, which would still cover the entire micro-hole interface; however, the rate of evaporation of the aqueous sample must be taken into account at such low volumes.

Fig. 4. Differential pulse stripping voltammograms of Cd^{2+} ion transfer from the gel, after the assisted transfer by ETH 1062 (10 mM). The pulse conditions were potential increment of 2 mV, pulse potential of 10 mV and pulse duration of 50 ms (scan rate is 20 mV s^{-1}). The scan was directed from high to low potentials to drive Cd^{2+} ion transfer from the organic to aqueous phase. From bottom to top: curve obtained without any cadmium ions, with 196 nM of Cd^{2+} ions in water, followed by 391 nM without any preconcentration (plating) of Cd^{2+} ions. The top voltammogram was obtained after a preconcentration step for 391 nM Cd^{2+} ions in water by applying the potential at 600 mV for 30 s prior to analysis.

The tape ion sensor was finally integrated into a flow system (Metrohm flow cell prototype) to achieve a higher preconcentration of Cd^{2+} ions in the gel layer under a continuous solution flow (see Fig. 5). A representative differential pulse voltammogram of 1 μM Cd^{2+} ion detection is displayed in a right inset of the figure. The assisted transfer of Cd^{2+} ions by the ligand ETH 1062 across the