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Complete Electrolysis Using a Microflow Cell with an Oil/Water Interface

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A novel microflow cell with a nitrobenzene (NB)/water (W) interface was developed. A poly(tetrafluoroethylene) membrane filter was employed to prepare the NB/W interface which was formed over a thin channel (0.1 mm thick, 48 cm long) on a silver plate. The silver plate was electrolyzed in advance and served as an Ag/AgCl electrode for controlling the Galvani potential difference across the NB/W interface as well as detecting the current flowing through the interface. Using the microflow cell, complete electrolysis was accomplished for the interfacial transfer of a representative ion (i.e., tetramethylammonium ion). Thus, the present microflow cell was shown to be promising for coulometric (i.e., absolute quantitative) analysis of ions. Also, the microflow cell was shown to be useful for determination of the number of electrons for complicated charge-transfer processes at the oil/water interface.

In recent years, much attention has been paid to amperometric (or voltammetric) detection of ions with a liquid/liquid interface or an oil/water (O/W) interface.^{1–4} The amperometric detection is based on measurement of ion-transfer current, which is directly proportional to ion concentration and is therefore very suitable for flow injection analysis (FIA). So far, a variety of amperometric flow cells with the O/W interface have been reported.^{5–12} However, they are all designed to detect ion-transfer current due

to *partial* electrolysis of the sample aqueous solution. To the best of our knowledge, there has been reported no O/W-type flow cell that can accomplish *complete* electrolysis¹³ of the sample solution. If such a flow cell is realized, it will enable us to perform coulometric analysis of ions in a manner similar to conventional flow column electrodes utilizing glassy carbon granules or carbon fiber.^{14,15}

In this study, we constructed a microflow cell^{16,17} using the hydrophobic membrane-stabilized O/W interface,¹⁸ which is formed over a thin channel (0.1 mm thick, 48 cm long) on a silver plate. By using the microflow cell, we have accomplished complete electrolysis for the interfacial transfer of a representative ion (tetramethylammonium ion,¹⁹ TMA⁺). Also, it has been shown that the microflow cell is promising for determination of the number of electrons for heterogeneous electron-transfer reactions^{20,21} at the O/W interface.

EXPERIMENTAL SECTION

Chemicals. Tetrabutylammonium tetraphenylborate¹⁹ (TBATPB) and tetrapentylammonium tetraphenylborate²² (TPnATPB) were prepared as described previously. Analytical grade tetrabutylammonium chloride (TBACl) or tetrapentylammonium chloride (TPnACl) was occasionally contaminated by a trace amount of

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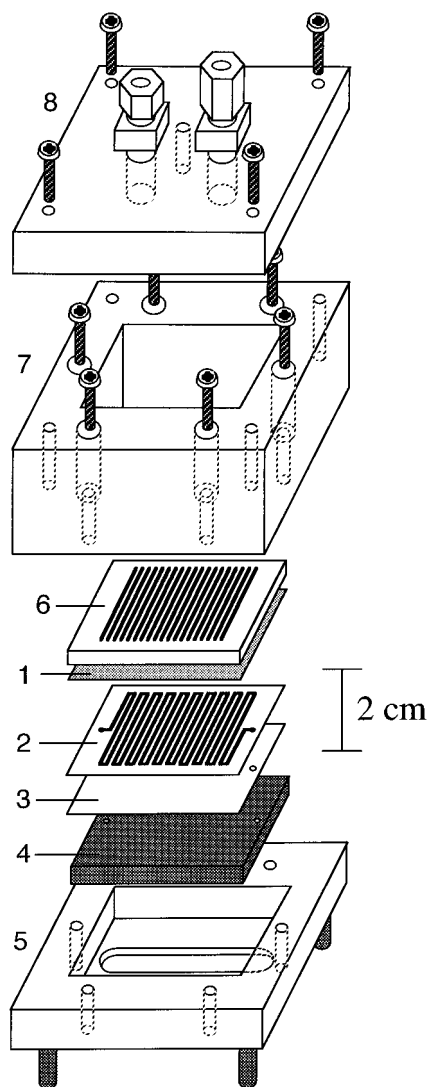


Figure 1. Cell construction: (1) PTFE membrane filter, (2) polyester gasket with a channel (1 mm wide; 48 cm long), (3) dialysis membrane, (4) silver plate, (5) Teflon pedestal with steel legs, (6) Teflon draining board (3 mm thick) with 19 slots (each being 1 mm wide and 23 mm long), (7) Teflon block with a square hole, and (8) Teflon lid with orifices for counter and reference electrodes and an air vent.

iodide ion, which was removed by metathesis with silver chloride in aqueous solution; the concentration of TBACl or TPnACl was determined by potentiometric titration with a standard silver nitrate solution. Analytical grade nitrobenzene (NB) as the oil-phase solvent was purified by shaking with active alumina overnight. The other reagents were of analytical grade.

Construction of a Microflow Cell. A silver plate ($30 \times 41 \times 5$ mm) was employed as the electrode for the aqueous mobile phase, which served as both the reference and counter electrodes. As seen in Figure 1, the silver plate was provided with two small orifices (0.9-mm diameter) for a solution inlet and outlet, into which Teflon tubes (0.86-mm outer diameter, 0.38-mm inner diameter) were inserted. The surface of the silver plate was polished in advance by using a $0.3\text{-}\mu\text{m}$ aluminum oxide lapping film (Sumitomo 3M, No. 15,000) and then preelectrolyzed to form a AgCl layer on it (see below). When the mobile phase contains redox species, the silver plate needs to be covered with a dialysis

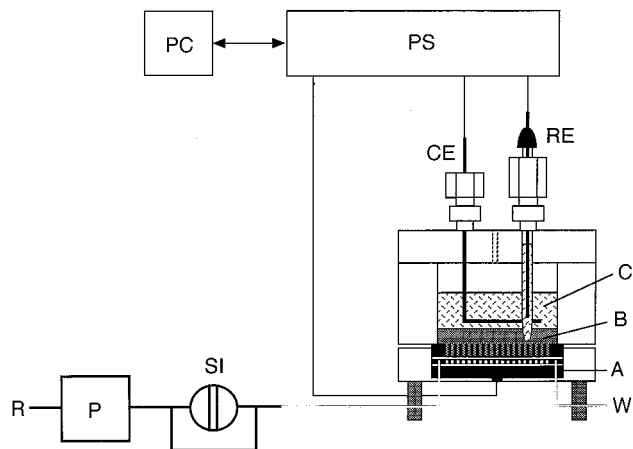


Figure 2. Scheme of the microflow electrolysis system: (A) silver plate, (B) NB phase, (C) 0.1 M LiCl aqueous solution, (RE) reference electrode, (CE) silver counter electrode, (SI) sample injector, (P) pump, (R) solution reservoir containing a 0.1 M LiCl aqueous solution, (W) waste, (PS) potentiostat, and (PC) personal computer.

membrane (Viskase, $20\text{ }\mu\text{m}$ thick). On this silver plate, a thin channel (1 mm wide, 48 cm long) was formed by using a polyester gasket (an OHP film of 0.1-mm thickness), on which a poly-(tetrafluoroethylene) (PTFE) membrane filter (Advantec, T010A047A, $70\text{ }\mu\text{m}$ thick, with $0.10\text{-}\mu\text{m}$ pore size) and a Teflon draining board were piled up as shown in Figure 1. These laminated plates were pressed into a Teflon pedestal by using a Teflon block and six screws. After the necessary solutions were supplied to the flow cell, a Teflon lid furnished with counter and reference electrodes was screwed down.

The NB/W interface was prepared in the microflow cell by pouring a 5-mL NB solution containing a supporting electrolyte (0.1 M TBATPB or 0.1 M TPnATPB) onto the PTFE membrane filter through the Teflon draining board (Figure 2). Because NB is toxic, its handling should be done under the hood by using safety groves. Since the PTFE membrane is hydrophobic, the NB/W interface is formed at the lower surface of the membrane. Next, a 0.1 M LiCl aqueous solution was gently applied onto the NB solution. In this aqueous solution, a square-spiral silver counter electrode (1-mm diameter, 10 cm long) was immersed. The reference electrode was an Ag/AgCl electrode immersed in a TBACl or TPnACl aqueous solution held in a Luggin capillary; the tip of the capillary was located in the NB solution.

The pretreatment of the silver plate was performed as follows: The flow cell was constructed in the same manner as illustrated in Figure 1, except that the silver plate was not covered with the dialysis membrane and the PTFE membrane was replaced by a dialysis membrane (Viskase, $20\text{-}\mu\text{m}$ thick). A 2% KCl aqueous solution was then poured onto the dialysis membrane, and the same solution was made to flow through the channel by using a peristaltic pump (flow rate, $180\text{ }\mu\text{L min}^{-1}$). Under these conditions, the surface of the silver plate, being in contact with the flow channel, was electrolyzed in the dark for several hours by using a 3-V dry battery that was connected in series to a $1\text{-k}\Omega$ resistor. This electrolysis formed a brownish AgCl layer on the silver plate, which served as an Ag/AgCl electrode.

Electrochemical Cell Systems. The microflow cell for the coulometric detection of TMA^+ is expressed as

	I	II	III	IV	
	0.1 M TBACl	0.1 M TBATPB	PTFE	mobile phase	
Ag/AgCl			membrane	0.1 M LiCl	AgCl/Ag (A)
	(W)	(NB)	(NB)	(W)	

Here the silver counter electrode is omitted, which was immersed in a 0.1 M LiCl aqueous solution contacting with the NB phase. A 20–200- μ L aliquot of a 0.5–2.0 mM TMACl aqueous solution was injected into the mobile phase. The left-side Ag/AgCl electrode serves as the reference electrode for the NB phase, while the right-side Ag/AgCl electrode (i.e., the electrolyzed silver plate) serves as both reference and counter electrodes for the W phase.

For the determination of the number of electrons for the heterogeneous electron-transfer reaction between L-ascorbic acid (AH_2) and chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone; denoted by Q),^{23–25} the following electrochemical cell was used:

	I	II	III	IV	V	
	0.02 M TPnACl	0.1 M TPnATPB	PTFE	mobile phase	dialysis	
Ag/AgCl	0.1 M MgSO_4	20 mM Q	membrane	0.1 M LiCl	membrane	AgCl/Ag (B)
	(W)	(NB)	(NB)	(W)	(W)	

As in cell A, the silver counter electrode is omitted, which was immersed in a 0.1 M LiCl aqueous solution contacting with the NB phase. A 100- μ L aliquot of a 0.2 mM AH_2 aqueous solution was injected into the mobile phase, whose pH was adjusted to 7.0 with 0.05 M phosphate buffer.

If we assume that the ohmic drop is correctly compensated in potentiostatic measurements and that the Ag/AgCl electrode for the W phase functions as an ideal nonpolarizable electrode (i.e., its potential remains unchanged during the current flow), the applied potential (E) between the two Ag/AgCl electrodes is related to the Galvani potential difference ($\Delta_{\text{O}}^{\text{W}}\phi$) between the NB/W interface by

$$E = \Delta_{\text{O}}^{\text{W}}\phi + \Delta E_{\text{ref}} \quad (1)$$

where ΔE_{ref} is a constant that depends only on the reference electrode system. Supposing that liquid junction potentials of the PTFE and dialysis membranes are negligible, ΔE_{ref} can be regarded as identical with that for the cell used previously,²² i.e., 323 or 289 mV, respectively, for cell A or B at 25 °C.

Apparatus. Figure 2 shows the scheme of the microflow electrolysis system, which comprised a peristaltic pump (Iuchi, CTP-1), a sample injector (Rheodyne, model 7125), and the microflow cell. The flow rate was usually set at 180 $\mu\text{L min}^{-1}$. A homemade potentiostat was used in order to control the $\Delta_{\text{O}}^{\text{W}}\phi$ of the NB/W interface and detect the ion-transfer current. A positive feedback circuit mounted in the potentiostat was employed with

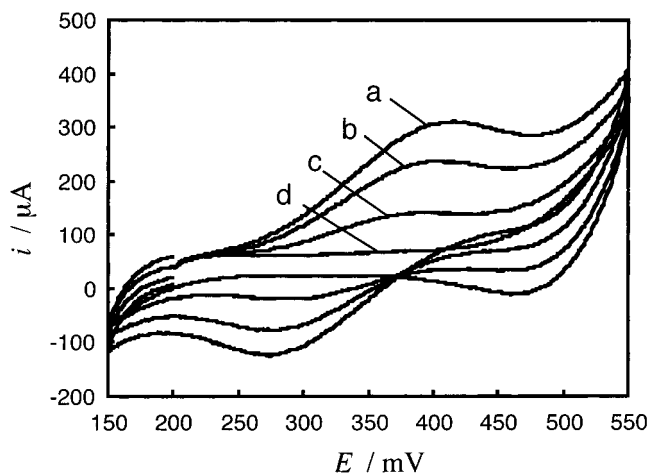


Figure 3. Cyclic voltammograms for the transfer of TMA^+ at the NB/W interface, which were recorded by using the microflow cell (Figure 1) under quiescent conditions; 0.1 M LiCl aqueous solutions containing (a) 0.6, (b) 0.4, (c) 0.2, and (d) 0 mM TMACl were provided in advance to the microflow cell. The potential scan was applied from 200 mV to 550 mV in the positive direction, followed by the negative to 150 mV, and then back to the initial potential. Scan rate, 50 mV s^{-1} .

the intention of compensating the solution resistance ($\sim 90 \Omega$). The coulometric and voltammetric data acquisition was controlled by means of a 16-bit personal computer (NEC, PC9801VM) equipped with a 12-bit analog-to-digital converter and a 16-bit digital-to-analog converter.

RESULTS AND DISCUSSION

Preliminary Experiments. In our initial experiments, a dialysis membrane was used instead of the PTFE membrane in order to prepare a NB/W interface in a microflow cell. However, a complete electrolysis was not accomplished, the electrolysis efficiency not going over 30%. Since a dialysis membrane is hydrophilic, an O/W interface is usually formed on the membrane surface adjacent to the O phase.^{26,27} Accordingly, an ion in the mobile W phase should cross the dialysis membrane until it transfers across the O/W interface. In the preliminary experiments, some of the transferring ions were supposed to pass through the flow channel without transferring across the O/W interface. Then, we changed the dialysis membrane to a porous hydrophobic PTFE membrane to form an O/W interface on the membrane surface adjacent to the mobile W phase. Hundhammer and Wilke¹⁸ employed a similar porous hydrophobic membrane (poly(ethylene terephthalate) membrane) to stabilize a NB/W interface.

Voltammetric Responses. Figure 3 shows cyclic voltammograms recorded after providing 0.1 M LiCl aqueous solutions containing several concentrations of TMACl to the microflow cell (Figure 1, cell A). The voltammetric measurements were carried out under quiescent conditions. As seen in Figure 3, well-developed voltammetric waves for the transfer of TMA^+ at the NB/W interface were obtained in a similar manner as reported.¹⁹ The positive-current peak is due to the transfer of TMA^+ from W

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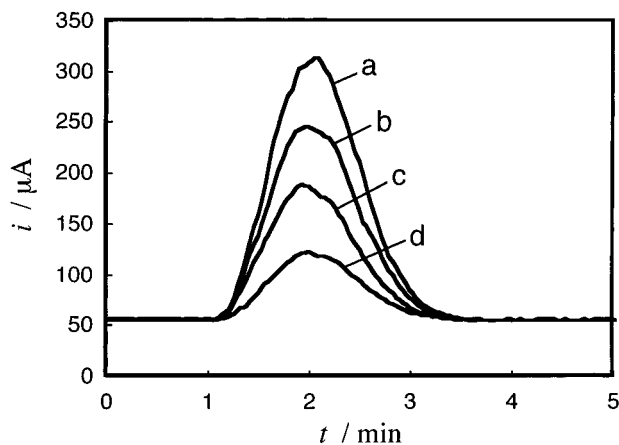


Figure 4. Coulometric curves obtained with the microflow cell (cell A) to which a 100- μ L aliquot of a sample solution containing (a) 2.0, (b) 1.5, (c) 1.0, or (d) 0.5 mM TMA⁺ was injected. Applied potential, 500 mV.

to NB, whereas the negative-current peak is due to its transfer back to W. Thus, it was shown that the NB/W interface formed by using a PTFE membrane in the microflow cell could function as a polarizable interface in the same manner as ordinary NB/W interfaces.

Nevertheless, the peak separation was found to increase with the TMA⁺ ion concentration, being much larger than the value of ~ 60 mV for a reversible wave of the transfer of a univalent ion. Since the transfer of TMA⁺ at the NB/W interface is known to be very fast (i.e., electrochemically reversible),^{19,28} the large peak separation may be ascribed in part to polarization of the Ag/AgCl electrode for the W phase due to the current flow. Also, it seems likely that an unequal potential distribution over the NB/W interface formed on the long channel arose from imperfect compensation of the ohmic drop. Such incompleteness in the voltammetric measurements, however, hardly affected the coulometric measurements described below.

Coulometry of TMA⁺. Figure 4 shows the coulometric curves obtained with the microflow cell (cell A) to which a 100- μ L aliquot of a sample solution containing several concentrations of TMA⁺ was injected. The electrode potential (E) was set at 500 mV, where TMA⁺ ions in the mobile W phase would be completely "electrolyzed" or thoroughly transported to the NB phase (cf. Figure 3). Immediately after the potentiostatic operation was started, a positive current probably due to transfer of supporting electrolyte ions (TPB⁻, Li⁺, or both) was observed but rapidly reduced to a constant value, which seems to be due to the transfer of Li⁺ being constantly provided from the mobile phase. Then a sample solution was provided to the flow cell to record a coulometric curve as shown in Figure 4. As seen in the figure, an almost symmetrical current peak due to the TMA⁺ ion transfer was obtained for every concentration. When the injection volume was increased to 200 μ L, however, a slight deformation of the current peak, i.e., "tailing", was observed (not shown).

Provided that complete electrolysis is accomplished, the quantity of electricity, being obtained from the peak area, should be proportional to the mole number of the transferring ion in the

Table 1. Electrolysis Efficiency^a (%) for the Transfer of TMA⁺ at the NB/W Interface

injection volume, μ L	TMA ⁺ concentration, mM			
	0.5	1.0	1.5	2.0
20	91 \pm 0	93 \pm 2	99 \pm 1	93 \pm 3
50	94 \pm 4	90 \pm 4	99 \pm 1	99 \pm 0
100	98 \pm 2	92 \pm 1	91 \pm 1	91 \pm 1
200	96 \pm 1	91 \pm 0	92 \pm 0	90 \pm 1

^a Mean of four repeat measurements.

sample solution. In Table 1, the electrolysis efficiencies evaluated from the peak areas are shown for different concentrations of TMA⁺ (0.5–2.0 mM) and injection volumes (20–200 μ L). Under these conditions, the electrolysis efficiency was over 90%, showing the accomplishment of almost complete electrolysis. Thus, the present microflow cell appears to be promising for absolute quantitative analysis of ions. We would like to add that the present technique has great potentialities for the determination of nonredox species such as ionic and ionizable drugs, ionic surfactants, or some metal ions (alkali/alkaline earth metals).

In the reported O/W-type flow cell,^{9,10} a four-electrode configuration has been adopted, in which the Galvani potential difference between the O/W interface can be controlled more accurately than in a three- or two-electrode configuration. However, a four-electrode configuration is cumbersome and unsuitable for designing a thin-layer cell for complete electrolysis. In the present flow cell, the electrolyzed silver plate serves as both reference and counter electrodes. Hence, some polarization of the electrode due to current flow is inevitable, so that the concentration of a transferring ion should be kept lower than millimolar level. However, we would like to stress that a simpler three-electrode configuration has effectively functioned to realize a thin-layer flow cell for complete electrolysis.

Determination of the Number of Electrons for Heterogeneous Electron-Transfer Reactions. In recent years, much attention has been paid to heterogeneous electron-transfer reactions at the O/W interface.^{20,21} This is because the O/W interface is the simplest and most promising model for understanding electron transport in biomembranes (e.g., respiratory chain, free-radical scavenging antioxidants, etc.).^{29,30} So far, some voltammetric studies have been performed on heterogeneous electron-transfer reactions for biologically significant compounds which include AH₂,^{23–25} flavin mononucleotide (FMN),³¹ and β -nicotinamide adenine dinucleotide (NADH).³² However, as discussed in the literature, such heterogeneous electron-transfer reactions are not necessarily simple. For clarification of the reaction mechanisms, it seems fundamentally important to determine the number of electrons (n) involved in the charge-transfer reactions.

In this study, we have applied the microflow cell to the determination of n for the electron-transfer reaction between AH₂

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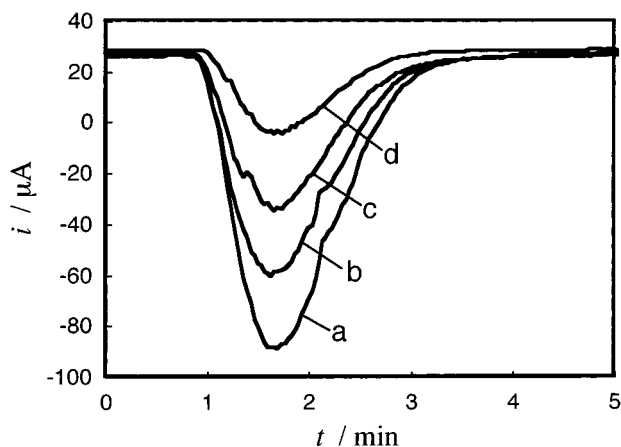
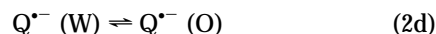
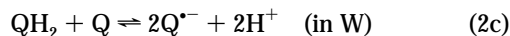
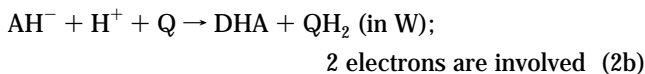


Figure 5. Coulometric curves obtained with the microflow cell (cell B) to which a 100- μ L aliquot of a sample solution containing (a) 0.4, (b) 0.3, (c) 0.2, or (d) 0.1 mM AH_2 was injected. Applied potential, 100 mV.

in W and Q in NB.^{23,24} Figure 5 shows the coulometric curves obtained with the microflow cell (cell B) to which a 100- μ L aliquot of a sample solution containing 0.1, 0.2, 0.3, or 0.4 mM AH_2 was injected. The electrode potential (E) was set at 100 mV, where AH_2 in the mobile W phase (pH 7.0) would be completely electrolyzed.²⁴ As seen in Figure 5, a well-defined current peak was observed for every AH_2 concentration. The quantity of electricity required for the oxidation of AH_2 was evaluated from the peak area, and then the n value was calculated by using the relation $n = Q/(F[\text{AH}_2]V)$, where Q is the quantity of electricity (in C), F the Faraday constant (96 485 C mol⁻¹), $[\text{AH}_2]$ the concentration of AH_2 (in mol L⁻¹), and V the injection volume

(in L). The n value determined was 1.91, 1.98, 2.06, or 2.05 (for one molecule of AH_2) at 0.1, 0.2, 0.3, or 0.4 mM AH_2 , respectively. The average n value of 2.00 ± 0.07 is in line with the proposed mechanism:²⁴



In this mechanism, Q is partly extracted into the W phase, where it undergoes an irreversible two-electron reduction by ascorbate (AH^- , the dominant species in pH 6–8) producing the hydroquinone form of chloranil (QH_2) as well as dehydro-L-ascorbic acid (DHA). As shown in eq 2c, QH_2 can proportionate in the presence of Q to form the semiquinone radical anion ($\text{Q}^{\bullet-}$), which subsequently transfers to the O phase at negative potential differences (eq 2d). According to this mechanism, the oxidation of 1 mol of AH_2 leads to the interfacial transfer of 2 mol of univalent $\text{Q}^{\bullet-}$. This is consistent with an n value of ~ 2 determined by using the microflow cell. Thus, the present microflow cell has been shown to be promising also for clarification of complicated charge-transfer processes at the O/W interface.

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