

# Mathematical modelling for the preparation of platinum–solid-polymer-electrolyte by counter-current diffusion

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## Abstract

A mathematical model is proposed for the counter-current diffusion of hexachloroplatinic acid in perfluorinated Nafion membranes using sodium borohydride as a reducer. The model equations are employed to describe the metallic platinum (Pt) concentration profiles across the membrane. Diffusivities are obtained from permeation measurements and then the theoretical data are compared with experimental results which are obtained by electron dispersive microanalysis spectroscopy. There is a good agreement between the simulated model equation and the experimental results. It is expected that this model can provide an idea of the development of the new Pt–solid-polymer-electrolyte (Pt–SPE) electrode. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Mathematical model; Counter-current diffusion; Concentration profile; Permeation measurement; Platinum; Solid-polymer-electrolyte

## 1. Introduction

Water electrolysis employing a solid-polymer-electrolyte (SPE) has been investigated widely for hydrogen production. It is well known that the method used to prepare the electrocatalyst affects markedly the performance of the electrocatalyst in water electrolysis. Various preparation methods have been used, namely: chemical deposition using cation and anion metal salts, hot pressing, electrodeposition, sputtering, vapour deposition [1–4].

The counter-current diffusion process is a type of chemical deposition method using anion metal salts. The process is accomplished by diffusing a metal ion into one side of the film and diffusing a reducing agent into the opposite side. The reaction of preparing electrocatalyst can be controlled if diffusivity data are known. In addition, there is no abrasion of the electrocatalyst during the water electrolysis because the electrocatalyst is prepared in a wet condition. The counter-current diffusion process has the advantage in that it can be performed on a free-standing film and does not require electric current.

Van Oss [5] has reported that morphological complexity is observed when the precipitation reaction was coupled with counter-current diffusion [6]. Manring [7] has investigated the electroless deposition of silver as an interlayer within polymer films. Manring et al. [8], Mazur and Reich [9] and Reich et al. [10] have examined the electrochemical growth of metal interlayers in polyimide film. Dee [11] and Dee et al. [12] have reported on the kinetics of metal interlayer growth in polyimide film. Dewulf and Bard [13] showed that the rate constant of the electrochemical deposition reaction is so large that the formation rate of platinum is determined by the concentration of the reactants (metal ion and reductant), while the morphology depends markedly on the concentration of reactants. The formation of platinum in the membrane film can be controlled by the mass-transfer rates of the reactants.

In this study, the electrocatalyst is prepared by counter-current diffusion and the location of deposition of electrocatalyst is predicted from the diffusivity data. To control the location of deposition of Pt, the diffusion of  $\text{PtCl}_6^{2-}$  and  $\text{BH}_4^-$  in the Nafion membrane film is investigated and a mathematical model for counter-current diffusion is proposed. The mathematical model has been utilized to estimate the diffusivity of Pt ions and the concentration profile within the membrane. It is compared with experimental data obtained from electron dispersive microanalysis spectroscopy.

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## 2. Experimental

### 2.1. Materials

Nafion 117 perfluorosulfonic membrane (Dupont de Nemours, equivalent weight 1100 g mol<sup>-1</sup> and dry thickness 0.178 mm) was chosen as the SPE. Before electrode deposition, a two-step standard procedure of cleaning was followed for every sample, namely, (i) immersion for 1 h in boiling HNO<sub>3</sub>-H<sub>2</sub>O(1:1 vol.%) solution to remove impurities; (ii) immersion for 1 h in boiling deionized water (resistivity of 1 MΩ at 25°C) to introduce a reproducible amount of water into the membrane. Hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) and sodium borohydride (NaBH<sub>4</sub>) were purchased from Aldrich and Duksan, respectively.

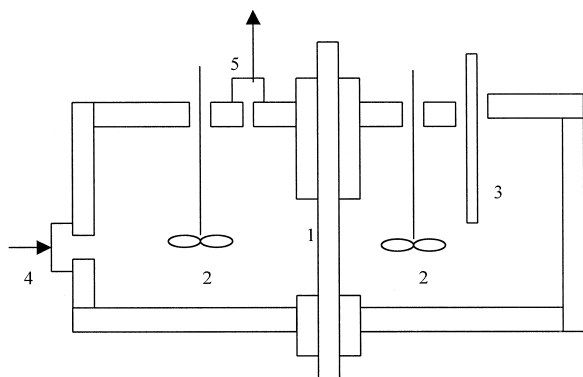
### 2.2. Measurement of diffusion coefficients in the membrane

A schematic diagram of the apparatus used for measurement of the diffusion coefficient of H<sub>2</sub>PtCl<sub>6</sub> and NaBH<sub>4</sub> within the membrane by counter-current diffusion is shown in Fig. 1. As the volume of the compartment was large, the concentration changes near the boundaries were neglected. The area of the membrane exposed to the solution was 5.06 cm<sup>2</sup>. The solution of each compartment was stirred to remove concentration polarization. The temperature was maintained at 25°C.

The diffusion coefficients of PtCl<sub>6</sub><sup>2-</sup> in Nafion membrane were estimated by measuring the flux through the membrane between two half-cells, one contained 0.040 M PtCl<sub>6</sub><sup>2-</sup> (pH = 1), the other 1 M HCl. The concentration of PtCl<sub>6</sub><sup>2-</sup> in the HCl compartment was monitored spectrophotometrically at 260 nm until it reached 4.0 × 10<sup>-5</sup> M. The flux of solution for steady-state conditions under linear diffusion is given by Eq. (1):

$$J = \frac{DKC_0}{d} \quad (1)$$

where:  $K$  is the partition coefficient of PtCl<sub>6</sub><sup>2-</sup> between the aqueous solution and the Nafion membrane;  $d$  is the



1. Membrane 2. Impeller 3. Sampling port  
4. Solution input 5. Solution output

Fig. 1. Cell used for membrane ionic flux measurement.

membrane thickness;  $D$  is the diffusion coefficient of PtCl<sub>6</sub><sup>2-</sup> in the membrane [14–17].

The partition coefficient of the PtCl<sub>6</sub><sup>2-</sup> between aqueous solution and the membrane was measured spectrophotometrically after soaking a membrane in 0.040 M PtCl<sub>6</sub><sup>2-</sup> for 72 h [18]. The partition coefficient of the BH<sub>4</sub><sup>-</sup> was also measured by the above method.

### 2.3. Measurement of the rate constant of the reaction between PtCl<sub>6</sub><sup>2-</sup> and BH<sub>4</sub><sup>-</sup>

The rate constants of the reactions in the polymer film cannot be measured directly [19]. Schelly et al. [20] reported that the determination of the rate constant of a fast irreversible reaction in solution differ from that of a reversible reaction and it is possible to measure it when the initial concentration of reactants are in the range of 10<sup>-4</sup> to 10<sup>-7</sup> M. Therefore, in this work, the rate constant was measured at an initial concentration of 1.0 × 10<sup>-4</sup> M [20].

The rate constant of the reaction between PtCl<sub>6</sub><sup>2-</sup> and BH<sub>4</sub><sup>-</sup> was determined by monitoring the appearance of colloidal platinum particles with a spectrophotometer (Shimadzu 160) after mixing solutions of the reactants.

The small platinum particles (< 200 Å) suspended in solution have an optical absorption between 200 and about 600 nm with a maximum at 260 nm. This absorption has been treated theoretically by Dewulf and Bard [13]. The integrated absorbance (area under the absorption spectrum) should be linearly proportional to the amount of platinum metal present. At low initial reactant concentration, this absorption was used to monitor the formation of platinum from the reaction between NaBH<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>. By plotting the results from a second-order rate law, the rate constant was obtained.

### 2.4. Distribution of platinum concentration in the membrane

The Nafion 117 membrane (geometrical area 5.06 cm<sup>2</sup>) was placed with one surface held in contact with H<sub>2</sub>PtCl<sub>6</sub> of various concentrations and the other surface held in contact with NaBH<sub>4</sub> of various concentrations. The reducing agent solution continuously penetrates through the membrane and comes into contact with the metal acid solution. The reducing agent, borohydride, was allowed to penetrate the SPE to reduce Pt ions to Pt metal at the surface of the membrane. The metallic platinum concentration profiles across the membrane were obtained by electron dispersive microanalysis spectroscopy.

### 2.5. Sample characterization

The concentration of the PtCl<sub>6</sub><sup>2-</sup> transferred through the Nafion membrane was obtained from the standard curve

by measuring the maximum absorbance using a spectrophotometer (Shimadzu 160) at 260 nm. Also, inductively coupled plasma–MS was used to determine the concentration of  $\text{BH}_4^-$ . The concentration profiles of Pt across the membrane were obtained by means of an electron dispersive microanalysis spectroscopy (JSM 6400).

### 3. Diffusion–reaction model

The counter-current diffusion process is illustrated schematically in Fig. 2. In such diffusion, a free-standing polymer is arranged as a membrane that separates the solution of a reducing agent,  $\text{R}^-$ , at one surface ( $x = 0$ ) and solution of metal ions,  $\text{M}^+$ , at the opposite surface ( $x = L$ ). The two components diffuse into the membrane and simultaneously react with each other to form reduced Pt in the membrane.

In this analysis:  $D_m$  and  $D_r$  are diffusion coefficients for transport of metal ions and reducing agent in the solvent-swollen polymer, respectively;  $K_m$  and  $K_r$  are equilibrium sorption coefficients that govern the partition of the metal ions and reducing agent between the solutions (concentrations  $[\text{M}^+]_s$  and  $[\text{R}^-]_s$ ) and the film (concentrations  $[\text{M}^+]_l$  and  $[\text{R}^-]_0$ ). The reduction of metal is assumed to be governed by a second-order rate law with a rate constant of  $k'$  for reduction by  $\text{R}^-$ .

A general diffusion–reaction model can be formulated as follows. Let  $Q(x, y, z, t)$  represent the metal density distribution that expresses the quantity of metal within an incremental volume element at location  $\{x, y, z\}$  following a deposition that is terminated at time  $t$ .

If the metal is produced in a heterogeneous second-order chemical reaction with a rate constant  $k'$  for reduction of  $\text{M}^+$  by reducing agent,  $\text{R}^-$ , then  $Q$  is given by:

$$Q(x, y, z, t) = \int_0^t k' [\text{M}^+] [\text{R}^-] dt. \quad (2)$$

So long as transport is sufficiently slow to influence the overall kinetics, the concentrations will vary with location, except under steady-state conditions. In order to simplify Eq. (2), assuming diffusion to be the sole transport mechanism, the time-dependent concentration profiles are gov-

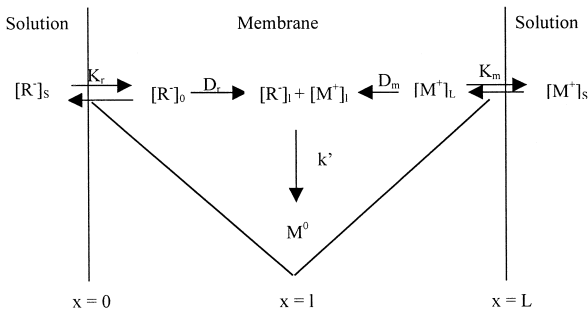


Fig. 2. Dynamics involved in counter-current diffusion experiment.

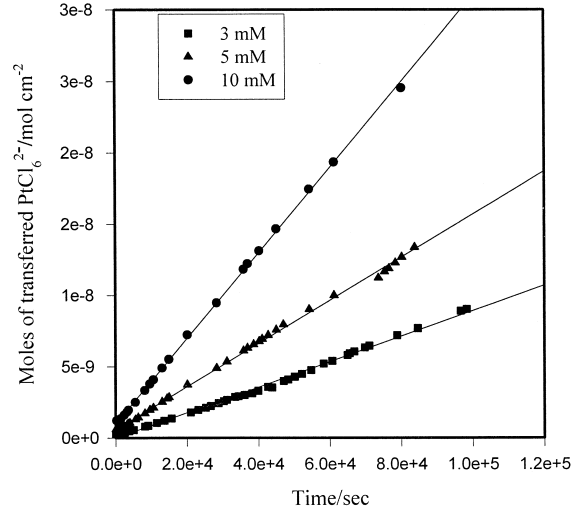


Fig. 3. Moles of transferred  $\text{PtCl}_6^{2-}$  as a function of time.

erned by simultaneous equations for the reaction rate law and Fick’s second law of the counter-current diffusion [12,21–23], i.e.,

$$\frac{\partial [\text{M}^+]}{\partial t} = D_m \nabla^2 [\text{M}^+] - k' [\text{M}^+] [\text{R}^-] \quad (3)$$

$$\frac{\partial [\text{R}^-]}{\partial t} = D_r \nabla^2 [\text{R}^-] - k' [\text{M}^+] [\text{R}^-] \quad (4)$$

By assuming a uniform concentration of reactants along planes parallel to the film, Eqs. (3) and (4) become one-dimensional and Laplacian and simplify to  $d^2/dx^2$ , i.e.,

$$\frac{\partial [\text{M}^+]}{\partial t} = D_m \frac{d^2}{dx^2} [\text{M}^+] - k' [\text{M}^+] [\text{R}^-] \quad (5)$$

$$\frac{\partial [\text{R}^-]}{\partial t} = D_r \frac{d^2}{dx^2} [\text{R}^-] - k' [\text{M}^+] [\text{R}^-] \quad (6)$$

Eqs. (5) and (6) can be solved by numerical methods for suitably defined boundary conditions.  $[\text{M}^+]_l$  and  $[\text{R}^-]_0$  are assumed to be in equilibrium with the solutions of concentrations  $[\text{M}^+]_s$  and  $[\text{R}^-]_s$ , respectively. The relevant boundary conditions are summarized as follows. For  $t = 0$

$$[\text{M}^+]_x = 0 \text{ for } 0 < x < L \quad (7)$$

$$[\text{R}^-]_x = 0 \text{ for } 0 < x < L \quad (8)$$

For  $t > 0$

$$[\text{M}^+]_l = K_m [\text{M}^+]_s, \quad (9)$$

$$[\text{R}^-]_0 = K_r [\text{R}^-]_s, \quad (10)$$

$$\frac{d[\text{M}^+]}{dt} = 0 \text{ for } x < 0, \quad (11)$$

$$\frac{d[\text{R}^-]}{dt} \text{ for } x > L. \quad (12)$$

The theoretical profile of the concentration is obtained from the above partial derivative equations and boundary

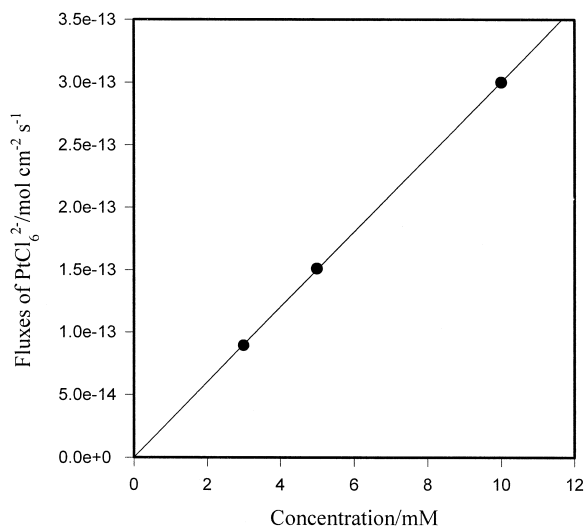


Fig. 4. Fluxes of transferred  $\text{PtCl}_6^{2-}$  to  $\text{H}_2\text{PtCl}_6$  concentration.

conditions. In this case, the computer program used to solve the model equations is a modified IMSL program (MATH/LIBRARY) [24].

#### 4. Results and discussion

##### 4.1. Diffusion coefficients of $\text{PtCl}_6^{2-}$ in the membrane

The moles of transferred  $\text{PtCl}_6^{2-}$  as a function of time with Pt aqueous solution concentration are shown in Fig. 3. The linear portion represents steady-state conditions and the slope of the line is the steady-state flux,  $J = DKC_0/d$ . The flux change of  $\text{PtCl}_6^{2-}$  in the membrane as a function of Pt concentration is shown in Fig. 4. The transferred flux of Pt is found to be proportioned to the initial concentration of Pt in aqueous solution.

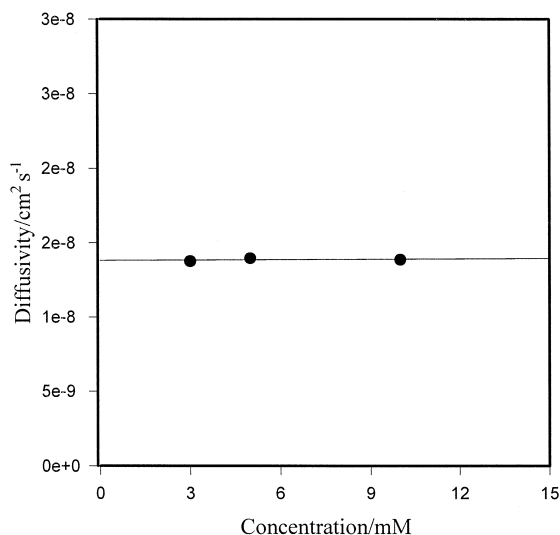


Fig. 5. Diffusivities of transferred  $\text{PtCl}_6^{2-}$  to  $\text{H}_2\text{PtCl}_6$  concentration.

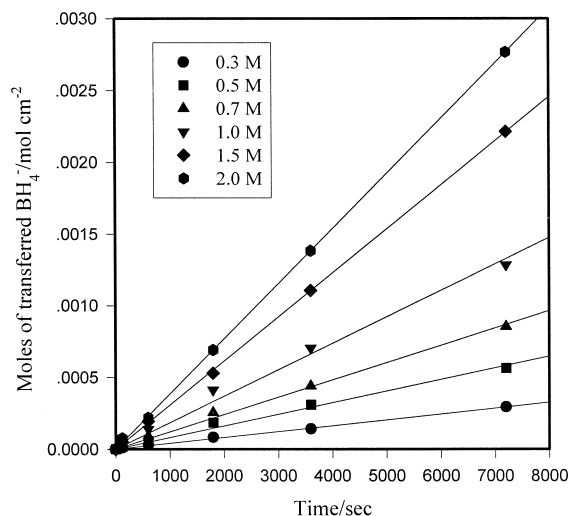


Fig. 6. Moles of transferred  $\text{BH}_4^-$  as a function of time.

The partition coefficient of  $\text{PtCl}_6^{2-}$  was estimated from the standard curve by measuring the absorptivity using a spectrophotometer set at 260 nm. The partition coefficient for  $\text{PtCl}_6^{2-}$  between Nafion 117 and aqueous solution was measured spectrophotometrically after soaking a membrane in 0.04 M  $\text{PtCl}_6^{2-}$  for 72 h. The absorbance of the Nafion 117 was 0.127, while that of the  $\text{PtCl}_6^{2-}$  soaked membrane was 0.645. If the molar absorptivity of  $\text{PtCl}_6^{2-}$  in the Nafion is taken to be the same value as that in water, the equilibrium concentration is  $1.54 \times 10^{-3}$  M; the partition coefficient,  $K = [\text{PtCl}_6^{2-}]_{\text{Naf}}/[\text{PtCl}_6^{2-}]_{\text{aq}}$ , is 0.0385 [13]. The coefficients calculated from these data are shown in Fig. 5.

##### 4.2. Diffusion coefficients of $\text{BH}_4^-$ in the membrane

Using inductively coupled plasma, the flux of  $\text{BH}_4^-$  was obtained from the concentration of  $\text{NaBH}_4$  for the mod-

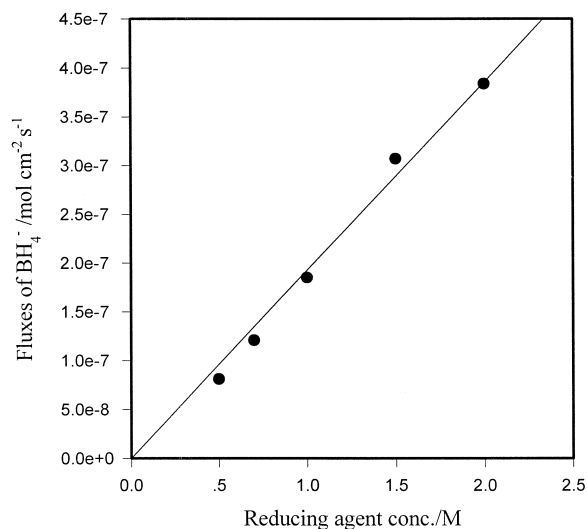


Fig. 7. Fluxes of transferred  $\text{BH}_4^-$  to reducing agent concentration.

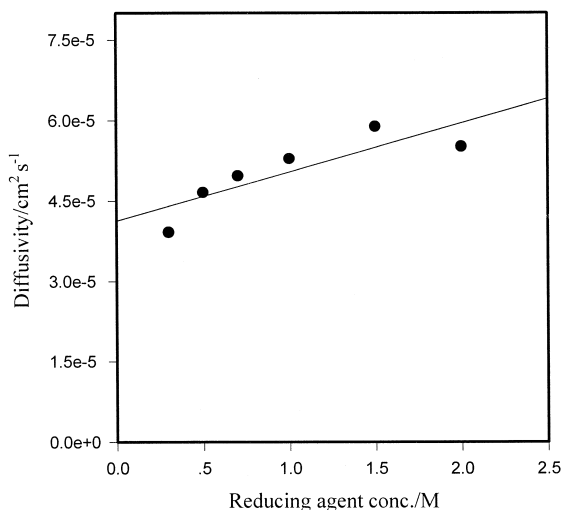


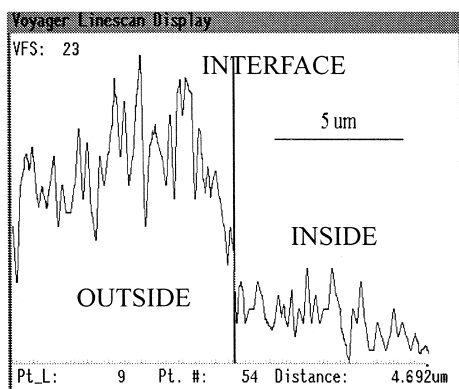
Fig. 8. Diffusivities of transferred  $\text{BH}_4^-$  to reducing agent concentration.

elling of the Pt–SPE composite. As the reducing agent concentration is increased, the concentration of  $\text{BH}_4^-$  transported per unit area of membrane is increased. This indicates that the flux of transported  $\text{BH}_4^-$  increases with increasing concentration of reducing agent, as shown in Fig. 6.

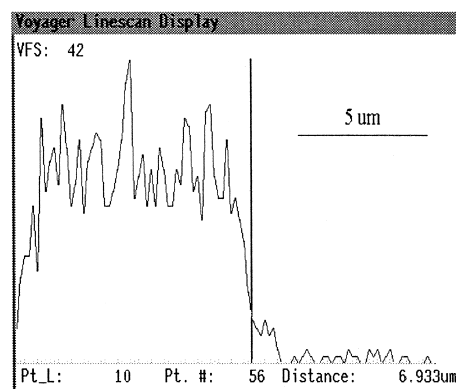
Also, Fig. 7 shows that the flux of  $\text{BH}_4^-$  increases linearly with increasing concentration of reducing agent. The values are approximately in the range of  $10^{-7}$  mol  $\text{cm}^{-2}$   $\text{s}^{-1}$ . It should be noted that the flux of  $\text{BH}_4^-$  is greatly larger than that of  $\text{PtCl}_6^{2-}$  in this system. When a high concentration of reductant is used, its diffusion into the Nafion will be sufficiently fast that Pt will be reduced before it can diffuse to a significant distance from the membrane. Consequently, a higher concentration distribution of Pt should be obtained from the Pt deposited membrane. On the other hand, when a low concentration of reductant is used, its diffusion into the membrane will be slow so that the Pt ions have a sufficient time to diffuse to the Nafion–solution interface. Therefore, it is possible to get Pt in the middle or the other side of the Nafion membrane. Nevertheless, the amount of the deposited Pt should be less. In addition, it is found that the deposited Pt is concentrated nearer the surface as observed in other work [25]. The diffusivity, obtained from Eq. (1), increases linearly with increasing reductant concentration (Fig. 8).

#### 4.3. Simulated concentration profiles

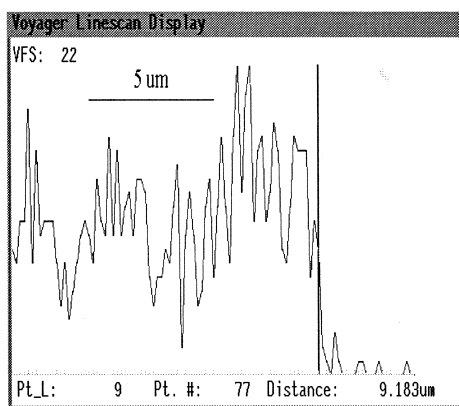
Concentration profiles of Pt for analyzing the preparation mechanism of Pt–SPE were obtained from the experi-



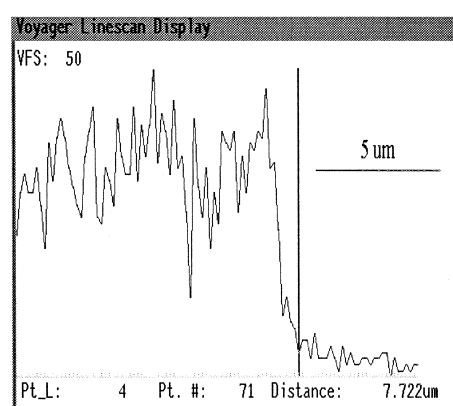
(a)



(b)



(c)



(d)

Fig. 9. Electron microprobe concentration profiles for the cross-section of Pt–SPE. (a)  $\text{NaBH}_4$ ; 0.1 M,  $\text{H}_2\text{PtCl}_6$ ; 0.005 M (b)  $\text{NaBH}_4$ ; 1.0 M,  $\text{H}_2\text{PtCl}_6$ ; 0.005 M (c)  $\text{NaBH}_4$ ; 2.0 M,  $\text{H}_2\text{PtCl}_6$ ; 0.005 M (d)  $\text{NaBH}_4$ ; 1.0 M,  $\text{H}_2\text{PtCl}_6$ ; 0.010 M.

mental parameters (diffusivity, initial concentration of  $\text{H}_2\text{PtCl}_6$  and  $\text{NaBH}_4$ ).

The EDS results according to the various concentrations of reducing agent with Pt aqueous solution of various concentrations are shown in Fig. 9. It is found that reduction of the Pt occurred on the membrane in the direction of the Pt solution. The terms, denoted as the inside and outside in Fig. 9, indicate the membrane part and solution part to the boundaries of the membrane and solution, respectively.

Because the diffusion coefficient of the  $\text{BH}_4^-$  in the membrane and the initial concentration of the  $\text{BH}_4^-$  are larger than those of  $\text{PtCl}_6^{2-}$ , the location of deposited Pt obtained by calculated concentration profiles is restricted in the direction of the Pt aqueous solution. The differences are in order of  $10^3$  and  $10^2$ , respectively. The concentra-

tion profiles of Pt for the proposed model were simulated in terms of various concentrations of the reducing agent in a Pt aqueous solution concentration of 5 or 10 mM. The kinetic constant used for the model equation analysis was obtained by spectroscopic measurements which monitored the formation of Pt particles with time. Its value was  $1.51 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

The simulated concentration profiles of reactants of various concentrations as determined by the mathematical model are shown in Fig. 10. Irrespective of the concentration of reductant ( $\text{BH}_4^-$ ) and metal ions ( $\text{Pt}^{2+}$ ), the concentration profiles are not greatly modified, namely, the Pt concentration dropped drastically at the surface of membrane and this indicates the diffusion limiting process of Pt ions in preparation of the Pt–SPE electrode. This result is in good agreement with the concentration profiles of Pt

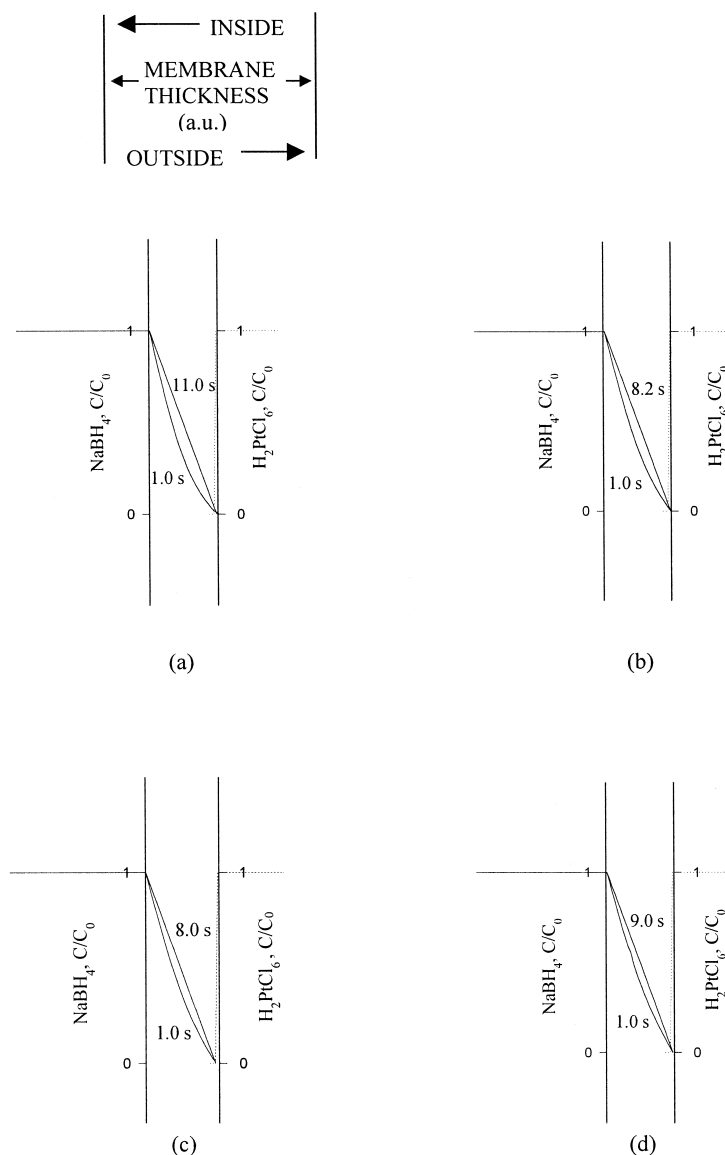


Fig. 10. Pt concentration profile according to reactants of various concentration. (a)  $\text{NaBH}_4$ : 0.1 M,  $\text{H}_2\text{PtCl}_6$ : 0.005 M (b)  $\text{NaBH}_4$ : 1.0 M,  $\text{H}_2\text{PtCl}_6$ : 0.005 M (c)  $\text{NaBH}_4$ : 2.0 M,  $\text{H}_2\text{PtCl}_6$ : 0.005 M (d)  $\text{NaBH}_4$ : 1.0 M,  $\text{H}_2\text{PtCl}_6$ : 0.010 M.

obtained by EDS. At higher reductant concentration, the region of reaction can only move slightly in the direction of the Pt aqueous solution side. This implies that reduction in the diffusivity of the reductant can control the Pt concentration profile in the Pt–SPE electrode. This could be achieved by selection of a bulky reductant. The mathematical model appears to be effective in estimating the location of Pt in the membrane when the Pt–SPE electrode is prepared by the counter-current diffusion process. Based on this study, it is expected that a new Pt–SPE electrode can be designed to enhance the performance of water electrolysis. To prove the validity of the model equation, changes in the location of deposited Pt by control of the diffusivities of reactants will be examined in future work.

## 5. Conclusions

It has been shown that a conductive metallic interlayer can be formed within the membrane by counter-current diffusion of  $\text{NaBH}_4$  and  $\text{H}_2\text{PtCl}_6$ . Using model equations, the metallic platinum concentration profiles across the membrane have been computed. The calculated data compare well with experimental data obtained by electron dispersive microanalysis spectroscopy. It is possible to predict the concentration profiles of Pt after reaction. The model can be used to predict location of deposition.

It is found that the Pt–SPE composite is deposited at the location where the relative diffusivity of metal ion and reductant is low. The mathematical model appears to be effective in estimating the location of Pt in the membrane when a Pt–SPE electrode is prepared by counter-current diffusion.

Based on this study, it is expected that a new Pt–SPE electrode can be designed to enhance the performance of water electrolysis.

## 6. Nomenclature

$C_i$	Concentration of species $i$ (M)
$D_i$	Diffusivity of species $i$ ( $\text{cm}^2 \text{ s}^{-1}$ )

$d$	Membrane thickness (cm)
$J$	Solute flux ( $\text{mol cm}^{-2} \text{ s}^{-1}$ )
$k$	Kinetic constant ( $\text{M}^{-1} \text{ s}^{-1}$ )
$K_i$	Partition coefficient of species $i$
$[\text{M}^+]$	Concentration of metal ion (M)
$[\text{R}^-]$	Concentration of reductant ion (M)
SPE	Solid-polymer-electrolyte

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