THE DIFFUSION OF VARIOUS ANIONS IN A POLYACETYLENE CATHODE OF A SECONDARY LITHIUM BATTERY

ZEN-ICHIRO TAKEHARA*, KIYOSHI KANAMURA*, SHUN-ICHI YONEZAWA**
and TETSURO HANAWA***

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida-Hommachi, Sakyo-ku, Kyoto 606 (Japan)

Summary

The diffusion coefficients of the anions, BF_4^-, ClO_4^-, and PF_6^-, were estimated as 2 - 4×10^{-14} cm^2 s^{-1}. The diffusion of anions in polyacetylene was treated as cylindrical diffusion. The diffusion coefficients were obtained by such a treatment, because the electrode surface area and the concentration of anions in polyacetylene were not needed in the estimation of the diffusion coefficients. The diffusion resistances estimated from the diffusion coefficient were compared with the charge transfer resistance in the potential region 3.6 V - 3.0 V *versus* Li/Li^+. The rate determining step on charge or discharge of a polyacetylene electrode was the anion diffusion process.

Introduction

Conducting organic polymers have been investigated by many workers in order to develop positive and negative electrodes for a lithium secondary battery [1 - 3]. The discharge and charge reactions proceed through doping and undoping processes involving various anions and cations. Polyacetylene is a well known conducting polymer and is prepared by the Shirakawa method [4]. Polyacetylene film consists of many fibrils, which are bundles of CH chains bonded by the Van der Waals force. In the course of the discharge and charge, the anions or cations diffuse in the fibril. Thus the rates of the charge and discharge reactions of polyacetylene may be limited by the diffusion of the dopants in the fibril. The diffusion behavior of anion dopants in polyacetylene has been examined in order to improve the discharge and charge characteristics of a polyacetylene electrode. Will [5] estimated the diffusion coefficients of the anions in a polyacetylene film to

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*Authors to whom correspondence should be addressed.
**Present address: Rakuto Kyoto Prefecture High School, Azugawa-mukai Yamashina-ku, Kyoto 607, Japan.
***Present address: Department of Applied Chemistry, Faculty of Engineering, Osaka University, Senri-oka, Suita-city, Osaka 565, Japan.

be 10^{-12} cm^2 s^{-1} using a current pulse method and assuming one dimensional linear diffusion. MacDiarmid estimated the diffusion coefficient to be 4×10^{-18} cm^2 s^{-1} [6].

The diffusion coefficients in fibrils, however, differ with author. In this study, the diffusion coefficients of BF_4^-, ClO_4^-, and PF_6^- in polyacetylene fibrils were estimated by assuming cylindrical diffusion.

Experimental

The thickness and density of a polyacetylene electrode, made by pressing *trans*-polyacetylene powder together with a binder, were 0.3 mm and 0.3 g cm^{-3}, respectively. Polyacetylene has a porous network structure consisting of many fibrils each of about 1 μm dia., as shown in Fig. 1. It is believed that anions diffuse more quickly in the interstitial spaces between the polyacetylene fibrils than in the fibrils themselves. On charge, the anions diffuse in the interstitial spaces between the fibrils and are oxidized anodically on the fibril surfaces. They then diffuse into the polyacetylene fibrils. The diffusion coefficient in the fibril solid phase is smaller than that in the liquid phase of the interstitial spaces among the fibrils. Thus, in this study, it was assumed that the electrochemical reaction of polyacetylene was controlled by the slow diffusion of anions within the fibrils.
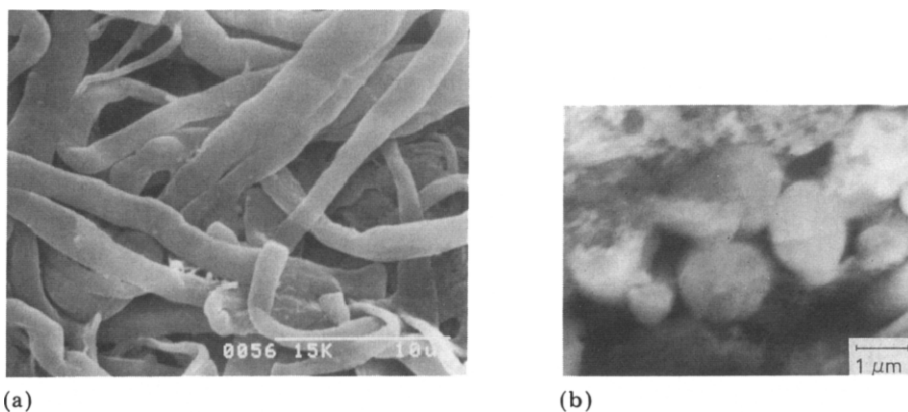

(a) (b)

Fig. 1. Scanning electron micrographs of polyacetylene film. (a) Network of polyacetylene fibrils; (b) cross section of polyacetylene fibril.

Cylindrical diffusion of anions in polyacetylene fibrils

In this study, the process of undoping anions from the polyacetylene on discharge was examined. In the initial steady state, anions are distributed uniformly in the doped polyacetylene. The electrode potential of the polyacetylene was then changed suddenly to a lower potential. The concentra-

tion of dopant anion, A, on the surface of the polyacetylene fibril changes according to the electrode potential of the following redox reaction:

$$(CH)_x + A^- \rightleftharpoons [(CH)_x A] + e^- \qquad (1)$$

Doping and undoping is regarded as a reversible redox reaction between dopant anion, A^-, and dopant, A, according to eqn. (1) [7]. Thus, the concentration of dopant A on the electrode surface can be controlled by the electrode potential.
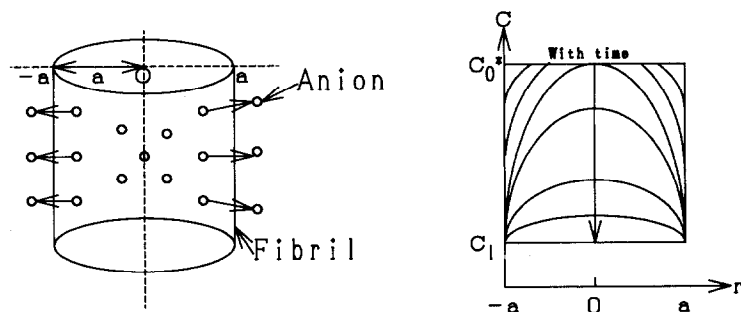

Fig. 2. Concentration profiles after the potentiostatic discharge of a charged electrode.

Figure 2 shows the change in the concentration profile after a potential step discharge has been applied. A finite cylindrical diffusion can be applied for the diffusion behavior. Fick's diffusion law may be described as follows:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) \qquad (2)$$

where D is the diffusion coefficient of dopant A in the polyacetylene fibril and C is the concentration of dopant anion in polyacetylene. The initial conditions and the boundary conditions are given by:

$$t = 0, \qquad 0 < r < a, \qquad C = C_0^* \qquad (3)$$

$$t > 0, \qquad r = a, \qquad C = C_\ell \qquad (4)$$

The solution of eqn. (2) was obtained using Laplace and Fourier transformations.

$$J_t/J_\infty = 2 \sum_{n=1}^{\infty} \exp(-\beta_n^2 \tau) \qquad (5)$$

where

$$J_\infty = \frac{FD(C_0^* - C_\ell)}{a} \qquad (6)$$
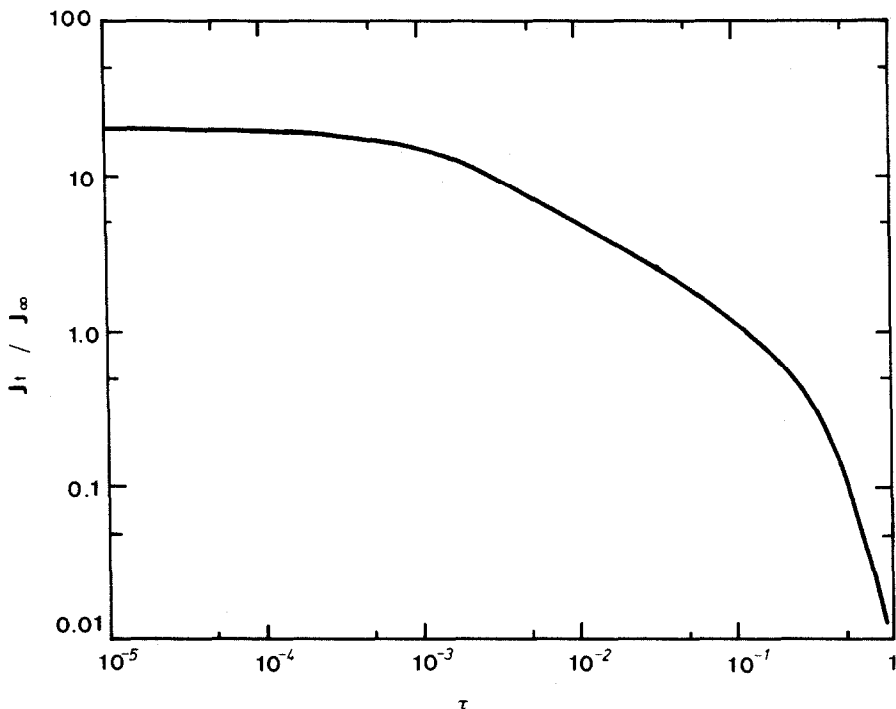
$$\tau = \frac{Dt}{a^2} \qquad (7)$$

Fig. 3. Theoretical current–time transient during the potentiostatic discharge.

and where J is the flux of dopant anion in the polyacetylene fibril. The numerical solutions of eqn. (5) at various dimensionless time intervals (τ) can be calculated using the numerical solution for the Bessel function:

$$J_n(x) = \frac{x^n}{2^n n!} \left\{ 1 - \frac{x^2}{2(2n+2)} + \frac{x^4}{8(2n+2)(2n+4)} \cdots \right\} \tag{8}$$

Thus, the relation $\log(J_t/J_\infty)$ *versus* $\log \tau$ is determined, as shown in Fig. 3. Therefore, when the undoping of anions from polyacetylene fibril is limited by cylindrical diffusion, the current–time transient after the potentiostatic discharge is as shown in Fig. 3.

Charge is carried by carbocations of polyacetylene and anions. The mobility of the carbocations is greater than that of the anions. In other words, the transference number of anions in polyacetylene is much smaller than that of carbocations. Therefore, anions do not migrate via the potential gradient in polyacetylene, but via the chemical potential gradient. The surface concentration of anions during electrochemical potential step undoping is assumed to be constant at all times after the potential step, assuming that the charge transfer resistance is much smaller than the diffusion resistance. The width of the potential step in the experiments was large enough to establish a constant concentration of anions at the polyacetylene surface.

Results and discussion

Figure 4 shows the current–time transient during discharge by the potential step method. The circles are the observed values obtained by the potential step 3.80 V - 3.15 V *versus* Li/Li$^+$ in propylene carbonate with 1.0 M LiClO$_4$. The solid line is the theoretical curve of eqn. (5). Though the observed curve deviated from the theoretical curve during the initial period, after 10 min the experimental values agreed with the theoretical values. Since the polyacetylene electrode has a porous structure, as indicated by the low density, 0.3 g cm^{-3}, the capacity of the electrical double layer of the porous electrode is very large. Initially, both the current corresponding to the anion undoping from polyacetylene and the current corresponding to the charging of the electrical double layer may be measured. Polyacetylene fibrils have a high crystallinity, confirmed by X-ray diffraction. However, there are some defects in its structure. The dopant in such defects diffuses faster than that in the crystalline portion of the fibril. The deviation during the initial period may also be caused by defects.

The anion mobility in polyacetylene fibrils is assumed to be cylindrical diffusion. It is possible to diffuse parallel to the direction of the CH chain. In this case, the anion motion is assumed to be one dimensional linear diffusion, and the current–time transient obeys the Cottrell equation, which has a slope of 1/2 on a log–log scale. The slope of the initial current–time
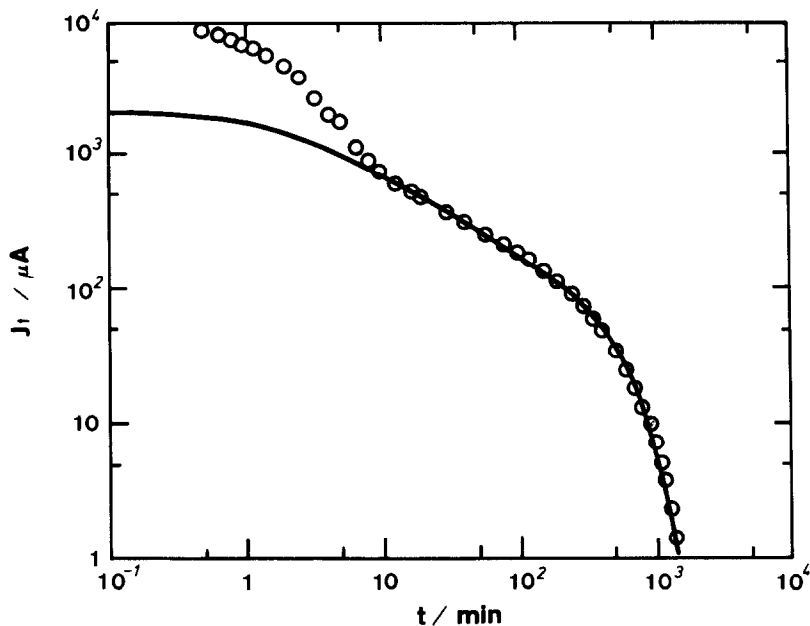

Fig. 4. Current–time transient during the potentiostatic discharge of polyacetylene from 3.80 V to 3.15 V *vs.* Li/Li$^+$ in propylene carbonate with 1.0 M LiClO$_4$. ○, experimental values; ———, theoretical curve.

TABLE 1

Diffusion coefficients of various anions in polyacetylene fibrils

Electrolyte	Diffusion coefficient (cm^2 s^{-1})
1.0 M LiClO$_4$/PC	2.4×10^{-14}
0.5 M LiClO$_4$/PC	3.6×10^{-14}
0.1 M LiClO$_4$/PC	4.2×10^{-14}
1.0 M LiBF$_4$/PC	4.4×10^{-14}
1.0 M LiPF$_6$/PC	2.3×10^{-14}

PC: propylene carbonate.

transient was not 1/2. Therefore, these results indicate that linear diffusion did not significantly contribute to the anion mobility. Probably, the assumption of one dimensional linear diffusion applies to the short period, i.e., less than 1 min.

Nevertheless, the experimental curve was in good agreement with the theoretical curve from 10 min after the potential step. This agreement allows us to calculate the diffusion coefficient using eqn. (7). Diffusion coefficients of various anions in polyacetylene are summarized in Table 1. All diffusion coefficients were of the order of 10^{-14} cm^2 s^{-1}. These are much smaller than those in solution. The diffusion coefficients obtained did not depend greatly on the concentration of the electrolyte or the kind of anion. However, it seems that the diffusion coefficient may depend, to some small extent, on the size of the dopant. The diffusion coefficients of BF$_4^-$, ClO$_4^-$, and PF$_6^-$ are estimated to be 4.4×10^{-14} cm^2 s^{-1}, 2.4×10^{-14} cm^2 s^{-1}, and 2.3×10^{-14} cm^2 s^{-1}, respectively. From these results, it can be seen that the undoping process is controlled by diffusion of anions within the polyacetylene.

The anion diffusion coefficient obtained was so small that it can be approximated by linear diffusion at short times. Because the diffusion depth of the anions is about 100 Å, which is much smaller than the diameter of the polyacetylene fibril used, the Warburg impedance, W, can be used:

$$W = \sigma^{-1/2} - j\sigma^{1/2} \tag{9}$$

The diffusion coefficient of ClO$_4^-$ in the electrolyte is much larger than that in the polyacetylene fibril, D_0. Therefore,

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}} \left[\frac{1}{D_0^{1/2}C_0^*} \right] \tag{10}$$

where A is the true surface area of the polyacetylene electrode and D_0 is the diffusion coefficient of dopant A in the polyacetylene fibril. Since the true density of polyacetylene is 1.16 g cm^{-3} [8] and the density of the polyacetylene electrode used in this experiment is 0.3 g cm^{-3}, the surface area of a polyacetylene electrode of 1 cm^3 was calculated to be 1.03 m^2. The surface area of polyacetylene weighing 7.07 mg was estimated to be 2.43 ×

10^{-2} m^2. The diffusion coefficient, D_0, of ClO$_4^-$ in polyacetylene was about 4×10^{-14} cm^2 s^{-1}.

C_0^* is the concentration of ClO$_4^-$ doped in the polyacetylene fibril. The amount of ClO$_4^-$ is controlled by the electrode potential. The relationship between the open circuit potential, V_{OC}, and the doping level, y, was given by Kaneto *et al.* [9] as

$$V_{OC} = 3.43 + 0.14 \ln(y) \tag{11}$$

The relation between y and C_0^* is given by

$$C_0^* = \frac{\dfrac{M_s}{M} \times (y/100)}{V} \tag{12}$$

where M_s is the weight of the polyacetylene sample, M the molecular weight of CH, and V the volume of the polyacetylene sample. In this way, C_0^* was determined at each doping level. σ values at various electrode potentials were easily determined, and these and the doping levels at various electrode potentials are summarized in Table 2. Warburg impedances were calculated by substituting values in Table 2 into eqn. (9).

Figure 5 shows the charge transfer resistance and the diffusion resistance at various electrode potentials. The charge transfer resistances used were previously obtained from the impedance measurement, using the same electrode and cell [10]. The diffusion resistances calculated at 10, 1, 0.1, 0.01 Hz are also shown in Fig. 5. Though the diffusion coefficients at much lower frequencies than 0.01 Hz can be calculated, such "resistances" are not strictly correct, because one dimensional linear diffusion cannot be assumed. The diffusion depth at much lower frequencies is too large to

TABLE 2

y values and σ values at various electrode potentials

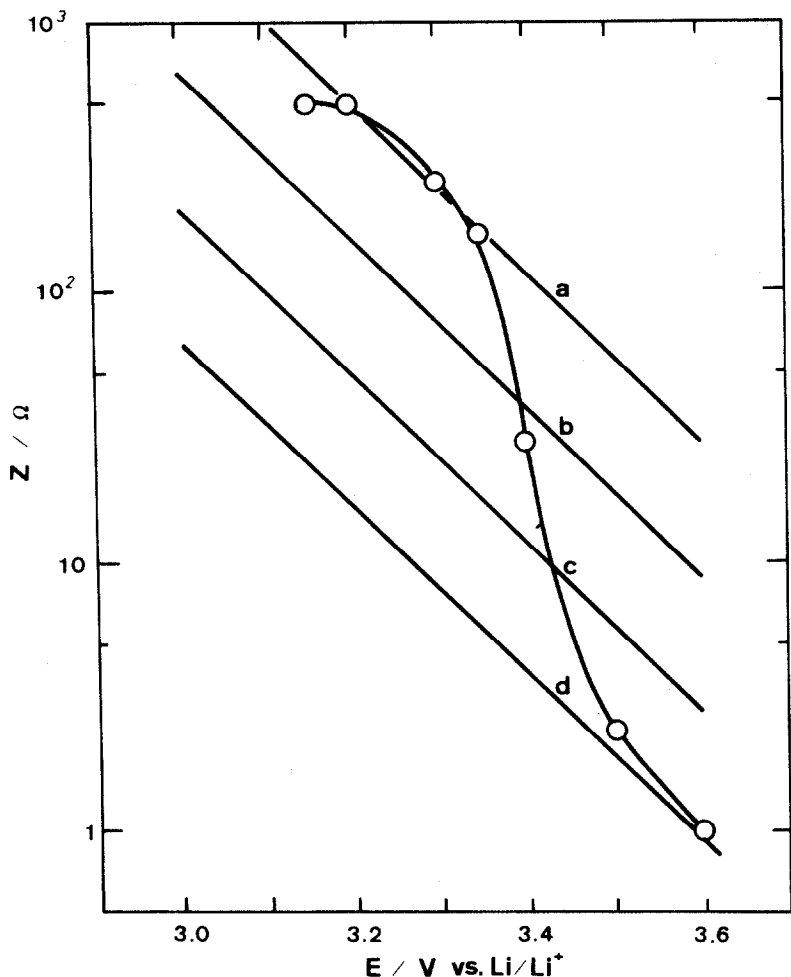| Potential (V *vs.* Li/Li$^+$)	y (Dopant level) (%)	σ (s$^{-1/2}$)
3.60	3.37	5.014
3.55	2.36	7.166
3.50	1.65	10.24
3.45	1.15	14.63
3.40	0.807	20.93
3.35	0.565	29.89
3.30	0.395	42.75
3.25	0.276	87.50
3.20	0.193	125.09
3.15	0.135	125.09
3.10	0.095	177.76

Fig. 5. Dependence of the diffusion and charge transfer impedances on the open circuit potential of a polyacetylene electrode at various frequencies. ———, Diffusion impedance: a, 0.01 Hz; b, 0.1 Hz; c, 1 Hz; d, 10 Hz; ○, charge transfer resistance.

assume one dimensional diffusion. The diffusion resistance depends on the frequency (eqn. (9)).

At 10 Hz, the diffusion resistance is smaller than the charge transfer resistance in the potential region 3.6 V - 3.0 V. The difference between the two resistances increases as the electrode potential is lowered. At 0.01 Hz, the diffusion resistance is larger than the charge transfer resistance in the potential region 3.6 V - 3.4 V. However, in the potential region less than 3.3 V, the charge transfer resistance is comparable with the diffusion resistance. Both the diffusion resistance and the charge transfer resistance change with the electrode potential. In other words, the discharge and

charge characteristics of the polyacetylene electrode depend on the doping level of the anions in it.

From these results, the behavior of the impedance of a polyacetylene electrode can be understood. At higher open circuit potentials, e.g., $E = 3.6$ V, the total impedance at high frequencies ($\geqslant 10$ Hz) is limited by the charge transfer resistance. At 10 Hz, the impedance is controlled by both the diffusion and the charge transfer resistances. At lower frequencies ($\leqslant 10$ Hz), the diffusion resistance is much larger than the charge transfer resistance. However, at lower potentials, e.g., $E = 3.2$ V, the diffusion resistance is smaller than the charge transfer resistance in the frequency region 10 Hz - 0.1 Hz. When the impedance of the polyacetylene electrode is measured at lower potentials, it is not of the Warburg type. This is in good agreement with our results on the impedance of polyacetylene electrodes [10]. Therefore, it is reasonable to assume that the diffusion of anions in polyacetylene fibrils must be treated as cylindrical diffusion.

In either case, the diffusion coefficients of anions in polyacetylene were so small that the discharge of polyacetylene was controlled by diffusion, especially at high rates of discharge. In order to develop a high performance polymer battery, the process of anion diffusion in the polymer must be improved.

Acknowledgements

References

1 P. J. Nigrey, A. G. MacDiarmid and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (1979) 594.
2 C. K. Chiang, M. A. Drucy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. J. Park and H. Shirakawa, *J. Am. Chem. Soc.*, *100* (1978) 1015.
3 G. C. Farrington, B. Scrosati, D. Frydrych and J. DeNuzzio, *J. Electrochem. Soc.*, *131* (1984) 7.
4 H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (1977) 578.
5 F. G. Will, *J. Electrochem. Soc.*, *132* (1985) 2351.
6 J. H. Kaufmann, E. J. Mele, A. J. Heeger, R. Kaner and A. G. MacDiarmid, *J. Electrochem. Soc.*, *130* (1983) 571.
7 R. Huq and G. C. Farrington, *J. Electrochem. Soc.*, *131* (1984) 819.
8 H. Shirakawa and T. Yamabe, *Gosei Kinzoku*, Kagaku Dojin, 1980, p. 30.
9 K. Kaneto, M. Maxfield, D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, *J. Chem. Soc., Faraday Trans.*, *78* (1982) 3417.
10 Z. Takehara, K. Kanamura and T. Hanawa, *J. Power Sources*, *20* (1987) 231.