Functional Metal–Porphyrazine Derivatives and Their Polymers. Part 11.† Secondary Fuel Cells based on Oxygen Reduction at a Platinum Electrode modified by Metal–2,9,16,23-Tetracarboxyphthalocyanine covalently bound to Poly(2-vinylpyridine–styrene)

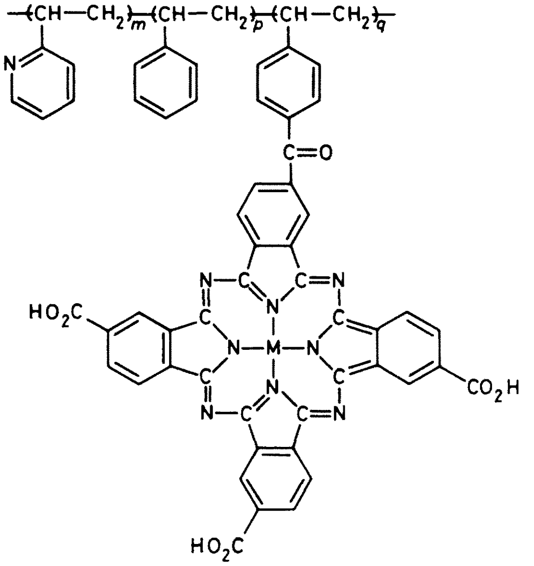
Okikazu Hirabaru, Tomohiro Nakase, Kenji Hanabusa, Hirofusa Shirai,* Kiichi Takemoto, and Nobumasa Hojo
Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda-shi, 386 Japan

---

A new type of secondary fuel cell is described in which molecular oxygen evolved by electrolysis of water in the charging process is stored in the polymer matrix of metal–2,9,16,23-tetracarboxyphthalocyanine covalently bound to poly(2-vinylpyridine–styrene) (M = $\mathrm{Fe^{III}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Cu^{II}}$) on a platinum electrode, and then electrocatalytically reduced in the discharging process in 30% KOH aqueous solution. The constant-current charge–discharge curve for the platinum electrode modified by the cobalt–copolymer, charged for 30 min at 500 μA, followed by a 100-μA discharge, showed a stable plateau at about −0.24 V *vs.* saturated calomel electrode. The discharge capacity was 833 A h per kg of the cobalt–phthalocyanine, about 20 times that for the corresponding electrode modified by vacuum deposition of monomeric cobalt–phthalocyanine. For this cell there was no significant decay in its characteristics after over 30 charge–discharge cycles. After the charge the e.s.r. spectrum showed a signal assigned to a $\mathrm{Co^{III}{-}pc{-}O_2^-}$ radical [pc = phthalocyaninate(2−)]. The higher capacity of the cobalt–copolymer complex seems to be due to the activation and storage of dioxygen evolved upon charging. The capacity decreased in the order $\mathrm{Co^{II}} > \mathrm{Fe^{III}} \gg \mathrm{Cu^{II}} > \mathrm{Ni^{II}}$. The cathodic reactions of the electrode modified by the cobalt-copolymer are discussed.

Metal phthalocyanines have attracted considerable interest because of their structural similarity with naturally occurring metal porphyrins. In previous papers we have studied the preparation as well as the chemical properties of some soluble metal–phthalocyanine derivatives which have peripheral functional groups and the polymers made from them.[1–13] In recent years much attention has been paid to the electrocatalytic properties of phthalocyanine and porphyrin complexes in the cathodic reduction of oxygen with hydrogen in fuel cells.[14–28] Quite recently, we have developed a secondary fuel cell based on oxygen reduction at a vacuum-deposited platinum electrode coated with polymer.[13] In this system molecular oxygen evolved by electrolysis of water in the charging process is stored in a polymer-coated electrode containing metal phthalocyanine, and then, is electrocatalytically reduced in the discharge process.

We have also reported on the catalase-like activity of metal–2,9,16,23-tetracarboxyphthalocyanine complexes covalently-bound through a CO group to poly(2-vinylpyridine–styrene). The iron(III) derivative was a remarkably effective catalyst for H_2O_2 decomposition.[9,11] Such iron(III)- and cobalt(II)-polymer complexes are of the five-co-ordinated high-spin type, one axial co-ordination site being occupied by an N atom of a pyridine group.[10] They may also be highly effective catalysts for electrocatalytic reactions.[29] Therefore, we investigated the properties as a secondary cell and the electrochemical mechanism of a platinum electrode modified with such derivatives.



M = $\mathrm{Fe^{III}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, or $\mathrm{Cu^{II}}$

$m = 0{\cdot}50$, $p = 0{\cdot}48 - 0{\cdot}39$, $q = 0{\cdot}02 - 0{\cdot}11$

Experimental

The metal–2,9,16,23-tetracarboxyphthalocyanines (M = $\mathrm{Fe^{III}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, or $\mathrm{Cu^{II}}$) and the corresponding tetra-acid chlorides were prepared as described previously.[6] Styrene, 2-vinylpyridine, and the solvents were purified by repeated distillations under reduced pressure. 2,2′-Azobisisobutyronitrile (aibn) was recrystallized three times from ethanol. The other reagents were of analytical grade from commercial origin and used without further purification.

Poly(2-vinylpyridine–styrene) was prepared from the corresponding monomers under a nitrogen atmosphere with aibn as initiator.[30] Yield: 25 g (60% conversion of monomers); inherent viscosity ([η]) = 0.62 dl g^{-1} in dimethylformamide (dmf) at 30 °C. The composition of the copolymers was determined by ^{1}H n.m.r. in CD_3OD solution; $[\text{styrene}]_{\text{unit}}/[\text{2-vinylpyridine}]_{\text{unit}} = 1.08$.

---

† Part 10 is ref. 13.

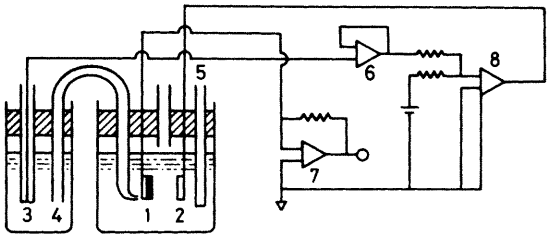


Figure 1. Diagram of the electrochemical cell: 1 = working electrode; 2 = counter electrode (Pt); 3 = reference electrode (s.c.e.); 4 = agar salt bridge (KCl); 5 = Ar gas inlet; 6 = electrometer; 7 = current–voltage converter; 8 = power amplifier

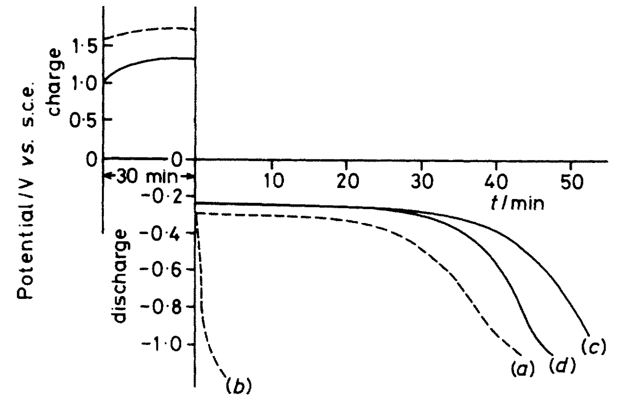


Figure 2. Constant-current charge–discharge curves for the platinum electrode modified by copolymer alone [(*a*), (*b*)] and by the cobalt–copolymer [(*c*), (*d*)] in 30% KOH aqueous solution at 25 °C. The charging current was 500 μA for 30 min and the discharging current 100 μA. Argon bubbling was carried out in cases (*b*) and (*d*)

The metal–phthalocyanine complexes covalently bound to poly(2-vinylpyridine–styrene) were prepared and purified as follows.[9,10] To a solution of a copolymer (4 g, 0.038 mol) and the metal–phthalocyanine tetra-acid chloride (2 g, 0.002 mol) in nitrobenzene (1 g, 0.0075 mol) was added $AlCl_3$. After stirring for several hours at room temperature, the reaction mixture was extracted with hexane followed by benzene using a Soxhlet extractor until no nitrobenzene could be detected. The product was filtered off and washed with alkaline water in order to remove the free metal–phthalocyanine. The copolymer-bound derivative was purified by dissolving in methanol and reprecipitating with excess of light petroleum (b.p. 30—70 °C). I.r. (film): 1 700 (carboxyl C=O stretching) and 1 650 cm^{-1} (ketone C–O stretching). Content of metal–phthalocyanine in the copolymer: 1.5—5.8 mol %.

For coating the surface of the platinum electrode the solvents benzene, methanol, and tetrahydrofuran (thf) were purified by repeated distillations under reduced pressure. Potassium hydroxide was of analytical grade from commercial origin and used without further purification.

Platinum sheets (surface area 1 cm^2) were polished mechchanically with fine grades of emery paper (grade 1 000). Then the sheets were washed with distilled water by a ultrasonic cleaner, treated with alkaline detergent (Dipsol 334S, Dipsol Co.), and rinsed with 6 mol dm^{-3} HCl. Finally, their surface sheets were washed with distilled water using a ultrasonic cleaner, and dried. The electrodes thus treated were dipped into methanol containing 5% of the metal–copolymer and dried in air at about 40 °C for 40 min.

Electrodes modified with monomeric metal-phthalocyanines (M = Fe^{III}, Co^{II}, Ni^{II}, or Cu^{II}) were obtained as follows.[13] The metal-phthalocyanine was first vacuum deposited onto the platinum sheet.[31] The latter was then dipped into methanol containing 5% of poly(2-vinylpyridine–styrene) and dried in air at about 40 °C for 40 min. The crystal structures of the metal–phthalocyanines on the sheets, as determined by *X*-ray diffraction, were of the α form.

Discharge curves were measured by using the cell shown in Figure 1 for a 30 min charge at 500 μA, followed by a 100-μA discharge. The reference electrode was a saturated calomel electrode (s.c.e.) connected by a Ruggin capillary, and the counter electrode was a platinum sheet (surface area 1 cm^2). The agar salt bridge contained 3.3 mol dm^{-3} KCl. The charge–discharge curves were measured potentiostatically with a model HA-501 potentiostat/galvanostat (Hokuto-Denko Co.) (Figure 1). Cyclic voltammograms were obtained with a model HA-501 potentiostat/galvanostat, (Hokuto-Denko Co.), model 164 sweep generator (Wavetek), and *x*–*y* recorder (model TYP-3083, Yokogawa Co.). Conventional two-compartment cells were employed. A potassium chloride-saturated calomel reference electrode was used. Its potential was in the range 0.4 to −1.1 V *vs.* a standard s.c.e. in the supporting electrolytes employed. Experiments were conducted at 25 ± 0.1 °C.

U.v.–visible spectra of methanol, benzene, and thf solutions of the metal–copolymers were recorded on a JASCO-UVIDEC-505 apparatus. E.s.r. spectra were measured with a Varian E-line spectrometer and 100-kHz field modulation using the *X*-band (9 196 GHz at 123 K) and microwave power of 100 mW. After the charge, the film of cobalt–copolymer coated on the platinum electrode was cooled in a liquid-nitrogen bath, peeled off the platinum sheet, and placed in quartz tubes (inside diameter 4 mm) for measurements at 123 K. *g* Values were calculated using solid diphenylpicrylhydrazyl (dpph) as reference.

Results and Discussion

The Constant-current Charge–Discharge Characteristics.— The constant-current charge–discharge curves for a platinum electrode modified with the metal–copolymer or only copolymer in 30% KOH aqueous solution at 25 °C with and without argon bubbling are shown in Figure 2 for a 30-min charge at 500 μA, followed by a 100-μA discharge. These measurements were made after a number of initial charge–discharge cycles of the cell. In the charging process oxygen was evolved from the surface of the electrode and hydrogen from a counter electrode. In the discharge curve for the platinum electrode modified only with the copolymer the plateau capacity was obtained at about −0.30 V *vs.* s.c.e. [Figure 2(*a*)]. With argon bubbling the plateau capacity remarkably decreased [Figure 2(*b*)]. The reason for this may be the desorption of oxygen which is evolved by electrolysis of water in the charge process and stored in the polymer matrix. In order to remove such stored oxygen, after the charge the electrode was allowed to stand for 24 h under vacuum, whereupon the plateau capacity remarkably decreased. The discharge curve for the platinum electrode modified with the cobalt–copolymer showed a stable plateau at about −0.24 V *vs.* s.c.e. [Figure 2(*c*)], different from that for the electrode modified with only the copolymer. With argon bubbling the plateau capacity for the cobalt–copolymer slightly decreased [Figure 2(*d*)].

Figure 3 compares the constant-current charge–discharge curves for all the metal–copolymers immobilized on the surface of platinum sheets with argon bubbling in 30% KOH aqueous solution at 25 °C. The order of decreasing plateau capacity is Co^{II} > Fe^{III} $\gg$ Cu^{II} > Ni^{II} in agreement with

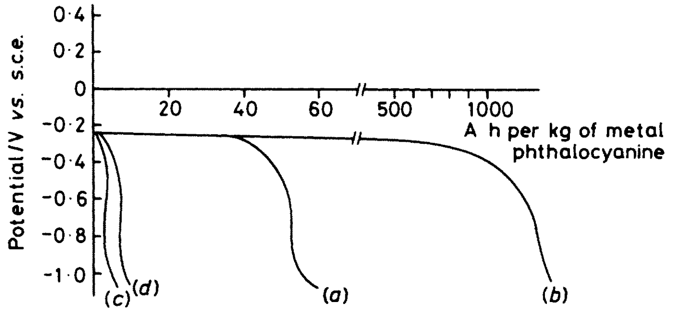


Figure 3. Constant-current charge–discharge curves of the platinum electrode modified by metal–copolymer in 30% KOH aqueous solution at 25 °C with Ar bubbling. The charging current was 500 μA for 30 min and the discharging current 100 μA. M = Fe^{III} (*a*), Co^{II} (*b*), Ni^{II} (*c*), and Cu^{II} (*d*)

Table. Discharge capacities for platinum electrodes modified by metal–copolymers

M	Contents of metal–phthalocyanine (wt. %)	Discharge capacity (A h per kg of metal complex)
Fe^{III}	6.8	37.5
Co^{II}	1.5	833.3
Co^{II}	4.9	125.0
Ni^{II}	5.5	4.2
Cu^{II}	4.3	2.9

Electrolyte: 30% KOH, with argon bubbling, 25 °C. The charging current was 500 μA for 30 min, and discharging current was 100 μA.

that for the electrodes first modified by vacuum deposition of the metal–phthalocyanine followed by polymer coating.[13] Metal–phthalocyanines are known to be electrocatalytic in oxygen reduction.[14–18] Jasinski [28] used cobalt–phthalocyanine in alkaline electrolyte. Alt *et al.*[27] investigated metal–phthalocyanines (M = Fe, Co, or Ni) as catalysts for the cathodic reduction of oxygen in acidic electrolytes, and a similar order was found, explained on the basis of simple molecular-orbital considerations.

From these findings, the cobalt- and iron–phthalocyanines in the polymer matrix may contribute to the storage and activation of oxygen generated on the platinum surface in the charging process. Iron(II)- and cobalt(II)-phthalocyanines are known oxygen carriers.[32] Therefore, phthalocyanine containing Fe^{II} may be more active than the corresponding iron(III) or cobalt(II) derivatives. The discharge capacities (A h per kg metal–phthalocyanine) for modified platinum electrodes are listed in the Table, and compared with those for electrodes modified first by vacuum deposition of the metal–phthalocyanine followed by polymer coating. The capacity was found to decrease in the order $Co^{II} > Fe^{III} \gg Cu^{II} > Ni^{II}$, in close agreement with that obtained for the electrodes modified by vacuum deposition, *etc.*[13] The electrodes modified with iron(III)- and cobalt(II)-copolymer had higher discharge capacities, compared with the corresponding electrodes modified by vacuum deposition. The value for the cobalt–copolymer was about 20 times that for monomeric cobalt–phthalocyanine. The iron(III)- and cobalt(II)-copolymers were found to be very effective as secondary fuel cells. The open circuit voltage, V_{OC} (*vs.* Zn), of the cell was 1.2 V, and the discharge capacity was of 833.3 A h kg^{-1} based on the weights of the cobalt–phthalocyanine.[33,34] There was no significant decay in its characteristics after over 30 charge–discharge cycles.

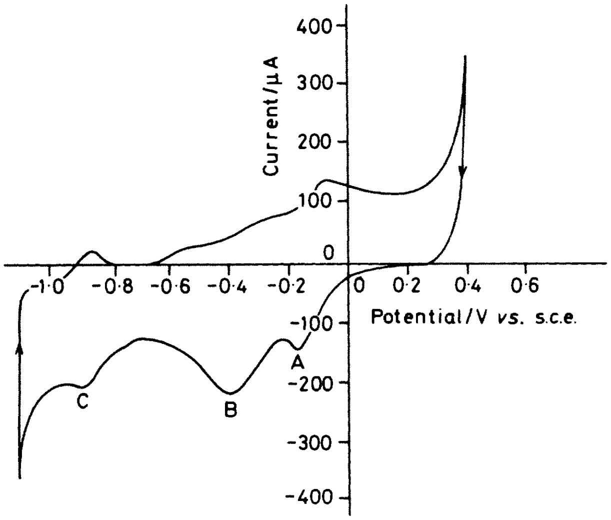


Figure 4. Cyclic voltammogram for platinum electrode modified by cobalt–copolymer. Electrolyte: 30% KOH aqueous solution. Sweep rate: 7.5 mV s^{-1}. Argon saturated

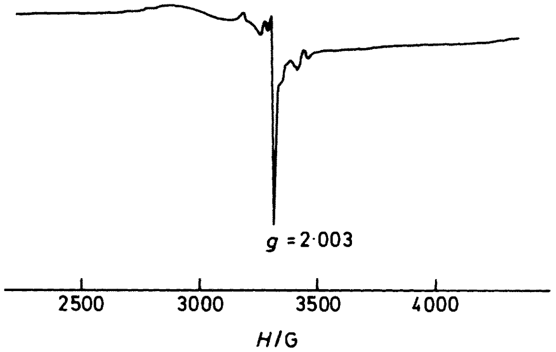


Figure 5. E.s.r. spectrum at −140 °C (1 G = 10^{-4} T) of a cobalt–copolymer film cooled in a liquid-nitrogen bath and peeled off the platinum electrode. Spectrometer setting: microwave frequency 9.19 GHz, power 100 mW

The cathodic reaction for a electrode modified by cobalt(II)-*copolymer.* A cyclic voltammogram for this electrode in 30% KOH aqueous solution is shown in Figure 4. There are three peaks in the anodic sweep. Peak B is based on the reduction of a surface platinum oxide formed in the cathodic sweep, peak A is comparable to the potential for O_2 reduction and appeared to be governed by the redox potential ($Co^{III} \rightarrow Co^{II}$) of the cobalt–phthalocyanine as described previously,[13,23] and peak C also corresponds to the reduction ($Co^{II} \rightarrow Co^{I}$) of the cobalt.[13]

After the charge, the cobalt–copolymer film was peeled off the electrode and cooled in a liquid-nitrogen bath. The e.s.r. spectrum of the film at −140 °C is shown in Figure 5. The signal at $g = 2.003$ has previously been assigned to a cobalt(III)-phthalocyanine–hyperoxide radical generated by oxidation of the phthalocyanine ring.[10] Recently, Raynor and others [35,36] have concluded that this sharp signal arises from a charge-transfer interaction between the phthalocyanine and co-ordinated dioxygen with the formation of a ligand radical cation and reduced dioxygen. Before the charge or after the discharge, the signal was not observed. This fact indicates that the species formed by the reaction of the cobalt–phthalocyanine with the dioxygen molecule evolved from electrolysis of water in the charging process is stored in the polymer matrix.

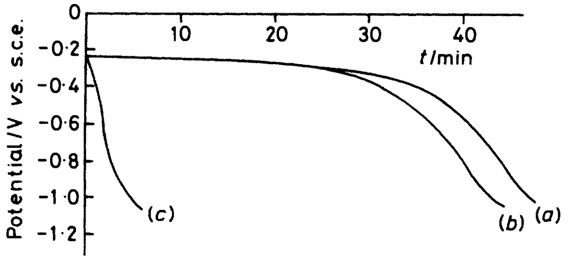


Figure 6. Constant-current charge–discharge curves for the platinum electrode modified by coating from tetrahydrofuran (*a*), methanol (*b*), and benzene (*c*) solutions of cobalt–copolymer in 30% KOH aqueous solution at 25 °C with Ar bubbling. The charging current was 500 μA for 30 min and the discharging current 100 μA

As has previously been pointed out, the copolymer-supported metal–phthalocyanines are of the five-co-ordinate high-spin type, and one axial co-ordination site is occupied by an N atom of a pyridine group. Such a geometry would seem favourable for the formation of a dioxygen complex.[29,37]

From these results and the mechanism proposed by Yeager and co-workers,[22] the mechanism in equations (1)—(7) explains the behaviour of the cell [pc = phthalocyaninate-(2−)].

(*i*) Charging process

$$2H_2O \longrightarrow 2H_2 + O_2 \qquad (1)$$

$$Co^{II}\text{-}pc + O_2 \rightleftharpoons Co^{II}\text{-}pc\text{-}O_2 \qquad (2)$$

$$Co^{II}\text{-}pc\text{-}O_2 \rightleftharpoons Co^{III}\text{-}pc\text{-}O_2^- \qquad (3)$$

(*ii*) Discharging process

$$Co^{III}\text{-}pc\text{-}O_2^- \xrightarrow{e^-} Co^{II}\text{-}pc\text{-}O_2^- \qquad (4)$$

$$Co^{II}\text{-}pc\text{-}O_2^- \xrightarrow{e^-} Co^{II}\text{-}pc + O_2H^- + OH^- \qquad (5)$$

$$O_2 + H_2O \xrightarrow{2e^-} O_2H^- + OH^- \qquad (6)$$

(stored free oxygen in polymer matrix)

$$O_2H^- \longrightarrow \tfrac{1}{2}O_2 + OH^- \qquad (7)$$

Influence of the Coating Solvents on the Platinum Electrode.— The constant-current discharge curves for the platinum electrode modified by the coating from benzene, methanol, or tetrahydrofuran (thf) solutions of the cobalt–copolymer in 30% KOH are shown in Figure 6. The plateau capacities seem to depend on the type of coating solvent; that is, the electrodes modified by coating from methanol and tetrahydrofuran solutions showed stable plateau capacities, while that from benzene had no capacity. The capacity was found to decrease in the order thf > methanol ≫ benzene = 0. Figure 7 shows electronic spectra of the cobalt–copolymer in the different solvents. There are peaks at around 630 and 660 nm in the visible region due to a dimer and a monomer respectively.[38] The magnitude of the absorption coefficients at 660 nm decreased in the solvent order of thf > methanol ≫ benzene. Therefore, the concentration of monomer decreases in the same order in these solvents. It is well known that such a species is preferred for the formation of the dioxygen adduct.[29,37] We have previously suggested that the dimerization of metal–phthalocyanine rings, attached to copolymer chains, is sterically hindered by the latter and the concentration of monomer is higher than of the dimer in the polymer matrix.[6]

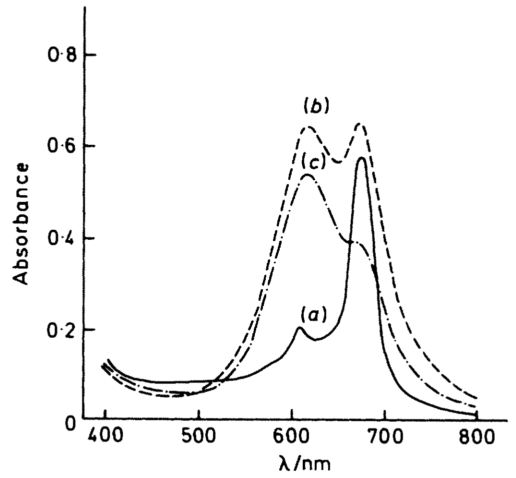


Figure 7. Electronic spectra of the cobalt–copolymer (5×10^{-5} mol dm^{-3}) in tetrahydrofuran (*a*), methanol (*b*), and benzene (*c*) solutions

As shown in the Table, the discharge capacity per kg of cobalt–phthalocyanine for the electrode modified by the polymer complex containing about 4.9 wt. % cobalt–phthalocyanine was lower than that containing about 1.5 wt. %. At higher concentrations of cobalt–phthalocyanine, dimerization may occur during the film formation. The high efficiency of the present derivatives seems to be due to the activation and the storage of dioxygen evolved upon charging.

Acknowledgements

We thank Dr. M. Kaneko (The Institute of Physical and Chemical Research) for useful discussions.

References

1 Part 1, H. Shirai, S. Yagi, A. Suzuki, and N. Hojo, *Makromol. Chem.*, 1977, **178**, 1889.
2 H. Shirai, K. Kobayashi, Y. Takemae, and N. Hojo, *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 343.
3 Part 2, H. Shirai, K. Kobayashi, Y. Takemae, A. Suzuki, O. Hirabaru, and N. Hojo, *Makromol. Chem.*, 1979, **180**, 2073.
4 H. Shirai, A. Maruyama, K. Kobayashi, and N. Hojo, *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 661.
5 Part 3, H. Shirai, A. Maruyama, K. Kobayashi, N. Hojo, and K. Urushido, *Makromol. Chem.*, 1980, **181**, 565.
6 Part 4, H. Shirai, A. Maruyama, K. Kobayashi, N. Hojo, and K. Urushido, *Makromol. Chem.*, 1980, **181**, 575.
7 Part 5, H. Shirai, A. Maruyama, M. Konishi, and N. Hojo, *Makromol. Chem.*, 1980, **181**, 1003.
8 Part 6, H. Shirai, A. Ishimoto, N. Kamiya, K. Hanabusa, K. Ohki, and N. Hojo, *Makromol. Chem.*, 1981, **182**, 2429.
9 H. Shirai, S. Higaki, K. Hanabusa, and N. Hojo, *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21**, 157.
10 Part 7, S. Higaki, K. Hanabusa, H. Shirai, and N. Hojo, *Makromol. Chem.*, 1983, **184**, 691.
11 H. Shirai, S. Higaki, K. Hanabusa, and N. Hojo, *J. Chem. Soc., Chem. Commun.*, 1983, 751.
12 Part 9, O. Hirabaru, N. Tonami, S. Higaki, K. Hanabusa, H. Shirai, K. Takemoto, and N. Hojo, *Oyo Butsuri*, 1983, **52**, 1051.
13 Part 10, O. Hirabaru, T. Nakase, K. Hanabusa, H. Shirai, K. Takemoto, and N. Hojo, *Angew. Makromol. Chem.*, in the press.
14 H. Jahnke, M. Schönborn, and G. Zimmermann, *Top. Curr. Chem.*, 1976, **61**, 135.
15 J. Zagal, R. K. Sen, and E. Yeager, *J. Electroanal. Chem.*, 1977, **83**, 207.

16 V. S. Bagotsky, M. R. Tarasevich, K. A. Radyushkina, O. A. Levina, and S. I. Andrusyova, *J. Power Sources*, 1977—1978, **2**, 233.

17 J. A. R. van Veen and C. Visser, *Electrochim. Acta*, 1979, **24**, 921.

18 J. P. Randin, *Electrochim. Acta*, 1974, **19**, 83.

19 F. Beck, *J. Appl. Electrochem.*, 1977, **7**, 239.

20 A. J. Appleby and M. Savy, *Electrochim. Acta*, 1977, **22**, 1315.

21 R. Sen, J. Zagal, and E. Yeager, *Inorg. Chem.*, 1977, **16**, 3379.

22 J. Zagal, P. Bindra, and E. Yeager, *J. Electrochem. Soc.*, 1980, **127**, 1506.

23 P. Forshey, T. Kuwana, N. Kobayashi, and T. Osa, *Adv. Chem. Ser.*, 1982, **201**, 601.

24 K. Shigehara and F. C. Anson, *J. Electroanal. Chem.*, 1982, **132**, 107.

25 K. Shigehara and F. C. Anson, *J. Phys. Chem.*, 1982, **86**, 2776.

26 J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, and F. C. Anson, *J. Am. Chem. Soc.*, 1980, **102**, 6027.

27 H. Alt, H. Binder, and G. Sandstede, *J. Catal.*, 1973, **28**, 8.

28 R. Jasinski, *Nature (London)*, 1964, **201**, 1212.

29 O. Hirabaru, T. Nakase, K. Hanabusa, H. Shirai, K. Takemoto, and N. Hojo, *J. Chem. Soc., Chem. Commun.*, 1983, 481.

30 Y. Iwakura, Y. Tamikado, M. Yamaguchi, and K. Takei, *J. Polym. Sci.*, 1959, **39**, 203.

31 O. Hirabaru, T. Nakajima, and H. Shirai, *Shinku*, 1979, **22**, 273.

32 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

33 T. Yamamoto, S. Kuroda, and A. Yamamoto, *Inorg. Chim. Acta*, 1983, **65**, L175.

34 H. Jahnke and M. Schönborn, *3es Journees Int. d'Etude des Piles á Combustible, Bruxelles*, 1969, p. 60.

35 J. B. Raynor, M. Robson, and A. S. M. Torrens-Burton, *J. Chem. Soc., Dalton Trans.*, 1977, 2360.

36 J. Zwart and J. H. M. C. van Wolput, *J. Mol. Catal.*, 1979, **5**, 235.

37 E. Tsuchida, *J. Macromol. Sci. Chem.*, 1979, **13**, 545.

38 J. H. Furhop, S. Besecke, W. Vogt, J. Ernst, and J. Sabramanian, *Makromol. Chem.*, 1977, **178**, 1621.

Received 6th April 1983; *Paper* 3/527