JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 77–84

Effect of method of preparation of FePc oxygen reduction catalyst on the activity of practical air electrodes

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Received 20 February 1984; revised 30 March 1984

The catalytic effects if iron phthalocyanine (FePc) on two types (A and B) of practical air electrodes were examined, and compared with those of cobalt phthalocyanine (CoPc). For Type A electrodes, polytetrafluoroethylene (PTFE) powder was heat-treated at 400° C. For Type B electrodes, PTFE dispersions were used with treatment at 250° C. Both FePc and CoPc showed high H_2O_2 decomposition rates, which resulted in low oxygen electrode polarization at high current density. However, the catalytic effects for Type A electrodes were not shown at low current density (< 1 mA cm^{-2}), despite the fact that a 4-electron reduction process took place on FePc at these current densities. For the Type B electrodes, the effect of FePc at low current density became clearer: under these conditions, the electrode with FePc showed a higher potential than that with CoPc and showed a higher open circuit potential (OCV) (0.218 V). Type B electrodes showed good performance in the entire current density region compared with Type A electrodes. With FePc catalysts, Type B electrodes showed a larger current region for the 4-electron process (0–0.1 mA cm^{-2}) compared with Type A electrodes (0–0.02 mA cm^{-2}). The improved performance of Type B electrode is considered to be due to the presence of many pores as a result of the PTFE 'yarn' connecting carbon substrate particles.

1. Introduction

The development of high energy metal–air batteries requires that typical air electrode performance should be upgraded. An attempt to realize this objective involves preparing an improved active catalyst for air electrodes. Noble metals, such as platinum or silver, have been mainly used as active catalysts for these electrodes and the oxygen reduction mechanisms on these catalysts have been studied in detail [1–12].

On the other hand, catalysts cheaper than the noble metals have been intensively examined. For example, inorganic catalysts such as Li doped NiO [13], $La_{1-x}Sr_xCoO_3$ [14–19] and $NiCo_2O_4$ [20–23], together with organic catalysts, such as metal porphyrins, metal phthalocyanines and their derivatives, have been studied in respect to the O_2 reduction mechanism [24–48]. It has been reported that iron phthalocyanine (FePc), iron porphyrin and their derivatives go via the 4-electron process [30, 36] and that cobalt porphyrin dimer also goes via the same mechanism [38]. In addition, the effects of the substrate on the electrode performance have been examined [49, 50].

Few studies have been reported on the performance of a practical air electrode using these materials [27]. In the present work, the catalytic effects of several organic materials were examined for practical air electrodes. Furthermore, for FePc electrodes, the influence of the substrate, of preparation methods and of optimally prepared catalysts were estimated and compared with that for CoPc.

2. Experimental details

2.1. *Catalysts used for tests*

Samples of iron, copper, nickel, cobalt and zinc phthalocyanines (FePc, CuPc, NiPc, CoPc, ZnPc)

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and ferric benzoilacetonate ($Fe(bzac)_3$) were purchased from Eastman Kodak Co. while cyanocobalamine (VB_{12}) and haemoglobin were purchased from Kishida Chemical Co. and chlorophyll, ferrocene, ferric and cobalt acetonates ($Fe(acac)_3$, $Co(acac)_2$) were obtained from Kanto Chemical Co. Copper bis-α-benzoinoxymat ($Cu(bzox)_2$) was synthesized from α-benzoinoxym and copper acetate.

2.2. *Catalyst substrate*

The carbon substrates used were

(a) a carbon powder (C; specific surface area [SSA] 2 $m^2 g^{-1}$; provided by Nippon Carbon Co.),
(b) a mixture of C and acetylene black (AB; SSA 74 $m^2 g^{-1}$; Denki Kagaku Kogyo Co.) and
(c) a mixture of C and activated charcoal (AC; SSA 740 $m^2 g^{-1}$; Kanto Chemical Co.).

In the case of (a), test electrodes were made of C and polytetrafluoroethylene (PTFE) powder (Seiken Kogyo Co.) in a ratio of 5:3 with a catalyst, if necessary. In the case of (b) and (c), the test electrodes were made of a mixture of carbon substrate (70 wt %) and PTFE powder (30 wt %).

Furthermore, to fabricate the improved air electrodes, we used a substrate of (d) C and AB in a ratio of 1:1 (36 $m^2 g^{-1}$).

2.3. *Catalyst preparation*

Catalysts were prepared in three different ways.

(a) Mixing; catalysts were mixed with the carbon substrate and PTFE powder to yield catalyst: substrate of 2:5 wt %.

(b) Impregnation; the samples of metal phthalocyanines (MPc) were dissolved in 96% H_2SO_4, added to the carbon substrate and then precipitated onto the substrate by pouring the mixture into ice–water to yield MPc: substrate of 1:8 wt %. The improved electrodes were made in the MPc: substrate range 1:200 to 1:20 wt %.

(c) Evaporation; for FePc and CoPc, evaporation was carried out onto the carbon substrate and PTFE powder test electrodes. Due to the high resistivity of the phthalocyanines, care was taken to prevent thick film formation on the electrode by using heat treatment.

2.4. *Electrode preparation*

All test electrodes were prepared under the following conditions.

Type A. The carbon substrate and the PTFE powder (together with the catalyst when the mixing method was used) were mixed by a homogenizer for *c*. 30 min. A 16 mm diameter disc was made by pressing in a brass vessel containing 0.4 g of mixed powder onto an Ni screen (Furuuchi Chemical Co.) current collector at 400 kg cm^{-2}. The vessel was then heated at 400° C for 30 min.

The improved air electrodes were prepared as follows:

Type B. The carbon substrates with FePc and an aqueous dispersion of PTFE (60%; Mitsui Fluorochemicals Co.) were mixed and kneaded with ethanol and water. The mixture was then rolled into a sheet and an Ni screen (Exmet Co. 3Ni7-3/0) together with a porous PTFE sheet (Nitto Denko Co. NTF5205) were applied to one side and pressed at 82.5 kg cm^{-2} and 250° C for 30 min.

2.5. *Electrochemical measurements*

2.5.1. Polarization. The air electrode (2 cm^2) was placed into a PTFE cell with a Pt foil counter electrode, 1 N KOH electrolyte and a saturated calomel reference electrode (SCE) or Ag–AgCl reference electrode. Potential results were corrected to the standard hydrogen electrode scale. Polarization curves (log i–E) were obtained by scanning at a rate of 0.6 mV s^{-1}, using a potentiostat, log converter and function generator (Princeton Applied Research Co. Model 331).

2.5.2. Dependence of OCV on O_2 pressure. Variations in the open circuit potential (OCV) as a function of oxygen partial pressure were determined with the same experimental system as used in the polarization measurements. To prevent the influence of irreversibly adsorbed O_2 on the surface of the test electrode, the OCV was measured with increasing O_2 partial pressure in the range 1–100% (oxygen in nitrogen) at a total pressure of one atmosphere. After waiting *c.* 3–10 min to attain equilibrium the OCV value was recorded.

Table 1. Polarization characteristics for air electrodes with catalysts

Catalyst	*Potential* E *(V)*				
	0 (mA cm^{-2})	1 (mA cm^{-2})	5 (mA cm^{-2})	10 (mA cm^{-2})	20 (mA cm^{-2})
FePc*	0.217	0.12	0.052	0.012	−0.048
Pt black	0.22	0.10	0.052	0.022	−0.018
$Co(acac)_2$	0.12	0.082	0.022	−0.008	−0.048
FePc‡	0.21	0.082	0.008	−0.035	−0.088
Ag	0.17	0.082	−0.028	−0.068	−0.098
CuPc†	0.14	0.077	0.017	−0.008	−0.048
$Fe(acac)_3$	0.17	0.062	−0.008	−0.038	−0.068
CoPc†	0.17	0.052	0.017	0.002	−0.018
VB_{12}	0.21	0.052	0.012	−0.004	−0.028
$Cu(bzox)_2$	0.15	0.052	−0.008	−0.008	−0.078
Haemin†	0.16	0.052	−0.018	−0.048	−0.098
$Fe(bzac)_3$	0.13	0.032	−0.023	−0.053	−0.098
Without	0.14	0.032	−0.023	−0.058	−0.088
NiPc†	0.13	0.012	−0.048	−0.078	−0.118
ZnPc†	0.094	0.012	−0.048	−0.078	−0.118
Chlorophyll	0.10	0.012	−0.048	−0.088	−0.128
Ferrocene†	0.18	0.007	−0.038	−0.068	−0.108
Haemoglobin	0.13	−0.028	−0.108	−0.158	−0.228

Catalyst content is 0.05 g: * 0.1 g, † 0.03 g, ‡ 0.02 g.

2.6. H_2O_2 *decomposition rate measurements*

Hydrogen peroxide decomposition rate measurements were conducted to examine the catalytic effect of the electrodes for the decomposition of HO_2^- intermediate. A 3 wt % H_2O_2 solution (5 ml) was added to 1 N KOH containing 0.05 g of catalyst (50 ml) and the O_2 gas volume evolved was measured. The peroxide solution was prepared by dilution of stabilizer-free 30 wt % H_2O_2 (Mitsubishi Gas Chemical Co.), which was standardized by titration with $KMnO_4$ solution.

3. Results and discussion

3.1. *Catalytic effects of materials*

Table 1 gives the polarization characteristics for Type A air electrodes with catalysts prepared by mixing, listed in the order of potential at 1 mA cm^{-2}. The order of effectiveness at 1 mA cm^{-2} was FePc* > Pt black > Ag = FePc‡ = $Co(acac)_2$ > CuPc‡ > $Fe(acac)_3$ > CoPc. NiPc, ZnPc, chlorophyll, haemoglobin and ferrocene showed no catalytic effects. FePc has been reported as having good overall activity, approaching Pt in its ability to catalyse oxygen reduction [28]. CoPc is also reported to be a good catalyst, although its O_2 reduction process is different from that on FePc [28, 36]. Polymeric CoPc shows high activity at large current and is more stable than polymeric FePc [33]. Both $Co(acac)_2$ and $Fe(acac)_3$ have been reported as being good catalysts [47]. The present results show similar catalytic effects, for example, FePc has an activity close to that of Pt black. CoPc and VB_{12} give lower potentials than that of Pt black in the lower current density region, but show a high potential at more than 1 mA cm^{-2}.

3.2. H_2O_2 *decomposition effects*

The H_2O_2 decomposition rates for several catalysts are summarized in Table 2. Both FePc and CoPc decompose H_2O_2 to evolve O_2, and therefore are good catalysts for decomposition of the intermediate (HO_2^-), if this is produced during O_2 reduction. Both haemoglobin and $Cu(bzox)_2$ were soluble in the electrolyte.

The relationships between the O_2 evolution

Table 2. Kinetics of decomposition of reaction intermediates for different catalysts

Catalyst	*O_2 evolution rate (ml s^{-1})*
AC*	3.33×10^{-3}
Pt black	6.54×10^{-2}
FePc	2.67×10^{-2}
CoPc	3.64×10^{-2}
VB_{12}*	5.36×10^{-3}
$Cu(bzox)_2$	2.50×10^{-1}
Haemoglobin	5.00×10^{-2}

*Heat treatment at 400° C for 30 min.

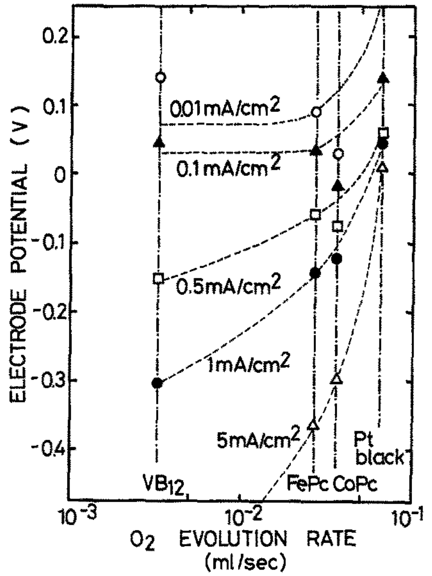

Fig. 1. Relationship between O_2 evolution rate and electrode potential at constant current density.

rate from the H_2O_2 decomposition reaction and electrode potential for electrodes of Substrate 1 prepared by mixing at constant current densities are shown in Fig. 1. Electrodes with catalyst showing a low decomposition rate showed lower potentials, which were more pronounced at higher current density. Comparing FePc and CoPc, the reversed order of potentials under current densities of < 0.5 mA cm^{-2} as a function of H_2O_2 decomposition rate suggests that a different electron process takes place on FePc, perhaps a direct 4-electron process.

3.3. *Relationships between OCV and O_2 partial pressure*

The OCVs (V_0) of air electrodes with and without FePc or CoPc made by several methods were measured under an O_2–N_2 atmosphere in the p_{O_2} range 0.01–1 atm. They were plotted as a function of ln (p_{O_2}). Typical results are shown in Fig. 2. The values of $V_0 - \ln(p_{O_2})$ slope and the OCV at $p_{O_2} = 0.21$ are listed in Table 3. These data give some practical information though their precise scientific meaning is not totally clear. The FePc electrodes (6, 8 and 9 in Table 3) showed higher OCV and smaller variations of OCV with p_{O_2} (line 1 in Fig. 2). However, other FePc electrodes showed lower OCV and larger variations of OCV with p_{O_2} (line 2 in Fig. 2). For CoPc electrodes, OCVs were lower than FePc electrodes (except 7 and 14), in spite of having large H_2O_2 decomposition rates (line 3 in Fig. 2). Electrodes without catalyst were less active (line 4 in Fig. 2).

3.4. *Influence of preparation methods on performance*

For FePc and CoPc, the influence of catalyst preparation methods on air electrode performance was examined. Polarization curves for air electrodes made by different preparation methods are shown in Fig. 3 for FePc and in Fig. 4 for CoPc. The electrodes made by Method 6 showed the

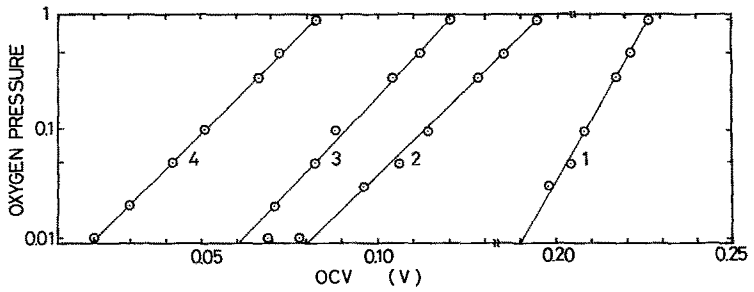

Fig. 2. Dependences of OCV on O_2 pressure for electrodes: Curve 1, evaporated FePc [Substrate a]; 2, mixed FePc [Substrate a]; 3, evaporated CoPc [Substrate a]; 4, without catalyst [Substrate b].

Table 3. Dependence of OCV on O_2 partial pressure

Catalyst	*Preparation method*	*Substrate*	*Values of* $V_0 - ln\,(p_{O_2})$ *slope* *(V decade^{-1})*	$E_{p_{O_2}=0.21}$ *(V)*
1. Without	–	a	0.028	0.068
2. Without	–	b	0.031	0.060
3. Without	–	c	0.026	0.077
4. FePc	a	a	0.031	0.123
5. FePc	b	a	0.031	0.116
6. FePc	b	b	0.016	0.147
7. FePc	b	c	0.026	0.081
8. FePc	c	a	0.018	0.214
9. FePc	c	b	0.018	0.127
10. FePc	c	c	0.030	0.096
11. CoPc	a	a	0.026	0.092
12. CoPc	b	a	0.031	0.103
13. CoPc	b	b	0.030	0.129
14. CoPc	b	c	0.033	0.103
15. CoPc	c	a	0.030	0.100
16. CoPc	c	b	0.030	0.124
17. CoPc	c	c	0.033	0.082

Method: (a) Mixing, (b) impregnation, (c) evaporation.
Substrate: (a) C only (2.2 m^2 g^{-1}), (b) C and AB (22 m^2 g^{-1}), (c) C and AC (210 m^2 g^{-1}).

highest activity for both FePc and CoPc. The advantage of Method b is that it coats the catalyst thinly and uniformly on the carbon substrate compared with other methods so that the catalyst is not only on the electrode surface but also in the electrode pores.

For some electrodes (5, 7, 10, 12, 14, 17 in Table 3), an extraordinarily high OCV was observed. It is believed that the adsorbed O_2 on the electrode surface resulted in the high OCV, considering $E_{p_{O_2}=0.21}$ in Table 3.

The electrodes using Substrates b and c (calculated SSA values: 22 and 210 m^2 g^{-1}, respectively) showed higher potential than that using Substrate a in the region > 1 mA cm^{-2}. Comparing current densities at the same potential, the former showed a current density of about one decade larger than the latter in this region. The results indicate that an active air electrode should consist of a substrate with larger SSA than 20 m^2 g^{-1}.

3.5. *Improved air electrode*

Though FePc showed a 4-electron reduction process at low current density, the results for Type A electrodes did not clearly show any predominant effects of FePc.

We, therefore, examined Type B electrodes with a PTFE dispersion for FePc and CoPc to improve this performance. Fig. 5 shows the polarization curves for electrodes prepared using FePc by three methods and using CoPc by impregnation. The potentials for these types of electrode are higher than that for the Type A electrode. The electrode of Method b (impregnation) showed the highest potential of all. The effect of FePc (4-electron process) is clearly shown in the polarization curves shown in lines 2 and 5; at low current densities, < 10 mA cm^{-2}, the potential using FePc is higher and its Tafel slope ($-$ 0.036 V decade^{-1}) is less than that for CoPc.

For the Type B electrode impregnated with FePc, the current range showing high potential is wide (0–0.1 mA cm^{-2}) compared with that for type A (0–0.02 mA cm^{-2}). It is suggested that the current range for the 4-electron process is larger for the Type B electrode than for the Type A electrode. Vertical sectional SEM views of both types of electrode are shown in Fig. 6. It is clearly shown that the active particles are connected with a 'yarn' of PTFE for the Type B electrode. It is

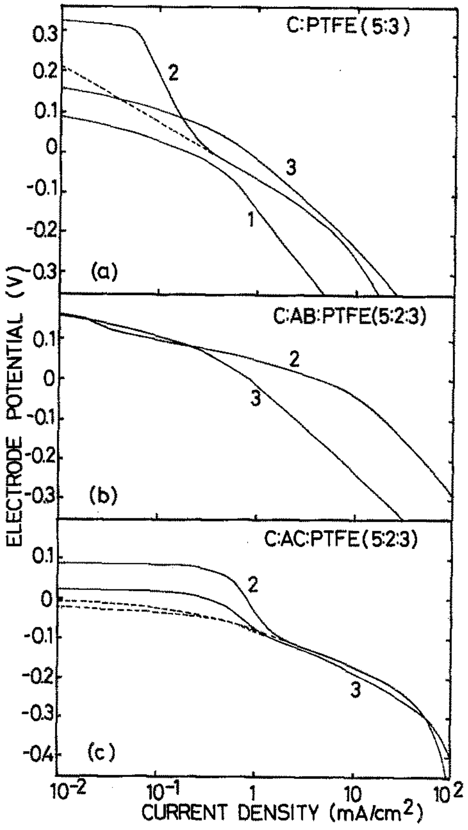

Fig. 3. Polarization curves for Type A electrodes with FePc consisting of (a) Substrate a, (b) Substrate b, and (c) Substrate c: Curve 1, Method a; 2, Method b; 3, Method c. Dotted lines show polarization curves for $p_{O_2} = 0.21$ atm.

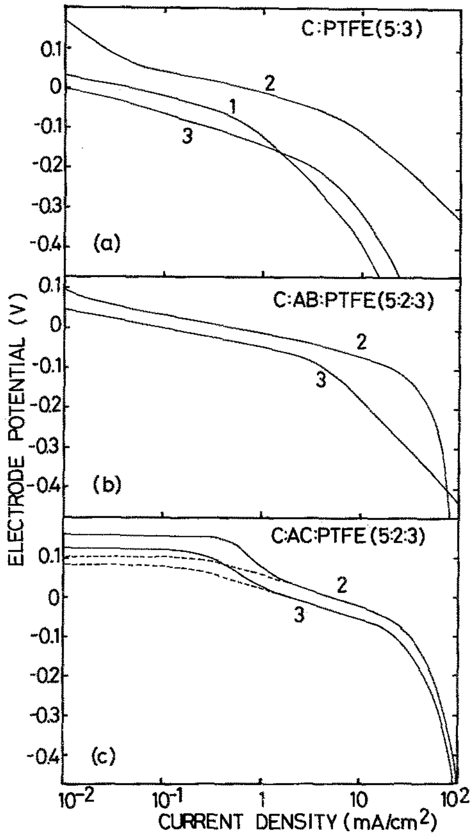

Fig. 4. Polarization curves for Type A electrodes with CoPc consisting of (a) Substrate a, (b) Substrate b, and (c) Substrate c: Curve 1, Method a; 2, Method b; 3, Method c. Dotted lines show polarization curves for $p_{O_2} = 0.21$ atm.

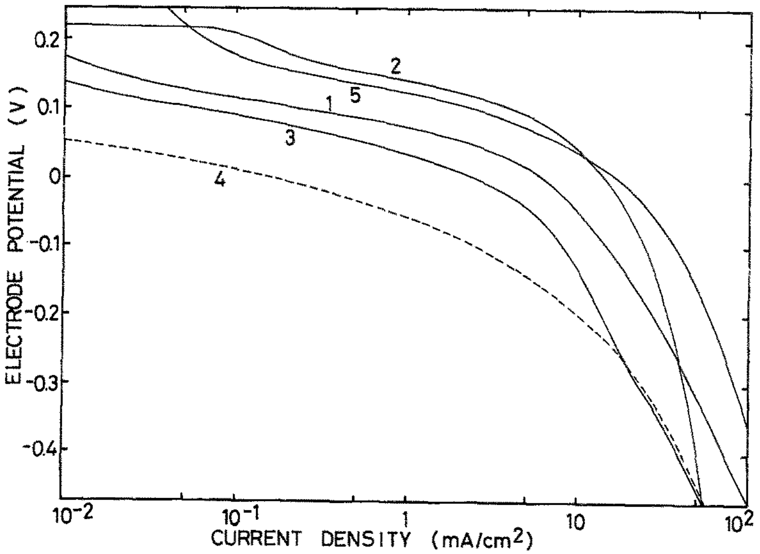

Fig. 5. Polarization curves for Type B electrodes: Curve 1, mixed FePc; 2, impregnated FePc; 3, evaporated FePc; 4, impregnated CoPc; 5, impregnated FePc (large SSA substrate, SSA = 360 m^2 g^{-1}).

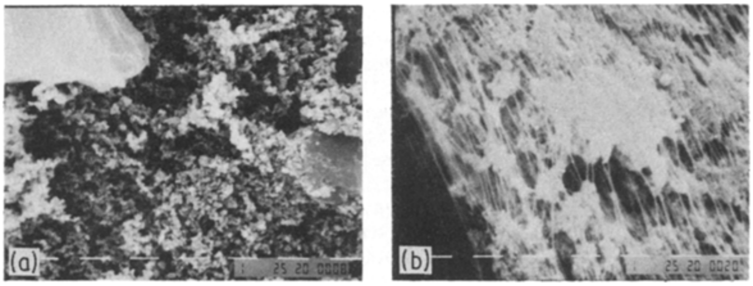

Fig. 6. Vertical sectional SEM views of electrodes. One division is 1 μm: (a) Type A electrode, (b) Type B electrode.

suggested that there are many more effective pores for O_2 reduction in the Type B electrodes, so that they showed a better performance than that of Type A electrodes, even though both have almost the same SSA.

Fig. 7 shows the dependence of electrode potential on the amount of FePc used to impregnate the electrodes. The electrode prepared using 0.2 g FePc for 8 g of substrate (6.9×10^{-4} g m^{-2}) showed the highest potential and the best performance.

4. Conclusion

The catalytic effects of FePc and CoPc on practical air electrodes of two different types (A and B) were examined to determine the influence of the method of catalyst preparation and of the carbon substrate.

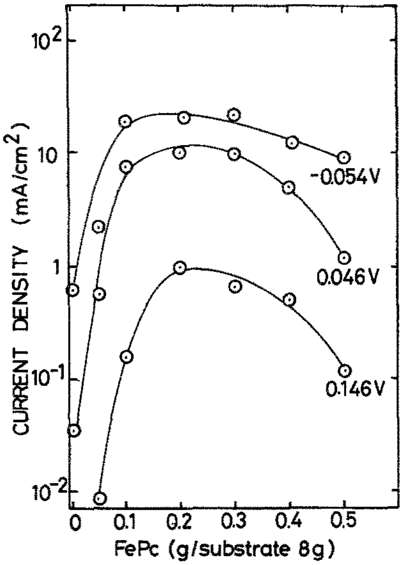

Fig. 7. Dependence of electrode potential on amount of FePc used in impregnating electrodes (SSA = 36 m^2 g^{-1}).

Both FePc and CoPc showed high H_2O_2 decomposition rates which resulted in low polarization at high current density.

The Type B electrodes showed better performance over the whole range of current densities than the Type A electrodes. Especially, the Type B electrode impregnated with FePc showed a very long current region corresponding to the 4-electron reduction process (0–0.1 mA cm^{-2}), compared with the Type A electrode impregnated with FePc (0–0.02 mA cm^{-2}). It is suggested that the Type B electrodes have many pores because of the presence of the PTFE 'yarn' connecting carbon substrate.

The electrode impregnated with catalyst showed the higher potential. The advantage of impregnation lies in supporting the catalyst more thinly and uniformly.

The electrode made using substrates with specific surface area of > 20 m^2 g^{-1} showed high potentials at large current densities.

Acknowledgement

The authors wish to express their gratitude to Mr T. Okada, Mr C. Uemura and Mr T. Inamura for their helpful guidance and discussions during the course of this research.

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