JOURNAL OF APPLIED ELECTROCHEMISTRY **15** (1985) 441–445

The influence of catalyst-supporting methods on electrochemical activity and the resultant stability of air electrodes activated with iron phthalocyanine

TOSHIRO HIRAI, JUN-ICHI YAMAKI, AKIHIKO YAMAJI

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki-ken, 319–11 Japan

Received 7 June 1984; revised 15 August 1984

To improve the performance of air electrodes, the dependence of iron phthalocyanine (FePc) catalytic effects on preparation methods was examined. The methods used were mixture (Electrode 1), impregnation (Electrode 2) and direct synthesis (Electrode 3). Electrodes 2 and 3 showed higher potentials during cathodic polarization up to 10 mA cm^{-2} than Electrode 1. The rate of chemical destruction of H_2O_2 decreased in the order Electrode 3 > Electrode 2 > Electrode 1. Electrode 3 showed the smallest potential drop for a discharge at 10 mA cm^{-2}, 0.09 V after 50 h. However, the potential of Electrode 2 decreased with discharge, becoming 0.09 V lower than that of Electrode 3 after a 50 h discharge at 10 mA cm^{-2}. Once the potential drop occurred, the potential was not recovered by resting or by drying the electrode. The potential drop may be caused by deactivation of FePc. One possible reason for such deactivation is the presence of H_2SO_4, which remained on the electrode after impregnation of the FePc–H_2SO_4 solution.

1. Introduction

Iron phthalocyanine (FePc) is recognized as an active catalyst for oxygen reduction [1, 2]. However, the activity may depend on the preparation methods and the supporting materials [3]. Several methods of preparation of organometallic compounds have been carried out. These include evaporating the catalyst onto inert electrodes [3, 5], impregnating a catalyst solution [3, 6, 7], painting the electrodes with a suspension of the catalyst in an adequate solvent [3, 8], mixing the catalyst with supporting materials to create the electrodes [9, 10] and directly synthesizing the catalyst onto the carbon supports [7, 11].

Kozawa *et al.* [3] compared the activities of metal phthalocyanines which were supported by impregnation, evaporation and painting. They claimed that impregnation produced the most active electrode of the three methods. In a previous paper [12], it was shown that impregnation was a better method than mixture and evaporation, and the overpotential of the air electrode was reduced by the use of a polytetrafluoroethylene (PTFE) emulsion as an electrode binder. Kreja and Plewka [7] on the other hand, reported that the poly-FePc electrodes supported by impregnation and direct synthesis showed nearly the same polarization characteristics.

In the present study, FePc was deposited on carbon supports in three ways (mixture, impregnation and direct synthesis) and air electrodes were fabricated from the supports. The effects of FePc preparation methods on overpotential of the improved air electrode and its deactivation with discharge were then studied.

2. Experimental details

2.1. *Catalyst preparation*

FePc was prepared on carbon supports by the following three methods [a reagent grade of FePc (Eastman Kodak Co.) was used for Methods (1) and (2)]:

0021–891X/85 $03.00 + .12

(1) Mixture method, where FePc was mixed with carbon supports.

(2) Impregnation method, where FePc (0.05–0.5 g) was dissolved in 150 cm^3 of 96% H_2SO_4 and precipitated on 8 g of carbon supports by pouring into 2 l of ice-water. After filtration, the carbon supports with FePc were washed with distilled and ion-exchanged water until the pH of the filtrate reached 7.

(3) Direct synthesis method, where phthalonitrile, $FeCl_3$, urea and the carbon supports were mixed and reacted at 300° C for 70 h in a N_2 atmosphere. The temperature was then raised to 350° C and the reactants were heated for two additional hours. The product was purified by extraction with ethanol in a Soxhlet apparatus.

2.2. *Electrode preparation*

Carbon powder (C, Nippon Carbon Co.) and acetylene black (AB, Denki Kagaku Kogyo Co.) were used as carbon supports with a 1:1 weight ratio. FePc was prepared on the carbon supports as described above. The FePc-prepared carbon supports were then mixed in a ratio of 4:1 with PTFE emulsion (60 wt % solution, Mitsui Fluorochemicals Co.) and kneaded with ethanol and water. The mixture was rolled into a sheet. A nickel 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} 250° C for 30 min. The electrode sheet was finally cut into 30 mm diameter discs.

2.3. *Electrochemical measurements*

The air electrode was set into a PTFE cell with a Pt foil counter electrode, 1 N KOH electrolyte and a saturated calomel reference electrode (SCE). Polarization curves were obtained by scanning at a rate of 0.6 mV s^{-1}, using a potentiostat, log converter and function generator (Priceton Applied Research Co., Model 331).

Discharge studies were galvanostatically carried out using an electrometer (Takeda Riken Co.) and constant current source (Kikusui Denshi Co.). All measurements were carried out at room temperature (20–25° C). The potential of SCE in 1 N KOH was 0.244 V vs NHE.

2.4. *H_2O_2 Decomposition rate measurements*

Decomposition rates of hydrogen peroxide were measured in order to examine the catalytic effects of the electrodes on the decomposition of the HO_2^- intermediate. Five milliliters of 30 wt % H_2O_2 solution (Mitsubishi Gas Chemical Co.) were added to 50 cm^3 of 1N KOH containing 0.05 g of the carbon supports with FePc, and the evolved O_2 gas volume was measured at room temperature (20–25° C).

2.5. *Amounts of residual H_2SO_4 on carbon supports*

Carbon supports with FePc were boiled in distilled and ion-exchanged water for 8 h. The filtrate was titrated with 10^{-3} M KOH.

3. Results and discussion

3.1. *Optimum amount of FePc supported on the electrodes*

Cathodic polarization of the mixed, impregnated and directly synthesized electrodes (Electrodes 1, 2 and 3) with various amounts of FePc are shown in Table 1, 2 and 3, respectively. The FePc amounts

Table 1. Polarization characteristics for FePc-mixed electrodes in 1 N KOH at room temperature (20–25° C)

FePc amount	*Electrode potential vs SCE (V)*					
g (supports + PTFE g^{-1})	*OCV*	*0.01 mA cm^{-2}*	*0.1 mA cm^{-2}*	*1 mA cm^{-2}*	*5 mA cm^{-2}*	*10 mA cm^{-2}*
0	−0.118	−0.224	−0.250	−0.328	−0.440	−0.528
0.02	+0.028	−0.040	−0.119	−0.156	−0.206	−0.252
0.03	+0.031	−0.020	−0.109	−0.144	−0.212	−0.266
0.04	+0.024	−0.068	−0.120	−0.156	−0.248	−0.317
0.06	+0.042	−0.088	−0.128	−0.170	−0.278	−0.350

Table 2. Polarization characteristics for FePc-impregnated electrodes in 1 N KOH at room temperature (20–25° C)

FePc amount g (supports + PTFE g^{-1})	Electrode potential vs SCE (V)					
	OCV	0.01 mA cm^{-2}	0.1 mA cm^{-2}	1 mA cm^{-2}	5 mA cm^{-2}	10 mA cm^{-2}
0	−0.118	−0.224	−0.250	−0.328	−0.392	−0.440
0.005	+0.028	−0.126	−0.146	−0.212	−0.392	−0.482
0.01	+0.032	0	−0.092	−0.128	−0.176	−0.214
0.02	−0.026	−0.040	−0.042	−0.090	−0.130	−0.160
0.03	−0.014	−0.048	−0.062	−0.100	−0.142	−0.180
0.04	−0.054	−0.058	−0.064	−0.126	−0.200	−0.270
0.05	−0.080	−0.082	−0.090	−0.154	−0.226	−0.295

(per electrode material weight) for the electrodes which showed the highest potential at 1 mA cm^{-2} in the Tafel-like region were 0.03 g g^{-1} for Electrode 1, 0.02 g g^{-1} for Electrode 2 and 0.029 g g^{-1} for Electrode 3, respectively. The polarization curves in these optimum conditions are shown in Fig. 1.

Electrodes 2 and 3 showed higher potentials up to 10 mA cm^{-2} than Electrode 1, while in the higher current region, Electrode 3 showed the highest potential. Electrode 1 showed the largest polarization, which may be caused by the absence of the FePc layer on the carbon supports. From a calculation using the area of the FePc molecule (1.15 nm × 1.15 nm) and the specific surface area (SSA) of carbon supports (36.4 m^2 g^{-1}), the impregnated carbon supports (0.03 g g^{-1}) are suggested to be covered with monomolecular FePc layer.

Oxygen evolution rates from the H_2O_2 solution containing carbon supports for three methods are shown in Table 4. A high decomposition effect is shown for direct synthesis, which may bring about low polarization at high current density.

It has been reported that the concentrated H_2SO_4 can remove the central Fe atom from FePc [13] and sulphonate FePc at high temperatures [14]. The results of atomic absorption analysis showed that 7% of the central Fe atoms were removed from FePc by treatment with the same procedure as impregnation. In the infrared spectrum, the absorption peak of the SO_3H group could not be detected for the H_2SO_4 treated FePc sample with the same procedure as impregnation. It is therefore suggested that a decreasing number of central Fe atoms, such as this, is one possible reason for the lower activity of Electrode 2.

3.2. *Potential stability with time*

Discharge potentials at 10 mA cm^{-2} are shown in Fig. 2 for three electrodes. Potential drops between the starting point and after 50 h were 0.1 V for Electrode 1, 0.17 V for Electrode 2 and 0.09 V for Electrode 3. The latter (curve 3) showed the highest potential with a very small potential change for at least 50 h. Though Electrode 2 (curve 2) showed an initially higher potential than the electrode with metal-free phthalocyanine (H_2Pc) by impregnation

Table 3. Polarization characteristics for FePc-directly synthesized electrodes in 1 N KOH at room temperature (20–25° C)

FePc amount g (supports + PTFE g^{-1})	Electrode potential vs SCE (V)					
	OCV	0.01 mA cm^{-2}	0.1 mA cm^{-2}	1 mA cm^{-2}	5 mA cm^{-2}	10 mA cm^{-2}
0	−0.118	−0.224	−0.250	−0.328	−0.392	−0.440
0.005	−0.027	−0.128	−0.160	−0.240	−0.416	−0.478
0.015	+0.007	+0.004	−0.092	−0.128	−0.156	−0.174
0.019	−0.040	−0.050	−0.074	−0.108	−0.146	−0.176
0.029	+0.034	+0.022	−0.066	−0.098	−0.124	−0.144
0.047	−0.040	−0.041	−0.052	−0.129	−0.212	−0.302
0.070	−0.036	−0.037	−0.052	−0.121	−0.210	−0.272

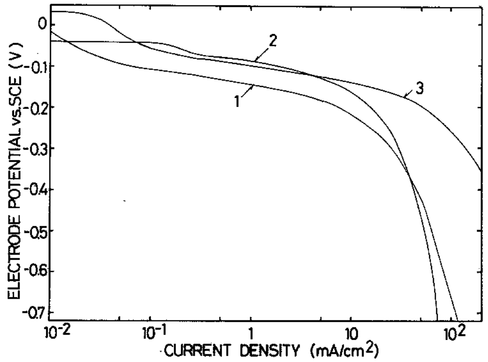

Fig. 1. Polarization curves for electrodes with FePc by different supporting methods in 1 N KOH at room temperature (20–25° C). Curve 1: mixture method, 2: impregnation method, 3: direct synthesis method.

(curve 5), their potentials became nearly equal after 34 h. The potential of Electrode 2 reached a saturated value of −0.33 V after 20 h discharge at 10 mA cm^{-2} with a change of within 0.03 V after that. The corresponding saturated potential values and time at other discharge currents were −0.29 V after 50 h, −0.31 V after 40 h and −0.72 V after 20 h at 1, 5 and 20 mA cm^{-2}, respectively.

It is possible that the potential drop was caused by a diffusion limitation in the electrolyte or the increase of electrolyte penetration into the electrode. Tests were conducted to check these possibilities. Discharge tests at 10 mA cm^{-2} with intervals of 14 h after every 10 h discharge were carried out for Electrode 2. Significant potential recovery was not found after each interval. Furthermore, Electrode 2 was washed with water and dried after the 50 h discharge test at 10 mA cm^{-2}. The potential was almost constant after 4 h with no potential recovery found. From these results, we conclude that the potential drop of Electrode 2 was caused by the deactivation of the material composing it, with accompanying irreversible damage.

Table 4. O_2 Evolution rates according to H_2O_2 decomposition reaction for carbon supports with and without FePc at room temperature (20–25° C)

Sample	*O_2 Evolution rate ($cm^3 g^{-1} s^{-1}$)*
Without FePc	0.0404
Mixed FePc	4.25
Impregnated FePc	5.85
Directly synthesized FePc	7.84

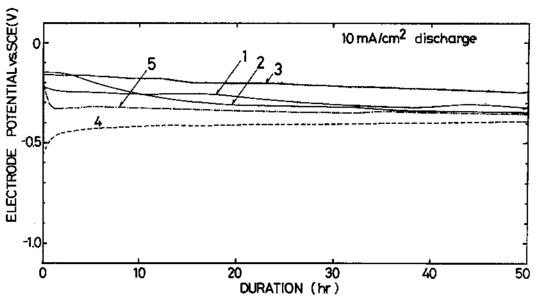

Fig. 2. Dependence of the potential drop at constant current density 10 mA cm^{-2} on the time for the electrodes in 1 N KOH at room temperature (20–25° C). Curve 1: mixed FePc, 2: impregnated FePc, 3: directly synthesized FePc, 4: without catalyst, 5: impregnated H_2Pc.

The amounts of remaining H_2SO_4 on the impregnated carbon supports were evaluated by refluxing the supports and by titrating with 10^{-3} M KOH. The results are shown in Table 5. Carbon supports treated with H_2SO_4 exhibited 19 times as much acidic material on the carbon surfaces as those which were untreated. FePc-impregnated carbon supports exhibited 116 times as much as those without FePc (untreated with H_2SO_4). This deactivation may be caused by the residual H_2SO_4 which removes Fe atoms from FePc.

The impregnated carbon supports were refluxed with distilled and ion-exchanged water for 8 h to remove the H_2SO_4. The other impregnated carbon supports were immersed in 0.1 or 1 N KOH for 8 h at room temperature and washed with distilled and ion-exchanged water until the pH of the filtrate reached 7. The curves are nearly the same. The

Table 5. Amount of acid materials on the surfaces of various carbon supports

Sample	*Amount of acid materials*	
	($mol\,g^{-1}$)	*($mol\,m^{-2}$)*
Without FePc (untreated)	4.10×10^{-6}	1.08×10^{-7}
Without FePc (washed with water)	1.80×10^{-7}	4.74×10^{-9}
Without FePc (treated with H_2SO_4, washed with water)	3.38×10^{-6}	8.89×10^{-8}
With FePc of 0.2 g (treated with H_2SO_4, washed with water)	2.09×10^{-5}	5.50×10^{-7}

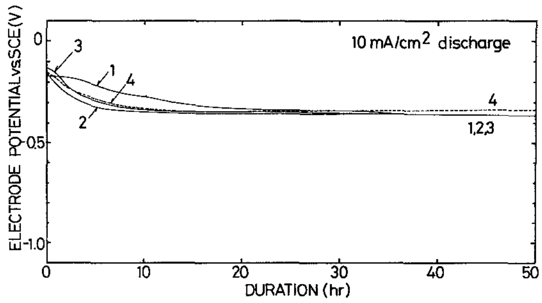

Fig. 3. Dependence of potential drop at constant current density 10 mA cm^{-2} on time for the electrodes with FePc in 1 N KOH at room temperature (20–25° C). Curve 1: untreated, 2: refluxed with water for 8 h, 3: treated with 0.1 N KOH for 8 h, 4: treated with 1 N KOH for 8 h.

potential decreased from −0.12 to −0.32 V for the first 10 h, and was then constant. The values were the same as those for the untreated electrode (Electrode 2) after 36 h. The H_2O_2 decomposition rate was decreased to 1.30 ml g^{-1} s^{-1} by treating with 1 N KOH for 8 h. It was impossible to remove H_2SO_4 without the deactivational process during the treatments.

4. Conclusion

Three catalyst supporting methods, mixture, impregnation FePc–H_2SO_4 solution and direct synthesis, were examined to improve the performance of air electrodes. The optimum amounts of FePc were determined in these electrodes. The FePc amounts (per electrode material weight) for the electrodes which showed the highest potential at 1 mA cm^{-2} in the Tafel-like region were 0.03 g g^{-1} by mixture (Electrode 1), 0.02 g g^{-1} by impregnation (Electrode 2) and 0.029 g g^{-1} by direct synthesis (Electrode 3), respectively. Electrodes 2 and 3 showed the lowest polarization among the three electrodes. The H_2O_2 decomposition rate was in the order of direct synthesis > impregnation > mixture. Electrode 3 showed the smallest potential drop for discharge at 10 mA cm^{-2}, 0.09 V after 50 h. However, Electrode 2 showed a remarkable potential drop during discharge, becoming 0.09 V lower than that of Electrode 3 after 50 h. Once the potential drop occurred, the potential was not recovered by resting or drying the electrode. The potential drop may be caused by the deactivation of FePc. One possible reason for such deactivation is the presence of H_2SO_4 on the air electrode.

Acknowledgement

The authors wish to thank C. Uemura and T. Okada for helpful suggestions.

References

[1] A. Kozawa, V. E. Zilionis and R. J. Brodd, *J. Electrochem. Soc.* **118** (1971) 1705.
[2] J. Zagal, P. Bindra and E. Yeager, *ibid.* **127** (1980) 1506.
[3] R. J. Brodd, V. Z. Leger, R. F. Scarr and A. Kozawa,National Bureau of Standards Special Publication, **455** December (1974) 253.
[4] M. Savy, C. Bernard and G. Magner, *Electrochim. Acta* **20** (1975) 383.
[5] A. J. Appleby, J. Fleisch and M. Savy, *J. Catal.* **44** (1976) 281.
[6] A. Kozawa, V. E. Zilionis and R. J. Brodd, *J. Electrochem. Soc.* **117** (1970) 1470.
[7] L. Kreja and A. Plewka *Electrochim. Acta* **27** (1982) 251.
[8] A. J. Appleby and M. Savy, *ibid.* **21** (1975) 567.
[9] H. Meier, W. Albercht, V. Jshirwitz and E. Zimmerhackl, *Ber. Bunsenges. Phys. Chem.* **77** (1973) 843.
[10] R. Jasinski, *J. Electrochem. Soc.* **112** (1965) 526.
[11] L. Kreja and A. Plewka, *Electrochim. Acta* **25** (1980) 1283.
[12] T. Hirai, J. Yamaki and A. Yamaji, *J. Appl. Electrochem.* in press.
[13] Y. Bansho, J. Kuwabara, T. Sekiguchi and K. Yamanari, *J. Chem. Soc. Jpn.* (1972) 1712 in Japanese.
[14] Y. Hosoda, 'Senryo Kagaku' Gihou-do, Tokyo (1973), in Japanese pp. 386–95.
[15] J. R. Golstein and A. C. C. Tseung, *J. Phys. Chem.* **76** (1972) 3646.