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OXYGEN REDUCTION ON GLASSY CARBON ELECTRODE MODIFIED BY POLYMER AND COBALT PHTHALOCYANINE

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Catalytic activities and the lifetime of chemically modified glassy carbon electrode by polystyrene(PS) and cobalt phthalocyanine(CoPC) were investigated in the reduction of oxygen by the measurements of current-potential curves in 6N KOH aqueous solutions. The PS coated electrode behaved in the same manner as the glassy carbon electrode without treatment(GCE), without any obvious current decrease and potential shift of the wave. The electrode coated with the PS containing the CoPC showed higher catalytic activities than the GCE during a long continuous operation, which had a longer life than the electrodes on which the CoPC was directly attached by the adsorption or the chemical modification.

The chemically modified electrode have become of general interest lately,[1] because they may have various possibilities to the new electrode reactions. Their preparation and application are reviewed by Osa et.al.[2),3)] In spite of many researches on the modification, however, the few electrodes have received practical application because of their short lifetime. The modification technique is expected to be further improved. In this respect, polymers are attracting attention which play the role of binders between substrates and catalysts.[4)] Besides, for polymer coated electrodes, some polymer effects which promote the catalytic activities or selectivities are expected.[5),6)] The present study describes the effect of the polymer coating on glassy carbon electrodes for the reduction of oxygen.

Glassy carbon rods(GC20, 5mm diameter, Tokai Carbon,Inc.) were polished mechanically at one end with successively finer grades of emery paper(final grade of #3000 of Nikken Kogyo Inc.) and alumina pastes(#8000) on a rotating felt to have mirror finish. Then the rods were washed with distilled water, dipped into the dichloromethane containing polystyrene(PS)(1%) and cobalt phthalocyanine(CoPC)(ca,10^{-5} mole) for several hours, taken out of the solution, quickly shaken to remove the excess solution and dried in air at about 100 °C for 30 min. The polymer film on the electrode was visible. The PS and the dichloromethane were of commercially available and were used without further purification. The CoPC was synthesized and purified in our laboratory.

Current-potential curves were obtained in 6N KOH aqueous solution with the linear potential sweep voltammetry from the rest potential where the electrode potential was held for several minutes passing O_2 over the solution after several successive sweeps under O_2 bubbling. The electrolytic cell was the glass cell of conventional design which has three compartments for test, counter and reference electrode. A platinum coil and a Hg/HgO(6N KOH) were used for the counter and the reference

electrode, respectively.

Typical current-potential curves for the reduction of oxygen are shown in Fig.1. Comparing curves a with b, it is seen that the polystyrene-coated electrode(PSE) behaves in the same manner as the GCE. The curve c indicates that the PSE containing the CoPC has the higher catalytic activities than the GCE. The electrodes on which the CoPC was directly attached by adsorption or chemical modification showed also similar activities.[7),8),9),10)] But we would like to emphasize here that the PSE containing the CoPC does not decrease its activities during a long continuous operation (even after several days and several hundreds potential sweeps between +0.6V and -1.2V vs. SCE). While the former electrode lost their activities in half a day of operation in the same solution. The long life of the PSE is due to the strong adsorption of the PS which protects the catalysts from poisoning. Similar experiments were made on the films of polyvinylalcohol or polyacryronitrile, but they were destroyed immediately in 6N KOH. The detailed investigation on the role of the polymer is now in progress.

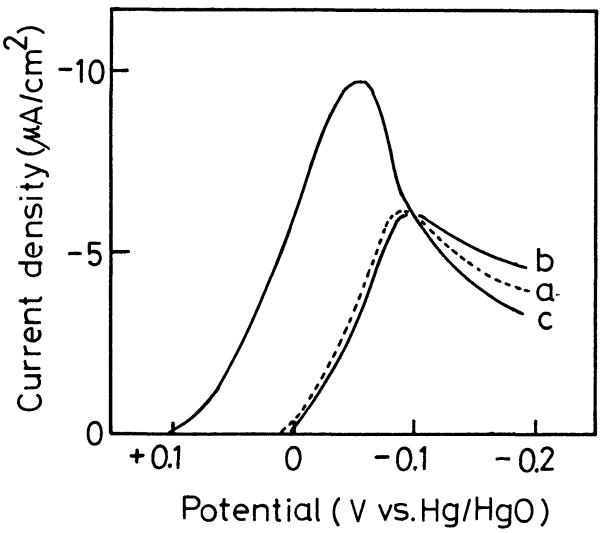

Fig.1 Current-potential curves for oxygen reduction on glassy carbon electrode in oxygen saturated 6N KOH aqueous solution at 24°C. sweep rate; 2mV/s. a, without treatment; b, coated with PS; c, coated with PS containing CoPC.

Literatures

1) J.C.Lennox and F.Murray, J.Electroanal.Chem., 78,395(1977).
2) T.Osa, Kagaku, 34,534(1979).
3) M.Fujihira and T.Osa, Denkikagaku, 45,270(1977).
4) N.Oyama and F.C.Anson, J.Am.Chem.Soc., 101,3450(1979).
5) M.R.Van De Mark and L.L.Miller, J.Am.Chem.Soc., 100,3223(1978).
6) J.B.Kerr and L.L.Miller, J.Electroanal.Chem., 101,263(1979).
7) H.Alt, H.Binder and G.Sandstede, J.Catal., 28,8(1973).
8) K.A.Radynshkina, R.Kh.Barshtein, B.D.Berezin, M.R.Tarasevich and S.D.Levina, Elektrokhimiya, 9,395(1973).
9) A.J.Appleby and M.Savy, Electrochimica.Acta., 21,567(1976).
10) A.J.Appleby, J.Fleish and M.Savy, J.Catal., 44,281(1976).

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