NOTES

Foreign Gas Behavior of Oxygen Reduction Reaction on a Gas Diffusion Hybrid Polymer Electrode

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Recently, a new method has been developed for the preparation of conductive polymers hybridized with conventional non-conductive polymers.[1-5] Niwa *et al.* synthesized a conductive polymer film by the electrochemical polymerization of pyrrole into polyvinyl chloride (PVC) and polyvinylidene fluoride coated on a conductive substrate.[1,2] In this hybrid polymer, the binder polymer used such as PVC may function not only as a supporter for a brittle conductive polymer but as a functional material for controlling the properties of the hybrid polymer.[2,6-8]

Our previous work[8] showed the effectiveness of the hybrid polymer film composed of polypyrrole (PPy), various binder polymers and metal phthalocyanines (M–Pc) in promoting O_2 electrochemical reduction as a gas diffusion electrode in an alkaline solution. In such a gas diffusion hybrid polymer (GDHP) electrode, it was suggested that the reactant species of the electrode reaction, *e.g.*, O_2 molecules and OH^- ions, could migrate to the active center of the M–Pc catalyst included in the film through the diffusion of the species into the binder polymer.

Along with previous works,[8,9] further investigation was done in this study, *i.e.*, an attention was paid to the influence of foreign gases (N_2, CO, CO_2, and SO_2) on O_2 reduction on the GDHP electrode composed of PPy conductive polymer, PVC binder polymer and cobalt phthalocyanine (Co–Pc) crystalline powder used as a catalyst for the electrode reaction. The results obtained suggested the effectiveness of the GDHP electrode for gas sensing application.

EXPERIMENTAL

Pyrrole (Tokyo Kasei Kogyo Co., Ltd.) was distilled under reduced pressure and stored in an nitrogen atmosphere. Tetra-*n*-butylammonium perchlorate (Tokyo Kasei Kogyo Co., Ltd.) was purified by recrystallization from the mixed solvent of ether and acetone. Co–Pc was prepared by the reaction of cobalt dichloride with isophthalonitrile in 1,8-diazabicyclo-[5.4.0]-7-undecene by refluxing in nitrobenzene at 210°C for 6 h. The BET surface area of the Co–Pc crystalline powder obtained was $3.00 \, m^2 \, g^{-1}$. PVC (SUMIRIT EX-13, mo-

lecular weight; 80000, Sumitomo Kagaku Co., Ltd.) was used without further purification.

The details of the preparation method for the GDHP electrode were described in our previous paper.[8,9] The major points are highlighted here. A mixture of Co–Pc and PVC powder with equiweight ratio was added to dimethylformamide, then dispersed by stirring for 30 min at 50°C on a magnetic stirrer. The PVC binder polymer film containing Co–Pc catalyst was obtained by casting the dispersion solution on an indium–tin–oxide (ITO) glass plate and drying in vacuo. The electrochemical polymerization of pyrrole was carried out using the ITO glass plate coated with the binder polymer as a working electrode in an electrolytic solution composed of tetrabutylammonium perchlorate and 0.1 M pyrrole solution of acetonitrile. The charge density for the polymerization was adjusted to be $2.5°C\,cm^{-2}$ under a potentiostatic electrolysis at 2.0 V vs. $Ag/AgNO_3$. The hybrid polymer film thus prepared was then stripped from the working electrode for electrochemical measurements.

The GDHP electrode was tested as a cathode for various gas reduction reactions in a half cell with a Hg/HgO reference electrode, a Pt counter electrode and 1 M KOH electrolytic solution. Various gases, N_2, CO, CO_2, and SO_2, were mixed with the O_2 feed gas at a given molar ratio, and then introduced into the gas compartment of the cell with a flow rate of $100\,ml\,min^{-1}$. The potential of the working GDHP electrode was controlled by a potentiostat/galvanostat (HA501, Hokuto Denko Co., Ltd.) and the output was fed into a recorder (Servo 105, Graphtec Co., Ltd.). In the polarization measurements, an ohmic drop (IR drop) due to the resistance of the electrolytic solution was calibrated by a current interrupter method. All electrochemical measurements were done at 25°C. The reduction product of SO_2 reduction was analyzed by a Raser Raman spectrometer (RAMANOR-U1000, Jobin Yvon Co., Ltd.).

Gas adsorption characteristics of Co–Pc and PVC powder were examined to identify the type of adsorption by static apparatus as follows: the sample (0.5 g) was taken into a Pyrex glass vessel connected to a high vacuum system, and then evacuated at 25°C for 1 h under a high vacuum ($\sim 10^{-3}$ Pa) prior to the introduction of a given amount of the gas (O_2, CO, CO_2, SO_2, and their mixtures). The adsorption was done at 25°C for all adsorbate gases. After reaching equilibrium of adsorption, the amount of the gas adsorbed onto the sample was calculated from the equilibrium pressure measured by a MacLeord gauge. The surface area of Co–Pc catalyst was obtained by a BET method using ethylene gas at liquid oxygen temperature.

RESULTS AND DISCUSSION

Figure 1 shows the change in the electrode potential when introducing 50 mol% of N_2 and CO, respectively, into the O_2 feed gas at a current density of $0.05\,mA\,cm^{-2}$. A very quick response of the potential was observed for every on-off of the N_2 supply, while a rather slow response and large polarization loss were
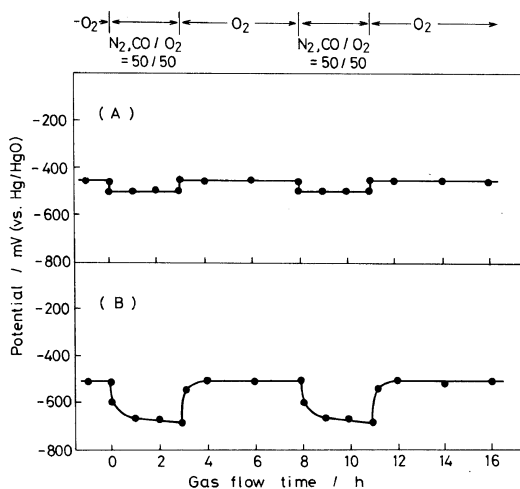

Figure 1. Change in potential of GDHP electrode when introducing N_2 (A) and CO (B) into O_2 feed gas at $0.05\,mA\,cm^{-2}$ in 1 M KOH at 25°C.
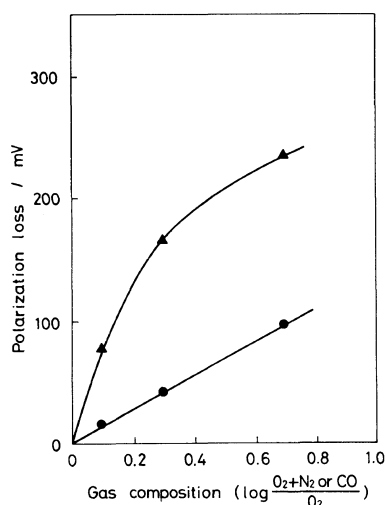
Figure 2. Relationship between gas composition and polarization loss due to introduction of N_2 (●) and CO (▲) into O_2 feed gas.

Figure 3. Change in potential of GDHP electrode when introducing CO_2 into O_2 feed gas at $0.05\,mA\,cm^{-2}$ in 1 M KOH at 25°C.

observed for CO. The potential responsibility observed in the case of N_2 was almost the same as that in the previous work,[8] where a somewhat different composition of the GDHP electrode, PMP binder polymer and Pd–Pc catalyst, was used. When the pure gas of N_2 or CO was supplied to the electrode, the potential decreased immediately toward the potential for H_2 evolution. This behavior means that no electrochemical reduction of CO occurs at least in this potential range. Figure 2 shows the relationship between the feed gas composition and polarization loss due to foreign gas supplied to the O_2 feed gas. A linear relation was obtained for the case of N_2, indicating a Nernst-like dependence of O_2 pressure on the polarization loss of potential. The polarization loss due to the introduction of N_2 is attributed to a mere blocking effect of N_2 against the adsorption of O_2 at the active center of the catalyst. For the case of CO, one can notice a nonlinear, large dependence of O_2 pressure on the polarization loss of potential. This implies another effect of CO in addition to the dilution effect as observed in the case of N_2. It is well known that there exists a relatively
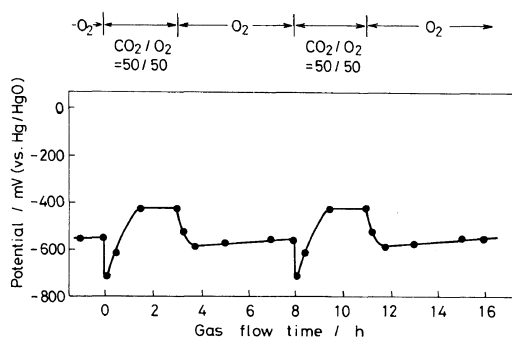
strong chemical interaction of central metal atoms in the M–Pc with CO molecules,[10] resulting in poisoning of CO against catalytic reactions.[11] The behavior of CO shown in Figure 2 seems to come from such a poisoning of CO against the catalytic activity of Co–Pc for the electrochemical O_2 reduction. The CO poisoning in the present case should, however, not be irreversible but reversible (i.e., temporary poisoning) as indicated from a smooth recovery in the electrode potential when removing CO as shown in Figure 1(B). This temporary poisoning is somewhat different from that of metallic catalysts. In the case of the M–Pc catalyst, the central metal is considered to have less electron density to form a carbonyl complex than in cases of metallic catalysts, because the central metal is co-ordinated with a large phthalocyanine ring. Therefore, the CO molecules chemisorbed on the central metal could be relatively smoothly removed to recover catalytic activity for oxygen reduction.

The change in the electrode potential when introducing CO_2 into the O_2 feed gas is shown in Figure 3. There is an unusual response in the case of CO_2. A very quick decrease in potential was observed just after introducing CO_2, followed by a gradual increase and then a steady state of potential which was higher than that for the oxygen reduction reaction in 1 M KOH electrolytic solution. The steady

state with the higher potential may be indicative of a cathodic reaction of CO_2. From the thermodynamic data, the equilibrium potential for the electrochemical reduction of CO_2 can be calculated by assuming a two-electron reduction mechanism, as follows;

$$CO_2 + 2H^+ + 2e^- = CO + H_2O$$
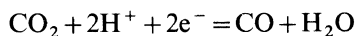
$$E_O(V \text{ } vs. \text{ Hg/HgO})$$
$$= -0.201 - 2.303(RT/F)pH$$

where R, T, and E are gas constant, absolute temperature and Faraday constant, respectively. As suggested by the previous work,[8] the electrode reaction on the GDHP electrode is considered to proceed through diffusion of the reaction species, such as feed gas molecules, water molecules and OH^- ions into the electrode bulk, i.e., into the PVC binder polymer and the PPy conductive polymer. Therefore, properties of the electrolytic solution impregnated in the electrode bulk should be taken into account for reaction on the GDHP electrode. The quick decrease in the potential just after introducing CO_2 as shown in Figure 3 can be explained by the potential change toward the CO_2 reduction potential in the impregnated electrolytic solution at high pH. With a longer time of CO_2 gas flow, the impregnated electrolytic solution could become gradually more acidic because of the dissolution of CO_2 into the electrode bulk, resulting in a higher reduction potential of CO_2. Also, possibly the equilibrium potential of O_2 reduction changes toward a more anodic level with decrease in pH of the impregnated electrolytic solution, as follows;

$$O_2 + 4H^+ + 4e^- = H_2O$$
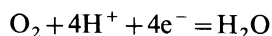
$$E_O(V \text{ } vs. \text{ Hg/HgO}) = 1.131 - 2.303(RT/F)pH$$

Therefore, the potential of the steady state after introducing CO_2 could be a mixed potential of these CO_2 and O_2 reductions. It is noteworthy that the potential behavior of the GDHP electrode attributed to the introduction of CO_2 is completely different from that of conven-

tional gas diffusion electrodes, as reported by the authors,[12,13] where dilution effects of CO_2 on the electrochemical reduction of O_2 were observed. The major difference between the GDHP electrode and the conventional gas diffusion electrode is the kind of catalyst used for the electrochemical reduction, i.e., the GDHP electrode contains a Co–Pc catalyst, while a perovskite-type metal oxide catalyst is used for the conventional gas diffusion electrode. Furuya et al.[14] reported CO_2 electrochemical reduction on a gas diffusion electrode with various kinds of M–Pcs in a CO_2 saturated $KHCO_3$ electrolytic solution. For the electrode with Co–Pc catalyst, they found that the electrode exhibited a catalytic activity with an efficiency of 90—100%. In general, the reduction of CO_2 is considered to proceed in an aqueous electrolytic solution competitively with the evolution of H_2. The results obtained here would not be the case, probably because of a low polarization loss coming from the appreciably low current density, 0.05 mA cm^{-2}, and also because of the mixed potential of CO_2 and O_2 reductions as mentioned above.

Two types of the GDHP electrodes with and without catalyst were used to investigate the effects of SO_2 on O_2 reduction. Figure 4 shows the change in the electrode potential when introducing SO_2 into the O_2 feed gas for these GDHP electrodes. Similarly to the case of CO_2,
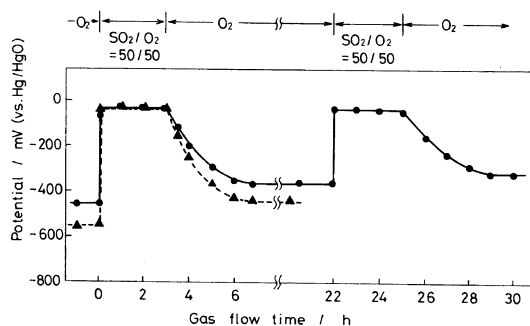

Figure 4. Change in potential of GDHP electrode with catalyst (●) and without catalyst (▲) when introducing SO_2 into O_2 feed gas at 0.05 mA cm^{-2} in 1 M KOH at 25°C.

a steady state with a higher potential than that in the pure O_2 feed gas was also observed in both electrodes although in this case a sharp increase in potential was obtained just after introducing SO_2. It is interesting that the potential value in the steady state is almost the same in both electrodes, while the potential value of the GDHP electrode with catalyst is higher in the pure O_2 feed gas than that of the GDHP electrode without a catalyst. These results indicate that Co–Pc catalyst has an activity for the O_2 reduction regardless of the reaction in the steady state after introducing SO_2. After these experiments, a yellow material was found to be deposited on the gas side surface of the electrode. From Raman spectroscopic analysis for this material, it was found to be solid sulfur. In addition to the potential increase of the O_2 reduction accompanied with decrease in pH of the electrolytic solution impregnated in the bulk of the electrode, this result should be indicative of the electrochemical reduction of SO_2, as follows:

$$SO_{2(gas)} + 4H^+ + 4e^- = S_{(solid)} + 2H_2O$$
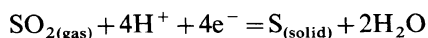
$$E_0(V \ vs. \ Hg/HgO) = 0.156 - 2.303(RT/F)pH$$

As will be discussed later, it was found that PVC binder polymer has a great solubility of SO_2. From this fact, it is thought that the electrolytic solution impregnated in the bulk of the GDHP electrode becomes immediately more acidic. In such a situation, the potential could move toward the reduction potential of SO_2 at around pH = 7 with the introduction of SO_2 into the feed gas. In fact, the permeation of acidic electrolytic solution to the gas side surface of the electrode was found after the experiment. Based on the behavior of the potential in the steady state in Figure 4, it does not appear necessary for the existence of Co–Pc catalyst to occur SO_2 reduction on the GDHP electrode, the reasons for which are to be discussed later in detail. Also one can notice for the case of SO_2 that recovery in the electrode potential is fairly slow and not
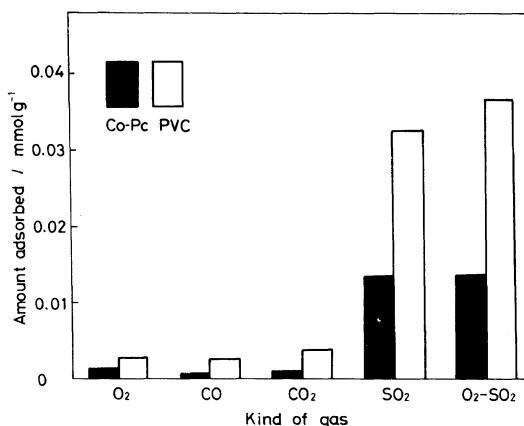

Figure 5. Amounts of various gases adsorbed on Co–Pc and PVC at 25°C under initial introduction pressure of 2.66 kPa for pure gases and of each 2.66 kPa (total pressure, 5.32 kPa) for O_2 and SO_2 mixed gas.

complete until 22 h even after cutting off the flow of SO_2, implying some composition changes of the electrolytic solution. We made the same measurement using 0.5 M K_2SO_3 electrolytic solution. Similar behavior was found in this case.

Figure 5 shows the amounts of various gases adsorbed on Co–Pc and PVC powder, respectively, at 25°C under an initial introduction pressure of 2.66 kPa for pure gases and each 2.66 kPa (total pressure, 5.32 kPa) for O_2–SO_2 mixed gas. Only a small amount adsorbed on Co–Pc was observed for O_2, CO, and CO_2, while a much greater amount was found for SO_2. It was also found that the amount adsorbed of SO_2 was almost the same level as that for O_2–SO_2 mixed gas. No noticeable change in the adsorption rate was observed between pure SO_2 and O_2–SO_2 mixed gas. Therefore, SO_2 molecules should be adsorbed selectively on Co–Pc without any disturbance of the coexistence of O_2. Similar features for the gas adsorption were obtained for the case of PVC although the amount adsorbed was greater in every adsorbate gas than for Co–Pc, particularly in SO_2 and O_2–SO_2 mixed gas. The active site for the gas adsorption on Co–Pc is considered to be on the central Co atom of
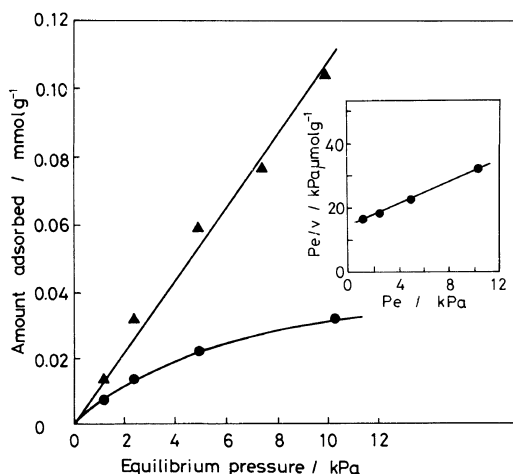
Figure 6. Adsorption isotherms of SO_2 on Co–PC (●) and PVC (▲) at 25°C. Inserted figure is Langmuir type isotherm of SO_2 on Co–PC at 25°C. P_e and v represent equilibrium pressure and amount adsorbed of SO_2, respectively.

Co–Pc molecule. It is very interesting that PVC has much ability for gas adsorption although it does not have any active sites such as Co–Pc. In order to clarify this fact, the adsorption characteristics of SO_2 were investigated for Co–Pc and PVC, respectively (Figure 6). A linear relationship between the amount adsorbed and equilibrium pressure (Henry law) was obtained for PVC. This definitely indicates the absorption of SO_2 into PVC. On the other hand, a Langmuir-type isotherm was found for the adsorption of SO_2 on Co–Pc as shown in the inserted figure, indicating a monomolecular layer adsorption which may include a chemical adsorption of SO_2 on the central Co atom of Co–Pc molecule, such as observed for the adsorption of NH_3 on Zn–Pc.[15] Since the SO_2 reduction proceeded on the GDHP electrode without Co–Pc catalyst as shown in Figure 4, the reduction site for the SO_2 reduction would be at the conductive PPy as well as at the Co–Pc

catalyst. The dissolution of SO_2 through the electrode into the electrolytic solution may be due to the large SO_2 absorption ability of the PVC binder polymer.

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