OXYGEN REDUCTION ON GAS DIFFUSION ELECTRODES IN ALKALINE SOLUTION

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Introduction

It is very important that an oxygen reduction reaction on the gas diffusion electrode in the alkaline solution. For example, they are alkaline fuel cell, oxygen cathode for the chlor-alkali electrolysis (1), air cathode of the zinc-air battery, etc. This gas diffusion electrode is composed of PTFE dispersion, carbon blacks and a catalyst (2). The catalysts was used various metal and metal oxide. Ag and Pt catalysts were studied (3, 4). During the previous studies, we found also that even a gas diffusion electrode with no supported catalyst on the reaction layer showed activity for oxygen reduction, although the activity was lower than that with Ag or Pt catalyst by ca 100 mV in terms of the electrode potential. However, no mechanistic studies on the gas diffusion cathodes with and without loaded catalyst were conducted in the former reports to investigate the role of the catalyst.

Purpose of the paper is to conduct comparative mechanistic studies of oxygen reduction on the gas diffusion cathodes with Mn, Co, Fe, Ni, Ag and without catalyst in order to investigate the role of catalysts in the oxygen reduction.

Experimental method

The reaction layer (RL) was made from a hydrophilic carbon black (Ketjen Black) with catalysts and a hydrophobic carbon black (No.6, Denki Kagaku Kogyo, Inc.) and polytetrafluoroethylene (D-1, Daikin Kogyo, Inc.). The gas diffusion electrodes with and without catalysts on the reaction layer will be called hereafter the Metal-C-Electrode and C-electrode, respectively. The gas-supply layer (GSL) was made from a hydrophobic carbon black and polytetrafluoroethylene. A cupper net with 1mm mesh and 0.1mm thick was integrated in the gas-supply layer and used as a current collector.

The metal catalysts (0.3 – 0.001 mg cm^{-2}) were loaded on Ketjen Black by ion-exchange method.

To prepare the RL and GSL the constituent materials were first dispersed in aqueous solutions with a surfactant. Then, the solutions were filtered to separate the aggregates of the constituent materials that were then rolled into sheets of RL and GSL, respectively. The surfactant was removed from the sheets by the ethanol extraction procedure. A gas diffusion electrode was made by hot pressing the sheets of the RL and GSL with the cupper mesh at 380°C and 4.9 MPa for 1min.

Potential of the gas diffusion electrode was measured for applied current densities in 32wt% sodium hydroxide solution at 80°C while supplying pure oxygen gas. A reversible hydrogen electrode in the same solution (RHE) at the same temperature was used as the reference electrode, to which the potential of the gas diffusion electrode was referred. The electrochemically active area of the electrodes was 12.56 cm^2 (geometrical).

The cyclic voltammograms (CV) of the Metal-C and the C-Electrode were measured in 32 wt% NaOH at 80°C under nitrogen or oxygen atmosphere. The CV measurements were conducted in the potential range between 0.4V and 1.5 V at 0.1 to 1.0 V s^{-1}.

Result and discussion

I-V performances of oxygen reduction at the Metal-C and the C-Electrodes are shown in Fig.1. It can be seen that the C-electrode with no catalyst shows reasonable activity for oxygen reduction, although its potential is lower than the Mn-C, Ag-C and Co-C Electrode by ca 100mV in the entire region of the current densities studied. However, Ni-C and Fe-C Electrodes are lower than the C Electrode. The ladder of the oxygen

reduction performance is Mn-C > Ag-C > Co-C > C > Ni-C > Fe-C.

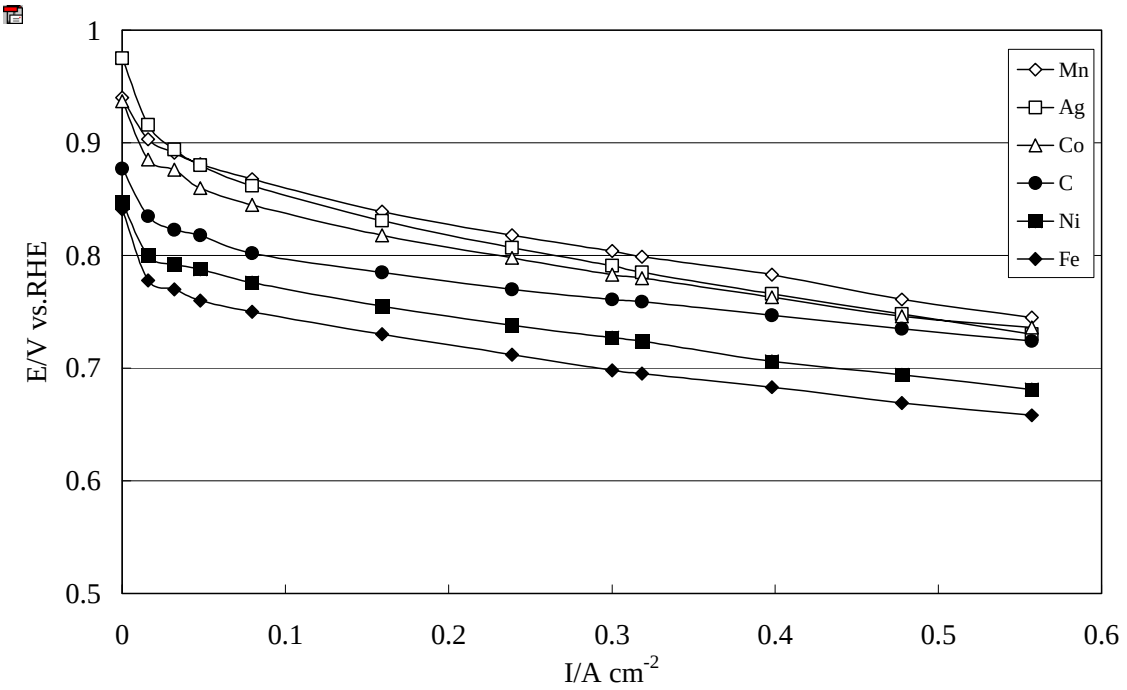

Fig.1 *I-V performances of oxygen reduction at the Metal-C and C-Electrodes*

Figure 2 shows the cyclic voltammograms of the Metal-C and the C-Electrode observed in oxygen atmosphere. The cathodic current observed on each electrodes below ca 0.8 V are due to oxygen reduction, while the voltammetric feature observed above 0.8 V is specific to each electrode. The Mn-C and Co-C Electrode show similar feature to that observed in nitrogen atmosphere corresponding to oxidation/reduction on the Ag surface, while there is a broad anodic current peak around 1.2 V for the C-, Ni-C and Fe-C Electrode which is absent in nitrogen atmosphere. In view of the mechanism of the oxygen reduction on the C-, Ni-C and Fe-C Electrode, origin of the anodic current peak observed on the Ni-C, Fe-C and C-Electrode are most likely oxidation of $H_2O_{2\ produced}$ during negative potential sweep. Production of H_2O_2 during oxygen reduction on the C-Electrode was suggested based on the number of electrons determined from the rate of oxygen consumption. Results of the CV measurements showed in Fig. 2 gives another support for the H_2O_2 formation during oxygen reduction on the Fe-C, C- and Ni-C Electrode.

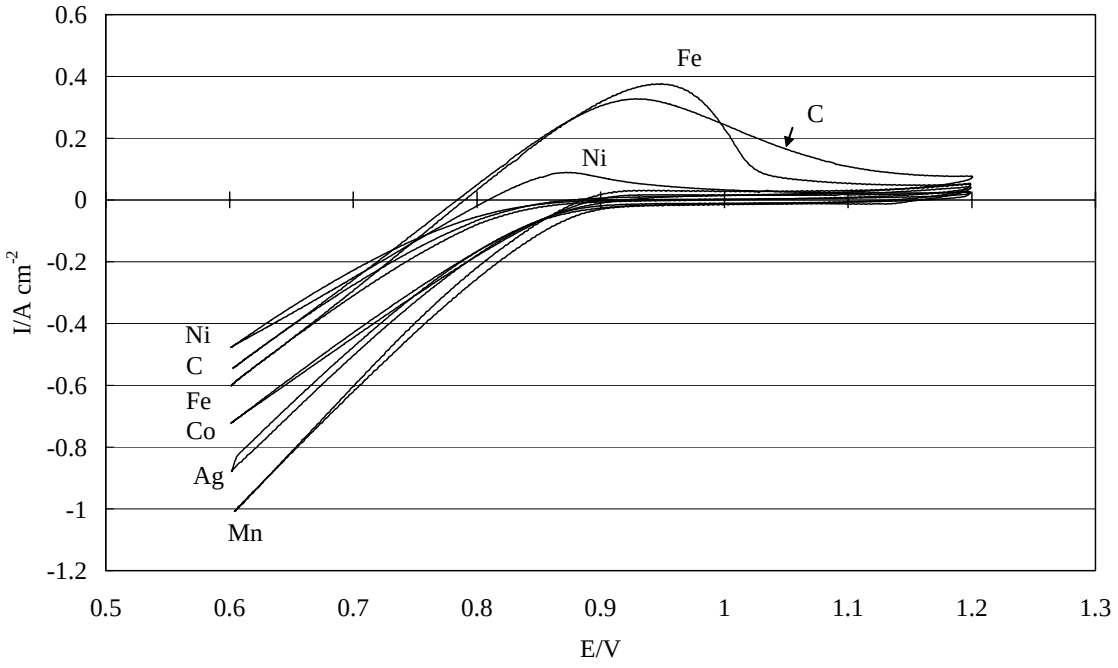

Fig.2 *The cyclic voltammograms of the Metal-C and the C-Electrodes.*

Conclusion

Comparative studies of oxygen reduction on gas diffusion electrodes Mn, Co and Ag catalyst in the reaction layer has shown that addition of silver not only enhances oxygen reduction but also affects the reaction mechanism and promotes the four-electron reduction of oxygen to produce OH^-. Fe, Ni and C catalysts production of H_2O_2 as the major reaction intermediate predominates on the carbon support as demonstrated by the CV measurements.

References

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