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HIGHLY ACTIVE Ag/C ELECTRODE FOR OXYGEN DEPOLARIZED CHLOR-ALKALI ELECTROLYTIC CELL

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The polytetrafluoroethylene-bonded carbon electrode on which silver was loaded by "ion exchange method" gave 300 mA/cm^2 at -0.12 V (vs. Hg/HgO) for the reduction of oxygen in 9 mol/dm^3 NaOH at 80 °C, and it may be useful for the oxygen depolarized chlor-alkali electrolytic cell. The high activity of the electrode was found to come from the fine dispersion of silver and the oxidation-treatment of carbon surface.

A new type of electrolytic cell for the brine electrolysis which utilizes cathodic reduction of oxygen instead of hydrogen evolution has become of interest from an energetic point of view.$^{1)-3)}$ It is said that the use of an oxygen cathode in the membrane cell will reduce the cell voltage by a ca. 1 volt (or a ca. 30 percent reduction in electrical energy).$^{3)}$ In order to develop this type of electrolytic cell, one needs highly efficient, inexpensive oxygen electrodes which are stable under severe operational conditions. In spite of active studies in the fields of fuel cells and metal-air batteries to develop efficient oxygen electrodes, the performance of the electrodes so far obtained is still insufficient for the brine electrolysis. We report here that the performance of PTFE (polytetrafluoroethylene)-bonded carbon electrodes on which metal catalysts are supported depends greatly on the mode of catalyst-loading and that, in the case of silver-loaded catalysts, the "ion exchange method" gives the most effective electrode. The effects of the silver dispersion and the oxidation-treatment of the carbon substrate are also described.

Amorphous carbon powder (Kishida Chemical) with BET specific surface area 128 m^2/g was used for preparing electrodes. After the loading of catalysts by various methods, the carbon powder (ca. 40 mg) was mixed with ca. 26 mg of PTFE suspension (Daikin Kogyo, 61 wt% solid content). The paste obtained was applied on a 100 mesh nickel screen to form a PTFE-bonded carbon electrode of 1.76 cm^2 area, 0.05 cm thickness and 23 mg/cm^2 bulk density. The electrode was then cured at 300 °C for 0.5 h in a stream of a mixture of nitrogen and hydrogen (7 : 3, volume ratio). The electrochemical reduction of oxygen was carried out in a "floating" half cell$^{4)}$ in 9 mol/dm^3 NaOH at 80 °C under a pure oxygen flow. The potential of the working electrode was regulated vs. an Hg/HgO reference electrode by using a potentiostat (Hokuto Denko, HA-303). A platinum plate (4 cm^2) was used as the counter-electrode.

Silver (1.5 ~ 6.5 wt%), which was mainly used as electrode catalyst in this work,

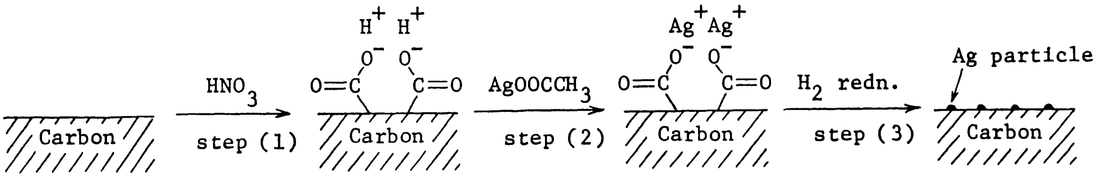

Fig. 1 Schematic diagram for the ion exchange method

was loaded on the carbon powder by three methods: (i) commercial silver powder (Mitsuwa Chemical, 99.9 % purity, 325 mesh), after reduction-treatment, was mechanically mixed with the carbon, (ii) the carbon was impregnated with 0.1 mol/dm^3 $AgNO_3$ followed by a thermal treatment for 2 h at 450 °C, and (iii) silver ions were "ion-exchanged" on the carbon surface as described below. The above-mentioned carbon electrodes will be denoted by Ag/C(M), Ag/C(Im), and Ag/C(IE), respectively. The silver particle size was determined by X-ray diffraction analysis (Rigaku Denki, D-3F) or electron microscopic observation (JEOL, JEM-1000 of HVEM LAB, Kyushu University, 1000 kV).

The ion exchange method for supporting metal catalysts on carbon is known in the field of heterogenous catalysis.$^{5)}$ Ag/C(IE) in this work was prepared in the following way. (1) Treatment of the carbon surface with 7 mol/dm^3 HNO_3 for 5 h at 95 °C to introduce surface acidic groups (such as carboxylic groups). (2) Exchange of protons of the acidic groups with silver ions in 0.02 mol/dm^3 $AgOOCCH_3$ at 25 °C for 2 days. (3) Reduction of the exchanged silver ions to fine silver particles in a hydrogen flow for 0.5 h at 200 °C. Each step is schematically shown in Fig. 1.

The electrochemical reduction of oxygen on carbon electrodes in known to proceed via hydrogen peroxide ions in alkaline solutions$^{6)}$: $H_2O + O_2 + 2e \rightarrow HO_2^- + OH^-$, $HO_2^- \rightarrow OH^- + (1/2)O_2$. Preliminary experiments confirmed that the addition of noble metal catalysts to the carbon electrode promoted the activity for the electrochemical oxygen reduction in the order Ag > Pt > Pd > Au. As the order agrees with the catalytic activity order reported$^{7)}$ for the catalytic decomposition of H_2O_2, the high activity of silver in the electrode reaction is considered to come from its catalytic ability to decompose HO_2^- ions which are produced on the carbon in the cathodic oxygen reduction.

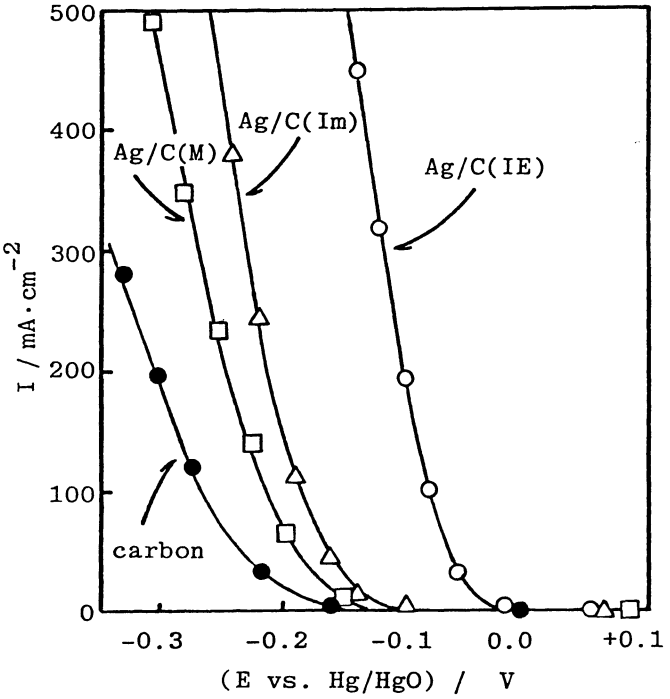

Fig. 2 I - E curves on various carbon electrodes with 6.5 wt% Ag catalyst (9 mol/dm^3 NaOH, 80 °C).

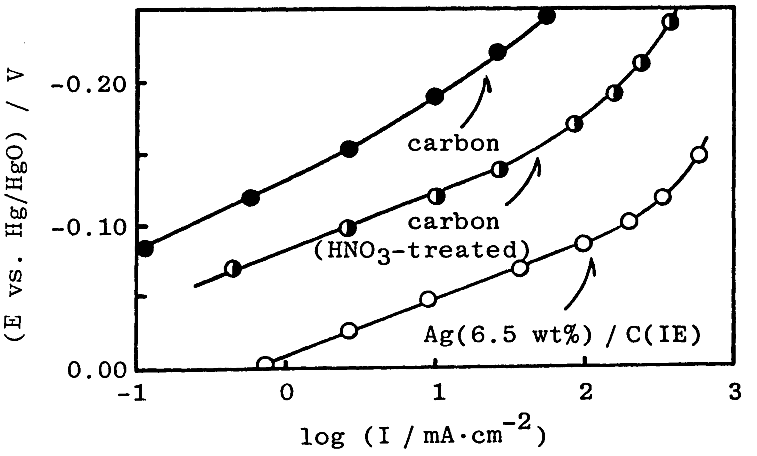

Fig. 3 Cathodic Tafel plots on various carbon electrodes (9 mol/dm^3 NaOH, 80 °C).

Fig. 2 shows cathodic polarization curves for the carbon electrodes with or without 6.5 wt% (1.6 mg/cm^2-electrode area) silver catalyst in 9 mol/cm^3 NaOH at 80 °C. It is seen that any of the three electrodes loaded with silver exhibits higher current density than the electrode without silver at the same potential (e.g., -0.2 V), that is, the activity of the carbon electrode is increased by the presence of the silver catalysts. It is also evident that the degree of the increase depends very much on the way of catalyst loading, giving the electrode activity order Ag/C(IE) >> Ag/C(Im) > Ag/C(M). The overpotential of the Ag/C(IE) electrode was 0.38 V at 300 mA/cm^2 with respect to the equilibrium potential (+0.26 V vs. Hg/HgO) for $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$: the voltage is ca. 0.2 V smaller than that of the carbon electrode without silver. The activity of the Ag/C(IE) electrode appears to be enough for practical use in the chlor-alkali cell.

Two factors are conceived for the high activity of the Ag/C(IE) electrode shown in Fig. 2, i.e., the oxidation-treatment of the carbon, and the presence of the finelly dispersed silver particles. The E-log I curves for the cathodic oxygen reduction were given in Fig. 3 on the three types of electrodes, that is, the non-treated carbon electrode, the HNO_3-treated carbon electrode (see the step (1) in Fig. 1), and Ag(6.5 wt%)/C(IE). It is seen that the electrode activity (the current density in the Tafel region) of the HNO_3-treated carbon is ca. 10 times higher than that of the non-treated carbon. This shows that the oxidation-treatment increases the activity of the carbon electrode significantly. This effect seems to be ascribed to the formation of the surface acidic groups, but further investigation is necessary for this phenomenon. The effect of the presence of the silver catalyst can be evaluated from a comparison of the electrode activity between Ag(6.5 wt%)/C(IE) and the HNO_3-treated carbon. The current density of Ag/C(IE) is ca. 80 times higher than that of the HNO_3-treated carbon in the Tafel region. This fact indicates that

Table 1 Silver particle size in Ag(6.5 wt%)/C

		Ag/C(IE)	Ag/C(Im)
Ag particle size nm	X-ray[a)]	6.5	12.5
	HVEM[b)]	5 ~ 8	10 ~ 20

a) Determined by X-ray diffraction analysis.
b) Determined by high voltage electron microscopic observation.

the effect of the presence of silver on the electrode activity is much more remarkable than that of the surface-treatment. The large effect of the presence of silver in Ag/C(IE) is probably associated with the finely dispersed state of silver particles. As shown in Table 1, the silver particle size in Ag/C(IE) was almost one half of that in Ag/C(Im). The effect of the particle size is more clearly shown by an experiment in which the silver particle size in Ag/C(IE) was changed by changing the temperature of the reduction of the silver ion-exchanged carbon (step (3) in Fig. 1). The silver particle sizes and the current densities at 0.4 V overpotential are shown in Table 2. Evidently the electrode activity (the current density) increases with the silver dispersion, i.e., with the decrease in particle size.

Table 2 Correlation between Ag particle size and electrochemical activity of Ag(4.4 wt%)/C

	Reduction temperature 200°C	 400°C	 550°C
Ag particle size[a)] / nm	6.3	7.3	9.4
Current density[b)] / $mA \cdot cm^{-2}$	345	200	120

a) Determined by X-ray diffraction analysis.
b) Overpotential: 0.4 V, 9 mol/cm^3 NaOH, 80 °C.

A stability test was carried out by subjecting the Ag/C(IE) electrode to a short-term operation at 500 mA/cm^2 in 9 mol/dm^3 NaOH at 80 °C. No appreciable increase in overpotential was observed during 10 h. The degradation of the electrode, e.g., the coagulation of the silver particles and the dissolution of the silver into the electrolyte, does not seem to have taken place to any significant extent at least for such a short period. However, a long-term stability test of this electrode is necessary for the practical use.

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