Degradation Evaluation of Gas-Diffusion Electrode in Oxygen-Depolarized Cathode for Chlor-Alkali Membrane Cell

Keiichi Okajima, Kenji Nabekura, Takaya Kondoh, Youhei Shibuya and Masao Sudoh

Department of Materials Science and Chemical Engineering, Shizuoka University
3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan

The kinetics of oxygen reduction on gas-diffusion electrode has been extensively investigated, but quantitative data on the electrode characteristic or the mechanism of the electrode degradation are not sufficient. Therefore, it is necessary to have quantification of the electrode degradation. The cathodic properties of oxygen reduction on the gas-diffusion electrode were determined by an impedance method. Comparing the electrodes using Ag and Pt catalysts, the electrode characteristics were evaluated by the impedance parameters. The surfaces of the gas-diffusion electrodes were analyzed by XPS.

The electrodes tested in this study were as follows; P-1 and P-2 were basic gas-diffusion electrodes produced by Tanaka Noble Metal Co. 0.56 mg/cm^2 of Pt catalyst was loaded on the electrode. P-1 was a virgin electrode and P-2 was a used one for short-term. A-1~3 electrodes were the prototype gas-diffusion electrodes with Ag nano-particle catalyst. A-1 was a virgin electrode and A-2 was an used one for short-term. A-3 was used one for long-term. The electrochemical measurements were carried out in a three-electrode cell containing 30 wt % NaOH electrolyte maintained at 353 K. The gas-diffusion electrode was mounted into a PTFE holder containing a silver ring current collector and an inlet pipe to feed the oxygen gas. The electrode area exposed to the electrolyte was 3.14 cm^2. A platinum plate was used as the counter electrode. An RHE was connected to the cathodic compartment via a silicon tube through a Luggin capillary whose tip was placed close to the working electrode surface. A Nyquist plot was obtained at the potential of 860 mV (vs. RHE) with AC voltage amplitude of 5 mV. Figure 1 shows a simplified structure model of a gas-diffusion electrode, and an equivalent circuit for AC impedance analysis. The AC impedance analysis supplies information on the charge-transfer resistance and the double-layer capacitance of the electrode during the oxygen reduction process.[1)] The symbols of the figure shows that R_s is the electrolyte resistance, C_d is the double-layer capacitance, R_{ct} is the charge-transfer resistance, and Z_d is the diffusion impedance.

Figure 2 shows Nyquist plots for oxygen reduction on the P-1, P-2 (standard) and A-1 to A-3 (Ag catalyst loaded) electrodes at 353 K and the simulation curves. The Nyquist plots of all electrodes present semicircles. The diameters of the Nyquist plots increased with increasing the working time. Table 1 depicts impedance parameters calculated by the AC impedance analysis of the electrodes at 353 K. The charge-transfer resistance increased at 5.4 times in comparison with P-2 electrode and P-1 electrode. In A-3 electrode and A-1 electrode, increase of R_{ct} was 4.2 times, though A-3 electrode was used for long-term. Figure 4 shows the XPS spectra of the A-1~3 electrodes. As the electrode degradation progressed from the A-1 electrode to A-3, peaks of F and C decreased and that of O increased. Na was detected on A-2 and A-3 electrodes. The degradation with use of the electrode surface was clarified by the XPS analysis.

1) M. Sudoh, T. Kondoh, N. Kamiya, T. Ueda and K. Okajima, *J. Electrochem. Soc.*, **147** 3739 (2000).

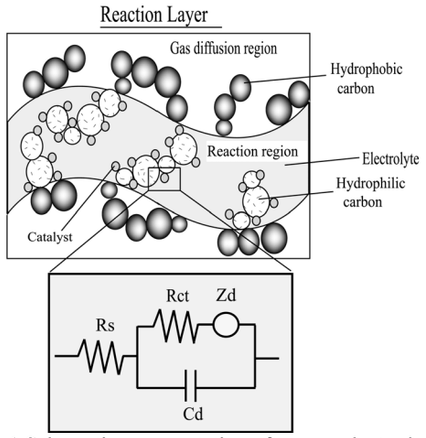

Fig. 1 Schematic representation of porous electrode and the equivalent circuit for the AC impedance analysis.

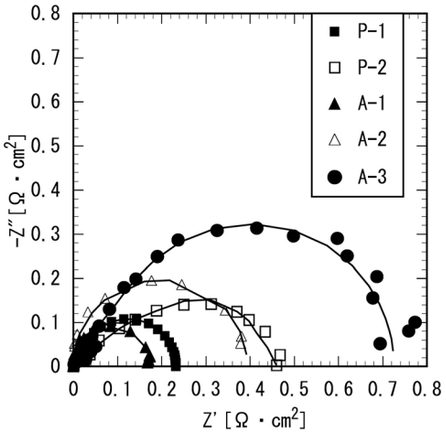

Fig. 2 Nyquist Plots of different electrodes at E=860 mV (vs. RHE).

Table 1 Impedance parameters on various electrodes at 353K.

Electrode	C_d [mF/cm^2]	R_{ct} [Ω cm^2]
P-1	16.7	0.114
P-2	23.1	0.615
A-1	14.4	0.166
A-2	29.3	0.376
A-3	38.4	0.695

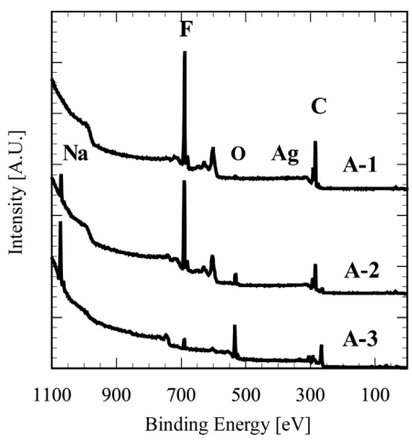

Fig. 3 XPS spectra of A-1, A-2 and A-3 electrodes.