



Accelerated degradation testing of gas diffusion electrodes for the chlor-alkali process[☆]

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Abstract

The chlor-alkali industry consumes large amounts of energy. The gas diffusion cathode has been investigated for energy saving modifications. To commercialize the process, an electrode of high durability is required. Electrolytic operating factors causing electrode deterioration were examined. Under the condition of low oxygen concentration operation, the degradation of the electrode was significantly accelerated. The life of the electrode was also estimated by an acceleration test. The relationship between the logarithm of the life and the operating overvoltage was linear. Using this relation, the life of a possible mass production electrode was assumed to be five years or more.

1. Introduction

At present, chlorine, caustic soda and hydrogen are produced in Japan by the ion-exchange membrane process. The main problem in the electrolysis process is the high power consumption. In the chlor-alkali industry, oxygen diffusion electrodes have been developed to replace conventional hydrogen evolution electrodes in chlor-alkali membrane cells since the 1980s [1–3]. For energy saving, a new electrolysis technology combined with a gas diffusion electrode has been researched since 1993 [4–11].

To commercialize this technology, a highly-durable electrode is essential. To improve GDE durability, an acceleration test which can degrade the electrode in a short period is necessary in order to determine the life of the electrode. Acceleration test equipment was installed to determine the factors that accelerate degradation. Furthermore, the durability of a possible mass production electrode was estimated by using the acceleration test and the life estimation equation was introduced.

2. Experimental details

2.1. Gas diffusion electrodes

The gas diffusion electrodes consisted of a reaction layer, a gas supply layer and a current distributor. The

reaction layer was made from hydrophobic carbon black, hydrophilic carbon black, PTFE and a Ag catalyst. The thickness of the layer was about 100 μm . The gas supply layer was made from hydrophobic carbon black and PTFE. The thickness of the layer was 700–800 μm . An Ag mesh as the current distributor was buried in the gas supply layer. The gas supply layer and the reaction layer were joined by a hot-press technique [12–16].

2.2. Acceleration test

Figure 1 shows the cell for the acceleration test. The test was carried out in a chlor-alkali process. Chlor-alkali cells with an effective area of 33.4 cm^2 were used. The anolyte of purified brine was supplied from the cell bottom, and the catholyte was circulated by keeping the outlet concentration of sodium hydroxide at 32 wt%. Oxygen gas added with nitrogen was supplied from the cell top. The temperature of the anolyte, catholyte and reactant gas, catholyte concentration and oxygen concentration were controlled by a computer. Standard electrolysis conditions, were: current density 3 kA m^{-2} ; temperature 88 $^{\circ}\text{C}$; catholyte concentration 32 wt% NaOH; and oxygen concentration 93%.

The degradation factor was examined using the current density, oxygen concentration, temperature and catholyte concentration. To evaluate the degradation of the electrode, the overvoltage (anode overvoltage + cathode overvoltage) was measured by the current interrupt ion method.

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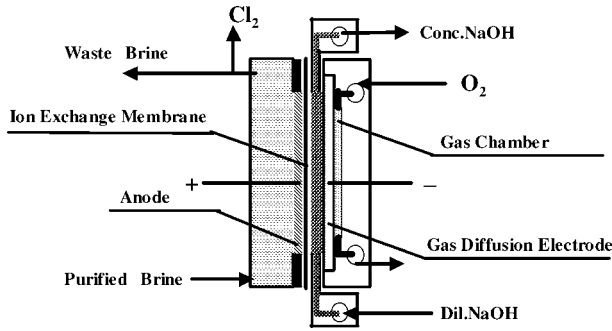


Fig. 1. Electrolytic cell for acceleration test.

2.3. Analysis

The Na-distribution in the cross section of the electrodes after electrolysis was measured by electron probe microanalysis (EPMA) to estimate the wetting depth of the electrodes after electrolysis.

2.4. Life estimation of the gas diffusion electrode

An acceleration test at low oxygen concentration was carried out, and the durability of a current trial electrode was also investigated. The life of an electrode was judged from the occurrence of a rise in the overvoltage. This was defined as the time up to the overvoltage rising to 0.75 V when returning to standard conditions after the accelerated conditions.

3. Results and discussion

The result of a long-term test is shown in Figure 2. Electrode 1 consisted of the reaction layer, the gas supply layer, and Ag mesh as the current distributor. Electrode 2 was similar to electrode 1 except for the Ag mesh, where porous Ni coated with Ag was used. The overvoltage (anode overvoltage + cathode overvoltage) of electrode 1 increased from 0.48 to 0.75 V after three years (1200 days). Electrode 1 was degraded. Electrode

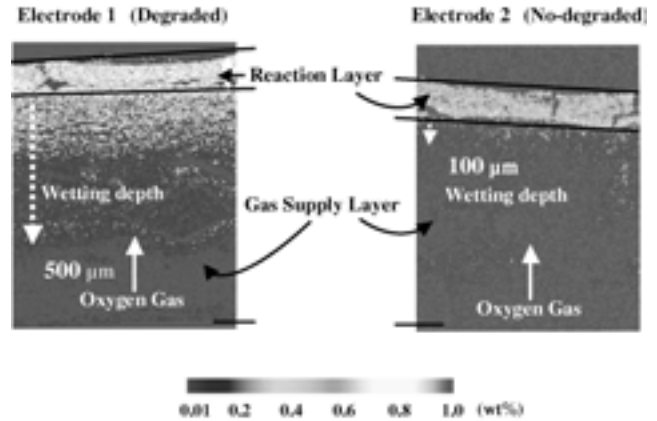


Fig. 3. Na-distribution in the cross section of long-term run electrodes. Bright area signifies Na rich.

2 suffered a voltage increase from 0.45 to 0.50 V. Electrode 2 showed no degradation.

To investigate the cause of the degradation, The Na-distribution in the cross section of electrodes 1 and 2 was measured by electron probe microanalysis (EPMA). The results of the analysis are shown in Figure 3. The wetting depth of electrodes 1 and 2 were about 500 μm and 100 μm, respectively. The degraded electrode received heavy Na (catholyte) intrusion. Therefore, it was thought that the degradation was caused by a heavy coverage at the reaction points because of the catholyte intrusion into the gas supply layer.

3.1. Operating factors to accelerate degradation

The factors to accelerate the degradation of the electrode were investigated and their effect on the operating conditions are shown in Table 1 along with results.

Electrode A in this test was the same type as electrode 1 for the long-term test.

The current density, temperature and catholyte concentration for run 1 were changed to higher than the standard condition. However, the degradation of the electrode was only a 56 mV overvoltage increase. Only

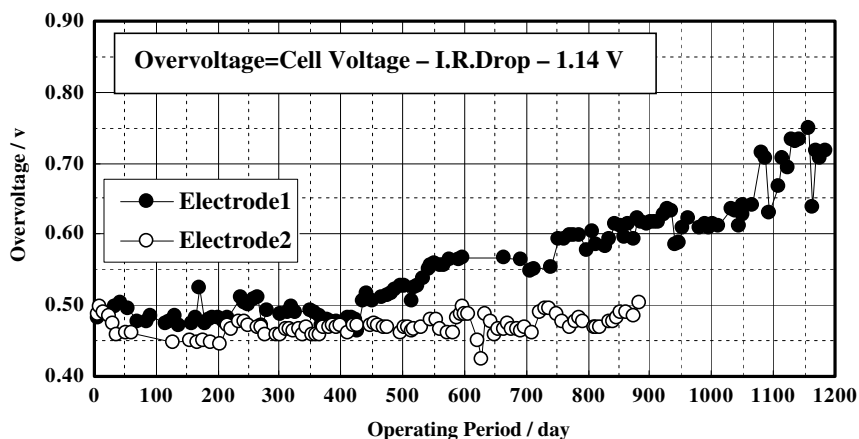


Fig. 2. Long-term test Electrode size: 1 dm²; Current density: 3 kA m⁻²; temperature: 80 °C; catholyte concentration: 32 wt% NaOH.

Table 1. Operation factors

Acceleration test	Run 1	Run 2
Operating conditions		
Current density/k Am ⁻²	6	3
Temperature/°C	98	88
NaOH conc./wt. %	37	32
Oxygen conc./%	93	46
Supply gas		
O ₂ /Nml min ⁻¹	50 (1.4 times of stoichiometry)	50
N ₂ + Ar/Nml min ⁻¹	4	54
Results		
Operating period/day	62	37
Overvoltage increase/mV	56	294
Wetting depth/μm	165	600

the oxygen concentration in run 2 was changed to lower than the standard condition. The degradation was a very remarkable 294 mV. Therefore, the oxygen concentration was identified as the operating factor that accelerated the degradation.

Figure 4 shows the Na-distribution in the cross section of electrodes after runs 1 and 2 by EPMA. The wetting depth of the electrodes for run 1 and 2 were about 165 μm and 600 μm, respectively. With the same results as the long-term test, the degradation electrode had a significant Na (catholyte) intrusion.

Figure 5 shows the relationship between wetting depth and overvoltage. The wetting depth and overvoltage increase were linearly related at 0.5 mV μm⁻¹. As a result of both the acceleration test and long-term test overlapping on the same line, the degradation of the electrode after the acceleration test and long-term test seemed to occur by the same mechanism of catholyte intrusion into the gas supply layer (wetting progress). Therefore, the acceleration test at a low oxygen concentration is effective for the life estimation of the electrode.

3.2. Acceleration test at low oxygen concentration

An example of the relation between oxygen concentration and overvoltage for electrode A is shown in

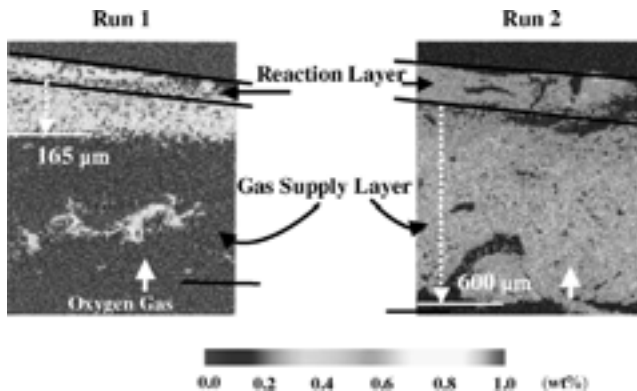


Fig. 4. Na-distribution in the cross section of electrodes. Bright area is Na rich.

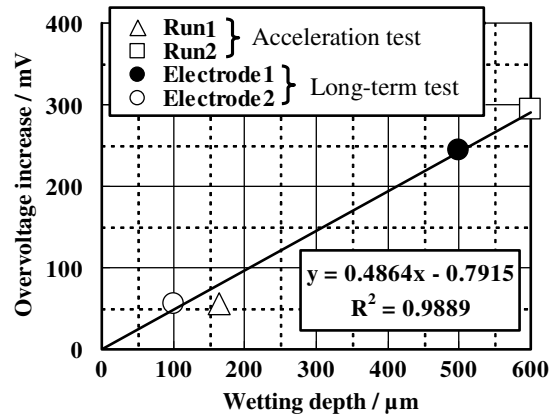


Fig. 5. The relationship between wetting depth and overvoltage.

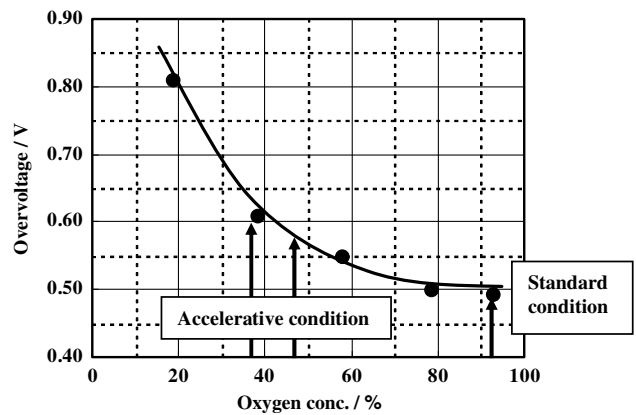


Fig. 6. The relationship between overvoltage and oxygen concentration.

Figure 6. The overvoltage of the electrode rose significantly at low oxygen concentration.

The overvoltage change of electrode A during the acceleration test is shown in Figure 7, where the oxygen concentration was 93%, 47% and 37%. The life of the electrode depended on the initial overvoltage during the acceleration test rather than the oxygen concentration.

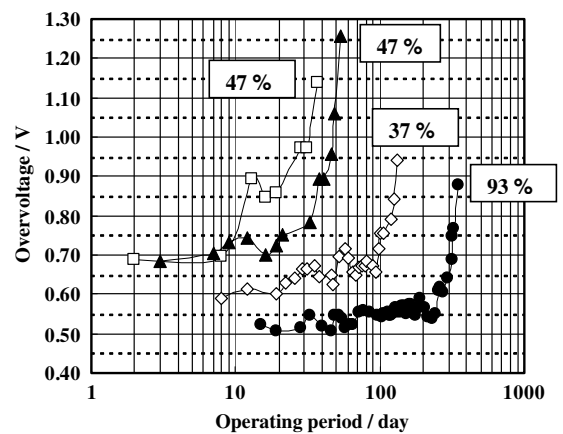


Fig. 7. Acceleration tests of electrode A under the conditions of various oxygen concentration.

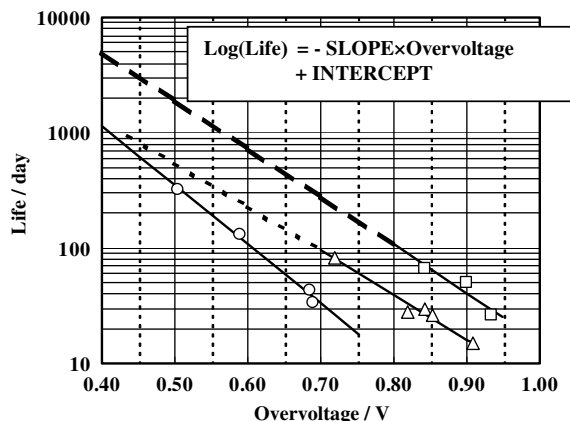


Fig. 8. Life estimation of the electrodes of A(O), B(Δ) and C(\square). Current density: 3 kA m^{-2} ; temperature: $88 \text{ }^\circ\text{C}$; catholyte concentration: 32 wt% NaOH.

It is assumed that the high overvoltage promotes the formation of hydrogen peroxide which oxidizes the carbon. The life of the electrode was plotted versus the initial overvoltage during the acceleration test in Figure 8. The relationship between the logarithm of the life of the electrode and the overvoltage was linear. Using this relation, the life of the electrode follows the equation:

$$\log(\text{Life/day}) = -\text{Slope} \times (\text{Overvoltage/V}) + \text{Intercept}$$

The life of electrode A was estimated to be about 1.7 years (630 days) at an overvoltage of 0.45 V under standard conditions (93% of oxygen concentration).

The results for electrodes B and C are also shown in Figure 8. These electrodes were also fabricated in a similar manner to electrode A. The Slope of these three kinds of electrode were about the same. The intercept, was different, but the three kinds of electrode consisted of the same material. It was assumed that the dispersion condition between the carbon and PTFE within the electrode was different. The durability of these elec-

trodes is improving, and the life of the improved electrode was assumed to be five years or more.

In conclusion, the electrode degradation was accelerated at low oxygen concentration. The logarithm of electrode life was linearly dependent on the operating overvoltage. Using this relationship, the life of the most recent trial electrode was estimated to be more than five years.

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