

Short communication

Improving MEA durability by using surface-treated catalysts

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Abstract

In order to improve the durability of membrane electrode assemblies (MEAs), surface treatments of carbon-supported Pt catalysts are studied. When treating catalysts with amines, especially hindered amine light stabilizers (HALS), durability testing of an MEA drastically improved. The amino groups in the molecule of HALS are considered to react with carboxyl groups on carbon support to form complexes. It was confirmed that hydrogen peroxide formation is retarded in the case of HALS-added catalyst by using a hydrogen peroxide test paper. Together with the results of the catalyst surface treatments using nitric acid and dehydrated ethanol, it was clarified that surface functional groups, carboxyl and/or hydroxyl groups, on the carbon support play an important role in the generation of hydrogen peroxide during fuel cell operation.

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1. Introduction

Hydrogen is the focus of world attention because it is clean and environmentally friendly. Proton exchange membrane fuel cells (PEMFCs), which use hydrogen and oxygen as fuels, have been considered one of the most promising power sources of the future. In order to establish PEMFCs as a practical power source, however, the system is required to have more stable performance. It is reported that membrane electrode assemblies (MEAs) tend to fail with pinholes in the membrane in too short a time for the realization of PEMFCs [1–2]. Peroxide radicals, which are derived from hydrogen peroxide, are generally blamed for the chemical degradation of the perfluorinated sulfonic acid (PFSA) membranes. Although a large number of studies [3–4] have been made on membrane degradation by peroxide radicals, little is known about the relationships between hydrogen peroxide formation and catalysts. We reported [5] that MEA durability can be drastically improved by using a heat-treated catalyst, pointing out that surface functional groups, hydroxyl and/or carboxyl groups, on the carbon support are responsible for the hydrogen peroxide formation that can lead to the membrane degradation in an MEA. The heat-treated catalyst, however, has a larger platinum crystalline diameter and has less organic contaminant

remaining on carbon support than a non-heat-treated catalyst because of the treatment at a very high temperature. It has not been excluded that the smaller platinum crystalline diameter or organic contaminant might promote hydrogen peroxide formation. This study shows that the MEAs using catalysts whose acidic surface functional groups are neutralized have better durability even though the platinum crystalline diameter remains the same and organic contaminant is not removed.

2. Experimental

2.1. Amine-treated catalysts

2.1.1. MEA preparation

Carbon-supported Pt catalyst (46%Pt/Ketjen: catalyst-A) or carbon-supported Pt/Ru catalyst (30%Pt–23%Ru/Ketjen: catalyst-B), water, ethanol and ionomer solution (Flemion, 910 equivalent weight (EW); Asahi Glass Co. Ltd.) were mixed with a homogenizer. The ratio of ionomer to carbon support was 0.8. Amine-treated catalyst inks were formulated in the following manner. Catalyst-A or catalyst-B and water were stirred and this was followed by the addition of an ethanol solution of amine instead of ethanol in the case of the reference ink described above. There should be no difference between the amine-treated catalyst inks and the reference ink in terms of organic contaminant on carbon support. The suspension was

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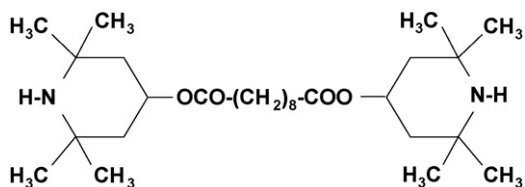


Fig. 1. Chemical structure of LA77.

mixed with a homogenizer. Amines used were tripropylamine and bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (LA77, a product of Adeka Corporation). LA77 is one of the hindered amine light stabilizers (HALS) with a chemical structure as shown in Fig. 1.

Catalyst inks were coated to fabricate thin-layer electrodes, which were transformed via a decal method onto Flemion membrane (910EW, Asahi Glass Co. Ltd.) to prepare an MEA. The MEA, which has an active electrode area of 25 cm² was assembled into a test cell.

2.1.2. OCV testing

Open circuit voltage (OCV) testing was carried out under condition 1 in Table 1.

Catalyst-A and B were used for the cathode and anode, respectively. In the case of amine-treated catalysts, 4 wt.%-tripropylamine-added anode and 10 wt.%-tripropylamine-added cathode, 5 wt.%-LA77-added anode and 7 wt.%-LA77-added cathode were used. Added amounts are expressed in weight percentage per catalyst. X-ray diffraction showed that platinum crystalline diameters of both 7 wt.%-LA77-added catalyst-A and 5 wt.%-LA77-added catalyst-B were 2–3 nm and 3–4 nm, respectively, which were the same values as those of catalysts without LA77.

2.1.3. Durability testings and polarization measurement of an MEA

Durability testing was carried out under the condition 2, and polarization curves were obtained under the condition 3 in Table 1.

2.1.4. MEA operation and the fluoride ion release rate (FRR)

In order to compare the effect of surface treatment of catalysts on MEA degradation, the FRR was determined, operating the MEA at 0.2 A cm⁻² under condition 4 in Table 1. The product water from the test cell was trapped in a 0.1N potassium hydrox-

ide aqueous solution. The amount of fluoride ion in the product water was measured with an ion chromatography, Dionex DX-320 system, equipped with an Ion Pac AS12A column. The FRR was determined based on the amount of fluoride ion, the period of sampling time and the area of a membrane.

2.1.5. Zeta potential measurements

LA77 (1–13 wt.% per catalyst) containing catalyst inks were formulated by adding an ethanol solution of LA77 to a mixture of catalyst and water followed by the addition of ionomer solution (Flemion, 910EW; Asahi Glass Co. Ltd.) while homogenizing the suspension. Zeta potential was measured by using a zeta potential analyzer, ESA-9800 (Matec Applied Science). With ESA-9800, pH can be measured simultaneously with zeta potential.

2.1.6. Determination of hydrogen peroxide concentration

A hydrogen peroxide test paper (Ryoko Chemical Co. Ltd.) was used to determine the hydrogen peroxide concentration in a catalyst suspension where hydrogen is bubbled. The concentration was able to be determined using a standard color table over a range of 0–25 ppm with an accuracy of about 30%.

2.2. Other catalyst treatments

2.2.1. UV/ozone treatment

Catalysts were spread on a glass plate and underwent ultraviolet (UV)/ozone treatment (70–90 °C, 10 mW cm⁻²) for 20 min using an UV/ozone treating device, NL-UV342 (Japan Laser Electronics).

2.2.2. Dehydrated ethanol treatment

The required amount of dehydrated ethanol (Junsei Chemical Co. Ltd.) to formulate a catalyst ink was added to a catalyst under nitrogen atmosphere and the mixture was left overnight. Water and ionomer solution (Flemion, 910EW; Asahi Glass Co. Ltd.) were added to the mixture and homogenized in the same manner described in Section 2.1.1.

2.2.3. Nitric acid treatment

One hundred grams of 20% nitric acid was added to 5 g of catalyst and the slurry was kept stirred with a magnetic stirrer at 60 °C for 20 h. After filtration the catalyst was washed with a large amount of pure water until the pH of the water after washing became neutral. The catalyst was dried at 120 °C under nitrogen atmosphere overnight.

Table 1
Operating conditions

Conditions	Current density (A cm ⁻²)	Pt badings		Membrane thickness (×10 ⁻⁶ m ⁻¹)	Cell temperature (°C)	Humidity		Stoichiometry	
		Anode (mg cm ⁻²)	Cathode (mg cm ⁻²)			Anode (%RH)	Cathode (%RH)	H ₂	Air
1	0	0.20	0.40	50	90	50	50	2.0	2.0
2	0.2	0.35	0.60	30	90	34	34	1.4	2.5
3	0.2	0.50	0.50	50	70	81	100	1.4	2.5
4	0–1.0	0.35	0.60	30	70	81	100	1.4	2.5

Pressure: ambient pressure.

2.2.4. Determination of surface functional groups

Carbon-supported catalysts were treated with an aqueous solution of Na₂CO₃ and NaOH so that the functional groups on the carbon support would convert to sodium salt depending on the basicity of the alkali. The number of functional groups were titrated in a manner reported in the literature [6].

3. Results and discussion

3.1. Amine-treated catalysts

3.1.1. OCV testing

Carbon-supported catalysts (catalyst-A and B) were treated with amines, HALS (LA77) or tripropylamine, so that the amino groups would react with the acidic functional groups such as hydroxyl and/or carboxyl groups on the carbon support. We conducted open circuit voltage (OCV) durability testing of MEAs with an amine-treated catalyst to both anode and cathode. Under the condition of OCV, hydroxyl radicals are produced from hydrogen peroxide, which is formed from oxygen and hydrogen at low anode potentials. A membrane in the MEA is vulnerable to hydroxyl radicals and OCV testing is, therefore, used to accelerate the degradation of MEAs. Fig. 2 shows the results of OCV testing of MEAs with amine-treated catalysts.

An MEA using a HALS-added catalyst lasts more than 200 h, maintaining a small fluoride ion release rate (FRR) of $1-2 \times 10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$, and an MEA using a tripropylamine-treated catalyst lasts for about 120 h with an FRR of $1-2 \times 10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$, whereas a conventional MEA degrades within 100 h, with an accelerating release of fluoride ion. After a sudden drop of cell voltage, a few pinholes were observed in the membrane for all three MEAs by the postmortem analysis. The catalyst treatment with LA77 is more effective than that with tripropylamine; this is because HALS, LA77, has much smaller solubility to water, less than 0.05 g per water (20 °C), and remains in the electrode, while tripropylamine, which has a solubility of 2.6 g per water (20 °C), will easily be removed from the electrode where water is produced during MEA operation. Although the HALS-added catalyst gives an improvement in OCV testing, the MEA using a heat-treated catalyst lasts more

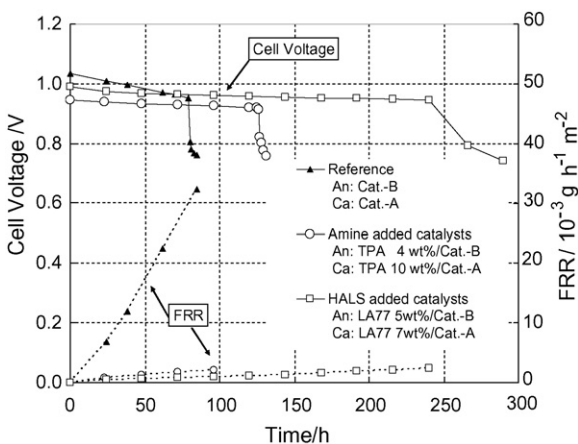


Fig. 2. OCV testing of MEAs with amine-treated catalysts.

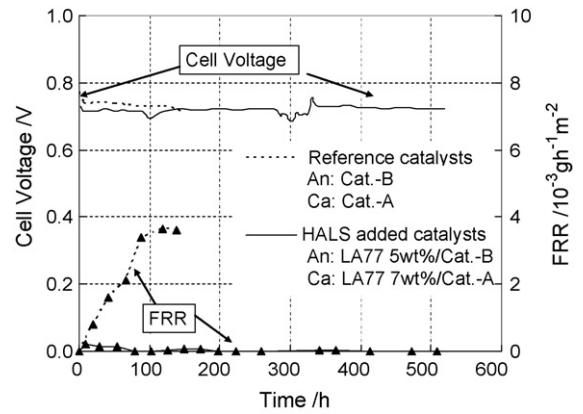


Fig. 3. Durability testing of an MEA with HALS-added catalysts operated at 0.2 A cm^{-2} .

than 700 h with an FRR of less than $0.2 \times 10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$ as reported in our previous paper [5]. The FRR in the case using a HALS-added catalyst is about 5–10 times as large as that in the case using a heat-treated catalyst. This probably indicates that HALS in the electrode is not so stable and is gradually decomposed under the OCV conditions or there might be some surface functional groups on carbon support, such as hydroxyl or carbonyl groups, which do not react with HALS.

3.1.2. Durability testing of an MEA using a HALS-added catalyst

An MEA using a HALS-added catalyst was continuously operated at 0.2 A cm^{-2} to see the long-term effect of the surface treatment on fuel cell performance. Fig. 3 shows the trends of cell voltage and the FRR for 500 h. Although the FRR for the operation of a reference MEA increases with the passage of time, an MEA using a HALS-added catalyst keeps a cell voltage of about 0.72–0.73 V, maintaining a very small FRR. No pinhole was observed for the MEA after the operation of 500 h.

3.1.3. HALS in the catalyst layers and its working mechanism to curb hydrogen peroxide generation

Polarization curves for the MEA using HALS(LA77)-added catalysts and the reference MEA are indicated in Fig. 4.

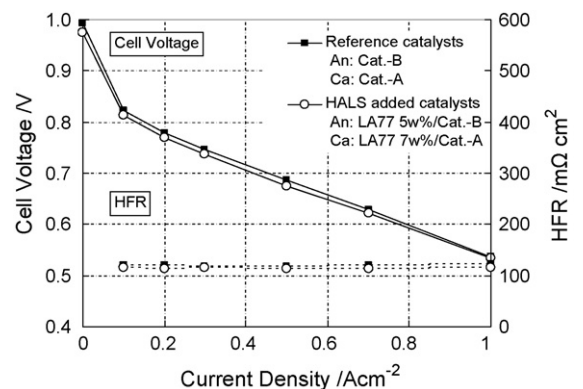


Fig. 4. Comparison of polarization curves for MEAs between HALS-added catalysts and reference catalysts.

Table 2
Number of –NH groups in HALS (LA77) and other functional groups on carbon support and ionomer to formulate 1 g of HALS-added catalysts

		Functional groups (10^{-3} mol g-cat $^{-1}$)	
		Cathode (Cat.-A)	Anode (Cat.-B)
HALS (LA77)	–NH	0.19	0.14
Carbon	–COOH	0.37	0.13
Support	–OH	0.09	0.05
Ionomer	–SO ₃ H	0.32	0.29

The numbers of –NH groups in HALS (LA77) and other functional groups on carbon support and ionomer to formulate one gram of HALS (LA77)-added catalysts are presented in Table 2. Although the number of the –NH group is 48% of that of the –SO₃H group in the anode and the number of the –NH group is 59% of that of the –SO₃H group in the cathode, the difference in cell voltage between the MEA using a HALS-added catalyst and that of the reference MEA is 9 mV at 0.2 A cm $^{-2}$ in Fig. 4. It is noteworthy that the performance does not deteriorate much despite the addition of a considerable amount of organic compound, HALS, to both cathode and anode. The drop in cell voltage could be ascribed to the poisoning of platinum catalyst by HALS. In Fig. 3 the average cell voltage for the first 100 h is 716 mV, which is 5 mV smaller than the average cell voltage for 100–200 h, showing that the poisoning compound is gradually removed during fuel cell operation. At the beginning we were concerned that HALS in the cathode would significantly deteriorate the performance of MEAs, but it seems that HALS does not have a major influence on the oxygen reduction on Pt surface in which hydrogen peroxide is believed to be an intermediate.

The small difference in the polarization curves suggests that the –SO₃H groups that facilitate proton transfer are not affected by the –NH groups, and that the –NH groups are most likely to form complexes with the –COOH groups. Hindered amine light stabilizers (HALS) are widely used as additives for plastics such as polypropylene, polyethylene, and polyvinylchloride. It is proposed that HALS terminate radical chain reactions by trapping radicals and degrading hydro-peroxide compounds [7,8]. This mechanism, however, applies to the HALS with independent –NH groups, and does not apply to the HALS-added catalysts. We also confirmed that no improvement in MEA durability was observed if HALS was added to membranes or HALS was mixed with ionomer first instead of catalysts when formulating a catalyst ink. Zeta potential measurements were conducted to assess the surface charge on the catalyst particle in the catalyst ink. The zeta potential is a function of the surface charge of the particle and the nature of the solvents in which the particle is dispersed, and it reflects the effective charge on the particles and is related to the electric repulsion. The zeta potential of catalyst inks as a function of the amount of added HALS is shown in Fig. 5.

Both of the zeta potentials of the cathode and anode inks are negative without HALS, but the potential becomes 0 mV when HALS is added 3–7 wt.% to the catalysts. The pH of the anode and cathode catalyst inks are 3.8 and 5.1, respectively. Whereas, the pH of the LA77-5%-added anode and LA77-7%-added cathode catalyst inks become 5.0 and 6.3, respectively. These results

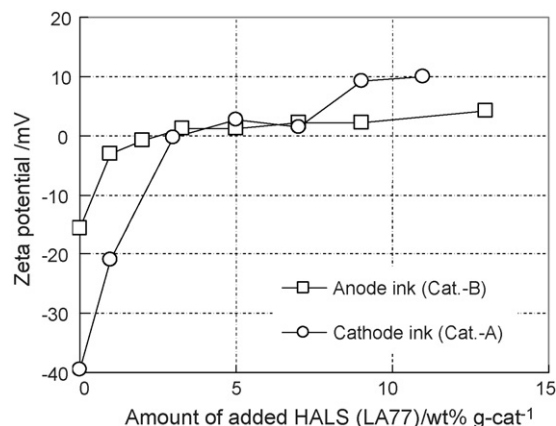


Fig. 5. Change in zeta potential of anode and cathode inks as a function of the amount of added HALS.

suggest that the amino groups in the molecule of HALS react with the surface carboxyl groups on carbon support to afford amide complexes. It is generally believed that cross-over oxygen to the H₂-covered anode catalyst forms hydrogen peroxide. Hydroxyl radicals or hydrogen peroxide radicals generated from hydrogen peroxide attack the membrane and degrade it, releasing fluoride ions [9]. It was found in our previous paper [5] that the functional group density of the catalyst had a larger impact on the fluoride ion release rate than the mere number of functional groups. When carboxyl groups on carbon support are converted to amide complexes by adding LA77, the FRR in OCV testing and durability testing becomes very small. We already reported [5] that MEAs using alkali-treated catalysts gave smaller FRR than the MEA using a non-treated catalyst when a carbon-supported Pt catalyst was treated with an aqueous solution of NaOH or an ethanol solution of EtONa so that the surface functional groups on carbon support would be converted to sodium salt. It is also known that carbonyl and hydroxyl groups play a part in industrial hydrogen peroxide production using the anthraquinone process [10]. We, therefore, presume that the active sites for the hydrogen peroxide formation have something to do with functional groups on carbon support or the surface of carbon support near the functional groups and that removing functional groups on carbon support or converting them to other forms will curb hydrogen peroxide formation in MEAs.

3.1.4. Determination of hydrogen peroxide

Liu and Zuckerbrod reported [11] that they determined the concentration of hydrogen peroxide within the proton exchange membrane by an electrochemical technique and that hydrogen peroxide forms on the anode by reduction of oxygen that crosses over through the membrane from the cathode side. We employed a hydrogen peroxide test paper to make a rough estimate of the hydrogen peroxide concentration in a catalyst suspension where hydrogen is bubbled. The hydrogen peroxide concentrations were as follows: 10–25 ppm in the suspension using a catalyst-A and 2–5 ppm in the suspension using a 7 wt.% HALS added catalyst-A. It is obvious that hydrogen peroxide formation is retarded by adding HALS to the catalyst.

Table 3
Catalyst treatments and the fluoride ion release rate (FRR) during MEA operation

	Anode	Cathode	FRR ($10^{-3} \text{ g h}^{-1} \text{ m}^{-2}$)			Time (h)	Anode catalyst	
			Anode	Cathode	Total		COOH groups ($10^{-3} \text{ mol g-cat}^{-1}$)	COOH density ($10^{-6} \text{ mol m}^{-2}$)
1a	Cat.-A	Cat.-A	0.88	0.47	1.35	99	0.56	1.82
1b	Cat.-A/UV-O ₃ treatment	Cat.-A/UV-O ₃ treatment	0.79	0.59	1.38	9	0.72	2.34
1c	Cat.-A/dehydrated EtOH	Cat.-A/dehydrated EtOH	0.02	0.05	0.07	56	–	–
2a	Cat.-B	Cat.-A	0.04	0.05	0.09	51	0.19	0.60
2b	Cat.-B/UV-O ₃ treatment	Cat.-A/UV-O ₃ treatment	0.02	0.05	0.07	100	0.19	0.60
2c	Cat.-B/HNO ₃	Cat.-A/HNO ₃	0.21	0.59	0.80	100	0.44	1.38
2d	Cat.-B/LA77 (5 wt.%)	Cat.-A/LA77(7 wt.%)	0.00	0.00	0.00	70	–	–

Cat.-A: 47%Pt/C (B.E.T. 308 m² g⁻¹), Cat.-B: 30Pt-23%Ru/C (B.E.T. 319 m² g⁻¹).

3.1.5. Other catalyst treatments

In addition to the amine treatment of catalysts, we treated catalysts with ultra-violet (UV)/ozone, dehydrated ethanol, and nitric acid in order to examine the effect of surface treatment of catalysts on the FRR. UV/ozone treatment is commonly used to remove low molecular weight organic contaminants from surfaces. When treated with dehydrated ethanol the carboxyl groups on catalysts should be esterified. Nitric acid treatment removes metallic or organic contaminants from a surface and produces a highly oxidized surface. Table 3 shows the FRR during MEA operation using surface-treated catalysts. The functional group density of a catalyst was defined as the number of surface functional groups per specific surface area (S. Surf. Area).

UV/ozone treatment of catalyst-A slightly increases the number of carboxyl groups, but the number does not change in the case of catalyst-B. Nitric acid treatment increases the number of carboxyl groups both on catalysts-A and B. The FRR becomes smaller when using a catalyst whose carboxyl groups are esterified with dehydrated ethanol, whereas the FRR becomes larger when a catalyst with more surface carboxyl groups is used. Considering the fact that the FRR remains almost the same when using UV/ozone treated catalysts, we may say that the surface contaminants of as-received catalysts do not play an important role in hydrogen peroxide formation. These results show that surface carboxyl groups on anode carbon support are mainly responsible for hydrogen peroxide formation, which is in good agreement with the conclusion of our previous paper [5].

4. Conclusion

Amine-treated catalysts, especially HALS-added catalysts, for both electrodes improve OCV durability of an MEA by

more than double, maintaining a small fluoride ion release rate (FRR). Together with the result that the FRR becomes small when a dehydrated ethanol-treated catalyst or a heat-treated catalyst is used in an MEA, it was confirmed that the active sites for the hydrogen peroxide formation in MEAs during fuel cell operation or OCV testing are related to the functional groups on carbon support or the surface of carbon support near the functional groups. Zeta potential measurements suggest that the amino groups in a molecule of HALS react with the surface carboxyl groups on carbon support to afford amide complexes. It seems that the generation of hydrogen peroxide is impeded when functional groups on carbon support are converted to other forms.

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