Improving MEA Durability by Using a Catalyst with a Small Number of Functional Groups on Its Surface

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In order to improve the durability of MEAs, surface functional groups on catalysts were focused. It was found that functional groups such as hydroxy and carboxyl groups are responsible for the OCV degradation of MEAs. By applying a heat-treated catalyst, which has a small number of functional groups on its surface, to both cathode and anode of an MEA, the OCV durability was drastically improved.

The proton-exchange membrane fuel cell (PEMFC) is attracting worldwide attention today. An membrane electrode assembly (MEA), the critical part of power generation in PEMFC, is made up of a membrane and catalytic electrodes which are attached to both sides of the membrane. The two catalyst layers are composed of a metal, such as Pt, dispersed carbon and a polymer electrolyte that has a similar structure to the membrane. Although fluorinated proton-exchange polymers are much less likely to degrade than hydrocarbon-based polymers, decomposition does occur in severe operating conditions such as high temperatures and low humidity, which has been a problem. It is generally believed that hydroxyl radicals attack the polymer to decompose and produce fluoride ions.[1] Hydroxyl radical is generated as a result of the decomposition of hydrogen peroxide which is produced from hydrogen and oxygen by a catalytic reaction.

In order to prove authors' hypothesis that hydrogen peroxide production has something to do with the catalyst surface, especially the surface functional groups such as carboxyl or hydroxy groups, some alkali-treated catalysts were prepared: A carbon-supported Pt catalyst was treated with an aqueous solution of Na_2CO_3, NaOH, or an ethanol solution of EtONa so that the functional groups on the catalyst would convert to sodium salt depending on the basicity of the alkali.[2]

Carbon-supported Pt catalyst and ionomer solution (Flemion®, 910 equivalent weight (EW); Asahi Glass) were used to fabricate thin-layer electrodes, which were transferred via a decal method onto Flemion membrane (910EW, Asahi Glass) to prepare an MEA. Using the alkali-treated catalysts, MEAs, which had Pt loadings of 0.5 mg/cm^2 for both anode and cathode, were operated under the following conditions. Cell temp.: 70 °C, An/Ca = 81/100%RH, stoic.: H_2/air = 1.4/2.5, ambient pressure. Table 1 indicates that MEAs using alkali-treated catalysts give fluoride ion release rates in reverse order of pK_a, the basicity of the alkali used. Humidity at the anode (An) and cathode (Ca) is expressed in %RH, % relative humidity.

Table 1. Effect of base treatment of catalysts[a]

MEAs	Electrodes		Basicity	F ion/10^{-3} g·h^{-1}·m^{-2}			Time
	Anode	Cathode	/pK_a	Anode	Cathode	Total	/h
1	No Treatment	No Treatment	—	1.07	0.42	1.49	94
2	Na_2CO_3	Na_2CO_3	10.25	0.24	0.04	0.28	32
3	NaOH	NaOH	15.74	0.00	0.05	0.05	32
4	EtONa	EtONa	20.58	0.00	0.03	0.03	62

[a]Catalyst: 55%Pt/C, Surface functional groups: COOH = 0.49, OH = 0.15 (mmol/g-cat).

The effect of the functional group of catalysts on the fluoride ion release rates was investigated by using a variety of catalysts, whose properties, such as number of surface functional groups and specific surface area, were measured as summarized in Table 2. The functional group density of a catalyst was defined as the number of surface functional group per specific surface area (S. Surf. Area).

MEAs were operated under the following conditions: cell temp.: 70 °C, An/Ca = 81/100%RH, stoic.: H_2/Air = 1.4/2.5, ambient pressure. The relationship between the functional group (Fn. Grp.) density of catalysts and the fluoride ion release rates are shown in Tables 3 and 4. Fluoride ion was detected by an ion chromatography after a certain length of time.

As illustrated in Figure 1, when a fixed cathode catalyst was used to see the effect of the anode catalysts, the smaller the functional group density of the anode catalyst, the smaller the fluoride ion release rate. On the other hand, when a fixed anode catalyst was used to see the effect of the cathode catalysts, it was found that the functional group density of the cathode catalyst has little influence on the fluoride ion release rate. This result suggests that hydrogen peroxide, the source of hydroxyl radical, is mainly produced by crossover of oxygen to the H_2-covered Pt anode catalyst.

As the number of surface functional groups (Surf. Fn. Grps.) of catalyst seems to play an important role in the fluoride ion release rate, i.e., the degradation of MEAs, heat-treatment of a

Table 2. Properties of catalysts

Catalysts	Surf. Fn. Groups (10^{-3} mol/g-cat)			B.E.T. S.Surf. Area	Fn. Grp. Density /10^{-6} mol·m^{-2}
	–COOH	–OH	Total: A	(m^2/g-cat): B	A/B
Pt 30%–Ru 23%/C	0.19	0.07	0.26	319	0.82
49% Pt/C	0.24	0.08	0.32	344	0.93
36% Pt/C	0.54	0.15	0.69	401	1.72
47% Pt/C	0.56	0.14	0.70	308	2.27
55% Pt/C	0.50	0.12	0.62	256	2.42
Pt 27%–Ru 13%/C	0.25	0.05	0.30	121	2.48
50% Pt/C	0.63	0.26	0.89	327	2.73
40% Pt/C	0.66	0.11	0.77	146	5.27

Table 3. Effect of the anode catalyst (fixed cathode: 47%Pt/C)

Anode Catalysts	Fn. Grp. Density /10^{-6} mol·m^{-2}	F ion/10^{-3} g·h^{-1}·m^{-2}			Time /h
	A/B	Anode	Cathode	Total	
Pt 30%–Ru 23%/C	0.82	0.04	0.08	0.13	75
36% Pt/C	1.72	0.03	0.38	0.40	107
47% Pt/C	2.27	0.55	0.19	0.75	59
55% Pt/C	2.42	0.71	0.10	0.81	107
Pt 27%–Ru 13%/C	2.48	0.02	0.45	0.47	82
40% Pt/C	5.27	0.91	0.30	1.22	11

Table 4. Effect of the cathode catalyst (fixed anode: Pt30%–23%Ru/C)

Cathode Catalysts	Fn. Grp. Density /10^{-6} mol·m^{-2}	F ion/10^{-3} g·h^{-1}·m^{-2}			Time /h
	A/B	Anode	Cathode	Total	
36% Pt/C	1.72	0.00	0.00	0.00	79
40% Pt/C	5.27	0.01	0.11	0.12	83
47% Pt/C	2.27	0.04	0.08	0.13	75
49% Pt/C	0.93	0.01	0.14	0.15	85
55% Pt/C	2.42	0.02	0.17	0.19	80
50% Pt/C	2.73	0.15	0.28	0.43	132

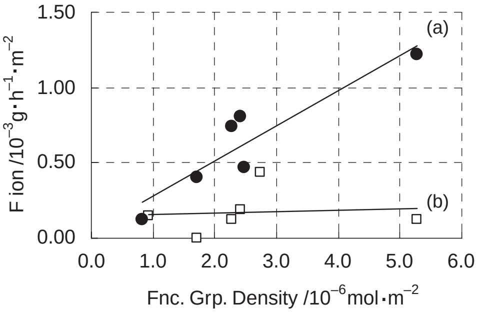

Figure 1. Effect of the functional group density on the fluoride ion release rate: (a) effect of the anode catalysts (fixed cathode: 47%Pt/C), (b) effect of the cathode catalysts (fixed anode: Pt30%–23%Ru/C).

Table 5. Comparison of catalyst properties

Catalysts	Surf. Fn. Grps (10^{-3} mol/g-cat)			S.Surf.Area B.E.T.	Pt[b]	Fn. Grp. Density	Pt Cryst. Diameter
	–COOH	–OH	Total	(m^2/g-cat)	(m^2/g-Pt)	/10^{-6} mol·m^{-2}	/nm
47% Pt/C	0.56	0.14	0.70	308	137	2.27	3–4
HT-47% Pt/C[a]	0.12	0.01	0.13	350	78	0.37	4–5

[a]Heat-treated 47%Pt/C. [b]Determined by the CO adsorption method.

catalyst at 700–900 degrees Celsius for about 15 min under an argon atmosphere, was carried out to reduce the number of surface functional groups of a catalyst. The properties of before and after the heat-treatment of the catalyst are compared in Table 5.

Open circuit voltage (OCV) durability testings of MEAs were conducted using MEAs with a heat-treated catalyst to both cathode and anode. OCV testings are used to accelerate the degradation of MEAs because hydroxyl radicals severely attack an membrane in the MEA.[3] Under the condition of OCV, hydroxyl radical is produced from hydrogen peroxide, which is formed from oxygen at the low anodic potentials where the Pt electrode is covered with hydrogen.[4] As shown in Figure 2, an MEA using a heat-treated catalyst for both electrodes lasts for over 700 h with a fluoride ion release rate of 0.1–0.2 × 10^{-3} g h^{-1} m^{-2}, whereas a conventional MEA degrades within 100 h.

Polarization curves in Figure 3 show no significant difference in cell voltage at 100%RH, but an MEA with a heat-treated anode catalyst gave slightly lower cell voltage than a conventional MEA at 53%RH.

It is concluded that surface functional groups, hydroxy and/or carboxyl groups, on the catalysts are responsible for the generation of hydroxyl radicals that degrade the membrane in an MEA. Catalysts with a small number of surface functional groups are membrane-friendly and will contribute to the development of durable MEAs.

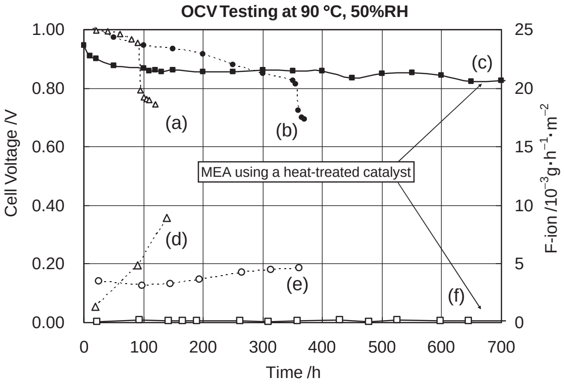

Figure 2. Change in cell voltage and fluoride ion release rates of MEAs. Catalysts used, (a), (d): An/Ca = std/std, (b), (e): An/Ca = HT/std, (c), (f) An/Ca = HT/HT, where std = 47%Pt/C, HT = heat-treated 47% Pt/C. Conditions: Pt loadings: An/Ca = 0.2/0.4 mg/cm^2, membrane thickness: 50 µm, Cell temp.: 90 °C, An/Ca = 50/50%RH, Stoic.: H_2/Air = 2/2, ambient pressure.

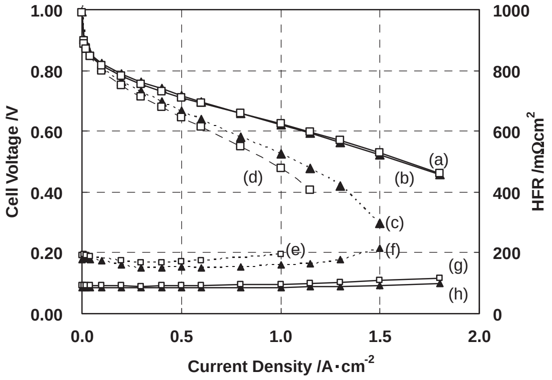

Figure 3. Polarization curves (a), (b) and high frequency resistance, HFR (g), (h) at An/Ca = 100/100%RH. (a), (g): MEA using An/Ca = std/std, (b), (h): MEA using An/Ca = HT/std. Polarization curves (c), (d) and HFR (e), (f) at An/Ca = 53/53%RH. (c), (e): MEA using An/Ca = std/std, (d), (f): MEA using An/Ca = HT/HT, where std = 47%Pt/C, HT = heat-treated 47%Pt/C. Conditions: membrane 40 µm, cell temp. 80 °C, stoic. H_2/air = 1.4/2.0, ambient press.

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