

Study of Oxide Supports for PEFC Catalyst

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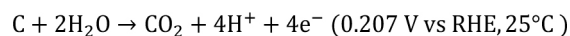
ABSTRACT

Polymer electrolyte membrane fuel cell (PEFC) systems for fuel cell vehicles (FCVs) require both performance and durability. Carbon is the typical support material used for PEFC catalysts. However, hydrogen starvation at the anode causes high electrode potential states (e.g., 1.3 V with respect to the reversible hydrogen electrode) that result in severe carbon support corrosion. Serious damage to the carbon support due to hydrogen starvation can lead to irreversible performance loss in PEFC systems. To avoid such high electrode potentials, FCV PEFC systems often utilize cell voltage monitor systems (CVMs) that are expensive to use and install. Simplifying PEFC systems by removing these CVMs would help reduce costs, which is a vital part of popularizing FCVs. However, one precondition for removing CVMs is the adoption of a durable support material to replace carbon. For this reason, tin oxide and titanium oxide were examined as cathode and anode support materials, respectively, since these materials are more stable under high potentials than carbon. Membrane electrode assemblies (MEAs) with titanium oxide- and tin oxide-supported platinum (Pt) catalysts were prepared and compared with conventional carbon-supported Pt catalysts. The results of this study found that MEAs using these metal oxide supports achieved equivalent performance to conventional carbon-supported Pt catalysts. These metal oxide supports were also more durable under a high potential (1.3 V) than carbon-supported Pt catalysts.

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BACKGROUND AND OBJECTIVES

Polymer electrolyte membrane fuel cell (PEFC) systems require higher performance and durability for application as a power source in next-generation vehicles. Carbon is used as the typical support material for PEFC catalysts due to its large surface area and high electrical conductivity. However one issue of carbon supports in PEFC systems is corrosion (Fig. 1). The corrosion mechanism can be expressed by Equation (1) [1][2].



(1)

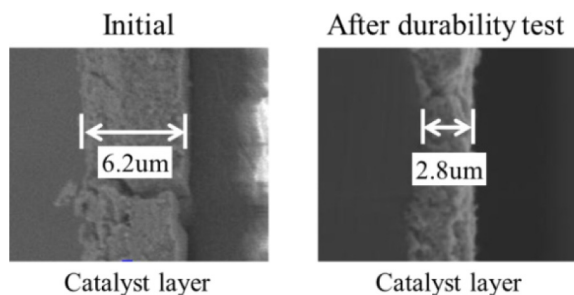


Figure 1. Thinning of catalyst layer caused by carbon corrosion.

Carbon corrosion accelerates the growth of the carbon-supported platinum (Pt) particles. This reduces the number of available sites for the oxygen reduction reaction, which is necessary for power generation. In addition, it also adversely affects the transportation of electrons, gasses, and protons, which can lead to irreversible

performance loss in PEFC systems [3]. In particular, hydrogen starvation at the anode causes high electrode potentials that accelerate carbon support corrosion.

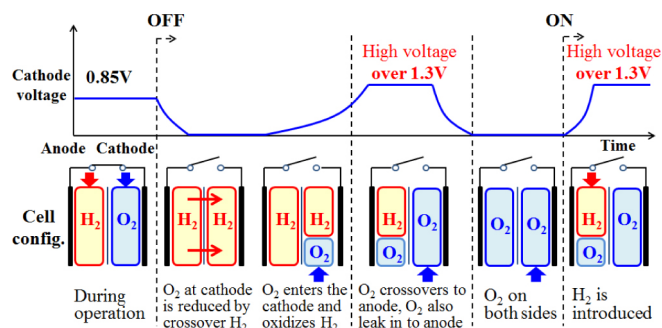


Figure 2. Mechanism of high potential generation at cathode in PEFC.

Partial hydrogen starvation refers to the co-existence of hydrogen and air at the anode and is caused by the gradual crossover of air to the anode side when the hydrogen supply is interrupted after the PEFC is stopped. A partial hydrogen starvation state is likely to occur when the PEFC system is re-started after a long period. As shown in Fig. 2, when partial hydrogen starvation occurs at the anode, a high potential in excess of 1.3 V is applied to the cathode on the opposite side. In contrast, if total hydrogen starvation occurs at the anode, a high potential in excess of 1.3 V is applied to the anode (Fig. 3). This total hydrogen starvation state can be caused if the gas channels become blocked. To help prevent hydrogen starvation and avoid high electrode potentials, FCV PEFC systems often utilize cell voltage monitor systems (CVMs) that are expensive to use and install. Simplifying PEFC systems by removing these CVMs would help reduce costs, which is a vital part of popularizing FCVs. However, one precondition for removing CVMs is the adoption of a durable support material to replace carbon. For this reason, tin oxide and titanium oxide were examined as cathode and anode support materials, respectively, since these materials are more stable under high potentials than carbon. Membrane electrode assemblies (MEAs) with titanium oxide- and tin oxide-supported platinum (Pt) catalysts were prepared and compared with conventional carbon-supported Pt catalysts. The results of this study found that MEAs using these metal oxide supports achieved equivalent performance to conventional carbon-supported Pt catalysts. These metal oxide supports were also more durable under a high potential (1.3 V) than carbon-supported Pt catalysts.

voltage monitors (CVMs). Simplifying PEFC systems by removing such expensive components would help to greatly reduce costs, which is a vital part of popularizing FCVs. Therefore, Toyota Motor Corporation has started to develop supports that are stable under high potentials as a key part of simplifying high potential-prevention systems in future fuel cell vehicles (FCVs).

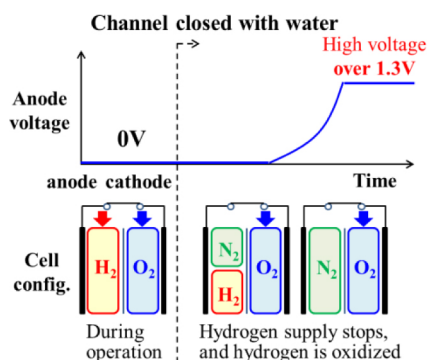


Figure 3. Mechanism of high potential generation at anode in PEFC.

Figure 4 shows the relationship between pH and potential in a Pourbaix diagram. The diagram indicates that both titanium oxide and tin oxide are more stable under high potential FC environments than carbon and are promising durable support materials [4]. Tin oxides doped with tungsten or antimony and titanium oxides having oxygen defects (for example, Ti_4O_7 is the titanium oxide with the highest conductivity) are known to exhibit high conductivity. For these reasons, a number of reports have examined their suitability as an FC catalyst support material to replace carbon [5]–[12]. The mechanism that generates conductivity in tin oxide is stable under oxidation conditions even at high temperature, but it is not unstable under reduction conditions over 80°C . In contrast, the mechanism that generates conductivity in titanium oxide is stable under reduction conditions even at high temperature, but it is not unstable under oxidation conditions over 80°C . Based on the above, we judged that the tin oxide support should be used for anode and the titanium oxide support should be used for cathode, respectively.

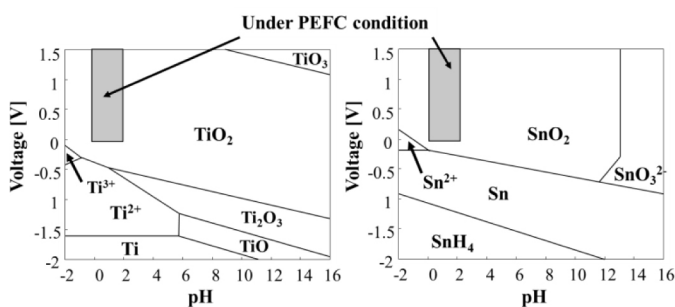


Figure 4. Pourbaix diagram of tin and titanium.

EXPERIMENTAL METHODS

Catalyst Preparation

The oxygen-deficient titanium oxide-supported Pt anode catalysts (Pt particle diameter: 2.5 nm) used in this research were supplied by Sakai Chemical Industry Co. Ltd. (Sakai, Japan). The reference Ketjen-supported Pt anode catalysts (Pt particle diameter: 2.5 nm)

were supplied by Cataler Corporation (Kakegawa, Japan). Cataler Corporation also supplied the carbon-supported Pt-cobalt (Co) alloy catalysts used in the membrane electrode assembly (MEA) evaluations to determine the feasibility of application to the anode. The tungsten-doped tin oxide-supported Pt cathode catalysts (Pt particle diameter: 2.5 nm) were supplied by Mitsui Mining & Smelting Co., Ltd. (Haraichi, Ageo-shi, Japan). The reference acetylene black carbon-supported Pt cathode catalysts (Pt particle diameter: 2.5 nm) were supplied by Cataler Corporation. The anode catalysts used in the MEA evaluations to determine the feasibility of application to the cathode were the Ketjen-supported Pt anode catalysts (Pt particle diameter: 2.5 nm) described above.

Catalyst Layer Preparation

The catalyst ink was obtained by combining the catalyst, ionomer, and solvent so that the weight ratio of the ionomer and oxide support was 0.116 and the solid component concentration was 24wt%. This solution was then dispersed for six hours at 300 rpm in a planetary ball mill using zirconia beads with a diameter of 1 mm. The ionomer was supplied by DuPont (Nafion ionomer, product name: DE2020CS) and the solvent was a mixture of deionized water, ethanol, and tert-butyl alcohol. The catalyst layer sheet was prepared by coating the catalyst ink on a Teflon sheet and drying. In this case, the amount of catalyst ink coating was adjusted so that the amount of Pt per 1 cm^2 of the catalyst layer was 0.2 mg on the cathode and 0.05 mg on the anode. The catalyst layer sheets for the carbon-supported cathodes were manufactured in the same way as the oxide-supported catalysts, except that the weight ratio of the ionomer and carbon was 0.75. In the case of the catalyst layer sheets for the carbon-supported anodes, the weight ratio of the ionomer and carbon was 1.2.

MEA Preparation

The MEAs (active area: 1 cm^2) were prepared by cutting pieces from the manufactured anode and cathode catalyst layer sheets. These were then layered with proton exchange membranes (DuPont NR212) in a thermal molding press (conditions: 130°C , 31 kgf/cm^2 , 20 minutes). Table 1 shows the specifications of the manufactured MEAs.

Table 1. Specifications of MEA.

MEA		Cathode	Anode
(A) Pt/W-SnO ₂	Catalyst/support	Pt/W-SnO ₂	Pt/Ketjen
	Pt loading	0.2 mg/cm ² -MEA	0.05 mg/cm ² -MEA
	Ionomer/support weight ratio	0.16	1.2
(B) Pt/AB reference of (A)	Catalyst/support	Pt/acetylene black	Pt/Ketjen
	Pt loading	0.2 mg/cm ² -MEA	0.05 mg/cm ² -MEA
	Ionomer/support weight ratio	0.75	1.2
(C) Pt/TiOx	Catalyst/support	PtCo/acetylene black	Pt/TiOx
	Pt loading	0.35 mg/cm ² -MEA	0.05 mg/cm ² -MEA
	Ionomer/support weight ratio	0.75	0.116
(D) Pt/Ketjen reference of (C)	Catalyst/support	PtCo/acetylene black	Pt/Ketjen
	Pt loading	0.35 mg/cm ² -MEA	0.05 mg/cm ² -MEA
	Ionomer/support weight ratio	0.75	