Journal of Power Sources 305 (2016) 17–21

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Clarifying the chemical state of additives in membranes for polymer electrolyte fuel cells by X-ray absorption fine structure

Toshihiro Tanuma [a], [*], Takanori Itoh [b]

[a] Asahi Glass Research Center, 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa, 221-8875, Japan
[b] AGC Seimi Chemical Co. Ltd., 3-2-10 Chigasaki, Chigasaki-shi, Kanagawa, 253-8585, Japan

HIGHLIGHTS

- X-ray absorption fine structure technique was applied to fuel cell membranes.
- The chemical states of Ce and Mn in the membrane were directly observed.
- The valence state of Ce was observed to be 3+ before and after the degradation test.
- Mn with low and high valence states (2+ and 3+) existed after the degradation test.
- The reaction rate of Ce/Mn with hydroxyl/hydroperoxyl radicals are discussed.

GRAPHICAL ABSTRACT

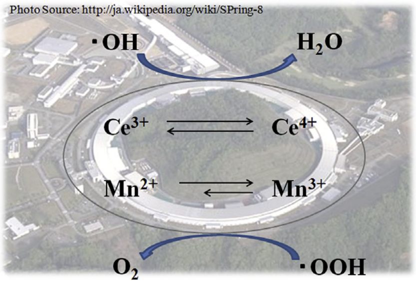


Photo Source: http://ja.wikipedia.org/wiki/SPring-8

ARTICLE INFO

Article history:
Received 6 April 2015
Received in revised form
26 June 2015
Accepted 16 November 2015
Available online 29 November 2015

Keywords:
Fuel cell
XAFS
Membrane degradation
Cerium
Manganese

ABSTRACT

Cerium and manganese compounds are used in the membrane for polymer electrolyte fuel cells (PEFCs) as radical scavengers to mitigate chemical degradation of the membrane. The chemical states of cerium and manganese in the membrane were investigated using a fluorescence X-ray absorption fine structure (XAFS) technique. Membrane electrode assemblies (MEAs) were subjected to open circuit voltage (OCV) condition, under which hydroxyl radicals attack the membrane; a shift in absorption energy in X-ray absorption near edge structure (XANES) spectra was compared between Ce- and Mn-containing membranes before and after OCV testing. In the case of the Ce-containing MEA, there was no significant difference in XANES spectra before and after OCV testing, whereas in the case of the Mn-containing MEA, there was an obvious shift in XANES absorption energy after OCV testing, indicating that Mn atoms with higher valence state than 2+ exist in the membrane after OCV testing. This can be attributed to the difference in the rate of reduction; the reaction of Ce^{4+} with ·OOH is much faster than that of Mn^{3+} with ·OOH, leaving some of the Mn atoms with higher valence state. It was confirmed that cerium and manganese redox couples reduced the attack from radicals, mitigating membrane degradation.

1. Introduction

Hydrogen is the focus of world attention because it is clean and environmentally friendly. As PEFCs use hydrogen and oxygen as fuels, they are considered one of the most promising technologies,

---

[*] Corresponding author.
E-mail address: Toshiihiro-tanuma@agc.com (T. Tanuma).

http://dx.doi.org/10.1016/j.jpowsour.2015.11.055

for such applications as distributed generation, telecommunication backup power, cogeneration, and automotive. Fuel cell vehicles have already been on the market since 2014. Perfluorinated sulfonic acid (PFSA) membranes (e.g. Flemion, Nafion) are commonly used in PEFCs. Although they have better physical properties and chemical stability, compared to hydrocarbon-based membranes, decomposition does occur in severe operating conditions such as high temperature and low humidity. Accordingly, a great number of studies concerning membrane degradation have been carried out with the aim of improving performance and durability [1–3]. It is generally accepted that hydroxyl or hydroperoxyl radicals attack the PFSA membrane to decompose and produce fluoride ions during fuel cell operation. Such radicals are thought to be generated as a result of the decomposition of hydrogen peroxide formed at the electrodes, or in a reaction between hydrogen and oxygen, originating from hydrogen/oxygen crossover, on the surface of the platinum catalyst [4]. Several strategies have been proposed to reduce membrane degradation. Trogadas and Endoh disclosed that Mn and Ce compounds are extremely effective in mitigating PFSA membrane chemical degradation [5,6]. They suggested that such compounds function as highly reversible and stable redox quenchers of hydroxyl peroxide radicals. Approximately 0.1–1 wt% of Mn and Ce compounds are typically introduced to the PFSA membrane by doping, or PFSA dispersion containing additives is used to prepare mitigated PFSA membranes [7,8]. Although a great number of studies have been made on the degradation mitigation effect of Mn and Ce compounds in total [5,7–13], little research has been done on direct observation of the actual chemical state of the additives within the membrane.

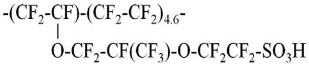
The XAFS technique is the most suitable for the chemical state analysis of atoms such as Mn and Ce. A great number of studies using XAFS were made on carbon supported platinum catalysts [14–17], but it has never been tried in the analysis of membranes for PEFCs. We have employed a fluorescence XAFS technique using a 19 element Ge solid state detector (SSD) system, which enables measurements with increased sensitivity to low element concentrations of additives in the membrane. This paper is the first to report on the chemical state of Mn and Ce in the membranes, which are added to improve durability of the membrane used in PEFCs.

2. Experimental

2.1. Perfluorinated sulfonic acid polymer dispersion containing manganese carbonate or cerium carbonate

Powder of $MnCO_3$ and $Ce_2(CO_3)_3$ was added to PFSA polymer dispersion (solid content 28.1 wt%, 910 equivalent weight (EW), dispersion in ethanol/water = 6/4; Asahi Glass Co., Ltd.) so that each cation in the separate polymer dispersion became 5.5 mol/g-polymer (ca. 0.3 mol%), then mixed with a magnetic stirrer until the carbonates were dissolved completely. The chemical structure of the PFSA polymer is shown in Fig. 1.

Although the incorporation of Ce^{3+} and Mn^{2+} in the membrane is effective in reducing the chemical degradation rates of the PFSA membrane in PEFCs, it was reported that there is a tradeoff between durability and cell performance; the more cation loadings, the lower the cell voltage. The performance losses are not dominated by increasing cell resistance at the high cation loadings [3]. Studies show that the majority of observed losses in MEAs are thermodynamic in nature where the cations migrate toward the cathode under load [18]. With the aim of facilitating analysis by XAFS technique, we added 5.5 mol/g-polymer of cation to the PFSA polymer membrane.



$$\begin{array}{l} -(CF_2-CF)-(CF_2-CF_2)_{4.6}- \\ \qquad\quad | \\ \qquad\quad O-CF_2-CF(CF_3)-O-CF_2CF_2-SO_3H \end{array}$$

Fig. 1. Chemical structure of the PFSA polymer.

2.2. Membranes with or without manganese or cerium carbonate

The PFSA polymer dispersions and slurry were coated onto a poly(ethylene-co-tetrafluoroethylene (ETFE)) film by using an applicator and dried in a convection oven at 80 °C for 15 min to fabricate a 25 μm membrane containing Mn or Ce carbonate. A 25 μm membrane without additives was also prepared in the same manner, using the polymer electrolyte dispersion. Finally, the membranes were heat treated in a convection oven at 160 °C, under N_2 atmosphere for 30 min.

2.3. Fabrication of membrane electrode assemblies

The catalyst slurry was prepared by mixing catalyst, water, ethanol, and ionomer (PFSA polymer dispersion) with a planetary ball mill (LP-4, Itoh Seisakusho Lt.). The ratio of ionomer to carbon support was 0.8. Carbon-supported Pt catalyst (50 wt%Pt/C, Tanaka Kikinzoku Kogyo) was used for both the anode and cathode. The catalyst slurry was coated onto an ETFE film to fabricate a thin-layer electrode, which was transferred via decal method onto the 25 μm membrane. The Pt loading was 0.4 mg/cm^2 for the anode and cathode decals. Membrane electrode assemblies (MEAs) were assembled by hot-pressing (130 °C, 1.5 MPa, 5 min) so that the catalyst layers were in contact with the membrane. The MEAs, which have an active electrode area of 25 cm^2, were assembled into a test cell. As a reference GDL, a GDL (X0086 IX51 CX173, hydrophobic treated GDL with an MPL, Freudenberg-NOK) was used for both the anode and cathode sides.

2.4. Fuel cell operation

The single cell fixture was composed of an MEA and a pair of graphite plates with a single serpentine flow channel of 0.8 mm width and 0.7 mm depth for the anode, and a single serpentine flow channel of 1.0 mm width and 1.0 mm depth for the cathode. Hydrogen and air/oxygen were supplied in a counter-flow configuration. For the wet condition, the cell temperature was kept at 80 °C, while the inlet anode and cathode humidity was maintained at 100% RH. For the dry condition, the cell temperature was kept at 80 °C, whereas the inlet anode and cathode humidity was maintained at 30%RH. For both conditions, the stoichiometric ratios of hydrogen and air were 1.4 and 2.0, respectively. After a conditioning operation of the cell at 0.7 A/cm^2 for 15 h under the wet condition, it was operated at 0.2 A/cm^2 for 150 h, under both wet and dry conditions.

2.5. Open circuit voltage testing

Under the condition of open circuit voltage (OCV), hydroxyl radicals are produced from hydrogen peroxide, which is formed from oxygen and hydrogen at low anode potentials. The membrane in the MEA is vulnerable to hydroxyl radicals, and OCV testing is therefore used to accelerate the degradation of MEAs [3]. The membrane in MEAs was hydrated by operating a single cell at 0.2 A/cm^2 for 150 h. Then, the cell was operated under OCV conditions (120 °C, anode/cathode 18/18%RH (inlet), H_2/Air stoichiometric ratios of 2.0/2.0 at 0.2 A/cm^2 equivalent flow, ambient pressure) for 150 h.