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# Analysis of cerium-composite polymer-electrolyte membranes during and after accelerated oxidative-stability test



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#### HIGHLIGHTS

- Ce-composite PEMs were evaluated in accelerated oxidative-stability test at OCV.
- During the test, the impedance, HFR, ICs, CVs, and LSVs were measured.
- <sup>1</sup>H NMR spectroscopy, GPC, FE-SEM, and EDS were conducted after the test.
- The in situ and post-test analyses determined what happened during the test.
- Ce radical scavengers aided the PEM's oxidative stability in fuel-cell operation.

#### ARTICLE INFO

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#### ABSTRACT

The oxidative stability of membranes constructed from a composite of pristine sulfonated poly(arylene ether sulfone) and cerium was investigated by conducting an accelerated oxidative-stability test at the open-circuit voltage (OCV). The membranes were analyzed in situ through OCV and impedance measurements, cyclic voltammetry, and linear-sweep voltammetry to monitor the electrochemical properties during the stability test. Although the high-frequency resistance of a composite membrane was slightly higher than that of a pristine membrane because of the exchange of protons from the sulfonic acid with cerium ions, the composite membrane maintained its potential for much longer than the pristine membrane. The effect of the cerium ions as radical scavengers was confirmed by analyzing the drain water and chemical structure after operation. These post-operation analyses confirmed that cerium ions improved the oxidative stability of the hydrocarbon-based polymer during fuel-cell operation. It is clear that the cerium-based radical scavengers prevented chemical surface area, while they rarely diffused outward from the membrane.

1. Introduction

Proton-exchange-membrane fuel cells (PEMFCs) are ecofriendly energy-conversion devices because they emit only water as a byproduct during power generation [1–3]. Among the components of a PEMFC, the proton-exchange membrane (PEM) plays a critical role as the electrolyte that conducts only protons (i.e., it is an insulator that does not conduct electrons) and a barrier that prevents the permeation of fuel and oxidants [4,5]. Polymers based on perfluorosulfonic acid (PFSA) are widely used for state-of-the-art PEMs because they exhibit excellent electrochemical performance and chemical stability [6,7]. However, they are expensive and unstable at high temperature because of their low glass-transition temperatures, which limit their application.

To overcome these drawbacks, hydrocarbon-based polymers have been studied as alternative materials to PFSA polymers because of their low cost, high thermal stability, and excellent performance as gas

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*Abbreviations*: CV, cyclic voltammetry; DMAC, *N*,*N*-dimethyl acetamide; DMF, *N*,*N*-dimethylformamide; DMSO-d6, *N*,*N*-dimethyl sulfoxide; ECSA, electrochemical surface area; EDS, energy-dispersive spectroscopy; FE-SEM, field-emission scanning electron microscopy; FRR, fluorine release rate; GPC, gel-permeation chromatography; HFR, high-frequency resistance; *I–V*, current–voltage; IC, ion chromatography; LSV, linear-sweep voltammogram; MEA, membrane-electrode assembly; NMR, nuclear magnetic resonance; OCV, open-circuit voltage; PDI, polydispersity index; PEMFC, proton-exchange-membrane fuel cell; PTFE, polytetrafluoroethylene; RH, relative humidity; SPES, sulfonated poly(arylene ether sulfone); TOC, total organic carbon

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barriers. Despite these advantages, they have several disadvantages like lower proton conductivity and lower intrinsic chemical stability than those of PFSA polymers. To enhance the proton conductivity, researchers have explored the introduction of a separation between the hydrophilic and hydrophobic phases in these hydrocarbon-based polymers [8–13], and the resulting well-defined morphology facilitates proton transport even in environments with low relative humidity (RH). As a result, block copolymers or graft copolymers, which have welldefined morphology in the nanoscale, show outstanding electrochemical performance comparable to that of PFSA polymers. In addition, their electrochemical performance is less dependent on humidity, thus allowing their application to be extended over wide temperature and RH ranges.

The long-term durability associated with chemical stability is also an important issue for hydrocarbon-based polymers [14-16]. Most hydrocarbon-based polymers have ether or thio-ether linkages between benzene rings because they are usually synthesized by a nucleophilic aromatic substitution reaction between halide monomers and hydroxyl (or thiol) monomers. In particular, the electron-rich ether and thioether linkages around sulfonic acid groups are known to be susceptible to attack by oxidative radicals [17]. Sulfonic acid groups are also reported to be unstable in the presence of radical species [18]. Therefore, incorporating radical scavengers into the polymer matrix is an effective way to improve the chemical stability [19]. It is well known that cerium ions serve as antioxidants in biological and fuel-cell applications [20-33]. They are also known to be very reactive to radical species; however, positive cerium ions can replace protons in sulfonic acid, leading to a decrease in proton conductivity. Cerium ions consume radical species through the following oxidation and reduction mechanisms [34]:

$$\operatorname{Ce}^{3^{+}} + \operatorname{OH} + \operatorname{H}^{+} \to \operatorname{Ce}^{4^{+}} + \operatorname{H}_{2}\operatorname{O}, \tag{1}$$

$$Ce^{3+} + OOH + H^+ \rightarrow Ce^{4+} + H_2O_2,$$
 (2)

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + OOH + H^+,$$
 (3)

$$Ce^{4+} + OOH \rightarrow Ce^{3+} + O_2 + H^+.$$
(4)

Fenton's test is commonly used to estimate the chemical stability of PEMs because transition-metal ions (e.g.,  $Fe^{3+}$ ,  $Cu^{2+}$ ) break down peroxide to radicals through the catalyzed Haber–Weiss reaction [35–37]. However, Fenton's test is not the same as an actual PEMFC test owing to the difference between their experimental conditions: Fenton's test is conducted in the liquid state, whereas a PEMFC is operated and tested under partially humidified conditions. Therefore, in our research, we carried out experiments in which PEMs were exposed to peroxide vapor to mimic the operating conditions of fuel cells [19]. Even though the experimental conditions were close to those in real-life applications, the best accelerated method for evaluating the oxidative stability is the open-circuit voltage (OCV)-hold test at the operating temperature and RH of a real fuel cell. In general, radical species are generated at the OCV from the reaction between hydrogen and oxygen at both the anode and cathode in the following sequence:

$$H_2 \rightarrow 2 H_2$$
, (5)

$$\mathrm{H} \cdot + \mathrm{O}_2 \to \mathrm{OOH},\tag{6}$$

$$\cdot OOH + H \rightarrow H_2O_2, \tag{7}$$

$$\mathrm{H}_{2} + \mathrm{O}_{2} \to \mathrm{H}_{2}\mathrm{O}_{2}, \tag{8}$$

$$H_2O_2 \rightarrow 2 \cdot OH$$
,

$$H_2O_2 + OH \rightarrow OOH + H_2O.$$
(10)

These equations indicate that the permeability of hydrogen and oxygen through the membrane is an important parameter that determines the kinetics of the generation of radical species. During fuelcell operation, hydrogen and oxygen are consumed to generate power, leading to decreases in their respective concentrations in each electrode. However, the highest concentrations of hydrogen and oxygen are maintained at the OCV, which lead to the maximum generation of radical species [38–40]. The setting might be the harshest condition for the oxidative-stability test of the membrane. Moreover, since the generation and diffusion of radical species might depend on the temperature and humidity, the degradation of a polymer membrane can be accelerated by changes in the temperature and humidity [18,41].

There have been a few studies on stability tests of membranes under open-circuit voltage condition [14,15,18,42–46]. They reported experimental results like the fluorine-release rate (FRR) and current-voltage (I-V) polarization curves obtained from OCV-hold tests to investigate the degree of degradation. Obviously, the OCV continues to decrease during the test owing to chemical degradation of the membrane-electrode assembly (MEA). However, it is very difficult to pinpoint the exact progression of degradation during the OCV test because the carbon support of the Pt catalyst and the PFSA ionomer binder at both electrodes can be degraded at the same time. Moreover, the condition of the catalyst is important because the generation of radical species occurs on its surface, as shown in Eqs. (5–10). Therefore, further analysis during or after the accelerated oxidative-stability test is necessary to closely investigate the degradation of the membrane.

In our earlier work, we already reported the effect of cerium radical scavengers on the oxidative stability of a membrane made of sulfonated poly(arylene ether sulfone) (SPES), a hydrocarbon-based polymer [19]. The cerium radical scavengers improved the oxidative stability of the SPES membrane even after exposure to hydrogen peroxide vapor and the accelerated oxidative-stability test at the OCV. In order to better understand the oxidative degradation of MEAs with hydrocarbon membranes, we conducted further in situ and post-test investigations in the study reported here to determine what really happened during the OCV test. The accelerated oxidative-stability test was conducted at 90 °C and 30% RH. During the test, the impedance and linear-sweep voltammograms (LSV) were measured to monitor the high-frequency resistance (HFR) and hydrogen cross-over current, respectively, which resulted from the degradation of the membrane. Cyclic voltammetry (CV) was also performed to check the state of the Pt catalyst, which could affect the generation of hydrogen peroxide. The degraded polymer fragment diffused outward through the outlet of the single cell, and the drain water from both the anode and the cathode was analyzed to estimate the degree of degradation. The degradation was confirmed by post-test analyses based on proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy and gel-permeation chromatography (GPC). In addition, field-emission scanning electron microscopy (FE-SEM) and energy-dispersive spectroscopy (EDS) were used to observe the migration of cerium ions.

#### 2. Experimental

#### 2.1. Preparation of membrane-electrode assembly (MEA)

A Nafion<sup>\*</sup> membrane (NRE212; thickness: ~50  $\mu$ m) was purchased from DuPont, USA, and used as received. Pristine SPES (SPES50) and a composite of SPES with 2 wt% Ce (the degree of sulfonation was 50% for SPES) was prepared according to a process developed in our previous work [19]. Both pristine and composite membranes were cast with a thickness of 50 ± 5  $\mu$ m to remove the effect of thickness on the long-term stability. For the electrode layer, carbon-supported platinum (HiSPEC<sup>\*</sup> 4000, Johnson Matthey, UK; 40 wt% Pt on C) and a 20 wt% Nafion<sup>\*</sup> dispersion (DE-2021) were used as the metal catalyst and binder, respectively. The total ionomer content was 20 wt% against the supported catalyst. The electrode was loaded onto both sides of the membrane by hot-pressing at 140 °C at a pressure of 17 bar, and the amount of Pt loaded onto each anode and cathode was 0.3 mg cm<sup>-2</sup>. The edge of the MEA was sealed with a support film to prevent mechanical failure caused by excessive membrane swelling or pressure,

(9)

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