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Durability of Nafion-hydrophilic silica hybrid membrane against trace radial species in polymer electrolyte fuel cells

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ABSTRACT

Durability of an organic–inorganic nanocomposite electrolyte membrane prepared by mixing hydrophilic fumed silica particles of an average size of 7 nm with Nafion ionomer was studied for the mitigation of chemical degradation of the membrane caused by trace radial species in polymer electrolyte fuel cells (PEFCs). Infrared (IR) spectroscopy indicated that the peak of C—F, S—O and C—O—C bands were not shifted to the higher wavenumber with an addition of 1 wt.% hydrophilic silica to the Nafion matrix. This suggests that hydrophilic silica had a catalyst activity for the decomposition of hydrogen peroxide and reduced the membrane degradation by trace radicals attack. Quantum chemical calculations (QCCs) using a model ionomer of trifluoromethanesulfonate (TFMS) and a model nanoparticle of $Si(OH)_4$ also implied that the nanoparticle was able to trap H, OH and OOH radical species before attacking the ionomer. The hydration of TFMS that induces deprotonation of sulfonic acid group in TMFS and formation of hydronium anion was confirmed also in the presence of trace radicals due to the ability of $Si(OH)_4$ to trap H radical.

1. Introduction

Degradation of proton exchange membranes is one of the most important factors limiting the lifetime of polymer electrolyte fuel cells (PEFCs) [1–4]. Degradation of the membrane in a fuel cell occurs via multistep chemical reactions including formation of trace radicals by a reaction of hydrogen peroxide with trace amount of metal ions and chemical degradation of the ionomer chain induced by the radicals [5,6]. Hydrogen radical (H·), hydroxyl radical (·OH) and hydroperoxy radical (·OOH) have been identified as the aggressive oxidative species responsible for the propagation of chemical degradation in perfluorosulfonic acid (PFSA) membranes [7–10].

Therefore, increasing the chemical stability is considered to be a key requirement to PEFCs. Electrolyte properties of the nanocomposite membranes have extensively been studied at a molecular level because of advantage of chemical properties arising from the organic matrix and that of thermal stability by the inorganic dispersion [11]. It has also been reported that dispersion of inorganic nanoparticles, such as SiO_2 and TiO_2 in a PFSA membrane, such as Nafion, shows an improvement of thermal and chemical stability of the membrane during the fuel cell operation [12–14]. Danmin et al. confirmed that the Ag/SiO_2 particles in a sulphonated poly(biphenyl ether sulfone) composite membrane had a catalyst activity for the decomposition of hydrogen peroxide and reduced degradation of membrane by ·OH and ·OOH radicals attack due to lower hydrogen crossover. Moreover, water uptake study and thermogravimetric analysis also indicated that the hydrophilic Ag/SiO_2 particles retain more water in the composite membrane [15].

Our previous work demonstrated that chemical degradation products, e.g. HF, CF_2O and SO_3H, were generated at the catalyst interface of PEFCs by hydrogen and oxygen feeding into the anode due to the H· and ·OH trace radicals attack [16]. The present study is aimed at examining and applying the trace radical scavenging properties of nanoparticles based on hydrophilic silica to mitigate the chemical degradation of the membrane. Nafion and hydrophilic fumed silica having an average particle size of 7 nm was mixed and immersed in a solution of 30% H_2O_2 for degradation tests. Chemical degradations in the membrane during the fuel cell operation were speculated from the results using infrared (IR) spectroscopy. In conjunction with experimental result, quantum chemical calculations (QCC) based on density functional theory (DFT) were performed to predict the chemical reactions on the nanocomposite membrane surfaces by using trifluoromethanesulfonate (TFMS) as a model of Nafion and $Si(OH)_4$ as a model of nonporous hydrophilic fumed silica, in the presence of H·, ·OH or ·OOH as the free radical species and a few molecules of H_2O as water content. Optimized configurations

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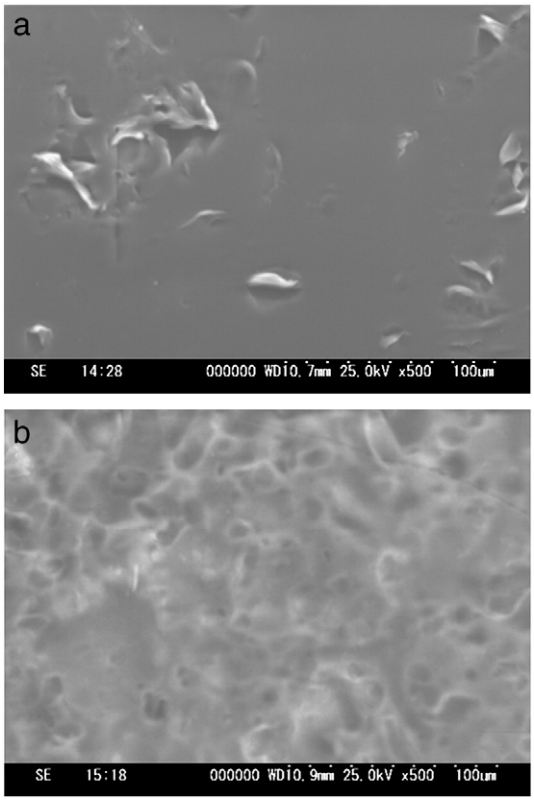

Fig. 1. SEM of the membrane surfaces (500×). (a) Nafion. (b) Nafion/Aerosil 380 1 wt.%.

of TFMS and their bond dissociation energy (BDE) will also be calculated to discuss the durability of Nafion-hydrophilic silica hybrid membranes.

2. Experimental

2.1. Sample preparation

A 20 wt.% Nafion solution in lower aliphatic alcohols and 30% H_2O_2 were purchased from Aldrich and used without further purification. Hydrophilic fumed silica having an average particle size of 7 nm (Aerosil 380) was obtained from Evonik. The Nafion solution was diluted in a methanol and water (4:1 wt ratio) mixture as the solvent to give a Nafion concentration of 0.6 mg·ml^{-1}. The silica nanoparticles were dispersed in the diluted Nafion solution with a content of 1 wt.% by ultrasonication for 30 min. The silica dispersed Nafion solution or the diluted Nafion solution without the nanoparticles was casted onto a silicone type release paper and dried at room temperature for one day. The casted membranes were carefully removed from the paper, finally ca. 150 μm thick samples were obtained, cut into ca. 1 cm^2 square and used for durability tests. Each sample was immersed in the 30% H_2O_2 solution at 80 °C for 0, 1, 4 and 8 h, and in deionized water for 1 h before the IR spectrometric analysis [17].

Table 1
Assignments of IR absorption bands. ν: stretching, ν_s: symmetric stretching, ν_{as}: antisymmetric stretching.

Wavenumber (cm^{-1})				Assignment
Nafion (80 °C×0 h)	Nafion (80 °C×8 h)	Nafion/Aerosil (80 °C×0 h)	Nafion/Aerosil (80 °C×8 h)	
1209	1219	1207	1209	C F (ν_{as})
1152	1155	1151	1151	C F (ν_s)
1057	1057	1057	1057	S O (ν_s)
970	972	968	966	C O C (ν)

2.2. SEM analysis

The Nafion and nanocomposite membranes before the degradation tests were observed with a Hitachi S-2300 scanning electron microscope (SEM). Its accelerating voltage and magnification were set at 25.0 kV and 500×, respectively.

2.3. IR spectroscopy

All the attenuated total reflection (ATR) IR spectra were collected using a Thermo Scientific Nicolet 380 Fourier transform IR spectrometer equipped with a DTGS detector and a germanium crystal at an incident angle of 45°. Penetration depth of an evanescent wave generated at the crystal/sample interface at 2000 cm^{-1} was calculated to be ca. 0.67 μm. All the spectra were collected with 64 scans at a resolution of 4 cm^{-1} and recorded in the range from 4000 to 675 cm^{-1}. Samples were pressed equally in all ATR measurements to avoid the differences in the size or shape. All spectra were collected and analyzed with Omnic 7.3 software [18].

2.4. QCC

QCC based on DFT was carried out with the Gaussian 03 program. The simulations were performed under conditions of a target temperature of 298.15 K and a pressure of 101.325 kPa (STP). The optimum structures and vibrational frequencies were calculated with a B3LYP functions and a 6-31++G(d,p) basis set. All the calculations refer to

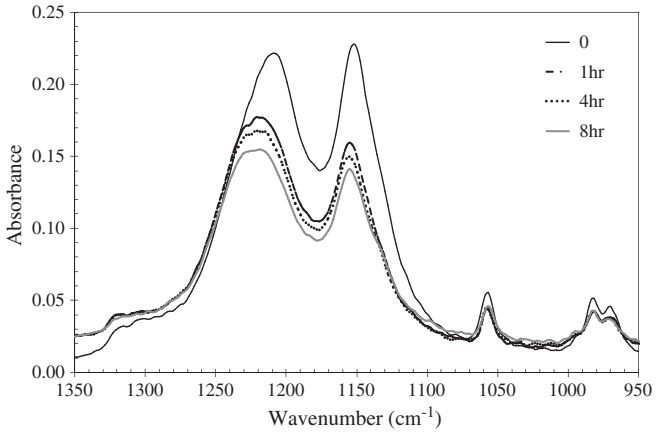

Fig. 2. Selected plots of the time-dependent IR spectra of Nafion membrane after durability test in 30% H_2O_2 at 80 °C.

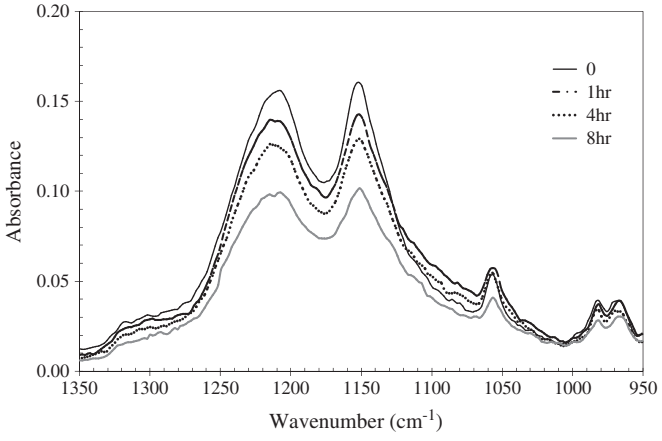

Fig. 3. Selected plots of the time-dependent IR spectra of Nafion/Aerosil 380 1 wt.% membrane after durability test in 30% H_2O_2 at 80 °C.