



Chemical degradation of Nafion ionomer at a catalyst interface of polymer electrolyte fuel cell by hydrogen and oxygen feeding in the anode

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ABSTRACT

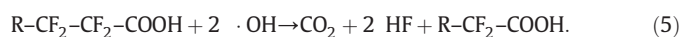
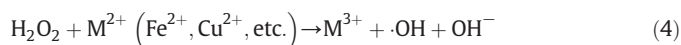
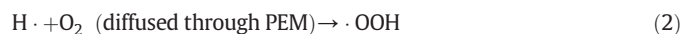
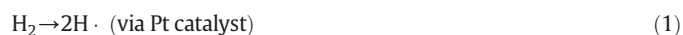
Chemical degradation products of a Nafion membrane on the catalyst interface of polymer electrolyte fuel cell (PEFC) by hydrogen and oxygen feeding into the anode were studied by high-performance liquid chromatography (HPLC). An acidic solution of pH 5.3 was obtained after the anode reaction and $5.0 \times 10^{-6} \text{ mol} \cdot \text{l}^{-1}$ of hydrogen fluoride was detected by HPLC. Degradation mechanisms of the ionomer induced by trace radical species were simulated by means of quantum chemical calculations using a model side chain terminal of trifluoromethanesulfonate (TFMS). The results indicate that H radicals and OH radicals generated by the reaction on the interface induce the production of hydrogen fluoride, carbonyl fluoride and sulfonic acids. The bond dissociation energies (BDE) of C–S and C–F bond in TFMS are calculated to be 214.5 and 569.6 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. It was clarified that the degradation of TFMS is affected not only by BDE but also by the behavior of fluorine atoms.

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1. Introduction

Durability is one of the most critical issues for commercialization of polymer electrolyte fuel cells (PEFC) [1]. Several macromolecular functions of proton-exchange membranes (PEM) have been required for stable and long-life operations of the fuel cells. Nafion, a perfluorosulfonic acid (PFSA) membrane developed by DuPont, has been widely applied as it is chemically stable, structurally durable and has a high proton conductivity when sufficiently hydrated [2–6].

Although many kinds of analogous PFSA based PEM have been developed, they do not adequately satisfy the demand for high performance fuel cell operations involving mechanical, thermal and electrochemical properties [7–10]. It has been believed that cumulative deterioration of the membrane is caused by trace radicals attacking the ionomer chain [11,12]. The generation of hydrogen radical, hydroxyl radical and degradation products by scission the ionomer chain is summarized as follows:



The performance of PEFC is known to be influenced by many parameters including the amount of trace radical and contamination of carbon monoxide (CO). Hori et al. investigated the lifetime properties of a single PEFC at 80 °C for up to 2500 h. Decrease in proton conductivity, increase in rate of hydrogen crossover and thinning membrane which directly related to PEFC power output were reported to be caused by the attack of the trace radical [13]. The adsorption of CO onto an anode catalyst also leads to the decrease in the output power of PEFC [14]. The trace amounts of CO in the hydrogen may be obtained by steam reforming of hydrocarbon fuels or a very expensive purification process should be applied [15]. Our previous work demonstrated that the adsorbed CO was removed by oxygen feeding into the anode for an oxidation reaction on the catalyst surface [14]. However, it is expected that the oxygen feeding directly into the anode causes chemical degradation of PEM.

In the present study, mechanisms of chemical degradation of PEM on the catalyst interfaces induced by oxygen feeding into the anode of a PEFC will be discussed. Chemical species generated and/or degraded on a Pt/Nafion interface during hydrogen and oxygen feeding was analyzed by high-performance liquid chromatography (HPLC). In conjunction with this, quantum chemical calculations (QCC) based on density functional theory (DFT) was performed to investigate the chemical reactions of trifluoromethanesulfonate (TFMS). The calculation was

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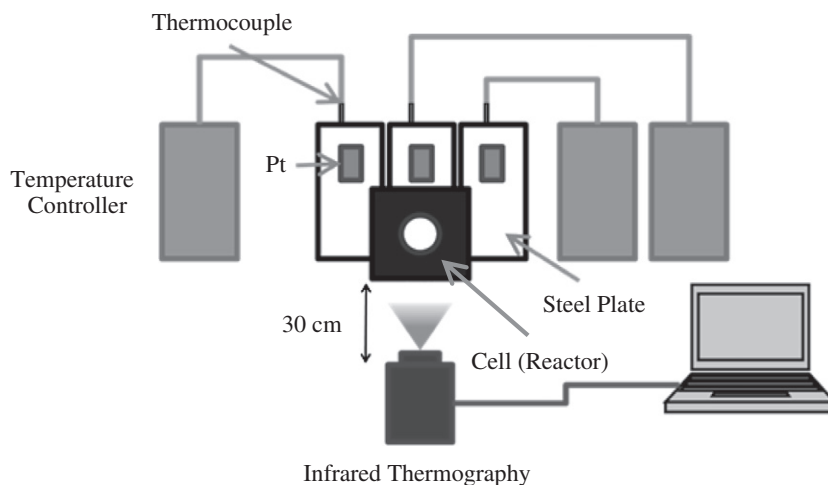


Fig. 1. Schematic diagram of the experimental system equipped with infrared thermography.

made for a model side chain terminal of Nafion ionomer, with 1–3 hydrogen radicals ($\text{H}\cdot$) and 1–3 hydroxyl radicals ($\cdot\text{OH}$). Degradation products of TFMS and their dissociation energy (BDE) will be discussed in detail.

2. Experimental

2.1. Sample preparation

A schematic diagram of the experimental system for this study is shown in Fig. 1. An infrared thermography (NEC Avio, InfRec Analyzer NS9500 Standard) was used to detect the temperature of the Pt/Nafion

interface inside the cell (reactor). The measured temperature was compared with a Pt-plated steel whose temperature was controlled. Fig. 2 shows the detailed illustrations of a laboratory-made reactor and its photograph. A Nafion (DuPont, N-117) membrane and the gas diffusion layer (GDL) were put between lower and upper parts of the reactor that was sealed using an O-ring. The carbon fiber based GDL that was integrated with the carbon-supported platinum catalyst of ca. $0.1 \text{ g}\cdot\text{m}^{-2}$ was used to effectively transport reactant gasses and electrons. Hydrogen and oxygen at flow rates of 6 and $3 \text{ ml}\cdot\text{min}^{-1}$, respectively were fed at standard temperature and pressure (STP) and exhausted at the upper side of the reactor. A liquid generated by the reactant gasses on the Pt/Nafion interface was collected after a 1 h

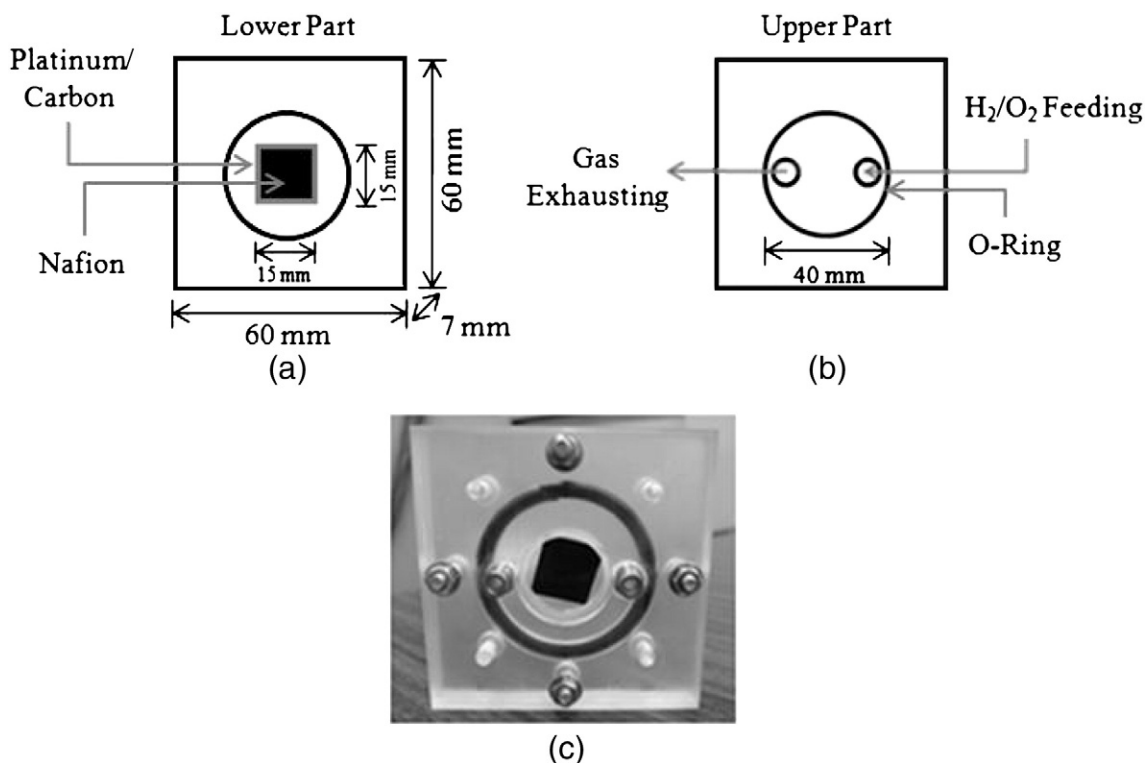


Fig. 2. Schematic design of the laboratory-made reactor. (a) Lower part, (b) upper part, (c) photograph of the reactor.

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