



A simple in situ characterization technique for the onset of the chemical degradation of PEM fuel cells' fluorinated membranes

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ABSTRACT

The onset of the chemical degradation of the fluorinated PEM fuel cells' membranes is characterized using an in situ novel technique. It is based upon measuring the pH of the water drained out from the cathode and the anode compartments using a flow pH meter connected to these outlets. It was found that the acidity of water increases significantly as the load increases if the cell operates at low temperature–low relative humidity (RH) condition after it was working at high temperature–high RH condition previously. Degradation rates were calculated from the pH measurements.

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1. Introduction

Durability is one of the main challenges for commercializing PEM fuel cells. The decrease of the PEM fuel cells' performance with time is attributed either to the degradation of one or more of the cell components [1–9] and/or to the decrease of the catalytic activity [10,11]. Electrolyte membranes are the main component of PEM fuel cells since they are responsible for the protons conduction. Its degradation can take place (i) chemically as a result of the attack of hydroxyl ($\cdot\text{OH}$) or hydroperoxyl ($\cdot\text{OOH}$) radicals on the polymer, (ii) mechanically as a result of non-uniform contact pressures, fatigue that takes place because of cycling temperature and humidity, pinholes and foreign materials introduced during the preparation, (iii) through changing of its morphology as a result of dryness, and/or (iv) through contaminations by ionic species from the bipolar plates, humidifiers and air which decrease its proton conductivity [9,12]. Cycling of load, temperature, and RH can result in an increase of the degradation rate by several orders of the magnitude [12]. Many techniques have been used in the literature to characterize the membrane degradation. Fluoride release rate (FRR) in the water drained out from the cathode and anode compartments is correlated to the chemical degradation of the fluorinated membranes [8,13–15]. Hydrogen gas cross-over mea-

suring is also used as an indicator for the chemical and mechanical degradation [8,16,17]. Impedance spectroscopy is also an effective technique in studying the change of the membrane resistance as a result of thinning of the membrane or formation of corrosion products [18]. Ex situ techniques, e.g., energy dispersive X-ray analysis (EDX) [19], fluorine nuclear magnetic resonance (^{19}F NMR) [15], X-ray photoelectron spectroscopy (XPS) [1] and X-ray diffraction (XRD) [12,20,21] were also used for characterization.

The aim of this work is to introduce an in situ, simple, and cost-efficient technique for the early detection of the onset of the chemical degradation of the fluorinated membranes within PEM fuel cells operating at different loads in a real time scale. In contrast with the pH measurements done before [22,23], the introduced pH measurements in this work for the water drained out from the cathode and anode compartments are in situ using a flow pH meter, which helped us in following the measurements under galvanodynamic conditions. In addition to that, the effect of cycling the temperature and the relative humidity and the presence of pollutants in air upon the pH measurements was studied.

2. Experimental

MEAs and a JARI standard type fuel cell were purchased from NF Corporation, Japan. The active area of the Nafion 112 membrane is 25 cm^2 ($5 \times 5\text{ cm}$) loaded with 1 mg cm^{-2} Pt catalyst at the cathode side and 1 mg cm^{-2} Pt–Ru (0.766 Pt and 0.234 Ru) at the anode side.

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MTB-36714 fuel cell system purchased from NF Corporation, Japan, was used to maintain the gases' pressures, temperatures, relative humidity (RH) and flow rates. It is worthy to mention that wherever RH is mentioned it refers to the relative humidity for both gas feeds.

The reference electrode was a reversible hydrogen electrode (RHE) with its own H₂ gas feed. This is to assure a constant hydrogen gas pressure for it.

For the pH measurements, a flow pH meter purchased from Analyticon Corporation, USA model number HM-30R was connected to the outlet of the cathode and anode compartments using a 50 cm polyethylene tube (so water drained out is cooled by air) in order to measure the pH of the water drained out from these compartments. The temperature of the water drained out never exceeded 30 °C. The pH meter was calibrated using pH buffers before and after each experiment. The measured pH values were corrected according to the temperature recorded by the pH meter during these measurements. It is worthy to mention that pH was measured for the liquid phase of water drained out from the electrode compartments.

Cyclic galvanodynamic polarization curves were measured by polarizing the cathode at different loads starting from 0 mA cm⁻², i.e. open circuit potential (OCP) to the load corresponding to 0 V vs RHE, and then scanning the load back at the same scan rate to the 0 mA cm⁻² at a temperature of 50 °C and an RH of 35%. The pH values were measured simultaneously every minute during the cyclic galvanodynamic measurements. The current scan rate was 0.5 A min⁻¹.

To check the effect of pollutants in the natural air on the pH of the water drained out from the cathode compartment, a pure artificial air was used (80% N₂ + 20% O₂). Purity of the artificial air was 99.9995%.

The effect of cycling the temperature and the RH on the pH of the water drained out from the cathode compartment was checked by comparing the pH values measured before and after working at high temperature–high RH condition. The high temperature–high RH condition chosen is 90 °C–100% RH for 10 h at OCP.

The gases' flow rates were kept constant during all the measurements at 300 and 1000 cm³ min⁻¹ for H₂ and air, respectively. The gases' pressures were kept constant accordingly at 1.5 and 25.3 kPa for H₂ and air, respectively. H₂ and air flew oppositely to each other.

3. Results and discussion

Fig. 1 shows the change in the potential and the pH as the load was cycled between 0 mA cm⁻² (open circuit potential) and the value corresponding to 0 V (it differs depending on the operating conditions of the fuel cell).

At OCP, pH was around 4.5 and then as the load was increased it increased and reached a pH value of 4.9 at a potential of 736 mV after which it decreased sharply and reached a pH value less than 1 as the load was increased. When the load's scan direction was reversed, the pH values remained almost the same as those during the forward scan at these high loads until the potential reached 649 mV, and then the pH started to increase again as the load was decreased. The final pH was 2.41 which is almost 2 pH units more acidic than the initial pH. In fact waiting for 20 min at OCP increased the pH to its initial value (4.5). These low pH values could be measured only when the MEA was fatigued at 90 °C and 100% RH for 10 h before it operates at the low temperature–low RH condition.

This can be clearly shown from Fig. 2 where the pH oscillated between pH 4 and 5 (no measured low pH values) as the load was increased from 0 A (OCP) to that corresponding to 0 V for a

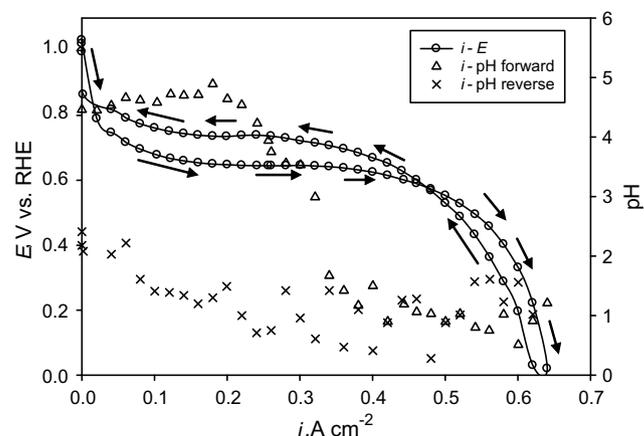


Fig. 1. The polarization behavior (solid line) and the pH variation (scattered symbols: Δ for the forward scan and \times for the reverse scan) upon cycling the load between OCP and 0 V at a temperature of 50 °C and an RH of 35%. The MEA was fatigued before measurements at a temperature of 90 °C and an RH of 100% for 10 h.

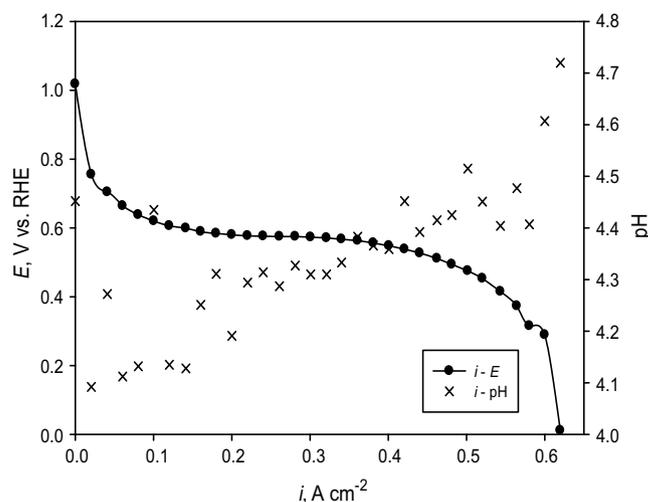
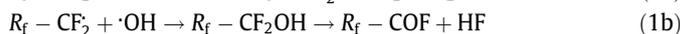
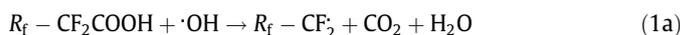


Fig. 2. The polarization behavior (solid line) and the pH (scattered symbol) variation as a function of load at a temperature of 50 °C and an RH of 35%.

non-fatigued MEA. Operating the fuel cell at higher temperatures and/or higher humidity values continuously resulted in pH values ranging between 4.5 and 7 (data not shown).

The measured low pH is assumed to result from one or more of the following chemical reactions:



Reaction (1) is the chemical degradation of the fluorinated membrane by $\cdot OH$ radicals (mentioned below). Reaction (2) is the dissolution of CO₂ in water while Reaction (3) is the Pt oxide formation. In fact, electrochemical reactions that produce protons can not be considered here since there will be no excess of H⁺ to be released from an overall electrochemical reaction.

Both Reactions (2) and (3) should be excluded from the possibility of being responsible for lowering the pH. This is supported by the following facts (the data are not shown). When using artificial

pure air instead of natural air, which contains CO₂, the pH difference in both cases was very small, and thus CO₂ dissolution in water is definitely not the major reason for measuring these low pH values. Also, measuring the pH change as a function of load and humidity has shown that pH increases significantly as the temperature and/or RH are increased. At higher temperature more Pt²⁺ ions exist and the Pt oxide formation is more favorable. If Reaction (3) is responsible for the measured low pH values, it would be expected to measure lower pH values at higher temperatures and RH values. As opposed to this expectation, the pH was found to increase at higher temperatures and/or higher RH values. Thus, the membrane chemical degradation is considered to be responsible for lowering the pH. Many reports support this conclusion. For example, Xie et al. and Healy et al. reported the existence of fluoride anions in the cathode outlet water which confirms the degradation of Nafion 112 membrane or the catalyst-layer recast ionomer, or both [14,22]. Also, Sethuraman et al. reported that the rate of H₂O₂ formation at the anode side is three orders of magnitude lower than that at the cathode side [24]. We have found that the pH of the anode water was constant and around a value of 4 (which is 3 pH units higher than cathode's water) which is almost the same difference in the rate of H₂O₂ production between both sides. In addition to that, they have found that H₂O₂ selectivity in the ORR increases as the water activity decreases (RH decreases) [24], which also agrees with the present observation where the low pH values was measured only at low temperature–low RH conditions. The role of H₂O₂ in lowering the pH is likely to be based on its decomposition to ·OH radicals by reacting with the Pt²⁺ (from corrosion of the catalyst), Ni²⁺, Fe²⁺ (from corrosion of end plates) and Cu²⁺ (from corrosion of bipolar plates) ions dissolved in the membrane [24,25]. These radicals attack the membrane causing its degradation and the production of HF which decreases the measured pH (see Eq. (1)). The reasons of measuring these low pH values only at low temperature–low RH conditions are (i) the increase in temperature decreases the stability of H₂O₂ (disintegrate to O₂ and water at high temperatures) which decreases the amount of ·OH radicals and (ii) increasing the RH decreases the amount of H₂O₂ produced during the ORR and this consequently decreases the amount of ·OH radicals.

Besides working at low temperature–low RH condition, the MEA must be operated at high temperatures–high RH before its operation at the low temperature–low RH condition in order to measure these low pH values (pH 1) where the initial working at high temperature–high RH conditions increased the amount of Pt²⁺, Fe²⁺, Ni²⁺, Cr²⁺ and Cu²⁺ significantly within the membrane (especially Ni²⁺ and Fe²⁺). It was reported that these cations enormously suppress the charge transfer step in the oxygen reduction reaction (ORR) that occurs at the Pt–ionomer interface [26] which might increase the selectivity of H₂O₂ formation. It is worthy to mention here that these cations do not affect the charge transfer step in the ORR at the normal Pt–electrolyte solution interface [27]. Therefore, in the presence of high concentrations of these metallic ions, the concentration of the formed HO· and HOO· radicals is much higher (since its formation depends on the presence of these transitions metal cations and the H₂O₂ molecules) and the degradation increases significantly as the load increases where more H₂O₂ molecules are formed. This agrees with the conclusions reported in the literature that cycling of load, temperature, and RH can result in an increase of the degradation rate by several orders of the magnitude [12]. Also, it might be attributed to the decrease in the Pt active area due to agglomeration [1] at elevated temperatures and high RH values which results in a significant generation of the peroxide during the working at lower temperature–lower RH conditions [28]. Wei et al. reported an agglomeration of the Pt nanoparticles at 95 °C where the particle's size increases from 7.5 to 12.2 nm [29].

The rate of degradation can be calculated based upon these pH measurements. The average pH in Fig. 1 is 2.1 while it is 4.3 in Fig. 2. Measuring the mass of the water collected at the end of Figs. 1 (1.86 g) and 2 (0.928 g) allowed calculating the fluoride release rate (FRR) which is equivalent to the H⁺ release rate. In Fig. 1, the fluoride release is 2.8×10^{-4} g in 66 min which is equivalent to $10 \mu\text{g cm}^{-2} \text{h}^{-1}$ which means that the whole fluorine content will be depleted after 750 h. In Fig. 2, the FRR was calculated to be $0.06 \mu\text{g cm}^{-2} \text{h}^{-1}$. This shows the danger of cycling the temperature and RH. It is inaccurate to calculate the rate of degradation from a single point (especially when the pH is very low) on the galvanodynamic polarization curve since this pH will increase with time as a result of the decrease of the concentration of the contaminating ions. Instead, a constant load should be applied and the average pH is calculated and then the degradation rate can be estimated. A constant load of 0.01 A cm^{-2} was applied for an MEA for 1 h at 50 °C–35% RH. Although during this measurement low pH values were recorded (less than 2), the average pH was 3.95 which is equivalent to a FRR of $1.63 \times 10^{-6} \text{ g h}^{-1}$ ($\approx 6.51 \times 10^{-8} \text{ g cm}^{-2} \text{h}^{-1}$).

4. Conclusions and summary

pH of the water drained out from the cathode side was found to decrease sharply starting from a certain load when the PEM fuel cell operates at low temperature–low RH condition after being working at high temperature–high RH condition. This agrees with what was reported before [8,13]. In situ pH measurements for this water using a flow pH meter enable an in situ qualitative and quantitative characterization for the onset and the amount of the chemical degradation of the PEM fuel cells' membranes. The effect of cycling the temperature and humidity was shown to increase the rate of degradation at least two orders of magnitude.

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