



# X-ray photoelectron spectroscopy investigation on electrochemical degradation of proton exchange membrane fuel cell electrodes



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## HIGHLIGHTS

- Electrochemically stressed electrodes at 20 °C and 70 °C were studied with XPS.
- Ionomer phase was found to protect catalyst from degradation.
- Catalyst layer ionomer degradation is more severe than the membrane degradation.

## ARTICLE INFO

### Article history:

Received 12 November 2014

Received in revised form

22 January 2015

Accepted 2 February 2015

Available online 3 February 2015

### Keywords:

XPS

Interface

Ionomer

Structure

Degradation

Lamination

## ABSTRACT

X-ray photoelectron spectroscopy studies were systematically carried out on the electrodes before and after the electrochemical stress tests in an aqueous electrolyte at 20 °C and 70 °C. The electrodes have different ionomer structures (no ionomer, only ionomer, physically mixed ionomer and hot pressed ionomer) but have identical, commercial catalyst and catalyst loading. A significant degree of carbon corrosion, platinum migration and ionomer degradation were observed in the electrodes after the treatment. The degradation of the ionomer in the electrode is more severe than that of membrane. The electrode structure and the corresponding interface are crucial for the catalyst performance and durability.

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## 1. Introduction

The durability issue is universally considered one of the greatest challenges preventing proton exchange membrane fuel cells (PEMFCs) from an actual stationary as well as portable energy supplier [1,2]. Platinum is so far the most effective catalyst catalyzing the electrode reactions of PEMFCs [3]. The most widely studied and applied catalyst in a PEMFC is platinum supported on high surface area carbon [4]. Degradation of such catalyst is commonly categorized into platinum degradation and carbon corrosion [2]. These two aspects interact and exaggerate each other. Such degradation mechanisms are commonly applied in accelerated stress tests (ASTs) for catalyst focused and support focused degradation protocol developments [5,6].

However, in a practical fuel cell construction, liquid electrolyte is no more applicable. Solid electrolyte ionomer is routinely impregnated in the electrode to extend the reaction zone. Only the catalysts participating in the three-phase boundary (TPB) [7] are electrochemically active. In general, the electrode structure can be optimized according to the following approaches. Firstly, gas phase accessibility may be modified with component hydrophobicity and pore former if necessary [8]. Its effects are generally related to mass transport limitation and water management issues [9,10]. Secondly, the electronic conducting phase concerns both support and catalyst. Major activities include the improvement of electronic conductivity of the catalyst support [11,12], better attachment between catalyst and support [13], and catalyst–support interactions [14]. Finally, in order to achieve a highly effective and durable electrode a robust continuous proton-conducting phase in the electrode structure is just as important as the other two phases [15]. Therefore, the focus of this study is placed on not only the catalyst and support, but also on the proton conductor in the catalyst layer.

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Nafion is one of the most widely studied and applied protonic conductors in proton exchange membrane fuel cells. The chemical structure of the polymer is shown in Fig. 1. The basic building block of Nafion is tetrafluoroethylene (Teflon) backbone and sulfonated perfluorovinyl ether side chain. The unique structure renders the polymer versatile applications as well as self-organizing properties in both homogenous [16] and heterogeneous [17,18] environments.

In our previous work [19], identical catalyst was found to possess significantly different electrochemical performance, especially with respect to the durability when the catalyst is in contact or not in contact with the ionomers. The reduction in the platinum catalyst performance (reduction of hydrogen adsorption/desorption ability in cyclic voltammetry) was due to the platinum degradation (detachment, dissolution and coalescence), carbon corrosion and ionomer degradation and change in the associated pore morphology and surface properties. We have also found [20] that the PEMFC components are of characteristic surface oxidation states and the fabrication conditions directly influence the electrode structure and surface chemistry of the pristine state.

However, the literature does not sufficiently address the degradation of the catalyst layer. Moreover, the commonly used electrochemical and other methods have failed in detecting the ionomer degradation. Besides, one of the general challenges in the fuel cell research is that there are too many factors affecting the total cell performance. Instability of one component may lead to degradation of other elements, which may not necessarily be unstable on its own under the same condition. In order to isolate problems and vary one parameter at a time, we have chosen to perform ex-situ electrochemical accelerated stress test (AST) on individual components and study the surface chemistry respectively utilizing X-ray photoelectron spectroscopy. Separate components simplify sample preparation for XPS and guarantee authenticity of the surface. Furthermore, we monitor the changes of composition and the degree of chemical oxidation of different electrode structures subjected to the stress at different temperatures.

## 2. Experimental

Catalyst powder Johnson Matthey Hispec 9100 (CP) was used as received. Catalyst ionomer electrode (CIE) was a mixture of CP and Nafion ionomer prepared according to a standard recipe [21]. Hot pressed catalyst ionomer electrode (CIE-L) was produced with a standard hot pressing (lamination) condition at 140 °C and 7 bar for 3 min. Laminated membrane electrode (M-L) is the membrane surface in a half membrane electrode assembly (MEA), where only one side of the membrane is laminated with the electrode. The interface region of the electrode and the conducting carbon layer (MEA-I) is the surface after peeling off the gas diffusion layer from a half MEA. The letters in the acronym represents the electrode type; the last two digits imply the treatment temperature and 0 means

pristine state.

The electrodes were subjected to the potential cycling between 0.4 and 1.6 V vs. RHE for 1600 cycles with sweep rate of 1 V/s in 1 M H<sub>2</sub>SO<sub>4</sub> (as a simulated fuel cell start and stop treatment) at both 20 °C and 70 °C. A glassy carbon rod was used as the counter electrode and a radiometer<sup>®</sup> Hg/Hg<sub>2</sub>SO<sub>4</sub> was used as the reference electrode. Ar purging was maintained during the measurements with a constant flow of 0.2 mL/s. The experiments were carried out with an electrochemical workstation (Zahner<sup>®</sup> IM6e). The connection between the sample and the device was established with a 0.2 mm thick gold wire. The electrochemical surface area (ECSA) was evaluated by determining coulombic charge transfer of monolayer atomic hydrogen adsorption.

After the CV treatments, the samples were carefully rinsed with ultra-pure water and left to dry in inert atmosphere. The surface or interphase of the various electrodes before and after the treatment was studied with XPS. The experiments were performed using a SPECS<sup>®</sup> system with MgK $\alpha$  (1253.6 eV) as the X-ray source at a power of 250 W. The survey spectra were scanned at a resolution of 2.5 eV, while the higher resolution spectra were scanned at 1.5 eV of resolution. The XPS data was analyzed using CasaXPS<sup>™</sup> and presented with Origin<sup>®</sup> Pro 9.1. All binding energies were calibrated with respect to C 1s: C–C peak at 284.5 eV.

## 3. Results and discussions

### 3.1. Electrochemical accelerated stress test

The various electrodes were used as working electrodes and electrochemically stressed under the same condition. The percentage change of the electrochemical surface area (ECSA) as an indication of the active platinum catalyst is presented in Fig. 2. The result clearly suggests that electrode structure has a great influence on the catalyst stability towards the potential cycling. Moreover, presence and robustness of the ionomer phase is vital for the catalyst performance. It follows the sequence (from the lowest to the highest) catalyst powder (CP), catalyst ionomer electrode (CIE), laminated catalyst ionomer electrode (CIE-L) and half membrane electrode assembly (HMEA), despite identical catalyst and catalyst loading were used for all electrodes. A similar trend is also observed at elevated temperature, but with higher degree of degradation. The utilization of the platinum nanoparticles depends not only on the catalyst itself, but also support carbon and surrounding proton conductive media, and their associated stability. The evolution of surface composition and oxidation states are the focus of this study.

### 3.2. Survey spectra and surface element content

Before and after the AST, the electrodes were studied using XPS.

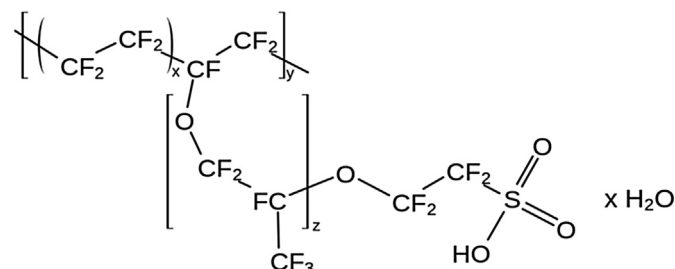


Fig. 1. Chemical structure of Nafion.

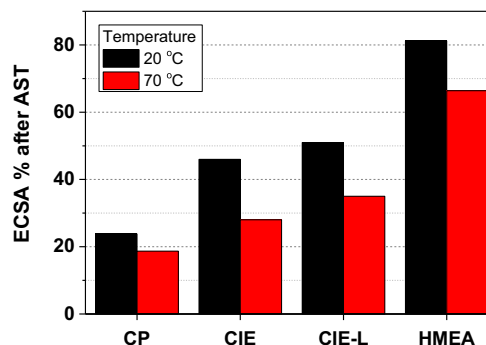


Fig. 2. Electrochemical accelerated stress test on various electrodes.

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