



Chemistry of carbon polymer composite electrode – An X-ray photoelectron spectroscopy study



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HIGHLIGHTS

- Surface oxidation state of PEMFC components and different electrodes were compared.
- The surface property of the catalyst layer is influenced by the electrode structure.
- Lamination can induce structure change in electrode.

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ABSTRACT

Surface chemistry of the electrodes in a proton exchange membrane fuel cell is of great importance for the cell performance. Many groups have reported that electrode preparation condition has a direct influence on the resulting electrode properties. In this work, the oxidation state of electrode components and the composites (catalyst ionomer mixtures) in various electrode structures were systematically studied with X-ray photoelectron spectroscopy (XPS). Based on the spectra, when catalyst is physically mixed with Nafion ionomer, the resulting electrode surface chemistry is a combination of the two components. When the electrode is prepared with a lamination procedure, the ratio between fluorocarbon and graphitic carbon is decreased. Moreover, ether type oxide content is decreased although carbon oxide is slightly increased. This indicates structure change of the catalyst layer due to an interaction between the ionomer and the catalyst and possible polymer structural change during electrode fabrication. The surface of micro porous layer was found to be much more influenced by the lamination, especially when it is in contact with catalysts in the interphase. Higher amount of platinum oxide was observed in the electrode structures (catalyst ionomer mixture) compared to the catalyst powder. This also indicates a certain interaction between the functional groups in the polymer and platinum surface.

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1. Introduction

Many advances have been achieved since the first demonstration of proton exchange membrane fuel cell (PEMFC). Non-precious metal catalysts [1], corrosion resistant catalyst supports [2] and improvements of catalyst – support attachment [3] are important milestones in the history of PEMFCs. Meanwhile, understanding and optimization of the electrode structure: water management [4], catalyst ionomer ratio [5], electrode fabrication conditions [6,7], are also of crucial importance for the advancement of the technology. Surface chemistry and morphology of the electrode, though still not well understood, are essential parameters influencing the

cell performance [8,9]. The delicate three-phase boundary (TPB), where proton, electron and gas meet and initiate the electrochemical reactions, has great impact on the catalyst utilization and cell lifespan.

Though the thickness of the catalyst layer (CL) is only around 20 μm , which is less than 5% of the total thickness of a membrane electrode assembly (MEA), CL is the heart of PEMFC, and is responsible for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). State of the art PEMFC catalyst layer consists of platinum supported by carbon and impregnated with proton conducting Nafion ionomer. The loading of the ionomer is typically in a range of 30–50% by weight [10,11], depending on the surface property of catalyst. Since the density [12] of Nafion is around 1.5 g/cm^3 , a composite electrode normally contains 40–60% ionomer by volume, depending also on hydration. This implies that the final morphology of the electrode has a significant contribution

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from the polymer phase. The interaction between the catalyst and the proton conductor is one of the most important factors affecting the electrode morphology. Moreover, Nafion thin film in the catalyst layer (less than 10 nm) is of a significantly different structure and property comparing to the bulk membrane as reported by many groups [13,14].

Due to its low molecular weight and minute thickness, Nafion ionomer in CL is nearly transparent to the most microscopic techniques [15,16]. Identification of the polymer requires normally tedious preparation of the samples for the microscopy such as staining with heavy metal ions [17], while the genuineness might be compromised. More convenient methods are various spectroscopies such as infrared [18], Raman [19], nuclear magnetic resonance [20,21] and X-ray photoelectron spectroscopy (XPS). Among those, XPS has the advantage of multi element analysis, non-destruction, high sensitivity, low sample demand and simple sample preparation.

There is a rich literature of chemical composition and oxidation state of Nafion membrane [22,23] and carbon supported platinum catalyst [24–26]. However, a fundamental study of various PEMFC components and electrode structure is currently missing in the literature. In this work, a systematic examination of carbon, platinum and Nafion polymer in various electrode structures was carried out using XPS. The spectra were investigated on various types of electrode designs. The oxidation state of carbon, oxygen, fluorine and platinum were discussed.

2. Experiment

Pristine Nafion 212 membrane (M) was used as received. The protective films on both sides were peeled off right before the XPS measurement. Thermally treated membrane (M-L) was hot pressed at 140 °C, 7 bar for 3 min (the same condition as lamination for electrode preparation). Commercially available catalyst Hispec 9100 (Johnson Matthey) with 57 wt.% platinum supported on high surface area carbon black was used for electrode preparation. A catalyst powder (CP) electrode was prepared by drop coating of catalyst water suspension on a piece of carbon paper (Toray Industries). A catalyst ionomer electrode (CIE) sample was prepared following a standard PEMFC electrode preparation recipe [2], where a catalyst – water/alcohol suspension of 30% Nafion ionomer (w/w) was coated onto a gas diffusion layer (GDL) Sigracet 35DC® (SGL Group). CIE-L was prepared by laminating CIE. The micro porous layer (MPL) is made by a mixture of active carbon and 20 wt.% polytetrafluoroethylene (PTFE), SIGRACET®. The same lamination treatment was applied to MPL, and the resulting

product is labeled as MPL-L. The MEA was constructed by laminating CIE onto membrane Nafion 212. MEA-I, the interphase between CIE-L and MPL-L in a MEA, was prepared by physically remove GDL from MEA by peeling. A list of the samples is shown in Table 1.

XPS analysis was performed using a SPECS® system. The spectrometer was equipped with a hemispherical analyzer and a monochromator and all XPS data presented in this study were acquired using Mg K α (1253.6 eV). The binding energies of the C 1s, O 1s, F 1s, and Pt 4f of the samples were calibrated with respect to C 1s: graphitized carbon peak at 284.5 eV. Survey spectra were collected at pass energy (PE) of 50 eV, resolution 2.5 eV over the binding energy range 0–1250 eV. High resolution multiplex data for the individual elements were collected at a PE of 25 eV, resolution 1.5 eV. Between 60 and 80 min X-ray exposure was applied on each sample. X-ray induced sample degradation and reproducibility were systematically studied. XPS data was analyzed using CasaXPS™. The background was subtracted using the non-linear, Shirley method. The position of the peaks fitting is within resolution of 0.2 eV.

3. Result and discussion

3.1. Survey

PEMFC components and electrodes of different structures were examined with XPS. Due to the low electron conductivity of the polymer, all membrane samples (M and ML) were found to charge and this led to a shift of 3–4 eV towards higher binding energy (BE). Such charging effects were not observed for any of the electrodes (CIE, MPL and MEA etc.) containing 20–30 wt.% polymer. This indicates that the electrodes are of good electron conductivity, since the polymer is rather homogeneously mixed among the catalyst/carbon, and the electrons can conduct through tunneling [27].

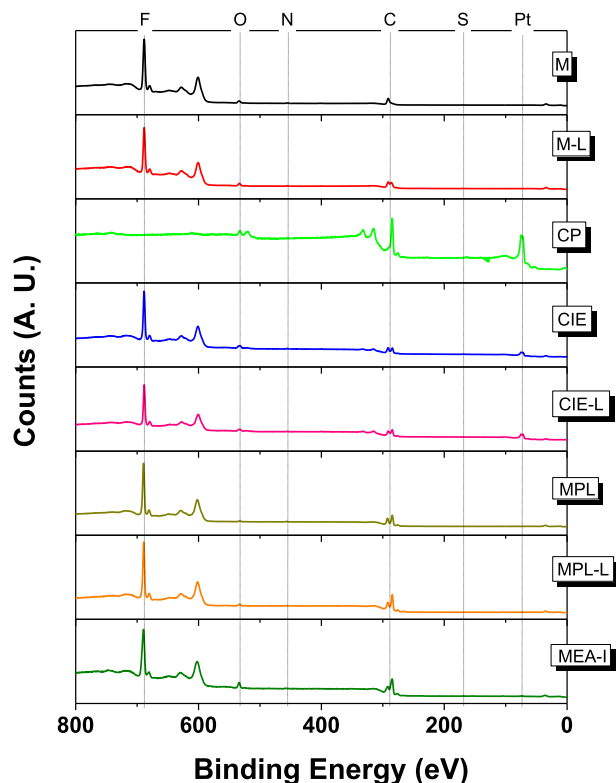


Fig. 1. Survey spectra of PEMFC components and electrodes.

Table 1
A list of samples.

Acronym	Description	Preparation
M	Membrane	Use as received
M-L	Laminated membrane	Hot pressing M at 140 °C, 7 bar for 3 min
CP	Catalyst power	Use as received
CIE	Catalyst ionomer electrode	Mixture of ionomer (30 wt.%) and catalyst
CIE-L	Laminated catalyst ionomer electrode	Hot pressing CIE at 140 °C, 7 bar for 3 min
MPL	Micro porous layer	Mixture of PTFE (20 wt.%) and active carbon
MPL-L	Laminated micro porous layer	Hot pressing MPL at 140 °C, 7 bar for 3 min
MEA-I	Interphase between CIE-L and MPL-L	Physically removing GDL from MEA, which was prepared by hot pressing CIE with Nafion 212 membrane at 140 °C, 7 bar for 3 min

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