# Modulation of the microstructure of the Ag/C-based alkaline cathode *via* the ionomer content for a bipolar membrane fuel cell

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## HIGHLIGHTS

- Ag/C based alkaline cathode was prepared for the bipolar membrane fuel cell.
- The microstructure of the Ag/C catalyst layer was modulated by ionomer content.
- 3D structure of the catalyst layer was characterized by nano-CT.

## GRAPHICAL ABSTRACT
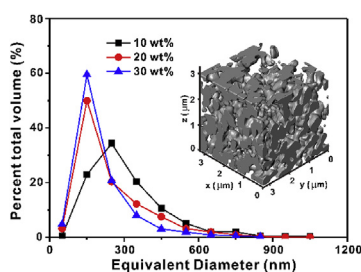
## ABSTRACT

Ag/C is evaluated as a cathode catalyst for a bipolar membrane fuel cell (BPMFC). The microstructure of the cathode catalyst layer is modulated *via* ionomer content, and the effects on BPMFC performance are studied. When the ionomer content is increased from 10 wt% to 30 wt%, the fuel cell performance is optimized at 19.3 mW/cm$^2$ with an ionomer content of 20 wt%. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) are conducted on the catalyst layer. EIS indicates that the charge transfer resistance is minimum, while CV suggests that the highest electrocatalytic activity of the catalyst is achieved with an ionomer content of 20 wt%. The microstructure of the catalyst layer is characterized using scanning electron microscopy (SEM) and nanometer-scale X-ray computed tomography (nano-CT). The SEM results show that excess ionomer cover on the surface of the catalyst, and the catalyst seems to form larger aggregates. Nano-CT, however, produces quite different results. The reconstructed 3D image of the catalyst layer reveals that the Ag/C catalyst tends to aggregate at low ionomer content. When the ionomer content is increased from 10 wt% to 30 wt%, the average diameter of the catalyst aggregation decreases from 313 nm to 210 nm.

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## 1. Introduction

The bipolar membrane fuel cell (BPMFC) is a new type of polymer electrolyte membrane fuel cell in which the polymer electrolyte membrane is a bipolar membrane. This membrane consists of a bipolar junction at the interface of the proton exchange membrane

(PEM) and the anion exchange membrane (AEM) where the PEM is directly contact with the AEM [1–4]. The PEM segment of the bipolar membrane is in contact with the acidic anode, while the AEM segment is in contact with the alkaline cathode. A BPMFC with this configuration has two advantages: 1) water generated at the PEM|AEM interface diffuses into both the PEM and AEM to provide fuel cell self-humidification, which simplifies the water management system, and 2) the alkaline cathode facilitates electrokinetics, allowing for a lower catalyst loading or for using non-noble catalysts, such as silver and nickel [5–8].

Previous investigations have suggested that BPMFCs have a very low performance of 0.64 mW/cm$^2$ at 50 °C [9]. Nevertheless, our lab has improved the power output of BPMFCs to 327 mW/cm$^2$ at 50 °C under anhydrous operating conditions by improving the contact interface between the PEM and AEM. This power output was comparable to that of a conventional PEM fuel cell [1].

Pt catalyst is used in the electrode of the BPMFCs because of its high electrocatalytic activity for the oxygen reduction reaction (ORR) in alkaline conditions. However, the scarcity and high cost of Pt impede its wide application in BPMFCs. Nevertheless, an attractive feature of BPMFCs is the elimination of platinum-group metal catalysts at the alkaline cathode. The ORR proceeds more easily in alkaline environments than in acidic environments, and several non-platinum catalysts are available for the ORR [10–13]. Non-Pt metal catalysts, such as Ag/C [14,15], Fe/N/C [12,16] and some non-precious alloys [17,18], have been used as cathode catalysts in anion exchange membrane fuel cells (AEMFCs), and they exhibit fuel cell performance comparable with that of the Pt-based catalyst. In our previous study, Ag/C was used as an alkaline cathode catalyst for a BPMFC, and it showed encouraging fuel cell performance and stability [1].

As one of the fundamental materials, the ionomer in the catalyst layers (CLs) not only acts as a physical binder, but also transfers ions. Its content significantly influences the ionic resistance, gas transmission and catalyst utilization [19]. Nafion Ionomer in electrodes have been studied a lot in proton exchange membrane fuel cells (PEMFCs). Similar conclusions have been achieved that electrons transport well at low ionomer content but the ionic conduction is poor. With the increase of ionomer content, the situation is completely different in which excess polymer would cover on the catalyst particles and hinder the electrons and reactants arriving on the reaction sites. Many factors, such as the ionomer type and catalyst loading, affect the optimal value of ionomer content. Even with the same catalyst loading, different kinds of ionomer have different optimal values [20–23]. Kaliaguine et al. found that the proper content of Nafion in anode was 25 wt%, while it was 35 wt% in cathode with a Pt loading of ~0.5 mg/cm$^2$ [24]. With the decrease of Pt loading, more Nafion is required to form well three-phase boundaries [25]. Meanwhile, the dispersion of the catalyst and the microstructure of the CLs are also changed greatly. Passalacqua et al. found that the total specific pore volume decreased when the Nafion content in CL was greater than 33 wt% [26]. Cho et al. revealed that a large number of catalyst particles agglomerated with the increase of dispersed ionomer [22]. However, the catalyst dispersion in CL remains unknown since SEM cannot distinguish the ionomer from the carbon-supported catalyst. Only information about porous phase, such as pore size and pore size distribution, can be obtained.

The development of nanometer-scale X-ray computed tomography (nano-CT) with a resolution of 50 nm offers the capability of investigating the morphology of carbon-supported catalysts in the CL. Solid materials with high atomic numbers ($Z$) absorb more radiation and hence can be distinguished from low-$Z$ materials and empty pores. Nano-CT has been used to investigate the morphology of solid oxide fuel cell electrodes [27,28]. However, there are only a few studies on the application of nano-CT to study the CL of polymer electrolyte fuel cells [29,30].

In this work, Ag/C was fabricated and used as the catalyst for the alkaline cathode of a BPMFC. CLs of Ag/C with different ionomer binder (quaternary ammonium polysulfone, QAPS) content were prepared and used to study the influence of the ionomer content on BPMFC performance and the CLs microstructure. The influences were evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in terms of electrode resistance and catalytic activity. Nano-CT was used to analyze the microstructure of the CLs. The computational reconstructions of the CLs provided visible information on the size and form of the catalyst particle agglomerates, and this can be used as criteria for evaluating electrode preparation in the future.

## 2. Experiment

### 2.1. Materials preparation

The carbon black-supported Ag catalyst (Ag loading of 50 wt %) was prepared via a chemical reduction method. Firstly, carbon black Vulcan XC-72 from Cabot (Billerica, MA) was dispersed in DI water in a reaction vessel, and a pre-calculated amount of AgNO$_3$ (Beijing Chemical Factory, China) was added to the vessel. This was incubated in an ice bath with vigorous stirring. Then, NaBH$_4$ (0.01 g/mL) was pumped into the Ag salt-carbon black mixture using a constant flow pump with a rate of 2.0 mL/min. The resulting slurries were washed with DI water, filtered, and dried according to the freeze-drying method.

### 2.2. BPM fabrication

The BPM was prepared by hot-pressing a pretreated Nafion membrane and a QAPS membrane. The Nafion membrane was pretreated with 5.0 wt% H$_2$O$_2$ and 0.5 mol/L H$_2$SO$_4$ following standard procedures. The QAPS membrane was cast and dried at 65 °C using a QAPS solution (2.0 wt%) in N,N-dimethylformamide (DMF). The thickness of the as-prepared QAPS membrane was ~10 μm. The QAPS membrane was then immersed in an aqueous 1.0 mol/L KOH solution overnight to exchange Cl$^-$ in the alkaline ionomer for OH$^-$. After several rinses in ultrapure water (Millipore, 18.2 MΩ at 25 °C) and pretreatment in ethanol, the QAPS membrane was hot-pressed with the pretreated Nafion membranes at 60 °C and 4 MPa for 10 min to form the BPM [1].

### 2.3. MEA preparation

The Pt-based acidic anode catalyst ink was prepared by mixing a Nafion solution (5 wt%), a Pt/C catalyst (40 wt%, BASF) and isopropyl alcohol. The Ag-based alkaline cathodic catalyst ink was prepared by a mixing QAPS solution (2 wt%), a Ag/C catalyst (50 wt%) and n-isopropyl alcohol. The inks were dispersed in an ultrasonic bath for 30 min before casting onto a Toray carbon paper (TGP-H-060) gas diffusion layer. The Pt loading in the acidic electrode was 0.4 mg/cm$^2$, and the Ag loading in the alkaline electrode was 1.0 mg/cm$^2$. The QAPS content of the prepared Ag-based alkaline cathode was 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt%, respectively. The alkaline cathodes were then immersed in aqueous 1.0 mol/L KOH solution to exchange Cl$^-$ in the alkaline ionomer for OH$^-$. Finally, both the Pt-based and Ag-based MEA were assembled by hot-pressing the acidic anode, the BPM, and the alkaline cathode together at 135 °C and 4 MPa for 90 s with the cathode facing the QAPS membrane.