



## Fine microstructure of high performance electrode in alkaline anion exchange membrane fuel cells



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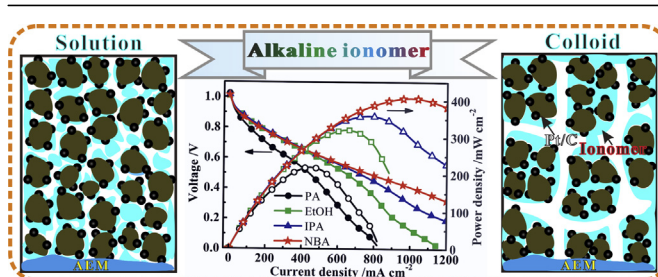
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### HIGHLIGHTS

- Microstructure of electrode with anion-exchange ionomer is studied and improved.
- The colloidal anion-exchange ionomer is prepared and evaluated for the first time.
- A high performance of  $407 \text{ mW cm}^{-2}$  in the alkaline fuel cell is obtained.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The electrode fabrication and resulting microstructure are the main determinates of the performance of alkaline anion exchange membrane fuel cells (AAEMFCs). In the present work, the electrode microstructure is adjusted by the ionomer content in catalyst layers as well as the dispersion solvent for catalyst inks. The ionomer content shows a strong influence on the cell active, ohmic and mass-diffusion polarization losses. Especially, an in-suit proof for the ionomer as the hydroxide conductor is first given by the cell cycle voltammogram, and the optimum content is 20 wt.%. Meanwhile, it is found that the ionomer either dissolves in the dielectric constant  $\epsilon = 18.3\text{--}24.3$  solutions (including ethanol, propanol and isopropanol) or disperses in the n-butyl acetate ( $\epsilon = 5.01$ ) colloid. Compared with these electrodes using the solution method, the colloidal electrode tends to form the larger catalyst/ionomer agglomerates, increased pore volume and pore diameter, continuous ionomer networks for hydroxide conduction, and correspondingly decreased ohmic and mass-diffusion polarization losses. Ultimately, when employing the optimum ionomer content and the colloid approach, the highest peak power density we achieved in AAEMFC is  $407 \text{ mW cm}^{-2}$  at  $50^\circ\text{C}$ , which can be taken as a considerable success in comparison to the current results in publications.

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## 1. Introduction

Alkaline anion exchange membrane fuel cell (AAEMFC) using a solid polymer membrane to replace the liquid caustic alkaline electrolyte, has been undergoing revolutionary developments in recent decades [1–3]. Compared with the proton exchange

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membrane fuel cell (PEMFC), AAEMFC has emerged some outstanding advantages to overcome the technical and cost issues, including the faster electrochemical reaction kinetics of both the fuel oxidation and oxygen reduction reaction, minimized corrosion issues, decreased fuel crossover rates and potentially improved water management, etc [1,4–9]. In particular, the fast reaction kinetics can reduce or remove the demand for noble metal electrocatalysts like platinum-based catalysts [2,7,10]. To fully realize these advantages, enormous efforts have been put into the research and development of AAEMFC. Unfortunately, the use of anion exchange membranes (AEMs) brings about new electrode design and assembly challenges, and the cell performance has not yet been satisfactory for the industrial and commercial application [1,11]. One of the major reasons is attributed to the lagging development of efficient membrane electrode assemblies (MEAs) due to the challenge in yielding optimal accessibility, stability and numbers of three phase boundaries (TPBs) where the catalysts, ionomers and reactants meet and react [9,12–16]. To build ideal TPBs and electrode architectures, the fabricated MEAs require a combination of high catalyst utilization, sufficient ion conduction, and flexible reactant and product transport in the CLs [17]. Research on advanced MEA design and preparation should be necessary to make the performance break through.

The MEA as the fuel cell's heart is typically composed of an AEM, catalyst layers (CLs) and gas diffusion layers [18]. Currently, the state-of-the-art method for creating the CLs is the catalyst coated membrane (CCM) where CLs are formed by directly coating catalyst slurry on both sides of the AEM. Its advantage over the traditional catalyst-coated gas diffusion electrode is the incorporation of more catalyst particles into the solid electrolyte media, where hydroxide are more easily to transport from the cathode to the anode [19]. The CLs play critical roles of reducing the reaction activation barrier as well as cost for fuel cell [20]. The catalyst slurry used to fabricate CLs is usually constituted of catalyst nanoparticles mixed with ionomer/binder and dispersion solvent. In a traditional PEMFC system, the use of Nafion ionomer in CLs can extend the TPBs of catalytic reaction. The Nafion ionomer serves as the physical binder and proton conductor in the porous CLs, and the molecular interaction between the catalyst particles and ionomer will play a significant role in governing the final microstructure and properties of the MEA [14,21–23]. However, the excessive ionomer enriched in the CL surface will cause a negative impact on the electrochemical reaction due to high shielding of Pt-based particles and the increased limitations of the reactant, product and electron transport [21]. Therefore, the optimization of the ionomer content is a critical step in achieving high-performance MEAs. Besides, in our previous work, the commercial anion-exchange ionomer AS-4 was identified with the high hydroxide conductivity and good stability in the AAEMFC using our home-made AEM [24].

As a matter of fact, it is known that the dispersion solvent for the catalyst ink controls the ionomer molecular morphology in solution and thus determines the final microstructure of ionomer in the CLs [25,26]. The low-boiling solvents such as ethanol (EtOH), propanol (PA) and isopropanol (IPA) are frequently used to dissolve the alkaline ionomer commonly with the quaternary ammonium hydroxide [24,27,28]. In the meantime, it was reported that the dielectric constant ( $\epsilon$ ) of the organic dispersion solvent determines the state of the Nafion ionomer used in PEMFCs, including solution when  $\epsilon > 10$ , colloid when  $3 < \epsilon < 10$  and precipitate when  $\epsilon < 3$ , respectively [25,29–31]. This is because the  $\epsilon$  value of a solvent molecule strongly relates to its polarizability, and characterizes the solvation and dispersibility to molecules/ions of another substance like ionomer. It is interested to note that ionomer dispersion states adjusted by the solvent'  $\epsilon$  can change the shapes of double layer region on catalyst surface and eventually influence the charge

transfer process [32,33]. However, the alkaline system with the anion-exchange ionomer is significantly different from the acidic PEM system with the Nafion ionomer due to the varied ionomers and membranes [1]. Additionally, some other properties of dispersion solvents, such as boiling point, relative volatilization rate and viscosity, also may cause a formidable influence on the electrode microstructure.

In the current study, we seek to investigate and understand the influences of the ionomer content in CLs and the dispersion solvents for the catalyst slurry on the electrode microstructure and corresponding performance. Using the optimized fabrication approach, our results indicated that the prepared electrode with improved microstructure obtained significantly high performance in AAEMFC.

## 2. Experimental

### 2.1. MEA fabrication

To prepare a CCM, the commercial 70 wt. % Pt/C particles (Johnson Matthey), 5 wt.% AS-4 solution (Tokuyama Corp.) and A-201 membrane (Tokuyama Corp.) were supplied as the electrocatalysts (both in the anode and the cathode), alkaline ionomer and AEM, respectively. Catalyst inks composed of the electrocatalyst, ionomer and dispersion solvent were homogenized for 1 h in an ultrasonic bath. The resulting inks were then sprayed onto both sides of the AEM. The Pt loading measured by weighting was about  $0.4 \text{ mg cm}^{-2}$  on each side including the anode and cathode. The ionomer content which was equal on each side was described as the dry weight proportion of the ionomer to the whole CL. Two pieces of carbon paper (Toray, TGP-H-060) were utilized as the anode and cathode gas diffusion layer, respectively. MEAs were prepared by hot-pressing the sandwich of the CCM and the gas diffusion layers at  $60 \text{ }^\circ\text{C}$  and 1 MPa for 2 min.

### 2.2. Characterization of CL microstructure

The surface morphology of the prepared CCMs was observed by the scanning electron microscope (SEM, JOEL JSM-7800F) with an accelerated voltage of 5 kV. The pore structures of electrodes were measured by the mercury intrusion porosimetry (MIP) with a Quantachrome PoremasterGT 60. The test pressure ranged from 200 psi to 30000 psi and the mercury contact angle was  $140^\circ$ .

### 2.3. Single cell tests

The prepared MEAs were assembled into fuel cells designed with an effective area of  $5 \text{ cm}^2$ . Fuel cell test were conducted at  $50 \text{ }^\circ\text{C}$  by passing  $\text{H}_2/\text{O}_2$  (100% relative humidity, RH) with the flow rate of  $100/200 \text{ mL min}^{-1}$  at 0.05 MPa, respectively. The  $i$ - $V$  curves, high-frequency resistance ( $R_{\text{HF}}$ ) and in-situ electrochemical impedance spectroscopy (EIS) spectra of single cells were measured and recorded by an electric load system (KMF2030, Kikusui Electronics Corp.). The EIS experiments were carried out at a current density of  $100 \text{ mA cm}^{-2}$  with a small-amplitude alternating current of  $10 \text{ mA cm}^{-2}$  and the frequency range was from 0.1 Hz to 10 kHz.

After the EIS test, the in-suit cell cyclic voltammogram (CV) was collected at  $50 \text{ mV s}^{-1}$  and  $50 \text{ }^\circ\text{C}$  between 0 V and 1 V to monitor the function of alkaline ionomer content in CLs.  $\text{H}_2$  gas (100% RH,  $100 \text{ mL min}^{-1}$ ) was supplied to the anode as counter electrode and reference electrode, and  $\text{N}_2$  gas (100% RH,  $300 \text{ mL min}^{-1}$ ) was fed into the cathode as working electrode.

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