

# Design of highly wettable microstructure for enhancing the oxygen-water transport dynamics in anode catalyst layers of PEMWE<sup>#1</sup>

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## ABSTRACT

Proton exchange membrane water electrolysis (PEMWE) has a certain fluctuating load following ability and is an effective way to realize renewable energy consumption. The performance and stability of PEMWE are seriously affected by the gas-liquid countercurrent that occurs at the interface of the anode catalytic layer (ACL) and the porous transport layer (PTL). In this work, polyethylene glycol (PEG) was used as an ACL ink additive to improve slurry stability and to control the wettability of the catalyst layer by varying the mass ratio of PEG to Nafion. Single flow channel modelling was used to obtain the water saturation of the ACL. The results show that the addition of PEG to the slurry can make the slurry more stable and improve the hydrophilicity of the ACL. When the mass ratio of PEG to Nafion is 5:5, the water contact angle of the catalytic layer is 72.3°, and the performance of the electrolyzer can reach 3.07 A·cm<sup>-2</sup>@1.9 V, which is 0.07 A·cm<sup>-2</sup> higher than that of DOE 2025 target. This paper is innovative and instructive for the design of CL/PTL interface in electrolyzer.

**Keywords:** proton exchange membrane water electrolysis, ink stability, anode catalyst layer structure, wettability

## NONMENCLATURE

### Abbreviations

PEMWE Proton exchange membrane water electrolysis

### Symbols

s water saturation

technology with fast start-up and shutdown advantages to match the volatility of renewable energy generation[1–4]. The PEM electrolyzer consists of end plates, bipolar plates (BP), porous transport layers and membrane electrode assembly (MEA)[5]. The anode catalyst layer (ACL) in the MEA is an important place for the reaction to take place, and plays a key role in the transfer of electrons, protons, and gas-liquid two-phase transport, which directly affects the performance of the PEMWE.

The countercurrent of water and oxygen constantly occurs on the surface of ACL, but the resistance to the desorption of product oxygen molecules is relatively large, and a large number of stagnant bubbles impede the transport of reactant water, reducing the effective active area of the catalytic layer[6–8]. Especially at high currents, the mass transfer loss increased significantly. The performance of the electrolyzer decreased significantly. This indicates the important role of the ACL in the two-phase flow of PEMWE. The structure and physicochemical properties of the ACL directly affect the performance of the PEMWE. The ACL is usually deposited on the PEM surface by ultrasonic spraying, screen printing and ink jet printing of catalyst inks. The catalyst inks therefore have a significant influence on the microstructure of the ACL. The structure and morphology of ionomers in the catalyst inks are related to solvent and ionomer adsorption behaviour on the catalyst.

In this paper, high-performance ACLs were prepared using polyethylene glycol (PEG) as a slurry additive. Highly water-soluble PEG as an additive can improve the stability of the ink and reduce the agglomerate particle size. The ACL wettability can be regulated by changing the mass ratio of PEG to Nafion in the ink. The electrochemical test results show that the ACL is the

## 1. INTRODUCTION

Proton exchange membrane water electrolysis (PEMWE) is the most promising hydrogen generation

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most hydrophilic and has the best performance in the electrolyzer when the mass ratio of PEG to Nafion is 5:5, and the experimental results are verified by single flow channel numerical simulation.

## 2. MATERIAL AND METHODS

### 2.1 MEA preparation

PEG nanosheets (Makllin, average MN=10000) were first dissolved in ultrapure water (Millipore, > 18.2 MΩ) to form a solution. ACL ink was prepared by blending IrO<sub>2</sub> catalyst (Alfa Aesar, 84.2wt%), Nafion solution (DuPont, 5wt%), PEG solution in mixed solvents (isopropyl alcohol and ultra-pure water). The following PEG/Nafion mass ratios were used to investigate the effect of PEG mass on MEA performance: 0:10 (Nafion), 1:9 (P1N9), 3:7 (P3N7), 5:5 (P3N7), 7:3 (P7N3), 9:1 (P9N1). The conventional ACL was prepared in the same way as above, except for the addition of PEG. Both ACL and CCL inks were ultrasonic sprayed on the two sides of a proton exchange membrane (Nafion 115), respectively. Subsequently, MEAs were boiled in 80 C ultra-pure water for 2 h to dissolve PEG, and this process was repeated for three times to ensure all the PEG has been removed. The active electrode area was 2.6×2.6 cm<sup>2</sup>. The precious metals loadings for the anode and cathode were 2.0 and 0.2 mg·cm<sup>-2</sup>, respectively.

### 2.2 Physical characterizations

The ACL thickness and surface were evaluated using scanning electron microscopy (SEM; VEGA3, TESCAN). The morphology of the dispersed IrO<sub>2</sub> catalyst agglomerates was observed by transmission electron microscopy (TEM; FEI Talos F200X, FEI Co., Ltd.). The particle size distribution (PSD) of 200 catalyst agglomerates randomly selected from TEM images was assessed using the ImageJ software. The stability of the catalyst inks was evaluated by measuring the zeta potential (Zetasizer Nano ZS90) and viscosity (MCR92).

### 2.3 Electrochemical characterizations

A commercial electrolyzer with a 2.6×2.6 cm active area (Mainz-PEM-04, Mainz Laboratory Equipment Co., Ltd.) was utilized to evaluate the PEMWE performance. Titanium fiber felts (~240 μm thickness, 50 % porosity, Bekaert Co., Ltd.) were used as the porous transport layers in both the cathode and anode. Electrochemical tests were performed using an electrochemical workstation equipped with a potentiostat and booster (Reference™ 3000 potentiostat & 30k Booster, Gamry Instruments). All testing procedures were operated at 80 °C with a water flow rate of 5 mL min<sup>-1</sup>. The

polarization curves were tested as follows: 0-0.04 A cm<sup>-2</sup> in 10 mA steps, 0.04-0.2 A cm<sup>-2</sup> in 20 mA steps, 0.2-1.6 A cm<sup>-2</sup> in 100 mA steps, and greater than 1.6 A cm<sup>-2</sup> in 200 mA steps. Each step was maintained for 2 min to ensure accurate and stable data. Electrochemical impedance spectra measurements were made in the range of 0.05 Hz-100 kHz with the current perturbations of ±200 mA to determine the high frequency resistance (HFR), charge, and mass transport impedance of different MEAs. The cyclic voltammetry (CV) curves were recorded at a scanning rate of 50 mV s<sup>-1</sup> from 0.2 to 1.4 V with H<sub>2</sub> fed to the cathode side and DI water fed to the anode side to calculate the ECSA. During the measurements, the anode was used as the working electrode and an N<sub>2</sub>-stream of 100 mL min<sup>-1</sup> was injected into its water loop, while the cathode was used as the reference/counter electrode and it was supplied with H<sub>2</sub> at 80 mL min<sup>-1</sup>.

### 2.4 Numerical model

In this study, a three-dimensional single-channel model is employed to compute the two-phase distribution inside the PEM electrolyzer (Fig. 1). All basic components including the bipolar plate (BP), porous transport layer (PTL), and membrane electrode assembly (MEA) are included in the model. The COMSOL Multiphysics software is employed to solve the above conservation equations. Before computation, mesh independence is ensured by examining five different mesh quantities: 46,000, 51,000, 56,000, 65,000, and 73,700. The mesh number of 65,000 is finally adopted in this study considering both computational accuracy and efficiency.

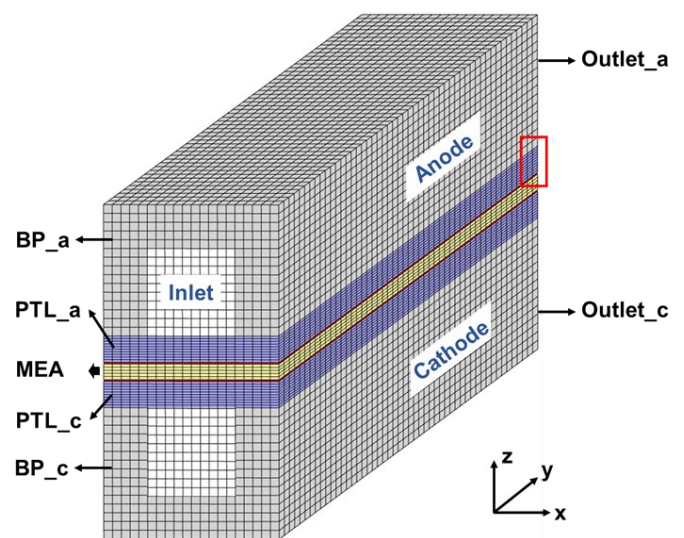


Fig. 1 Structure of single-channel model

### 3. RESULTS

#### 3.1 Catalyst inks stability

The viscosity of catalyst inks was measured with different mass ratio of PEG and Nafion (Fig. 2a). PEG is hydrophilic and lipophilic, the results indicated that PEG can increase the viscosity of catalyst inks. The viscosity of the ink increased with the PEG mass ratio. Dispersant lipophilic groups adsorbed on the surface of solid particles, hydrophilic groups for the solvation of aqueous media, and the expansion of the aqueous medium, which around the particles to form a charged protective barrier, double-layer surrounded by particles, electrostatic repulsion between particles to stabilize the dispersion. The main chain of nafion is hydrophobic and the side chains are hydrophilic. It has been thoroughly demonstrated that the effect of PEG can effectively promote the dissolution of the ionomer's main chains and side chains, increase the repulsive volume of the ionomer, and thus increase the viscosity of the dispersion. Zeta potential can be regarded as the effective surface potential (on the sliding surface) of the agglomerates in the ink, and is therefore an indicator of colloid stability: high zeta potential particles tend to agglomerate less than low zeta potential particles due to the greater electrostatic repulsion. (Fig. 2b). Zeta potential is negative, as bare  $\text{IrO}_2$  particles are negatively charged as well as Nafion ionomer due to the presence of sulfonate functional groups ( $-\text{SO}_3^-$ ), which is consistent with recent reports. Addition of PEG in the inks resulted in a higher negative zeta potential. When the mass ratio of PEG to Nafion is 5:5, the zeta potential of the ink is highest negative and the ink is most stable. The addition of an excessive quantity of PEG resulted in the coagulation of the slurry, a reduction in the absolute value of zeta potential, and a deterioration in the stability of the ink.

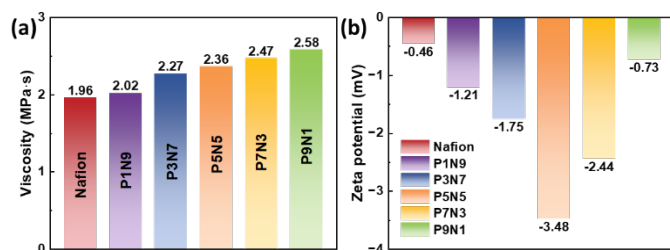


Fig. 2 (a) Viscosity, (b) Zeta potential of prepared inks

#### 3.2 Anode catalyst layer microstructure

Fig. 3 showed the surface morphology of the ACL prepared with different ratios of PEG to Nafion. With the

addition of PEG, the surface structure of the CL gradually transforms from dense to loose. The particle size of the particles deposited on the surface of the ACL decreased and there were no visible cracks on the surface. This demonstrated that PEG can promote ionomer dispersion in ink, make ionomer evenly distributed, and reduce the agglomeration degree of catalyst particles in inks. In addition to changes in surface morphology, a significant number of pits appear on the ACL surface after removal of PEG. With pore-forming agents being removed, a large number of microscale cavities are formed, and this would further increase active sites and enhance mass transfer.

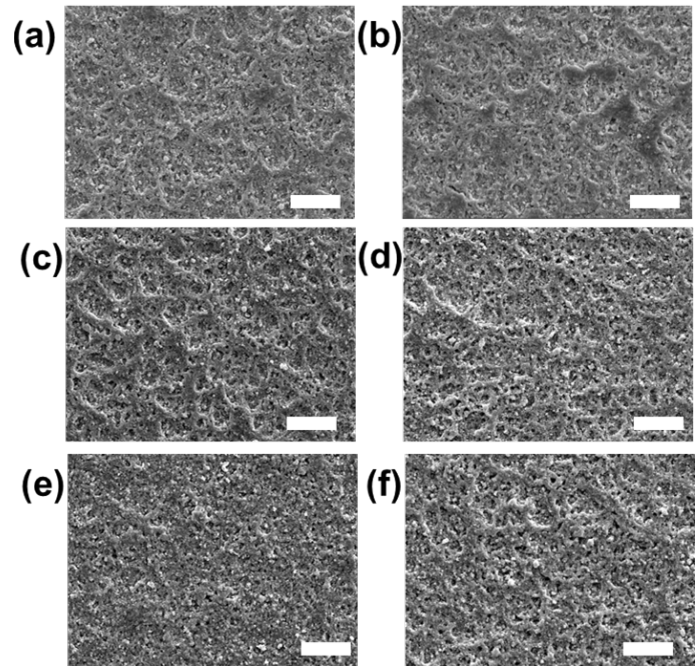


Fig. 3 The surface morphology of the ACL of (a) Nafion, (b) P1N9, (c) P3N7, (d) P5N5, (e) P7N3, (f) P9N1. Scale bar, 25  $\mu\text{m}$ .

The water contact angles of the ACL were measured to determine its hydrophilicity (Fig. 4). The traditional ACL was extremely hydrophobic, with a water contact angle of approximately  $139.8^\circ$ . The hydrophilicity of the catalyst layer decreased and then increased with increasing mass ratios of PEG. The addition of PEG to the inks increased the hydrophilicity, with morphological changes in the catalytic layer. The water contact angle of the ACL of P5N5, on the other hand, was generally small, approximately  $72.3^\circ$ .

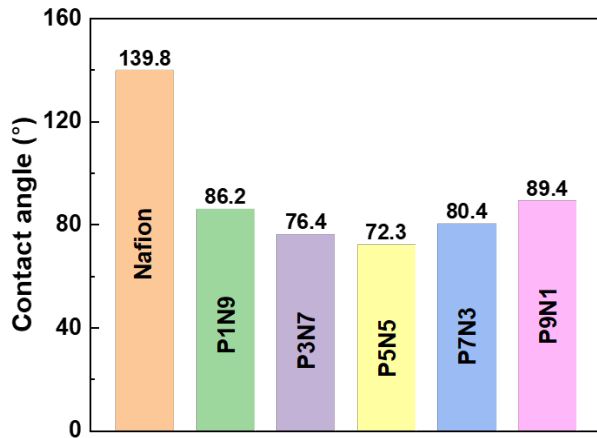


Fig. 4 The water contact angle of ACL

### 3.3 Electrochemical properties of the catalyst layer

The effect of the mass ratio of PEG to Nafion of the ACL on MEA performance was evaluated by LSV and CV testing (Fig. 5). As the mass of PEG increased, the PEMWE cell current density initially increased from  $2.92 \text{ A cm}^{-2}$  (P1N9) to  $3.05 \text{ A cm}^{-2}$  (P5N5), and then decreased to  $2.44 \text{ A cm}^{-2}$  (P9N1) under the voltage of 1.9 V. These changes in performance result from the variations in the ink stability and ACL microstructure (as described above). When the mass ratio of PEG to Nafion is 5:5, the ink is the most stable, the hydrophilicity of the catalytic layer increases and the PEMWE cell performance reaches the best.

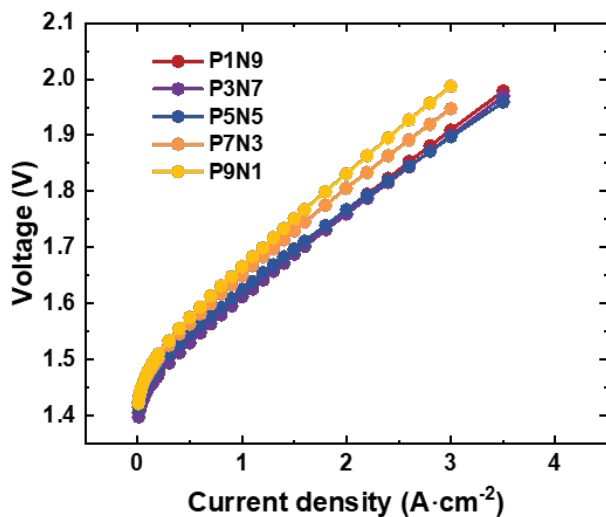


Fig. 5 LSV curves of MEA of different mass ratio of PEG to Nafion

### 3.4 Water saturation analysis

Fig. 6 showed the model prediction and comparison of water saturation in the different ACL with varied water contact angle. Fig. 6a showed the average liquid phase saturation (liquid water volume fraction) within the anode CL obtained from simulations for different CL contact angles. It showed that hydrophilic ACL (contact angle is  $72.3^\circ$ ) was the most liquid saturated within the CL, while the hydrophobic ACL (contact angle is  $139.8^\circ$ ) had the lowest liquid saturated within the catalyst film, only 24.7%. As the degree of hydrophilicity (hydrophobicity) of the ACL increased, the mass transfer of water into the ACL and the ability to expel the gas generated in the ACL were enhanced. This resulted in an increase in the content of liquid water in the CL, which facilitates the electrochemical reaction. Fig. 6b showed a cloud map of the distribution of the liquid water saturation in the y-z section in the vicinity of the outlet of the flow channel. It could further illustrate that when the difference in liquid water saturation within the PTL is not significant, hydrophilic treatment of CL could significantly increase the liquid water content within CL to facilitate the electrochemical reaction.

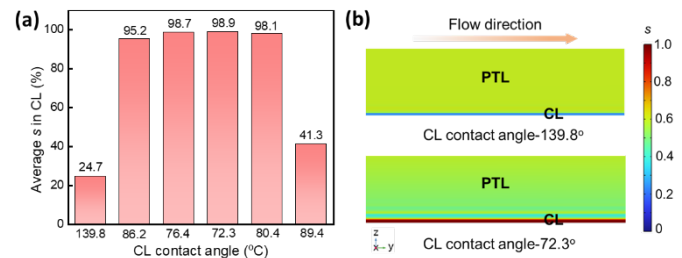


Fig. 6 (a) Average liquid saturation in the CL under different contact angles, (b) Liquid saturation distribution at the end of the flow direction for anode PTL and CL.

## 4. CONCLUSION

This study investigated the effects of the addition of PEG in catalyst inks on electrolyzer performance. The results showed that increasing the mass percentage of PEG in the ink reduces catalyst agglomerate particle size and improves slurry stability, resulting in increased MEA active area and improved electrolyzer performance. A catalysed ink with excellent stability and a MEA showing superior performance ( $3.05 \text{ A}\cdot\text{cm}^{-2}@1.9 \text{ V}$ ) can be prepared when the mass ratio of PEG to Nafion is 5:5.

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