

Solvent evaporation processes on the catalyst ink microstructures and electrochemical performance of proton exchange membrane fuel cell

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ABSTRACT

The microstructure of the catalyst layer has a great influence on the performance of the fuel cell. Industrial camera and optical microscope are used to observe the drying process and deposition of catalyst inks, and electrochemical tests are performed by linear sweep voltammetry. The focus is on the drying kinetics of the catalyst ink with different isopropyl alcohol (IPA) contents in the solvent and the effect on the formation of the microstructure. Experiments have found that the deposition height is symmetrical in the diameter direction. A coffee ring is formed at the edge of the deposition, and the slender aggregates are arranged in the shape of petals inside the edge. As the IPA content decreases, the deposition becomes more uneven, the circulatory flow is gradually activated, and a large number of particles run from the edge of the droplet to the center.

Keywords: Catalyst ink, Solvent evaporation, Drying kinetics, Catalyst layer, Microstructure, Proton exchange membrane fuel cell

1. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is a device that directly converts the chemical energy of fuel into electrical energy through electrochemical reaction. In order to boost the commercialization, it is necessary to reduce the cost and improve the performance of fuel cells. Some studies have shown that the non-uniformity of the microstructure of the catalyst layer (CL) is the root cause of the fuel cell malfunction [1, 2]. Spraying method is often used during the preparation of CL, and the ink is distributed on the membrane in the form of droplets. Therefore, the adjustment and optimization of the catalyst ink ratio contributes to the optimal design

of the CL structure and the improvement of cell performance.

Wang et al. [3] mainly studied the drying kinetics of the ink with different Nafion loadings. Their experiment showed that when the proportion of $W_{\text{Nafion}} / W_{\text{Nafion+Pt}}$ increases from 6.25% to 62.5%, a circulating formed inside the droplet. The pinning time of the contact wire increased, and the thickness of the coffee ring became wider. Zhao et al. [4] focused on the drying process of droplets under different dilution ratios and humidity. They achieved the phase separation and reconstruction of the catalyst and ionomer. However, most existing research focus on the catalyst ink droplet drying process without connecting with electrochemical testing, and many studies have not investigated the exact composition and quantity of the solvent in detail.

Therefore, this study will focus on the drying kinetics of different ratios of isopropanol and water used as catalyst solvent. The optical microscope (OM) and industrial camera are used to characterize the drying process and microstructure of catalyst ink. Moreover, a rotating disk electrode (RDE) is used for oxygen reduction reaction (ORR) test to characterize the catalyst activity.

2. EXPERIMENTAL

2.1 Catalyst Ink Preparation

The catalyst ink is prepared by mixing 20% Pt/C (Johnson Matthey, UK), Nafion solution (5 wt%), isopropanol (IPA, ENERGY, 99%) and ultrapure water (Milli-Q Advantage A10). The weight ratio of catalyst particles to ionomer maintains 3:1 in this study, which is widely adopted in industry [5-7]. The solid content (catalyst particles and Nafion polymers) concentration remains below 2%. Catalyst ink samples are prepared

using different IPA contents, and $W_{IPA}/W_{IPA+water}$ are 95%, 80%, 50%, and 20%, respectively, including the range of ratios found in the literature. The specific information of the catalyst ink used in this study is shown in Table 1. The catalyst and the organic solvent are mixed and ultrasonicated for ten minutes to disperse the catalyst particles. Then add Nafion solution and sonicate for 60 minutes.

The drying kinetics of the catalyst ink is observed using an industrial camera and an OM. The droplet dispensing system utilizes a syringe (Hamilton 7001 KH SYR, capacity of 1 μ L with resolution to 0.01 μ L) to control the volume of each droplet and to disperse the 1 μ L ink droplet onto the surface slides. The experiments are carried out at 298 K and repeated at least 6 times for each test.

Table 1. Materials in different catalyst inks

Materials	Case I	Case II	Case III	Case IV
Pt/C particles, %	0.6	0.6	0.6	0.6
Nafion Polymer, %	4	4	4	4
Isopropanol, %	90.63	76.32	47.7	19.08
Ultrapure water, %	4.77	19.08	47.7	76.32

2.2 Phase Distribution

Assume that the CL is homogeneous and isotropic. This means that the statistical average can be replaced by the volume average and the volume average can be further replaced by surface average. Therefore, the volume ratios, which can be evaluated by area ratios in 2D experimental images, can be used to evaluate the boundaries of intensity (or gray values) of each component when each pixel is assumed to represent an individual phase.

Table 2. Parameters for droplet deposition imaging analysis

Case #	I	II	III	IV
Diameter of deposition, mm	7.1	6.13	6.22	3.4
Area fraction of deposition, %	65.4	63.3	48.67	70.66
Area fraction of Pt/C, %	24.05	22.35	18.01	26.14
I_a	109	101	95	54
Pining time, S	6	17	57	185
Total time, S	21	23	90	281

Based on the above assumptions. The specific phase separation process is as follows: First, the deposition area fraction can be obtained according to the

deposition area and the total area of the image. Then the catalyst area fraction can be obtained. Subsequently, the number of catalyst pixels is obtained through the total number of pixels and the catalyst area fraction. Finally, a MATLAB programming is used to calculate the catalyst gray threshold and separate it out.

2.3 Optical Microscope

In this study, an optical microscope with ultra-depth of field is used to observe the microstructure of the catalyst ink deposition. The OM can focus parts at different heights and import multiple images to synthesize 3D images to show deposition thickness distribution.

2.4 Oxygen Reduction Reaction

Polytetrafluoroethylene (PTFE) is usually used as an insulator. Platinum wire or glass carbon are processed into a precise disk which is tightly nested in the insulator. A strong convection system is formed by driving the shaft of the disk electrode to rotate by the motor, and the current signal of the working electrode is collected by the upper brush to test the ORR performance of the catalyst [8].

In this experiment, 0.1 M $HClO_4$ is used as the electrolyte and a saturated calomel electrode is used as the reference electrode. The glassy carbon electrode is polished 100 times in the forward and reverse directions on the suede which mixed with alumina and water. The working electrode is connected to the speed controller, and the liner sweep voltammetry (LSV) test is performed at the speeds of 400, 800, 1200, 1600 and 2000 rpm. The voltage ranges from 1.2 V to 0.15 V vs RHE for unidirectional scanning, and the scanning speed is 10 $mV s^{-1}$.

3. RESULTS AND DISCUSSION

In order to better understand the influence of different IPA contents on the drying kinetics and microstructure formation of catalyst ink droplets, the following four droplet types calculated by weight, $W_{IPA}/W_{IPA+water}=95\%$, 80%, 50% and 20% are introduced and studied. The above four droplets are named IPA 95, IPA 80, IPA 50 and IPA 20, respectively.

3.1 Drying Kinetics

As the IPA content is decreased, the total drying time from contact line to final drying is increased. The specific time is shown in Table 2.

Fig. 1 shows a snapshot of the drying kinetics of the four samples. As shown in Fig. 1 (a), the droplets of IPA

95 appear as puddles. The surface tension from the edge to the center of the drop is insufficient, so there is no circulatory flow. For IPA 80 shown in Fig. 1 (b), a vortex is formed near the contact line, and the particles move randomly in the vortex. Interestingly, at the end of the drying process, a large number of particles at the edge of the droplet run together towards the center of the droplet. The white arrows in Fig. 2 (b) indicate the direction of particle movement. As the IPA content continues to be decreased to 50% shown in Fig. 1 (c), the particles rush to the edge contact line, and a large amount of liquid gathers at the edge and produces petal-like vortices, which then continue to expand and merge into larger vortices. At this concentration, the circulatory flow phenomenon is very obvious. As for the IPA 20 in Fig. 1 (d), the drying time is greatly increased due to the large amount of water in the solvent. At this time, the pinning phase of the contact line almost dominates the entire drying process, ultimately resulting in the widest coffee ring.

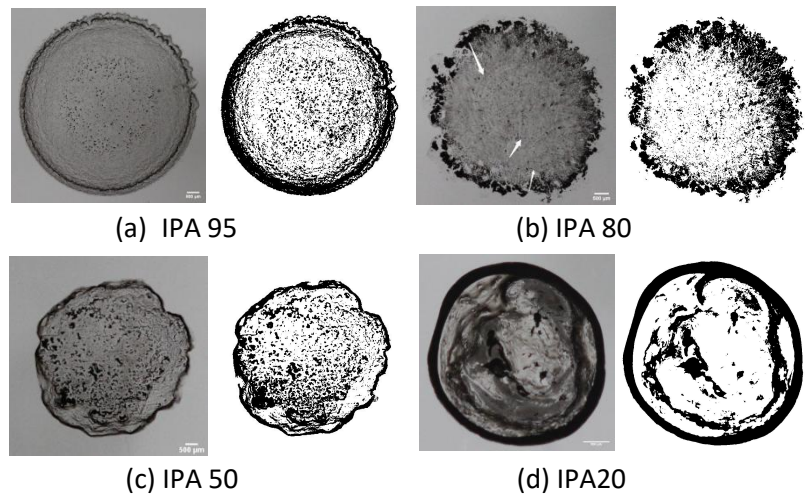


Fig. 2 Dried mode of catalyst ink droplet and catalyst phase separation.

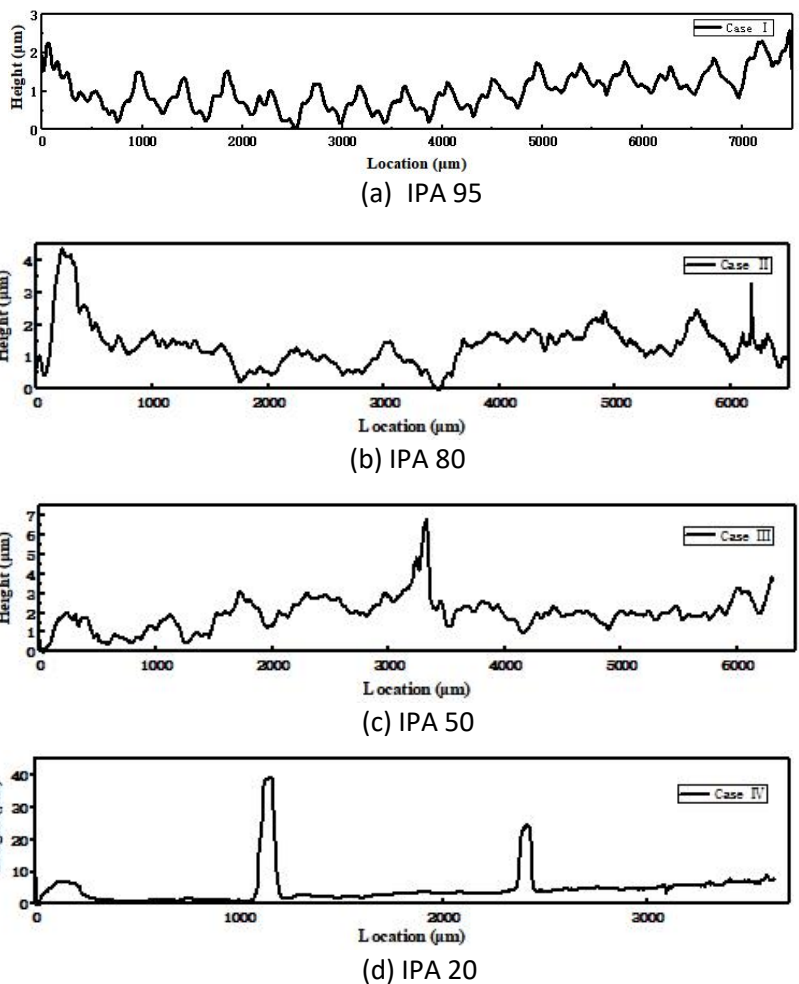
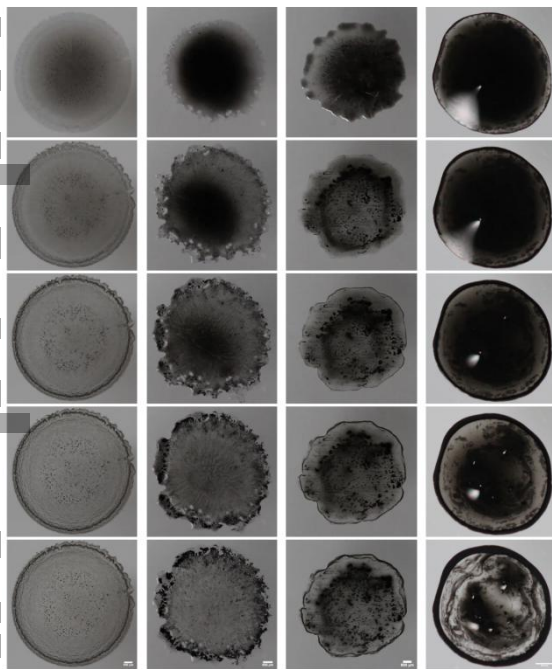


Fig. 3 Relative thickness distribution of catalyst deposition.



(a) IPA 95 (b) IPA 80 (c) IPA 50 (d) IPA 20

Fig. 1 Drying kinetics snapshots of four samples at $t = 0.0 t_{total}$ (row 1), $0.2 t_{total}$ (row 2), $0.4 t_{total}$ (row 3), $0.6 t_{total}$ (row 4), $0.8 t_{total}$ (row 5).

3.2 Microstructure of Deposition

Fig. 2 shows the deposition of catalyst inks under different contents and the catalyst images separated from the deposition with MATLAB. It can be seen from Fig. 2 that the deposition distribution is uneven. The particles gather at the edge of the deposition and the inside is relatively sparse. Among them, Pt/C

agglomerates are deposited inside the droplets in the form of curved slender leaves. A large number of particles run toward the center of the droplet making the deposition edge of IPA 80 more irregular and the droplet inside is more uneven. Whether this

phenomenon leads to more uneven distribution of CL remains to be further studied. There is a circulating flow inside the IPA 50 droplet, but there is no phenomenon that a large number of particles run to the center. IPA20 has the longest evaporation time, the widest coffee ring and the smallest diameter. Under the same evaporation conditions, the distribution of catalyst particles on the deposition surface of IPA 95 is more uniform.

In this study, the relative thickness along the diameter of the CL (the lowest point of deposition is zero) is discussed, as shown in Fig. 3. It can be seen from the Fig. 3 that the height of the deposition is symmetrically distributed about the center of the circle. In addition, with the decrease of IPA content, the height of the highest point of deposition increase from 2.58 μm to 39.5 μm . Therefore, the higher the IPA content, the more uniform the final distribution of catalyst particles.

3.3 Oxygen Reduction Reaction

Fig. 4 shows the LSV curves of different IPA contents at 1600 rpm. In general, indicators of oxygen reduction performance generally include initial potential, half-wave potential, and limiting current density. It can be seen from the figure that IPA 95 has the largest half-wave potential (0.84 V) and the highest limiting current density, indicating that IPA 95 has the highest ORR activity.

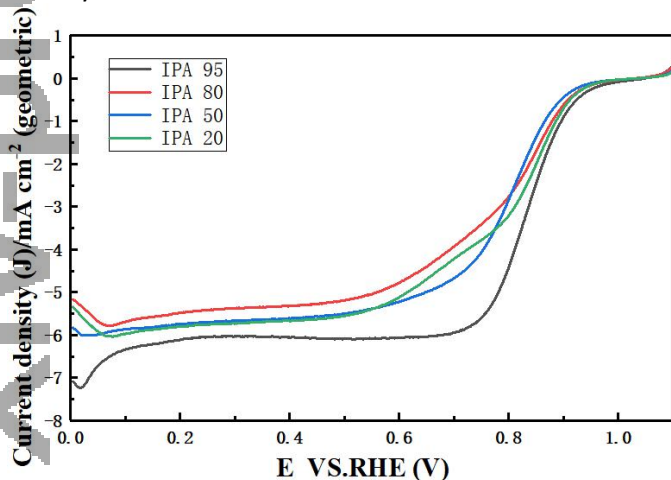


Fig. 4 LSV curves of different IPA content at 1600 RPM.

4. CONCLUSIONS

The solvent evaporation process in proton exchange membrane fuel cell (PEMFC) and its influence on the microstructure of the catalyst layer (CL) are studied in this study, with emphasis on the influence of different IPA contents, which deepened the understanding of drying kinetics. The experimental results show that the

solvent evaporation process has a great influence on the microstructure of the CL in terms of catalyst particle distribution and surface morphology, which in turn affects the performance of the CL. As the IPA content decreases, the surface tension from the edge to the center of the droplet increases, and the particles begin to flow in reverse. The deposition ultimately consists of a dense coffee ring at the edge and sparse area connecting with Pt/C aggregates inside. The deposition thickness is distributed symmetrically around the center of the circle in the diameter direction. In these four samples of different IPA contents, the catalyst particles of IPA 95 are most uniformly distributed and the deposition surface height difference is the smallest within 3 μm . In line with the desirable microstructure, IPA 95 has the highest half-wave potential and limiting current density, showing the highest ORR activity.

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