Electronic Supplementary Material

Exploration of the Oxygen Transport behavior in Non-precious Metal Catalyst-based Cathode Catalytic Layer for PEMFCs

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1 Experimental

1.1 Synthesis of catalyst used in CCL/DCL

Synthetic routes for Fe-N-C catalyst and Zn-N-C are shown in Fig. S1. Compared with the Fe-N-C catalyst, the Zn-N-C used for spraying the DCL was synthesized without adding catalytically active Fe and other elements, and the rest of the preparation and precursor heat treatment steps were the same as those for the Fe-N-C catalyst.

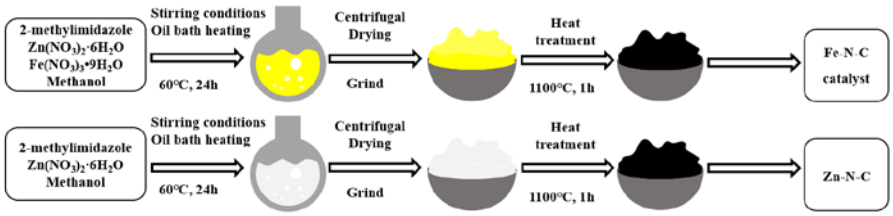

Fig. S1 Synthetic Routes of Fe-N-C catalyst and Zn-N-C.

1.2 Parameters of the flow channel

The flow channel used for oxygen transport resistance measurement consisted of 10 straight channels with ridge width, groove width, and groove depth of 0.5, 0.5, and 0.8 mm, respectively, and an active area of 2 cm × 1 cm. The values and corresponding units of parameters used in Eq. (7) are shown in Table S1.

Table S1 The parameters used in Eq. (7)

Parameters	Value	Unit
A	1.12	

B	1.01	
a	0.25	mm
d	0.8	mm
L	20	mm
N	10	
$D_{O_2}^{CH}$	0.201	$cm^2 \cdot s^{-1}$
P	151000	Pa
P_0	101325	
p_w	31300	
Q_{dry}	1.5	$L \cdot min^{-1}$

1.3 Preparation of MEAs

MEAs with DCL were fabricated using the spraying method. The CCL ink was prepared by dispersing commercial Pt/C catalyst (46.7%, mass fraction) in water/isopropanol solvent with Nafion solution (20%, mass fraction, DuPont), which was sprayed on either side of a Nafion 211 membrane to form the anodic and cathodic CLs after ball-milling for 12 h. The DCL ink was prepared using the same process, but Zn–N–C rather than Pt/C catalyst was used, which was further sprayed on the as-prepared CCL to form DCL (2 cm × 1 cm). The Pt loading on the anode and cathode were both ca. 0.1 mg cm^{-2}. The preparation steps of MEA with DCL were the same as above, but Fe-N-C catalyst rather than Pt/C catalyst was used in CCL, and the DCL was not sprayed.

1.4 MEA performance optimization

Before studying the oxygen transport, orthogonal experiments were designed for various parameters of MEA preparation to determine the best preparation method, so that the follow-up oxygen transport research would be more targeted.

Based on an I/C of 0.6, MEAs with different NPMC loadings were prepared and tested. Figure 7(a) shows that with the increasing NPMC loading, the performance of MEA first decreases, then increases, and then decreases. The performance of the MEA is the best at the catalyst loading of 5.28 mg/cm^2.

Using the NPMC loading of 5.28 mg/cm^2, MEAs with different I/C values were prepared and tested. Figure 7(b) shows that with the continuous increase in I/C, the performance of the MEA first increases and then decreases. The performance of the MEA is the best at the I/C of 0.4.

To explore the effects of Nafion EW, ink solvent ingredient, I/C, and NPMC loading on the performance of the MEA during the preparation of the MEA, an orthogonal experiment was designed with the peak power density of the MEA as the index. Table S2 lists the design and results of the

orthogonal test, and Fig. S2 shows the obtained polarization curves and peak power densities. The optimal parameters for MEA preparation are thus the following: ink solvent-ethanol, the I/C of 0.4, Nafion EW of 950 g/mol, and NPMC loading of 5.28 mg/cm^2.

To attain the best performance and make the follow-up oxygen transport research more targeted, based on the above optimal scheme, MEAs with different proton exchange membranes were prepared, and the peak power density of the optimal membrane electrode reached 553.65 mW/cm^2, as shown in Fig. 7© and (d). The thicknesses of Nafion 211, Nafion 212, and Nafion 115 are 25.4, 50.8, and 127 μm.

Table S2. The design and results of the orthogonal test based on 4 factors

No.	Nafion EW /(g·mol^{-1})	Ink solvent ingredient	NPMC loading /(mg·cm^{-2})	I/C	Peak power density /(mW·cm^{-2})
1	790	Isopropyl alcohol	4.11	0.4	189.48
2	790	Isopropyl alcohol : Ethanol = 1 : 1	5.28	0.6	130.50
3	790	Ethanol	6.46	0.8	126.76
4	900	Isopropyl alcohol	5.28	0.8	225.39
5	900	Isopropyl alcohol : Ethanol = 1 : 1	6.46	0.4	185.90
6	900	Ethanol	4.11	0.6	384.44
7	950	Isopropyl alcohol	6.46	0.6	227.88
8	950	Isopropyl alcohol : Ethanol = 1 : 1	4.11	0.8	126.24
9	950	Ethanol	5.28	0.4	445.63

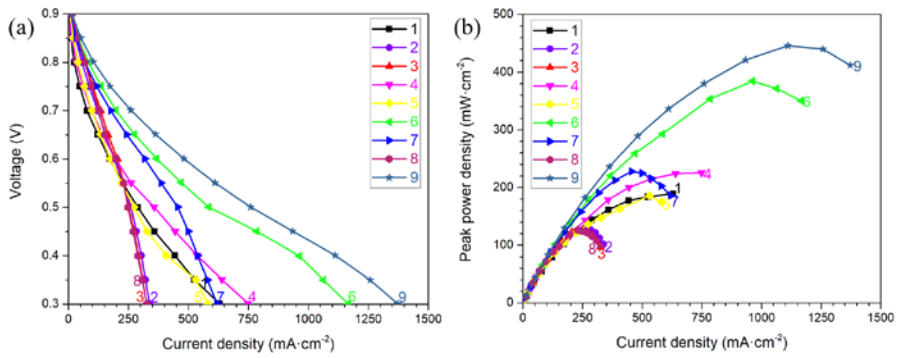

Fig. S2 Orthogonal experiment results.

(a) Polarization curves ; (b) peak power densities.