Supporting Information

Improved anode two-phase mass transfer management of direct methanol fuel cell by the application of graphene aerogel

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1. Characterization Methods

1.1 Electrochemical measurements

For the methanol crossover test we designed, cyclic voltammetry was applied on an electrochemical workstation (CHI660D, Chenhua Shanghai) using a three-electrode cell. A glassy carbon electrode (GCE) with the diameter of 5mm served as the working electrode while a 1 cm*1 cm Pt foil and Hg/Hg₂SO₄ electrode were chosen for counter electrode and reference electrode respectively. For the preparation of working electrode, GCE was first polished by alumina suspensions. The catalyst ink was obtained by dispersing 4 mg commercial Pt/C catalyst (40%Pt, Johnson Matthey) into 1 mL isopropyl alcohol uniformly, together with 20 μ L Nafion (5 wt. %, DuPont). Then 5 μ L catalyst slurry was dropped onto the GCE and dried under room temperature. The potential range was -0.65 V to 0.55 V, with the scan rate of 0.05 Vs⁻¹. The measurements were conducted at 298 K and the potentials documented were versus the Hg/ H₂SO₄ reference electrode.

1.2 Methanol crossover test

Methods for electrochemical measurements are as described above. During the test, the reservoir chamber at the anode was filled with a certain concentration of methanol solution, while the chamber connected to the cathode was filled with a fixed volume of 0.5 M H₂SO₄ (saturated with nitrogen). A certain voltage was applied to the anode using amperometric i-t method on the electrochemical workstation to maintain the output at 120 mA cm⁻². After a certain period, cyclic voltammetry was performed on the three-electrode cell system. According to the CV curve obtained, the methanol concentration

in the cathode chamber is calibrated. Combining with the volume of the solution in the chamber, we can calculate the amount of methanol permeating from anode to cathode during the operation of µDMFC. The method for the concentration calibration is as follows. First, the working electrode is activated in 0.5 M H₂SO₄ to achieve a steady response (as shown in FigureS1a). Second, standard solutions of different concentrations of methanol with 0.5 M H₂SO₄ were prepared. Then CV scans with the working electrode were conducted in the different standard solutions. CV curves obtained in the solution of methanol and 0.5 M H₂SO₄ show two oxidation peaks, one in the positive scanning direction, the other in the negative direction. According to the results, the relationship between the positive peak current density I_f and the methanol concentration can be obtained, and a fitting curve is made. Next, based on the I_f value of the CV measured in the cathode chamber, the corresponding methanol concentration is determined. It is worth noting that the working electrode corrected in the standard solution and the working electrode used in the cathode chamber must be the same electrode. The peristaltic pump was used to circulate the anode methanol solution during the test to maintain the concentration stable. Figure S1b exhibits the curves of performing linear sweep voltammetry (LSV) on the anodes of the test systems corresponding to MEA-JM and MEA-C30GA70, according to which the voltage applied on the anode can be determined to keep the output at 120 mA cm^{-2} .

1.3 Stability test

Stability test of the two μDMFCs with MEA-JM and MEA-C30GA70 were conducted at 298 K, operating with 3 M and 6 M methanol solution respectively. Both μDMFCs

maintain an output current density of 120 mA cm⁻², and the value of the output voltage is recorded every 120 s to obtain the power density-time curve.

2. Supplementary table and figures

Table S1. Statistics of methanol concentration and peak power density of $\mu DMFCs$ in

this work

	MEA-C100	MEA-JM	MEA-C30GA70	MEA-GA100
Methanol concentration at 333 K/ M	3	3	7	7
Methanol concentration at 298 K/ M	3	3	6	6
Peak power density at 333 K/ mW cm ⁻²	34.5	34.4	43.6	33.3
Peak power density at 298 K/ mW cm ⁻²	20.7	19.4	23.5	17.5



Figure S1. (a) CV curve of the working electrode in 0.5 M H₂SO₄; (b) LSVs of the anodes of the test systems corresponding to MEA-JM and MEA-C30GA70



Figure S2. Stability test of the two μ DMFCs with an output of 120 mA cm⁻²