INTRODUCTION

In contrast with pure H\(_2\) as a fuel, methanol has the advantages of higher volumetric energy density, higher security, easier production, storage, transport, and refueling.\(^1\) Its most common application in fuel cell technology is its direct electrochemical oxidation on PtRu anode of direct methanol fuel cell, though with low prohibitive electrical efficiency for large scale applications.\(^4\)

Recently, Avgouropoulos et al\(^5\) demonstrated the functionality of an internal reforming methanol fuel cell (IRMFC), where the methanol gets reformed by a catalyst incorporated into the anode compartment of a high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) single cell. The IRMFC has several advantages such as simplifying the system, increasing overall efficiency, reducing the weight and volume of the system and so on, which has potential applications in portable or stationary power supply system. Two kinds of IRMFC structures have emerged. One is designed in accordance with the standard IRMFC concept that the methanol reforming catalyst is in direct contact with a high temperature membrane electrode assemblies (MEAs). However, it has the defects that small amounts of unconverted methanol in the reformate will...
poison the MEA\textsuperscript{10} and H$_3$PO$_4$ released from the MEA will dissolve the reforming catalyst.\textsuperscript{8,11}

To avoid the negative effects of phosphoric acid and unconverted methanol, a second kind of IRMFC adding a nonporous thin plate between the reforming catalyst and the HT-PEMFC MEA is put forward.\textsuperscript{8,9,12-14} As shown in Figure 1A, it mainly includes a reformer and a HT-PEMFC single cell. So far, three kinds of reformers shown in Figure 1B-D used in the IRMFC have been reported.

The first is generally a monolithic reformer such as foamed copper carrying CuMnO$_x$ or CuMnAlO$_x$ proposed by Avgouropoulos et al\textsuperscript{9} The reformer per milliliter with 0.54 g catalysts can only supply less than 4 mL/min hydrogen at 473 K with more than 90% methanol conversion. When converting the hydrogen production to the active area of the MEA, the MEA per square centimeter can get less than 2 mL/min hydrogen, thus limiting the power density of the IRMFC single cell to less than 0.120 W/cm$^2$. When enlarged to a 70 W IRMFC stack, volumetric specific power of the stack can only reach 9.3 W/L. To reduce the volume of reformer, they design a novel ultrathin methanol reformer made up of a carbon paper carrying 90 mg/cm$^2$ of commercial CuO/ZnO/Al$_2$O$_3$ catalyst.\textsuperscript{12} However, the reformer per milliliter with 1.07 g catalyst can only provide less than 6 mL/min hydrogen at 483 K with more than 90% methanol conversion. The HT-PEMFC MEA per square centimeter can only get less than 2.5 mL/min hydrogen, thus limiting the power density of the IRMFC single cell to less than 0.300 W/cm$^2$. When enlarged to an 100 W IRMFC stack, volumetric specific power of the stack can reach 30 W/L,\textsuperscript{15} being among the highest reported in portable and stationary applications.

The third proposed by Mendes et al\textsuperscript{13,14} is a three-channel serpentine packed bed reformer made of gold-plated aluminum or graphite, usually carrying commercial CuO/ZnO/Al$_2$O$_3$ catalyst. The reformer per milliliter with 1.3 g catalyst can offer 5 mL/min hydrogen at 453 K and the HT-PEMFC MEA per square centimeter can get 6 mL/min hydrogen, thus expanding the power density of the IRMFC single cell to 0.330 W/cm$^2$. However, they do not optimize the reformer used in the IRMFC and there is still room for improvement of hydrogen production with a smaller reformer.

To produce more hydrogen with less volume, it is very important to improve catalyst utilization by enhancing heat and mass transfer in the reformer. According to early research by Lee et al\textsuperscript{16} and Karim et al\textsuperscript{17} at temperatures lower than 483 K there are no internal diffusion limitations and the major heat transfer resistance exists between the wall and catalyst particles due to the gas film in a packed bed reactor for methanol steam reforming (MSR) reaction on a commercial CuO/ZnO/Al$_2$O$_3$ catalyst. A. Karim et al showed that with the reactor diameter from 4.1 mm down to 1 mm, the temperature gradient of the bed dropped from 40 K to 22 K while the bed pressure drop increased a lot.

Therefore, in this paper a single channel serpentine packed bed reformer was designed and its bed size was optimized by experiment and numerical simulation to enhance heat transfer between the wall and catalyst particles and increase catalyst utilization while keeping a low pressure drop. The stability of the optimal reformer was also investigated. Then, it was integrated with a homemade HT-PEMFC MEA to make up an IRMFC single cell. The performance and stability of the IRMFC single cell was also investigated.
2 | RESULTS AND DISCUSSION

2.1 | Screening of MSR catalyst

To be integrated with a HT-PEMFC to make up an IRMFC, the reformer should be operated at 433-473 K, which requires the MSR catalysts to have high activity and selectivity. Among the MSR catalysts including copper-based and group 8-10 metal-based catalysts, copper-based catalysts especially for CuO/ZnO/Al2O3 are the most active and selective ones at low temperature.18

As shown in Figure 2A-C, the activity and selectivity of the two types of commercial CuO/ZnO/Al2O3 catalyst was compared at 453-473 K. It is obvious that catalyst B is more active than catalyst A, which is mainly due to their differences in composition and structure.19 To avoid the negative effect of unconverted methanol in the reformate on the HT-PEMFC MEA,10 it can be seen from Figure 2B that the methanol conversion should be more than 90%. In terms of selectivity, it is no longer a problem for these two catalysts with a less than 1% CO content in the dry reformate as shown in Figure 2C due to low working temperature and high S/M,20,21 since HT-PEMFC can tolerate CO content up to 5%.22 Therefore, taking both activity and selectivity into account, catalyst B was selected for the following study.

2.2 | Optimization of reformer bed diameter

Hydrogen production is affected not only by catalysts activity and selectivity, but also by catalyst utilization which is related to mass and heat transfer during MSR. The mass transfer process involves reactants external diffusion through bulk stream to the catalyst surface and internal diffusion through the catalyst pores to the open reaction sites. Taking the catalyst particle size (less than 0.75 mm) and the low operating temperature (453-473 K) into account, the effect of internal diffusion can be ignorable according to the precious study from Lee et al.16

The heat transfer process mainly involves heat transfer from the reformer wall to the catalyst bed and heat transfer in the catalyst bed. For MSR at 453-473 K, it has to be operated with low gas velocity to achieve high conversion.23 The low gas velocity dramatically lowers the effective thermal conductivity of the catalyst bed. Furthermore, the low ratio of reactor bed diameter to catalyst particle diameter (∆d/∆p < 10) and the low gas velocity tend to introduce a large heat transfer resistance between the wall and the catalyst particles.24 It is well known that the void fraction at the wall is larger than that in the center of the bed, and there are only limited number of contact points between the catalyst particles and the reactor wall. Hence, the major heat transfer resistance between the wall and the catalyst particles is due to the gas film.

To minimize the effect of transport limitations, the equivalent bed diameter of a single channel serpentine packed bed reformer is reduced. It can be inferred from Figure 3A that to achieve the same methanol conversion, for a given methanol flow rate at 453-473 K, 7% less catalyst weight would be needed for the 5 mm i.d. reformer compared with the weight of the 5.8 mm i.d. reformer, and about 10% less for the 3.8 mm i.d. reformer. In addition, it can be seen that compared with the 5.8 mm i.d. reformer, the pressure drop triples when reformer diameter is 5 mm, while increasing seven times for reformer diameter of 3 mm with nitrogen feed at the room temperature.

As specifically described in the Experimental Section, a 3D pseudo-homogeneous reactor model was established to analyze the effects of bed diameter on heat transfer. The simulating results are shown in Figure 4.

It can be seen from Figure 4A that the simulating results fit the experimental data very well. The difference between the
model and the data at low $W/F$ can be attributed to deactivation of the catalyst since the experimental data were obtained by starting at a low flow rate and increasing the flow rate with time (moving from right to left along the curve). Figure 4B-D shows the temperature profiles in the 3.8 mm i.d. reformer, $U_0 = 0.360$ m/s; $W/F = 122.5$ kg s/mol. (C) Temperature profile in the 5 mm i.d. reactor, $U_0 = 0.534$ m/s; $W/F = 122.5$ kg s/mol. (D) Temperature profile in the 5.8 mm i.d. reformer, $U_0 = 0.630$ m/s; $W/F = 122.5$ kg s/mol

As shown in Figure 5A,B, with the increase of bed length of the 5 mm i.d. reformer, the methanol conversion and the $H_2$ production increase. When the bed length increases to 1.5 L to load 0.45 g/mL reformer catalysts, the reformer per milliliter can reach 9.8 mL/min hydrogen at 453 K with more than 95% methanol conversion, almost twice as much as that by Mendes et al.\textsuperscript{13,14} with nearly one-third of their catalyst loading. It is enough to make a HT-PEMFC single cell with an active area of 45 cm$^2$ discharge at 1 A/cm$^2$ at 453 K and more than 2 A/cm$^2$ at 473 K. When integrating the reformer into an IRMFC single cell shown in Figure 5C, the pressure drop of the single cell anode is enhanced by less than 40% under $N_2$ feed at 473 K. In practical applications, the maximum pressure drop of IRMFC single cell anode will be less than 0.2 bars.

### 2.3 Optimization of reformer bed length

The reformer bed length is also an important factor affecting the hydrogen production. When integrated into an IRMFC stack, a reformer with appropriate bed length will be needed, since too short cannot load sufficient catalyst to produce enough hydrogen and too long will increase pressure drop.

As shown in Figure 5A, B, with the increase of bed length of the 5 mm i.d. reformer, the methanol conversion and the $H_2$ production increase. When the bed length increases to 1.5 L to load 0.45 g/mL reformer catalysts, the reformer per milliliter can reach 9.8 mL/min hydrogen at 453 K with more than 95% methanol conversion, almost twice as much as that by Mendes et al.\textsuperscript{13,14} with nearly one-third of their catalyst loading. It is enough to make a HT-PEMFC single cell with an active area of 45 cm$^2$ discharge at 1 A/cm$^2$ at 453 K and more than 2 A/cm$^2$ at 473 K. When integrating the reformer into an IRMFC single cell shown in Figure 5C, the pressure drop of the single cell anode is enhanced by less than 40% under $N_2$ feed at 473 K. In practical applications, the maximum pressure drop of IRMFC single cell anode will be less than 0.2 bars.

### 2.4 Stability test of the optimal reformer

As described above, the optimal reformer is a single channel serpentine packed bed reformer with an equivalent bed
diameter of 5 mm and a bed length of 30 cm. The used catalyst is commercial CuZnAlOx catalyst (HiFuel R120). For practical applications, long-term stability test of the optimal reformer was carried out under continuous methanol feed at 473 K. It can be seen from Figure 6 that the reformer was quite stable and less than 10% decline in methanol conversion was observed during the 100 hours period, which is similar to the results reported by Joan Papavasiliou et al.25 According to their research, the highly active CuZnAlOx catalyst (HiFuel R120) shows high tolerance under repeated on/off cycles. So the optimized reformer is promising to be integrated into an IRMFC single cell for portable, mobile, and off-grid applications.

2.5 | An IRMFC single cell electrochemical test

As shown in Figure 7, the integrated IRMFC single cell was mainly composed of the optimized reformer, polar plate, and a homemade HT-PEMFC MEA. Typical polarization curves (Figure 8A) measured at 473 K under two kinds of anode feed stream were obtained. It can be seen that when methanol aqueous solution and air is fed, the power density of the IRMFC single cell can reach 0.55 W/cm² at 473 K, which is the same as that with H₂ feed. From the previous research, it can be inferred that when 0.7 mL/min methanol aqueous solution (H₂O/CH₃OH = 1.5) is fed, the methanol conversion can reach 100% and the reforming products approximately contain H₂ (66%), CO₂ (22%), CO (1%), H₂O (11%). The effect of CO₂ dilution can be mitigated since the single cell works at 473 K and the hydrogen production is excessive (1.5@1.4 A/cm²), which is also found by Waller26 and Mendes et al.13 The poisoning effect of CO with presence of CO₂ can be relieved by certain water content in the products and higher working temperature (473 K).27-30 Additionally, certain water content have a positive effect on proton conductivity due to inhibiting the dehydration of phosphoric acid.31,32

To understand the influence of these two feeds on the fuel cell performance, an EIS analysis was performed. The Nyquist plots obtained at 1.0 A/cm², respectively, with hydrogen and methanol feed (Figure 8B) show a similar size of the semi-circles associated with anodic processes (high frequencies), cathodic processes (intermediate frequencies), and mass transfer process (low frequencies).33 The slight differences observed in the semi-circles (high and low frequencies) prove a weak influence of CO₂ dilution and CO poisoning, in accordance to what is observed in the polarization curves. The slightly lower ohmic resistance (interception of the Nyquist plot with the real axis) with methanol feed further indicates the inhibitory effect of water on dehydration of phosphoric acid.

When working at 453 K, the power density of the single cell can reach 0.450 W/cm² with methanol feed, which is 0.015 W/cm² lower than that with H₂ feed. The slight difference is likely to be mainly caused by unreacted methanol. From the above study, it can be inferred that the methanol
conversion in the reformer can reach 97% under 0.5 mL/min methanol aqueous solution feed at 453 K. However, the methanol conversion in IRMFC single cell may be different under the same feed since hydrogen consumption rate has an influence on the methanol reforming reaction.\textsuperscript{11} Under the open circuit, the increased pressure drop with no hydrogen consumption may inhibit the methanol reforming reaction\textsuperscript{21} and reduces methanol conversion to less than 97%, in accordance to the fact that open-circuit voltage with methanol feed is 83 mV lower than that with hydrogen feed observed in Figure 8C.

As the discharge current density increases, the hydrogen consumption rate increases and the pressure drop in the reformer decreases, thus probably increasing the methanol conversion to 97%. At 0.9 A/cm\textsuperscript{2}, the reforming products approximately contain H\textsubscript{2} (66%), CO\textsubscript{2} (22%), CO (0.3%), CH\textsubscript{3}OH (0.7%), H\textsubscript{2}O (11%). The effect of CO\textsubscript{2} dilution can still be weak since the single cell works at 453 K, and the hydrogen production is excessive (1.5@1.0 A/cm\textsuperscript{2}). The poisoning effect of CO can be further relieved by its lower content in the products. Additionally, the effect of methanol-water vapor mixture on performance is smaller, which is
mainly because the dilution and degrading effects for anodic process are balanced out by the enhanced mass transport according to the research of Samuel Simon Araya et al.34

The Nyquist plots obtained at 0.9 A/cm² at 453 K (Figure 8D), respectively, with hydrogen and methanol feed are nearly the same. Slight differences are observed in the semicircles (high and low frequencies) further prove a weak influence of CO₂, CO, and methanol-water vapor. The same ohmic resistance under methanol feed and under hydrogen feed, respectively, at 0.9 A/cm² may be due to the reduction of polycondensation of phosphoric acid at 453 K and poisoning effect of unreacted methanol species on the proton conductivity of the membrane.10,34

As described above, power density of the optimized IRMFC single cell reached 0.45-0.55 W/cm² at 453-473 K under CH₃OH solution and air feed, the highest since IRMFC single cell in existing reports generally worked at 0.1-0.36 W/cm².5,6,8,9,12-15 In addition, stability of the optimized IRMFC single cell was also investigated. As shown in Figure 9A, the IRMFC single cell performance at 0.5 A/cm² under hydrogen feed is attenuated by 3% with an overall degradation rate of 62.5 μV/h after the 320 hours stability test including 10 on/off cycles at 453 K. Relevant research shows that the degradation of phosphoric acid-doped PBI-based HT-PEMFCs under hydrogen feed is mainly due to the growth of the Pt catalyst particles, the oxidation of the carbon support, PBI membrane degradation, and loss of phosphoric acid electrolyte.35-38 Yu et al39 found that compared to steady-state conditions (433 K, 0.2 A/cm²), under variable load and start-stop conditions the loss rate of phosphoric acid increased from several to dozens of ng/cm²/h. Yuka Oono et al40 found that with the operating temperature increasing from 423 K to 463 K, the decay rates of HT-PEMFC single cells at 0.2 A/cm² increased from 3.6 to 47 μV/h. Similar to the results of A. Mendes et al, the rapid degradation of the HT-PEMFC MEA performance after each on/off cycle at 453 K is mainly attributed to the fast loss of phosphoric acid in PBI membrane and rapid catalytic layer attenuation.

As shown in Figure 9B, when methanol solution is fed, the corresponding attenuation rate is increased by nearly an order of magnitude in the 30 hours stability test. The fast decay is mainly caused by unreacted methanol, since CO content in reformate is less than 0.3%. Mendes et al14 and Samuel Simon Araya et al34 reported that methanol has negative effect on anode resistance, cathode resistance, and the ohmic resistances. The cathode resistance increased is mainly due to the methanol crossover from the anode to the cathode. As shown in Figure 9C, the open-circuit voltage of the single cell under methanol feed is gradually reduced, which illustrates an increase in unreacted methanol content.

The increase in methanol content can be attributed to the reformer attenuation at 453 K with high concentration methanol solution feed. At the beginning, the methanol conversion rate can be higher than 90%, less than 3% methanol by volume in the anode feed, in accordance to higher open-circuit voltage (917 mV) in Figure 9C. After 30 hours test, the methanol conversion rate can be lower than 90% and the open-circuit voltage is reduced to 880 mV. The decrease in the reformer performance is associated with the typical catalyst deactivation on the one hand, since copper-based commercial catalyst normally presents an initial lost in activity of ca. 20%, before reaching the steady state.2 On the other hand, the reformer attenuation is largely related to nonuniform flow distribution in the reformer. Noteworthy, after the
Experiments the reformer was opened and examined; the catalyst bed was nonuniform and some preferential flow paths were observed. The nonuniform bed will significantly reduce catalyst utilization and should be primarily responsible for the excessive decay of the reformer, which may be solved by replacing the crushed catalysts with uniformly shaped ones. In addition, the stability of the reformer in the IRMFC single cell can be further improved when raising the operating temperature of the reformer to 473 K or more by developing highly stable high-temperature (≥473 K) MEAs.

3 | CONCLUSIONS

A single channel serpentine packed bed reformer used in an IRMFC is designed and optimized by experiment and numerical simulation to enhance heat transfer and increase catalyst utilization. The optimal reformer per milliliter can supply 9.8 mL/min hydrogen at 453 K, almost twice as much as that by Mendes et al with one-third of their catalyst loading. The reformer was quite stable, and less than 10% decline in methanol conversion was observed during the 100 hours period. When integrated into an IRMFC single cell, the power density can reach 0.45–0.55 W/cm² at 453–473 K under CH₃OH solution and air feed, the highest in existing reports. Its application in portable or stationary power supply system.

4 | EXPERIMENTAL SECTION

4.1 | 3D pseudo-homogeneous model

The following assumptions have been made taking into account the features of the flow in the MSR reformer:

1. The flow is steady state; the fluid is an ideal incompressible gas;
2. The flow is laminar because Re is less than 10;
3. The reformer bed is a porous medium with isotropic and homogeneous porosity;
4. There are no temperature and concentration gradients between gas and solid in the catalyst beds;
5. The thermal radiation is negligible compared to convection.

The governing equations for the mass conservation can be written as:

$$\nabla \cdot (\gamma \rho \vec{v}) = 0$$  \hspace{1cm} (1)

The momentum equation can be expressed as:

$$\nabla \cdot (\gamma \rho \vec{v} \vec{v}) = -\gamma \nabla P + \nabla \cdot (\gamma \vec{T}) + \nabla \cdot (\nabla \rho) - \frac{\gamma^2 \mu}{K} \nabla \vec{v} + \frac{\gamma C_2}{2} \rho \nabla \cdot \vec{v}$$  \hspace{1cm} (2)

The energy equation is for fluid zones:

$$\nabla \cdot (\vec{v}(\rho E + P)) = \nabla \cdot (\lambda \nabla T - \sum_j h_j J_j) + S_h$$  \hspace{1cm} (3)

where \(\lambda_j\) is the thermal conductivity for fluid, \(J_j\)-diffusion flux of \(i\)-th component; \(E = h\) for an incompressible gas; \(h\) is the enthalpy; \(S_h\)-total heat of chemical reactions.

The equation of mass transfer of \(i\)-th component is:

$$\nabla \cdot (\gamma \rho \vec{v} \phi_i) = \nabla \cdot (\gamma \Gamma \nabla \phi_i) + \gamma S_{\phi_i}$$  \hspace{1cm} (4)

Methanol can be reformed by two overall reactions in a reformer filled with the catalyst CuO/ZnO/Al₂O₃ as described by Amphlett et al⁴¹ and Suh et al.⁴²

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \quad \Delta H = 49 \text{kJ/mol} \hspace{1cm} (5)$$

$$\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H = 90.7 \text{kJ/mol} \hspace{1cm} (6)$$

$$r_{\text{CH}_3\text{OH}} = -k_1 C_{\text{CH}_3\text{OH}} - k_2$$

$$k_1 = C_1 \left( A_1 + B_1 \ln \left( \frac{S}{M} \right) \right) e^{-E_1/(RT)} \quad k_2 = C_2 A_2 e^{-E_2/(RT)}$$

where \(S/M\) is the molar ratio of steam to methanol; \(A_1, B_1,\) and \(A_2\) are Amphlett’s constants for reforming and decomposition reactions, respectively. \(C_1\) and \(C_2\) are correction factors for reforming and decomposition reactions, which are determined empirically from the activity and effectiveness of catalyst.

The boundary conditions for the energy and mass balance equations are as follows: at the reformer inlet: \(T_0 = 473 \text{ K}\); \(S/M = 1.5\). At the reformer walls: The wall temperature is constant, \(T_w = 473 \text{ K}\). At the reformer outlet: \(P_{\text{out}} = 0 \text{ bar}\). The physical parameters and basic operating conditions are listed in Table 1, and the other physical properties of each species are referred to the existing literatures.

The commercial CFD code ANSYS Fluent (17.0) was used for the preparation of a mathematical model of the reformer. The governing equations were solved numerically using the finite volume method. The SIMPLEC algorithm was employed for pressure-velocity coupling and the second-order upwind spatial discretization was chosen for the momentum, energy, and species transport equations. The shape of the control volumes of the 3D computational grid was hexagonal to improve the convergence of the solution during the computation. The number of elements of grid verified by grid independence was equal N = 910 000. The convergence criteria for the normalized residuals were restricted to less than 10⁻⁴ for all species and 10⁻⁵ for the energy.
TABLE 1  Geometric parameters, physical properties, and operating conditions

| Parameter                          | Value                        |
|------------------------------------|------------------------------|
| Equivalent diameter of catalyst bed ($d_b$) | 3.8, 5.0, 5.8 (mm)          |
| Corresponding porosity of catalyst bed ($\varepsilon$) | 0.65, 0.49, 0.45          |
| Diameter of pellet ($d_p$)          | 0.7 mm                       |
| Porous surface area of pellet ($a_p$) | $4.72 \times 10^8$ m$^2$/m$^3$ |
| Mean pore size of pellet ($r_{pore}$) | $4.2 \times 10^{-9}$ m     |
| Density of catalyst ($\rho_s$)       | 2617.8 kg/m$^3$              |
| Thermal conductivity of catalyst ($k_s$) | 0.364 W/m/K                 |
| Specific heat capacity of catalyst ($C_p$) | 0.703 kJ/kg/K               |
| Molar ratio of steam to methanol ($S/M$) | 1.5                         |
| The reformer wall temperature ($T_w$) | 473 K                        |
| The contact time ($W/F$)             | 122.5 kg s/mol               |

4.2  Methanol reformer and anode plate

As shown in Figure 7B, the graphite reformer was a single channel serpentine packed bed reactor with outer dimensions of 10 cm × 10 cm × 0.6 cm. The equivalent diameter of reformer bed is, respectively, 3.8 mm, 5 mm, and 5.8 mm. The filled reforming catalysts were commercial CuO/ZnO/Al$_2$O$_3$ catalyst. Catalyst A (M615) was purchased from Lan Zhou Institute of Chemical Physics while catalyst B (HiFUEL R120) was from Alfa Aesar in unreduced form. The cylindrical reforming catalyst was crushed, sieved to 0.6-0.75 mm particle size, and then filled into the reformer. In order to match the reformer, the specific anode plate shown in Figure 7C is designed and used.

4.3  Preparations of the MEA

The homemade membranes of m-PBI were fabricated by solution casting from a polymer solution in N,N-dimethylacetamide. After complete evaporation of the solvent, the membranes were immersed in phosphoric acid (85 wt% H$_3$PO$_4$) at 353 K for at least 12 hours. Immediately after acid doping and removal of excess acid from the membrane surface, an acid doping level (ADL) of approximately 12 H$_3$PO$_4$ molecules per polymer repeat unit was determined gravimetrically.

About 60% Pt/C with Pt loading of 0.8 mg/cm$^2$ was used in the anode gas diffusion electrode. PtCo/C with Pt loading of 1.0 mg/cm$^2$ was in the cathode gas diffusion electrode. The H$_3$PO$_4$-doped membrane was sandwiched between the two electrodes and then was hot pressed at 423 K and 2500 LB for 10 minutes to produce the MEAs. FEP film with certain thickness was used as gaskets to achieve an appropriate compression in the single cell.

4.4  Methanol reformer measurement

A homemade evaporation chamber was connected directly to the methanol reformer inlet, while the methanol reformer outlet was connected directly to a gas chromatograph (Agilent Technologies, 7890B GC system) equipped with TCD and FID. The temperature of the line connecting the reformer outlet to the chromatograph is always maintained at 413 K to prevent condensation of the unconverted methanol. First, pure hydrogen is fed to the reformer to activate the reforming catalyst at 473 K for 4 hours, and then a variety of flow rate of methanol aqueous solution (H$_2$O/CH$_3$OH = 1.5) is introduced through a high-pressure constant flow pump at 453-473 K to evaluate the reformer.

4.5  Fuel cell measurements

A 45 cm$^2$ IRMFC single cell was assembled depending on the conformation described in Figure 6A. The single cell was first purged with pure hydrogen and air at 393 K and then discharged at 0.2 A/cm$^2$ for 10 hours at 473 K for activating the cell and the reforming catalyst simultaneously.

The cell temperature was set at 453-473 K. The cell performance was evaluated at atmospheric pressure under two kinds of different feed: (a) pure H$_2$, (b) methanol aqueous solution (H$_2$O/CH$_3$OH = 1.5). The electrochemical measurements (polarization curves and AC impedance) were carried out using an ELECTRONIC LOAD (KIKUSUI, PLZ664WA), a FC IMPEDANCE METER (KIKUSUI, KFM2150) and a FC SCANNER (KIKUSUI, KFM2150). Impedance data were obtained within a frequency range from 10 kHz to 0.1 Hz, and the stimulus amplitude was 5% of the applied current in galvanostatic impedance experiments.

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ORCID

Gongquan Sun https://orcid.org/0000-0002-6902-2270

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