Short Communication

Enhanced low-humidity performance of proton exchange membrane fuel cell by incorporating phosphoric acid-loaded covalent organic framework in anode catalyst layer

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HIGHLIGHTS

- A COF network was proposed to develop MEA with self-humidifying ability.
- The COF network possesses water retention and proton transfer abilities simultaneously.
- The COF network has excellent compatibility with Nafion ionomer and membranes.
- The MEA shows excellent low humidity performance at 60 °C and 38% RH.
- Durability test reveals the good stability of the MEA for low humidity operation.

ARTICLE INFO

ABSTRACT

Developing self-humidifying membrane electrode assembly (MEA) is of great significance for the practical use of proton exchange membrane fuel cell (PEMFC). In this work, a phosphoric acid (PA)-loaded Schiff base networks (SNW)-type covalent organic framework (COF) is proposed as the anode catalyst layer (CL) additive to enhance the PEMFC performance under low humidity conditions. The unique polymer structure and immobilized PA endow the proposed COF network with not only excellent water retention capacity but also proton transfer ability, thus leading to the superior low humidity performance of the PEMFC. The optimization of the additive content, the effect of relative humidity (RH) and PEMFC operating temperature are investigated by means of electrochemical characterization and single cell test. At a normal operation temperature of 60 °C and 38% RH, the MEA with optimized COF content (10 wt%) showes the maximum power density of

Covalent organic framework
Low-humidity performance

582 mW cm^{-2}, which is almost 7 times higher than that of the routine MEA (85 mW cm^{-2}). Furthermore, a preliminary durability test demonstrates the potential of the proposed PEMFC for practice operation under low humidity environment.

Introduction

Proton exchange membrane fuel cell (PEMFC) has been demonstrated to be one of the most promising power sources for electric vehicles, portable devices, and residential cogeneration systems [1,2]. However, the commercialization of PEMFC is currently hindered by several problems, such as the incomplete hydrogen infrastructure [3,4], costly noble metal catalysts [5—17] and complex water and heat managements. Among them, water management is a key concern because additional humidifying devices complicate the system and increase the cost of PEMFCs [18—20]. Self-humidification is then of great importance to popularize PEMFC as it can greatly simplify the system and reduce the manufacturing cost, which are attractive for the real application of PEMFC [21—23]. Of several self-humidifying techniques, employing hygroscopic substances as catalyst layer (CL) additive is a simplest but effective way to enable PEMFC operating under ambient low-humidity conditions [24,25]. Generally, simply mixing these substances (such as SiO_2 [26—33], TiO_2 [34,35], Al_2O_3 [36], agarose [37]) into CL could endow the membrane electrode assembly (MEA) with self-humidifying ability due to their superior water retention capacities. However, a shortcoming of these hygroscopic substances is that they usually do not have electron or proton transfer abilities, thus the introduction of these materials may result in high cell resistance, which could restrict the improvement of the PEMFC performance. On the other aspect, most hygroscopic oxides have poor compatibility with Nafion ionomer, which may deteriorate the interfacial contact between the Nafion membrane and the CL. Furthermore, these oxide particles are easily aggregated or get lost since they are not immobilized or bonded in the CL due to the poor compatibility with Nafion ionomer. Therefore, the addition of these hygroscopic oxides in CL were normally unfavorable to the cell durability and performance stability during long-term operation.

In recent years, newly emerged porous materials of covalent organic framework (COF) have shown great potential for electrochemical applications, such as fuel cells [38,39] and sensors [40], due to their custom-design functionalities (such as proton transfer ability), fine-tunable pore size, high porosity and surface area, as well as their excellent stability in PEMFC operating conditions such as high temperature and strong acid [41]. For example, Yang et al. [42] developed a series of COFs with phenolic hydroxyl groups (proton donor) and azo groups (proton acceptor) integrated into the COF skeleton. By loading with H_3PO_4, this COF materials (H_3-PO_4@COFs) was made into a solid electrolyte membrane in the MEA, which delivered a maximum power density of

81 mW cm^{-2} under H_2/O_2, 100% relative humidity (RH) and 60 °C. Although this performance surpassed all previously reported COF-based MEAs, it is still far inferior to the conventional Nafion-based MEAs for practical use. Furthermore, the leaching of guest molecules (e.g. H_3PO_4) should be considered when such COF materials were designed for long-term PEMFC operation, as it can affect proton conductivity and catalyst activity due to the possible adsorption effect of phosphate ions. Based on this consideration, Yin et al. [43] proposed a Schiff base networks (SNW)-type COF network to prepare a H_3PO_4 loaded COF-Nafion composite membrane for PEMFC operating under low humidity. By using melamine and terephthalaldeyde as polymer monomers, the SNW-1 COF network was obtained in their work with the major cavity diameter of ~0.52 nm, which matches the size of H_3PO_4 molecule (~0.37 nm), then the H_3PO_4 molecules can be effectively confined in these cavities and with low leaching rate. The single cell test showed that the MEA based on this composite membrane possessed a peak power density of 278 mW cm^{-2} with hydrous H_2/O_2 at 60 °C. Although this performance is a substantial improvement compared to pure COF membrane based MEAs, it is still too low to be considered for real applications. Therefore, a decent performance is a must for COF material being more widely considered in PEMFC applications.

Since H_3PO_4 loaded SNW-1 COF is well compatible with Nafion ionomer, it can also be employed in the CL of PEMFC to serve as hygroscopic agent due to its intrinsic hydrophilic groups (such as −NH−, -PO_3H_2) and abundant cavities. Furthermore, the immobilized H_3PO_4 could further hold the water in the cavities, which can greatly increase the water retention of the CL under low humidity conditions. Based on these reasons, we believe that simply introducing the SNW-1 COF into CL will enable the PEMFC with self-humidifying ability. It is envisaged that this COF-based CL possesses the water retention and proton transfer abilities simultaneously, and commercial Nafion membrane can be employed for MEA in this case, which could then greatly enhance the PEMFC performance for practical applications under ambient humidity conditions.

Experimental

SNW-1 COF network preparation and physical characterizations

The synthesis method of SNW-1 can be found in literature [41]. Briefly, melamine (AR, Aladdin), terephthalaldeyde (AR, Aladdin), and anhydrous dimethyl sulfoxide (AR, Aladdin) were added into a three-necked flask with a condensation

device. The mixture was then reacted in argon atmosphere for 72 h at 180 °C. After cooling down, the precipitate was separated by filtration and sequentially washed with N, N-dimethylformamide (AR, Aladdin), methanol (AR, Aladdin), and tetrahydrofuran (AR, Aladdin). Finally, the SNW-1 COF network was obtained by vacuum drying overnight at 120 °C.

The impregnation of H_3PO_4 was conducted by a vacuum assisted method [43]. First, the SNW-1 COF was vacuum treated at 120 °C for 24 h to remove residual solvent and air in the pores. After cooling down to 70 °C and keeping vacuum, 25 wt% H_3PO_4 solution was added to mix with SNW-1. Last, the vacuum was removed to press H_3PO_4 into the cavities of the COF. Finally, the PA-loaded SNW-1 COF was obtained after centrifuging, washing and vacuum drying at 60 °C.

The Fourier transform infrared (FT-IR) spectra of the SNW-1 and PA-loaded SNW-1 material was recorded by using spectrometer (Nicolet iS50 FT-IR), and the pore size distribution and surface area were measured by N_2 absorption with a Tristart II gas adsorption analyzer.

Preparation of MEAs

A catalyst-coated membrane (CCM) method [29] was employed to prepare MEAs for this work. Based on previous studies, the PEMFC performance under low humidity was mainly determined by the self-humidification of anode [44]. Therefore, the COF network was introduced into anode CL only. The catalyst ink for anode CL was obtained by ultrasonic dispersing the 40 wt% Pt/C (Johnson Matthey, USA), 5 wt% Nafion® solution (DuPont, USA) and the PA-loaded SNW-1 COF into appropriate amount of isopropanol solvent. The as-prepared catalyst ink was sprayed onto one side of Nafion-212 membrane (DuPont, USA) to form anode CL. The cathode CL was prepared as the same procedure except that no COF was added. To study the effect of the introduced COF amount, four MEA samples with various COF contents in anode CL were prepared, the specifications of these MEAs were included in Table 1. The Nafion content in the CLs of all these MEAs were 30 wt%. The effective area of the MEA was 4 cm^2.

Contact angle test

A contact angle meter (Dingsheng, JY-82B, China) were employed to determine the wettability of the CLs with various COF contents. A drop of water was placed on the dry and clean MEA surface and was measured by direct image analysis at room temperature. The contact angle is obtained by fitting the

tangent of the three-phase point of contact between the liquid surface and the solid surface [45].

Single cell test and electrochemical measurements

Together with two GDLs based on carbon papers (TGP-H-090, Toray, Japan), the MEA was assembled with a torque of 6 N m in a single cell test fixture (Fuel Cell Technologies, Inc, USA). The single cell performance was evaluated in a fuel cell test system (Arbin Instruments, USA). High pure hydrogen (≥99.999%) and oxygen (≥99.5%) were introduced into the anode and the cathode respectively, with the stoichiometric ratio of 2:1.5. Prior to testing, the MEAs were activated at 100% humidification by conditioning at 0.2−1 A cm^{-2} for 3−5 h to achieve a stable performance.

Electrochemical impedance spectroscopy (EIS) was used to study the polarization resistance of the MEAs under different operating conditions by using an electrochemical workstation (CHI660E, Shanghai Chenhua Instruments Co., China). The measurements were performed at 0.6 V with 5 mV amplitude in 0.1 Hz−20 KHz frequency range [46].
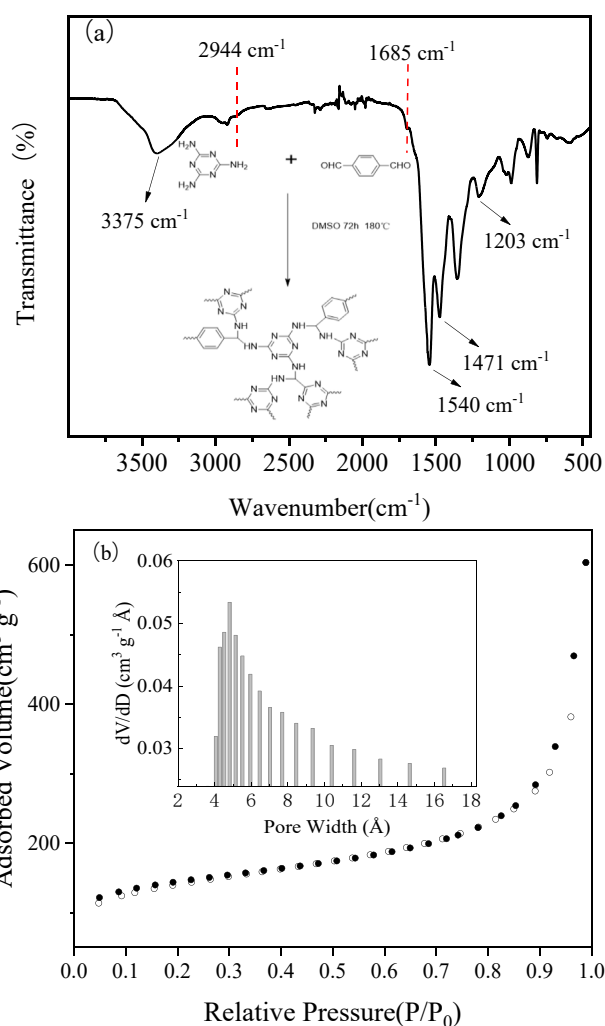

Fig. 1 − (a) FT-IR spectra and N_2 adsorption-desorption isotherms of SNW-1, (b) the inset in is the pore size distribution of the SNW-1 COF.

Table 1 − Specifications of the MEAs prepared in this study.

MEAs	Anode (0.1 mg_{Pt} cm^{-2})	Cathode (0.2 $mg_{Pt}$$cm^{-2}$)
MEA-C0	Pt/C, Nafion, 0 wt% COFs	Pt/C, Nafion
MEA-C5	Pt/C, Nafion, 5 wt% COFs	Pt/C, Nafion
MEA-C10	Pt/C, Nafion, 10 wt% COFs	Pt/C, Nafion
MEA-C20	Pt/C, Nafion, 20 wt% COFs	Pt/C, Nafion

Results and discussion

Physical characterizations of the SNW-1 COF

As previously reported, the SNW-1 COF network was built up between terephthalaldehyde and melamine based on Schiff base chemistry. The successful preparation of the SNW-1 COF material is confirmed by FT-IR spectra, as shown in Fig. 1(a). The spectral features are well consistent with previous result [43]. The bands corresponding to C=O stretching (1685 cm^{-1}) and C–H stretching (2944 cm^{-1}) in aldehydes is greatly attenuated in the spectra of the SNW-1 COF materials, indicating the completion of the polymerization. The ring stretching from triazine (1540 and 1471 cm^{-1}) and the distinct bands attributed to the N–H stretching (3375 cm^{-1}) are found in the spectra, which confirms the incorporation of the melamine into the networks. The band at ~1203 cm^{-1} pertains to C–N bonds, which further confirms the successful formation of Schiff base networks. The FT-IR spectra of the PA-loaded SNW-1 COF can be found in Fig. S1 (Supporting information), where a new band emerged at 1157 cm^{-1} can be detected and assigned to P=O stretching vibration [43], which confirms the successful impregnation of H_3PO_4 into SNW-1.

The porous structure and the pore size distribution of the SNW-1 COF material are analyzed by N_2 absorption measurement. As shown in Fig. 1(b), a steep gas uptake is displayed in the adsorption isotherms under low relative pressure, followed by a flat adsorption process, which is a typical feature for microporous materials. The Brunauer-Emmet-Teller (BET) surface area of the COF is up to ~600 m^2 g^{-1}, and no obvious hysteresis was observed upon desorption, suggesting a high cross-linking degree of monomers [41]. The major pore size of the SNW-1 is found to be 0.42–0.54 nm, which well matches the size of H_3PO_4 molecules (~0.37 nm) to be immobilized in its cavities.

Wettability of the anode CL

The wettability is normally a reflect of the water retention capacity of CL, which can be evaluated from the contact angle test. Fig. 2 presents photographs of the contact angles of the anode CLs with and without the addition of COFs. The water contact angle of the anode CL was obviously decreased with the increase of the amount of PA-loaded COF in the CLs, which clearly indicates that the addition of the COF improved the wettability, implying the increased water retention capacity of these CLs. However, it should be noticed that the contact angle was substantially decreased from 163.7° from 150.4° when just 5 wt% COF was introduced into the CL, however further increasing the COF amount to 10 wt% and 20 wt% only made minor changes (a gradually decrease of ~2°) on the CL contact angle. This could be due to that moisture was mainly retained in the cavities of the COFs (combined with PA), so the micropore surface in the CL can still maintain good hydrophobicity, then resulting in the higher contact angles compared to the CLs based on other hygroscopic additives [25]. It is assumed that a decent hydrophobicity can favor the remove of excess water and the gas transport inside the CL.
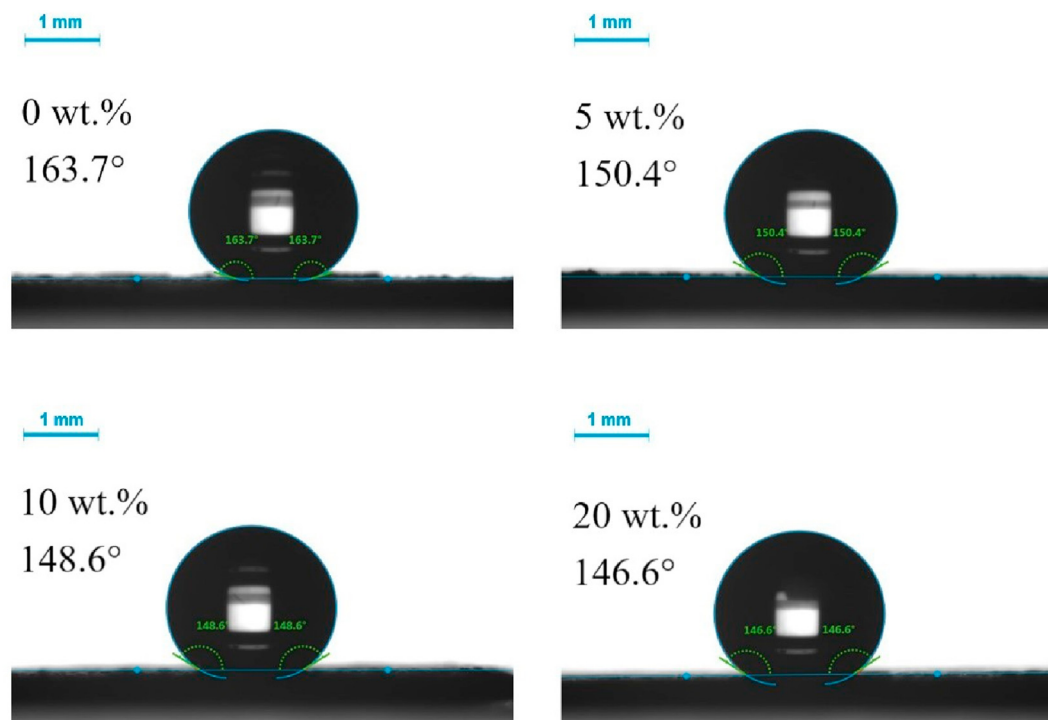

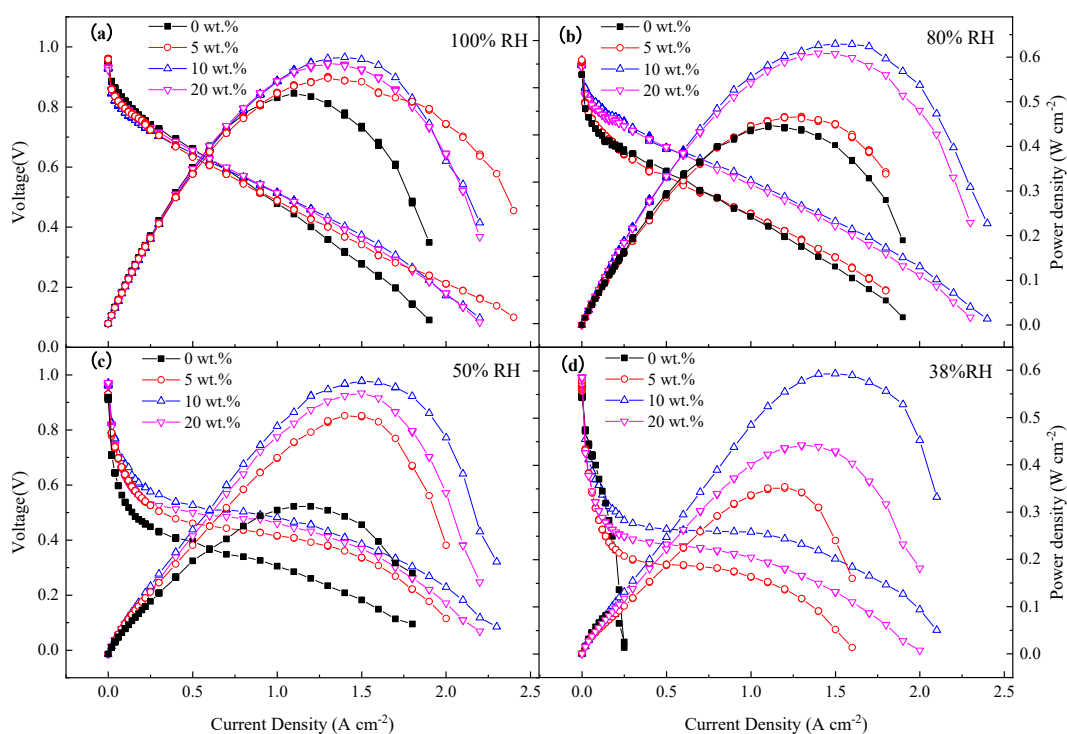Fig. 2 — The contact angles of MEAs with different amounts COFs in the anode CLs.

Fig. 3 – The performances of the MEAs with various COF loadings at 60 °C and different RH conditions. (a) 100% RH; (b) 80% RH; (c) 50%RH; (d) 38%RH.

Effect of COF loading on MEA performance under different RH conditions

Fig. 3 plots the polarization and power density curves of the MEAs with different COF amounts in the anodes (0, 5, 10, 20 wt %) at 60 °C and various humidification conditions (38, 50, 80, 100% RH). It is quite common hygroscopic additives in anode CL helps the improvement of PEMFC performance under low humidity as observed in many previous studies [24,47,48]. Surprisingly, the COF additive in this work can not only improve the cell performance at low humidity, but also elevate its performance at full humidification (Fig. 3(a)), especially at high current densities. The higher performances of these MEAs might be attributable to the unique properties of the PA-loaded COF network, i.e. the proton transfer ability and the abundant cavities containing PA molecules, which make it a proper proton conductor and water reservoir simultaneously, then a large quantity of water can be constrained inside the cavities, consequently reduced the risk of flooding at high humidification and finally leading to an enhanced performance in mass transfer region (i.e., at high current densities).

With reducing the RH, the advantage of the MEAs with COF additive was more obvious. It can be seen that the performance of the pristine MEA-C0 was significantly dropped when the RH was decreased from 80% to 38%, while the MEAs with COF network still showed decent performances at the same conditions (Fig. 3(b-d)). In addition, it was found that the content of the COF additive had certain effects on the MEA performances under various RHs. A relatively low content (e.g. 5 wt%) of the COF additive could impair the water retention of the anode while a higher (e.g. 20 wt%) COF content might greatly increase the cell resistance, then resulting in inferior performances at low RH conditions. Therefore, an optimal COF content of 10 wt% in the anode CL seems a compromise between retaining water and maintaining low ohmic resistance, thus showing the best performance among these MEAs. It should be mentioned that 38% RH was the limitation in this study determined by the test system and humidification temperature. As shown in Fig. 3(d), the MEA-C0 can hardly work at this RH, probably due to the serious dehydration of the CL and the Nafion membrane. In contrast, the COF-doped MEAs showed much better performances at this low RH, i.e., the voltage drop slowed down with the increase of current densities (>0.3 A cm^{-2}), which was attributable to the enhanced CL water retention and membrane hydration due to the increased water production at higher current densities. For the MEA-C10, its maximum power density can still reach 582 mW cm^{-2}, which was close to the performance at 80% and 100% RHs (585–626 mW cm^{-2}), and almost 6.85 times higher than that of pristine MEA-C0. These results distinctly demonstrated that the superior self-humidifying ability of the MEAs incorporating with the COF network.

Electrochemical impedance spectroscopy

To further explain the performance differences and validate the effect of the COF additive in anode CL, *in situ* impedance characterization on the MEAs was performed at low humidification of 38% RH, as shown in Fig. 4. Fig. 4(a) presents the Nyquist plots of the MEAs at the cell voltage of 0.6 V, and the cell ohmic resistances (R_Ω) and the cell charge transfer
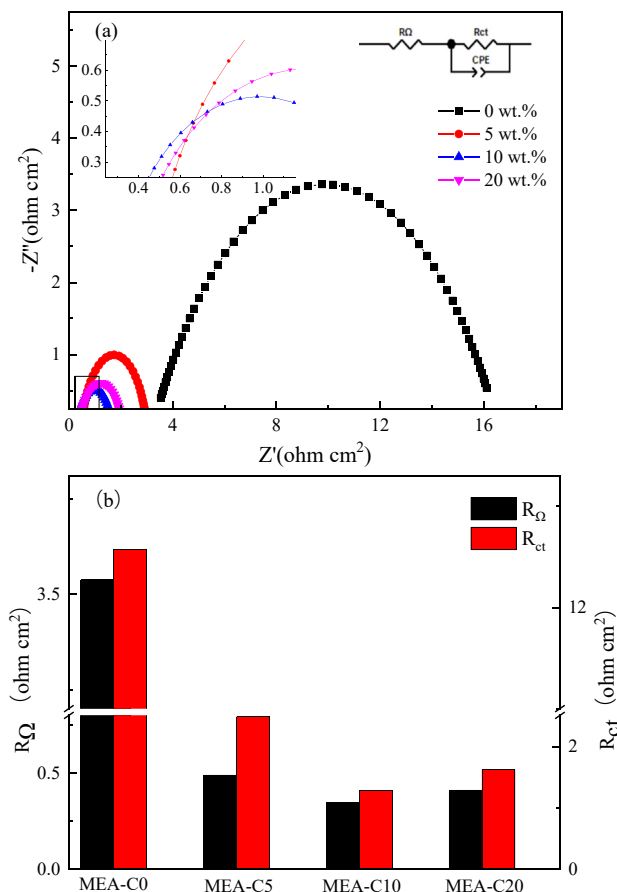
Fig. 4 − **The impedance spectra of MEAs containing various amounts of COF, (a) measured at 60C and 38% RH; (b) Bar graph showing resistance.**

Fig. 5 − **Comparison of single cell performances of MEA-C10 at various cell temperatures with 38% RH conditions.**

resistances (R_{ct}) were obtained by equivalent circuit fitting and the values were plotted in Fig. 4(b) for comparison. It can be seen that the cell ohmic resistances of the MEAs with the COF additive are around 0.35−0.49 Ω cm², which are much lower than that of the pristine MEA (3.54 Ω cm²). It is well known that the cell ohmic resistance consists of the resistances for both electron and proton conduction in and between MEA and other cell components. Although the addition of the COF network could increase the resistance for electron conduction in CL, the superior water.

Retention ability and the loaded PA molecules made a facile proton transport even at low humidification, consequently a low cell ohmic resistance can still be maintained. In contrast, the pristine MEA-C0 suffered with serious dehydration under low humidification, which greatly decreased the proton conductivity of Nafion ionomer and Nafion membrane, thereby leading to an extremely high cell ohmic resistance and charge transfer resistance due to the low proton transfer ability. Therefore, the EIS results further validated the advantages of the PA-loaded COF for the MEA operation under low humidification, and the 10 wt% additive was determined as an optimal content due to the minimum ohmic resistance and charge transfer resistance, as well as the best single cell performance under this low humidity operation.
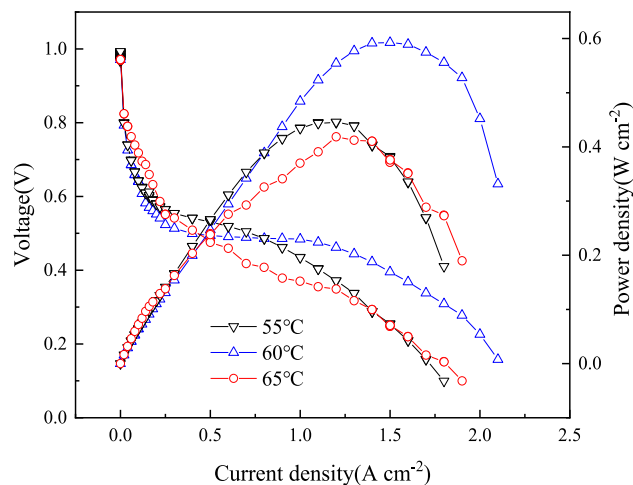
The effect of cell temperature on MEA performance

Generally, the operating temperature has important effect on the PEMFC performance at low humidity because the temperature can simultaneously affect the evaporation of water and the kinetics of electrode reaction. As shown in Fig. 5, the polarization curves of MEA-C10 at different temperatures (55, 60, 65 °C) and 38% RH were examined. The proper operating temperature was found to be 60 °C for the MEA at the low humidification condition, where the maximum power density was up to 582 W cm⁻², which is 31% higher than that operating at 55 °C. The superior performance at higher temperature is reasonable because the improved electrode reaction kinetics at higher temperature. However, high temperature could also accelerate the loss of moisture remained inside MEA, which could lead to the dehydration of the CL and the membrane at low humidity condition, then resulting in the
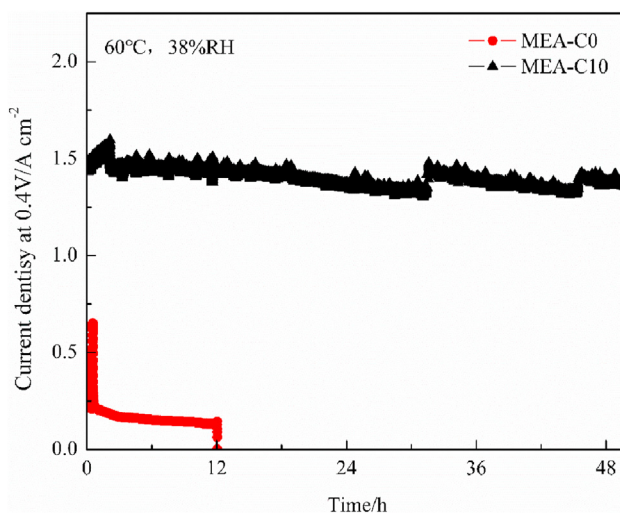

Fig. 6 − **Short-term discharge tests of MEA-C0 and MEA-C10 operating at 38% RH and cell temperature of 60 °C.**
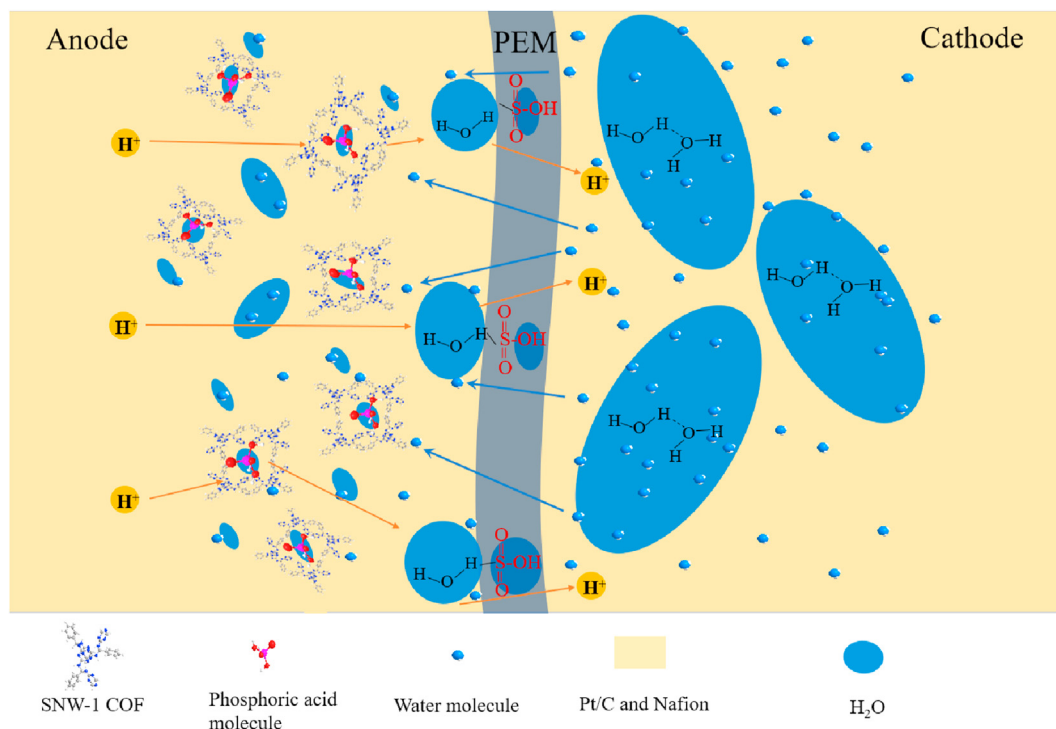
Fig. 7 – Illustration self-humidifying mechanism of the MEA with SNW-1 COF-based anode CL.

increased proton transfer resistance. This could be the reason for the cell voltage of the MEA-C10 decreasing sharply in ohmic polarization region (0.3–1.0 A cm^{-2}) at the cell temperature of 65 °C, consequently leading to the irregular changes in voltage with increasing current densities and the inferior single cell performance.

Stability

To evaluate the stability of the MEA with COF additive for low humidity operation, a preliminary durability test at constant voltage (0.4 V) on the MEA-C10 and MEA-C0 were conducted, as shown in Fig. 6. After 48 h running at 38% RH, the current density of MEA-C10 still remained at ~1.38 A cm^{-2}, which is equivalent to only 4.4% loss in the performance during this term. On the contrary, the pristine MEA-C0 showed a steep decrease in current density at the very beginning of operation, and it can hardly work after 12 h, indicating the serious dehydration of the MEA. It should be noticed that there was a few recovery in the performance of the MEA-C10 during the operation, such as at ~30th and 44th hours, which could result from the self-regulation and rebalancing of hydration due to the superior water storage capacity of the COF network with abundant micro cavities, suggesting that the proposed MEA possess the possibility for long-term operation at low humidity environment.

To further confirm the stability of the COF additive during PEMFC operation, the CL samples before and after the stability test were taken and examined by FT-IR, as shown in Fig. S2

(Supporting Information). Due to the existence of different ingredients in CL, the FT-IR spectra of the COF-based CL is quite different from the pure COF material. However, the main characteristic peaks of the SNW-1 COF, such as 1210 cm^{-1} (C–N), 1542 cm^{-1} and 1471 cm^{-1} (triazine) can still be observed in the spectra (Fig. S2a). Furthermore, there was almost no change on the spectra for the CL after 48 h operation (Fig. S2b), implying the good stability of the SNW-1 COF for PEMFC operation. This result is consistent with its physicochemical properties, i.e., excellent resistances toward strong acid and high temperature (up to 300 °C), as reported previously [41].

Based on the above results, the self-humidifying mechanism of the MEA with the COF additive is proposed and illustrated in Fig. 7. The water produced at cathode can be transferred to anode in the manner of back diffusion due to the concentration gradient [49], then it can be captured by the COF network (SNW-1) due to the hydrophilicity of H$_3$PO$_4$ and amino groups in SNW-1. Most water molecules could enter into the cavities of the SNW-1 due to the strong moisture absorption ability of the impregnated H$_3$PO$_4$ molecules. Thus, the cavities of the COF can act as like many small water reservoirs, which could adjust the balance of the water required in the CL for proton transport under low humification. Furthermore, the loaded H$_3$PO$_4$ molecules in the cavities can facilitate the proton transfer in the CL as explained in previous work [43], which make the COF additive simultaneously possess proton transfer and water retention abilities, consequently leading to enhanced performance and durability for PEMFC operation under low humidity conditions.

Conclusions

A self-humidifying MEA with H_3PO_4-loaded COF network (SNW-1) as anode additive was developed to improve the PEMFC performance under low humidity conditions. The results from the single cell tests and EIS measurements revealed that an optimal content of 10 wt% COF in the anode CL was capable to deliver the highest performance at various humidity conditions due to the minimum cell ohmic resistance and charge transfer resistance. At 60 °C and 38% RH, the maximum power density of the optimized MEA was up to 582 mW cm^{-2}, which is almost 7 times higher than that for the routine MEA (85 mW cm^{-2}). It is found that elevating cell temperature could impose negative effect on the low humidity performance of the PEMFC due to the enhanced dehydration of the MEA, where 60 °C was suggested as the proper operating temperature for this system by compromising a decent electrode reaction kinetics and restricted water evaporation. At last, a preliminary durability test (48 h) demonstrated the potential of the proposed MEA for practice application under low humidity environment. We conclude that the unique proton transfer ability, the good interfacial compatibility with Nafion matrix, and the superior water retention capacity are crucial features making the COF a promising alternative for developing self-humidifying PEMFCs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.12.153.

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