

# High Temperature PEMFCs for Heavy Duty Applications

- Challenges and Opportunities -

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**ABSTRACT:** Recently, high-temperature proton exchange membrane fuel cells (HT-PEMFCs) for heavy duty applications has attracted lots of attention. Instead of traditional phosphoric acid doped polybenzimidazole-based membrane (PA/PBI) which is only stable when operating between 140°C to 160°C and low current density, an ion-pair type of membrane was developed. The ion-pair membrane is based on quaternary ammonium-biphosphate ion-pair coordination. The ion-pair MEA has a much wider operating temperature (80°C-200°C) and stable for dynamic operation of fuel cells. This leads to the potential application of HT-PEMFC for heavy duty applications due to its better heat rejection, simpler water management and high fuel impurities tolerance. We review the state-of-the-art ion pair MEAs for performance and durability. Moreover, phosphoric acid (PA) effect to oxygen reduction reaction (ORR) was studied. Pt alloy catalysts were evaluated on both low temperature and high temperature rotating disk electrode to understand the PA poisoning and possible countermeasures. A few strategies were explored to improve ORR catalyst activity. Based on what we have learned for the evaluation results, we will share our perspectives on further improve the MEA performance in HT-PEMFCs.

**KEY WORDS:** high temperature PEM, ion-pair, ORR, phosphoric acid, MEA, fuel cell

## 1. INTRODUCTION

The focus of PEMFCs technologies has recently shifted from light-duty automotive applications to heavy-duty vehicle applications (HDV). <sup>(1)</sup> One of the most significant technical challenges of HDV fuel cells is the issue of heat rejection as the average operating temperature of HDV fuel cells can be 5-15 °C higher than light-duty vehicle fuel cells. In order to control the heat rejection, the voltage of fuel cell for HDV is usually limited to high voltage and low power density. <sup>(2)</sup> Moreover, it was estimated that 28-69% higher heat load will be generated depending on the driving condition despite higher efficiency of fuel cell than internal combustion engine. Therefore, 68-124% larger fan and radiator are required for packaging which can be an issue in HDVs.

There are several advantages to increase the fuel cell operating temperature to 160°C and above. The cost of fuel cell systems can be reduced by smaller fuel cell cooling system. Additionally, high-temperature and dry operation allows for the use of reformat hydrogen containing 2% carbon monoxide and enables operation of the system without a large humidifier or complex humidity controlling unit. <sup>(3)</sup>

Since traditional perfluorosulfonic acid (PFSA) electrolytes require adequate hydration and phosphoric acid-doped polybenzimidazole (PA-PBI) electrolytes suffer from PA leaching

at low temperature, high current density and dynamic operating conditions, the emerging ion-pair electrolyte shows promising stability within a wide operating temperature window. <sup>(2)</sup> The chemical structures of the ion-pair membrane and phosphonated polymer mixed with PSFA ionomer are shown in Fig.1. Because of the much stronger ion-pair interaction in PA-QAPOH than the acid-base interaction in traditional PA/PBI, the PA-QAPOH has much better PA retention ability. Furthermore, the tradition PTFE binder in PA/PBI MEA was replaced by phosphonated ionomer with high proton conductivity. Adding PFSA ionomer further improved the proton conductivity of the poly (2,3,5,6-tetrafluorostyrene-4-phosphonic acid) (PWN) ionomer and adjusted hydrophobicity of the electrode.

Here, we will compare the latest ion-pair MEAs performance to low temperature MEA performance. Through the comparison, we identified performance gap between HT-PEMFC and low temperature proton exchange membrane (LT-PEMFC). Further study of PA poisoning effect discloses the low ORR activity of catalyst in HT-PEMFC environment. Pt alloy catalyst and ionic liquid surface modification were explored to mitigate PA poisoning. At last, we will share our perspectives on further improve the MEA performance in HT-PEMFCs.

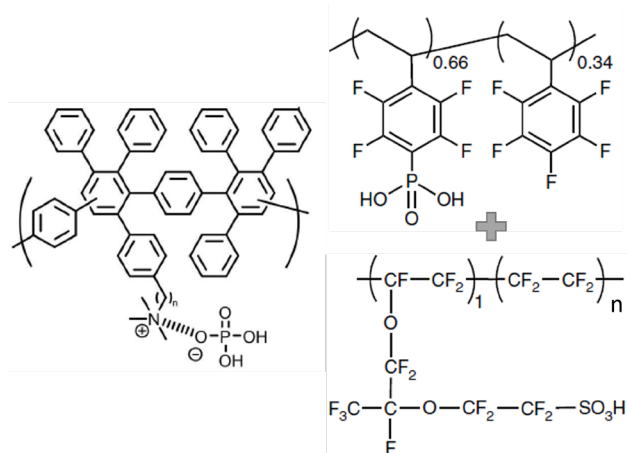


Fig. 1 Chemical structures of ion-pair membrane PA-QAPOH (left) and phosphonated polymer PWN-1.8 mixed with Nafion (right).

## 2. EXPERIMENTAL

Catalyst activity was evaluated with low temperature rotating disk electrode (LT-RDE) at room temperature with perchloric acid with and without 0.1M phosphoric acid. The Nafion to carbon ratio was 0.5. The catalyst loading on the electrode is 15  $\mu\text{gPt}/\text{cm}^2_{\text{GC}}$ . Cyclic voltammetry was conducted between 0.05-1.05 V at 100 mV/s in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  at 400 rpm for 30 cycles. Linear sweep voltammogram (LSV) was scanned from 0.05 to 1.05 V at 10 mV/s in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  at 1600 rpm. The electrolyte was then bubbled with Ar for 15 min. Three cycles CV(0.05-1.05 V) and 1 LSV scan are conducted in Ar-saturated 0.1 M  $\text{HClO}_4$ . The same electrode, after the ORR measurement in 0.1 M  $\text{HClO}_4$ , was then transferred to another cell with 0.1 M  $\text{HClO}_4$  + 0.1 M  $\text{H}_3\text{PO}_4$ . CV and LSV curves are obtained in Ar-saturated 0.1 M  $\text{HClO}_4$  + 0.1 M  $\text{H}_3\text{PO}_4$  and then in an  $\text{O}_2$ -saturated solution. The electrochemical surface area (ECSA) was determined from the average of hydrogen adsorption and desorption charges between 0.06 V - 0.4 V, assuming a specific charge of 210  $\mu\text{C}/\text{cm}^2_{\text{Pt}}$ . The kinetic current is determined from the equation  $i_K = \frac{i_L \times i}{i_L - i}$ , where  $i$  is the measured current at 0.9 V after subtracting the background (LSV measured in Ar),  $i_L$  is the diffusion limiting current measured at 0.4 V.

High temperature RDE (HT-RDE) was performed in pure phosphoric acid at 160°C. To avoid  $\text{H}_3\text{PO}_3$  generation (explanation in results and discussion section), CV was conducted in 0.6 -1.05 V for 30 cycles with continuous  $\text{O}_2$  bubbling. LSV was scanned from 1.05 V to 0.4 V at 1 mV/s. ECSA from LT-RDE was used to calculate the specific activity (SA).

Low temperatures MEA was fabricated with Gore membrane (12 $\mu\text{m}$ ), PtCo/C catalyst with 0.17mgPt/ $\text{cm}^2$  loading on cathode and Pt/C catalyst with 0.05mgPt/ $\text{cm}^2$  loading on anode. The cell was evaluated in a customized 4 $\text{cm}^2$  differential cell at 80°C with  $\text{H}_2/\text{Air}$  supply and 200kPa (abs.) backpressure.

## 3. RESULTS AND DISCUSSION

Fig. 2 shows the polarization curve of ion-pair MEA 160°C and our typical low temperature fuel cell MEA performance. The ion-pair MEA's performance is still much low than state-of-the-art low temperature MEA performance. At kinetic region, the ion-pair MEA shows lower activity compared to LT MEA. The cell voltage at 0.2A/ $\text{cm}^2$  of the ion-pair MEA is around 700mV and the LT-MEA is around 800mV. Despite the conclusion that high temperature should enhance the ORR reaction, the kinetic performance of ion-pair MEA by far is not comparable to LT-MEA.<sup>(4,5)</sup> It is generally agreed that the phosphoric acid poisoning including catalyst surface occupation and competition with ORR reaction intermediates is the main reason to the low activity.<sup>(6,7)</sup> Moreover, the Pt loading in ion-pair cathode is more than 3 times of the Pt loading in LT-MEA. The thicker electrode may also hinder the oxygen transfer. Nevertheless, the catalyst activity in ion-pair MEA with phosphoric acid as electrolyte needs to be improved for better kinetic performance.

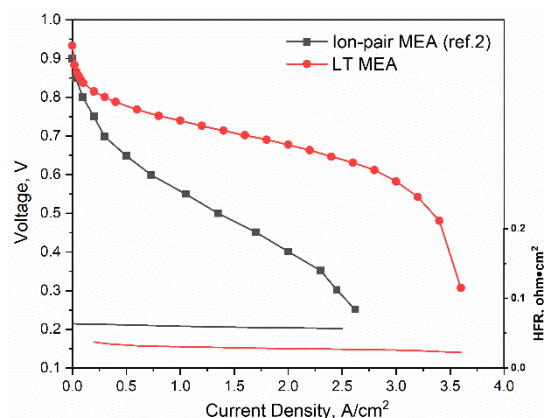


Fig. 2 performance comparison of ion-pair MEA at 160°C, anhydrous,  $\text{H}_2/\text{Air}$ , 148kPa (replotted from reference 2) and low temperature MEA performance at 80°C, 90%RH with  $\text{H}_2/\text{Air}$  and 200kPa(abs.) back pressure.

As emphasized when comparing the MEA performance between LT-MEA and HT ion-pair MEA, we conducted fundamental study on phosphoric acid poisoning aiming to understand the poisoning effect and develop more active catalyst. Fig. 3a and Fig. 3b compare Pt alloy (PtM) catalysts tested on RT-RDE with and without phosphoric acid. ORR specific activity reduces by ~10 times on Pt and PtM catalysts in PA solution. We

also found that active ORR catalysts in 0.1 M HClO<sub>4</sub> in general show higher activity in PA solution.

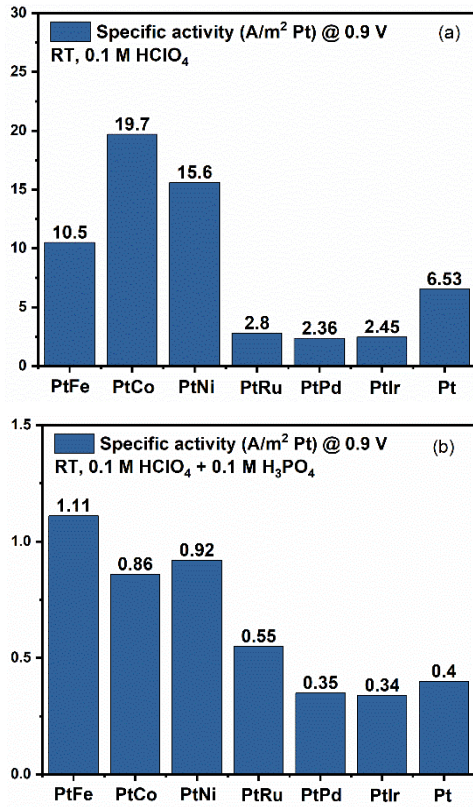


Fig. 3 Pt alloy catalysts tested on RT-RDE with 0.1M HClO<sub>4</sub> (a) and with 0.1M HClO<sub>4</sub> and 0.1M H<sub>3</sub>PO<sub>4</sub> (b)

It is important to point out that when conducting HT RDE using Pt disk electrode with pure phosphoric acid (Sigma Aldrich, 99.999%), an unknown peak (Fig. 4) was observed around 0.7V during ECSA test. This peak could be due to the reduction of H<sub>3</sub>PO<sub>4</sub> to H<sub>3</sub>PO<sub>3</sub> at 0.05 - 0.4 V: H<sub>3</sub>PO<sub>4</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>3</sub>PO<sub>3</sub> + H<sub>2</sub>O, then the generated H<sub>3</sub>PO<sub>3</sub> to be oxidized at a higher potential. This phenomenon has been observed by Sugishima and Wippermann<sup>(8, 9)</sup>. To mitigate the effect of oxidation peak, LSV from 1.05V to 0.4V at different rotation speed (900, 1100, 2500 rpm) was measured to fit in Koutecky-Levich equation (1) for catalyst activity calculation.

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{i_K} + \frac{1}{B} \omega^{-\frac{1}{2}} \quad (1)$$

The coefficient B is

$$B = 0.62nFAD_0^{2/3} \nu^{-1/6} C_0^* \quad (2)$$

where  $F$  is the Faraday constant,  $C_0$  is the concentration of dissolved O<sub>2</sub> in the electrolyte solution,  $D_0$  is the diffusion coefficient,  $\nu$  is the kinematic viscosity, and  $\omega$  is the rotation rate in rad/s.

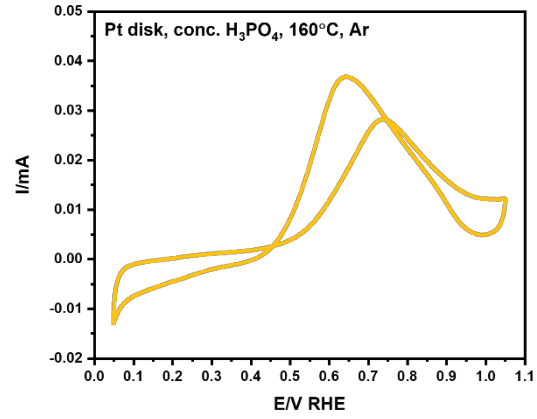


Fig. 4 CV on HT RDE using Pt disk electrode with pure phosphoric acid in Ar gas.

Fig. 5 shows the mass activity (MA) measured with HT-RDE setup. PtCo/C and PtPd/C catalysts show much higher MA than other Pt alloy catalyst we evaluated. The PtCo/C catalyst is more active on LT-RDE, therefore, even with PA poisoning, the MA is still higher than other catalysts. High activity of PtPd/C maybe due to high PA poisoning resistance and smaller particle size.

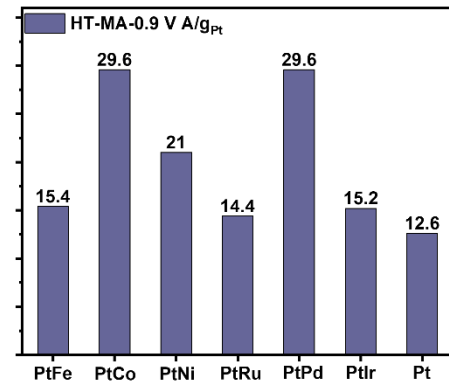


Fig. 5 Mass activity of different Pt alloy catalysts measured on HT-RDE with pure phosphoric acid electrolyte at 160°C.

Further investigation of mitigation of PA poisoning by surface modification was conducted. For LT PEMFC, ionic liquid surface modification has been reported as an effective method to enhance catalyst ORR activity and reduce poisoning from ionomer.<sup>(10, 11)</sup> We applied ionic liquid to the Pt/C catalyst and evaluated it with HT RDE. Fig. 6 shows the mass activity of Pt/C catalysts with and without ionic liquid surface modification. The ionic liquid can effectively improve the mass activity of the Pt/C catalyst. It's deduced that the ionic liquid formed a physical barrier to separate the PA with catalyst. Moreover, the ionic liquid itself is a proton conductor to facilitate the proton transfer even without water.<sup>(12)</sup> Different ionic liquid to carbon ratio leads to various level of mass activity improvement. The optimized ionic liquid to carbon weight

ratio seems to be around 0.05. It may be related to coverage of the ionic liquid on catalyst surface and thickness of the ionic liquid coating. Less coverage could leave more catalyst surface poisoned with PA, therefore limited the improvement. Abundant ionic liquid could form thick coating layer which reduces the oxygen transfer. These preliminary results indicate a different approach for HT-PEMFC catalyst improvement.

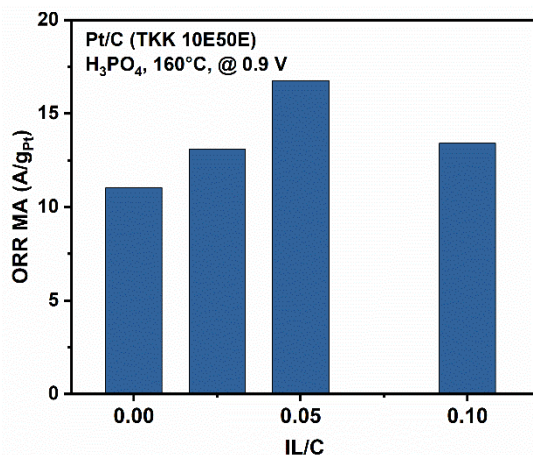


Fig. 6 Mass activity of Pt/C catalyst with different ionic liquid to carbon weight ratio measured on HT-RDE with pure phosphoric acid electrolyte at 160°C.

The high activity catalyst for HT ion-pair MEA is essential to improving MEA performance. However, we notice that the understands to the new ion-pair MEA materials limited. First, the high frequency resistance (HFR) of the membrane is  $\sim 75 \text{ m}\Omega \cdot \text{cm}^2$  which is 3 times of LT membrane. The thickness of the ion-pair membrane is reported to be 35 $\mu\text{m}$ . The thicker membrane compared to LT membrane's 12 $\mu\text{m}$  thickness may be the direct reason of the higher HFR. It could be necessary to reduce the thickness of ion-pair membrane. Secondly, as shown in Fig. 2, the high current density performance of the ion-pair MEA is significantly lower than LT-MEA. We deduce that the mass transfer is greatly hindered due to thicker electrode, liquid electrolyte ( $\text{H}_3\text{PO}_4$ ) with low oxygen solubility and diffusivity in the electrodes. Detailed analysis of the mass transfer behavior in the MEA should be conducted to better understand the limitation of current ion-pair MEA. Finally, recent reports on the solvent effect to the ionomer properties and new ionomer structure with high hydrophobicity for ion-pair MEA (Fig.7) indicating the ionomer is very important to the MEA performance not only the ionomer with less poisoning to catalyst is needed but also the oxygen transfer ability which could be the key to the major boost of high current density performance of ion-pair MEA. (13, 14) The

hydrophobic F7N55-bonded MEA exhibited higher performance in both the mass transport and the kinetic regions.

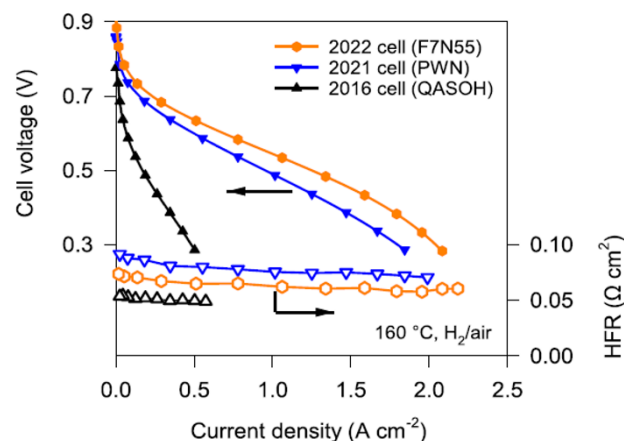


Fig. 7 Ion-pair MEA performance with ionomers with different hydrophobicity (water contact angle to catalyst layer with QASOH ionomer: 2.5°, PWN ionomer: 23° and F7N55 ionomer 163.8°). Reprinted with permission from Adhikari S, et al. Hydrophobic Quaternized Poly(fluorene) Ionomers for Emerging Fuel Cells. ACS Appl Energy Mater. 2022;5(3):2663-8. Copyright 2023 American Chemical Society.

While the performance gap between HT-PEMFC and LT-PEMFC is still significant, we believe that with fundamental understanding of the root causes of the low performance and new materials development, HT-PEMFC performance could be further improved to minimize the gap to LT-PEMFC. The obvious advantages of HT-PEMFC such as better heat rejection is essential to high power requirement applications like heavy-duty trucks. System design incorporating the HT-PEMFC stack should be conducted to fully evaluate the benefits of this technology. The stack materials and cooling technology for the HT-PEMFC system should also be investigated to accommodate the higher operating temperature.

#### 4. CONCLUSION

Through reviewing the state-of-the-art ion-pair MEA performance, we found that the MEA performance is still lower than LT-PEMFC and the catalyst loading is much higher than LT-PEMFC. In effort to improve the HT-PEMFC performance, catalyst poisoning effect was studied and confirmed that Pt alloy catalyst responses to PA poisoning differently. The RDE results show promising trend that catalyst activity at high temperature in phosphoric acid can be improved. We suggest that further works to improve ion-pair MEA performance may include PA resistant catalysts, more conductive membrane and ionomer with low poisoning to catalyst as well as mass transfer improvement.

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