

Advanced Ion-Pair High-Temperature Polymer Electrolyte Membrane Fuel Cells

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ABSTRACT: High-temperature proton exchange membrane fuel cells (HT-PEMFCs) for heavy-duty applications have gained significant attention due to their advantage in thermal management. Unlike the traditional phosphoric acid-doped polybenzimidazole (PA/PBI) based membrane, which is only stable when operating between 140°C to 160°C at low current density, an ion-pair membrane type 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 is stable for the dynamic operation of fuel cells. This advancement enhances HT-PEMFCs' potential for heavy-duty applications, providing improved heat rejection, simpler water management, and higher tolerance to fuel impurities. Our work focuses on improving the performance of the ion-pair membrane electrode assemblies (MEAs) by enhancing oxygen transfer and mitigating phosphoric acid (PA) poisoning of the oxygen reduction reaction (ORR). We explored carbon paper as a gas diffusion layer (GDL) to replace carbon cloth, aiming to enhance mass transfer in the MEA. Additionally, we used ionic liquid (IL) to shield the Pt catalyst from PA poisoning, thereby boosting catalytic activity. Based on these insights into advancing MEA performance, we will share our perspectives on further enhancing MEAs in ion-pair HT-PEMFCs for heavy-duty applications.

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

1. INTRODUCTION

The focus of PEMFCs technologies has recently shifted from light-duty automotive applications to heavy-duty vehicle applications (HDV). ⁽¹⁻³⁾ One of the most significant technical challenges of HDV fuel cells is heat rejection, as the average operating temperature of HDV fuel cells can be 5-15 °C higher than light-duty vehicle fuel cells. To control heat rejection, the fuel cell voltage for HDV is usually limited to high voltage and low power density. ^(4, 5) This significantly limits the fuel cell stack performance in HDVs.

The emerging ion-pair electrolyte shows promising stability within a wide operating temperature window. ⁽⁶⁻⁸⁾ The chemical structure of the ion-pair membrane is shown in Fig.1. Because of the much stronger ion-pair interaction between quaternary ammonium (QA) cations and negatively charged dihydrogen phosphate anions than the acid-base interaction in traditional PA/PBI, the ion-pair membrane has much better PA retention ability. ⁽⁹⁾ Furthermore, a phosphonate ionomer with high proton conductivity replaced the traditional PTFE binder in PA/PBI MEA. 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.

Phosphonated polymer mixed with PSFA ionomer is shown in Fig.2.

Here, we report our latest approaches to improving the ion-pair MEA performance. Carbon paper GDL was used to replace carbon cloth GDL to facilitate oxygen transfer in the MEAs. To overcome PA poisoning to the Pt catalyst for ORR reaction, we incorporated a novel high melting point ionic liquid to separate the catalyst from PA. Analysis of the MEAs was conducted to provide insights into the functions of carbon paper GDL and ionic liquid. By significantly boosting the ion-pair HT-PEMFC comparison, we are one step closer to applying the HT-PEMFCs in HDVs.

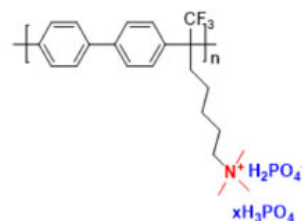


Fig. 1 Chemical structures of phosphoric acid (PA)-doped biphenyl-backbone ion-pair coordinated PEMs (ORION CMX)

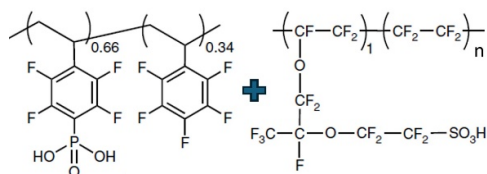


Fig. 2 Phosphonated polymer mixed with PSFA as ionomer

2. EXPERIMENTAL

High-temperature RDE (HT-RDE) was performed in pure phosphoric acid at 160°C to evaluate the activity of Pt with and without ionic liquid modification. The setup of the HT-RDE is shown in Fig. 3. LSV was scanned from 1.05 V to 0.4 V at 1 mV/s to calculate the mass activity (MA).

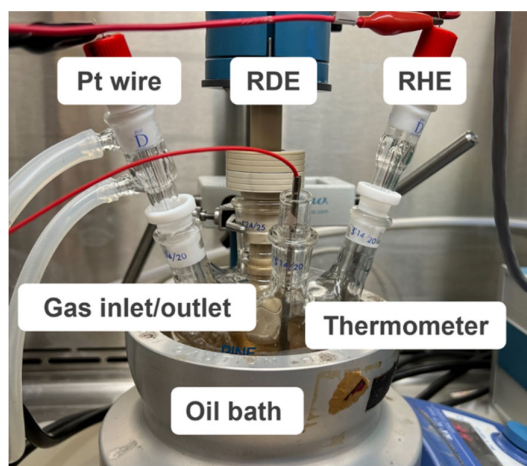


Fig. 3 HT-RDE setup for evaluation of Pt/C and IL-modified Pt/C catalysts

High-temperature ion-pair MEAs were fabricated with a PA-doped ORION CNX membrane (40μm). Carbon cloth GDL (W1S1009, CeTech) and carbon paper GDL (39BB, SGL Carbon) were evaluated by coating with a Pt/C catalyst (10E50E, TKK) with 0.7mgPt/cm² loading as the cathode and 0.4mgPt/cm² loading as the anode. Pt/C with an ionic liquid-to-carbon ratio from 0.1 to 0.2 was compared with pristine Pt/C in mitigating PA poisoning. The cells were evaluated in 5cm² cells with serpentine channels at 160°C with an H₂/Air supply and 148kPa (abs.) back pressure.

3. RESULTS AND DISCUSSION

Investigation of mitigation of PA poisoning by surface modification with ionic liquid was conducted. We applied ionic liquid to the Pt/C catalyst and evaluated it with HT-RDE. Fig. 4 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 from the catalyst. Different ionic liquid-to-carbon ratios lead to various

levels of mass activity improvement. The optimized ionic liquid-to-carbon weight ratio is 0.05 for HT-RDE. It may be related to the coverage of the ionic liquid on the catalyst surface and the thickness of the ionic liquid coating. Less coverage could leave more catalyst surfaces poisoned with PA, therefore limiting the improvement. Abundant ionic liquid could form a thick coating layer, reducing oxygen transfer. These preliminary results indicate a different approach for HT-PEMFC catalyst improvement.

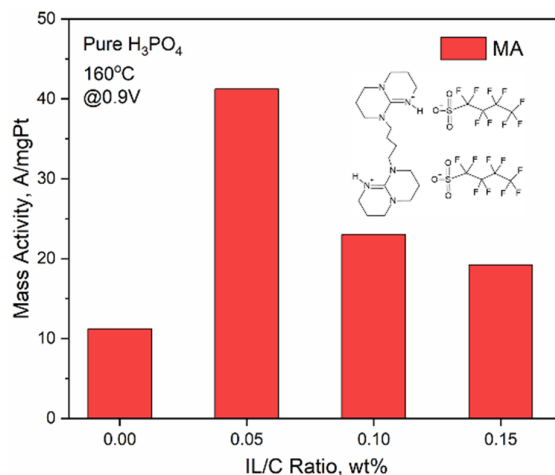


Fig. 4 Mass activity of Pt/C catalyst with different ionic liquid to carbon weight ratio measured on HT-RDE with pure phosphoric acid electrolyte at 160°C. The insert shows the chemical structure of the ionic liquid.

Fig.5 shows the comparison of HT ion-pair MEAs. Using carbon paper GDL significantly improves MEA performance. This is due to the better oxygen transfer in the carbon paper GDL. Fig.6 compares the gas transfer resistance (GTR) of the MEAs with carbon cloth and carbon paper GDL. The pressure-independent oxygen transfer resistance (R_{other}) of the MEAs is similar, indicating the GDLs have no impact on oxygen transfer from the ionomer to the catalyst surface. However, the carbon cloth GDL shows much higher molecular diffusion resistance (R_{molec}) than carbon paper GDL. Combining carbon paper GDL with ionic liquid modification gives the best MEA performance. The optimized ionic liquid-to-carbon weight ratio in MEAs is 0.15 instead of 0.05 on HT-RDE because of the different environments in HT-RDE and MEAs. In HT-MEAs, PA is absorbed into the electrode and retained within the catalyst layer. Water generated from the reaction may cause some dilution to the phosphoric acid with different oxygen transfer capabilities. Therefore, the results from HT-RDE may not be able to represent the exact conditions in HT-MEA fully. Nevertheless, the HT-RDE is a valuable screening tool for evaluating the catalysts; only a tiny quantity is required.

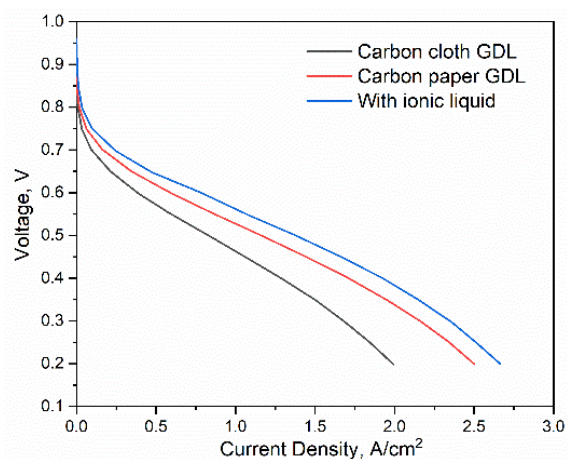


Fig. 5 MEA performance of HT ion-pair MEA with carbon cloth GDL, carbon paper GDL, and ionic liquid modification

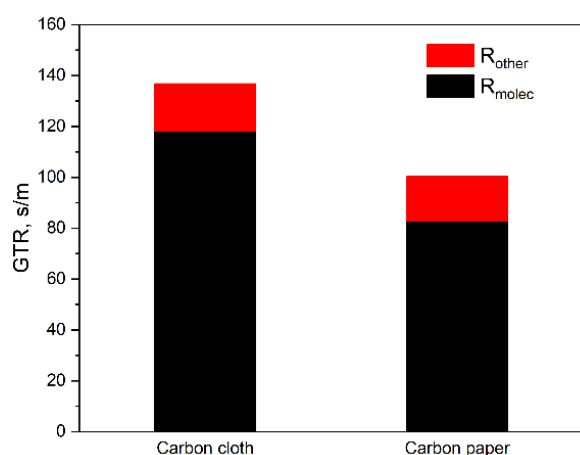


Fig. 6 Gas transfer resistance of HT ion-pair MEAs with carbon cloth GDL and carbon paper GDL

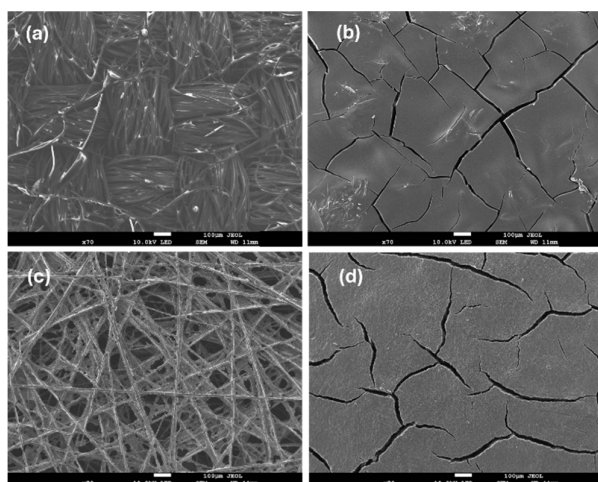


Fig. 7 SEM images of gas diffusion layers (GDLs): (a) Fiber side of the carbon cloth GDL, (b) Microporous layer (MPL) side of the carbon cloth GDL, (c) Fiber side of the carbon paper GDL, and (d) MPL side of the carbon paper GDL.

Fig. 7 shows the SEM images of the fiber side of the carbon cloth GDL (Fig. 7a), fiber side of the carbon paper GDL (Fig. 7c), MPL side of the carbon cloth GDL (Fig. 7b) and MPL side of the carbon paper GDL (Fig. 7d). Both GDLs show cracks on the MPL side. The cracks are normal since the MPL was made of carbon black and PTFE binder slurry and then coated on the carbon cloth or carbon paper substrates. Though how the cracks affect mass transfer in MEAs is still debatable, the cracks could facilitate the gas transfer since the HT-PEMFCs are operated under anhydrous conditions. The cracks may also help with PA redistribution, which is essential for HT-PEMFCs to avoid local flooding.

The fiber sides of the carbon cloth GDL (Fig. 7a) and carbon paper GDL (Fig. 7c) exhibit significant differences in their morphology, fiber arrangement, and structural characteristics, which could have a strong influence on their electrochemical performance in HT-PEMFCs. The carbon cloth GDL has a woven structure with densely packed, interwoven carbon fibers, creating a compact and tightly knit structure. Fibers are closely arranged with fewer large voids, leading to lower bulk porosity and a more rigid framework. The high-density structure provides good mechanical integrity, reducing deformation under compression. However, the low porosity can impede oxygen diffusion, making mass transport challenging in HT-PEMFC operation. The lack of large pores may increase phosphoric acid (PA) accumulation, potentially leading to flooding issues in the electrode.

The carbon paper GDL is a non-woven, randomly oriented carbon fiber network that contains randomly oriented carbon fibers with a more open, porous structure. The presence of PTFE-treated fibers helps improve hydrophobicity and gas permeability. The fiber network is less dense than carbon cloth, allowing for better mass transport of reactants and products. The increased porosity enhances oxygen diffusion, reducing mass transport resistance, which is particularly beneficial for HT-PEMFC cathodes. However, the looser fiber network may lead to higher contact resistance, requiring careful compression during MEA assembly to optimize interfacial contact.

SEM/EDS was also used to analyze the morphology of the IL-modified Pt/C catalyst. The elements mapping from EDS is shown in Fig. 8. It shows a uniform distribution of S and F from the ionic liquid. The IL coating can effectively block the PA from the Pt surface, significantly improving the MEA performance.

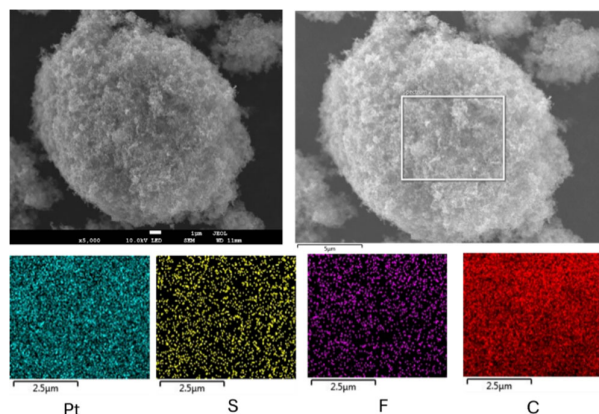


Fig.8 SEM/EDS of IL modified Pt/C catalyst (IL/C=0.15) and mapping of elements of Pt, S, F and C

The EDS spectra in Fig.9 shows the O, F and S peaks from the IL. The Pt and F weight percentage corresponds to IL/C=0.149, close to the designed IL/C ratio of 0.15.

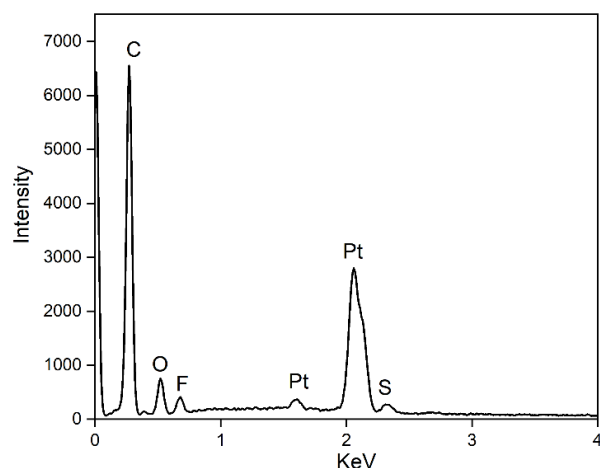


Fig.9 EDS of IL-modified Pt/C catalyst (IL/C=0.15)

4. CONCLUSION

By implementing carbon paper GDL, we significantly boosted the HT ion-pair MEA's performance. The RDE results show the much higher mass activity of Pt/C after surface modification by the ionic liquid. SEM/EDS confirmed the ionic liquid coating and loading on the Pt/C particles. MEAs utilize carbon paper GDL and ionic liquid-modified catalysts, showing promising MEA performance, the best state-of-the-art performance in literature. The positive trend of performance improvement shows a high potential for applying HT ion-pair MEAs in future HDVs.

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