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# Pt/CeO<sub>2</sub> Cocatalyst and porogen enhance performance of high-temperature proton exchange membrane fuel cells



Chaoran Huang<sup>1</sup>, Jie Yan<sup>1</sup>, Xueyao Wang, Zeren Gao, Ding Ma<sup>\*\*</sup>, Junrong Zheng<sup>\*</sup>

College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular Sciences, Peking University, 100871, Beijing, China

#### HIGHLIGHTS

• Synthesizing Pt/CeO2 Nanoparticles with Stable Oxygen Defects.

• Enhancing HT-PEMFCs Performance by Adding Pt/CeO<sub>2</sub> to the Cathode of 25 cm<sup>2</sup> MEA.

• Using (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> as a Pore-Forming Agent to Enhance Mass Transport Performance.

• Achieving a 33 % performance improvement.

#### ARTICLE INFO

Keywords: HT-PEMFC Pt/CeO<sub>2</sub> Porogen Cathode catalyst layer additives

# ABSTRACT

To address the issue of the slow oxygen reduction reaction (ORR) kinetics in high-temperature proton exchange membrane fuel cells (HT-PEMFCs), 0.2 wt% Pt/CeO<sub>2</sub> nanoparticles with oxygen vacancies are synthesized and incorporated into the cathode catalyst layer to enhance performance. Tests with 25 cm<sup>2</sup> single-cells reveal a significant enhancement in HT-PEMFCs performance with the addition of Pt/CeO<sub>2</sub>, reaching a peak power density of 432 mW/cm<sup>2</sup> at 160 °C, compared to 352 mW/cm<sup>2</sup> without the particles. Electrochemical impedance spectroscopy (EIS) analyses show a reduction in charge transfer resistance, suggesting improved O<sub>2</sub> activation. Additionally, oxygen diffusion is identified as a limiting factor in membrane electrode assembly (MEA) performance. To further enhance performance, ammonium oxalate is introduced as a pore-forming agent in the catalyst layer, increasing gas diffusion and reducing concentration polarization. Combining 10 % Pt/CeO<sub>2</sub> with 20 % ammonium oxalate increases the maximum power density to 467 mW/cm<sup>2</sup>, a 33 % improvement over pure catalysts. Structural analyses reveal that the pore-forming agent effectively alters the pore size distribution. This research highlights the potential of Pt/CeO<sub>2</sub> in accelerating ORR kinetics, enhancing HT-PEMFCs performance, and providing valuable insights for the design of catalyst layer additives in HT-PEMFCs.

# 1. Introduction

Hydrogen is an efficient and clean energy source, playing a crucial role in optimizing renewable resources and replacing fossil fuels. Fuel cells, particularly proton exchange membrane fuel cells (PEMFCs), convert hydrogen and oxygen into electricity with up to 60 % efficiency [1–3], and zero emissions [4]. When combined with heat utilization, their efficiency can exceed 80 % [5], making them ideal for applications in transportation, aerospace, and household energy [6–8].

Traditional Nafion-based PEMFCs require extremely pure hydrogen (99.999%) [9,10] because even trace amounts of CO (as low as 20 ppm)

can significantly degrade performance [11,12]. In contrast, high-temperature proton exchange membrane fuel cells (HT-PEMFCs), which operate at 140–190 °C using phosphoric acid-doped polybenzimidazole (PA/PBI) membranes, offer distinct advantages [13,14]. The higher temperature simplifies water management [15] and reduces dependence on humidity [16,17], besides enhancing tolerance to contaminants like CO. HT-PEMFCs can tolerate up to 5 % CO at 180°C [18], allowing for the use of less-purified hydrogen [19–22]. Additionally, the high-quality heat generated by HT-PEMFCs can be efficiently integrated with reformers and heat exchange systems [23,24]. These features provide significant advantages for various industrial and energy

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<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: junrong@pku.edu.cn, zhengjunrong@gmail.com (J. Zheng).

<sup>&</sup>lt;sup>1</sup> These authors contributed equally to this work and should be considered co-first authors.

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# applications [25,26].

However, the actual discharge performance of HT-PEMFCs is significantly lower than that of low-temperature proton exchange membrane fuel cells, primarily due to the low oxygen reduction reaction (ORR) activity of Pt catalysts in phosphoric acid [27]. This phenomenon, known as "phosphoric acid poisoning," occurs when phosphoric acid and its anions strongly adsorb on the Pt surface, hindering the reduction of oxygen molecules and leading to substantial overpotential losses [28]. Furthermore, the low solubility and diffusion coefficient of oxygen in phosphoric acid exacerbate the mass transport resistance within the electrode, intensifying concentration polarization and ultimately affecting the cell's output voltage and efficiency [27].

ORR limitations are the primary bottleneck limiting the HT-PEMFC performance [29]. To address the issues of slow ORR rates and catalyst limitations in high-temperature proton exchange membrane fuel cells (HT-PEMFCs), researchers have focused on modifying membrane materials [30–36], developing new catalysts [37], and improving catalyst layers [38] to enhance performance and extend the lifetime of the cells [39].

Compared to membrane material modifications and catalyst design, catalyst layer modification is more feasible in terms of preparation and can be optimized using existing commercial catalysts [28,40]. By introducing solid acids (e.g., phosphotungstic acid [41], phosphomo-lybdic acid [42], zeolite molecular sieves), nanometal oxides (e.g., Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> [43], ZrO<sub>2</sub> [34]), and nanometal phosphates (e.g., titanium pyrophosphate, zirconium hydrogen phosphate [44]) into the catalyst layer, it is possible to significantly enhance proton conductivity and improve the distribution of phosphoric acid, thus preventing acid flooding. Moreover, adjusting the surfactants, binders, and solvent ratios [45] in the catalyst ink can improve the dispersion of catalysts and binders, increasing the uniformity and performance of the catalyst layer [46]. The use of pore-forming agents is another important strategy, as they can regulate pore size distribution in the catalyst layer, improving gas diffusion and reducing concentration polarization [47].

In terms of enhancing the electrochemical activity and durability of catalysts, it has been found that supporting Pt and other metals on metal oxides (e.g., TiO<sub>2</sub> [48], SnO<sub>2</sub> [49], RuO<sub>2</sub> [50]) is an effective approach. The interaction between the metal and the oxide support not only inhibits the migration of metal nanoparticles but also promotes the adsorption of oxygen and the cleavage of O-O bonds on the Pt surface, thereby improving ORR activity. Cerium oxide (CeO<sub>2</sub>) begins to attract attention in fuel cell catalysis due to its unique properties [33,51]. CeO<sub>2</sub> can switch between Ce<sup>3+</sup> and Ce<sup>4+</sup> states, releasing or storing lattice oxygen in the process [37,52]. Oxygen vacancies in the CeO<sub>2</sub> surface can stabilize metal particles and enhance catalyst durability [53,54]. Additionally, the interaction between CeO<sub>2</sub> and Pt can promote oxygen adsorption and decomposition, further enhancing the ORR rate [52,55].

The Pt/CeO<sub>2</sub> system has been investigated in fields such as hydrogen production and ethanol steam reforming [56,57]. Furthermore, the combination of Pt/CeO<sub>2</sub> with graphene has been shown to significantly enhance its performance in alcohol electro-oxidation [58]. Research also indicates that increasing the interfacial area of metal oxides allows for the adsorption of more metal particles, enhancing charge transfer and stability. While smaller metal particles tend to exhibit higher catalytic activity, larger particles demonstrate better durability [58].

To address the bottleneck of slow ORR rates in HT-PEMFCs, this work proposes the synthesis of Pt/CeO<sub>2</sub> nanoparticles with stable oxygen vacancies. These nanoparticles will be mixed with PtCo/C catalysts and added to the cathode catalyst layer, with the expectation that the interaction between CeO<sub>2</sub> and Pt will promote O<sub>2</sub> adsorption and decomposition, thereby enhancing the ORR rate and improving HT-PEMFC performance. This study first uses CV and LSV tests to characterize the electrocatalytic performance of the mixed catalysts in solution, assessing their ORR performance. Subsequently, 25 cm<sup>2</sup> MEAs are prepared for single-cell testing. Through polarization curves and EIS tests, combined with TEM and SEM morphology characterization, the effect of different  $Pt/CeO_2$  additions on MEA performance is explored, and the stability of the cells is tested over an extended period. The aim of this research is to utilize  $Pt/CeO_2$  particles with oxygen vacancies to promote oxygen activation, improve mass transport within the catalyst layer of HT-PEMFCs, and optimize the overall performance of the fuel cells.

#### 2. Experimental methods

#### 2.1. Synthesis and activation of Pt/CeO<sub>2</sub>

The Pt/CeO<sub>2</sub> catalyst was prepared using an incipient wetness impregnation method. First, 500 mg of CeO<sub>2</sub> (BASF) was placed into a 10 mL crucible, followed by the addition of 250  $\mu$ L of deionized water and a suitable amount of a 37 mg/mL platinum solution (prepared from chloroplatinic acid). The mixture was stirred using a quartz rod until it formed a paste-like suspension and eventually became dry granules. The sample was then dried at room temperature for 24 h and subsequently calcined in a muffle furnace at 400 °C for 2 h, resulting in a final product containing 0.2 wt% Pt/CeO<sub>2</sub>.

The synthesized catalyst was placed into a reaction tube and reduced in a 30 mL/min 10 % H<sub>2</sub>/Ar at 400 °C for 2 h. Then the catalyst was rapidly cooled to room temperature, producing Pt/CeO<sub>2</sub>, which appeared as a purplish-gray powder in air.

# 2.2. Characterization of Pt/CeO2

**X-ray diffraction:** XRD was employed to characterize the crystal structure and verify the chemical composition of the Pt/CeO<sub>2</sub>. XRD measurements were performed using a Rigaku D/Max-PC 2500X diffractometer with Cu K\alpha radiation ( $\lambda = 0.1542$  nm). The operating conditions were set at 40 kV and 100 mA. The activated and passivated samples were pressed flat onto grooved slides for X-ray analysis.

Scanning Transmission Electron Microscopy (STEM): Scanning transmission electron microscopy (STEM) images were acquired on an aberration-corrected JEOL-ARM300F2 GRAND ARM2 with a delta corrector and a cold field-emission gun operated at 200 kV. The convergence angle was set to be 32 mrad. The Z-contrast STEM-HAADF images were collected in the range of 68–280 mrad. Electron energy-loss spectroscopy (EELS) was carried out with the same experimental setup using Gatan GIF detector. All reduced then passivated samples for electron microscopy characterization were prepared by directly dropping the ethanol-diluted sample suspension on TEM grids coated with holey carbon film.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM): SEM and TEM were used to examine the morphology, microstructure, and elemental distribution of the catalyst and membrane electrode assembly (MEA). SEM analysis was conducted using a Hitachi S-4800. TEM analysis was performed using a JEM-2100F microscope. EDS analysis was capable of detecting elements between 5B and 92U.

#### 2.3. Electrocatalytic performance testing

**Preparation of Catalyst Ink**: First, 4 mg of catalyst (and any additives such as Pt/CeO<sub>2</sub>) was dispersed in a solution containing 100  $\mu$ L of ultrapure water, 870  $\mu$ L of isopropanol, and 30  $\mu$ L of Nafion solution. The mixture was sonicated until a homogeneous suspension was achieved. Then, 10  $\mu$ L of the catalyst ink was drop-cast onto the Glassy carbon electrode (GCE) surface, forming a uniform catalyst film with a Pt loading of 16  $\mu$ g. The catalyst layer was air-dried before subsequent electrochemical testing, with the rotation speed set to 1600 rpm to ensure uniform mass transport [1].

**Electrochemical Testing:** Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were carried out in a three-electrode cell on CHI660e. GCE with a radius of 5 mm, Ag/AgCl, and Pt wire were used as

working electrode (WE), reference electrode, and counter electrode, respectively. CV measurements were conducted to estimate the electrochemically active surface area (ECSA) at a scan rate of 50 mV/s in  $N_2$ -saturated 0.1 M HClO<sub>4</sub> solution. LSV measurements, which were used to assess ORR activity, were performed in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution at a scan rate of 10 mV/s. Reference electrode potentials were calibrated using a saturated hydrogen electrode, and all results were converted to the reversible hydrogen electrode (RHE) scale [37].

### 2.4. MEA assembly

**Preparation of Catalyst Ink**: PtCo/C catalyst was dispersed in a 3:1 mixture of isopropanol and water. If additives like  $Pt/CeO_2$  or poreforming agents such as ammonium oxalate were required, they were added at this stage. PTFE was then added as a binder (20 % of the catalyst mass), and the mixture was sonicated for 1 h in an ice bath to ensure uniform dispersion [59].

**Fabrication of Gas Diffusion Electrode (GDE):** Once the catalyst ink was thoroughly mixed, it was sprayed onto pre-cut 5.5 cm  $\times$  5.5 cm carbon paper using an airbrush. The carbon paper was placed on a heated plate (set to 65–70 °C) to evaporate the solvent during spraying. The Pt loading for the cathode was 1 mg<sub>Pt</sub>/cm<sup>2</sup> and 0.6 mg<sub>Pt</sub>/cm<sup>2</sup> for the anode. The GDEs were then heat-treated at 350 °C in a tubular furnace under a nitrogen atmosphere for 30 min [60].

**MEA Assembly**: The MEA assembly consisted of an anode GDE, PBI membrane, and a cathode GDE, with insulating frames between them. The PBI membrane was purchased from BASF, with a thickness ranging from 350 to 450  $\mu$ m. The phosphoric acid weight content ranges from 40 % to 70 %, corresponding to a concentration of 700–900 mg/cm<sup>3</sup>. The assembly was hot-pressed at 135 °C under a pressure of 1 MPa for 5 min [61]. The resulting MEA had an effective area of 25 cm<sup>2</sup>.

#### 2.5. Single-cell testing

All cell tests were performed in a single-cell setup. The home-built fuel cell assembly is consisted of graphite bipolar plates with single serpentine flow-fields (channel cross section: 1 mm  $\times$  1 mm), and aluminum plates equipped with two 300-W heating rods and four PT100 temperature sensors to adjust the operational temperature of the cell. All gas flow rates were monitored using Alicat mass flow controllers. Both the anode and cathode operated at near-atmospheric pressure with no back pressure applied. Each MEA was activated at 160 °C and 0.6 A/cm<sup>2</sup> for 5 h until stable performance was achieved [62], typically resulting in a 50–60 mV improvement in voltage compared to the inactivated state [29].

**Polarization Curve Testing:** Polarization curves were measured using a DC electronic load in the constant current mode. The temperature was maintained at 160 °C, with a hydrogen stoichiometry  $\lambda_{Hz} = 1.35$  and air stoichiometry  $\lambda_{Air} = 2.5$  or oxygen stoichiometry  $\lambda_{Oz} = 2.5$ . Current density was gradually increased from 0 mA/cm<sup>2</sup> (open circuit) to 1200 mA/cm<sup>2</sup>, with the corresponding gas flow rates adjusted accordingly. Testing concluded when the cell voltage dropped below

300 mV [63-65].

**Electrochemical Impedance Spectroscopy (EIS):** EIS measurements were conducted using an Ivium XP20 electrochemical workstation at a constant current of  $0.4 \text{ A/cm}^2$ . The frequency range was 10 kHz to 0.1 Hz, with 10 points measured per decade. A perturbation amplitude of 7 mV was used. To ensure measurement stability, each test was conducted after the cell had operated under stable conditions for approximately 30 min [63,66–68].

# 3. Results and discussion

# 3.1. Physical characterizations of Pt/CeO<sub>2</sub>

Fig. 1(a) presents the XRD patterns of  $Pt/CeO_2$  prepared using the described method. No characteristic peaks of Pt metal are observed, indicating that Pt is well-dispersed on the  $CeO_2$  surface without forming large Pt particles.

STEM analysis further investigates the dispersion of Pt on CeO<sub>2</sub>. Fig. 1(b) shows the HAADF image and EELS results for Ce-L and Pt-M of 0.2 wt% Pt/CeO<sub>2</sub>, which indicates that Pt species exits in the form of small clusters on the catalyst surface.

The combined XRD, STEM results confirm that the synthesized  $Pt/CeO_2$  catalyst exhibits excellent Pt dispersion, primarily existing in clusters with a diameter of around 1 nm.

#### 3.2. Electrocatalytic performance

To explore the effect of adding  $Pt/CeO_2$  to PtCo/C catalysts on the oxygen reduction reaction (ORR) activity, a series of mixed catalysts containing varying amounts (5 %, 10 %, 15 %, and 20 % by weight) of  $Pt/CeO_2$  were prepared and tested in 0.1 mol/L HClO<sub>4</sub> solution using cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

As shown in Fig. 2(a), the CV results indicate that the electrochemically active surface area (ECSA) of Pt/C catalysts remains relatively unchanged after the addition of Pt/CeO<sub>2</sub>. This suggests that CeO<sub>2</sub> is evenly dispersed without significantly covering the active Pt sites. All catalysts exhibited typical hydrogen adsorption/desorption behavior within the potential range of 0–0.3V. The ECSA was calculated using the hydrogen desorption charge on the Pt surface, as shown by the following equation [37]:

$$ECSA = \frac{Q_{\rm H}}{0.21^* m_{\rm Pt}},\tag{eq.1}$$

where  $Q_{\rm H}$  represents the measured hydrogen desorption charge. 0.21  $mC/cm^2$  is the charge associated with monolayer hydrogen adsorption on Pt, and  $mg_{Pt}$  is the Pt loading. The calculated *ECSAs* are 54.7  $m^2/mg_{Pt}$  for the 5 % Pt/CeO<sub>2</sub> catalyst, 56.1  $m^2/mg_{Pt}$  for 10 %, 50.3  $m^2/mg_{Pt}$  for 15 %, 52.6  $m^2/mg_{Pt}$  for 20 %, and 56.7  $m^2/mg_{Pt}$  for PtCo/C.

In the LSV results, shown in Fig. 2(b), the half-wave potential ( $E_{1/2}$ ) first rises and then decreases as the Pt/CeO<sub>2</sub> content increases, reaching its peak when 10 % Pt/CeO<sub>2</sub> is added. Specifically, for the commercial



Fig. 1. Physical characterizations of Pt/CeO<sub>2</sub>. (a) XRD; (b) HAADF image and corresponding EELS spectra for Ce-L and Pt-M of 0.2 wt% Pt/CeO<sub>2</sub>.



Fig. 2. CV(a) and LSV(b) curves of mixed catalysts with varying Pt/CeO<sub>2</sub> ratios.

catalyst,  $E_{1/2}$  is 0.868 V. For the mixed catalysts, the  $E_{1/2}$  values were 0.868 V, 0.871 V, and 0.869 V for 5 %, 10 %, and 15 % Pt/CeO<sub>2</sub>, respectively, showing a slight increase of 3 mV. However, at 20 % Pt/CeO<sub>2</sub>, the  $E_{1/2}$  dropped to 0.846 V, which is 20 mV lower than that of PtCo/C. In terms of limiting current density, all catalysts containing Pt/CeO<sub>2</sub> surpassed the performance of the catalyst (5.62 mA/cm<sup>2</sup>). Specifically, the limiting current densities are 5.82 mA/cm<sup>2</sup> for 5 % Pt/CeO<sub>2</sub>, 5.87 mA/cm<sup>2</sup> for 10 %, 5.69 mA/cm<sup>2</sup> for 15 %, and 5.63 mA/cm<sup>2</sup> for 20 %, with the catalyst containing 10 % Pt/CeO<sub>2</sub> demonstrating the highest value.

The experimental results indicate that the addition of an appropriate amount of  $Pt/CeO_2$  can improve the limiting current density. However, as  $CeO_2$  content increases, its non-conductive nature raises the ohmic resistance of the catalyst layer, hindering proton-electron coupling in the ORR process and resulting in higher overpotential.

The ORR process involves multi-electron transfer, typically through

four-electron and two-electron pathways. The number of electrons transferred was calculated using the Koutecky-Levich equation [37]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{0.62nFD^{2/3}v^{-1/6}C\omega^{1/2}}$$
(eq.2)

where  $j_k$  and  $j_d$  are the kinetic and diffusion-limited current densities. *n* is the number of electrons involved in the ORR. *F* is the Faraday constant. *D* is the diffusion coefficient of oxygen in the electrolyte  $(1.93 \times 10^{-5} \text{ cm}^2/\text{s})$ . *v* is the kinematic viscosity of the electrolyte  $(1.00 \times 10^{-2} \text{ cm}^2/\text{ s})$ . *C* is the oxygen solubility in the electrolyte  $(1.2 \times 10^{-6} \text{ mol/L})$ , and  $\omega$  is the rotation speed. The calculated electron transfer number *n* is 4.04, indicating that the ORR primarily follows a four-electron pathway with high efficiency.



Fig. 3. Performance of MEA prepared with varying Pt/CeO<sub>2</sub> ratios. (a) polarization and power density curves; (b) peak power density; (c) Nyquist plot; (d) impedance values fitted to the equivalent circuit. (H<sub>2</sub>/Air,T = 160 °C).

## 3.3. Single cell performance

Based on the electrocatalytic performance tests,  $25 \text{ cm}^2$  MEAs were prepared with 5 %, 10 %, and 15 % Pt/CeO<sub>2</sub> added to the cathode catalyst. The polarization and power density curves for these MEAs working in air are shown in Fig. 3(a) and (b). After adding Pt/CeO<sub>2</sub>, both the output voltage and power density of the HT-PEMFC are improved, with a power density inflection point appearing between 1.0 and 1.1 A/ cm<sup>2</sup>. As the Pt/CeO<sub>2</sub> content increases, both the voltage and power density first increase and then decrease, reaching a peak with the 10 % Pt/CeO<sub>2</sub> addition. At a current density of 0.4 A/cm<sup>2</sup>, the output voltage varies among 582 mV (0 %), 614 mV (5 %), 635 mV (10 %), and 621 mV (15 %). The peak power densities are 352 mW/cm<sup>2</sup> (0 %), 393 mW/cm<sup>2</sup> (5 %), 432 mW/cm<sup>2</sup> (10 %), and 399 mW/cm<sup>2</sup> (15 %). This trend aligns with the changes in ORR limiting diffusion current observed in the solution phase.

Fig. 3(c) and (d) show the electrochemical impedance spectroscopy (EIS) data collected at i = 0.4 A/cm<sup>2</sup>, which clearly show two semicircles, corresponding to charge transfer and mass transport processes. Equivalent circuit fitting reveals that as Pt/CeO<sub>2</sub> content increases, the charge transfer resistance ( $R_{ct}$ ) significantly decreases from 16.9 m $\Omega$  (0%) to 12.2 m $\Omega$  (5%), 9.0 m $\Omega$  (10%), and 8.2 m $\Omega$  (15%). This indicates that O<sub>2</sub> is activated and dissociated on the Pt/CeO<sub>2</sub> surface, accelerating the ORR process. However, Pt/CeO<sub>2</sub> is a "double-edged sword," as it is non-conductive, and increasing its content leads to a rise in ohmic resistance, from 4.5 m $\Omega$  (0%) to 5.5 m $\Omega$  (15%). Excessive Pt/CeO<sub>2</sub> can hinder electron transfer, reducing the ORR performance. The mass transport resistance ( $R_{mt}$ ) remains relatively constant between 23 and 25 m $\Omega$ , which is much larger than the combined  $R_{ct}$  and ohmic resistance, indicating that oxygen diffusion is the main limiting factor in MEA performance.

In pure oxygen conditions (Fig. S1 in SI), the power density of the HT-PEMFC significantly increases. When i = 0.7 A/cm<sup>2</sup>, the output voltage remains above 0.6 V, nearly doubles compared to the value in air  $(i = 0.4 \text{ A/cm}^2)$ . Across the 0–1.2 A/cm<sup>2</sup> range, no power density inflection point was observed. The power density trend with increasing Pt/ CeO<sub>2</sub> content is consistent with the results in air, peaking at 10 % Pt/ CeO<sub>2</sub>. At 1.2 A/cm<sup>2</sup>, the power densities are respectively 534 mW/cm<sup>2</sup> (0%), 588 mW/cm<sup>2</sup> (5%), 613 mW/cm<sup>2</sup> (10%), and 601 mW/cm<sup>2</sup> (15 %), showing a 50 % improvement compared to in the air. EIS data in pure oxygen show that both  $R_{ct}$  and  $R_{mt}$  are significantly reduced, with  $R_{ct}$  decreasing from 4.5 m $\Omega$  (0 %) to 4.3 m $\Omega$  (5 %), 4 m $\Omega$  (10 %), and 3.5 m $\Omega$  (15 %). Meanwhile,  $R_{mt}$  remains in the range from 10 to 12 m $\Omega$ , and the ohmic resistance is unchanged. The changes in impedance are consistent with the improved performance, suggesting that adding Pt/ CeO<sub>2</sub> effectively reduces charge transfer resistance, thereby enhancing the overall performance of the fuel cell.

When  $\text{CeO}_2$  is not loaded with Pt, it is reduced in 10 % H<sub>2</sub>/Air to form a blue-violet  $\text{CeO}_{2\text{-x}}$  powder, but upon exposure to air, the powder quickly oxidized to pale yellow. Adding this reduced CeO<sub>2</sub> to the cathode catalyst not only doesn't improve the performance (Fig. S2), but also makes it worse. This occurs likely because CeO<sub>2</sub> itself is non-conductive, and when not loaded with Pt, it is quickly oxidized to Ce<sup>4+</sup>, lacking oxygen vacancies to activate oxygen, hindering electron transfer and reducing performance. Therefore, Pt loading and oxygen vacancies are crucial for CeO<sub>2</sub> to enhance oxygen activation and improve fuel cell performance.

XPS was used to evaluate the electronic structures of Pt (Fig. S3). The Pt-4f orbital of PtCo/C can be split into  $Pt^0$  (71.88 eV and 75.27 eV),  $Pt^{2+}$  (72.75 eV and 76.19 eV), and  $Pt^{4+}$  (78.62 eV) valences [37]. Compared to PtCo/C, the Pt satellite peaks of PtCo/C + Pt/CeO<sub>2</sub> shift slightly to lower binding energy by 0.2 eV ( $Pt^0$  (71.72eV and 75.12 eV) and  $Pt^{2+}$  (72.62 eV and 76.12 eV)). The lower binding energy of Pt valence in the composite catalysts, compared to PtCo/C, indicates electron transfer from CeO<sub>2</sub> to Pt, which modifies the Pt surface to an electron-rich phase. This modification may enhance the catalytic activity for ORR.

Related computational studies suggest that the ORR on Pt<sub>3</sub>Co and Pt/ CeO<sub>2</sub> follows a 4-electron process [69], and the energy required for the direct dissociation of O2 is quite high, typically following the OOH\*-OH\*-H<sub>2</sub>O pathway [70]. The formation of OOH\* is the rate-determining step of the ORR process. On Pt/CeO2, the adsorption energy of OOH\* is -2.54 eV [71], while on Pt<sub>3</sub>Co, the OOH\* adsorption energy is -1.37 eV [72]. Therefore, OOH\* is more easily formed on Pt/CeO2, which accelerates the ORR process. For OH\*, the adsorption energies on Pt/CeO<sub>2</sub> and Pt<sub>3</sub>Co are similar, at -2.45 eV and -2.58 eV, respectively, indicating that OH\* can form on both catalysts. Considering the physical model where Pt<sub>3</sub>Co and Pt/CeO<sub>2</sub> particles are sufficiently close (with particle sizes around 5 nm) and both are supported on a carbon substrate, the OOH\* and OH\* species can rapidly diffuse to the adjacent catalyst. Based on the above experimental results and DFT calculations, the proposed reaction mechanism is as follows: O<sub>2</sub> first forms OOH\* on Pt/CeO2, then OOH\* is converted to OH\* on both Pt/CeO<sub>2</sub> and Pt<sub>3</sub>Co, ultimately leading to the formation of H<sub>2</sub>O.

In the 100-h lifespan test (Fig. 4), an HT-PEMFC using PtCo/C + 10 % Pt/CeO<sub>2</sub> shows excellent stability. After 100 h at 160 °C and 0.6 A/ cm<sup>2</sup>, the voltage only drops from 568 mV to 559 mV, demonstrating a minimal degradation. This suggests that MEAs with Pt/CeO<sub>2</sub> not only exhibit higher initial power density but also maintain stable performance over prolonged operation. Consequently, Pt/CeO<sub>2</sub> holds significant potential as a cathode catalyst additive, enhancing efficiency in high-temperature PEM fuel cells.

MEA lifetime tests with the Accelerated degradation test (ADT) method were conducted to compare two catalysts, with a 10-s start-stop cycle: 10 s of startup at a constant current of 0.4 A/cm<sup>2</sup>, followed by 10 s of open-circuit. The experiment lasted for 100 h, with polarization curves measured every 20 h. As shown in Fig. S4, after 100 h of start-stop testing, the voltage at 0.4 A/cm<sup>2</sup> for the MEA with PtCo/C + Pt/CeO<sub>2</sub> decreased to 471 mV, while the PtCo/C decreased to 415 mV. After accelerated aging, the performance of the PtCo/C + Pt/CeO<sub>2</sub> catalyst remained superior to that of the PtCo/C catalyst, demonstrating its potential for long-term application.

After 100 h of operation, the cathode with the mixed  $Pt/CeO_2$  catalyst was characterized using TEM, as shown in Fig. S5. Each dot represents a nanoparticle. Both PtCo/C and  $Pt/CeO_2$  catalysts appear spherical with a particle size of approximately 5 nm, exhibiting a narrow size distribution, making it difficult to distinguish between them based solely on TEM images. Additionally, no noticeable aggregation of catalysts or additives was observed in the TEM images, indicating that the

Fig. 4. MEA lifetime test of cathode catalyst composed of PtCo/C+10 % Pt/ CeO<sub>2</sub> (i = 0.6 A/cm<sup>2</sup>).

0.8

catalyst slurry was well-dispersed during preparation. These findings further validate the stability of the mixed catalyst over prolonged operation.

Using TEM and EDS spectroscopy, further analyses of the  $Pt/CeO_2$ and PtCo/C catalyst distribution were conducted. Elements such as Pt, Ce, and O were uniformly distributed across the catalyst layer (Fig. 5), demonstrating that both PtCo/C and  $Pt/CeO_2$  were evenly dispersed during ink preparation. This uniform distribution facilitates rapid diffusion of  $O_2$  to PtCo/C for reduction, after being activated on  $Pt/CeO_2$ . This process improves the reaction rate at the three-phase boundary and enhances the overall performance of HT-PEMFC, leading to higher power output in operation.

# 3.4. Effect of porogen

In section 3.3.3, EIS testing revealed that the mass transfer process severely limits the performance of the MEA. The  $R_{mt}$  was 23 m $\Omega$ , significantly higher than the  $R_{ct}$  of 9 m $\Omega$ . In our previous study, using MEAs produced by BASF, it was found that ORR was the primary performance-limiting factor, with activation losses as high as 70 % [29]. The increased mass transfer resistance may be attributed to the spray coating process used for the homemade MEA. To fully utilize the potential of Pt/CeO<sub>2</sub> co-catalyst and minimize the impact of mass transfer limitations, porogen is introduced to accelerate mass transfer by creating pores within the cathode catalyst layer. Although ammonium bicarbonate is a common porogen, its low decomposition temperature (60 °C) causes it to decompose during the spraying process (set at 65–70 °C), resulting in pore closure as the catalyst ink fills the spaces. Hence, ammonium oxalate, with a higher decomposition temperature

(90 °C), was selected. It remains stable during the spraying process and fully decomposes into gas during heat treatment at 350 °C, leaving behind the desired pore structure.

Four types of MEAs containing 20 % ammonium oxalate by weight of PtCo/C catalyst were prepared, and their polarization curves were measured for comparison. (Fig. 6). After the addition of 20 % ammonium oxalate, the MEA output voltage and power are improved, with voltage increasing by 15–20 mV and peak power increasing as follows:  $48 \text{ mW/cm}^2$  (0 %), 24 mW/cm<sup>2</sup> (5 %), 37 mW/cm<sup>2</sup> (10 %), and 36 mW/cm<sup>2</sup> (15 %). The MEA's optimal power output still occurs at 10 % Pt/CeO<sub>2</sub>.

Next, 10 % Pt/CeO<sub>2</sub> was used to further explore the effect of porogen content on MEA performance. MEAs containing 10 %, 20 %, and 30 % ammonium oxalate were tested (Fig. 7). As the ammonium oxalate content increases, both voltage and power first increase and then decrease. The peak power is achieved with 20 % ammonium oxalate at 467 mW/cm<sup>2</sup>, a 33 % improvement over the 352 mW/cm<sup>2</sup> is achieved with catalysts alone.

As shown in Fig. 7(b), adding a porogen significantly reduces MEA impedance, particularly the low-frequency mass transport resistance. In air,  $R_{mt}$  is reduced by half: 11 m $\Omega$  (10 %), 9.3 m $\Omega$  (20 %), and 9.0 m $\Omega$  (30 %). The ohmic resistance is slightly increased from 5.7 m $\Omega$  (10 %) to 7.1 m $\Omega$  (30 %), suggesting that the pore structure impacts electron transport pathways.

In pure oxygen conditions, the polarization and power density tests (Fig. S8) show that at 1.2 A/cm<sup>2</sup>, the power densities are 617 mW/cm<sup>2</sup> (10 %), 673 mW/cm<sup>2</sup> (20 %), and 635 mW/cm<sup>2</sup> (30 %), representing a 50 % improvement over in the air. The MEA with 20 % ammonium oxalate outperforms the pure catalyst (534 mW/cm<sup>2</sup>) by 26 %. In pure



Fig. 5. STEM images of the cathode catalyst. (a) TEM image; (b)-(d) EDS spectra for Pt, Ce and O.



**Fig. 6.** The polarization and power density curves for HT-PEMFCs, with 20 % ammonium oxalate pore-forming agent added to the cathode catalyst layer (a) and (b); (c) peak power density. ( $H_2$ /Air,T = 160 °C).



Fig. 7. Performance of MEA prepared with varying (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> ratios. (a) polarization and power density curves; (b) Nyquist plot. (H<sub>2</sub>/Air, T = 160 °C).

oxygen, impedance further decreases, with the two capacitive arcs merging into one, making it difficult to distinguish two separate processes.

The introduction of porogen significantly improves the gas diffusion capacity, and at lower contents, it notably reduces the concentration polarization, enhancing MEA output performance. However, as porogen content increases, an overly porous structure could hinder electron and proton transport and the formation of a three-phase boundary. Therefore, as porogen content rises, the ohmic resistance increases, leading to a drop in the output voltage. Experimental results indicate that the appropriate amount of porogen effectively improves the mass transfer, greatly enhancing the overall performance of the HT-PEMFC.

The pore distribution in the gas diffusion electrode (GDE) was characterized by mercury intrusion porosimetry (MIP) and BET testing. The BET method is suitable for measuring pore sizes below 100 nm, whereas the micro-scale pores in the gas diffusion layer (GDL) cannot be effectively characterized using this method. Thus, mercury intrusion was employed for more accurate results. As shown in Fig. S9(a), with the

increase in the pore-forming agent content, the peak at 80 nm gradually rises from 0.29 (0 %) to 0.38 (30 %), indicating that the addition of the pore-forming agent significantly increases the number of pores in the catalyst layer. In the BET analysis shown in Fig. S9(b), a peak in the 50–80 nm range is also observed. As the pore-forming agent content increases, the peak rises from 0.039 (0 %) to 0.057 (30 %), which is consistent with the results obtained using MIP.

SEM images further confirm this observation. As shown in Fig. S10, the images of the catalyst without the pore-forming agent (a)–(c) can be compared to those with the agent added (d)–(f), where a noticeable increase in pore formation is visible. Particularly in images (e) and (f), the pore density becomes much more concentrated and prominent. In the cross-sectional view, the catalyst layer thickness in image (d) is 23  $\mu$ m, slightly higher than the 19  $\mu$ m of the catalyst without the poreforming agent, likely due to the more porous structure of the layer. These morphological changes indicate that the introduction of the poreforming agent significantly alters the pore structure of the catalyst layer, creating more pore channels, resulting in a looser and thicker layer, and

making surface cracks more apparent.

In conclusion, the addition of porogen alters the pore size distribution in the catalyst layer, effectively improving gas diffusion. When added in moderate amounts, it significantly reduces the concentration polarization, enhancing the MEA output. However, an excessive porogen content creates overly porous structures that hinder electron and proton transport, increasing the ohmic resistance and reducing the output voltage. The results demonstrate that an optimal amount of porogen can optimize the mass transfer and significantly improve the performance of HT-PEMFC.

### 4. Conclusion

To address the issue of slow oxygen reduction reaction (ORR) kinetics in HT-PEMFCs,  $Pt/CeO_2$  with oxygen vacancies and a Pt content of 0.2 wt% are synthesized and added to the cathode catalyst layer. CV and LSV tests indicate that adding  $Pt/CeO_2$  don't significantly affect the electrochemical active area of PtCO/C, with an optimal amount of  $Pt/CeO_2$  that can enhance the limiting current density. However, since  $CeO_2$  is non-conductive, increasing its concentration raises the ohmic resistance of the catalyst layer, impeding proton-electron coupling during ORR and leading to higher overpotential.

In a 25 cm<sup>2</sup> single-cell test, the effect of different Pt/CeO<sub>2</sub> concentrations on MEA performance is evaluated. Experimental results demonstrate improved output voltage and power density in HT-PEMFCs with Pt/CeO<sub>2</sub> addition. At 10 % Pt/CeO<sub>2</sub>, the performance peaks, with a maximum power density of 432 mW/cm<sup>2</sup> at 160 °C (H<sub>2</sub>/air). Additionally, the charge transfer resistance significantly decreases, indicating that Pt/CeO<sub>2</sub> can effectively activate O<sub>2</sub>. EDS mapping confirms the uniform distribution of Pt and Ce elements, suggesting that the performance enhancement is likely due to O<sub>2</sub> activation on Pt/CeO<sub>2</sub>, where O<sub>2</sub> binds with H<sup>\*</sup> to form OOH<sup>\*</sup>, then OOH<sup>\*</sup> is converted to OH<sup>\*</sup> on both Pt/CeO<sub>2</sub> and Pt<sub>3</sub>Co, ultimately leading to the formation of H<sub>2</sub>O. After a 100-h durability test, the voltage drops by only 9 mV, confirming the long-term stability of the hybrid catalyst.

EIS measurements reveal that limited oxygen transport hinders further performance improvement in HT-PEMFCs. To address this, ammonium oxalate is introduced as a pore-forming agent in the catalyst layer. The addition of 20 % by weight of ammonium oxalate improves the membrane electrode performance. When combined with 10 % Pt/ CeO<sub>2</sub> in the cathode, the maximum power density reaches 467 mW/cm<sup>2</sup> at 160 °C (H<sub>2</sub>/air), a 33 % increase compared to 352 mW/cm<sup>2</sup> with only catalysts. SEM, mercury intrusion porosimetry, and BET analyses indicate that the pore-forming agent significantly alters the pore size distribution in the catalyst layer. Appropriate amounts of pore-forming agents improve gas diffusion, reduce the concentration polarization, and enhance the MEA performance. However, excessive addition leads to overly porous structures, which hampers proton and electron transport, increases the ohmic resistance, and reduces the output voltage.

Thus, uniformly introducing  $Pt/CeO_2$ , which activates  $O_2$ , into the catalyst layer can significantly accelerate ORR kinetics, improve the HT-PEMFC performance, and ensure long-term operational stability. This approach offers valuable insights for the design of catalyst layer additives in HT-PEMFCs and has a broad application potential.

In future work, we will conduct additional characterizations and DFT calculations to further clarify the enhancement mechanism of  $PtCo/C + Pt/CeO_2$  for ORR. Additionally, we will employ the Distribution of Relaxation Times (DRT) technique to separate different frequency processes and confirm the role of  $Pt/CeO_2$ .

# CRediT authorship contribution statement

**Chaoran Huang:** Writing – original draft, Formal analysis, Data curation, Conceptualization. **Jie Yan:** Data curation, Conceptualization. **Xueyao Wang:** Data curation. **Zeren Gao:** Data curation. **Ding Ma:** Funding acquisition. **Junrong Zheng:** Writing – review & editing,

Funding acquisition.

#### 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2024.235996.

# Data availability

The authors do not have permission to share data.

#### References

- M. Inaba, H. Daimon, Development of highly active and durable platinum coreshell catalysts for polymer electrolyte fuel cells, J. Jpn. Petrol. Inst. 58 (2) (2015) 55–63.
- [2] M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, Z. Ogumi, Gas crossover and membrane degradation in polymer electrolyte fuel cells, Electrochim. Acta 51 (26) (2006) 5746–5753.
- [3] M. Ahmed, I. Dincer, A review on methanol crossover in direct methanol fuel cells: challenges and achievements, Int. J. Energy Res. 35 (14) (2011) 1213–1228.
- [4] J. Eppinger, K.-W. Huang, Formic acid as a hydrogen energy carrier, ACS Energy Lett. 2 (1) (2016) 188–195.
- [5] J. Zhang, D. Aili, S. Lu, Q. Li, S.P. Jiang, Advancement toward Polymer Electrolyte Membrane Fuel Cells at Elevated Temperatures, Research (Wash D C), 2020 9089405.
- [6] T. Nagashima, Y. Aoki, K. Kimura, M. Inaba, T. Doi, High-capacity LiNi0.8Co0.1Mn0.102 positive-electrodes in the nearly saturated and fluorinated acetate-diluted electrolyte solutions, ACS Appl. Energy Mater. 7 (2024) 2707–2714.
- [7] T. Doi, M. Hashinokuchi, M. Inaba, Solvation-controlled ester-based concentrated electrolyte solutions for high-voltage lithium-ion batteries, Curr. Opin. Electrochem. 9 (2018) 49–55.
- [8] T. Doi, Y. Shimizu, M. Hashinokuchi, M. Inaba, Dilution of highly concentrated LiBF4/propylene carbonate electrolyte solution with fluoroalkyl ethers for 5-V LiNi0.5Mn1.5O4Positive electrodes, J. Electrochem. Soc. 164 (1) (2017) A6412–A6416.
- [9] P. Pei, H. Chen, Main factors affecting the lifetime of Proton Exchange Membrane fuel cells in vehicle applications: a review, Appl. Energy 125 (2014) 60–75.
- [10] S. Ma, M. Lin, T.-E. Lin, T. Lan, X. Liao, F. Marechal, J. Van herle, Y. Yang, C. Dong, L. Wang, Fuel cell-battery hybrid systems for mobility and off-grid applications: a review, Renewable Sustainable Energy Rev. 135 (2021) 110119.
- [11] V.A. Sethuraman, B. Lakshmanan, J.W. Weidner, Quantifying desorption and rearrangement rates of carbon monoxide on a PEM fuel cell electrode, Electrochim. Acta 54 (23) (2009) 5492–5499.
- [12] C. Song, Y. Tang, J.L. Zhang, J. Zhang, H. Wang, J. Shen, S. McDermid, J. Li, P. Kozak, PEM fuel cell reaction kinetics in the temperature range of 23-120°C, Electrochim. Acta 52 (7) (2007) 2552–2561.
- [13] P. Moçotéguy, B. Ludwig, J. Scholta, R. Barrera, S. Ginocchio, Long term testing in continuous mode of HT-PEMFC based H3PO4/PBI celtec-P MEAs for μ-CHP applications, Fuel Cell. 9 (4) (2009) 325–348.
- [14] J. Chen, M. Perez-Page, C.M.A. Parlett, Z. Guo, X. Yang, Z. Zhou, H. Zhai, S. Bartlett, T.S. Miller, S.M. Holmes, Operando synchrotron-based X-ray study and intervention approaches of graphene-related-materials for investigating the performance and durability of HT-PEMFC, Chem. Eng. J. 487 (2024) 150670.
- [15] L. Lueke, H. Janssen, M. Kvesic, W. Lehnert, D. Stolten, Performance analysis of HT-PEFC stacks, Int. J. Hydrogen Energy 37 (11) (2012) 9171–9181.
- [16] Z. Jabbari, B. Nassernejad, N. Fallah, M. Javanbakht, N. Afsham, Fabrication of novel binderless anode via electrophoretic deposition for HT-PEMFC, Surf. Eng. 35 (12) (2019) 1013–1020.
- [17] N. Seselj, S.M. Alfaro, E. Bompolaki, L.N. Cleemann, T. Torres, K. Azizi, Catalyst development for high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC) applications, Adv. Mater. 35 (40) (2023) 2302207.

- [18] F.S. Nanadegani, E.N. Lay, B. Sunden, Corrigendum to "Computational analysis of the impact of a micro porous layer (MPL) on the characteristics of a high temperature PEMFC", Electrochim. Acta 337 (2020) 135552.
- [19] C. Fink, G. Laurenczy, CO2 as a hydrogen vector transition metal diamine catalysts for selective HCOOH dehydrogenation, Dalton Trans. 46 (5) (2017) 1670–1676.
- [20] S.J. Folkman, J. Gonzalez-Cobos, S. Giancola, I. Sanchez-Molina, J.R. Galan-Mascaros, Benchmarking catalysts for formic acid/formate electrooxidation, Molecules 26 (16) (2021) 4756.
- [21] Y. Zhang, X. Chen, B. Zheng, X. Guo, Y. Pan, H. Chen, H. Li, S. Min, C. Guan, K. W. Huang, J. Zheng, Structural analysis of transient reaction intermediate in formic acid dehydrogenation catalysis using two-dimensional IR spectroscopy, Proc. Natl. Acad. Sci. U. S. A. 115 (49) (2018) 12395–12400.
- [22] C. Hao, C. Shen, Y. Zhang, J. Liu, J. Zheng, Unveiling the pressure dependent deactivation mechanism of iridium-based catalysts for hydrogen production from formic acid aqueous solutions, Int. J. Hydrogen Energy 72 (2024) 744–754.
- [23] K.-w. T. Huang Sa), Junrong Zheng, S.A. Thuwal, Electricity Generation Devices Using Formic Acid, 2022.
- [24] Z.J.S. Huang Kuo-Wei Sa, ELECTRICITY GENERATION DEVICES USING FORMIC ACID, 2021.
- [25] S. Authayanun, M. Mamlouk, A. Arpornwichanop, Maximizing the efficiency of a HT-PEMFC system integrated with glycerol reformer, Int. J. Hydrogen Energy 37 (8) (2012) 6808–6817.
- [26] S. Authayanun, W. Wiyaratn, S. Assabumrungrat, A. Arpornwichanop, Theoretical analysis of a glycerol reforming and high-temperature PEMFC integrated system: hydrogen production and system efficiency, Fuel 105 (2013) 345–352.
- [27] D. Xue, J.-N. Zhang, Recent progress of antipoisoning catalytic materials for high temperature proton exchange membrane fuel cells doped with phosphoric acid, Industria. Chem. Mater. 2 (2) (2024) 173–190.
- [28] J. Zhang, J. Zhang, H. Wang, Y. Xiang, S. Lu, Advancement in distribution and control strategy of phosphoric acid in membrane electrode assembly of hightemperature polymer electrolyte membrane fuel cells, Acta Phys. - Chim. Sin. 0 (0) (2020), 2010071-0.
- [29] C. Huang, Z. Wu, J. Zheng, Effects of concentrated CO2 on the performance of a PBI/H3PO4 high temperature proton exchange membrane fuel cell, J. Power Sources 614 (2024) 235053.
- [30] M. Linlin, A.K. Mishra, N.H. Kim, J.H. Lee, Poly(2,5-benzimidazole)-silica nanocomposite membranes for high temperature proton exchange membrane fuel cell, J. Membr. Sci. 411–412 (2012) 91–98.
- [31] Y. Devrim, H. Devrim, I. Eroglu, Polybenzimidazole/SiO2 hybrid membranes for high temperature proton exchange membrane fuel cells, Int. J. Hydrogen Energy 41 (23) (2016) 10044–10052.
- [32] V. Atanasov, A.S. Lee, E.J. Park, S. Maurya, E.D. Baca, C. Fujimoto, M. Hibbs, I. Matanovic, J. Kerres, Y.S. Kim, Synergistically integrated phosphonated poly (pentafluorostyrene) for fuel cells, Nat. Mater. 20 (3) (2021) 370–377.
- [33] B. Lv, K. Geng, H. Yin, C. Yang, J. Hao, Z. Luan, Z. Huang, X. Qin, W. Song, N. Li, Z. Shao, Polybenzimidazole/cerium dioxide/graphitic carbon nitride nanosheets for high performance and durable high temperature proton exchange membranes, J. Membr. Sci. 639 (2021) 119760.
- [34] H. Zheng, M. Mathe, Enhanced conductivity and stability of composite membranes based on poly (2,5-benzimidazole) and zirconium oxide nanoparticles for fuel cells, J. Power Sources 196 (3) (2011) 894–898.
- [35] D. Schonvogel, J. Belack, J. Vidakovic, H. Schmies, L.M. Uhlig, H. Langnickel, P. K. Man Tung, Q. Meyer, C. Zhao, P. Wagner, Performance and durability of high temperature proton exchange membrane fuel cells with silicon carbide filled polybenzimidazole composite membranes, J. Power Sources 591 (2024) 233835.
- [36] D.E. Hussin, Y. Budak, Y. Devrim, Development and performance analysis of polybenzimidazole/boron nitride composite membranes for high-temperature PEM fuel cells, Int. J. Energy Res. 46 (4) (2021) 4174–4186.
- [37] F. Xu, D. Wang, B. Sa, Y. Yu, S. Mu, One-pot synthesis of Pt/CeO2/C catalyst for improving the ORR activity and durability of PEMFC, Int. J. Hydrogen Energy 42 (18) (2017) 13011–13019.
- [38] H.-S. Oh, Y. Cho, W.H. Lee, H. Kim, Modification of electrodes using Al2O3 to reduce phosphoric acid loss and increase the performance of high-temperature proton exchange membrane fuel cells, J. Mater. Chem. A 1 (7) (2013) 2578–2581.
- [39] L. Zhao, J. Zhu, Y. Zheng, M. Xiao, R. Gao, Z. Zhang, G. Wen, H. Dou, Y.P. Deng, A. Yu, Z. Wang, Z. Chen, Materials engineering toward durable electrocatalysts for proton exchange membrane fuel cells, Adv. Energy Mater. 12 (2) (2021).
- [40] J. Zhang, H. Bai, W. Yan, J. Zhang, H. Wang, Y. Xiang, S. Lu, Enhancing cell performance and durability of high temperature polymer electrolyte membrane fuel cells by inhibiting the formation of cracks in catalyst layers, J. Electrochem. Soc. 167 (11) (2020) 114501.
- [41] J. Zhang, S. Chen, H. Bai, S. Lu, Y. Xiang, S.P. Jiang, Effects of phosphotungstic acid on performance of phosphoric acid doped polyethersulfonepolyvinylpyrrolidone membranes for high temperature fuel cells, Int. J. Hydrogen Energy 46 (19) (2021) 11104–11114.
- [42] P. Gómez-Romero, J.A. Asensio, S. Borrós, Hybrid proton-conducting membranes for polymer electrolyte fuel cells, Electrochim. Acta 50 (24) (2005) 4715–4720.
- [43] S. Kattel, B. Yan, J.G. Chen, P. Liu, CO2 hydrogenation on Pt, Pt/SiO2 and Pt/TiO2: importance of synergy between Pt and oxide support, J. Catal. 343 (2016) 115–126.
- [44] S.S. Rao, V.R. Hande, S.M. Sawant, S. Praveen, S.K. Rath, K. Sudarshan, D. Ratna, M. Patri, a-ZrP nanoreinforcement overcomes the trade-off between phosphoric acid dopability and thermomechanical properties: nanocomposite HTPEM with stable fuel cell performance, ACS Appl. Mater. Interfaces 11 (40) (2019) 37013–37025.

- [45] F. Mack, T. Morawietz, R. Hiesgen, D. Kramer, R. Zeis, PTFE distribution in hightemperature PEM electrodes and its effect on the cell performance, ECS Trans. 58 (1) (2013) 881–888.
- [46] W.J. Lee, J.S. Lee, H.-Y. Park, H.S. Park, S.Y. Lee, K.H. Song, H.-J. Kim, Improvement of fuel cell performances through the enhanced dispersion of the PTFE binder in electrodes for use in high temperature polymer electrolyte membrane fuel cells, Int. J. Hydrogen Energy 45 (57) (2020) 32825–32833.
- [47] H. Li, Y. Min, F. Ji, C. Deng, S. Liu, Design and study on pore structure of cathode double catalytic layer in high-temperature proton exchange membrane fuel cell, Hua Hsueh Hsueh Pao 81 (9) (2023) 1135–1141.
- [48] H. Namazi, H. Ahmadi, Improving the proton conductivity and water uptake of polybenzimidazole-based proton exchange nanocomposite membranes with TiO2 and SiO2 nanoparticles chemically modified surfaces, J. Power Sources 196 (5) (2011) 2573–2583.
- [49] W. Cao, Y. Mao, B. Hu, Y. Yang, W. Zhou, Z. Shao, Significantly improved stability and water retention for Pt supported on W-doped SnO2 to catalyse the oxygen reduction reaction in proton exchange membrane fuel cells, J. Mater. Chem. A 12 (18) (2024) 10799–10807.
- [50] Potential-induced pitting corrosion of an IrO2(110)-RuO2(110)/Ru(0001) model electrode under oxygen evolution reaction conditions, Am. Chem. Soc. 9 (7) (2019) 6530–6539.
- [51] C. Spiel, P. Blaha, Y. Suchorski, K. Schwarz, G. Rupprechter, CeO2/Pt(111) interface studied using first-principles density functional theory calculations, Phys. Rev. B 84 (4) (2011).
- [52] D.C. Grinter, J. Graciani, R.M. Palomino, F. Xu, I. Waluyo, J.F. Sanz, S. D. Senanayake, J.A. Rodriguez, Adsorption and activation of CO2 on Pt/CeOX/ TiO2(110): role of the Pt-CeOx interface, Surf. Sci. 710 (2021) 121852.
- [53] D. Chai, W. Wang, F. Wang, W. Jing, P. Wang, Z. Lei, Heterogeneous Ir3Sn–CeO2/C as alternative Pt-free electrocatalysts for ethanol oxidation in acidic media, Int. J. Hydrogen Energy 42 (15) (2017) 9775–9783.
- [54] Y. Huang, B. Long, M. Tang, Z. Rui, M.-S. Balogun, Y. Tong, H. Ji, Bifunctional catalytic material: an ultrastable and high-performance surface defect CeO2 nanosheets for formaldehyde thermal oxidation and photocatalytic oxidation, Appl. Catal. B Environ. 181 (2016) 779–787.
- [55] X. Cheng, X. Jiang, S. Yin, L. Ji, Y. Yan, G. Li, R. Huang, C. Wang, H. Liao, Y. Jiang, S. Sun, Instantaneous free radical scavenging by CeO2 nanoparticles adjacent to the Fe–N4 active sites for durable fuel cells, Angew. Chem. Int. Ed. 62 (34) (2023).
- [56] D. Vovchok, C. Zhang, S. Hwang, L. Jiao, F. Zhang, Z. Liu, S.D. Senanayake, J. A. Rodriguez, Deciphering dynamic structural and mechanistic complexity in Cu/CeO2/ZSM-5 catalysts for the reverse water-gas shift reaction, ACS Catal. 10 (17) (2020) 10216–10228.
- [57] Z. Zhao, M. Wang, P. Ma, Y. Zheng, J. Chen, H. Li, X. Zhang, K. Zheng, Q. Kuang, Z.-X. Xie, Atomically dispersed Pt/CeO2 catalyst with superior CO selectivity in reverse water gas shift reaction, Appl. Catal. B Environ. 291 (2021) 120101.
- [58] V.r. Matolín, V. Johánek, M. Škoda, N. Tsud, K.C. Prince, T.s. Skála, I. Matolínová, Methanol adsorption and decomposition on Pt/CeO2(111)/Cu(111) thin film model catalyst, Langmuir 26 (16) (2010) 13333–13341.
- [59] A. Weiß, S. Schindler, S. Galbiati, M.A. Danzer, R. Zeis, Distribution of relaxation Times analysis of high-temperature PEM fuel cell impedance spectra, Electrochim. Acta 230 (2017) 391–398.
- [60] T.H. Wan, M. Saccoccio, C. Chen, F. Ciucci, Influence of the discretization methods on the distribution of relaxation Times deconvolution: implementing radial basis functions with DRTtools, Electrochim. Acta 184 (2015) 483–499.
- [61] H. Liu, L. Ney, N. Zamel, X. Li, Effect of catalyst ink and formation process on the multiscale structure of catalyst layers in PEM fuel cells, Appl. Sci. 12 (8) (2022) 3776.
- [62] M. Ma, L. Shen, Z. Zhao, P. Guo, J. Liu, B. Xu, Z. Zhang, Y. Zhang, L. Zhao, Z. Wang, Activation methods and underlying performance boosting mechanisms within fuel cell catalyst layer, eScience (2024).
- [63] J.L. Jespersen, E. Schaltz, S.K. Kær, Electrochemical characterization of a polybenzimidazole-based high temperature proton exchange membrane unit cell, J. Power Sources 191 (2) (2009) 289–296.
- [64] T.J. Schmidt, J. Baurmeister, Properties of high-temperature PEFC Celtec®-P 1000 MEAs in start/stop operation mode, J. Power Sources 176 (2) (2008) 428–434.
- [65] R.F. Mann, C.P. Thurgood, Evaluation of Tafel–Volmer kinetic parameters for the hydrogen oxidation reaction on Pt(110) electrodes, J. Power Sources 196 (10) (2011) 4705–4713.
- [66] C. Siegel, I. Buder, A. Heinzel, Sectional electrochemical impedance analysis of a high temperature polymer electrolyte membrane fuel cell with three types of flowfields, Electrochim. Acta 112 (2013) 342–355.
- [67] Q. Meyer, Y. Zeng, C. Zhao, Electrochemical impedance spectroscopy of catalyst and carbon degradations in proton exchange membrane fuel cells, J. Power Sources 437 (2019) 226922.
- [68] S. Latorrata, R. Pelosato, P. Gallo Stampino, C. Cristiani, G. Dotelli, Use of electrochemical impedance spectroscopy for the evaluation of performance of PEM fuel cells based on carbon cloth gas diffusion electrodes, J. Spectroscopy 2018 (2018) 1–13.
- [69] Q. Wang, T. Qi, B. Mi, Q. Huo, S. Tong, Z. Qin, K. Zhou, H. Wang, Mechanism of Pt3Co nanocatalysts to improve the performance for oxygen reduction reactions: DFT study on oxygen adsorption and durability of different facets, Mater. Sci. Eng., B 289 (2023) 116202.

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- [70] T.Q. Nguyen, M.C.S. Escaño, H. Nakanishi, H. Kasai, H. Maekawa, K. Osumi, K. Sato, DFT+U study on the oxygen adsorption and dissociation on CeO2supported platinum cluster, Appl. Surf. Sci. 288 (2014) 244–250.
- [71] J. Yan, W. Xiao, R. Zeng, Q. Hong, X. Li, L. Wang, Pivotal role of Ce3+ polarons on promoting oxygen reduction reaction activity of Pt1/CeO2 catalysts, J. Power Sources 603 (2024) 234393.
- [72] M. Matsutsu, DFT Insight into the Oxygen Reduction Reaction (ORR) on the Pt3Co (111) Surface, University of Cape, Town, South Africa, 2012.