



# Enhanced performance and stability of high temperature proton exchange membrane fuel cell by incorporating zirconium hydrogen phosphate in catalyst layer



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## HIGHLIGHTS

- Incorporating Zr(HPO<sub>4</sub>)<sub>2</sub> in the CLs of HT-PEMFC was evaluated.
- The optimal content of Zr(HPO<sub>4</sub>)<sub>2</sub> in the CLs was found to be 30 wt.%.
- High single cell performance was delivered by the electrodes with Zr(HPO<sub>4</sub>)<sub>2</sub>.
- The electrodes containing Zr(HPO<sub>4</sub>)<sub>2</sub> showed high durability for HT-PEMFC operation.

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## ABSTRACT

Zirconium hydrogen phosphate (ZHP) together with polytetrafluoroethylene (PTFE) polymer binder is incorporated into the catalyst layers (CLs) of ABPBI (poly(2,5-benzimidazole))-based high temperature polymer electrolyte membrane fuel cell (HT-PEMFCs) to improve its performance and durability. The influence of ZHP content (normalised with respect to dry PTFE) on the CL properties are structurally characterised by scanning electron microscopy (SEM) and mercury intrusion porosimetry. Electrochemical analyses of the resultant membrane electrode assemblies (MEAs) are performed by recording polarisation curves and impedance spectra at 160 °C, ambient pressure and humidity. The result show that a 30 wt.% ZHP/PTFE content in the CL is optimum for improving fuel cell performance, the resultant MEA delivers a peak power of 592 mW cm<sup>-2</sup> at a cell voltage of 380 mV. Electrochemical impedance spectra (EIS) indicate that 30% ZHP in the CL can increase the proton conductivity compared to the pristine PTFE-gas diffusion electrode (GDE). A short term stability test (~500 h) on the 30 wt.% ZHP/PTFE-GDE shows a remarkable high durability with a degradation rate as low as ~19 μV h<sup>-1</sup> at 0.2 A cm<sup>-2</sup>, while 195 μV h<sup>-1</sup> was obtained for the pristine GDE.

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## 1. Introduction

With the ever-present search for alternative energy sources taking up the majority of studies in recent years, Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are considered one of the most promising future power sources. Considering their capabilities of providing high efficiencies, high power densities and zero emission power sources [1], they have been extensively used in portable, transport and stationary applications. At present, the majority of

the research in this field focusses on low temperature PEMFCs (LT-PEMFCs) based on perfluorosulphonic acid (PFSA) membranes, such as Nafion<sup>®</sup>. These PFSA membranes have proton conductivities that are dependent upon their hydrated state and therefore they are limited to operation at temperatures up to 100 °C under ambient pressure in order to maintain a high water content in the membranes [2]. Several existing challenges on this technology are associated with the low operating temperature, which include; (i) the need for complex fuel processing systems, due to the sensitivity of the Pt catalyst to CO and S poisoning at lower temperatures, (ii) poor quality of the generated heat and thus a greater difficulty in transferring the heat away to be used in other processes and (iii) complex water management systems for the humidification of the

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electrolyte membrane [3–5].

The limitations of LT-PEMFCs have in recent years led to a shift in focus from LT-PEMFCs to high temperature PEMFCs (HT-PEMFCs), which have several promising attributes over their low temperature counterpart, that accompany operation at temperatures between (100 °C – 200 °C). These advantages of a higher operating temperature include but are not limited to; (i) faster reaction kinetics and as a result the oxygen reduction reaction (ORR) is significantly increased, (ii) increased CO tolerance leading to simpler fuel processing and thus a more cost effective fuel cell, (iii) higher quality of the generated waste heat resulting in easier removal of the heat due to the larger temperature gradient between the fuel cell and the ambient environment, leading to simpler fuel processing and ancillary systems and improving the overall efficiency of the fuel cells [5–7]. The higher operating temperature influences the type of electrolyte membrane used in HT-PEMFCs, and since proton conducting electrolytes such as Nafion® dehydrate at high temperature and low relative humidity (RH), electrolyte membranes have been developed which are more suitable for high temperature operation. Efforts were first focussed on modifying low temperature electrolyte membranes such as Nafion® with metal oxide particles to improve water retention and thermal stability and developing acid-base polymer membranes [8–11].

Amongst the acid-base polymer membranes proposed for HT-PEMFC, polybenzimidazole (PBI) membranes were first investigated by Savinell et al. [12], these membranes exhibited good proton conductivity when doped with phosphoric acid (PA), have good thermal and mechanical stability, low gas permeability, as well as requiring little to no humidification. Since Savinell et al. first proposed PBI as an electrolyte membrane, various studies have been undertaken using PBI as an electrolyte membrane in HT-PEMFCs [13–16]. Phosphoric acid doped poly(2,5-benzimidazole) (ABPBI) membranes have more recently been used as electrolyte membranes for their improved proton conductivity over conventional phosphoric acid doped PBI membranes, in addition to being cheaper to produce [17–19]. In this system, a proper amount of phosphoric acid is required to impregnate the membranes and the CLs in order to achieve good proton conductivities [20]. However, the phosphate anions might adsorb onto the surface of Pt and deactivate the catalyst [21], which causes sluggish kinetics of the ORR and limits the fuel cell performance. Moreover, the low permeability of oxygen in phosphoric acid electrolyte is also considered as a primary contributor to the lower performance compared with LT-PEMFC systems. While the majority of current studies have focused on improving the properties of the electrolyte membrane, less attention has been paid to the development of an ionomer for the CL. Since phosphoric acid is used as an ionomer in the CL, performance loss due to phosphate anion adsorption and the resultant loss in proton conduction in the CL occurs at elevated temperatures. Furthermore, phosphoric acid dehydration at high temperature can also cause proton conductivity loss in the CL. In order to maintain sufficient proton conductivity, incorporation of inorganic proton conducting materials into the CL has been considered [22].

Zirconium hydrogen phosphate,  $Zr(HPO_4)_2$  (ZHP) is an insoluble solid that has been intensively studied as a proton conducting solid electrolyte. ZHP exhibits a layered structure (which allows for intercalation of “guest” molecules) as well as cation exchange properties [23]. In addition to these cation exchange properties, it also displays good proton conductivity as a result of high proton mobility on the surface of ZHP [24], and high hygroscopicity at elevated temperatures which make it extremely attractive for use as polymer electrolyte [25,26]. At 80 °C, amorphous ZHP in water exhibits a proton conductivity of  $\sim 0.01 \text{ S cm}^{-1}$ , which has led to several studies in which ZHP is incorporated into non-conducting

polymers such as polytetrafluoroethylene (PTFE) [27,28] as well as conducting polymers such as Nafion® [29]. These electrolytes are modified with ZHP to improve the moisture content and thermal stability of these membranes [29–31]. Since the incorporation of ZHP into electrolyte membranes has proven to be beneficial for moisture content and improved performance at temperatures above 100 °C, its presence in the CL should be beneficial for similar reasons. Xie et al. investigated the influence of ZHP in the CLs of gas diffusion electrodes (GDEs) for MEAs based on Nafion® membrane and found that below 100 °C, the performance remained similar to GDEs containing Nafion® only, however, above 100 °C the ZHP/Nafion GDEs showed improved performance over the conventional Nafion GDEs [22]. For the same reasons, introducing ZHP into HT-PEMFC systems should also prove beneficial as there is a need for stable proton conductivity at elevated temperatures.

In this work, ZHP was incorporated into the CLs of ABPBI-based HT-PEMFC along with a non-conducting polymer (PTFE), without additional  $H_3PO_4$  doping, to evaluate the effects of ZHP on (i) the fuel cell performance and (ii) the stability of the resulted GDEs. In summary, this work expands on the work carried out by Xie et al. [22], by incorporating ZHP into the CLs of ABPBI-based HT-PEMFC. Similar techniques and methodologies are applied in this work, which at the same time, is considered to be a new step in the optimisation challenge of the HT-PEMFC systems.

## 2. Experimental methods

### 2.1. MEA fabrication

Catalyst inks composed of Pt/C (40 wt.%, Johnson Matthey, HiSpec™ 4000),  $Zr(HPO_4)_2$  (ZHP, Sigma Aldrich) and/or PTFE binder (60 wt.%, Electrochem Inc.) were dispersed in Isopropanol (Kimix) by ultrasonication (Grant Instruments, 38 kHz) for 2 h [32]. The PTFE binder was normalised in relation to the Pt/C catalyst, with 40 wt.% PTFE concentration used in all formulated inks, whereas the  $Zr(HPO_4)_2$  was normalised in relation to dry PTFE with varying concentrations used in the ink formulations. The catalyst inks were sprayed manually with an airbrush onto commercially available GDL (Freudenberg H2135 CX 196) until the desired Pt loading was achieved. All electrodes (anode and cathode) prepared in this study had a Pt loading of  $\sim 1.0 \text{ mg cm}^{-2}$ . It should be mentioned that the Pt loading used in this study is close to those in commercial MEAs [33], however it is much higher than those for Nafion-based LT-PEMFCs (generally  $\sim 0.4 \text{ mg}_{Pt} \text{ cm}^{-2}$  [34]) due to the effect of  $H_3PO_4$  as mentioned before. The PTFE binder loading in the CL was fixed at 40 wt.%, while the  $Zr(HPO_4)_2$  loading in the CL was varied from 20% to 50% in relation to dry PTFE. Finally, all prepared GDEs were cured at 200 °C in a vacuum oven (Binder GmbH). Table 1 shows the composition of all GDEs prepared for testing in this study. Commercially available Fumapem® (Fumatech) ABPBI membrane

**Table 1**  
Specifications of the GDEs.

GDE	Catalyst type (% Pt/ C)	Pt loading	wt.% ZHP in CL (re. dry PTFE)	wt.% PTFE (re. Pt/C)
GDE-1	40	$1 \text{ mg cm}^{-2}$	0	40
GDE-2	40	$1 \text{ mg cm}^{-2}$	20	40
GDE-3	40	$1 \text{ mg cm}^{-2}$	30	40
GDE-4	40	$1 \text{ mg cm}^{-2}$	40	40
GDE-5	40	$1 \text{ mg cm}^{-2}$	50	40

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