



# The effect of binder content on the performance of a high temperature polymer electrolyte membrane fuel cell produced with reactive spray deposition technology



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## ABSTRACT

The effects of polytetrafluoroethylene (PTFE) binder content in the catalyst layer of high temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) utilizing phosphoric acid doped Advent TPS<sup>®</sup> polymer electrolyte membranes (pyridine bearing aromatic polyethers, TPS) has been investigated in terms of both hydrogen/oxygen and hydrogen/air performance. The anode and cathode gas diffusion electrodes (GDE) were fabricated with different PTFE/carbon weight ratios by a flame based process known as the Reactive Spray Deposition Technology (RSDT) method in order to increase the active platinum (Pt) surface area, with a goal of decreasing overall Pt levels to a total loading of 0.1 mg cm<sup>-2</sup>. The electrodes, prepared with different amounts of PTFE binder, have been tested in a single cell, with a 25 cm<sup>2</sup> geometric area, under an operating temperature range of 160–200 °C. Tests measuring the Pt nanoparticle dispersion on the carbon supports, the pore size distribution, and the electrochemical surface area of the catalyst layer were also performed. The best cell performance was achieved with PTFE/carbon weight ratio of 0.9 over the entire range of operating temperatures. This optimal PTFE binder content resulted in well-developed Pt dispersion on the carbon support and small, uniformly sized pores which develop ideal capillary forces for distributing the phosphoric acid electrolyte evenly throughout the catalyst layer. This led to a high number of triple phase boundaries and maximized Pt utilization.

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## 1. Introduction

Among the various types of fuel cells, low temperature polymer electrolyte membrane fuel cells (LT-PEMFCs) are a promising energy conversion system due to high energy conversion efficiency, low emission level, and it is user friendly [1–3]. Nevertheless, LT-PEMFCs, operated below 90 °C, have some limitations which require complex and expensive balance of plant for humidification and carbon monoxide (CO) removal. CO adsorbs onto the platinum (Pt) catalyst and reduces the performance [4–6]. High temperature PEMFCs (HT-PEMFCs) are being studied to solve these problems by simplification of the system and improvement of efficiency under zero humidification conditions. The typical HT-PEMFCs operating temperature is in the range of 150–200 °C which allows for co-

generation of heat and power. HT-PEMFCs also have a high tolerance to fuel impurities, and a simpler system design. For example, the adsorption of CO on the Pt catalyst is not favored at temperatures above 150 °C [7,8], and HT-PEMFCs have improved water management as well as faster electrochemical kinetics [4,9,10]. The increased temperature leads to an increase in CO tolerance, an increase in the performance and durability, and a decrease in the overall cost of the fuel cell [11]. Only phosphoric acid doped polybenzimidazole (PBI) membranes meet the US Department of Energy targets for high temperature membranes operating under no humidification on both the anode and cathode sides [12]. In the case of phosphoric acid doped PBI the phosphoric acid is used as a proton conducting medium. Excellent thermal and chemical stability as well as mechanical properties have been reported [13–15] for this system. The outstanding conductivity qualities of phosphoric acid can be explained by the Grotthus-mechanism which detaches the transport of the charge from the transport of the charged species [16]. Conduction in phosphoric

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acid appears to be predominately protonic ( $tH \approx 0.975$ ) and structure diffusion is proposed as the operating fast conduction and diffusion mechanism [17].

Recent studies show, when using a commercial HT-PEM CELTEC-P1000 MEA, produced by BASF, a power density of  $100 \text{ mW cm}^{-2}$  at  $160^\circ\text{C}$  was achieved [18]. This is a much lower power density than that found for the LT-PEMFC electrodes. The lower power density is due to numerous issues. The issue of chemical and morphological instability of catalyst layer is of a greater concern at elevated temperature. Phosphoric acid tends to adsorb onto the surface of the Pt catalyst and therefore hampers the reaction kinetics. Moreover, the elevated operating temperatures promote carbon corrosion and therefore degrade the integrity of the catalyst support. Therefore, high Pt loading in the catalyst layer is needed which leads to high cost of HT-PEMFCs. This is a significant barrier for commercializing HT-PEMFCs. The cathode performance decays as a result of both a reduced catalytic activity due to the loss of platinum surface area, and increases in diffusion losses due to loss in the porosity of the electrode. Additionally, the binder material plays a key role in regulating the hydrophobicity and hydrophilicity of the catalyst layer. Moreover, electrolyte migration can result in decay due to three mechanisms: 1) electrolyte evaporation, 2) migration of the electrolyte from the cathode side to the anode side 3) electrolyte losses through either corrosion or through absorption by the bipolar plates. Thus, the main objective for HT-PEMFCs is the development of novel membrane materials, that are suitable for a temperature up to  $200^\circ\text{C}$  and a much higher power density.

There are several high temperature polymer membrane electrolytes that can operate close to  $200^\circ\text{C}$  which are commonly cited in the literature including the phosphoric acid doped PBI membrane [19–24] and pyridine bearing aromatic polyethers (TPS) membrane [25–31]. PBI, proposed by Aharoni and Litt [19], has been studied as a promising polymer electrolyte for HT-PEMFCs. Acid doped PBI shows high thermal stability and high ionic conductivities [20–24]. An alternative novel approach to acquire high ionic conductivity at high temperature is based on TPS. Aromatic pyridine repeating units have exceptional chemical and thermal stability in the main chain where the phosphoric acid is preferentially bonded, while the incorporation of polar pyridine group helps to possess phosphoric acid. The phosphoric acid doping level is expected to depend on the pyridine content in the polymer chemical structure. In a step to further increase the pyridine content, diols of the general structure II were synthesized and used for polymerization [25]. The selection of pyridine as the polar group was made because of the ability of the pyridine ring to react and be protonated by strong acids leading to high ionic conductivity [25–30]. For a given set of conditions, TPS behaves similar to pure phosphoric acid, reaching higher hydration levels compared to PBI. This could be related to acid retention properties [31]. Therefore TPS membranes, provided by Advent<sup>®</sup>, were used in this study.

The performance of HT-PEMFC is critically dependent on the selection of materials and optimization of individual components. The binder in the catalyst layer (CL) is one of the important factors that affects the performance of HT-PEMFCs by allowing for a good contact between Pt and the proton conducting network [32,33]. The binder controls the triple phase boundary between proton conductive electrolyte, electron conductive catalyst, and reactant gases. Even though the effect of the various types of binder in catalyst layer has been investigated [34–36], polytetrafluoroethylene (PTFE) binder is still the material of choice for the HT-PEMFCs. PTFE is favored because it can provide hydrophobic regions within the catalyst layer through which the reactant gas can access the catalyst sites.

In this study, the effect of varying the PTFE binder/Carbon weight ratio in the catalyst layer of the gas diffusion electrode (GDE) was examined via single cell ( $5 \times 5 \text{ cm}$ ) performance in the temperature range of  $160\text{--}200^\circ\text{C}$ . The objective is to significantly reduce Pt loading (total  $0.1 \text{ mg cm}^{-2}$ ) and optimize pore size and PTFE loading to obtain a maximum performance. For this purpose steady state polarization measurements in a single cell have been conducted under both  $\text{O}_2$  and Air. In order to reduce catalyst loading and improve catalyst utilization, as well as cell performance, Reactive Spray Deposition Technology (RSDT) has been used to deposit the catalyst.

In the RSDT method, a controlled precursor injection, and tightly controlled reaction zones for nanoparticle formation, provides a unique and continuous process approach for scaling up nanocatalyst fabrication at costs that are relevant for large-scale industrial applications. The RSDT process can be adjusted to give tight control ( $<2 \text{ nm}$ ) on metallic nanoparticle diameter and disperse them on carbon supports in an open atmosphere. The resulting catalyst is then directed at a substrate in a one-step fabrication process [37,38]. Previous studies also showed that specific activity for  $\text{O}_2$  reduction varied non-monotonically with particle size showing a relatively sharp peak in specific Pt activity at  $2.2 \text{ nm}$  diameter [38]. This size dependent behavior is associated with the effect of the oxygen binding energies on the change in the distribution of Pt sites and associated O-binding energies with varying particle sizes. The deposition of Pt nanoparticles from the vapor phase through an open atmosphere combustion processes has been studied by relatively few researchers [39,40]. The deposition method can significantly affect the morphology, specifically the macro structure of the GDE, and therefore the demonstration of benefits of this technique is required. The RSDT technique is a single step process which bypasses many steps necessary in traditional ink sputtering methods for fabricating thin Pt catalyst layers. Also, the use of vacuum chambers in competitive CVD methods causes high cost and limits the ability to fabricate multi-layer coatings, which is possible with RSDT [41]. In order to investigate how the PTFE binder/Carbon ratio affects the electrode structure and performance, the following techniques were employed: fuel cell polarization tests, transmission electron microscopy (TEM), scanning electron microscope (SEM), mercury porosimetry, and cyclic voltammetry (CV).

## 2. Experimental

### 2.1. Fabrication of Gas Diffusion Electrode

The GDE samples with different PTFE binder/carbon weight ratios of the CL were fabricated using RSDT. RSDT is a vapor-phase nanotechnology approach for making nano-sized particles through the combustion of metal-organic compounds dissolved in a solvent [42]. It is possible to make  $2\text{--}5 \text{ nm}$  diameter Pt nanoparticles. The least expensive organoplatinum compound, platinum cetylacetonate ( $\text{Pt}(\text{acac})_2$ , Colonial Metals, Elkton, MD) was used as the Pt source because  $\text{Pt}(\text{acac})_2$  is readily available and is not subject to potential halide or nitrate contamination [43,44]. Xylene, acetone (Sigma Aldrich, St. Louis MO) and thiol-free propane (Airgas East Inc, Cheshire CT) were used for the solvent. The Pt precursor solution (which consists of xylene, acetone, propane, and platinum (II) acetylacetonate) was pumped into an atomizing nozzle and then atomized to form very small droplets, less than  $1 \mu\text{m}$  in diameter, by using a nebulizer. These droplets were then injected into an oxygen stream and then ignited by a burner. Once ignited by oxy-methane pilot flames, the solvent in the droplets evaporated while the solute was left in a concentrated core. Pt particle nucleation and growth occurs in the high temperature flame reaction zone ( $1000\text{--}2000^\circ\text{C}$ ) [40]. The carbon support

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