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Ultra-low platinum loadings in polymer electrolyte membrane fuel cell electrodes fabricated *via* simultaneous electrospinning/electrospraying method

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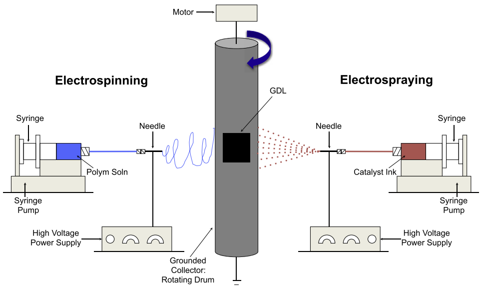
HIGHLIGHTS

- New electrospinning/electrospraying technique developed for fuel cell electrodes.
- Unique nanoparticle/nanofiber electrode morphology evidenced by microscopy.
- Ultra-low platinum loadings at high power densities were observed.
- Excellent platinum utilization of 0.024 g_{Pt} kW^{-1} was achieved.
- High electrochemical surface area was measured by cyclic voltammetry.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, membrane electrode assemblies (MEAs) were fabricated using a simultaneous electrospinning/electrospraying (E/E) technique to produce a unique nanoparticle/nanofiber cathode catalyst layer morphology evidenced by scanning electron microscopy. H_2/O_2 and H_2/air polymer electrolyte membrane fuel cell performance was evaluated for E/E MEAs at ultra-low Pt cathode loadings of 0.052 and 0.022 mg_{Pt} cm^{-2}, where maximum power densities of 1.090 and 0.936 W cm^{-2} (H_2/O_2) and 0.656 and 0.625 W cm^{-2} (H_2/air) were achieved at these two Pt loadings, respectively. This was compared to a conventional control MEA at a 0.42 mg_{Pt} cm^{-2} cathode catalyst loading with maximum power densities of 1.420 and 0.839 W cm^{-2} for H_2/O_2 and H_2/air, respectively. These results correspond to a significant reduction in Pt loading (5–12% of control) at only a modest reduction in power density (~66–78% of control) for the E/E electrodes. Excellent platinum utilization in the cathode of 0.024 g_{Pt} kW^{-1} (~42 kW g_{Pt}^{-1}) was achieved for the E/E electrode at 0.022 mg_{Pt} cm^{-2} cathode loading. Cyclic voltammetry results show an electrochemical surface area higher in the E/E electrodes compared to the control, which provides a rationale for the excellent platinum utilization results, where the E/E morphology results in more triple phase boundaries with more accessible Pt in the electrode.

1. Introduction

Proton exchange membrane (PEM) fuel cells have attracted considerable interest as alternative power sources for large market applications, such as transportation (hydrogen-fueled PEM fuel cell vehicles). This is because of their high efficiency, high energy and power density, low-to-moderate-temperature operation, rapid start-up time, with fuels from renewable sources with zero point-of-use green house gas emissions. In addition, research and development over the past several decades has contributed to advancements that overcome many of the major hurdles to bringing fuel cell vehicles to the market place, such as durability, reliability,

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lifetime performance, safety, and fuel storage. However, platinum (Pt), a rare precious metal, which is the most active catalyst for PEM fuel cells, is still a major factor that has limited the mass commercialization of fuel cell vehicles, where Pt contributes to a significant portion of the fuel cell engine cost [1,2]. Attempts to reduce this cost have led to research in alternative catalyst materials and alternative electrode designs.

First generation PEM fuel cells utilized un-supported Pt, which required high Pt loadings to achieve reasonable power densities [3]. Initial reductions in Pt loading in regards to alternative catalysts were achieved through the dispersion of Pt nanoparticles on high surface area carbon supports (Pt/C), i.e., supported Pt [1,4,5]. Other alternative catalyst materials that have been explored include non-noble metals, Pt alloys, Pt core–shell structures, and Pt supported thin films [6–10]. Early research on electrode design demonstrated that a significant reduction (approximately an order of magnitude) could be achieved by introducing the Nafion ionomer into the electrode [11]. These lower Pt loadings were achieved by increasing the triple phase boundary (TPB), which are the junction points where catalytic and electron conduction sites, reactant gases (pores), and proton conducting Nafion ionomer meet. Others have observed performance enhancements and reduced Pt loadings without significant performance loss through adjustments to this Nafion ionomer content in the electrodes [12–17]. More recently, alternative electrode designs have been explored with the attempt to expose more Pt surface area for the oxygen reduction reaction (ORR) and increase the TPB. Examples include electrospraying [18–21] and electrospinning [22,23] catalyst/ionomer mixtures to produce electrodes. Specifically, recent results from Pintauro and co-workers [22,23] demonstrate high PEM fuel cell power output with significantly lower Pt loadings compared to conventional electrodes.

Electrospinning is an intriguing approach to fabricate fuel cell electrodes. Previous results from our laboratory revealed the discovery of the natural formation of Nafion nanofibers in fuel cell electrodes with a careful *post mortem* (after fuel cell experiment) microscopy investigation [24]. A ~10% fuel cell performance improvement was observed specifically due to the formation of Nafion nanofibers, where only a small fraction of the Nafion ionomer were in nanofiber form [24]. These results suggest that Nafion nanofibers increase the TPB and designing fuel cell electrodes with higher Nafion nanofiber content may result in high power density fuel cells with much lower Pt loadings. Electrospinning is a technique that can produce high fidelity polymer nanofibers at high production rates. The production of Nafion nanofibers *via* electrospinning has previously been demonstrated by our laboratory and others [25–28]. Interestingly, the single Nafion nanofiber properties exhibit super high proton conductivity (as high as 1.5 S cm^{-1}), which is an order of magnitude higher than Nafion bulk films (~0.1 S cm^{-1}) [26]. The proton conductivity in single Nafion nanofibers increased exponentially with decreasing fiber diameter, where an oriented ionic nanostructure was observed in the axial direction of these fibers with small-angle X-ray scattering and provides the rationale for the enhanced conductivity [26]. These results motivate further investigation into Nafion nanofibers and the design of Nafion nanofiber-based electrodes for fuel cells.

In this study, electrospinning and electrospraying were combined in a simultaneous process to produce cathode catalyst layers for PEM fuel cells. Specifically, Nafion nanofibers and Pt/C nanoparticles were introduced separately and simultaneously by two different needles (see Fig. 1) using electrospinning and electrospraying, respectively, to produce unique nanoparticle/nanofiber electrodes. This electrospinning/electrospraying (E/E) technique differs from electrospinning or electrospraying alone, where a mixture of Nafion and Pt/C are expelled from the same needle. This E/E technique allows for a higher level of control over fiber size and Pt loading compared to other electrode fabrication techniques. In this paper, the cathode layers and subsequently membrane electrode assemblies (MEAs) were fabricated using the E/E technique and the morphology, fuel cell performance, and electrochemical surface area were investigated as a function of Pt loading and compared to MEAs fabricated with conventional electrodes.

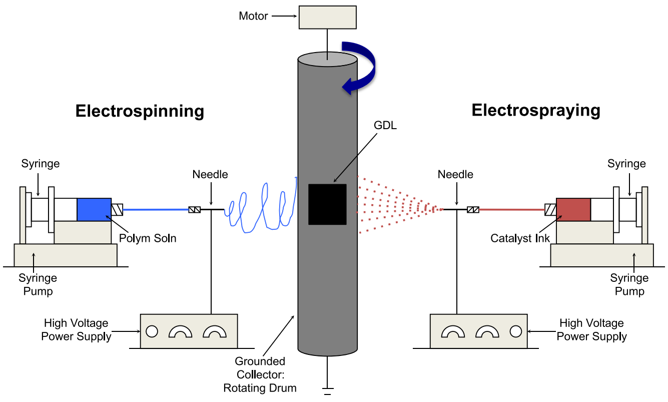

Fig. 1. Schematic of simultaneous electrospinning/electrospraying (E/E) two-needle system.

2. Experimental

2.1. Materials

Isopropanol (99.5%, Sigma–Aldrich), ethanol (99.5%, Decon Labs, Inc., 99.5%), Nafion solution (1000 EW, 5 wt% in a 3/1 v/v of isopropanol/water, Ion Power), poly(acrylic acid) (PAA; $M_V = 450{,}000$ g mol^{-1}, Aldrich), 20 wt% Pt on carbon catalyst (Pt/C; Vulcan XC-72, Premetek Co.), gas diffusion layer (GDL; SGL-25BC, Fuel Cells Etc.), and Nafion NR-212 membrane (1100 EW, ~50 μm (0.002 in) dry thickness, Ion Power) were used as received. Ultra-pure deionized (DI) water with resistivity ~16 MΩ cm was used as appropriate. Ultra high purity grade N_2, H_2, O_2 and ultra zero grade air were all purchased from airgas and used for all fuel cell experiments.

2.2. Two-needle electrospinning/electrospraying (E/E) system

Fig. 1 shows a schematic diagram of the simultaneous E/E apparatus used in this study. The custom-designed apparatus consists of two high-voltage power supplies (Model PS/EL50R00.8, Glassman High Voltage, Inc. and Model ES40P-10W/DAM, Gama High Voltage Research), two syringe pumps (Model NE-1000, New Era Pump Systems), two syringe needles (i.d. = 0.024 in., Hamilton), tubing (Pt. No. 30600-65, Cole–Parmer), and a grounded collector (aluminum foil coated cylindrical drum, o.d. = 4.85 cm). The collector drum is connected to a motor (Model 4IK25GN-SW2, Oriental Motor) to allow for rotation during the E/E process, where the rotational speed was set to 100 rpm. A GDL was adhered to the collector drum, where nanofibers/nanoparticles could be directly collected *via* the E/E process, where catalyst ink is electrosprayed and polymer solution is electrospun simultaneously. Details regarding catalyst ink and polymer solution preparation are described in the following section. The needle tip to collector distances, applied voltages, and solution flow rates were 15 and 9 cm, 10.5 and 12.5 kV, and 0.3 and 3 ml h^{-1} for the electrospinning and electrospraying processes, respectively.