Electrochimica Acta 139 (2014) 217–224

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effect of Polytetrafluoroethylene on Ultra-Low Platinum Loaded Electrospun/Electrosprayed Electrodes in Proton Exchange Membrane Fuel Cells

Xuhai Wang, Francis W. Richey, Kevin H. Wujcik, Roman Ventura, Kyle Mattson, Yossef A. Elabd*

Department of Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania 19104, United States

ARTICLE INFO

Article history:
Received 2 May 2014
Received in revised form 19 June 2014
Accepted 20 June 2014
Available online 11 July 2014

Key words:
electrospinning
nanofiber
fuel cell
Nafion
platinum

ABSTRACT

In this study, catalyst layers (CLs) were fabricated using a simultaneous electrospinning/electrospraying (E/E) technique to produce unique nanofiber/nanoparticle membrane electrolyte assemblies (E/E MEAs) evidenced by scanning electron microscopy. Specifically, the effect of polytetrafluoroethylene (PTFE) in these E/E MEAs on polymer electrolyte membrane (PEM) fuel cell performance was evaluated. E/E MEAs result in high fuel cell performance at ultra-low platinum (Pt) loadings with higher electrochemical surface areas as evidenced by cyclic voltammetry experiments. Without PTFE, an E/E MEA operated at 172 kPa (25 psi) back pressure results in a maximum power density of 1.090 W/cm^2 (H_2/O_2) and 0.647 W/cm^2 (H_2/air) with only 0.112 mg$_{Pt}$/cm^2 total Pt MEA loading. Introducing PTFE (at only 1 wt%) to the electrospinning process results in an E/E MEA operated at the same back pressure (172 kPa (25 psi)) with an even higher maximum power density of 1.240 W/cm^2 (H_2/O_2) and 0.725 W/cm^2 (H_2/air) at a lower total Pt MEA loading of 0.094 mg$_{Pt}$/cm^2. This corresponds to a significant reduction in Pt loading (16% of control) with only a modest reduction in power density (~86-87% of control), where the control MEA was produced using a conventional coating method and resulted in maximum power density of 1.420 W/cm^2 (H_2/O_2) and 0.839 W/cm^2 (H_2/air) at a Pt MEA loading of 0.570 mg$_{Pt}$/cm^2 (172 kPa (25 psi)). An excellent total MEA platinum utilization of 0.076 g$_{Pt}$/kW (~13.2 kW/g$_{Pt}$) was achieved with the E/E MEA with PTFE at only a 0.094 mg$_{Pt}$/cm^2 total Pt MEA loading. The improvement in E/E MEA with PTFE was a result of increased hydrophobicity of the nanofibers evidenced by contact angle measurements and improved PEM fuel cell performance at higher limiting current density in the mass transport region.

1. Introduction

Proton exchange membrane (PEM) fuel cells are an excellent alternative energy source for both stationary and mobile applications. However, currently the requirement for a significant amount of platinum (Pt), the most active catalyst for PEM fuel cells, limits the mass commercialization of PEM fuel cells [1,2]. In previous work in our laboratory [3], an alternative electrode design was explored to reduce the amount of required Pt, while still producing adequate PEM fuel cell power output. A simultaneous electrospinning/electrospraying (E/E) technique was employed to produce unique nanofiber/nanoparticle electrodes as evidenced by scanning electron microscopy (SEM). Specifically, Nafion nanofibers and Pt/C nanoparticles were introduced separately and simultaneously by two different needles using electrospinninig and electrospraying, respectively, to produce nanofiber/nanoparticle electrodes and subsequently membrane electrode assemblies (MEAs). In this previous study, only cathodes were produced via E/E process and anodes were produced using a conventional coating technique. The E/E MEAs in this previous study resulted in ultra-low Pt cathode loadings of 0.052 and 0.022 mg$_{Pt}$/cm^2, where maximum power densities (at 172 kPa (25 psi) back pressure) 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 (at 172 kPa (25 psi) back pressure) 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

---

* Corresponding author.
E-mail address: elabd@drexel.edu (Y.A. Elabd).

http://dx.doi.org/10.1016/j.electacta.2014.06.139

Pt cathode loading (5-12% of control) at only a modest reduction in power density (~66-78% of control) for the E/E MEAs. Excellent platinum utilization in the cathode of 0.024 g_{Pt}/kW (~42 kW/g_{Pt}) was achieved for the E/E MEAs at 0.022 mg_{Pt}/cm^2 cathode loading.

These lower Pt loadings were achieved by increasing the triple phase boundaries (TPBs), which are the junction points where catalytic and electron conduction sites, reactant gases (pores), and proton conducting Nafion ionomer meet. Cyclic voltammetry results confirm these findings, where increased electrochemical surface areas were observed for the E/E MEAs compared to the control, i.e., more accessible Pt in the cathode. This E/E technique differs from electrospinning [4,5] or electrospraying [6–9] alone, where a mixture of Nafion and Pt/C are expelled from the same needle. Contrastingly, the E/E technique allows for a higher level of control over fiber size and Pt loading compared to other electrode fabrication techniques.

In this study, we explore the impact of having both cathode and anode catalyst layers (CLs) prepared via the E/E technique and the effect of polytetrafluoroethylene (PTFE) in these nanofiber/nanoparticle CLs. Previously, the effect of PTFE in gas diffusion layers (GDLs), micro-porous layers (MPLs), and conventional CLs on fuel cell performance has been investigated [10–19]. Previous work [10,11] has shown that GDLs loaded with 5-30 wt% PTFE results in improved fuel performance due to an increase in hydrophobicity, which improves mass transport of the reactants from the gas flow channels to the CLs. However, excessive PTFE loading in GDLs results in poor fuel cell performance due to reduced electrical conductivity and gas permeability [12]. For some MEAs, a hydrophobic MPL is supported on the GDL substrate. Previous results have shown that ~10-30 wt% of PTFE in the MPL results in optimal fuel cell performance [13–15] due to increased pressure on cathode side, which improves water management in the fuel cell [11,13,16,17]. The effect of PTFE in CL on the performance of the fuel cell has been previously investigated for conventionally painted electrodes [18,19]. Uchida et al. [18] showed that the PTFE had an effect at high current densities, where flooding can limit fuel cell performance. Friedmann and Nguyen [19] optimized their MEAs by varying the ratios of Nafion, Pt/C, and PTFE in a two-step method to prepare the electrodes, where their results showed that a PTFE content of 10-24 wt% produced the best fuel cell performances. This previous work [10–19] demonstrates that a relatively high PTFE content (>10 wt%) in the GDL, MPL, and CL is required to improve fuel cell performance. Subsequently, the fuel cell performance decreases when excessive PTFE is added due reductions in pore size and electrical conductivity.

In this study, the effect of including PTFE in the E/E process and subsequently on the fuel cell performance/Pt loading ratio was explored. Both anodes and cathodes in the MEAs were produced via E/E process. This is the first study to investigate the effect of PTFE on nanofiber/nanoparticle CLs.

2. Experimental

2.1. Materials

Isopropanol (99.5%, Sigma-Aldrich), ethanol (99.5%, Decon Labs, Inc.), 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, 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. 60 wt% polytetrafluoroethylene (PTFE) dispersion in water (Aldrich) was diluted to 5 wt% with 3/1 v/v of isopropanol/water before use. Ultrapure 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

A custom-designed E/E apparatus was used and consists of two high-voltage power supplies (Model PS/EL50R00.8, Glassman High Voltage, Inc. and Model ES40P-10 W/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. The rotational speed of the collector drum was set to 100 rpm. A gas diffusion layer (GDL) was adhered to the collector drum, where nanofibers/nanoparticles could be directly collected via the E/E process and catalyst ink is electrosprayed and polymer solution is electrospun simultaneously. 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 for the electrospinning and electrospraying processes, respectively. 0.25-0.7 ml and 2.5-7 ml of solutions were electrospun and electrosprayed, respectively, resulting in catalyst layers of several micormeters in thickness on average. More details regarding the two-needle E/E apparatus are described in Wang et al. [3].

2.3. Membrane electrode assembly (MEA)

Catalyst ink used in the electrospraying portion of the E/E electrodes consisted of 20 mg Pt/C catalyst, 0.248 ml DI water, 0.043 ml Nafion solution, 0.171 ml isopropanol/water (3/1 v/v), and 1.970 ml ethanol. This mixture was sonicated for 3 min (Model CL-18, Qsonica Sonicator) prior to electrospraying. The polymer solution used in the electrospinning portion of the E/E electrodes consisted of 79.2/19.8/1 wt/wt/wt Nafion/PAA/PTFE. A 5 wt% polymer (Nafion, PAA and PTFE) solution was prepared by combining 131.1 mg PAA, 10494 mg of Nafion solution (5 wt%), 131.2 mg of PTFE solution (5 wt%), and 2491.7 mg isopropanol/water (3/1 v/v). This solution was stirred at ~70–80 °C for ~12 h to ensure complete dissolution. The solution was cooled down to ambient temperature before electrospinning. The catalyst ink and the polymer solution were used to make E/E electrodes as described in the previous section. After the E/E process, the E/E electrodes were annealed at 135 °C for 5 min.

MEAs were fabricated by sandwiching the Nafion NR-212 membrane between two catalyst-coated GDLs (anode and cathode catalyst layers) and hot pressing (heat press, Carver) for 5 min at 135 °C and 1.5 MPa (213 psi). All anode and cathode catalyst layers in this study were E/E electrodes, unless otherwise specified. Fuel cell performance of E/E anode/cathode MEAs were compared to MEAs where only cathodes were fabricated using E/E and where both anode and cathodes were prepared using a standard hand-painting GDL procedure (control). Details regarding the preparation of these MEAs can be found elsewhere [3].

2.4. Electrode characterization

Morphological characterizations of the E/E electrodes were investigated with scanning electron microscopy (SEM, Model FEI/Philips XL-30, 10 kV). SEM images of the E/E electrodes were collected after electrospinning/electrospraying of the nanofibers/nanoparticles on GDLs, but before MEA fabrication. All samples were sputter coated (Denton Desk II Sputtering System) with platinum at 40 mA for 30 s before SEM analysis. The nanofiber and nanoparticle diameters were measured using ImageJ software