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Long-term operation of a proton exchange membrane fuel cell without external humidification

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HIGHLIGHTS

- PEMFC electrodes with 0.2 $mg_{Pt}\,cm^{-2}$ Pt loading prepared by electrospraying.
- Long term testing of Pt/C catalysts with Pt concentration in the range 10–60 wt%
- MEAs tested for 1000 h in dry mode (dry H_2/dry air) with low performance loss, ≤3%
- Steady voltages of 515–611 mV reached at 0.2 A cm^{-2}, 40 °C and ambient pressure.
- Durability test (5000 h) at dry operation with a performance loss of 20% at 3800 h.

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ABSTRACT

Electrodes for proton exchange membrane fuel cells (PEMFCs) with a Pt loading of 0.2 $mg_{Pt}\,cm^{-2}$ were prepared by the electrospraying deposition technique and were used to build membrane electrode assemblies (MEAs). These MEAs were tested in a single-cell configuration under a non-humidified regime fed by dry H_2 and dry air. Long-term runs of 1000 h were performed for MEAs prepared from Pt/C catalysts with Pt percentages on the carbon support ranging from 10 to 60 wt%. The MEAs reached steady-state voltages in the approximate range of 500–600 mV at 200 mA cm^{-2}, ambient pressure, and a 40 °C cell temperature and exhibited almost no net performance loss. An even longer durability test of an MEA prepared from 20 wt% Pt/C demonstrated the suitability of the non-humidified regime for these electrosprayed electrodes. This MEA worked uninterruptedly for 5000 h with performance losses of 10% and 20% after 2200 and 3800 h, respectively. Moreover, an MEA prepared from the 60 wt% Pt/C catalyst was subjected to a long-term run under more efficient but more challenging conditions for non-humidified PEMFCs (a higher temperature, 60 °C, which favors thermal management, and a low air stoichiometry, $\lambda_{air} = 2$, which leads to high air utilization). Despite these harsh operating conditions, the non-humidified fuel cell reached a relatively stable voltage (≈0.6 V at 200 mA cm^{-2}) that was sustained throughout 1000 h of continuous operation.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) has long been recognized as a promising clean power generating device owing to its high efficiency, low pollutant emission, and ability to couple to renewable energies for hydrogen production [1,2]. Extensive research has been conducted during recent decades to make this technology competitive with current methods based on fossil fuels [3–5]. The US Department of Energy (DOE), in a recent revision of the Hydrogen and Fuel Cells Program for the period 2015–2020 [6], reported that most of the targets projected for the year 2020 have been or are close to being achieved (*i.e.*, power density, specific power, peak energy efficiency, and start-up). However, the report indicates that the durability and cost still require further improvement to meet the 2020 targets. The prices of various components and the need for peripheral equipment affect the fuel cell (FC) cost. To approach this goal, ultralow-Pt electrodes were prepared by electrospraying and showed extremely high Pt utilization [7–10]. Although, obviously, moderate specific powers were achieved, a tradeoff between the Pt loading and FC size can be reached to obtain the required FC power. On the other hand, the auxiliary humidification system that is usually added to FCs increases the cost of PEMFCs. The incoming gases are pre-humidified in most applications to prevent dehydration of the polymer electrolyte membrane (which occurs mainly at the gas inlets). This humidification degrades the overall FC

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efficiency, as the humidifiers and thermalized pipe lines represent parasitic power consumption [11]. Moreover, the addition of a humidification subsystem increases the complexity, cost, size, and weight of the FC. The latter is especially important in micro/mini FCs for portable power applications, where external humidification is impractical. On the other hand, the operation of a PEMFC without external humidification presents great advantages [12] such as mitigation of flooding phenomena caused by pre-humidified gases and the cooling effect of convective heat transfer and of removal of the latent heat of water from the cell. Among the main drawbacks of operation with dry gases are the poor air utilization (as air is usually supplied well above the stoichiometric factor) and drying of the membrane (especially at the gas inlets), which limits the range of cell operating temperatures [13].

Büchi and Srinivasan [12] demonstrated the feasibility of operating a FC without external humidification. Since then, many experimental studies of dry operation have been performed with conventional membrane electrode assemblies (MEAs) [14–19], and several water management strategies have been outlined [19–21]. More recent approaches have focused on the development of composite membranes by the addition of hydrophilic nanoparticles to improve the water retention and enhance the self-humidification of the membrane [22,23], whereas other researchers investigated the optimum hydrophobicity/hydrophilicity [24] and structure [25,26] of the gas diffusion layers. However, and despite the DOE report [6] pointing to durability as an important issue to improve, there is a lack of long-term tests under self-humidifying regimes beyond a few hours of continuous operation.

1.1. Motivation

This study demonstrates long-term operation of a PEMFC without external humidification. MEAs are prepared from current state-of-the-art and commercially available components (*i.e.*, the GDL, catalyst, and polymer electrolyte membrane), and electrospraying is used as the catalyst deposition method to prepare the electrodes. This technique, which has been reported elsewhere [7–10,27–30], has demonstrated greater Pt utilization in the generated electrodes than conventional deposition methods because of its ability to generate highly porous catalytic layers formed by Pt/C–ionomer clusters, which maximize the interfacial contact between the ionomer and the catalyst as well as the transport of gaseous reactants and the management of water [29,30]. Our research group has successfully used this technique repeatedly in combination with non-humidified regimes to enhance the FC performance in short-term tests [7–10], but we had not demonstrated long-term testing.

1.2. Methodology

Pt/C catalysts with a wide range of relative platinum concentrations (10–60 wt% Pt/C) were used to prepare electrodes with low Pt loading ($0.2\,\mathrm{mg_{Pt}\,cm^{-2}}$) by electrospray deposition following the procedure explained in the next section. Different MEAs with twin electrodes were tested for a long duration of about 1000 h. Each MEA was based on catalyst particles with different Pt/C concentrations. The range of air stoichiometries suitable for a steady-state voltage under non-humidified regimes was also studied. Furthermore, a durability test of 5000 h was performed with an MEA operating under the optimized air stoichiometry. Although the degradation issues are outside the scope of this work, post-mortem analyses were performed to shed some light on the causes of the performance losses.

2. Experimental

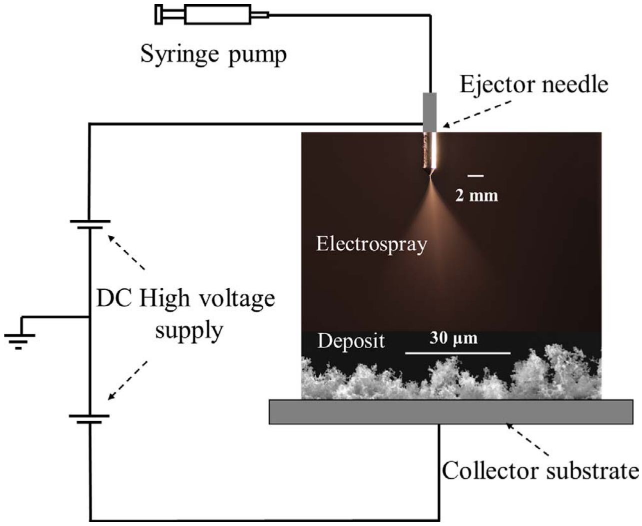

Fig. 1. Scheme of the experimental setup for electrospray deposition. Electrospray and deposit are shown at different scales [27].

Catalytic inks were prepared by mixing the catalyst, ethanol as solvent and Nafion® (Aldrich, 5 wt% in lower aliphatic alcohols and water) as ionomer. Catalysts with different percentage of Pt supported on carbon nanoparticles were used for preparing the catalytic inks: 10 wt% Pt/C, 20 wt% Pt/C, and 60 wt% Pt/C (Johnson Matthey HiSpec 2000, 3000 and 9100, respectively). In the catalytic ink (and therefore, also in the resulting electrodes as the ethanol and the aliphatic alcohol evaporate), the dry Nafion® to supporting C weight ratio was always fixed at 1:1.3, accordingly to our previous studies where the Nafion® loading was optimized for the electrospraying deposition method [9]. The catalytic inks were subjected to ultrasonic stirring for 1 hour to achieve a good dispersion of the catalyst. Commercial gas diffusion layers (GDL) based on non-woven carbon cloth coated with a carbon microporous layer (MPL, Freudenberg H24C3) were used. Electrodes with a Pt loading of $0.2\,\mathrm{mg_{Pt}\,cm^{-2}}$ and active area of 5 $\mathrm{cm^2}$ were prepared by electrospraying the catalytic ink and collecting the solid residue (Pt/C particles and ionomer) on the MPL of these GDLs. Fig. 1 shows a scheme of the electrospray experimental setup [7,27]. The ejector needle and the collector plate are connected to two independent DC high voltage power supplies (Bertan 205B-10R) with opposite polarity. A syringe pump (KDS 100) drives the catalytic ink through a silica capillary tube into the metallic needle at a selected flow rate. When a suitable electrical potential difference is imposed between the needle and the substrate, the catalytic suspension pumped through the needle forms a stable cone-jet structure at the tip of the needle [31] and the emerging jet breaks up in a spray of tiny charged droplets. The substrate is set to an opposite polarity with respect to the needle and the electric field drifts the charged droplets toward the substrate without losses, with the solvent (ethanol) evaporating along the flight. As the droplet evaporates, the electrostatic repulsion forces between ions on the surface of the droplet can surpass the surface tension forces (the so-called Rayleigh limit) and the droplet undergoes a Coulomb explosion breaking up into even smaller droplets. Thus, depending on the operating conditions, aggregates or even single catalyst particles can reach the substrate generating a dendritic-like and highly porous deposit [27]. The main control parameters in the electrospraying process are: the flow rate of the catalytic suspension, the voltages applied to the ejector needle and to the collector substrate and the needle-substrate distance which were chosen to maintain a stable cone-jet with steady droplet formation in the electrospray [31]. Here, a flow rate of $0.2\,\mathrm{ml\,h^{-1}}$ was selected to obtain a catalytic deposit made of small clusters, each cluster formed by aggregation of a few Pt/C catalyst and Nafion® particles. The voltage drop was set at 9 kV to get a stable operation of the electrospray in the cone-jet mode during the whole deposition time and a needle-substrate distance of 7 cm was chosen to ensure the complete evaporation of the ethanol in the catalytic ink droplets ejected by the needle throughout its flight-time. Note that the