# Study of superhydrophobic electrosprayed catalyst layers using a localized reference electrode technique

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## HIGHLIGHTS

- Superhydrophobic catalyst layers prepared by electrospray technique.
- Electrosprayed cathode catalyst layers improve homogeneity of cell performance.
- Performance gain attributed to improved water transport in catalyst layer.
- High Pt/C ratio in electrosprayed cathode produces optimum performance.

## ARTICLE INFO

## ABSTRACT

The performance of electrosprayed cathode catalyst layers in a polymer electrolyte membrane fuel cell (PEMFC) is studied using a localized reference electrode technique. Single cells with an electrosprayed cathode catalyst layer show an increase of >20% in maximum power density under standard testing conditions, compared with identical cells assembled with a conventional, state-of-the-art, gas diffusion cathode. When operated at high current density (1.2 A cm$^{-2}$) the electrosprayed catalyst layers show more homogeneous distribution of the localized cathode potential, with a standard deviation from inlet to outlet of <50 mV, compared with 79 mV for the conventional gas diffusion cathode. Higher performance and homogeneity of cell response is attributed to the superhydrophobic nature of the macroporous electrosprayed catalyst layer structure, which enhances the rate of expulsion of liquid water from the cathode. On the other hand, at low current densities (<0.5 A cm$^{-2}$), the electrosprayed layers exhibit more heterogeneous distribution of cathode potential than the conventional cathodes; this behavior is attributed to less favorable kinetics for oxygen reduction in very hydrophobic catalyst layers. The optimum performance may be obtained with electrosprayed catalyst layers employing a high Pt/C catalyst ratio.

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## 1. Introduction

Within commercial polymer electrolyte membrane fuel cell (PEMFC) stacks, the presence of lateral inhomogeneities in current density and electrode potential across the active area of individual cells can have a significant effect on both performance and lifetime. The principal sources of such inhomogeneities are the concentration gradients originating in the flow field during operation as a consequence of reactant consumption and accumulation of liquid water towards the cathode outlet [1–3]. Such heterogeneities may increase with time and cause local anode [4,5] and cathode [6,7] degradation, and the formation of pinholes in the membrane [8].

In order to reduce lateral inhomogeneities and improve performance and durability of the fuel cell, high rates of water transport are required. Water transport within a cell is a complex process involving concentration and thermal gradients through porous media. Under steady-state operation conditions, water generated in the cathode catalyst layer (CL) is removed from the adjacent gas diffusion layer (GDL), and the membrane. Eikerling considers the CL as a 'watershed' regulating these opposite hydraulic fluxes [9]. The fraction transported through the GDL toward the cathode flow field is favored by thermal and humidity gradients in the cathode [10], and this leads to the evaporation of water from the GDL surface into the channel, and/or its emergence in the form of liquid droplets

[11]. Within the flow field channel, water is dragged by the gas flow until it is expelled. Slow liquid water transport in the GDL and/or flow field leads to accumulation, which is the main limitation for power generation under normal operation conditions in a fuel cell, and may cause cathode flooding and cell failure [12—14]. The remaining fraction of water generated in the cathode CL diffuses through the membrane (back diffusion) driven by the activity gradient imposed by water content and transport properties of the membrane and the anode. Part of this water fraction returns to the cathode by electro- and thermo-osmosis [15], and the rest is expelled through the anode flow field. Water transport in the anode is rarely a limitation in performance, although under certain operation conditions it may accumulate causing localized hydrogen starvation and cell damage [16,17].

The cathode CL has a dominant influence on water transport processes in the cell [9,18,19]. Under steady state operation water transport occurs in liquid and vapor phases through a porous structure with mixed wettability [18,19]. The transport rate within the CL depends on the morphology that determines fundamental properties such as diffusivity, permeability, and liquid/vapor interfacial area [9]. Morphology and pore size distribution control the vapor diffusion mode (Knudsen or molecular diffusion), capillary forces for liquid transport, and the gradients towards the GDL and the membrane.

A possibility to improve water transport in the cell and mitigate cathode flooding is by engineering CLs with an appropriate morphology, able to enhance transport rate and gradients towards the adjacent layers, induce a favorable water partition between the anode and the cathode, and improve in-plane water distribution and lateral homogeneity of the cell performance. CLs with different morphologies can be prepared as a function of composition [20,21] and deposition method [22—24]. Common methods, and most appropriate for large scale production, are those originating from a liquid suspension, or 'ink', of the catalyst powder and the ionomer, to be applied as a thin film [25]. The ink application process determines the structure and morphology of the film as well as the distribution and interaction of the ionomer with the catalyst particles. Methods such as impregnation (doctor blade), airbrushing, electrospraying, and ink-jetting can be used for deposition of inks. Among these, one method leading to a particular pore size distribution and film morphology is the electrospray technique, which is based on ejection of the ink under the influence of a strong electric field [24,26]. Electrosprayed CLs show higher porosity than conventional layers due to a larger contribution above 1 μm pore size [24]. They have shown superior performance as PEMFC cathodes attributed to improved catalyst particle accessibility and facile water transport and expulsion. Other aspects of interest associated with this deposition method are the formation of uniform, crack-free, layers with good adherence to different substrates (e.g. microporous layers on GDL, Nafion films). These characteristics together with its high reproducibility and high yield, above 95% from beaker to layer, show great promise for both fundamental study and commercial application of the electrospray method.

Local performance and water transport properties of cells with electrosprayed CLs can be tested by means of techniques applicable in single cells with lateral resolution. The localized reference electrode technique, developed at the National Physical Laboratory (NPL), UK, is able to probe locally the cathode potential during operation and obtain information about performance heterogeneities in single PEMFCs [27]. This technique employs a unique "through-plate" reference electrode geometry, with a narrow salt bridge connection through the end plates of the cell hardware facilitating a localized measurement of electrode potential at the point of contact with the electrode. The salt bridge, consisting of fine Nafion tubing, makes contact with the back of the GDL, with the ionic pathway through the GDL to the electrode surface achieved by carefully impregnating the GDL with Nafion solution at the point of contact of the salt bridge. An array of nine measurement locations connected to nine separate reference electrodes provides a map of electrode potential distributed over the active area of the cathode. The localized reference electrode technique is especially suited to the study of large area 'commercial scale' electrodes, where significant concentration profiles can be established within the flow field of the cell during operation. The heterogeneity of the cell performance is characterized by means of localized i-V curves, where i is the cell current density, and V corresponds to the local cathode potential measured against an external standard reference electrode.

In this work, single cells with electrosprayed CLs in the cathode have been studied by means of the localized reference electrode technique. Electrosprayed layers with variable Pt/C ratio have been deposited on Nafion membranes, and their porous morphology and hydrophobicity are compared with those of conventional, state-of-the-art, CLs. The general performance of single cells with the layers in the cathode is studied with polarization curves and electrochemical impedance spectroscopy (EIS). The localized response is studied with the reference electrode technique, in order to determine the effect of the electrosprayed CL on the homogeneity of performance.

## 2. Experimental

### 2.1. Electrospray deposition of the CL on the membrane

CLs were deposited on Nafion NRE212 membranes following the procedure described elsewhere [28]. Three CL types were deposited using different Pt/C ratios, according to manufacturers' specifications of three commercial catalysts: ES20 with 20 wt% Pt (Pt on Vulcan carbon black XC72R, E-TEK); ES40 with 40 wt% Pt (Pt on Vulcan carbon black XC72R, HiSPEC 4000 Alfa Aesar GMBH); and ES60 with 60 wt% Pt (Pt on high surface area advanced carbon support, HiSPEC 9100 Alfa Aesar GMBH). The study is based on the differences in composition of the CLs (Table 1), although it is noted that the 60 wt% catalyst contains a different carbon support. Suspensions of the catalyst and the ionomer (Nafion in 5 wt% solution, Aldrich) were prepared in isopropanol (Panreac), keeping constant the total platinum loading (0.25 mg cm$^{-2}$, referred to active electrode area) and ionomer loading (15 wt%, referred to CL mass), which is the optimal amount for the 20 wt% catalyst determined from previous work [26]. Suspensions were ultrasonically stirred for 1 h before deposition. For electrospray deposition, a high dc voltage (9 kV) was applied between the needle and the substrate, while the suspension was maintained in a thermostated (22 °C) beaker, under ultrasonic stirring, and at a low $N_2$ overpressure (0.1 bar$_g$) to force the flow towards the needle through a silica capillary (150 μm diameter). The deposition was carried out directly onto

**Table 1**
Properties of the CLs studied.

| Cathode CL | Catalyst [Pt] | CL [Nafion] | CL [Pt] | CL Pt/C | CL Nafion/C |
|---|---|---|---|---|---|
| Units | wt% | wt% | mg cm$^{-2}$ | | |
| ES20 | 20 | 15 | 0.25 | 0.25 | 0.21 |
| ES40 | 40 | 15 | 0.25 | 0.67 | 0.25 |
| ES60 | 60 | 15 | 0.25 | 1.5 | 0.28 |
| Commercial | 30 | 30 | 0.25 | 0.43 | 0.61 |