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Spotlight on Applications

Electrospray Deposition: A Breakthrough Technique for Proton Exchange Membrane Fuel Cell Catalyst Layer Fabrication

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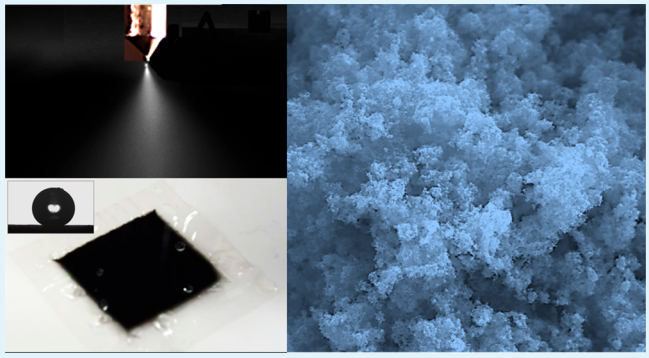
ABSTRACT: This Spotlight article presents the state-of-the-art of electrospray deposition technique applied to the fabrication of proton exchange membrane fuel cell (PEMFC) components, mainly focusing on catalyst layers in gas diffusion electrodes. The atomization of a suspension of particles over a substrate under the influence of a strong electric field results in the growth of a film with macroporous morphology and many interesting properties. This so-called electrospray deposition has reported many noteworthy beneficial effects for the fabrication of the catalyst layers of gas diffusion electrodes of PEMFCs. The electrosprayed catalyst layers prepared from suspensions of catalyst particles and ionomers present a dendritic macroporous morphology with superhydrophobic character that improves the water management inside the cell and increases the performance by ∼20% with respect to standard electrodes prepared by airbrushing. Other interesting effects observed with electrosprayed catalyst layers are increased catalyst utilization and water absorption capabilities of the ionomer, improved performance under nonhumidified conditions, and a reduction in catalyst degradation. In addition, the electrospray deposition decreases platinum losses during fabrication thanks to the attractive electrostatic forces between the ion mist and the substrate compared with regular ink-based spray methods.



KEYWORDS: *PEM fuel cells, electrospray, electrohydrodynamic spray, review, superhydrophobic electrodes*

1. INTRODUCTION

Electrospray is a method of liquid atomization based on the ejection of a solution or a suspension under the influence of a strong electric field. The electric field imposed by applying a potential difference between the liquid flowing out of an ejector needle and the substrate gives rise to the formation of a mist of ionized droplets with a narrow size distribution.[1] Unlike common spray methods, mechanical forces play a minor role in the atomization process, so the term *electrohydrodynamic spray* is commonly used to designate electrospray and to avoid ambiguity with other spray techniques that also apply an electric field to charge the particles after the atomization occurs.[2] However, after the exact meaning is clarified, the term electrospray will be used hereinafter for the sake of simplicity.

Electrospray has been reported to be useful for a number of applications that require thin solid films, such as solar cells, fuel cells, lithium batteries, microelectronic devices, piezoelectric actuators, and chemical sensors,[3] and is a widespread technique in the development of materials for energy applications.[4] Specifically, in the PEMFC research field, it has gained importance for the fabrication of catalyst layers, showing improved performance in comparison with conventional techniques and becoming a reliable technique that does not require a big capital investment compared with other techniques.

1.1. A Brief Historical Note. After the discovery of the electrospray phenomenon in the beginning of the twentieth century,[5] the first use of electrospray as a deposition technique was reported by Tilney in 1953. In fact, Tilney described two different processes called No. 1 and No. 2 used by the Ransburg Company of Indianapolis. No. 1 was an electrostatic-assisted spray-painting process using air atomized spray, whereas No. 2 was defined as a development that "represents a fundamental departure from all previous methods of applying coating materials to any surface", reporting a process only governed by the electrostatic force with the ability to produce considerably finer particles that cannot be achieved by other means.[6] The process was developed by Ransburg's housewares

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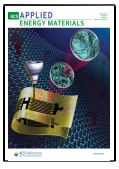

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factory from 1940 onward, which manufactured kitchen and other metal goods, to reduce the waste of paint associated with regular handspray painting methods. As a result of their investigation, several patents were assigned to the Ransburg Electro Coating Corp. during the 1950s, describing the methods and the experimental apparatus for electrostatic atomization.[7−9] Some years later, in 1965, Tilney reported the use of two basic types of atomizing heads of general use, that is, a rotating bell and a flat disc, and described the latest advances in the technology in the metal finishing sector.[10] In 1966, Hines described the electrospray painting technique as "an accepted industrial process" and reported the use of a knife edge atomizer with experimental data and some approximate formulas relating fluid properties and the electrical field in the system.[11]

1.2. Principles of the Electrospray Process. Electrospray of a plane liquid presents different functioning modes depending on the physical properties of the liquid (electrical conductivity, surface tension, and viscosity), its flow rate, the applied voltage between the ejector and the counter electrode, the geometry of the system, and the dielectric strength of the environment. Cloupeau and Prunet-Foch distinguish three main cases: (i) Drops are produced directly at the end of the capillary or the meniscus, (ii) the formation of a jet breaks up droplets, and (iii) the two preceding types occur together.[12] The second mode constitutes the well-known cone-jet mode, where the meniscus takes the form of an inverted cone ("Taylor cone"), extended at its apex by a jet whose breakup produces the droplets.

In the electrospray of a suspension of particles, the most appropriate mode for the deposition of thin films is the cone-jet ejection followed by aerosol formation. (See Figure 1.) At

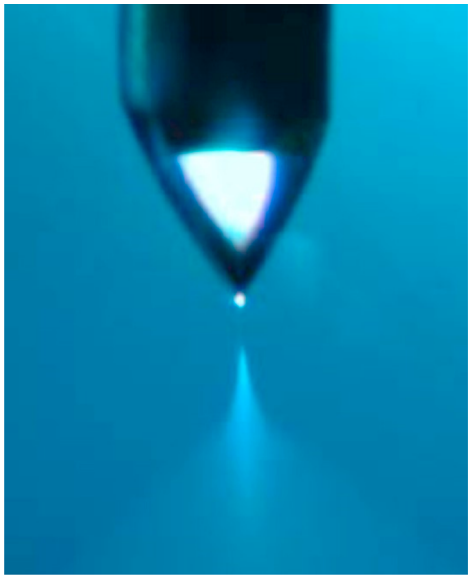

Figure 1. Electrospray in cone-jet mode with aerosol formation. Reprinted with permission from ref 13. © 2018 Elsevier.

the ejector-needle end, the meniscus adopts the Taylor cone, where particles become ionized. In the apex of the cone, a jet is formed and is ultimately decomposed into a mist of particles and solvent droplets dispersed in the space over the substrate. Whereas the solvent evaporates, the particles deposit under electrostatic interaction on the substrate acting as a counter electrode. The mechanism of electrospray deposition in the cone-jet mode therefore has four stages: cone formation and its stability, the production of charged droplets, solvent evaporation from the charged droplets, and deposition of the particles. For an analysis of the fundamental physics of the cone-jet mode, one may check a recent review by Rosell-Llompart et al.[13]

The electric field at the electrospray capillary tip produces the separation and migration of positive and negative ions and charged particles in the volume of the suspension. Figure 2

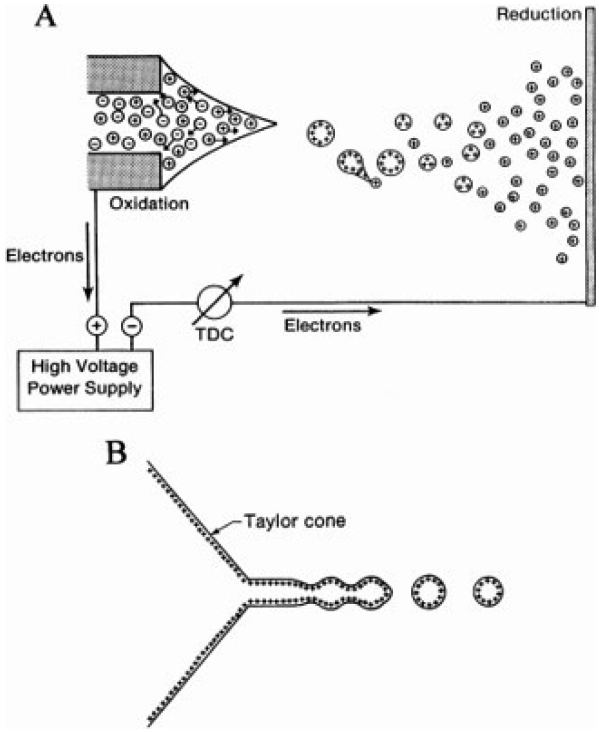

Figure 2. (A) Schematic representation of the electrospray process in cone-jet mode and (B) detail of the primary drop formation from the charged jet. Reprinted with permission from ref 14. © 2000 John Wiley and Sons.

depicts the tip of a capillary under positive ionization mode, in which positive ions and particles are generated and dragged to the surface of the liquid, converging into a meniscus, while negative ions are pushed into the capillary, where they discharge by transferring electrons to the metallic surface to keep the required average macroscopic electroneutrality. The repulsion of the positive ions is able to overcome the surface tension of the liquid and expand the liquid into the Taylor cone, extending into a liquid jet at the least stable point of the meniscus. This charged jet easily breaks up into individual charged droplets proportional to the jet diameter. All of those charged droplets are driven away from each other by Coulombic repulsion and spread along the direction of the electric fields.[14]

The charge of the droplets produced in the jet stream are distributed on droplet surfaces with equidistant spacing to minimize the potential energy.[15] While the droplet is moving to the substrate, it is subjected to two forces acting in opposite directions. One is the surface tension of the droplet, aiming to retain its spherical shape, and the other is the Coulombic repulsion between the charges on the surface, trying to break down droplet spheres. As the droplet travels, the thermal energy provided by the ambient gas causes droplet shrinkage

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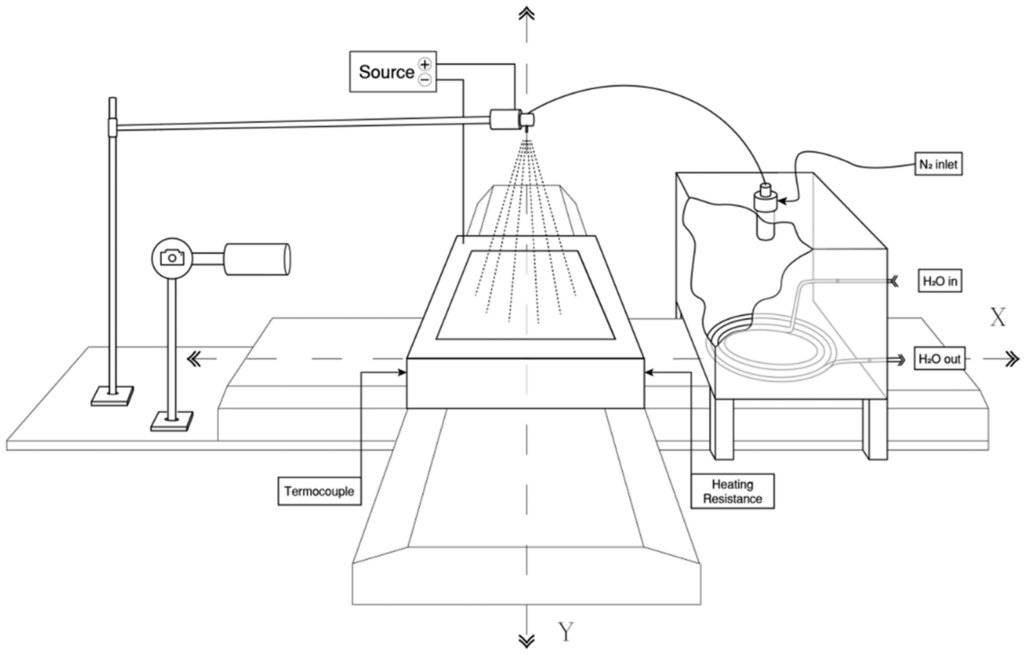

Figure 3. Schematic representation of the electrospray deposition setup used at CIEMAT.

due to solvent evaporation, whereas the charge remains constant, thus increasing the repulsive forces. When the mutual repulsion of charges is high enough to overcome the surface tension of the droplet, the shrinking droplet volume leads to droplet fission, releasing a jet of smaller, charged progeny droplets. Continued droplet fission will not only reduce the size of the droplet but also increase the charge-to-mass ratio. The process of solvent evaporation and Coulomb fission occurs repeatedly to generate smaller and smaller progeny droplets until the liquid is eliminated and only the charged solid particles remain.[16] Consequently, the electrospray deposition of particles can be considered a dry process if the experimental conditions for the full elimination of solvent in the aerosol phase are accomplished. Dry deposition is essential to have a film morphology dictated solely by electrostatic forces among particles and the substrate.

1.3. Electrospray as a Film Deposition Technique. Electrospray is a suitable technique for fabricating thin films of a controlled morphology. Because thin-film properties strongly depend on the size of the particles or the drops forming the layer, electrospray can produce films of excellent quality, reducing the number of voids, flaws, and cracks and ensuring a homogeneous thickness and morphology throughout the film.[17] A conductive or semiconductive substrate is necessary to avoid film charging during deposition, rendering an unstable process with pulsations and eventually interruption; however, the AC current on insulating substrates allows a reduction in the amount of surface charging.[18]

Solvent selection will play a fundamental role in the deposition process and final layer properties, drastically changing the surface morphology of the film depending on the solvent characteristics. Using a solvent with a lower vapor pressure results in particles of smaller size with smoother surface morphology. In this case, it is highly probable that the particles and solvent arrive together at the substrate, like in normal spray processes, where particle arrangement mechanisms are governed by ink rheology, solvent interactions, and postdeposition treatments, which changes the morphology of the film. In contrast, solvents with a high vapor pressure, and consequently a faster evaporation rate, allow dry particles to arrive at the substrate that arrange under pure electrostatic forces, which makes possible dendritic growth and the formation of highly porous surfaces.[19] Therefore, the appropriate selection of the solvent and the parameters of the deposition is essential for the deposition of dry particles, which characterizes electrospray deposition in comparison with standard ink-based spray methods.[20]

To gain more insight into the use of the cone-jet mode for the deposition of thin films, Rietveld et al. made an exhaustive literature review of the studies of the parameters affecting each of the four subprocesses in cone-jet electrospray deposition (i.e., cone stability, jet breakup, flight evaporation, and film deposition). However, having a fixed spray geometry and ink composition, the main free parameters remaining for electrospray experiments are the flow rate, the voltage, and the temperature of the substrate and of the ink. These three factors will determine the droplet evolution that will ultimately lead to different film morphologies. The surface energies of the particles and the substrate may also play an important role in the structure of the deposited film.[21]

The setup required to perform the electrospray deposition of thin films is relatively simple to gather and assemble in a laboratory. An example is in Figure 3, depicting a scheme of a medium laboratory-size setup assembled at CIEMAT's facilities, which allows deposition on substrates up to 200 cm^2. The ink suspensions are prepared in vials with a volume of 20 cm^3 and immersed in an ultrasonic bath to achieve a better ink homogenization. Afterward, ink vials are screwed to an adapted head that is connected to a N_2 inlet on the side and a capillary fitting on its top. This fitting allows the removal or modification of the position of the flexible borosilicate capillary while maintaining a gastight vial.

During the deposition process, the catalyst ink is maintained in a thermostatic bath under ultrasonic stirring. The liquid sample is fed to the tip of the needle through the capillary by applying a small N_2 overpressure inside the vial. A dead volume

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is used as a buffer for pressure, which is controlled by a piezoelectric sensor and a high-precision manual pressure regulator. The metal needle is embedded in an insulating Teflon support and attached to a metallic arm, allowing for the regulation of the distance of the needle to the substrate. A high dc voltage (typically 1−10 kV) is imposed between the needle and the substrate by means of a high voltage source. The charged particles are attracted to the substrate and are deposited according to a pattern that can be controlled by masks made of insulating material. The substrate base has ceramic heating resistances underneath to control the substrate temperature and is mounted on an XY stage that allows deposition on large areas. Additionally, a digital camera is mounted on a secondary structure, allowing for online monitoring of the process.

Overall, the electrospray technique is cheap and easy to handle. It requires a relatively low capital investment for a basic setup compared with chemical or physical vapor deposition, and the control of the process is governed by means of two fundamental parameters: the liquid flow and the applied voltage. On top of that, the deposition efficiency for solid particles is normally close to 100% thanks to the attractive electrostatic force with the substrate. The main drawback of this technique is probably the limited ionization rate of the suspension at the nozzle, which must be complete to avoid the ejection of uncharged droplets, leading to deposition rates in the range of a few milligrams of solid (Pt/C catalyst) per hour. New nozzle configurations have been proposed to increase the deposition rate, like the use of multinozzles,[22] multicapillary nozzles,[23] and slit-nozzle systems.[24]

2. DISCOVERING THE POTENTIAL OF ELECTROSPRAYED CATALYSTS IN PEMFCs

One must go back to the first decade of this century to find the first reports on the application of the electrospray deposition technique in PEMFCs. It is difficult to state the first application of the electrospray technique for PEMFC electrode preparation, but it may comprise reports in conferences and regular publications by three groups from the United States, Japan, and Spain from 2003 to 2006. Figure 4 graphically depicts the first 10 years of investigations, from the pioneers of the application of electrospray in PEMFC to the advances in the following years.

Baturina and Wnek deposited Pt/C catalyst layers on both sides of a Nafion 112 membrane using an ink dispersed in ethanol with no membrane electrode assembly (MEA) hot pressing. Their results were promising and showed good performance at 80 °C and pressure of 3 bar.[25] Before that, they demonstrated the feasibility of the technique by depositing Pt/C onto glassy carbon and studying the particle size distribution and dispersion, electrocatalytic activity, and catalyst utilization.[26] In 2004, Wnek also participated in a publication in which Nafion membranes were fabricated using electrospray. The physical properties of the electrosprayed Nafion membranes, that is, the water uptake, dimensional changes, and electrical conductivity, were similar to those of Nafion 117 films, with the exception of an unusually high water uptake. These electrosprayed membranes absorbed as much as 15 wt % more water compared with the commercial ones.[27] Simultaneously, Umeda et al. also explored the feasibility of a technique for the deposition of catalytic inks on Nafion membranes using catalyst dispersions diluted in a mixture of methanol, isopropanol, and water[28] and characterized the

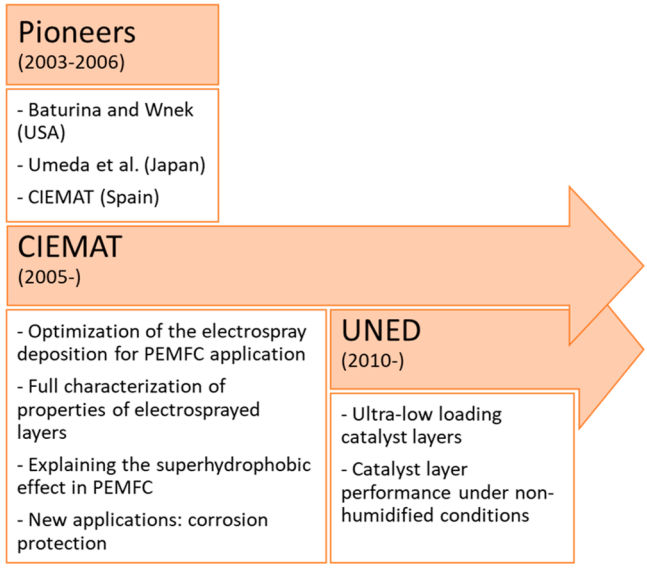

Figure 4. Graphic overview of the first 10 years of research in electrospray deposition for PEMFC application.

MEAs obtaining similar performances as cells prepared by air-spraying.[29] However, after those promising results, they stopped publishing works related to the electrospray deposition technique.

In parallel, the Fuel Cells group at CIEMAT published their first works on the use of electrospray for the fabrication of catalyst layers for PEMFCs in 2005[30,31] and have been applying this technique ever since. In their first work, the electrochemical characterization of electrosprayed layer was carried out with a rotating disk electrode, showing that the electrosprayed film in a direct liquid electrolyte contact had lower performance for oxygen reduction compared with airbrushed or manually impregnated films.[30] However, such difficulty in the interaction with a liquid electrolyte was not encountered for oxygen reduction in a single PEMFC, where Pt/C catalyst layers deposited on top of a gas diffusion layer by using an ink dispersed in a complex mixture of solvents (butyl acetate, ethanol and glycerol) reported higher platinum utilization and a performance increase as a cathode when compared with the other deposition methods.[31] Later work showed that high-boiling-point solvents remain within the film, and although this mixture shows high mass specific area, pure isopropanol is preferred as a solvent due to its lower boiling temperature.[32] Optimization of the catalyst loading at the cathode showed a maximum at 0.17 $mg{\cdot}cm^{-2}$ with Pt/C (containing 20 wt % Pt), corresponding to the minimum value of catalytic layer resistance. Additionally, an optimal 15 wt % of Nafion concentration was found to be optimal for electrospray-deposited electrodes, which is significantly lower than the values reported for the standard preparations methods.[33] The use of electrospray resulted in catalyst layers with a better distribution of the Nafion around the catalyst particles and the formation of structures with high macroporosity, as can be seen in Figure 5.[34] Such film structure leads to an improved electroactive area and cell performance in comparison with airbrushed layers, as shown in the polarization curves depicted in Figure 6. Additionally, single cell testing demonstrated that catalyst layers directly deposited on top of the Nafion membrane showed better catalyst layer−membrane ionic

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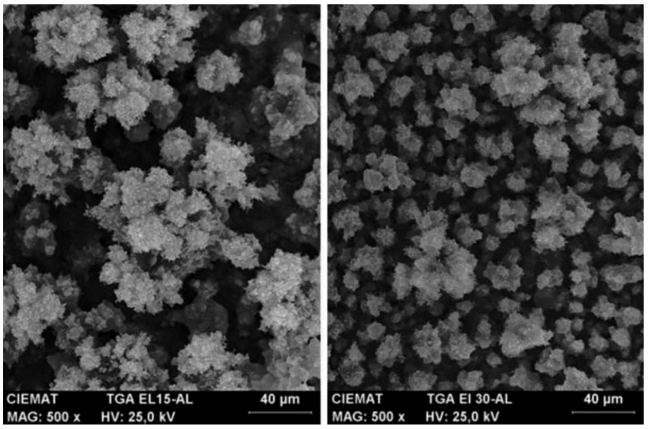

Figure 5. Electronic microscopy pictures of the morphology of electrosprayed catalyst layers. Reprinted with permission from ref 34. © 2010 IOP Publishing.

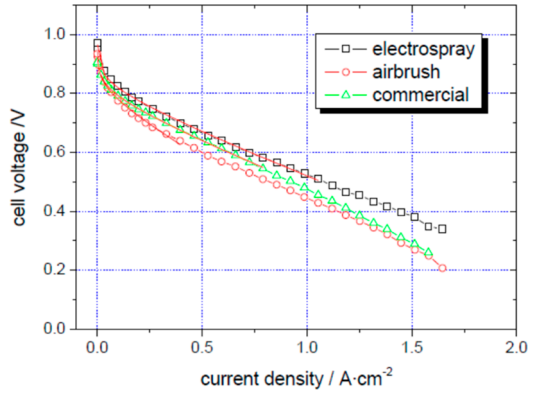

Figure 6. Polarization curves of PEMFC single cells with different cathodic catalyst layers: electrosprayed, airbrushed, and commercial. Reprinted with permission from ref 34. © 2010 IOP Publishing.

contact than the layers deposited on the gas diffusion layer, allowing a reduction in the internal resistance in the cell.[35]

Since 2010, another group from Spain has started publications with the electrospray deposition of catalyst layers focused on the minimization of the platinum catalyst loading.[36,37] Cathodic catalyst layers onto carbon papers reported platinum loadings as low as 0.012 mg·cm^{-2} with high power outputs per gram of platinum,[36] with a much higher optimum Nafion content in the range of 30−50 wt % with dry gases and a cell temperature of 80 °C.[37] They reported that the overall platinum utilization reached values larger than 30 kW·gPt^{-1} under certain conditions with Pt loadings of 0.01 mg·cm^{-2} in both the anode and cathode catalytic layers.[38] Moreover, they demonstrated the suitability of low-loading electrosprayed catalyst layers for scaling-up processes to elaborate electrodes up to 25 cm^{2}[39] and for long-term and stable operation under nonhumidified conditions.[40]

3. UNDERSTANDING THE PROPERTIES OF ELECTROSPRAYED CATALYST LAYERS

Within the first 10 years of investigations (from 2005 to 2015) in the field of PEMFC, electrosprayed layers showed improved performance values compared with conventional catalyst layers and the ability to obtain excellent performances with ultralow catalyst loadings. The interest in electrospray use was extended to other fuel cell groups, but the differences from the standard deposition methods were yet to be explained. For instance, its catalytic activity for oxygen reduction was found to be very similar, even somewhat reduced, in comparison with the standard methods,[30] whereas the fuel cell performance was enhanced over 20% with electrosprayed cathodes, so much effort was put in over the last several years to unravel the reasons behind such an enhancement. The main findings that aim to explain the electrosprayed layer behavior are compiled in Figure 7 and are described in detail in this section.

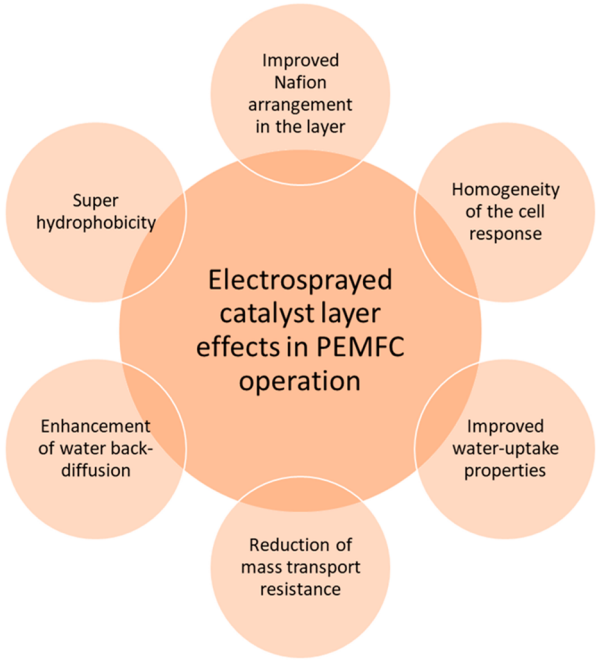

Figure 7. Main findings explaining the breakthrough properties of electrosprayed catalyst layers.

An analysis of the deposition process may help us to understand the mechanisms leading to the morphology of the electrosprayed layers. Most of the authors have reported high macroporous structures with dendritic shapes caused by deposition in the electric field under electrostatic interactions with the substrate of particles free of solvent. For instance, Tang and Gomez reported different properties of the deposits depending on the volatility of the solvents and their ability to achieve complete evaporation before reaching the substrate.[41] Koh et al. confirmed that the use of high boiling point solvents results in the deposition of dense and much less porous layers.[42]

The use of simulation tools has also been explored to achieve a better understanding of the morphology of electrosprayed layers. Castillo et al. performed Monte Carlo simulations to predict the bulk porosity and surface roughness depending on the approaching velocity of the particles to the substrate[43] and empirical calculations of experimental parameters to obtain a stable cone-jet for two different suspensions: carbon nanoparticles in ethanol and catalytic inks formed by Pt/C and Nafion in ethanol.[44] Higuera considered that the image field may overcome the applied field close to the substrate and govern the particle stacking and film morphology. Using Monte Carlo simulations, he proposed scaling laws for the size of micro islands and crevices with an applied field and particles size.[45]

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In addition to the study of the deposition processes, the most important advances over the past decade were focused on explaining the origin of the improved properties of the catalyst layers in PEMFCs. (See Figure 7.) In particular, electrospray-deposited from suspensions of platinum nanoparticles supported on carbon black (Pt/C) and dissolved ionomer polymer chains, typically Nafion, in a solvent like isopropanol have been shown to significantly improve their performance. Although the ability of the electrospray to produce superhydrophobic layers was already reported in polymer coatings,[46] this property did not receive much attention in PEMFC applications until some of the last published works by CIEMAT researchers. For instance, hydrophobicity was first considered in two publications devoted to the in situ study of electrosprayed cathodic layers by the use of a localized reference electrode technique, that is, incorporating an array of reference electrodes that enables the measurement of cell current as a function of the local cathode potential.[47,48] The superhydrophobic nature of the layers can be appreciated in Figure 8, in which water contact angle measurements result in

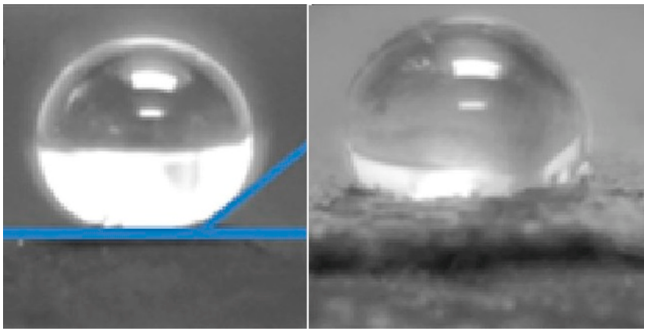

Figure 8. Electrosprayed layer (left) and the commercial electrode (right) during water contact angle measurements. Reprinted with permission from ref 47. © 2016 Elsevier.

a value of 159° for the electrosprayed layer, whereas a commercial electrode presented a value of 109°. The hydrophobic properties of Pt/C layers are believed to favor a faster water removal that contributes to improving the performance and the homogeneity of the cell response.[47] Additionally, the superhydrophobicity of the catalyst layer is also believed to retard the kinetics of corrosion of the carbon support, thus reducing the cathodic layer degradation.[48]

A thorough physicochemical study of carbon black−Nafion composites was performed using scanning electron microscopy, X-ray photoelectron spectroscopy, the water contact angle, and thermal stability to explain the superhydrophobic nature of the layers. This set of techniques attempted to unravel the interactions between the carbon black surface and the Nafion, determining the characteristic structure and properties of the resulting layers. The study revealed a strong and stable interaction between the sulfonic groups of the Nafion and the carbon black surface, which is probably the result of the fast desolvation of the adsorbed ionomer during the ionization process. This interaction is believed to favor a better coverage of the carbon surface with the polymer chains and leads to a particular arrangement of the Nafion with fluorocarbon backbones oriented toward the outer part of the aggregates.[49]

Electrosprayed catalyst layer properties were further analyzed ex situ for a more complete insight into their unparalleled properties. Mass-transport properties were studied by the hydrogen limiting-current technique and correlated with their water-vapor uptake capability.[50] The results showed a reduction in the mass-transport resistance for electrosprayed layers and an enhancement of the water-uptake capability due to the particular morphology and distribution of the ionomer phase. The enhanced water-vapor uptake of electrosprayed layers combined with their very low wettability and superhydrophobic character, allow for an optimal catalyst layer with low mass-transport resistance and high ionic conductivity.[50] The transport properties of electrosprayed catalyst layers have revealed an unprecedented reduction in the mass-transport limitations at low loadings when compared with conventional layers. This is probably the reason behind the excellent performances using ultra-low-loading catalysts reported by other authors.[36]

To prove the hypothesis of previous studies that the water transport could be affected by the presence of electrosprayed layers, a single cell study of water transport was performed by measuring the water output from the cathodic and anodic gas exhausts.[51] The study showed that electrosprayed layers in the cathode of a PEMFC in combination with a standard (more hydrophilic) anode enhance the back diffusion of water from the cathode to the anode. Figure 9 shows the water fraction

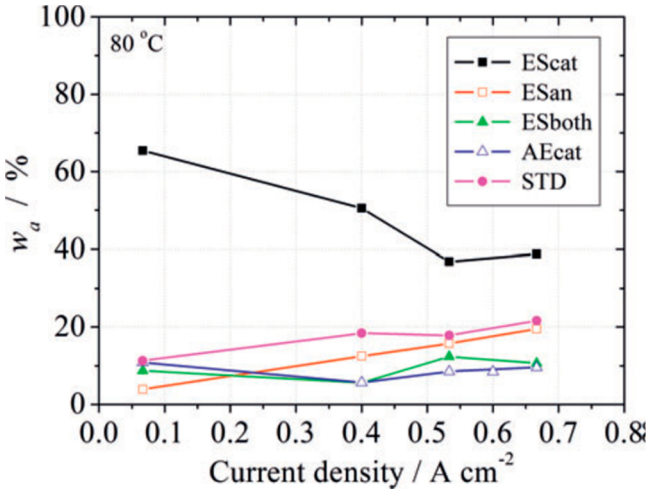

Figure 9. Water fraction recovered from the anode of a single PEMFC, at 80 °C, for five different cell configurations: EScat (with electrosprayed catalyst layer in cathode), ESan (electrospray in anode), ESboth (electrospray in cathode and anode), AEcat (airbrushed catalyst layer in cathode), STD (commercial electrode in anode and cathode). Reprinted with permission from ref 51. © 2018 John Wiley and Sons.

recovered in the cathodic exhaust using different MEA configurations, in which the cathodic electrosprayed layer is proven to push up to 60% of the total produced water in the cell operation. The superhydrophobic character of the electrosprayed layer gives rise to operation under lower saturation conditions and lower water permeability compared with the conventional layers. Larger water back diffusion toward the anode improves the membrane and anode humidification, decreases the internal resistance of the cell, and, as a result, improves the performance (>20% in maximum power density) and the stability of the cells.[51]

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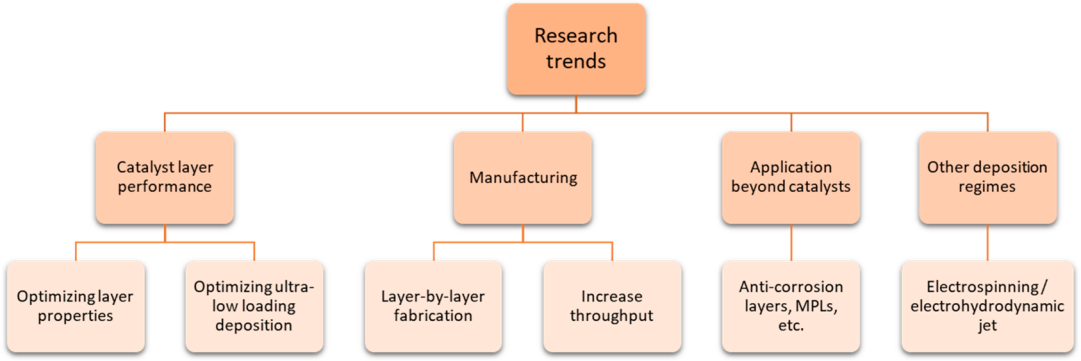

Figure 10. Research trends in electrospray deposition for PEMFC applications.

4. LATEST WORKS AND INNOVATIVE APPROACHES

Over the last several years, the use of the electrospray deposition technique has started to gain importance, as observed in a number of works by several research groups. The main trends in electrospray studies for PEMFC applications are compiled in Figure 10 and are divided into four main research topics, that is, research on catalyst layer performance, innovative manufacturing approaches, the application of electrospray beyond catalyst layers and the study of other deposition regimes beyond cone-jet.

For instance, some groups are pushing toward the optimization of catalyst layer performance, mainly by optimizing layer properties. Liu et al. studied the optimization of operating voltage and catalyst ink flow, obtaining a maximum of 1.4 $W{\cdot}cm^{-2}$ when operating the fuel cell at 2 bar.[52] The improvement in the transport resistance in cathodic layers reported by the Fuel Cells group at CIEMAT was confirmed by Cho et al.[53] Interestingly enough, they also reported significant differences in the catalyst layer transport resistance depending on the ionization mode. A more innovative approach was studied by Arai et al., in which the deposition of multilayered catalyst layers with different ionomer/carbon ratios was studied, forming different physical structures depending on the ratio and resulting in an increase in the performance of the cell when compared with homogeneous layers.[54]

The feasibility of using electrospray to deposit functional catalyst layers with ultralow platinum loadings, as reported by Garcia-Ybarra's group, has also been confirmed in other research laboratories. They have found improved mass activity values at 0.05 $mg{\cdot}cm^{-2}$ platinum loading due to the increased efficiency of gas mass transport[55] and the reduced O_2 transport resistance with low platinum loadings.[56] Recently, Liu et al. also reported excellent results of ultralow platinum loadings, obtaining a peak platinum utilization of 56 $kW{\cdot}gPt^{-1}$ with Pt loadings as low as 0.01 $mg{\cdot}cm^{-2}$ on coated gas diffusion layers.[57]

Even though the technique is mainly focused on the fabrication of catalyst layers, some authors are also using the electrospray to form carbon layers to be used in other parts of the fuel cell. For instance, Conde et al. prepared carbon-based superhydrophobic layers as protective coatings on metal surfaces, producing resistant films to corrosion in acidic media and opening the possibility to use them as coatings in metallic fuel cell components.[58] In this case, the superhydrophobicity of the coating prevents the contact of the metallic surface with water and limits electrochemical corrosion processes. Chingthamai et al. studied the optimal conditions for carbon black microporous layer deposition, obtaining films with acceptable air permeability, electrical conductivity, and coating adhesion.[59] Other authors studied the effect of carbon deposits next to the catalytic layers. For example, Koh et al. reported the fabrication of nanosized dense-structured layers to create a dual-layered electrode that improves self-humidification operation,[60] whereas Okuno et al. fabricated three-layered catalysts, alternating Pt/C and carbon layers, to examine the effect of platinum distribution on the cell performance.[61] There are also reports related to the use of noncarbon layers, such as Nafion/CeO_2 structures introduced between the interface of the membrane and the cathodic catalyst, which showed an improvement under low-humidity conditions due to the hygroscopic effect of the oxide.[62]

Electrospray is also reported as an appropriate technique for the whole, layer-by-layer fabrication of membrane-electrode assemblies. For instance, Wang et al. successfully achieved the fabrication of a membrane-electrode assembly by the sole use of the electrospray deposition technique. They manufactured both catalytic layers and the Nafion membrane on top of a gas diffusion layer for direct methanol fuel cell application. Even though the cell performance was not optimal, it showed the robustness and potential of electrospray for the industrial fabrication of fuel cell components.[63] The group continued their investigation in layer-by-layer membrane-electrode assemblies, depositing up to seven layers with a structural gradient in which the porosity of the subsequent layers was modified to improve the performance of the cell.[64]

Some innovative deposition approaches are being explored other than the standard cone-jet regime for electrode fabrication. For instance, the use of electrohydrodynamic jet deposition, which is formed at lower potentials than the cone-jet, resulted in the uniform deposition of fuel cell catalysts. This technique showed excellent spatial resolution capabilities, producing uniform catalyst layers with widths as low as 3 μm, ideal for the production of microfuel cells.[65] However, no data about the resulting layer morphologies have been reported, so it is unclear whether the properties described for regular electrosprayed layers are maintained. Additionally, the use of simultaneous electrospinning/electrospraying techniques to produce Pt/C-coated Nafion fibers is reported to improve the cell performance with low platinum loadings. This effect is attributed to an increase in the triple-phase boundary accessibility provided by a unique nanoparticle/nanofiber catalyst layer morphology.[66,67] Recent work shows the possibility to prepare nanometric arrays of particles with electrospray by using a focusing mask, which may be of interest

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Table 1. Electrosprayed Catalyst Layer Most Relevant Properties and Improvements in Cell Operation

	electrosprayed layer	conventional layer	ref
	Catalyst Layer Properties		
increased electroactive area	44 $m^2 \cdot gPt^{-1}$	32 $m^2 \cdot gPt^{-1}$	34
increased macroporosity	12 $m^2 \cdot gC^{-1}$	2.5 $m^2 \cdot gC^{-1}$	34
superhydrophobicity	>150°	<120°	49
reduced catalyst mass-transport resistance	~20 $s \cdot m^{-1}$ @ 0.025 $mgPt \cdot cm^{-2}$	~80 $s \cdot m^{-1}$ @ 0.025 $mgPt \cdot cm^{-2}$	50
improved water-vapor uptake	>20 wt %	<10 wt %	50
	Improvements in Fuel Cell Operation		
improvement in cell performance	0.66 $W \cdot cm^{-2}$ (@ 1 bar)	0.51 $W \cdot cm^{-2}$	51
	1.4 $W \cdot cm^{-2}$ (@ 2 bar)	-	52
reduction of optimum catalyst loading	0.17 $mgPt \cdot cm^{-2}$	0.25 $mgPt \cdot cm^{-2}$	33
reduction of optimum Nafion content	15 wt %	30 wt %	33
attenuation of catalyst degradation	−0.2 dV/dN decay rate	−0.3 dV/dN	48
improvement in water back-diffusion	40−60%	15−20%	51
excellent catalyst utilization at ultralow loadings	56 $kW \cdot gPt^{-1}$ @ 0.01 $mgPt \cdot cm^{-2}$	-	57
high stability under nonhumidified conditions	3% performance loss in 1000 h	-	40

for fundamental studies of electrosprayed catalyst and catalyst layer fabrication.[68]

The inclusion of new materials in catalytic ink formulations is also being explored by some research groups. Electrospray deposition of some innovative catalyst support materials has been reported, such as graphene,[69] carbon nanotubes,[70] Ta-doped SnO_2,[71] and Ni-doped TiO_2 nanofibers.[72] The publication of the first investigation dealing with the fabrication of platinum group metal-free catalyst layers with the objective of reducing the inherent mass-transport limitations of this type of catalyst is also remarkable.[73] The addition of surfactants to create additional porous structures allowing the modification of the layers after deposition has also been tested.[74] There are some successful attempts to expand the use of electrospray deposition to other type of fuel cells by depositing specific catalyst inks, such as Pt/C with polybenzimidazole for high-temperature PEM,[75] Pt/C with polyvinylpyrrolidone for an anion exchange membrane,[76] Pt−Ru/C with Nafion for direct methanol,[63] and palladium black with Nafion for direct formic acid fuel cells.[77]

5. CONCLUDING REMARKS AND FUTURE PERSPECTIVES

In the past decade, electrospray deposition has received increasing attention in the fuel cell research community for the preparation of catalyst layers of fuel cell electrodes. Electrospray is a powerful technique that can boost PEMFC performance using low catalyst loadings and help to solve some of the main limitations of this technology, such as water management and mass-transport limitations. Additionally, it is an easily scalable technique, requires low capital investment, and can effectively reduce platinum catalyst losses associated with the classical deposition methods.

The electrospray deposition technique is a breakthrough for the deposition of catalyst layers of PEMFC. Departing from conventional Pt/C and ionomer ink compositions, without requiring any other additive, electrospray produces catalyst layers with macroporosity and hydrophobicity that optimize the water interaction and mass-transport properties in the electrodes of the cells. In the cathodic electrode, the electrosprayed catalyst layers increase the cell performance by an average of 20−25% in peak power density under the standard testing conditions. Water management by the electrosprayed cathodic catalyst layers allows for higher current densities and stability of the cells.

A summary of the most relevant properties of electrosprayed catalyst layers measured ex situ and the most remarkable improvements reported in fuel cell operation is presented in Table 1. In this table, values were selected by prioritizing studies that compared electrosprayed layers with conventional layers using the same experimental setups and conditions.

In perspective, by playing a role in the fundamental and technical aspects of electrodes and MEA preparation, the electrospray deposition technique may contribute to palliating some of the main problems faced in the deployment of PEMFC related to cost and durability. For fundamental research studies, electrospray provides a method for electrode fabrication with high control and reproducibility that can be easily engaged in systematic studies of new catalysts, ionomers, supports, and electrode structures. The main target is the catalyst layer of the electrodes, where reproducible porous structures for fast mass transport and chemical stability are required; however, application to other parts of the PEMFC cell is also considered, like the microporous layer,[59] current collector protection,[58] and membrane deposition.[63] In this way, an integrated, additive fabrication for electrodes and MEAs is attained, which connects to technological objectives of the highest interest to use electrospray for the industrial fabrication of PEMFC electrodes. Being a low-cost method that can be used under normal ambience conditions and with the highest deposition efficiency of costly materials, its application for mass production principally relies on speeding up the deposition rates without altering the electrospray conditions. Some solutions have been proposed based on the application of multinozzle systems.[22−24] Electrospray could integrate in this way a fully additive manufacturing process for the mass production of electrodes and MEAs of the highest quality.

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