# Appendix II: Composite Nano-structured Solid Acid Fuel Cell Electrodes via Electrospray Deposition<sup>1</sup>

#### **A2.1. Introduction**

Due to their high efficiency, the possibility of cheap interconnects, and fuel flexibility, intermediate temperature fuel cells are attractive alternatives to combustion engines and could contribute significantly toward alleviating the energy crisis. Not only do solid acid fuel cell operating temperatures fall into the intermediate range, the true solid state proton conducting electrolyte provides many practical simplifications compared to existing technologies such as phosphoric acid or alkaline fuel cells.<sup>1</sup>

It is well known that most low and intermediate temperature fuel cells are performance limited by the rate of oxygen reduction at the cathode. In order to catalyze the reactions, precious metals, such as platinum are most often used. Current platinum utilization at 10 mg cm<sup>-2</sup> is not cost-effective when considering large-scale commercial applications.<sup>2</sup> Therefore, significant research efforts are needed for the discovery of non-precious metal catalysts and/or for a more efficient utilization of costly platinum. In the case of platinum, the oxygen reduction is a multistep reaction, occurring at the boundary between the electrolyte, catalyst and the gas phase—the triple phase boundary, where the simultaneous and coordinated transport of electrons, ions, and gas molecules can occur.<sup>2</sup> An increase of triple phase boundary per unit area of electrode could increase the number density of catalytically active sites and therefore fuel cell performance. The aim of the

<sup>&</sup>lt;sup>1</sup> This work was completed in collaboration with Áron Varga

presented work is to fabricate an interconnected, porous, three dimensional composite nanostructure of the electrolyte and catalyst, potentially reducing the amount of platinum necessary for a given performance.

In order to increase the number density of the triple phase boundary at the electrode, it is thought to be necessary to match the feature size of the electrolyte to that of the catalyst,<sup>2</sup> which is already commercially available in the form of 10 nm diameter nanoparticles see figure A2.1. Here, a given Pt nanoparticle can be in contact with multiple electrolyte particles, hence significantly increasing the triple phase boundary sites per Pt nanoparticle, which in turn increases their utilization or reduces the amount by weight necessary for a given performance level.

In order to reduce the size of CsH<sub>2</sub>PO<sub>4</sub> to match the Pt nanoparticle size, we have utilized electrospray. Electrospray is a widely used tool for aerosolizing a liquid.<sup>3</sup> It relies on electrostatic forces to expel micrometer sized droplets from a charged liquid. Here, a solution is pumped through a capillary, forming a cone at the capillary tip, called the Taylor cone.<sup>4</sup> The high electric field at the tip of the cone induces the emission of a fine spray of charged droplets. It is thought that as the droplets are accelerated toward the grounded substrate, evaporation of the solvent leads to charge concentration, inducing breakup of the droplet and ultimately forming submicron to nanoscale particles that can be deposited on the substrate. As a fuel cell fabrication tool, electrospray has been employed to produce dense, thin-film electrolytes for SOFCs<sup>5,6</sup> and PEMFC electrodes.<sup>7</sup> A wide range of chemical and physical parameters can be varied to tune the characteristics of the resultant structure that can range from dense thin films to porous electrodes. These parameters include solvent concentration, solution composition,

(affecting solution conductivity, surface tension, viscosity), spraying temperature, drying gas flow rate, and spray geometry (e.g., tip-to-substrate path length, spraying direction).

#### A2.2. Experimental Method

#### A2.2.1. Deposition

The electrospray apparatus used for these experiments is shown in figure A.2.2. It consists of a stainless steel capillary (I. D. 127 µm, O. D. 1.6 mm, L 50 mm) that has been machined to a point with a half angle less than the Taylor cone half angle. The sharpened end of the capillary opposes an aluminum pedestal (O. D. 25.4 mm) where the The pedestal temperature was controlled with a feedback substrate is mounted. controlled system using a heat rope. Between the capillary and the pedestal, a positive bias in the 4 to 6 kV range is applied so as to maintain a stable Taylor cone. The substrate-capillary distance can be varied between 25 to 40 mm by sliding the capillary in or out the chamber. These parts are enclosed in an aluminum housing with two plastic end caps made of Delrin (polyoxymethylene) to electrically isolate the capillary and the pedestal (the end caps limit the upper operating temperature of the system to the plastic melting point of 175°C). The housing is independently heated in a manner similar to the Visualization of the Taylor cone was achieved with two glass windows pedestal. (diameter  $\sim 12$  mm) epoxied into the side of the housing at opposite sides. The light from one window provided sufficient contrast to observe the Taylor cone directly through the second window. Two additional ports were made in the housing so that nitrogen gas could be introduced into the chamber at a fixed flow rate controlled with a mass flow controller. Nitrogen was chosen as the drying gas as it is less susceptible to electrical breakdown than a noble gas. A flow rate of 1000 sccm was chosen to aid evaporation.

The nitrogen is exhausted through a hole in the pedestal behind where the substrate rests. Before entering the housing, the nitrogen is independently heated with a third temperature controller to the same temperature as the housing. The pedestal was used to avoid dripping of excess solution onto the substrate due to common instabilities during the spraying process. It was found, that any dripping resulted in re-dissolution of the electrolyte and coarsening of the nanostructure (not presented in this paper). Holding the substrate on the pedestal was accomplished with a press-fit aluminum ring. Here, carbon paper (Toray TGP-H-120) was utilized as the substrate. It is cheap, inert with respect to CsH<sub>2</sub>PO<sub>4</sub>, and can serve as a current collector due to its high electrical conductivity. The solution was pumped via a sealed and pressurized container in order to avoid ratcheting effects present in syringe pumps. The air pressure was controlled between 0.1 and 0.2 psig obtain a flow rate of 5 and 15  $\mu$ L min<sup>-1</sup>, measured by weighing the sealed container before and after the spraying process. The current carried by the flux of charged particles to the substrate was measured by a picoammeter (Keithley 480 Digital 3.5 Digit Bench Picoammeter) connected in series between the ground wire and the pedestal. The critical parameters are summarized in table A2.1.

#### A2.2.2. Solution Properties

A series of solutions was prepared with a composition ranging from 10 to 50 mol% methanol in water.  $CsH_2PO_4$  is soluble in water and also readily dissolves in all water-methanol solutions investigated at a concentration of 10 g L<sup>-1</sup>. In separate experiments, platinum black (Alfa Aesar, Ward Hill, MA; nominal ~30 m<sup>2</sup> g<sup>-1</sup>) and platinum, nominally 40% on carbon black (Alfa Aesar Ward Hill, MA), and multiwalled carbon nanotubes (MWCNTs) were added each to the water methanol mixture.

Concentrations of 5 g L<sup>-1</sup> of platinum black and platinum on carbon nanoparticles, and of  $<1 \text{ mg L}^{-1}$  of MWCNTs were used. A stable colloidal suspension was obtained via the addition of the commonly used surfactant, polyvinylpyrrolidone (PVP; Alfa Aesar, MW 8000),<sup>11</sup> at a concentration of 20 g L<sup>-1</sup>.

#### A2.2.3. Oxygen Plasma Treatment

The surfactant polyvinylpyrrolidone (PVP) was subsequently removed from the surface of the structure with an oxygen plasma treatment to ensure active surface sites were not blocked. The radio frequency (13.56 MHz) plasma was generated by inductively ionizing an argon-oxygen gas mixture (Ar flow: 7.5 sccm, O<sub>2</sub> flow: 2.5 sccm) with a copper wire coil wound around a quartz chamber. The electrosprayed carbon paper substrate was placed on a pedestal in the afterglow portion of the plasma and treated for 4 minutes using a plasma power of 150 W with a chamber pressure of 136 mTorr. PVP removal was confirmed using infrared spectroscopy (Nicolet 860 Magna series FTIR).

#### A2.2.4. AC Impedance Measurements

Symmetric electrochemical cells have been fabricated using dense CsH<sub>2</sub>PO<sub>4</sub> electrolyte and two identical, electrosprayed carbon paper pellets as the electrode. The electrolyte was obtained by cold-pressing CsH<sub>2</sub>PO<sub>4</sub> powder for 20 minutes under a uniaxial pressure of 34 MPa.<sup>1</sup> The electrosprayed electrodes were lightly pressed onto the electrolyte by a compression holder, tightening screws via a torque wrench to avoid excessive damage of the microstructure and obtain good ionic conductivity across the interface. Two stainless steel porous plates were placed on either side of the symmetric

cell in order to give uniform gas diffusion to the surface of the electrode as depicted in figure A2.3. Impedance data was collected in a symmetric humidified hydrogen environment at 240°C with a Solartron impedance analyzer operating at a voltage amplitude of 10 mV over frequencies ranging from 10 mHz to 1 MHz. Hydrogen was supplied at a rate of 25 sccm and humidified flowing through a water bubbler held at 80°C.

#### A2.3. Results and Discussion

Initially, a three dimensional, interconnected, porous structure of  $CsH_2PO_4$  was obtained (figure A2.4.), by electrospraying an aqueous solution of  $CsH_2PO_4$ . The critical parameters are summarized in table A2.2. The average feature size was directly measured on the SEM micrograph to be circa 300 nm. The X-ray diffraction pattern of the nanostructure (figure A2.5.) confirmed no change in the CsH<sub>2</sub>PO<sub>4</sub> structure after the spraving process. A typical deposition rate of 5 mg hr<sup>-1</sup> and deposition efficiency of 50%-70% was measured by weighing the sample and solution before and after deposition with a precision balance. The sample surface coverage was complete but non-uniform. The thickness of the nanostructure ranged from 20 µm at the center of the sample to 10 µm at the edge. It is thought that the non-uniformity of the deposition results from statistical variations of the charge carried by each droplet and the radial decrease of the electric field strength. The dominant force acting on the charged droplets and particles is thought to be electrostatic in nature. Their flight path follows electric field lines and the number density of deposited particles correlates with the strength of the electric field. Experiments that varied the substrate temperature over a range from 65°C to 140°C with all parameters constant, resulted in no dramatic change of the morphology of the

nanostructure. Hence, it is thought that the fractal nature of the nanostructure is created by complete evaporation of the solvent before  $CsH_2PO_4$  particles are deposited, with deposition preferentially onto protrusions created by already deposited structures, rather than vigorous evaporation of the solvent when the droplets arrive on the substrate, creating voids.

Certain combinations of electrospray and solution parameters, see table A2.2, leads to non-complete evaporation of the solvent, and the deposition of  $CsH_2PO_4$  splats onto the substrate. A dense thin film of the electrolyte can form as shown in figure A2.6.

With exposure to atmosphere,  $C_{sH_2}PO_4$  readily absorbs water from air as it is highly hydrophilic. Its mechanical properties deteriorate,<sup>8</sup> leading to agglomeration of the nanostructure and the complete loss of its fractal nature. figure A2.7A,B show the start of agglomeration after two days in ambient conditions and the subsequent full collapse of the nanostructure with complete loss of porosity and high surface area after seven days in ambient conditions.

It has been found that cospraying with certain additives stabilizes the nanostructure. Electrospraying the colloidal suspensions of platinum on carbon, platinum black, and carbon nanotubes, stabilized with PVP resulted in similarly porous, interconnected, three-dimensional nanostructures as in the case of pure CsH<sub>2</sub>PO<sub>4</sub> solution, with the added benefit of even smaller feature size of 100 nm. Figure A2.8A-C show the stabilized nanostructures. Figure A2.8A,B depicts the platinum black and PVP stabilized structure after two days in ambient conditions and 12 hour dwell time at fuel cell operating conditions, i.e., 30% humidity and 240°C. From AC impedance measurements, we have some indication that the removal of surface PVP, deposited during the

electrospraying, enhances the electrodes' performance. On three separate samples, the impedance of electrodes with surface PVP present was ca. twice as large as of electrodes with surface PVP removed. Oxygen plasma treatment was identified to remove surface PVP but leave the morphology of the nanostructure intact. figure A2.9 shows the IR signal before and after plasma treatment. The main absorption peak of PVP at around  $1600 \text{ cm}^{-1}$  is not present in the plasma treated sample, while the extra peaks around  $2300 \text{ cm}^{-1}$  are most likely due to CO<sub>2</sub> adsorption on the sample surface.

A key finding of the presented work is the confirmation of structural stability of the nanocomposite electrodes, during normal fuel cell operating conditions. AC impedance measurements utilizing oxygen plasma treated platinum-black/CsH<sub>2</sub>PO<sub>4</sub> composite electrodes in a symmetric cell configuration over a 10 hour period show no significant electrode degradation. An electrode resistance of 4  $\Omega$  cm<sup>2</sup> was observed with a platinum loading of 0.1 mg cm<sup>-2</sup>, figure A2.10. A similar result is routinely observed for conventionally fabricated composite electrodes but with a platinum loading of 10 mg cm<sup>-2</sup>.<sup>9</sup>

#### A2.4. Summary

The viability of the cheap and scalable, hence technologically relevant fabrication method of electrospray deposition as a solid acid fuel cell electrode fabrication tool has been demonstrated. A three dimensional, porous, interconnected  $CsH_2PO_4$  nanostructure has been created with an average feature size of 100 nm. The stability of the nanostructure at fuel cell operating conditions (240°C and 30% humidity) over a time period of 10 hour has been shown. An electrode impedance of 4  $\Omega$  cm<sup>2</sup> has been achieved with a platinum loading of 0.1 mg cm<sup>-2</sup>. Further reduction of the electrolyte

feature size in order to match the size of the catalyst nanoparticles and increase the density of triple phase boundary sites, and an optimization of the electrode composition will be necessary to reach the state of the art electrode resistance reported in 2007.<sup>1</sup>



Figure A2.1. Fuel Cell Electrode Particle Size Comparison.

**1A.** Current state of the art solid acid fuel cell electrode: platinum nanoparticles with micron size electrolyte particles. **1B.** Composite electrode with equal catalyst and electrolyte particles size resulting in more catalytically active triple phase boundary sites.



Figure A2.2. Schematic of the Electrospray.

Electrospray setup using inverted geometry.

## Table A2.1. Critical Electrospray Parameters.

Critical electrospray parameters to be optimized for smaller feature size.

| Solution Properties  | Electrospray Properties  |  |
|--|--|--|
| methanol concentration<br>CDP concentration<br>solution surface tension<br>solution conductivity | solution flow rate<br>nitrogen flow rate<br>capillary to substrate distance<br>temperature |  |



## Figure A2.3. Fuel Cell Assembly.

Symmetric cell assembly.



Figure A2.4. Nano-structured CDP.

**4A.** Porous interconnected three-dimensional  $CsH_2PO_4$  structure obtained via electrospraying. **4B.** Electrosprayed  $CsH_2PO_4$  structure with average feature size of 300 nm.



Figure A2.5. X-ray Diffraction of CDP.

X-ray diffraction pattern of electrosprayed CsH<sub>2</sub>PO<sub>4</sub>.



Figure A2.6. Dense CsH<sub>2</sub>PO<sub>4</sub> Film.

Dense thin film of CsH<sub>2</sub>PO<sub>4</sub> obtained via electrospray deposition.



Figure A2.7. Effect of Aging on Nano-structure.

**7A.** Agglomeration of nanostructure after two days in ambient conditions. **7B.** Fully-collapsed CDP nano-structure after 7 days in ambient conditions.



Figure A2.8. Stabilized Electrode Nano-structure.

8A. Platinum-black and PVP stabilized composite electrode nano-structure.
8B. Platinum on carbon and PVP stabilized composite electrode nano-structure.
8C. Multiwalled carbon nanotube and PVP stabilized composite electrode nano-structure.



Figure A2.9. FTIR of Electrosprayed Electrode.

FTIR spectra of electrosprayed sampled before and after oxygen plasma treatment, confirming the removal of PVP.



### **Figure A2.10. Impedance Plot**

AC impedance spectra for electrosprayed nano-structured electrodes in a symmetric hydrogen gas and symmetric geometry configuration and a platinum loading of  $0.1 \text{ mg cm}^{-1}$ .

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