**Spontaneous formation of nanoparticles on electrospun fibers for fuel cell electrodes**

Norbert Radacsi1,2,[[1]](#footnote-1)\*, Fernando Diaz Campos3, Calum R. I. Chisholm3 and Konstantinos P. Giapis1

1Chemical Engineering, California Institute of Technology, 1200 E. California Blvd, Pasadena, CA, 91125, USA; Tel: +1 626 568 4180

2The School of Engineering, Institute for Materials and Processes, The University of Edinburgh, Robert Stevenson Road, Edinburgh, EH9 3FB, U.K.

3SAFCell Inc. 36 S. Chester Ave, Pasadena, CA 91106, USA Tel: +1 626 200 5327

ABSTRACT: **Nanofibers spontaneously decorated with nanoparticles were synthesized by nozzle-free electrospinning, showcasing the latter as a novel, inexpensive and scalable method for depositing high-surface area composites. Layers of nanofibers of the intermediate-temperature proton conducting electrolyte cesium dihydrogen phosphate, (CsH2PO4, CDP), were deposited from homogeneous undersaturated solutions of CDP and polyvinylpyrrolidone (PVP), uniformly over large area substrates. Under certain conditions, the nanofibers develop CDP nanoparticles on their surface, which increases the exposed electrolyte surface area and ultimately enhances electrocatalytic performance. Indeed, fuel cell tests on cathodes made of processed nanoparticle-decorated CDP nanofibers produced higher cell voltage, as compared to state-of-the-art electrodes.**

KEYWORDS: Solid acid fuel cell, nanostructured composite electrode, electrospray deposition, nanoparticles, decorated nanofibers

The promise of nanotechnology cannot be realized without efficient and inexpensive production of nanometer-sized objects, which must further be prevented from coalescing into larger objects devoid of nanoscale properties. This is particularly true for nanoparticles, which may possess special optical, electrical, magnetic, and catalytic properties1,2 different from those of the bulk. Thus, supporting nanoparticles to keep them apart is also necessary to take advantage of their nanoscale properties over long periods of time. Lastly, immobilizing nanoparticles makes their handling easier and safer.

Incorporation of functional nanoparticles within an electro-spun fiber is a timely topic in the field of electrospinning research3. Electrospinning is a versatile technique that uses high voltage for the production of fibers of polymers, inorganic materials, and composites, with diameters ranging from tens of nanometers to several micrometers4. Electrospinning from clear solutions tends to produce nanofibers with smooth surface, thus as-deposited composites have large surface area determined by the nanofiber diameter. One way to further increase the surface area of the composite is to place nanoparticles on the nanofiber surface5,6, a difficult task when the nanoparticles are dispersed in the solution from which the fibers are formed. While a few may end up on the skin of the fibers, most nanoparticles become embedded into the fibers, and do not contribute to the surface area. A process that ensures facile and uniform distribution of particles on the fiber surface could increase significantly the surface area of the produced composite.

We report here the spontaneous formation of electrolyte salt nanoparticles on electrospun nanofibers containing polyvinylpyrrolidone (PVP) or polyvinyl alcohol (PVA). Cesium dihydrogen phosphate (CDP) is an electrolyte used in intermediate-temperature solid acid fuel cells (SAFCs). Presently, fabrication of the cathode electrode is based on pressing micron-sized CDP powder into a porous pellet, followed up by chemical vapor deposition of a platinum-precursor to coat the exposed CDP surface with Pt. The resulting cathode structure provides the three-phase boundary needed for catalysis by covering the ionic conductor with a porous platinum network that is both electrically conductive and gas accessible. Increasing the three-phase boundary can boost performance substantially. Using smaller diameter CDP particles to form higher surface area porous electrodes runs into the particle-coalescence problem. Creating a CDP porous network by electrospray deposition provides a more resilient structure of smaller nanoparticles, which improves the power output of SAFCs7. In the present work, the interest is in depositing fibers loaded with immobilized CDP nanoparticles as an alternate method for fabricating cathode electrodes. There are several ways for decorating electrospun nanofibers with nanoparticles, such as by immersing electrospun fibers into solutions of dispersed nanoparticles, or by reducing *in situ* an appropriate precursor at the nanofiber surface, or via hydrothermal processes8–11. These methods add complexity by increasing the number of processing steps.

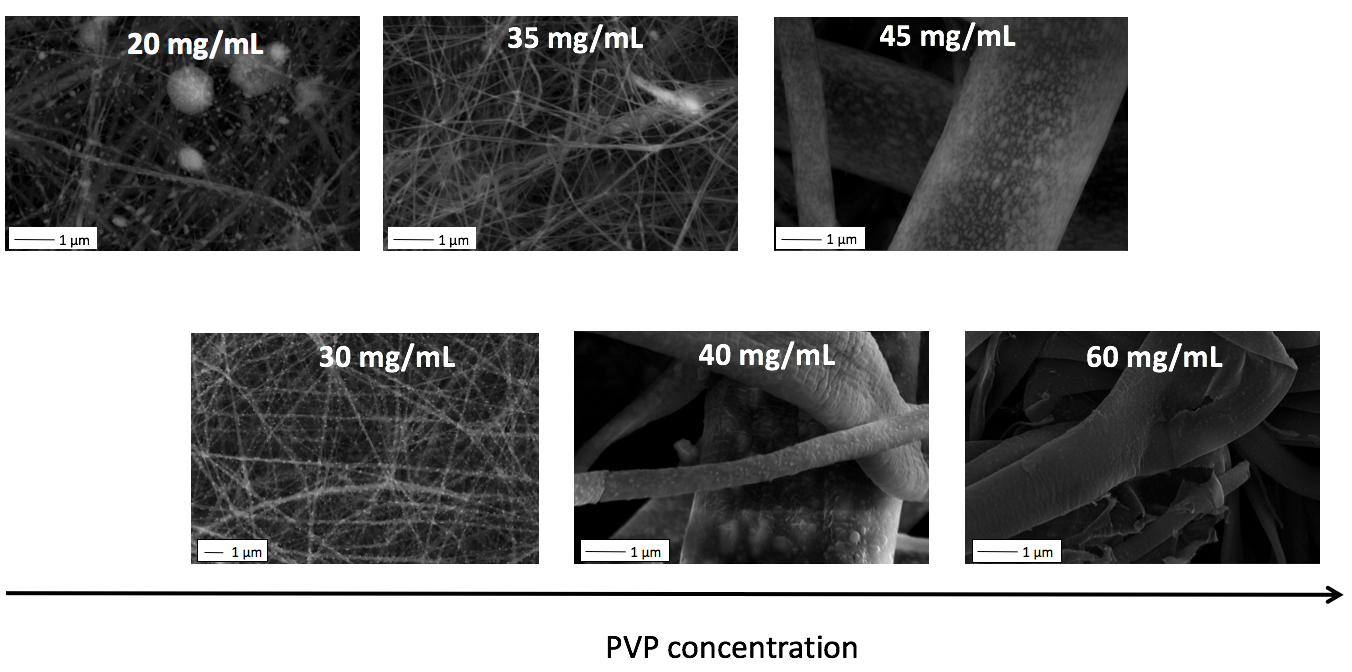
**Results**

Here we demonstrate the spontaneous fabrication of nanoparticle-decorated nanofibers in a single-step nozzle-free electrospinning process, as shown in Figure 1. Nozzle-free electrospinning provides the same product as a conventional electrospinning, but the yield of nanofibers is significantly enhanced, making it suitable for industrial production. The process starts by preparing a clear solution of aqueous CDP plus additives. The solution is fed into an electrospinning bath, where a rotating cylindrical electrode (drum) is partially immersed (Figure S1). Electrospinning commences when Taylor cones form on the surface of the drum, and electrostatic forces overcome the surface tension of the liquid solution. The produced fibers are deposited onto a biased and heated substrate. As the nanofibers cure during the deposition or afterwards, nanoparticle crystals emerge spontaneously on the surface of the nanofibers (Figure S2).



**Figure 1.** Schematic demonstration of the electrospinning process resulting in nanoparticle-decorated nanofibers from a clear solution. There are multiple Taylor cones forming on the rotating electrode immersed into the solution.

Two parameters were identified to play significant role in the process of forming nanoparticles on the fiber surface. The role of the solute concentration was considered first. The CDP salt and polymer concentrations were varied and their effect on nanostructure morphology and production rates was assessed. We tested nine different CDP concentrations: 10, 25, 30, 35, 40, 50, 60, 70 and 120 mg/mL, eleven different PVP concentrations: 12, 15, 20, 25, 27, 29, 30, 33, 35, 45 and 60 mg/mL, and two different PVA concentrations: 15 and 30 mg/mL. Interestingly, when PVP was used in the electrospinning process, the nanoparticle formation was observed only when the CDP concentration was 50 mg/mL. Increasing PVP concentration at this fixed CDP value, results in concomitant increase in fiber diameter, nanoparticle size, and nanoparticle density (Figure 2). Thus, by changing the PVP concentration, the size of the nanofibers and nanoparticles, and the spacing of such nanoparticles along the nanofiber surface can be controlled over a wide range. Using 30 mg/mL PVP concentration, nanoparticle decorated nanofiber composite mats with a mean diameter of the nanofibers being 123.9±32 nm, and the mean diameter of the nanoparticles being 104.5±28 nm can be achieved (Figure S2). The nanoparticle density is 29 particles/µm2.

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**Figure 2.** With increasing concentration of PVP in increments of 5, the electrospun fiber diameter increases. The nanoparticle size and density on the fibers also increase. Above 30 mg/mL PVP concentration no polymer beads are present. The (nano)fiber diameter is the smallest at 30 mg/mL PVP concentration.

The role of the polymer was considered next. When using PVA, the nanoparticle formation was observed only when the CDP concentration was 30 mg/mL. Polymer-type affects the nanoparticle size and density, albeit at different concentrations. The nanofiber composite mat produced from the 15 mg/mL concentration solution featured nanoparticle size of 188.5 ±43 nm, slightly lower than the one fabricated from the 30 mg/mL PVA solution, which was 218 ±69 nm (Figure 3). The nanoparticle density was higher for the lower PVA concentration (15 mg/mL), than for the higher PVA concentration (30 mg/mL): 28 vs. 17 particles/µm2, respectively.



**Figure 3.** PVA fibers decorated with CDP nanoparticles. **Left:** Mean nanoparticle size: 188.5 ±43 nm. Nanoparticle density: 28 particles/µm2. **Right:** Mean nanoparticle size: 218 ±69 nm. Nanoparticle density: 17 particles/µm2.

The formation of the multiple Taylor cones on the drum electrode surface results in rapid deposition of nanofibers over large areas (see Figure S3). An example of a 109 cm2 area CDP-PVP composite solid acid fuel cell electrode, with ~100 nm electrolyte nanoparticles on the surface on 50 – 200 nm nanofibers is shown in Figure 4. The deposition rate is around 900 mg/hr in the mentioned laboratory scale setup12.

**Figure 4.** Left: Multiple Taylor-cones emerging on the surface of the rotating stainless-steel electrode at +50 kV potential difference. Right: The fuel cell electrolyte, CDP, electrospun directly on a carbon paper from a clear CDP-PVP solution. A homogeneous and uniform film was obtained in just 10 minutes of electrospinning deposition.

BET measurements of as-spun CDP-PVP composite fibers showed a surface area of 21 m2/g compared to 2.4 m2/g, that is used for a SAFCell, Inc. standard cathode electrode. The electrospun composite mat was treated in a furnace at 300 °C for 12 hours under ambient conditions to remove the remaining solvents and part of the polymer (see figure S4). Then, platinum (Pt) nanoparticles were deposited on the electrodes by chemical vapor deposition. Electrochemical impedance and fuel cell testing of the 50 mg/mL CDP - 30 mg/mL PVP electrode at the 2“ benchmark (~15 cm2 active area) showed that the fabricated nanocomposite cathode possessed standard conductivity of 20 mΩ cm2 as shown by an area-specific resistance measurement (Figure S5). Using nanoparticle-decorated fibers for the cathode electrode improved the cell voltage at every current density as compared to the state-of-the-art SAFCell, Inc. standard (Figure 5). This constitutes a significant improvement in the field of SAFCs. The increase in cell voltage is likely due to the increase in available triple phase boundary. The peak power density showed that the fuel cell had the same stability as the SAFCELL Standard electrode (Figure S6).



**Figure 5.** The cell voltage at different current densities. The blue line represents the electrospun sample with the nanoparticle-decorated nanofibers. The black line shows SAFCell Inc.’s standard electrode. The electrospun sample has improved cell voltage at every current density.

**Discussion**

Nanoparticle formation on the fiber surface appears to require a crystallizable salt at a certain concentration. During deposition, drying, and later curing of the nanofibers, the solute is drawn out of the bulk and/or from the surface to form nanoparticle crystals on the surface of the nanofibers. Growth of the nanocrystals involves the transport of the solute into nucleated crystals. This may occur by dissolution of the solute into nanopores of the polymer nanofiber surface (e.g., by incomplete drying which leaves solvent in the fiber, or by solvent (water) supplied from ambient air during curing of the fibers). Regardless of how the solute is dispersed within the pores of the nanofiber, it has been discovered that the dissolved solute will diffuse out through the pores onto the surface of the nanofiber, where evaporation will lead to nucleation and growth of the nanocrystals. Different solvents with different boiling points play a key role in the nanoparticle formation mechanism. CDP, PVP and PVA are all soluble in water13, but the solubility of CDP in water is significantly higher (around 1300 mg/mL)14 than the solubility of the polymers. Thus, CDP is still in a dissolved form when the polymer fiber solidifies. This would still leave a film of the second solvent around the fibers, e.g., water-DMF. DMF promotes CDP crystallization. As the temperature of the nanofiber rises and water evaporates, the film breaks up, forming liquid islands on the nanofiber surface. Once supersaturation reaches its maximum, there is a driving force for nucleation from the liquid solution islands, and nanoparticles are formed on the fiber surface (e.g., via heterogeneous nucleation). As the nanofiber containing the solute dries and cures, diffusion supplies additional solute to grow the nanoparticles.

**Methods**

CsH2PO4 (CDP) was prepared by precipitation from an aqueous solution of Cs2CO3 and H3PO4, as described previously15. Cs2CO3 (99.9%), purchased from Alfa Aesar, and H3PO4 (ACS, 85% w/w aqueous solution) were combined in a molar ratio of 1:2 in aqueous solution and subsequently precipitated in methanol, followed by drying of the collected solid in air at 120 ℃. The synthesis of pure CDP was confirmed by X-ray powder diffraction. Polyvinylpyrrolidone (PVP; Alfa Aesar, Mw 1,300,000 u) and 99.8 % anhydrous dimethylformamide (DMF) were purchased from Sigma-Aldrich and 99.8% methanol from BDH. All chemicals were used without further purification. Aqueous solutions were prepared as follows: 5 g CDP and 3-6 g PVP (molecular weight: 1.3 million) were dissolved in 50 mL DI water and 40 mL ethanol (or methanol) in separate bottles, respectively. In a third beaker 10 mg polyaniline was dissolved in 10 mL DMF. When all the three beakers showed clear solutions, they were mixed together. For the PVA solution preparation, 3 g CDP was dissolved first in 50 mL DI water, then 1.5 or 3 g PVA (high molecular weight) was added to the solution. Upon observing a clear solution, 40 mL methanol was added to it. In a different beaker 10 mg polyaniline was dissolved in 10 mL DMF, and added to the main solution. Toray carbon paper without any PTFE coating was purchased from Fuel Cell Earth, USA. A home-built nozzle-free electrospinning setup was used to produce the nanoparticle decorated nanofibers. During the fabrication, the CDP concentration was fixed at 30 mg/mL, the potential difference between the electrodes was 50 kV (+45 kV DC on the rotating electrode immersed in the solution, and -5 kV DC on the collector electrode), and the distance between the top of the rotating electrode and collector was 140 mm. A 2400 W heat gun directed on the substrate provided hot air, which heated the substrate to 120 °C. The distance between the heat gun and rotating collector electrode was 192 mm. The collector electrode was rotating with 300 rpm, while the rotating electrode immersed in the solution was rotating with 3 rpm. For pictures of the setup see Figure S1 in Supplementary Information. The produced samples for the fuel cell tests were heat treated in a tube furnace that was inside a fume hood. The sample was placed in the center of a quartz tube, with both ends open. The temperature was increased in 3 steps to 300 °C using a heating rate of 5 °C/min (first 200 °C for 2h, then 230 °C for 2h, and finally 300 °C). The sample was left at 300 °C for 12h to remove the majority of the polymer (see Figure SX). Then the heat-treated product was sieved, and hand spread on a 2“ electrode for fuel cell testing (see Figure S8). The two half-cells were pressed together with 1 tons for 3 seconds. The operating conditions for the fuel cell measurements were: 0.30atm pH2O, 250 °C; flow rates of 70 sccm 100% H2 at the anode and 150 sccm air at the cathode. For visualization of the nanostructure, a ZEISS 1550 field emission scanning electron microscope (SEM) was used at 10 kV.

**Acknowledgements**

The authors thank Miguel Gonzalez of Caltech for his assistance. The information, data, or work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000495.

**Keywords:** Solid acid fuel cell, nanostructured composite electrode, electrospray deposition, nanoparticles, decorated nanofibers

**Authors’ contributions**

NR and KPG designed the experiment and co-wrote the paper. NR deposited, treated, and characterized the electrospun materials, FDC built the fuel cells, and tested the samples. CRIC interpreted the electrochemical data. KPG supervised the project.

**Competing financial interests**

The authors declare no competing financial interests.

**Materials & Correspondence:**

Dr. Norbert Radacsi. Tel.: +441316513571. E-mail address: [n.radacsi@ed.ac.uk](mailto:n.radacsi@ed.ac.uk)

**Data availability.** The data that support the findings of this study are available from the corresponding author upon reasonable request.

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1. \* \*Corresponding author. Tel.: +441316513571. E-mail address: n.radacsi@ed.ac.uk [↑](#footnote-ref-1)