

## Activity of Electrospayed Solid-Acid Nanostructures Measured by in-situ Electrochemical Atomic Force Microscopy

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Conducting atomic force microscopy (AFM), combined with cyclic voltammetry offers many advantages for measuring electrode kinetics in fuel cell systems. The use of a conducting AFM probe as a nanoelectrode eliminates the need for a reference electrode, enabling isolation and characterization of a single electrode-electrolyte interface. The feasibility of using a nanoscale probe as a fuel cell electrode has been examined for the polymer electrolyte membrane system at room temperature [1-2], and in addition, for the solid acid electrolyte system [3]. This technique, furthermore, permits studies of the spatial dependence of mechanistic phenomena while providing controllable electrode-electrolyte contact areas.

Solid acid compounds have been demonstrated as viable proton conducting electrolytes for fuel cells [4], with peak power densities of  $\sim 400$  mW/cm<sup>2</sup> at  $\sim 240$  °C [5]. Such fuel cells provide several advantages over polymer membrane fuel cells, including improved kinetics due to higher operating temperatures, impermeability to fuels, and the elimination of the need for complex water management systems.

Nanostructures of cesium hydrogen sulfate, CsHSO<sub>4</sub>, was selected as a model electrolyte to perform conducting AFM measurements for temperatures up to 145 °C. CsHSO<sub>4</sub> nanoparticles were deposited by electrospay from water-methanol solutions of 10 g L<sup>-1</sup> CsHSO<sub>4</sub>. Measurements were taken with a PicoSPM atomic force microscope (Series 4500, Agilent Technologies) equipped with an environmental chamber and hotstage set to 170 °C to attain a CsHSO<sub>4</sub> surface temperature of 150 °C. Electrochemical measurements were carried out using an externally connected potentiostat equipped with a femtoammeter and a frequency response analyzer (Modulab, Solartron Analytical). Working electrodes were platinum-coated Si-based AFM probes (MikroMasch) with spring constant of 5 N m<sup>-1</sup> and tip radius of 40 nm.

Solid acid (CsHSO<sub>4</sub>) feature sizes of 100 nm were observed by AFM (Figure 2). The complete current–voltage characteristics of the Pt | nano-CsHSO<sub>4</sub> interfaces were measured at various points across the electrolyte surface and reveal a variation of the oxygen reduction kinetics with position. Data analysis of the Pt | CsHSO<sub>4</sub> experiments, within the Butler–Volmer framework, yielded exchange coefficients ( $\alpha$ ) for charge transfer ranging from 0.1 to 0.3 as shown in Figure 3. Offset potential were observed as a function of particle size indicate its higher sensitivity to spatial heterogeneities relative to bulk CsHSO<sub>4</sub>.

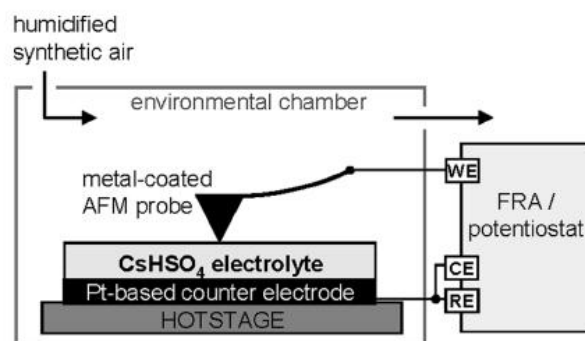


Figure 1. Schematic of conducting AFM setup detailing the catalyst (working electrode) | CsHSO<sub>4</sub> electrolyte interface | Pt (counter and reference electrode) [3]

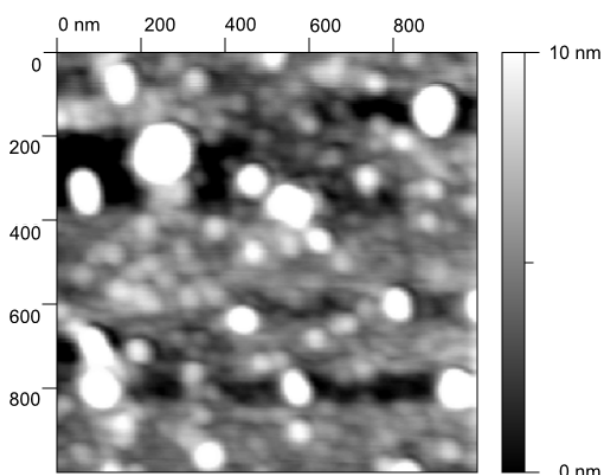


Figure 2. Topography of electrospayed cesium hydrogen sulfate nanoparticles measured by atomic force microscopy.

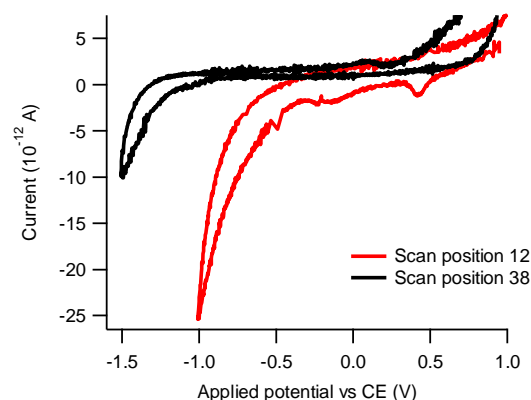


Figure 3. Particle size dependent offset bias observed by cyclic voltammetry of electrospayed CsHSO<sub>4</sub> electrolyte were carried out at  $\sim 150$  °C with a scan rate of 100 mV s<sup>-1</sup>.

### References

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