Activity of Electrosprayed 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 ~ 400 mW/cm² at ~ 240 ºC [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, CsHSO₄, was selected as a model electrolyte to perform conducting AFM measurements for temperatures up to 145 ºC. CsHSO₄ nanoparticles were deposited by electrospray from water-methanol solutions of 10 g L⁻¹ CsHSO₄. 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 CsHSO₄ 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⁻¹ and tip radius of 40 nm.

Solid acid (CsHSO₄) feature sizes of 100 nm were observed by AFM (Figure 2). The complete current−voltage characteristics of the Pt | nano-CsHSO₄ 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 | CsHSO₄ experiments, within the Butler−Volmer framework, yielded exchange coefficients (α) 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 CsHSO₄.

Figure 1. Schematic of conducting AFM setup detailing the catalyst (working electrode) | CsHSO₄ electrolyte interface | Pt (counter and reference electrode) [3]

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

Figure 3. Particle size dependent offset bias observed by cyclic voltammetry of electrosprayed CsHSO₄ electrolyte were carried out at ~ 150 ºC with a scan rate of 100 mV s⁻¹.

References