Holey Sheets: Durable Dendritic Platinum Catalysts for Fuel Cells

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Motivation—Polymer electrolyte membrane (PEM) fuel cells are an energy efficient and environmentally benign energy conversion technology for portable, stationary, and automotive applications. However, the poor durability of fuel cell components such as the membrane electrode assembly (MEA) impedes their successful commercialization. A major factor determining the lifetime of the MEAs is the loss of surface area and thus activity of the platinum-based electrocatalysts. Currently, platinum nanoparticles are supported on electrically conductive materials such as carbon black or carbon nanotubes where they are vulnerable to the processes of corrosion, dissolution, ripening/sintering, and migration and coalescence. The introduction of Sandia-developed methods for nanostructuring the Pt electrocatalyst offers novel new approaches for the enhancement of electrocatalyst stability.

Accomplishment—Recently, we reported nanostructures composed of dendritic platinum sheets, including flat nanosheets, spherical nanocages, nanowire networks, and foam-like nanospheres. We have now found that some of these Pt nanostructures show remarkable stability as electrocatalysts in PEM fuel cells (Fig. 1). Moreover, our studies suggest that the high stability of these dendritic Pt catalysts is due to the formation of persistent nanopores in the sheets. The conversion of the dendritic sheets to holey sheets was found to preserve much of their initially very high surface area. Our experiments and simulations demonstrate that the novel topography of the holey sheets renders them extraordinarily resistant to loss of surface area. Specifically, Monte Carlo simulations (Fig. 2) show that the holey sheets are resistant to sintering, hole migration, and coalescence processes that could drastically reduce surface area. The simulations also elucidate the rapid conversion of the dendritic sheets to holey sheets, with most of the holes having sizes near a critical 3-nm diameter. These holes are persistent, while larger or smaller holes are unstable. TEM images of flat dendritic sheets, taken at 2-minute intervals during heating by the electron beam, verify the predicted stability of the holes that form near the critical size and verify that the conversion from a dendrite to a holey sheet is fast and that the sheet thickness is persistent and near optimum.

An interesting parallel can be drawn between two alternative methods of preventing surface area losses due to sintering and ripening. For supported nanoparticles on carbon, small particles dissolve, allowing larger particles to grow, and resulting in lower surface area. Similar ripening occurs for the holes in nanosheets, but because of their optimum hole size they are metastable and thus preserve surface area. In addition, corrosion at the Pt-carbon interface frees particles to migrate to other particles where they rapidly coalesce, giving a large decrease in surface area. In contrast, holes can migrate and coalesce only by slow diffusion within the Pt sheets.

Significance—Materials nanoengineering is providing new opportunities for major improvements in conventional technologies such as fuel cells. Our demonstration of the possibility of sintering-resistant morphologies for metal nanostructures offers exciting possibilities for efficient, long-lived fuel cells. The simulations elucidate the principles that lead to such structures and point the way to further improvements and new applications.

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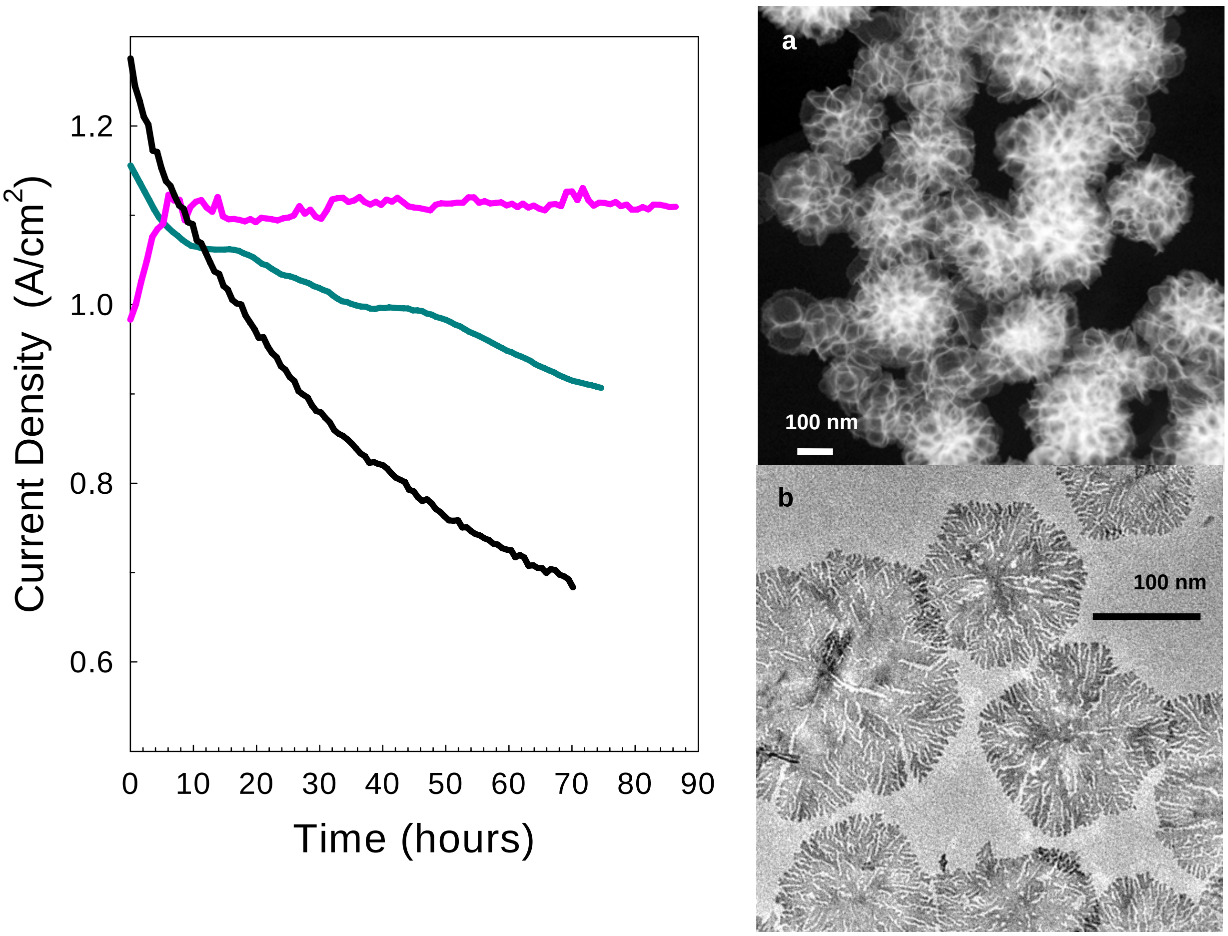

Figure 1. Durability tests of MEAs at 0.5 V for the dendritic Pt nanospheres (magenta) shown in (a), nanosheets (cyan) shown in (b), and platinum black (black). Dark field TEM images of the Pt nanospheres (a) and bright field images of the flat nanosheets (b).

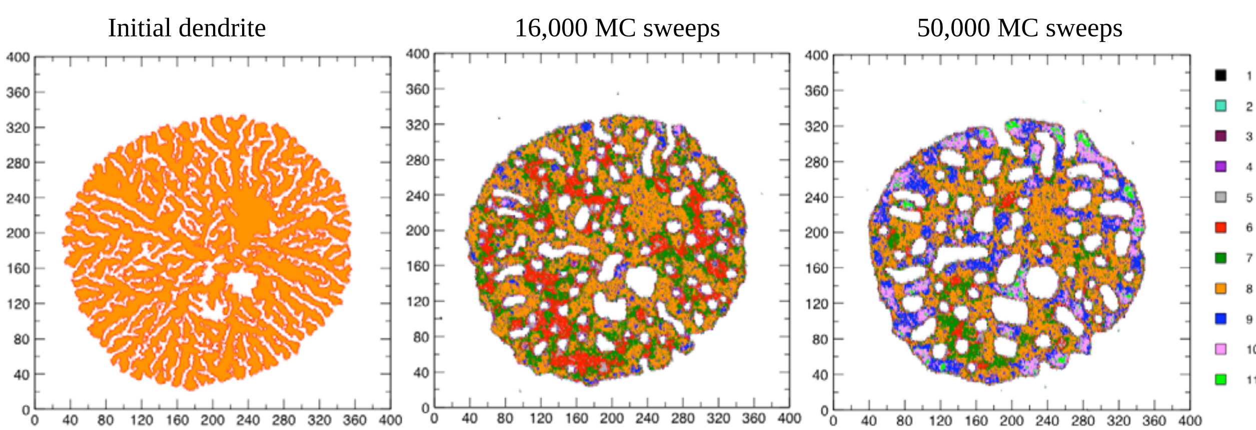

Figure 2. Monte Carlo simulations provide color-coded thickness maps of the dendrites that elucidate the dendrite-to-holey sheet conversion and some of the other unique properties of the holey sheet structures such as hole-hole interactions and specific areas of thickening and thinning.