

## Controlled Modification of Colloid-Imprinted Carbon Nanostructures for Application as PEM Fuel Cell Catalyst Supports

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Fuel cells are energy conversion devices that are capable of cleanly and efficiently converting chemical energy from the reactants (typically H<sub>2</sub> and O<sub>2</sub>) directly into electrical energy, with proton exchange membrane fuel cells (PEMFCs), which operate at relatively low temperatures (60 and 80 °C), being ideal for transportation and portable power applications. Presently, the cathode catalyst layer in a PEMFC consists of Pt nanoparticles deposited on a high surface area microporous (< 2 nm diameter pores) carbon support (typically Vulcan carbon XC-72R (VC)). Unfortunately, the pores of VC are too small to accommodate the ~3 nm Pt nanoparticles and the Pt nanoparticles therefore reside primarily on the outer VC surface. As a result, Pt deposition on VC occurs on only a fraction of the total surface area, making it difficult to achieve small, uniformly distributed Pt nanoparticles on conventional VC.

For this reason, there is significant interest in carbon materials that have much higher surface areas and larger pore diameters than VC, allowing for a more uniform distribution of Pt nanoparticles. One approach has been the use of surfactant-templated mesoporous silica to template the formation of ordered mesoporous carbon (OMC)<sup>1-3</sup>, pore diameters between 2 and 7 nm. However, these carbons suffer from transport losses at high currents, attributed to diffusion limitations in their relatively narrow pores and ohmic limitations through their thin, amorphous walls<sup>1,5,6</sup>. We have been focusing on the use of colloid-imprinted carbon (CIC) supports<sup>6-8</sup>, synthesized by imprinting a mesophase pitch carbon with silica colloids of controllable diameter, followed by carbonization and then dissolution of the silica colloids in NaOH<sup>9</sup>, with a past focus particularly on CICs having 15 and 26 nm pores. Here, we examine the effect of both larger CIC pore diameters as well as carbon wall thickness on the kinetics of the oxygen reduction reaction (ORR), after loading these carbon supports with Pt nanoparticles.

Four colloid-imprinted carbons (CICs) having pores of 15 (CIC-15), 26 (CIC-26), 50 (CIC-50), and 80 (CIC-80) nm were synthesized (all with 100% pore depths), loaded with 10 wt % Pt, and then evaluated as oxygen reduction (ORR) catalysts using 3-electrode experiments in O<sub>2</sub>-saturated sulfuric acid solutions. All four Pt/CICs were found to have a very similar electrochemically active Pt surface area (ECSA), suggesting that all four catalysts should be equally active, neglecting any CIC support effects. As the electrochemically determined ECSAs matched closely with the predicted Pt surface areas based on XRD measurements (assuming spherical Pt nanoparticles), the four Pt/CICs were all found to have close to 100 % Pt utilization.

It was also found that the ORR activity of the 10 wt. % Pt/CIC-26 catalyst is much lower than that of the other three catalysts, as seen by the 10 wt. % Pt/CIC-26 catalyst

having a higher ORR Tafel slope than expected. Gas sorption and transmission electron microscopy (TEM) have shown that, while CIC-26, CIC-50, and CIC-80 all possess an ordered (hexagonally close packed) porous structure, the CIC-15 pores are randomly arranged, leading to thicker walls for CIC-15 than would otherwise be expected. Through TEM tomography methods, the wall thicknesses of all four CICs were measured, giving average values of 10, 1.5, 10, and 25 nm for CIC-15, CIC-26, CIC-50, and CIC-80, respectively. It is suggested that, for an average wall thickness > 10 nm, the limiting ORR current is reached before resistive losses through the CIC walls become severe enough to be manifested in the observed ORR currents. For walls 1.5 nm thick (CIC-26), resistive losses are encountered at much earlier overpotentials and result in the lower ORR activity (higher ORR Tafel slope) of the Pt-loaded CIC-26 catalyst vs. the other three catalysts.

As further confirmation of this hypothesis, modelled Tafel plots have been generated based on porous electrode theory, neglecting any contribution from diffusion. These theoretical Tafel slopes clearly demonstrate that the observed trends in ORR activity of the four Pt/CIC catalysts cannot be explained based purely on differences in pore diameter. However, when the differences in wall thickness between the four CICs are also considered, the calculated Tafel slopes are found to match very well with the experimentally observed ORR Tafel slopes. Overall, this work highlights the importance of carbon wall thickness in the design of porous carbon supports.

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