

## Supercritical CO<sub>2</sub> Assisted Preparation of Pt Nanoparticles on Polyamide Aerogel Derived N-Doped Carbon Aerogels as ORR Electrocatalysts

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Carbon aerogels (CAs) obtained by the pyrolysis of polymeric aerogels, are excellent support materials for ORR electrocatalysts due to their high surface area, porosity, and electrical conductivity. Recently, heteroatom doped (N,S,B,P) CAs are gaining increasing attention since these dopants are known to improve ORR activity especially in alkaline media. Among polymeric aerogels, polyamide aerogels (PAs) prepared by the room temperature reaction of an aromatic isocyanate with pyromellitic acid (PMA). They inherently contain abundant N-functionalities distributed throughout the highly crosslinked polymer network and have high carbonization yield due to the aromatic isocyanate employed making them attractive for preparation of N-doped CAs. Metal incorporation to carbon aerogels is crucial to obtain highly active electrocatalysts, however, commonly used methods such as wet impregnation compromises the pore structure of aerogels and generally results in poor dispersion of metal nanoparticles and poor control of loading. Supercritical CO<sub>2</sub> assisted preparation of mono/bimetallic nanoparticles on various aerogels has proven to preserve the pore structure of aerogel as well as yielding an extremely fine distribution of metal nanoparticles. We have combined the advantageous properties of polyamide-driven CAs with the powerful supercritical CO<sub>2</sub> deposition technique to prepare Pt nanoparticles on N-doped CA electrocatalysts for ORR. Polyamide wet gels were prepared via the reaction of tris(4-isocyanatophenyl) methane (TIPM) and PMA in THF. After gelation and curing monolithic wet gels were washed with acetone and dried via supercritical drying with CO<sub>2</sub> to obtain PAs. PAs were then pyrolyzed at 800 °C under Ar flow (CPA). Some monoliths were also etched with CO<sub>2</sub> upon pyrolysis at 1000 °C (ECPA) to increase the surface area. Pt-CPA and Pt-ECPA composites were prepared via supercritical deposition with scCO<sub>2</sub> (SCD) followed by thermal conversion at 600 °C under N<sub>2</sub> flow. Pt content of the Pt-CPA and Pt-ECPA were determined as 28 and 33 wt.%, respectively which were quite close to the desired value of 30 wt.% showing high controllability through SCD. Bulk N content of Pt-CPA and Pt-ECPA were very close to each other (3.1 and 2.6 wt.%, respectively) and surface N content was 3.4 and 1.6 wt.%, respectively indicating that N atoms were homogeneously distributed throughout the electrocatalysts. XPS showed only metallic Pt peaks without any surface segregation suggesting that Pt nanoparticles were homogeneously distributed. XRD also confirmed the presence of Pt nanoparticles. Pt peaks were sharper for Pt/CPA and the particle size was calculated as 4.3 nm using Sherrer equation and (220) peak whereas for Pt/ECPA, the (220) peak was very broad indicating Pt nanoparticles were smaller than 2 nm. The larger Pt nanoparticles on CPA were attributed to the macroporosity and lower surface area so that Pt atoms during conversion had room to grow whereas on ECPA due to high microporosity, Pt atoms were confined in the pores. TEM images showed Pt nanoparticles were homogeneously distributed in both CPA and ECPA, even though Pt-CPA had a greater Pt nanoparticle size showing the power of SCD technique. Electrocatalytic performance of the electrocatalysts were determined via cyclic voltammetry and rotating disk electrode techniques in both acidic (0.1 HClO<sub>4</sub>) and alkaline (0.1 M KOH) electrolyte and compared to the commercial Pt-C electrocatalyst. Both Pt-CPA and Pt-ECPA electrocatalysts exhibited higher electrochemical surface area (ESA) than the commercial Pt-C in acidic media. Pt-ECPA exhibited the highest ESA due to the smallest Pt nanoparticle size. Furthermore, Pt-ECPA showed improved ORR mass activity, three times the mass activity of commercial Pt-C in acidic electrolyte whereas Pt/CPA showed only a little improvement in mass activity. Pt-ECPA also performed much better in alkaline media when compared to Pt-CPA and Pt-C with an onset potential of 0.96 V (vs. RHE) at 0.1 mA/cm<sup>2</sup> whereas Pt-CPA showed very similar performance to Pt-C indicating the importance of pore structure and evidently, Pt dispersion.

