

IMPROVING OXYGEN REDUCTION REACTION CATALYSTS FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Polymer electrolyte membrane fuel cells include proton exchange membrane fuel cells (PEMFCs) and hydroxide exchange membrane fuel cells (HEMFCs). PEMFCs use a proton conducting electrolyte, generating an acidic environment, while HEMFCs employ a hydroxide conducting electrolyte, providing a basic environment. For both types of fuel cells, the cathode's oxygen reduction reaction (ORR) is sluggish and controls the fuel cell performance. Therefore, this thesis focuses on improving the activity and durability of ORR catalysts.

PEMFCs, the more mature technology, have been commercially implemented in fuel cell cars like the Toyota Mirai and Honda Clarity. However, PEMFCs are expensive because they require a large amount of platinum (Pt) catalyst to overcome the large ORR overpotential and the rapid catalyst degradation caused by the acidic operating environment. Current PEMFCs use Pt nanoparticles supported on amorphous carbon black as ORR catalysts. These catalysts have activity and durability concerns resulting from both the Pt nanoparticles and the amorphous carbon support. The strategies to improve catalyst activity and durability include generating a support-less catalyst, increasing the durability of the catalyst support, and switching to a basic environment.

A transition to unsupported catalysts with an extended surface structure improves specific activity and durability and in turn, the cost-effectiveness of the entire fuel cell. Pt-coated copper nanowires (Pt/CuNW) exemplify these desirable catalytic traits. Improving this platform, post-synthetic processing is used to further enhance the ORR performance of the Pt/CuNW catalyst. Specifically, annealing followed by electrochemical dealloying increases activity by introducing geometric lattice tuning through Cu alloying. The resultant bimetallic PtCu-coated copper nanowire (PtCu/CuNW) catalyst yields ORR specific and mass activities of $2.65 \text{ mA cm}_{\text{Pt}}^{-2}$ and $1.24 \text{ A mg}_{\text{Pt}}^{-1}$, surpassing the respective DOE targets (SA and MA) of $0.72 \text{ mA cm}_{\text{Pt}}^{-2}$ and $0.44 \text{ A mg}_{\text{Pt}}^{-1}$. PtCu/CuNWs demonstrate enhanced durability over Pt nanoparticle catalysts by maintaining 64.1 % of its active surface area after undergoing 30,000 cycles of a potential cycling accelerated durability test (0.6 - 1.1 vs RHE). Post durability PtCu/CuNWs outperformed the DOE targets with a SA and MA of $1.50 \text{ mA cm}_{\text{Pt}}^{-2}$ and $0.477 \text{ A mg}_{\text{Pt}}^{-1}$.

Alternately, increasing catalyst support durability through the introduction of a more durable carbon support has also been accomplished. Highly graphitic and cost-effective cup-stacked carbon nanofiber supports have the potential to address the support durability concerns. Pt supported on carbon black (Vulcan XC-72) and cup-stacked carbon nanofibers as well as each carbon support alone underwent a high potential (1.4 V vs RHE) accelerated durability test in acidic and basic environments using rotating disk electrode techniques. It was shown that in all environments the cup-stacked carbon nanofiber support demonstrated higher durability and the

catalysts tested in the basic environment had better overall stability compared to their acidic counterpart.

HEMFCs have the potential for incorporating a wide variety of non-precious metal catalysts and promise to dramatically lower the fuel cell cost. One commercially available non-precious metal catalyst is Acta 4020. This carbon-based catalyst, containing 3.5 wt. % transition metals, when compared to state-of-the-art Pt/C catalysts demonstrates comparable ORR performance and superior durability while exposed to a potential cycling (0.6 – 1.1 V vs RHE) accelerated durability test. Fuel cell testing also demonstrates the feasibility of incorporating this catalyst into the cathode electrode of a HEMFC.