N-doped Graphene-Supported PtRu Direct Methanol Fuel Cell Electrocatalysts

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Significant advances in catalytic activity and durability of electrocatalytic materials are still needed for commercialization of direct methanol fuel cells (DMFC) Further development of this technology also requires improved utilization of the noble metal catalysts, such as Pt and Ru. Modification of carbon support materials with nitrogen dopants has been recognized as an attractive approach to modify catalyst-support interactions with potential benefits in catalyst utilization, catalytic activity and durability [1, 2, 3]. N-doped carbon materials have been studied as supports for Pt catalysts in hydrogen fuel cells and more recently for PtRu catalysts in direct methanol fuel cells. Most of the work has been conducted in acid media, while studies of nitrogen doping and performance of these catalysts in alkaline media is negligible.

The unique structure and properties of graphene nanosheets make them a very promising alternative to carbon black supports [4]. Effects of nitrogen doping on the properties and performance of graphene supports has been the subject of intensive interrogation. It is clear that one of the biggest challenges associated with the graphene supports is poor dispersion of this material during electrode preparation. In this talk, we will discuss our recent findings using graphene supports for Pt-Ru catalysts in both acid and alkaline media.

Graphene oxide was synthesized by modified Hummer's method [5]. Further reduction of graphene oxide was performed by means of hydrazine at room temperature. Functionalization of graphene sheets with nitrogen is performed using nitrogen ion implantation. This technique was previously employed to incorporate nitrogen functional groups onto the surface of HOPG substrates and carbon black supports with both types of functionalized substrates demonstrating improved PtRu nanoparticle stability [2]. Implantation of graphene for 1 hour using beam current of 13 mA results in incorporation of ~ 10 at% of nitrogen with a variety of nitrogen functionalities present. Deposition of Pt-Ru is conducted by sputtering from a single, alloyed, Pt-Ru target onto the carbon support material [3]. This method provides for tunability and reproducibility, as demonstrated previously on undoped and N-doped carbon black supports.

Electrochemical performance and stability of PtRu catalyst supported on undoped and N-doped graphene are evaluated using rotating disk electrode (RDE). In-house undoped and nitrogen-doped catalyst are compared to three commercially available reference materials, 30 wt% PtRu/Carbon (JM5000), 60 wt% PtRu/Carbon (JM10000) and PtRu black (JM6000). Figure 1 demonstrates that the in-house graphene-supported PtRu electrocatalyst improves precious metal utilization as compared to unsupported and supported commercial benchmarks. To facilitate systematic study of the performance of catalysts supported on graphene-based materials, their evaluation in RDE is combined with investigation of the ink dispersions using SEM analysis.

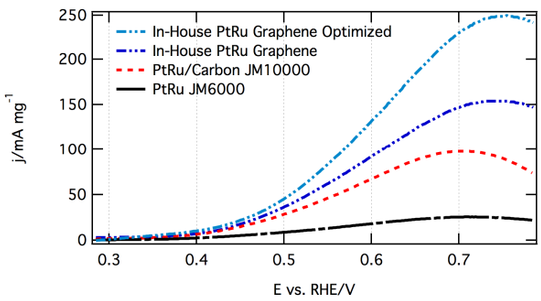

Figure1. Methanol oxidation cyclic voltamograms for PtRu electrocatalysts obtained in 0.5 M NaOH + 0.5 M MeOH, at room temperature, 10 mV/s.

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