

Performance of Nitrogen-Modified Commercial Catalysts in Acid and Alkaline Media

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For the last few decades a significant effort has been placed on improving knowledge and performance of acid based fuel cell systems. This focus has led to important breakthroughs that have improved performance and durability of this technology. Durability of Pt-based electrocatalysts can be greatly enhanced by improving catalyst-support interactions through nitrogen modification of the support structure [1-3]. It is well known that the kinetics of the methanol oxidation reaction are more facile in alkaline than in acid solutions, reducing the barriers to commercialization in alkaline systems [4]. However, very limited work has been done on understanding performance of electrocatalysts supported on nitrogen-modified carbon supports in alkaline media, mainly due to carbonation in the electrolyte, an issue that is raising less concern as research of new electrolytic membranes progresses. [5].

In this work we use one of the best-known commercial catalysts for the methanol oxidation reaction (Johnson Matthey10000, 60wt% PtRu) in its as-received state, and compare it against the same sample post-modified with nitrogen ion implantation. Compositional and morphological analyses are carried out using transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). XPS spectra confirm that ion implantation leads to the incorporation of nitrogen functionalities into the carbon support of JM1000.

Performance and durability of the unmodified and post-modified JM10000 are evaluated using cyclic voltammetry rotating disk electrode (RDE) in acid and alkaline solutions. Initial CO-stripping surface area measurements reveal consistently higher surface electrochemically-active surface area (~5 m²/g higher) for the nitrogen-modified samples compared to their unmodified counterparts. Despite the higher surface area for the nitrogen-modified samples, the initial methanol

oxidation reaction (MOR) performance (in both acid and alkaline media) is similar for both samples. Durability

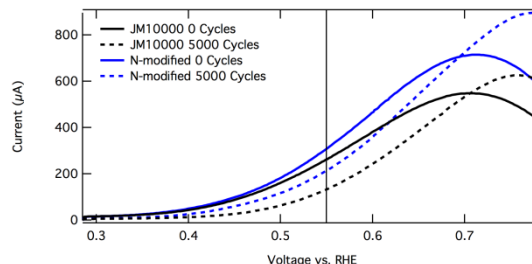


Figure 1: The MOR performance before and after cycling for JM10000 and JM10000 post modified with nitrogen in alkaline media (1M NaOH+1M CH₃OH).

studies were carried out to 5000 electrochemical cycles and intermittently interrupted to measure the changes in electrochemically active surface area as a function of cycling time. In these studies the nitrogen-doped samples consistently displayed ~30% higher surface area, regardless of media. Also, after cycling a significant improvement in performance was observed, with only ~20% loss in MOR performance at .55V vs. RHE was retained after cycling for the N-modified samples compared to ~50% reduction in performance after cycling for the unmodified sample.

These results help underscore the potential benefits of nitrogen modification in both acid and alkaline solutions. This data also shows that industry-leading benchmarks can be improved upon by a simple post-doping process.

References

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