

## Influence of Transition Metal on Oxygen Reduction Activity of Metal-Nitrogen-Carbon Electrocatalysts

Selvarani Ganesan, Nathaniel Leonard  
& Scott Calabrese Barton

Department of Chemical Engineering  
& Materials Science

Michigan State University, East Lansing, MI 48824, USA

Metal-Nitrogen-Carbon (MNC) based catalysts show superior activity and stability for oxygen reduction (ORR). Among the transition metals used in MNC catalysts, iron yields the highest ORR activity. These catalysts are synthesized by pyrolyzing iron in the form of iron acetate, melamine as a nitrogen precursor, and a carbon (Ketjenblack® 600JD) in a closed ampoule [1]. Excess iron that is unreacted during synthesis needs to be removed to avoid contamination of the fuel cell electrolyte. This is accomplished by leaching, a process that involves dispersing the synthesized catalyst with 0.5 M sulfuric acid at 80°C for five hours. However, this leaves an uncertain amount of iron in the catalyst after the leaching process. To understand the ORR mechanism on MNC catalysts it is important to know the exact quantity of iron in the catalyst, because this allows for an understanding of active sites that lead to high activity.

The present study, iron loading in MNC catalysts was varied from 1.15 wt. % to 4.6 wt. % and unreacted iron was leached from the catalysts. A quantitative estimation of Fe<sup>2+</sup> in the leached solution was performed using UV-VIS spectroscopy with 1, 10 phenanthroline penev [2]. Iron content in the catalyst was calculated based on the concentration of Fe<sup>2+</sup> in the leached solution as compared to the nominal amount of added during synthesis

The amount of iron that was leached from the catalysts with greater weight percent iron increased between the 1.15 wt. % iron and the 4.6 wt. % iron. However, the amount of iron was leached at high iron loadings was small, and did not increase proportionally with nominal iron loading (Fig. 1).

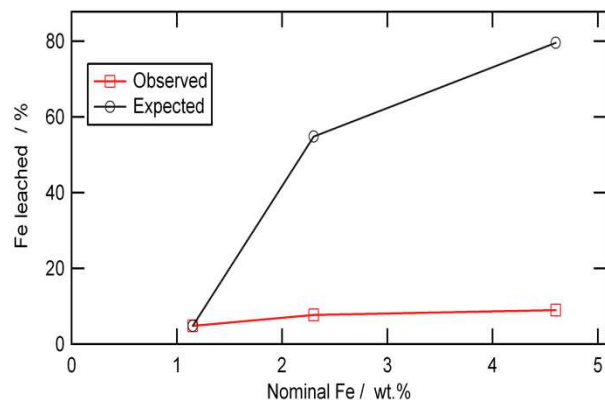
In order to understand the contribution of iron in MNC catalyst on ORR, MNC catalyst comprising 4.6 wt. % iron was leached with hot aqua regia for 24 h to remove the entire iron from MNC. The ORR performance of resulting catalyst was carried out in oxygen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> and compared with un-leached MNC catalyst (Fig. 2). In addition, ORR performance of MNC prepared without iron also included. These results clearly indicate that iron participating as one of the components of MNC's active site.

### ACKNOWLEDGEMENT

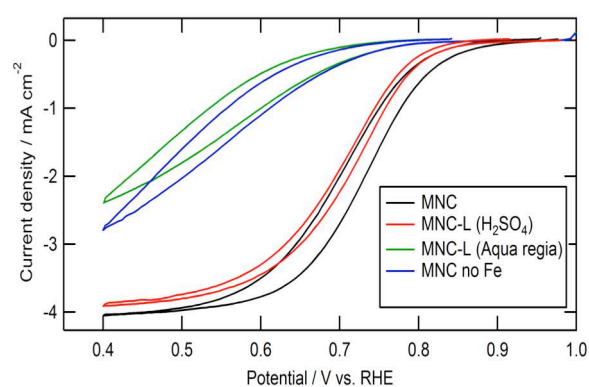
We gratefully acknowledge the partial financial support from the U.S. Department of Energy (EERE), under a Non PGM Catalyst development effort (Contract no EE 0000459) lead by Northeastern University (Sanjeev Mukerjee, P.I.).

### REFERENCES

1. V. Nallathambi, N. Leonard, R. Kothandaraman and S. Calabrese Barton, *Electrochemical and Solid State Letters*, **14**, B55-B58 (2011).
2. K. I. Penev and K. Mequanint, *Phys. Med. Biol.*, **58**, 1823-38 (2013).



**Figure 1.** Estimation of iron in the leached solution of MNC catalysts using UV-VIS spectroscopy at room temperature.



**Figure 2.** ORR performance for various MNC based catalysts in oxygen saturated 0.5M H<sub>2</sub>SO<sub>4</sub> scan rate: 5 mV/s, rotation rate: 1200 rpm at room temperature.