

Metal-nitrogen-carbon based non precious metal catalyst for oxygen reduction: Acid vs. Alkaline

Selvarani Ganesan, Nathaniel Leonard
and

Scott Calabrese Barton

Department of Chemical Engineering and Material
Science

Michigan State University, East Lansing, MI 48824, USA

The increasing cost of precious metals has accelerated efforts to replace Pt-group metals with cost-effective non-precious metal catalysts for the oxygen reduction reaction (ORR) in low-temperature fuel cells, such as Polymer Electrolyte Fuel Cells (PEFCs) and Direct Methanol Fuel Cells (DMFCs). Among the non-precious metal catalysts, carbon materials doped with nitrogen and transition metals have received considerable attention lately due to their high ORR activity, superior stability, excellent electron conductivity and low cost. Although the reasons behind the enhanced activity and stability of heat-treated metal nitrogen carbon (MNC) based catalysts remain unclear, remarkable progress has been achieved in identifying the chemical nature of their catalytic sites.

Fe-based MNC catalysts have attracted attention due to their reasonable activity and stability. In addition to the transition-metal and nitrogen precursors, the carbon-support and the method by which these catalysts are synthesized play a critical role in determining the activity of the catalyst towards ORR. In our approach, a nitrogen source (melamine), a high surface area carbon source (Ketjenblack® 600JD) and a metal precursor (iron-acetate) are pyrolyzed together in a closed container (quartz ampule), generating autogenic pressure due to melamine evaporation and subsequent decomposition. The synthesis is designed to increase the activity of the nitrogen precursor around the carbon-support while maintaining nitrogen mobility, thereby increasing the density of nitrogen-based catalytic sites [1, 2]. As nitrogen is believed to be a component of the catalytic site, increasing the surface nitrogen density could potentially increase active site density.

Iron stabilized by nitrogen on high surface area carbon structures has proven to be active for ORR, but activity in acidic environment is limited. However, in alkaline media, nitrogen doped carbon material show pronounced catalytic activity [3], which is close to or even surpasses the Pt-based catalysts. Such catalysts also exhibit selectivity towards ORR in the presence of a methanol, enabling concentrated methanol feed and increased volumetric energy density in DMFCs. In this study, comparative performance measurements were conducted for MNC catalyst in O₂-saturated 0.1 M KOH (pH = 13) and 0.1 M HClO₄ (pH=1) using a potential scan rate of 5 mV s⁻¹ and an electrode rotation rate of 1200 rpm (Figure 1). The results (alkaline medium) were normalized with respect to acid scale (pH=1) for comparison. As observed in Figure 1, the cathodic current at 0.9V vs. RHE for ORR in 0.1M KOH is 3.4 mA cm⁻², whereas in 0.1M HClO₄ electrolyte it is 0.15 mA cm⁻². For a given catalyst, a 20-fold increase in kinetic activity between acidic and alkaline media was observed.

In order to examine the methanol tolerance of MNC catalysts in alkaline electrolyte, oxygen reduction

was studied in the presence of methanol at various concentrations and results are presented in Figure 2. For comparison, ORR data for MNC in the absence of methanol are also shown. It is found that, MNC catalyst shows no activity towards methanol oxidation even with high concentration that is 6M. These results confirm that MNC catalysts possess tremendous activity towards ORR in alkaline medium, but are also highly tolerant of the presence of methanol.

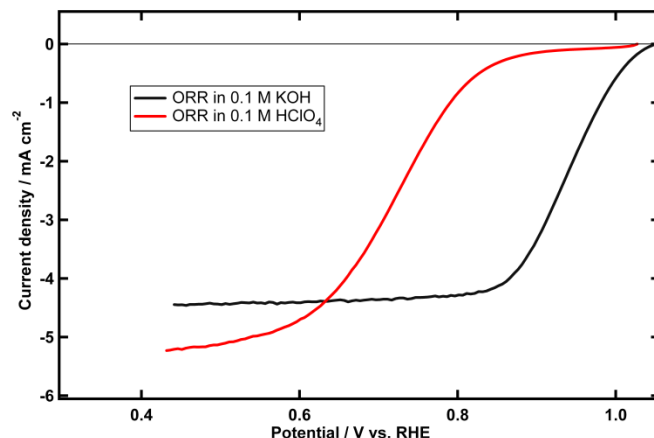


Fig. 1 ORR performance of MNC catalyst, scan rate: 5 mV/s, rotation rate: 1200 rpm at room temperature.

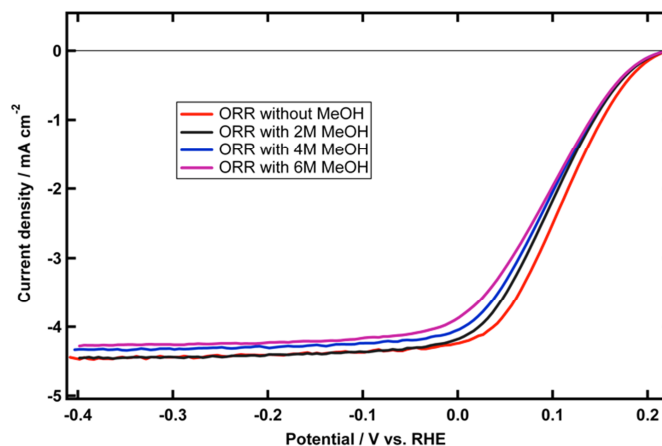


Fig. 2 ORR performance of MNC catalyst in presence and absence of methanol, scan rate: 5 mV/s, rotation rate: 1200 rpm at room temperature.

References

1. R. Kothandaraman, V. Nallathambi, K. Artyushkova and S. Barton, *Appl. Catal., B*, **92**, 209 (2009).
2. V. Nallathambi, N. Leonard, R. Kothandaraman and S.C. Barton, *Electrochem. Solid-State Lett.*, **14**, B55 (2011).
3. N. Ramaswamy and S. Mukerjee, *Advances in Physical Chemistry*, **2012**, Article ID 491604 (2012).