Scale-Up of Metal-Nitrogen-Carbon Electrocatalyst Synthesis by High-Pressure Pyrolysis

Selvarani Ganesan, Nathaniel Leonard
& Scott Calabrese Barton

Dept. of Chemical Engineering & Materials Science
Michigan State University, East Lansing, MI 48824, USA

The exploration of non-noble electrocatalyst alternatives to platinum has been of intensive interest for oxygen reduction (ORR) in fuel cells. Among the non-precious metal catalysts, Fe-based MNC catalysts have attracted attention due to their reasonable activity and stability. 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 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. As nitrogen is believed to be a component of the catalytic site, increasing the surface nitrogen density could potentially increase active site density [1, 2].

The bottleneck issues with quartz ampoule based, high-pressure MNC syntheses are weakness of quartz material at high temperature, the complexity of ampoule loading and sealing, single use of ampoules, inability to analyze process temperature, pressure, and composition, and scale-up. As nitrogen is believed to be a part of the catalytic site, increasing the surface nitrogen density could potentially increase active site density, but in a quartz ampoule, nitrogen precursor content is limited by ampoule failure. Therefore, in order to overcome the aforementioned issues, a laboratory-scale reactor was designed.

The large reactor was designed using stainless steel to sustain high pressure and temperature. Commonly, sealing is one of the critical issues with high temperature and pressure reactors, additionally, in the case of MNC catalyst preparation; there is a fair chance for organic corrosive decomposition products that may also severely affect the sealing. Therefore, to overcome the above-mentioned issues, the reactor was designed with two different temperature zones: the high temperature zone used for catalyst pyrolysis, and low temperature zone for end sealing and product analysis. To monitor the auto generic pressure inside of reactor with respect to time, an analog pressure gauge was connected at the low temperature end. To release the pressure after pyrolysis from reactor or trapping decomposed gas, a three-way valve was connected in between to reactor and pressure gauge. Schematic illustration of large reactor (laboratory scale) is given in Figure 1. During the pyrolysis process the high temperature end was inserted into the center of furnace and the low temperature end was kept outside of the furnace. To retain the exact mass ratio between melamine and the carbon of the quartz ampoule in the large reactor, a quartz rod covered the excess volume of large reactor. The total volume of reaction area was 40 ml, almost 17 times larger than the small ampoule.

Preliminary results obtained from scaling up of this approach are promising, as evident by MEA data (Figure 2), for comparison, MEA data for small scale (quartz ampoule) is also incorporated. Although, the design and scale-up up to laboratory scale are promising in the view of fuel cell performance. There is need to increase the batch size, optimize the C/N ratio to realize maximum performance and online/post analysis of decomposition products during catalyst synthesis in order to understand catalyst formation mechanism and active sites.

REFERENCES

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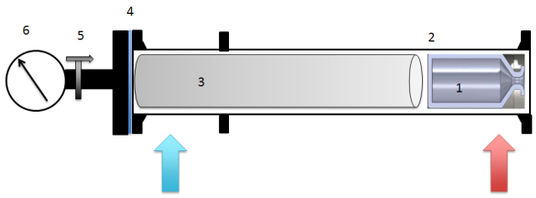

Figure 1. Schematic diagram of large reactor (1) reaction vial, (2) steel jacket, (3) quartz rod, (4) silicone gasket, (5) three-way valve and (6) pressure gauge. Arrows: in red, high temperature zone, blue low temperature zone.

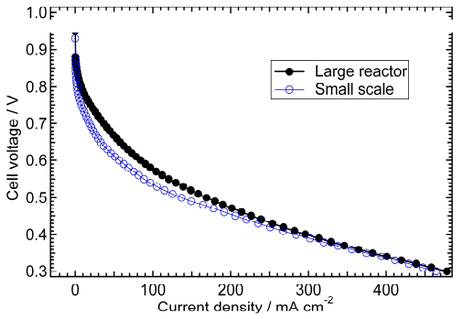

Figure 2. Comparative performance of MEAs comprising MNC catalysts prepared in large reactor and small ampoule.