Investigation of Activity and Stability towards Oxygen Reduction Reaction of Pt Catalyst with Heteroatom Doped Ordered Mesoporous Carbon Support

Bong Ho Lee[a], **Do Hyung Kim**[a], **Seung Woo Lee**[a], **Ji Yeon Lee** [a],
Yun Seok Choi[b], **Ji Man Kim**[b] **and Chanho Pak**[a,*]

[a] *Graduate Program of Energy Technology, School of Integrated Technology, Institute of Integrated Technology,*
Gwangju Institute of Science and Technology, Gwangju, 61005 Republic of Korea
[b] *Department of Chemistry, Sungkyunkwan University, Suwon, 16419, Republic of Korea*
* *Email:chanho.pak@gist.ac.kr*

Abstract: Activity and stability for oxygen reduction reaction (ORR) is significantly important for the polymer electrolyte membrane fuel cell (PEMFC), which is promising next propulsion system and has been studied continuously to increase the performance of the PEMFC. In this study, the Pt catalysts supported on different ordered mesoporous carbon (OMC) supports having heteroatom such as N or S are investigated for ORR. The stability test of activity for the ORR was conducted using accelerated degradation test. Pt/S-OMC showed the superior activity for the ORR initially and higher stability than other Pt catalyst using N-OMC and Vulcan carbon support, respectively.

Keywords: Oxygen reduction reaction, Heteroatom doped, Ordered mesoporous carbon.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is received worldwide attention because it can be used in the fuel cell electric vehicle (FCEV), which are about to start to commercialization as the ultimate eco-car having high efficiency and zero-emission. Despite many advantages of FCEV, there are still challenges to address for the wide expansion of FCEV such as stability and cost. Especially, the sintering of Pt nanoparticle induced by Ostwald ripening and carbon corrosion during the operation and startup/shutdown resulted in the degradation of the activity for oxygen reduction reaction (ORR) in the cathode. Many researchers have been studied metal oxide support to increase the stability of a support, however metal oxide supports have the limitation that small surface area and low electrical conductivity.[1]

In this study, heteroatom doped ordered mesoporous carbon (S-OMC and N-OMC) was investigated as a support for the Pt catalyst to increase the metal-support interaction, which have high surface area and ordered mesopore structure.[2] The thermal stability of Pt nanoparticles on the N-OMC and S-OMC is compared to the Pt catalyst supported on the Vulcan carbon, which is the one of the commercial carbon support. Electrochemical stability for ORR activity is investigated by the accelerated degradation test (ADT) method. The stability of ORR activity by the Pt/S-OMC is almost maintained after ADT and superior to the Pt/N-OMC and Pt/VC catalyst, which is attributed to the strong interaction between the Pt and S atom in the S-OMC.

2. Experimental

2.1. Preparation of Catalysts Pt/VC, Pt/S-OMC, and Pt/N-OMC

Chloroplatinic acid hydrate (Heesung metal) was used as a precursor and Vulcan XC-72R (Cabot, VC hereafter) was used as a commercial carbon support. Pt was deposited on different carbon supports by simple polyol method. Different carbon support was sonicated in ethylene glycol and distilled water for 30min and chloroplatinic acid hexahydrate was dissolved in distilled water. Pt precursor solution was poured into dispersed carbon solution. Then Pt precursor was reduced in 110℃.[3] After washing and drying of as-prepared Pt catalysts, Pt/VC, Pt/S-OMC, and Pt/N-OMC were heat-treated at 300, 600℃ under the hydrogen flow.

2.2. Electrochemical measurement

The electrochemical measurement was conducted using three electrode system. Pt/C ink was made that Pt/C 0.0050g was dispersed in H_2O 3.98 ml, Isopropyl alcohol 1 ml, 10wt% Nafion solution 0.02 ml.[4] After 1 hour of sonication and 5 minutes of resonance mixing, Pt/C ink was coated on rotating disk electrode (RDE, diameter = 5 mm, area = 0.196 cm^2). Pt loading was 20ug/cm^2. Activation cycle was that potential range from 0.05 to 1.2V_{RHE} and scan rate 100mV/s. Cyclic voltammetry was measured that 0.05 to 1.2V_{RHE}, scan rate 50mV/s. Accelerated degradation test was conducted 0.6 to 1.0V_{RHE}, scan rate 0.5V/s.[5]

3. Results and discussion

3.1. Thermal stability

Pt crystalline sizes were almost ~3nm in three different carbon supports from XRD pattern. After 600℃ heat-treatment of catalyst, Pt crystalline size increases just 60% in S-OMC (2.86 nm to 4.73 nm). However, Pt crystalline sizes increase 500% in Vulcan (2.12 nm to 12.75 nm) and 280% in N-OMC (2.20 nm to 8.5 nm). This result showed Pt/S-OMC has higher thermal stability than Pt/VC and Pt/N-OMC, which indicates that the S-OMC has more strong metal support interaction than the N-OMC and Vulcan carbon support.

3.2. Electrocatalytic activity and stability

Electrochemical surface area of Pt/S-OMC, Pt/N-OMC, and Pt/VC was 108 m^2/g_{Pt}, 74.48 m^2/g_{Pt}, and 83.36 m^2/g_{Pt}, respectively, which means that S-OMC provides a good dispersion of Pt nanoparticles. Before ADT, Pt/SOMC was high ORR activity than other carbon supports. After 4000 cycles of ADT, the half-wave potential of Pt/S-OMC was decreased 6mV, however in case of Pt/N-OMC and Pt/VC decreased 28mV, 13mV respectively. This results implied that S-OMC support interacts with Pt nanoparticles and this Pt-S interaction was attributed to enhance the electrochemical stability of Pt/S-OMC.

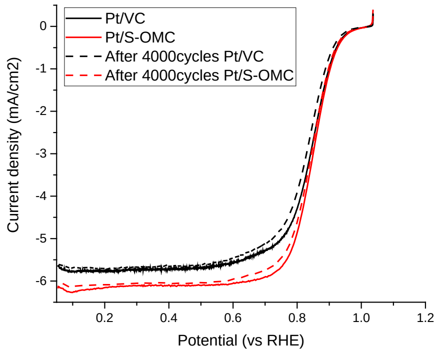

Figure 1. ORR polarization curve before and after ADT.

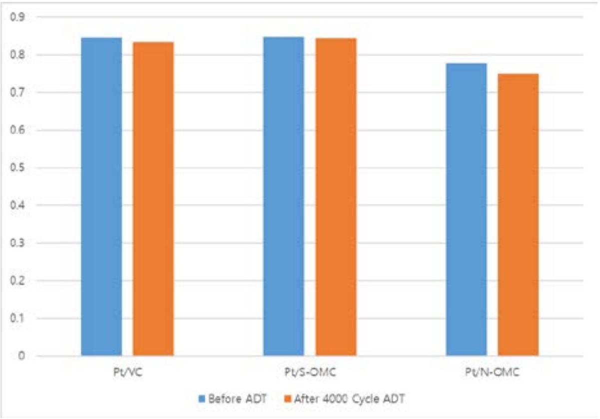

Figure 2. Half wave potential before and after ADT.

4. Conclusions

In conclusion, the thermal and electrochemical stability of different carbon supports (Vulcan, S-OMC, N-OMC) were investigated by the accelerated degradation test and heat-treatment. After 4000 cycle of ADT, half wave potential of Pt/S-OMC was decreased just 0.7%, which implies that Pt-S interaction helps to increase the stability. From the results, Pt-support interaction has an impact on thermal and electrochemical stability, among which the Pt-S interaction appears to have the positive effect on the Pt catalyst.

References

1. Z. Zhang, J. Liu, J. Gu, L. Su and L. Cheng, Energy Environ. Sci., 7(2014) 2535.
2. K. Kwon, S. Jin, C. Pak, H. Chang, S.H. Joo, H.I. Lee, J.H. Kim, J.M. Kim, Catal. Today, 1 (2011) 186.
3. D.J. You, K. Kwon, S.H. Joo, J. Kim, J.M. Kim, C.Pak, Int. J. Hydrogen Energy 37 (2012) 6880.
4. T. Reier, M. Oezaslan, and P. Strasser, ACS catal. 2 (2012) 1765.
5. E. Pizzutilo, S. Geiger, J.-P. Grote, A. Mingers, K. J. J. Mayrhofer, M. Arenz and S. Cherevko, J. Electrochem Soc, 163 (2016) F1510.