Investigation of IrRu-based OER Catalysts using Heteroatom doped-Ordered Mesoporous Carbon Supports for Reversal Tolerant Anode of PEMFC

Seung Woo Lee, Do Hyung Kim, Bong Ho Lee, Ji Yeon Lee, and Chanho Pak*
Graduate Program of Energy Technology, School of Integrated Technology, Institute of Integrated Technology,
Gwangju Institute of Science and Technology, Gwangju, 61005 Republic of Korea
**Email:chanho.pak@gist.ac.kr*

Abstract:

In fuel cell electric vehicles (FCEVs), hydrogen fuel starvation occurs under various transient operation conditions, which causes carbon corrosion in the anode leading to cell failure. To prevent cell degradation, the oxygen evolution reaction (OER) catalysts have been suggested as one of the strategies for reversal tolerant anode (RTA) strategy. In this study, IrRu-based OER catalysts using different heteroatom-doped ordered mesoporous carbon supports were investigated to improve the activity towards OER. The activity for OER is the highest in the case of S-OMC, which means the electronic structure of Ir would be changed by the increased metal-support interaction.

Keywords: Oxygen evolution reaction, Reversal tolerant anode, IrRu alloy

1. Introduction

Fuel-Cell Electric Vehicles (FCEVs) have been considered as an attractive automobile due to high energy density, high-efficiency, and zero-emission features. Despite many advantages of FCEV, there are still challenges to address for the wide expansion of FCEV such as stability and cost.

In particular, during FCEVs drive operation, the various transient condition cause hydrogen fuel starvation, leading to cell reversal voltage. This reversed high cell potential induces simultaneous water electrolysis and carbon oxidation reaction at the fuel cell anode. As one of the possible strategies for reversal tolerant anode (RTA), application of the oxygen evolution reaction (OER) catalyst has been studied to promote the water electrolysis rather than the carbon oxidation in the anode.[1-4]

In this study, IrRu-based OER catalyst[3] was investigated for the RTA. Particularly, heteroatom (N or S) doped mesoporous carbon materials (N-or S-OMC) were adapted as the OER catalyst supports with the purpose of increasing the interaction between metal and supports.[5-7] As a result, IrRu alloy supported on the S-OMC support displayed the improved OER activity compared to the activated carbon (Ketjen Black, KB 300J) and N-OMC support, which could be attributed to the strong interaction between Ir and S in the S-OMC proved by the XPS measurement.

2. Experimental

The impregnation method was used to prepare IrRu-based OER catalyst in this study. First, carbon supports were dispersed in ethanol, following metal precursor solutions were put in the mixture. Through the evaporation-drying process was used, and then powder was dried at 353K for overnight. Finally, this powder was reduced in the tube furnace under the H_2 atmosphere. The temperature was increased gradually to 573K. Through the analysis of N_2 adsorption/desorption and BJH, the specific area and pore size distribution (PSD) of the S-OMC, N-OMC, and KB300J were measured.

All electrochemical tests were measured with three electrodes electrochemical cell at room temperature with 0.1M $HClO_4$ purged with N_2. The working electrode was prepared as follows[8]: firstly, five mg of the catalyst was dispersed in a 5ml solution containing 1.00ml isopropanol solution and 10μL Nafion solution (10wt%); secondly, 10μL catalyst ink was dropped GC-RDE.

3. Results and discussion

The XRD pattern (not shown here) for $IrRu_4$ nano-particles revealed the presence of well-defined diffraction peaks; 43.85° is observed, which implies that the materials have hexagonal closed packing structure. Figure 1 indicates that S-OMC and N-OMC have ordered mesopore size compared to KB300J which has mainly microporous feature. The specific surface area for S-OMC, N-OMC, and the activated carbon respectively is as follows: $1020m^2/g$, $606m^2/g$, and $882m^2/g$. Particularly, mean pore size for sulfur doped OMC and nitrogen doped OMC is respectively 4.45nm and 5.84nm

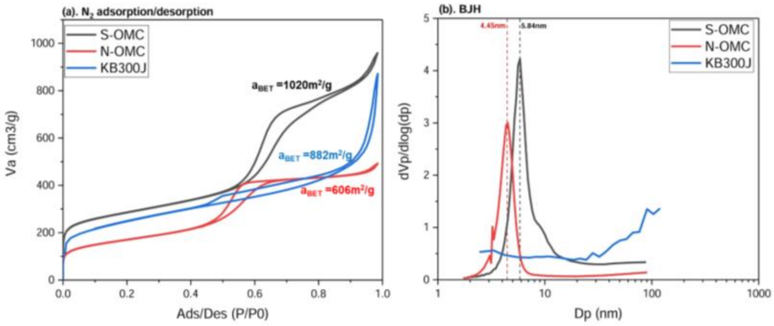

Figure 1. (a) N_2 ads/desorption graph (b) BJH plot for carbon supports

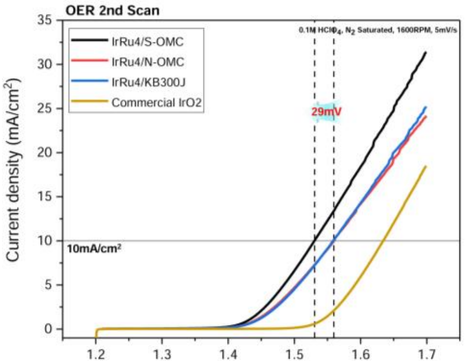

Figure 2. OER activity for $IrRu_4/C$ and IrO_2

To identify electron effect of between metal and doped-carbon supports, XPS measurements were conducted. XPS data indicated that among the OER catalysts, an active material with S-OMC has the largest binding energy shift compared to the with KB300J. In the Ir $4f_{7/2}$ XPS scan, OER catalyst with KB300J exhibited the binding energy centered at 61.15eV, which is in good agreement with values of Ir metallic state. However, the binding energy of Ir in IrRu-based/S-OMC catalyst was 62.38eV for Ir $4f_{7/2}$. It means that the strong interaction between S and Ir nano-particles in the catalyst.

In the electrochemical measurement, all of the home-made OER catalysts at $10mA/cm^2$ showed at least an over-potential of 75 mV lower than the commercial IrO_2. As shown in Fig. 2, in case of an active material with S-OMC was observed the highest OER activity. These results were explained by the electron effect which results in strong interaction between metal and supports.

4. Conclusions

In this study, IrRu alloy catalysts using various carbon supports were investigated. Ultimately, this research was conducted to apply the RTA strategy for PEMFCs. XRD pattern indicates that since all of the utilized carbon supports have a large specific surface, Ir and Ru metal were well deposited on carbon supports. XPS analysis was performed to confirm the effect of heteroatom (N or S) doped mesoporous carbon for OER activity. In particular, IrRu-based/S-OMC was observed the largest binding energy shift for Ir $4f_{7/2}$. Thanks to the strong interaction between Iridium and sulfur, IrRu alloy supported on the S-OMC support was shown the highest OER activity. In consideration durability issue, further study to improve the stability of IrRu-based/S-OMC is ongoing work.

References

1. H. Lim, W.H. Lee, Y. Jeong, and H.S. Kim, ECS. 164(14) (2017) 1580-1586
2. B.K. Hong, P. Mandal, J.-G. Oh, S. Litster, J. Power Source. 328 (2016) 280-288
3. E. You, M. Min, S.-A. Jin, T. Kim, and C. Pak, ECS Abstr., (2016)
4. C. Qin, J. Wang, D. Yang, B. Li, and C. Zhang, Catalysts Rev., 197(6) (2016) 1-21
5. C. Massue, V. Preifer, X. Huang, J. Noack, A. Tarasov, S. Cap and R. Schlogl, ChemSusChem. 10 (2017) 1943-1957
6. H.-S. Oh, H.N. Nong, T. Reier, A. Bergmann, M. Gliech, J.F. Araujo, E. Willinger, R. Schlogl, D. Teschner, P. Strasser, J. Am. Chem. Soc. 138 (2016) 12552−12563.
7. H.I. Lee, S.H. Joo, J.H. Kim, D.J. You, J.M. Kim, J.N. Park, H. Chang and C. Pak. J. Mater. Chem. 19 (2009) 5934-5939
8. T. Reier, M. Oezaslan, and P. Strasser, ACS Catal., 2 (2012) 1765-1772