Investigation on pH influence on PtRu/C catalyst prepared by polyol method for methanol electro-oxidation

Seong Ihl Woo[1*], S. Li[1], M. K. Jeon[1] and H. Daimon[2]
[1]*Dept. of Chemical and Biomolecular Eng. & Center for Ultramicrochemical Process Systems, Korea Advanced Institute of Science and Technology, Yuseong, Daejeon 305-701 (Republic of Korea)*
[2]*Hitachi Maxell Ltd., Development & Technology Division, New Device Center, Device Material Gr., Tsukuba, Ibaraki 300-2496 (Japan)*
*siwoo@kaist.ac.kr

Introduction

Direct methanol fuel cells (DMFCs) are widely studied for application in portable power sources of high power density and short recharge time. Though the easy handling of liquid fuel of methanol is the best merit of DMFC, low electro-oxidation activity of methanol in anode of DMFC is one of the major obstacles of low performance of DMFC. To effectively remove intermediate CO, PtRu alloy catalyst was introduced instead of pure Pt [1].

There are many reports on synthesis method of the PtRu catalysts such as impregnation, micro-emulsion, and colloidal methods [2]. Recently, polyol method was introduced as a new synthesis route of electro-catalysts [3]. The polyol method could provide small particle size and uniform distribution of particle size. However, detail study on synthesis condition was not studied in the previous report. In the present study, we investigated on pH influence on PtRu/C catalyst prepared by polyol method. By changing pH, particle size change was obtained and methanol electro-oxidation activity was measured.

Materials and Methods

PtRu/C catalysts were prepared by the polyol method. H_2PtCl_6 and $RuCl_3$ were used as Pt and Ru precursors, respectively. Ethylene glycol was used as a solvent and reducer. NaOH was used to adjust pH of precursor solutions. Then carbon support (Vulcan XC72R) was added to the precursor solution. Reduction was carried out at 197 oC for 3 h under N2 flowing. After the reduction, the catalyst powders were washed with DI water and ethanol. Finally, the catalysts were dried at 100 ^{o}C overnight. Catalyst loading was 40 wt% for all samples.

For characterization of the samples, X-ray diffraction (XRD), transmission electron microscopy (TEM), Thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) were used for physical analysis. For electrochemical analysis, CO-stripping and methanol electro-oxidation were performed in a glass three-electrode beaker cell.

Results and Discussion

Summary of the results are shown in Table 1. Particle size was significantly dependent on pH. Smallest particle size was obtained from pH 11. At higher or lower pHs, particle size growth was observed. Electrochemically active surface area followed the results of particle size. However, the catalyst synthesized at a pH of 3 showed largest methanol electro-oxidation activity in spite of intermediate particle size of 5 nm. This result indicates that the optimum particle size for methanol electro-oxidation is about 5 nm.

Table 1. Summary of crystalline analysis, CO stripping analysis, Pt utilization and methanol electro-oxidation of PtRu/C catalyst synthesized at different pH.

Synthesis pH	1	3	7	11	13.5
Crystalline analysis					
Particle size (nm) from XRD	7	5	2.4	1.8	3.4
Lattice parameter (Å)	3.90172	3.90192	3.90130	3.88328	3.89545
X_{Pt}(at.%)	80.4	80.56	80.06	65.64	75.38
CO stripping analysis					
CO stripping area (mC cm^{-2})	70.56	99.80	112.67	137.33	104
S_{EAS} (m^2 g^{-1})	35.00	52.50	59.24	73.25	54.70
Pt utilization					
S_{CSA} (m^2 g^{-1})	51.02	71.43	148.81	198.41	105.04
Pt utilization efficiency	0.70	0.74	0.40	0.37	0.52
Methanol electro-oxidation					
i_p (mA cm^{-2})	8.3	25.5	10.0	6.2	11.3
MA (A g^{-1})	518.75	1593.75	625.00	387.50	706.25
SA (A m^{-2})	14.82	29.06	10.55	5.29	12.94

Significance

This report shows pH influence on PtRu/C catalyst prepared by polyol method. Smallest particle size was obtained at a pH of 11, however, maximum methanol electro-oxidation activity was observed at a pH of 3, where the particle size was 5 nm.

References

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