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学位論文題目	Development of Non-platinum Electrode Catalyst for Polymer Electrolyte Fuel Cell
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## 論文内容要約

### Chapter 1 : Introduction

Polymer electrode fuel cell (PEFC) is expected to use as a household and mobile scale energy systems, because PEFC works at lower temperature ( $<373\text{K}$ ) than the other one. Since PEFC electrode catalyst is necessary to promote the reaction and generate, Platinum (Pt) and Pt alloys are well known as the best electrocatalyst of its anode and cathode electrode. However, because Pt is noble and expensive so that its resource is actually limited, the development of non-Pt catalyst materials is strongly required. For the promotion of PEFC performance of the Pt-alternative catalyst, the control in oxygen reduction reaction (ORR) kinetics is so important that the alternative materials have been studied to develop in pursuit of the similar activities as Pt electrode. As carbon (C) or nitrogen (N) share free electron with transition metal, they have similar properties to Pt<sup>1</sup>. Therefore, transition metal carbide and nitride can be used as the alternative materials. As metal combine with C, free electron transfer from metal to C. In addition, the metal lattice expands and the metal-metal distance increases by C, incorporating in the metal structure. The increased metal-metal distance causes contraction of the metal d-band. The d-band contraction leads to increase in density of states near the fermi level compare with parent metal. Therefore metal carbide has similar catalytic properties to precious metal. In addition, nanosizing of these particles is expected to enhance the catalytic activity due to the increase in surface area. From the viewpoint of interaction of the strength between metal surface and oxygen (O) on the density of state, formation of Ni and Co carbides or borides can be applied for the electrode catalysis of ORR. Their d-band centers seem to position in near Pt or Pt compounds ( $E = -3.1 \sim -2.6 \text{ eV}$ ). Therefore, Ni and Co compounds were expected to show high catalytic activity. However, carbides are generally formed by carburization in CO gas or mechanical alloying. Solid-state reaction takes a long time and wastes much energy. In addition, the products contain many defects and contaminations from the erosion of milling tools. Therefore, catalytic performance of those

materials on ORR has not been well known yet.

In this thesis, we will focus on the preparation of Ni and Co boride and carbide nanoparticles (NPs) for the electrode catalyst of ORR of PEFC as substitution material of Pt by use of liquid phase synthesis.

## Chapter 2 : Preparation of Nickel boride and carbide nanoparticles on carbon carrier and their electrode catalytic activity on oxygen reduction reaction

Ni is well known as a good hydrogenation catalyst material. In particular, Ni based catalyst used on solid oxide fuel cell (SOFC). Although Ni is also used as a part of Pt alloys in PEFC on cathode, ORR performance of Ni alone is not enough high as to use as a cathode electrode. Therefore, development of Ni catalyst activity is necessary and NiB and NiC is expected to show better ORR performance.

Ni boride NPs on C carrier (NiB) were prepared by the following procedure.  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and C carrier was dispersed into ion exchanged water.  $\text{NaBH}_4$  was added into the solution. Then, the solution was stirred for 30 min. The particles were separated by centrifugation. The crystal structure of the prepared NiB/C NPs were amorphous with composition ratio Ni : B = 90 : 10. As stable NiB structure is  $\text{Ni}_3\text{B}$  (Ni : B = 75 : 25), B ratio is small in prepared NiB structure. Because of carrier C electron negativity is bigger than B,  $\text{Ni}^+$  connected with C and B was difficult to combine with  $\text{Ni}^+$ . In addition, B also have affinity with C, B adsorbed on carrier C and reacted with O. When the ORR performance of them was evaluated, the activity was very low compared with carrier or Ni metal NPs. In addition, the catalytic life was very short because of due to their decomposition during ORR. Therefore, the obtained NiB/C NPs were not suitable to use as an electrode catalyst on ORR of PEFC.

Ni carbide NPs on C carrier (NiC/C) were prepared by the

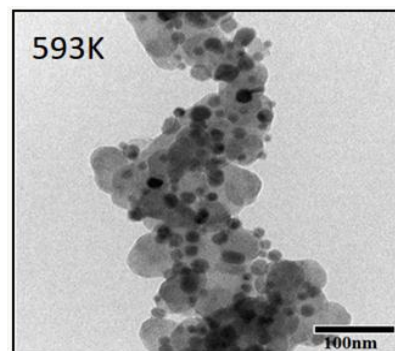


Figure 1 TEM image of as-synthesized NiC/C nanoparticles

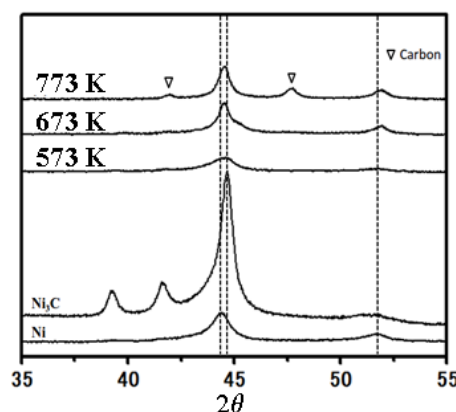


Figure 2. XRD patterns of NiC nanoparticles after heat treatment.

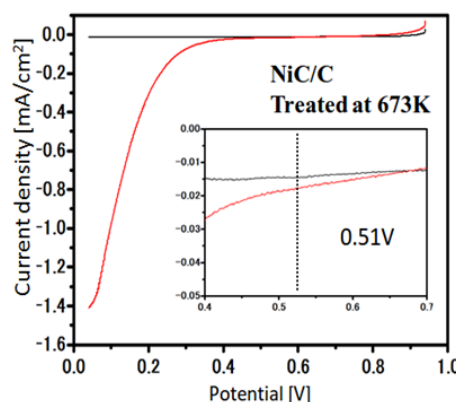


Figure 3. ORR onset potential of prepared  $\text{Ni}_3\text{C}/\text{C}$  and thermally treated  $\text{Ni}_3\text{C}/\text{C}$

following procedure.  $\text{Ni}(\text{acac})_2 \cdot n\text{H}_2\text{O}$  was added into oleylamine and then dissolved at 333 K for 30 min. C support added the solution and then heated up to 533 ~ 593 K under  $\text{N}_2$  atmosphere for 1 h. The black precipitate in the solution was separated by centrifuge and then washed with hexane and ethanol. Figure 1 shows TEM image of the prepared NiC/C NPs at 593 K. The NPs with the size of 10 - 20 nm were found well dispersed on C carrier. From XRD pattern, the crystal structure was identified as hcp- $\text{Ni}_3\text{C}$  structure. In order to enhance the catalytic activity by change of electrical structure which was operated by crystal structure, the prepared  $\text{Ni}_3\text{C}$  NPs were thermally treated in  $\text{N}_2$  atmosphere at 673 K. After treatment, main peak shift was observed on between Ni and  $\text{Ni}_3\text{C}$  phase (Fig.2). From this shift suggested that the desorption of C from  $\text{Ni}_3\text{C}$  phase and  $\text{Ni}_3\text{C}$  phase is most stable structure among Ni-C structures, the obtained Ni-C phase might become more unstable state than  $\text{Ni}_3\text{C}^2$ . ORR performance of the prepared NiC/C NPs is summarized in Figure 3. The onset potentials of the prepared Ni/C,  $\text{Ni}_3\text{C}/\text{C}$  and annealed NiC/C NPs as their ORR activities were measured by LSV method. Formation of Ni-C structure increased ORR catalytic activity (0.36V). In addition, destabilization of electrical structure of NiC structure improved ORR performance (0.51V). The d-band center was close to Fermi Energy by thermal treatment. O desorption might be enhanced and ORR performance was increased.

### **Chapter 3 : Preparation of Cobalt boride and carbide nanoparticles on carbon carrier and their electrode catalytic activity on oxygen reduction reaction**

In chapter 2, d-band center is increased by preparation of unstable structure. Increase of electron density might improve ORR activity. However, it is difficult to prepare  $\text{Ni}_2\text{C}$  and NiC structure. On the other hand, Co based boride and carbide have stable structures:  $\text{Co}_3\text{B}$ ,  $\text{Co}_2\text{B}$ ,  $\text{Co}_3\text{C}$  and  $\text{Co}_2\text{C}$ . In this chapter 3, we will focus the preparation of cobalt boride and carbide NPs. Their crystal structural stability and ORR performance are discussed. It might be higher electron density and show higher ORR performance than  $\text{Ni}_3\text{C}$ .

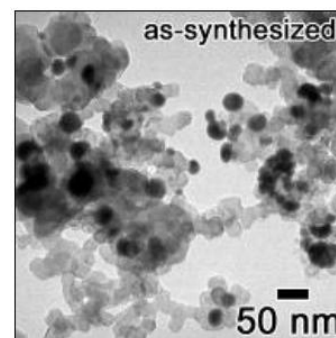


Figure 4. TEM image of CoB/C nanoparticles.

Co boride NPs on C carrier (CoB/C) were prepared by the similar condition of NiB NPs. Figure 4 shows TEM image of as-synthesized CoB/C NPs. The NPs were dispersed on C carrier. Their crystal structure was amorphous. The onset potential on ORR of the NPs was low and showed similar the potential of C carrier. In addition, the CoB NPs were decomposed to metal Co and boron oxide ( $\text{B}_2\text{O}_3$ ) during ORR.

On the other hand, Co carbide NPs on C carrier (CoC/C) prepared by thermal decomposition method

showed higher electrode catalytic activity on ORR compared with NiB, NiC and CoB nanoparticles.

#### **Chapter 4 : Durability of prepared boride carbide**

The prepared Ni and Co borides NPs were amorphous and easily decomposed in the solution during ORR. B of the NPs was easily oxidized during ORR due to weak bond between metal and B. Therefore, increase of stability of Ni-B and Co-B should be necessary to use electrode catalyst of ORR. On the other hand, Ni and Co carbide showed higher durability compared with borides. In addition, CoC NPs showed higher catalytic activity on ORR and durability than that of NiC NPs.

#### **Chapter 5 Conclusion**

In this thesis, Ni, Co based boride, and carbide NPs on C carrier were prepared by liquid phase method. ORR activity was increased by Ni-C, Co-C combines. Co<sub>2</sub>C/C showed higher ORR performance than the obtained Ni<sub>3</sub>C/C and thermally treated NiC/C.

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