

Preparation of Co₂C nanoparticles as Pt-substitution PEFC catalyst

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Polymer electrolyte fuel cell (PEFC) is generally used as a household energy system. Although Pt and Pt alloys are well known as the best electrocatalyst of PEFC, Pt is noble and rare element and then very expensive. PEFC becomes costly due to the increase in Pt use so that the generalization is prevented. Therefore, development of Pt-free electrode catalyst is now strongly required. We have focused our attention on Co₂C nanoparticles because Co₂C is one of the candidate of alternative materials of Pt. In this study, we have studied the preparation of Co₂C/C nanoparticles on carbon carrier (Co₂C/C) and their electrocatalytic activity with durability on oxygen reduction reaction (ORR).

Co₂C/C's were prepared by the following method. Cobalt(II) acetylacetonate (129 mg, 0.50 mmol) was dissolved in oleylamine (50 ml) at 50 °C for 30 min. Then, carbon carrier (50 mg) was added into the solution and well dispersed by ultrasonic irradiation. The resulting dispersion was heated up to 320 °C under an Ar atmosphere, and kept for 30 h at the temperature. Black-colored solids, thus obtained, were collected by centrifugation and washed with hexane by filtration. Vulcan XC-72, OSAB, Ketjen Black EC600JD, and multi-walled carbon nanotube (MWCNT) were used as the carbon carriers. The resulting Co₂C/C's were abbreviated as Co₂C_{vul}, Co₂C_{OSAB}, Co₂C_{Ket}, and Co₂C_{MWCNT}, respectively. The ORR activity was evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in a 0.10 M HClO₄ aq. solution. The CV measurement was swept for 10,000 cycles to evaluate the durability of the catalysts.

Fig.1 shows the transmission electron microscopic (TEM) images of the prepared Co₂C/C's. It was observed that Co₂C nanoparticles were supported on the carbon carriers as primary nanoparticle states for all

the samples. X-ray diffraction (XRD) measurement revealed that the nanoparticles had a Co₂C crystal structure. Fig.2 exhibits LSV profiles of Co₂C/C's. All the samples show ORR activity. The current densities of Co₂C/C's, measured by CV, were drastically increased by the 10,000 cycles of the sweeps. The results suggested that the surfaces of the freshly-prepared Co₂C/C catalysts might be oxidized to form an oxidized layer among the purification procedure, and the oxidized layer on the Co₂C/C catalysts was reduced by the repeated CV measurements to increase the ORR activity. It was revealed that Co₂C_{vul} showed the highest ORR activity (current density: -4.02 mA/cm²; onset potential: 0.66 V) among the present Co₂C/C catalysts. The durability tests also indicated that Co₂C_{vul} was the most stable catalyst for ORR. The current density observed for 15,000 cycles was decreased by 13% compared with the corresponding 5,000 cycles of sweeps. The decrease in the performance was smaller than that of the Pt-based catalyst (37%). In conclusion, Co₂C/C's prepared in the present study have a large potential for the Pt-alternative catalyst for PEFC.

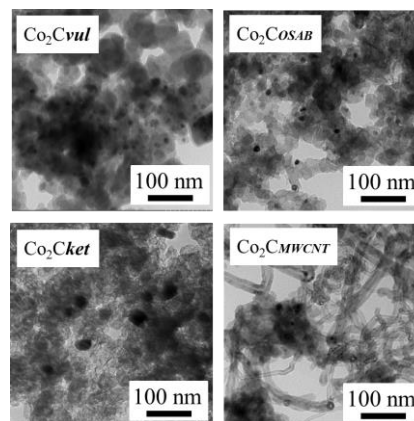


Fig. 1 TEM images of Co₂C/C's prepared in the present study.

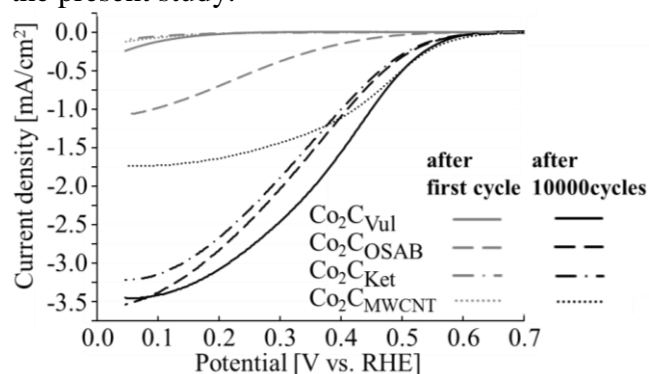


Fig. 2 LSV profiles of Co₂C/C's at the first cycle and 10,000th cycles.