

Structure and Characterizations of Co_{rich} core-Pt_{rich} shell/C Electrocatalyst for Oxygen Reduction Reaction Prepared by the Thermal Decomposition and Transmetalation Reactions

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In this study, a novel method was developed to synthesize the nanostructured Co_{rich} core-Pt_{rich} shell/C used as the electrocatalyst of ORR by the methods of thermal decomposition and the transmetalation. The electrocatalytic activity for ORR may be enhanced by the presence of transition metal located within the core due to the structure and electronic effects caused by the partial alloying and vacant d-orbital from the transition metal, and the dissolution of the transition metal is expectably reduced due to the protection by Pt on the shell. The thermal decomposition of dicobalt octacarbonyl (Co₂(CO)₈) was firstly used to prepared Co nanoparticle, and then mixed with the carbon support (XC-72) to prepare nanosized Co/C. Platinum acetylacetonate (Pt(acac)₃) was added into the solution containing nanosized Co/C particle to prepare the nanostructured Co_{rich} core-Pt_{rich} shell/C electrocatalyst by the cementation of Pt onto Co as shell (Fig. 1). The atomic ratios of Co/Pt in the preparation of Co_{rich} core-Pt_{rich} shell/C were designed to be 2.75, 5.52 and 8.25, respectively.

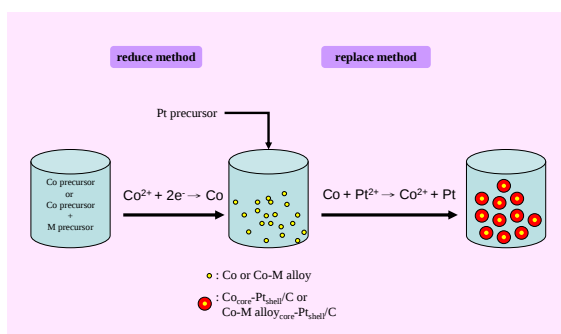


Figure 1. The procedures of synthesizing catalysts.

The particle size of Co_{rich} core-Pt_{rich} shell on the carbon support analyzed by TEM was found to be in the range of 2 ~ 5, 2~6 and 3~7 nm, respectively, when the atomic ratio of Co/Pt in the preparation was set to be 2.75, 5.52 and 8.25. A near perfect core-shell structure was demonstrated from the 0.82% alloying degree of Co_{rich} core-Pt_{rich} shell(2.75:1)/C calculated based on XRD analysis data as illustrated in Fig.1. As shown in Fig. 2, the electroactive areas of Co_{rich} core-Pt_{rich} shell/C with the designed atomic ratios of 2.75, 5.52 and 8.25 were 82.99, 106.74 and 85.89 m² g⁻¹, repetitively. Using Co_{rich} core-Pt_{rich} shell/C prepared with the various atomic ratios as electrocatalysts, the linear sweeping voltammograms and the results of ORR in 0.5 M HClO₄(aq) with saturated dissolved O₂ at 25°C were shown in the following. The open circuit potential (OCP) of ORR on Co_{rich} core-Pt_{rich} shell/C with atomic ratios of 2.75, 5.52 and 8.25 were obtained to be 0.9855, 0.9865 and 0.9815 V. The maximum mass activity (MA) and specific activity (SA)

of ORR at the overpotential of 100 mV were experimentally obtained to be 13.55 A g⁻¹ and 35.04 mA cm⁻² for Co/Pt atomic ratio of 5.52. The maximum MA and SA of the home-made Co_{rich} core-Pt_{rich} shell/C were 2.96 and 6.46 folds for comparing with the commercial Pt/C electrocatalyst (E-TEK, 20%). The results indicated that Co_{rich} core-Pt_{rich} shell/C prepared by the thermal decomposition and the transmetalation in this project exhibited a high electrocatalytic activity to ORR. The study of the mechanisms and the effect of Co on the electrocatalytic activity are our future works.

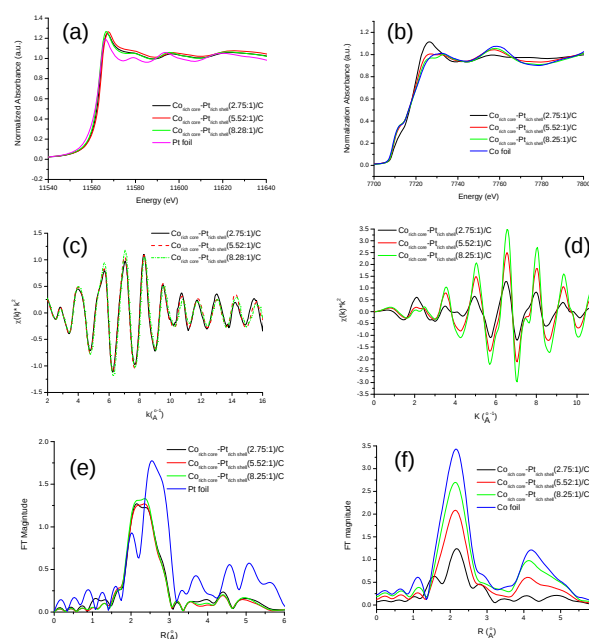


Figure 2. (a) Normalized XANES spectra near Pt L₃-edge (b) Co K-edge; (c) k^2 -weighted EXAFS data at Pt L₃-edge (d) Co K-edge; (e) FT-EXAFS spectra at Pt L₃-edge (f) Co K-edge.

As can be seen in Fig. 2 (a) that all of Pt contain in the catalysts tend to the same oxidation state with Pt foil (Pt⁰). As Fig. 2 (b) shown, the white line intensity of Co in each of catalysts decreased with the increasing Co/Pt atomic ratio but the oxidation state were partial Cobalt oxide. The result of Fig. 2 (c), (d) shown the amplitude of oscillations of catalysts on Pt L₃-edge were similar indicate the shell structure of the catalyst were similar. But the amplitude of oscillations of catalysts on Co K-edge were different due to the different core structure. As shown in Fig. 2 (e), the Pt contain in the catalyst bond with Co. The Co in the core tend to Co metal due to the interatomic distance were similar (Fig. 2 (f)).