In-Situ XAS Study: Formation Mechanism of PtPd Nanoclusters in PVP-Protected Ethylene Glycol System

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Nowadays, many efforts have been focused in the field of energy conversion devices especially on direct methanol fuel cells (DMFCs). However, still DMFC technology is hindered by two challenging issues: poor electrochemical kinetic reactions and high methanol crossover. The major problems of the cathode electrocatalyst in DMFCs are the slow oxygen reduction reaction (ORR) even on Pt due to the coverage of OH absorption on the Pt active site from the water activation in the potential region 0.7-1.0 V and mixed potential caused by methanol crossover. These practical problems greatly declined the efficiency of DMFCs during the real operations.

The promising approach to solve these problems is by designing the bimetallic nano-electrocatalysts which exhibit the high ORR activity and methanol-tolerance ability. Further, the electron configuration of bimetallic NPs was tunable by alloying with the secondary metal and changing the atomic composition. The oxygen chemisorption on the metal surface required two unpaired electrons from the d-band of the metal in the ORR kinetic mechanism. Thus, the correlation between d-band density of state and ORR activity were extensively discussed in recent studies. The “volcano” type relationship between ORR activities on the Pt monolayer deposited on various single crystal substrates (111) and calculated d-band center has been established by J. Zhang et al. NØrskov et al. proposed the d-band model correlating the changes of density of states with the bonding strength of chemisorptions. They concluded that the tensile or compressive force of Pt monolayer cause the shift in the d-band center.

At the initial stage of metal precursor, a peak between 1.3 and 2.2 angstrom attributed to the Pd-Cl bond from Pd-K edge. After the addition of sodium hydroxide, a new peak appeared at 2.6 angstrom which contribute to the Pd-Pd, indicated the reduction of palladium ions at this stage. The structure parameter was extracted from Feffit 7.0 software, and the $N_{Pd\text{-}Cl}$ is found to be 4.45 in absence of sodium hydroxide. Under basic environment, EG was released electron by the oxidation of EG (oxalic acid and oxalie aldehyde). The palladium precursor was reduced by utilizing the electron from the EG oxidation. Further, the $N_{Pd\text{-}Cl}$ decreased to 1.74 and $N_{Pd\text{-}Pd}$ is found to be 3.71 after the addition of NaOH. This confirmed the nucleation of palladium at this stage. There are two peaks between 1.8 and 3 angstrom in both Pd-K edge and Pt-L_3 edge after heating, their bond distance shifted forward compared to the Pd foil. This result reveals the presence of hetermetallic bonding at this step. (Fig.1) After adjusting the pH, the magnitude of Pt-Cl bond reduced to half of that of initial metal precursor, revealing that the $PtCl_6^{2-}$ ion was reduced to $PtCl_4^-$ ion. From the structure parameter (local coordination number), it confirm the previous observation. The peak was shifted toward comparing to the peak of Pt foil, indicated the formation of PtPd nanoclusters (shown as Fig.2).

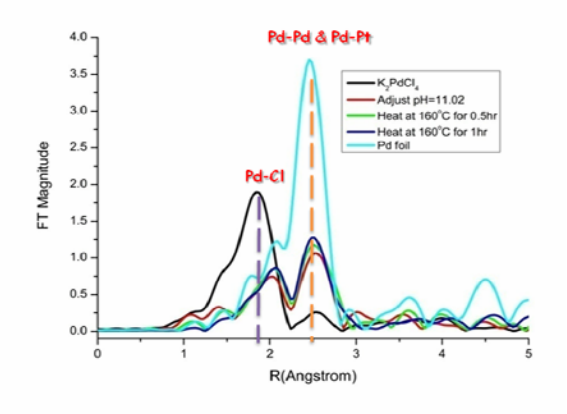

Figure 1. The FT-EXAFS spectra of home-made synthesized PtPd nanocluster at Pd-K edge during the various reaction stages.

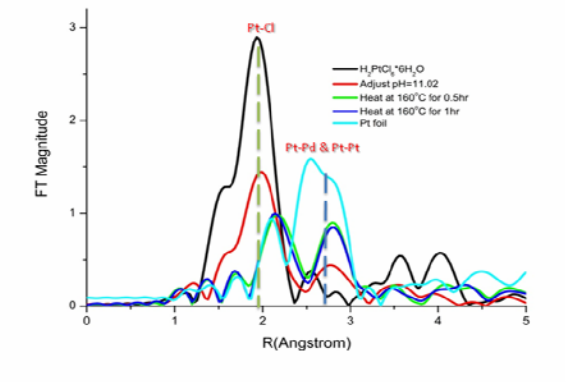

Figure 2. The FT-EXAFS spectra of home-made synthesized PtPd nanocluster at Pt-L3 edge in the various reaction stages.