

Heterogeneous Assembly of Pt-Clusters on Highly Disordered Co-Crystal for Oxygen Reduction Reaction Application

Dinesh Bhalothia^{1,2}, Che Yan², Wei Yeh², and Tsan-Yao Chen^{2,3*}

¹ Institute of Electronics Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

² Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan

³ Institute of Nuclear Engineering and Science, National Tsing Hua University, Hsinchu 30013, Taiwan.
fortuner2014@gmail.com

Abstract

Oxygen reduction reaction (ORR) at fuel cell cathode has substantial overpotential, limiting the power output efficiency. Efficient catalytic interfaces with low noble-metal loading are therefore essential to accelerate sluggish ORR kinetics. Herein, facile strategy for preparing carbon-supported Co₉₅Pt₅ nanocatalysts (NCs) with low platinum (Pt) loading and high Pt utilization via thermal reduction treatment in carbon monoxide (CO) atmosphere is reported. By cross-referencing results of microscopy, X-ray spectroscopy and electrochemical analysis, we demonstrate that the Pt atoms tend to form disordered atomic clusters capping on Co nanoparticle surface. The values of un-filled d-states (h_{T_s}) extracted from X-ray absorption near-edge spectroscopy was used to calculate the d-band vacancies of Pt. Accordingly, CoPt-CO570 (reduced in CO atmosphere at 570 K) possesses the lowest h_{T_s} value (0.302) (i.e., the lowest Pt d-band vacancies) among experimental samples, indicating a strong electron relocation from Co atoms. For providing further evidence, structural and electrochemical properties for H₂ and NaBH₄ reduction prepared CoPt NCs are compared as control. This work represents an appealing step towards the structural design of low Pt and high activity catalysts for fuel cell cathode catalysts.

Keywords - oxygen reduction reaction, fuel cell, overpotential, nanocatalysts.

Introduction

Confirmed near depletion of fossil fuels along with their serious climatic impact have become the biggest preoccupations attracting the common interest of researchers to find potential green alternatives. In this important field, fuel cells provide a bridge for efficient interconversion of chemical to electrical energy without increasing the carbon footprints¹⁻². Despite their great merits, the commercial viability of fuel cells is hampered by sluggish kinetics of oxygen reduction reaction (ORR) at cathode³. The ORR is a complex and most important chemical reaction for realizing the fuel cell technology. Cathodic nanocatalyst (NCs) consumes the highest energy input (i.e., over potential, 0.3 to 0.4 volt) among components in an alkaline fuel cell (AFC).^{1, 2, 3} Tremendous efforts (by manipulating particle shape, surface composition, heterogeneous intra-/inter- particle interfaces, and surface decoration by cluster in NC) have been devoted to overcome such a long-standing issue. Little assessments have proved to simultaneously raising both the two ends by a substantial extent due to the intrinsic trade-offs between bond strength and activation energy of material. Beyond performance considerations, material cost is the last stumbling stone in front of heterogeneous NCs in redox reaction applications. Effective strategies in solving those issues have been widely studied but promising and efficient, however, are still far away to attain commercial standards.

Experiments

Carbon-supported CoPt NCs were prepared via a deposition-precipitation (DP) method. The total metal loading with respect to carbon (i.e., metal/carbon) was maintained at 40 wt.%, whereas the Co/Pt atomic ratio was 95:5. Initially, aqueous solutions of H₂PtCl₆·6H₂O (99%, Sigma-Aldrich)

with CoCl₃·3H₂O (99%, Sigma-Aldrich) were mixed in the desired stoichiometry, co-deposited onto commercial carbon black (Vulcan XC-72R) at 340 K at pH 8 by 0.25 M NaOH, and reduced by isopropyl alcohol (IPA, ECHO Chemical). Afterwards, the as-deposited catalysts were heat-treated at given temperatures (470 or 570 K) under flowing H₂ or CO/Ar (10/90 vol.%) gas for 1 h, and named CoPt-H470, CoPt-H570, or CoPt-CO570. To prepare CoPt-NaBH₄, the reduction process of as-deposited CoPt was carried out with excessive NaBH₄. In addition, the Pt/C (46 wt.%, TKK, Tanaka Kikinzoku Kogyo) catalyst was used for comparison in this study.

The physical properties of experimental NCs are determined by cross referencing results of microscopy and X-ray spectroscopy techniques. The electrochemical measurements were carried out at room temperature using a potentiostat (CH Instruments Model 600B) equipped with a three electrode system.

Results

XRD patterns of the CoPt NCs reduced under different conditions are shown in Fig.1. For CoPt-CO570, the diffraction pattern with broad peaks suggests the co-existence of CoPt and Co phases.

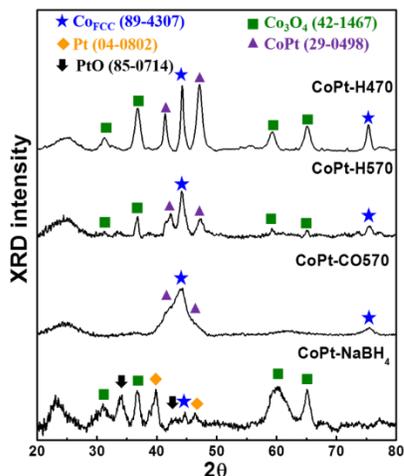


Fig. 1. XRD patterns of CoPt-H470, CoPt-H570, CoPt-CO570, and CoPt-NaBH₄ catalysts.

The electron relocation to Pt atoms is consistently revealed by the features in the XANES; where intensity (H_A) and width (W_A) of the absorption peak (white line, i.e., peak A) illustrate respectively to the extent of the electron vacancy and splitting of the 5d_{5/2} orbital. Shown in Fig. 2, the highest H_A is attributed to the largest extent of Pt-O chemisorption (or PtO) in CoPt-NaBH₄ among experimental NCs. Such a phenomenon is consistent to the results of XRD again proving the co-precipitation of Pt in CoO₂ surface. Among all experimental NCs, the lowest H_A is the second indication proving the largest extent of electron relocation to Pt atoms in CoPt-CO570.

Results of d-band vacancy in experimental NCs further elucidate the mentioned scenarios above. Such a parameter can be estimated by using a well-known h_{TS} value by using the integration areas of deviation spectra at Pt L₃-edge. The h_{TS} values (which correspond to the fractional change in the number of d-band vacancies relative to the reference material (f_d)) can be estimated by:

$$f_d = \frac{\Delta A_3 + 1.11 \Delta A_2}{(A_3 + 1.11 A_2)_r} \quad (1) \text{ and}$$

$$\Delta A_2 = A_{2s} - A_{2r}, \text{ and } \Delta A_3 = A_{3s} - A_{3r} \quad (2);$$

where A_2 and A_3 are the areas under the Pt L₃ absorption edges of the sample (s) and reference (r) material. The d-band vacancies of Pt in the sample can be calculated using the equation of the relation. The value of unfilled d-states in the reference material (h_{Tr}) was evaluated from band structure calculations to be 0.3.

$$h_{TS} = (1 + f_d) h_{Tr} \quad (3)$$

According to the literature, a higher alloying degree decreases the h_{TS} value by local electron relocation and localization around Pt atoms and promotes the ORR performance. Catalysts with lower h_{TS} values had lower unfilled d-states, weaker bonds, less Pt oxide formation, and less-pronounced white lines, leading to the promotion of ORR kinetics. Pt/C had the highest h_{TS} value and the lowest ORR activity among all catalysts. On the other hand, h_{TS} values of CoPt-CO570 and CoPt-H470 were as low as 0.302 and 0.304, suggesting that they have more d-band electrons transferred from Co to Pt, leading to higher ORR activities than Pt/C.

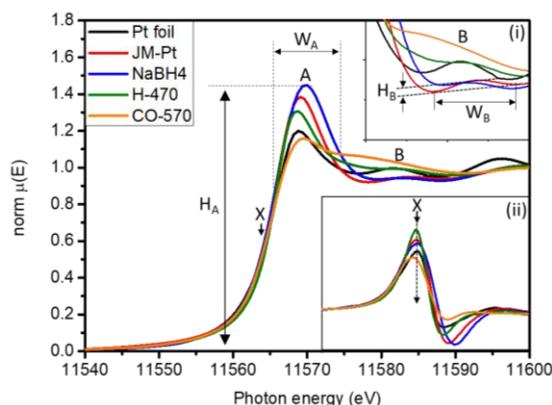


Fig. 2. XAS spectra of experimental CoPt NCs in near-edge region.

Linear sweep voltammetry (LSV) curves of CoPt NCs have been shown in Fig.3. Accordingly, CoPt-CO570 NC shows highest onset potential.

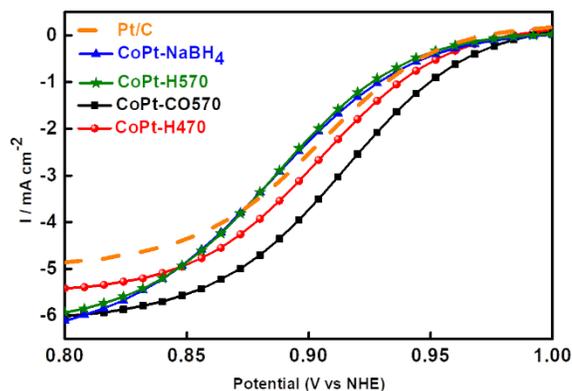


Fig. 2. XAS spectra of experimental CoPt NCs in near-edge region.

Discussion

In this study, a novel annealing reduction by the strong chemical bond of CO to Pt is developed to synthesis the CoPt nanocrystal with atomic Pt clusters decorating in Co metal core surface.

Acknowledgement

The authors express their gratitude to the staff of National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan for the help in various synchrotron-based measurements. T.-Y. Chen acknowledges the funding support from the Ministry of Science and Technology, Taiwan (MOST 106-2112-M-007-016-MY3).

References

- [1] B.C. Steele, A. Heinzl, Nature. 414 (6861):345-52 (2001).
- [2] J.K. Nørskov, J. Rossmeisl, A. Logadottir, and L. Lindqvist, J.Phys.Chem.B, 108 (46),pp 17886–17892 (2004).
- [3] N.Markovic, H. Gasteiger and P.N. Ross, J. Electrochem. Soc. 144(5): 1591-1597 (1997).