

Semi Quantized Charge Enables High-Rate Oxygen Reduction Reaction Performance of NiO_x-Monomers Anchored Co@Pd Nanoarchitecture

Dinesh Bhalothia¹, Che Yan¹, and Tsan-Yao Chen^{1,2*}

¹ Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan

² Institute of Nuclear Engineering and Science, National Tsing Hua University, Hsinchu 30013, Taiwan.
fortuner2014@gmail.com

Abstract

The prohibitive cost and scarcity of the noble-metal catalysts needed for catalyzing the oxygen reduction reaction (ORR) are major limitations for the wide-spread market introduction of fuel cell technology. Identifying materials design with expected properties can accelerate the development of efficient and economical transition-metal-based catalysts. In this context, we proposed novel tri-metallic nanocatalysts (NCs) consisting of NiO_x monomers decorated Pd nano-islands over Co-oxide base (namely CPN). To the optimum case, as-prepared CPN nanocatalyst (NC) with 1 wt.% of Ni-loading (i.e. CPN-1) exhibits an outstanding mass activity (MA) of 16184.6 mA_{mgNi}⁻¹, which is 241.5-times improved as compared to that of commercial J.M.-Pt/C (67.1 mA_{mgPt}⁻¹) NC. By cross-referencing the results of the spectroscopic, microscopic and electrochemical analysis, we demonstrated that such an enhanced performance is attributed to the quantum confinement of charge, resulting in the lower energy barrier of O₂ splitting and subsequent relocation of O-atoms on the CPN NC surface.

Keywords - oxygen reduction reaction, nanocatalysts, quantum confinement, mass activity.

Introduction

Fuel cells are accepted as the ultimate solution to combat an ever-growing energy imbalance along with adverse climatic issues and it is estimated that they will bring about an energy revolution when commercialized [1]. However, the intrinsically sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode counterpart severely restricts the overall performance of fuel cells and hinder their commercial viability. The noble-metal (especially Pt) based nanocatalysts (NCs) are considered as “the Holy Grail” to boost the ORR kinetics [2]. Unfortunately, the high cathodic overpotential owing to the strong adsorption of oxygen species [3], the varying activities with different exposed facets [4], and so on diminishes its capability in redox applications. Regardless of performance considerations, the obstinately high price and scarcity are key issues detaining Pt-based NCs at fuel cell cathode. Despite various notable assessments proposed in past decades [5-6], the omnipotent NC with the reconcilable balance between performance and economic considerations is still in vain. To this end, herein, we developed a brand-new next-generation Pt-free nanoarchitecture containing NiO_x monomers decorated Pd nano-islands over Co-oxide base underneath (namely CPN) via wet chemical reduction method on carbon black support. As-fabricated CPN NC with a metal loading of 1 wt.% outperforms the commercial J.M.-Pt/C NC with a record high mass activity (MA) of 16184.6 mA_{mgNi}⁻¹.

Experiments

NiO_x monomers decorated Co@Pd (CPN) NCs were fabricated via wet chemical reduction method with proper sequence and reaction time controls on metal ions adsorption and subsequent reduction. Prior to NCs synthesis, carbon support (UR-XC72, UniRegion Bio-Tech.) is acid-treated in 4.0 M H₂SO₄ at 80°C for 6 hours

for the sake of strengthening the attachment of metallic crystals on their surface. Then after, the metal ions were reduced sequentially in a controlled environment by using NaBH₄ as a reducing agent.

The physical properties of experimental NCs are determined by cross-referencing the 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

The atomic-level configuration of experimental NCs is unveiled by utilizing the results of Co, Pd and Ni K-edge XAS analysis. For instance, **Figure 1a** presents the XANES spectrum of CPN NCs compared with standard Co@Pd. Accordingly, the two absorption peaks “M” and “N” are corresponding to the 1s → 5p and 1s → 4f electron transitions, respectively. The variable intensities of absorption edges in the Pd K-edge spectrum indicate the different extent of charge relocation between Pd and the neighboring atoms (Ni in the present study) together with the extent of chemisorbed oxygen on the Pd atoms. In this context, the highest absorption peaks intensity for the CPN-1 NC implying the lowest confinement of Pd nano-islands by NiO_x monomers, which is obvious due to the only 1 wt.% loading of Ni. Besides, the position of the inflection point (I_p) is attributed to the oxidation state of the Pd atoms. Consequently, all the CPN NCs exhibits a similar inflection point position to that of Co@Pd reflecting their metallic characteristics.

Moreover, looking into the FT-EXAFS spectra (**Figure 1b**) at Pd K edge, it is evident that the intensity of the Pd-O (Peak O in **Figure 1b**) is highest for CPN-1 NC, which is consistent with former XANES analysis, indicating that the oxygen chemisorption on Pd atoms in CPN-1 NC is highest.

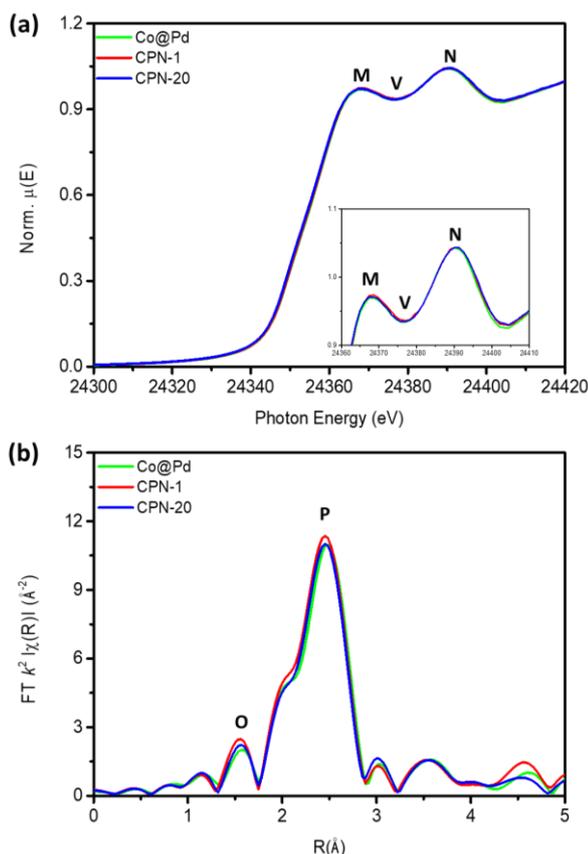


Fig. 1. X-ray absorption spectroscopy of CPN NCs compared with the control sample. (a) XANES and (b) FT-EXAFS spectra of CPN NCs at Pd k-edge, compared with Co@Pd.

The electrocatalytic ORR performance of CPN NCs was evaluated by linear sweep voltammetry (LSV) analysis in 0.1 M KOH (pH:13) electrolyte solution. **Figure 2a** depicts the LSV curves of CPN NCs compared with Co@Pd and commercial J.M.-Pt/C catalyst. Accordingly, the half-wave potential ($E_{1/2}$) and onset potential (V_{oc}) for CPN-1 NC is 0.873 and 0.924 V vs RHE, respectively. These values are highest among experimental NCs under investigation, indicating a lower energy barrier for ORR pathways and thus higher electrocatalytic ORR performance of CPN-1 NC. To further assess the ORR activity, mass activities (MA) (**Figure 2b**) of experimental NCs are obtained via normalizing the kinetic current densities (denoted as J_k) at 0.85V vs. RHE with respect to the Ni-loading (in case of CPN NCs). Unsurprisingly, the CPN-1 NC demonstrates an outstanding MA of 16184.6 $\text{mA mg}_{\text{Ni}}^{-1}$ at 0.85 V vs. RHE. Compared to the commercial J.M.-Pt/C catalyst (67 $\text{mA mg}_{\text{Pt}}^{-1}$ 0.85 V vs. RHE), this MA value is improved by 241.5-times, with an ultra-low Ni-loading of ~1 wt.%. such an enhanced MA is attributed to the unique charge confinement on NCs due to discrete energy levels of Ni atoms. Besides, a sharp fall down in MA is observed when the amount of the “Ni” is raised to 20 wt.% (similar to Pt-loading in J.M.-Pt/C), which can be rationalized by the blockage of surface-active sites via formation of a NiOx thin layer on catalysts surface.

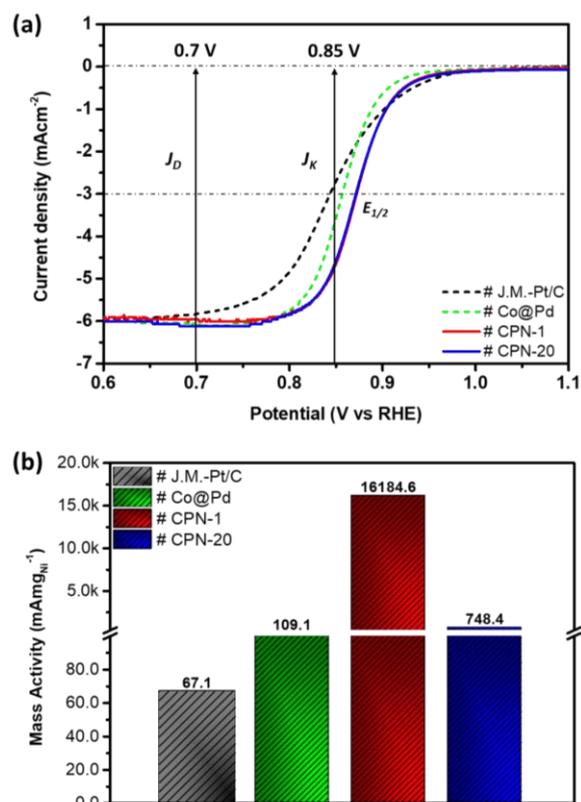


Fig. 2. Electrochemical results of CPN NCs. (a) LSV curves and (b) corresponding ORR mass activity at 0.85 V (vs. RHE) of CPN NCs compared with Co@Pd and commercial J.M.-Pt/C catalysts.

Acknowledgement

The authors express their gratitude to the staff of the 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 108-3116-F-007-001, MOST 109-3116-F-007-001-, and MOST 109-2112-M-007-030-MY3.).

References

- [1] B.C. Steele, A. Heinzl, *Nature*. 414 (6861):345- 52 (2001).
- [2] D. Bhalothia, L. Shuan, Y.-J. Wu, C. Yan, K.-W. Wang and T.-Y. Chen, *Sustainable Energy & Fuels*, 2020, **4**, 2541-2550.
- [3] J.K. Nørskov, J. Rossmeisl, A. Logadottir, and L. Lindqvist, *J.Phys.Chem.B*, 108 (46),pp 17886–17892 (2004).
- [4] N.Markovic, H. Gasteiger and P.N. Ross, *J. Electrochem. Soc.* 144(5): 1591-1597 (1997).
- [5] D. Bhalothia, C.-Y. Lin, C. Yan, Y.-T. Yang and T.-Y. Chen, *ACS Omega*, 2019, **4**, 971-982.
- [6] D. Bhalothia, Y.-J. Fan, T.-H. Huang, Z.-J. Lin, Y.-T. Yang, K.-W. Wang and T.-Y. Chen, *The Journal of Physical Chemistry C*, 2019, **123**, 19013-19021.