Electronic Supplementary Information

Porous Pt₃Ni with Enhanced Activity and Durability towards

Oxygen Reduction Reaction

Shuying Mi, Na Cheng, Hao Jiang, Chunzhong Li^{*}, Haibo Jiang^{*}

Key Laboratory for Ultrafine Materials of Ministry of Education, East China University of Science and Technology, Shanghai 200237, P. R. China

*Corresponding author. E-mail: jianghaibo@ecust.edu.cn (Prof. H. Jiang) and czli@ecust.edu.cn (Prof. C. Li). Tel: +86 021 64250996 (Prof. H. Jiang) and +86 021 6425094 (Prof. C. Z. Li)

Materials and methods

1 Chemicals

Platinum(II) acetylacetonate (Pt(acac)₂, 98%), nickel(II) acetylacetonate (Ni(acac)₂, 97%) and dodecyltrimethylammonium chloride (DTAC, 99%) were purchased from Aladdin-reagent Inc. (Shanghai, China). Oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇COOH, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Oleylamine (CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂, C18: 80-90%) was purchased from Macklin Inc. (Shanghai, China). Acetic acid (CH₃COOH, AR) and cyclohexane were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Isopropanol ((CH₃)₂CHOH, AR) and Nafion (5 wt.% in lower) were purchased from Titan Scientific Co., Ltd (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

2 DFT models and calculations

Yeager et al. proposed reductive and dissociative adsorption of O_2^* -20* as being rate-determining.¹ And First-principles computations have shown that there are two possible O_2 absorbed states on the Pt (111) surface. One is bridge site with an O-O stretching vibrational frequency of 850 cm⁻¹ and the other one is the face site with the vibrational frequency of 690 cm^{-1,2} Under the lower oxygen molecular coverage conditions, oxygen molecular tends to be absorbed parallel on the bridge site of the atom on the catalyst surface.^{3, 4} Therefore, in this paper, only bridge site was taken into consideration and all the calculation was finished in Dmol³ package.⁵ The density functional theory (DFT) method was applied for theoretical calculation. The calculation of the electronic structure and the exchange correlation potential was based on the generalized gradient approximation and Perdew-Burke-Emzerhof (GGA-PBE) method.⁶ The valence electrons were expanded by double numerical basis set and polarization function. The energy and electronic configuration of each model were calculated on the basis of Monkhorst-Pack 4×4×1 k-point mesh. The convergence value of energy was 1×10⁻⁵ Ha. Maximum allowable torque and step size were set as 0.004 Ha/Å and 0.005 Å, respectively. As for the transition state, LST/QST method was used.⁷⁻⁹ The final activation energy was obtained under the condition of one imaginary frequency. The frequency spectrum was shown in Figure S11 below and the imaginary frequency was circled in the red oval.

In order to eliminate the interaction between the units as far as possible, the thickness of the vacuum layer was installed, which was 10 Å. All the models were optimized by means of fully relaxing the atoms in the top three layers while fixing the rest of the atoms in their equilibrium positions under stress. Besides, according to element mapping and ICP-AES results, herein, Pt atoms were substituted by Ni atoms stochastically whereas the overall atom molar was maintained as 3:1 (Pt/Ni).



Figure S1. (A) XRD pattern of as-prepared PNC-Pt₃Ni (PDF#04-0802Pt, PDF#04-0850Ni) before and after annealing at 250 °C, (B) XPS pattern of PNC-Pt₃Ni after annealing at 250 °C.



Figure S2. TEM of PNC-Pt₃Ni/C before (A) and after annealing at 250 $^{\circ}$ C (B).



Figure S3. The tendency of the content and molar ratio of Pt/Ni at different reaction time stages: 3, 5, 20, 30 and 60 minutes. Here red broken line represents the content of Pt; Black represents Ni; Blue represents the molar ratio of Pt/Ni.



Fig. S4. Morphology change with different dose of DTAC as mapping agent. (A) 0, (B) 5 mg, (C) 25.9 mg, (D) 51.8 mg DTAC.



Figure S5. Structural analysis recorded under different precursor ratios. Pt:Ni=(A) 1:0. (B) 1:1 (PNC-Pt₃Ni). (C) 1:2. (D) 1:3. (F) XRD pattern comparison of diverse element ratio of catalysts resulted from the different precursor ratio



Figure S6. Structure of Pt-Ni alloy with different ratio of solvent. (A) OM/OA: 5/0, (B) OM/OA: 3:2, (C) OM/OA: 2.5/2.5, (D) OM/OA: 2:3.



Figure S7. TEM images of as-prepared PNC-Pt₃Ni/C (A) and Pt/C (B) with loading amount of 20%.



Figure S8. TEM images after 10,000 potential cycles. (A) Pt/C. (B) PNC-Pt₃Ni/C. (C) PNC-Pt₃Ni/C annealed at 400 °C for 3 hr. (D) ORR polarization curves of the PNC-Pt₃Ni/C catalyst (initial) and after calcination at 400 °C, the inset of D is the CV curves of these catalysts.



Figure S9. (A) The associated electrochemical impedance spectroscopy (EIS) of PNC-Pt₃Ni/C and Pt₃Ni-400/C recorded at -0.05 V within a frequency range from 100K Hz to 0.1 Hz (amplitude at 5 mV). (B) The equivalent circuit model for PNC-Pt₃Ni/C and Pt₃Ni-400/C.



Figure S10. The illustration of O_2^* adsorption on (A) reactant of Pt (111). (B) transition state of Pt (111). (C) product of Pt (111). (D) reactant of PNC-Pt₃Ni (111). (E) transition state of PNC-Pt₃Ni (111) and (F) product of PNC-Pt₃Ni (111).



Figure S11. The frequency spectrum under the condition of obtained activation energy for Pt_3Ni . Only one imaginary frequency was shown after the optimization, which was -413.64 1/cm. The green arrow from the insert represents the vibration direction of atoms.

Catalyst		PNC-Pt₃Ni/C	Pt/C	After ADT	
				PNC-Pt ₃ Ni/C (loss percent)	Pt/C (loss percent)
ECSA (m²/g)		75.335	81.640	59.092 (21.56%)	56.851 (30.36%)
Specific (mA/cm²)	Activity	0.789	0.120	0.766 (2.92%)	0.092 (23.33%)
Mass Activity (A/mg _{Pt})		0.594	0.098	0.453 (23.74%)	0.052 (46.94%)

Table S1. Calculated ECSA, specific activities and mass activities of PNC-Pt₃Ni/C and Pt/C catalysts before and after ADT.

Reference

- 1. S. J. Clouser, J. C. Huang and E. Yeager, *Journal of Applied Electrochemistry*, 1993, **23**, 597-605.
- 2. X. G. Wang and G. B. Fisher, *Phys Rev Lett*, 2007, **99**, 066101.
- 3. X. G. Wang and G. B. Fisher, *Physical Review Letters*, 2007, **99**.
- 4. J. L. Gland, B. A. Sexton and G. B. Fisher, *Surface Science*, 1980, **95**, 587-602.
- 5. B. Delley, *Journal of Chemical Physics*, 2000, **113**, 7756-7764.
- 6. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1997, **78**, 3865.
- 7. Q. G. Jiang, Z. M. Ao, S. Li and Z. Wen, *Rsc Advances*, 2014, **4**, 20290-20296.
- 8. S. T. Zhang, H. Yan, M. Wei, D. Evans and X. Duan, *Rsc Advances*, 2014, **4**, 30241-30249.
- 9. N. Govind, M. Petersen, G. Fitzgerald, D. King-Smith and J. Andzelm, *Computational Materials Science*, 2003, **28**, 250-258.