

Supplementary Information

Improvement of oxygen reduction reaction and methanol
tolerance characteristics for PdCo electrocatalysts by Au
alloying and CO treatment

Yu-Chen Wei, Chen-Wei Liu, Kuan-Wen Wang*

Institute of Materials Science and Engineering, National Central University

Taoyuan 32001, Taiwan

*To whom correspondence should be addressed,

E-mail: kuanwen.wang@gmail.com

Fax: 886-3-2805034, Tel: 886-3-4227151 ext 34906

Current address: Institute of Materials Science and Engineering, National Central
University, No.300, Jhongda Rd., Taoyuan 32001, Taiwan.

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Experimental section:

1. Preparation of Catalysts:

Carbon-supported Pd₇₅Co₁₀Au₁₅ catalysts (20 wt. % metal loading) were prepared through the deposition-precipitation (DP) route. Metal precursors of Pd(NO₃)₂, Co(NO₃)₂·6H₂O and HAuCl₄ in the desired stoichiometry were dissolved in DI water and co-deposited onto the commercial carbon black (Vulcan XC-72R) at 340 K at pH value to near 9. Afterwards, the solution was stirred, filtered, and dried at 320 K for 24 h. The dried catalysts were then reduced under a flow of H₂/N₂ (10/90 vol. %) at 390 K for 1 h and named as PdCoAu catalysts. Moreover, the as-reduced catalysts were heat-treated under CO atmosphere (CO/Ar = 10/90 vol. %) at T = 470-570 K and those samples were designated as COT for simplicity. The home made Pd/C and commercial E-TEK Pt/C catalysts (20 wt %) were used for the comparison of catalytic activity. Moreover, the Co/C and Au/C (20 wt %) catalysts were also synthesized by a similar way for the comparison.

2. Characterization of Catalysts

XRD characterization: The phases and structures of various catalysts were characterized by a Shimadzu XRD using CuK_α radiation operated at 40 kV and 25 mA. The XRD profile was obtained at a scan rate of 0.024° s⁻¹ for the 2θ values ranging from 35 to 50°.

HR-TEM characterization: The morphologies of various alloy catalysts were observed by using high resolution transmission electron microscopy (JEOL-2100) equipped with a LaB₆ electron gun and operated at 200 kV. Briefly, the powder alloy catalysts were ultrasonically suspended in 2-propanol. Afterwards, the suspension was then immediately dropped and dried on carbon supported on a 200 mesh/inch copper grids.

TPR characterization: For the determination of outmost surface species of all catalysts, the technique of TPR was exploited. In each TPR analysis, a sample of approximately 20 mg was inserted into a U-shape quartz tube and pre-oxidized in air at ambient temperature (300 K) for 1 h. Subsequently, the pre-oxidized alloy catalysts were reduced by a flow of 20 % H₂ in N₂ at a flow rate of 30 mL min⁻¹ as increasing the temperature from 120 to 550 K at a heating rate of 7 K min⁻¹. For the examination of Co/C catalysts, the temperature range was set from 300 to 800 K. While the reduction process started, the rate of hydrogen consumption presented in the TPR profile was measured automatically by thermal conductivity detector (TCD). Moreover, silica gel and molecular sieve absorbents were utilized for the purpose of water removal before the flowing gas reached the detector.

3. *Electrochemical measurements of catalysts*

The CO stripping test was assessed by using a glassy carbon (GC, area = 0.196 cm²) as working electrode in a conventional three-electrode configuration. A Pt wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All potentials throughout this study were referred to the NHE. 5 mg of catalysts were ultrasonically suspended in 2-propanol and Nafion solution (5 wt. %) to obtain the ink, and then spread on the GC electrode (8 μL of catalysts ink). For the examination of CO voltammetric stripping experiment, CO was adsorbed (CO_{ads} species) initially onto the surface of catalysts at a constant voltage of 0.1 V in the CO-saturated 0.1 M HClO₄ for 20 min. After the course of absorption of CO_{ads} species, the N₂-saturated 0.1 M HClO₄ was used for CO stripping study. Two cyclic voltammetry (CV) scans were collected between 0.05 and 1.2 V with a scan rate of 50 mVs⁻¹. The first potential sweep was conducted to electro-oxidize the adsorbed CO and the second sweep was to verify the complete oxidation of adsorbed species. Furthermore, the electrochemical surface area (ECSA) was hereafter calculated by the

integration of charges associated with the oxidation of CO peak and by the use of assumed value for desorption of monolayer CO_{ads} of near 420 μCcm⁻².

Linear sweep voltammetry (LSV): The equipment for measuring the electro-catalytic activity toward ORR of catalysts and the preparation approach of catalysts ink was the same as that for the CO stripping measurement. For the ORR measurement, 20 μL of the slurry was deposited on the GC electrode. The estimated Pd metal loading on the GC electrode was about 19 and 13 μg for Pd/C and PdCoAu catalysts, respectively.. The rotating disk electrode (RDE) at a rotational rate of 1600 rpm in O₂-saturated 0.1 M HClO₄ with or without 0.5 M CH₃OH solutions was applied. Prior to each test, the electrode was cycled by several times between 0.05 and 1.2 V to produce clean surfaces and activate the catalysts. During each measurement, a moderate O₂ gas flow was kept above the electrolyte to maintain the bulk concentration of O₂ molecular in the 0.1 M HClO₄ electrolyte. For the comparison of ORR activity on all alloy catalysts, the current density is calculated from the experimental data based on the mass-transfer correction for RDE by the following formula derived from the Koutecky–Levich (K-L) first order equation:

$$I_k = \frac{I_d I}{I_d - I} \quad (1)$$

where I is the experimentally measured current density during the ORR, I_k is the mass transport free kinetic current density and I_d is the diffusion-limited current density.¹⁻³ Moreover, the mass activity is obtained by the normalization of kinetic current to the weight of Pd.⁴ All of the ORR activity reported in this study is compared within the mixed kinetic-diffusion region at $E = 0.75$ V as suggested and employed by some literatures.⁵⁻⁷ On the other hand, according to the K-L equation, the I_d term is equal to $0.62nFAD^{2/3}Cv^{-1/6}\omega^{1/2}$ where A is geometric area of the electrode of 0.19625 cm², C is bulk O₂ solubility of 1.18×10⁻⁶ mol cm⁻³, D is diffusion coefficient of 1.9×10⁻⁵ cm²

s^{-1} and ν is kinematic viscosity of $8.93 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ in 0.1 M HClO_4 solution. By taking account these parameters, the electron transfer numbers (n) per oxygen molecular during the ORR can be approximately estimated.¹⁻³

Table S1 Results of ECSA and ORR activities of various catalysts.

Samples	ECSA ^a (cm ²)	ORR activity (at E = 0.75 V)			
		Without methanol		With 0.5 M methanol	
		I _k ^b (mAcm ⁻²)	MA ^b (Ag _{Pd})	I _k ^b (mAcm ⁻²)	MA ^b (Ag _{Pd})
Pd/C	8.6	0.5	5.2	0.1	1.0
PdCoAu	7.0	1.5	22.6	0.7	10.5
CO470	5.3	1.7	25.6	1.3	19.6
CO520	5.0	2.1	31.7	1.7	25.6
CO570	4.9	1.8	27.1	1.0	15.1

^a Electrochemical surface area (ECSA): the ECSA is estimated by integrating the charges associated with electro-oxidation of CO_{ads} species.

^b Kinetic current density (I_k): the kinetic current at E = 0.75 V is calculated by using the L-K equation.

^c Mass activity (MA): the mass activity is obtained by the normalization of kinetic current to the weight of Pd.

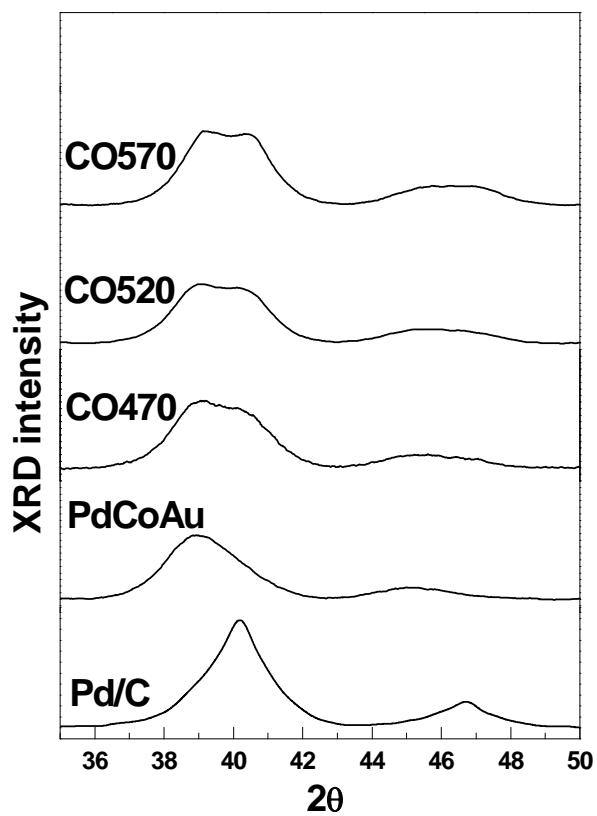


Figure S1 The original XRD patterns of Pd and various alloy catalysts.

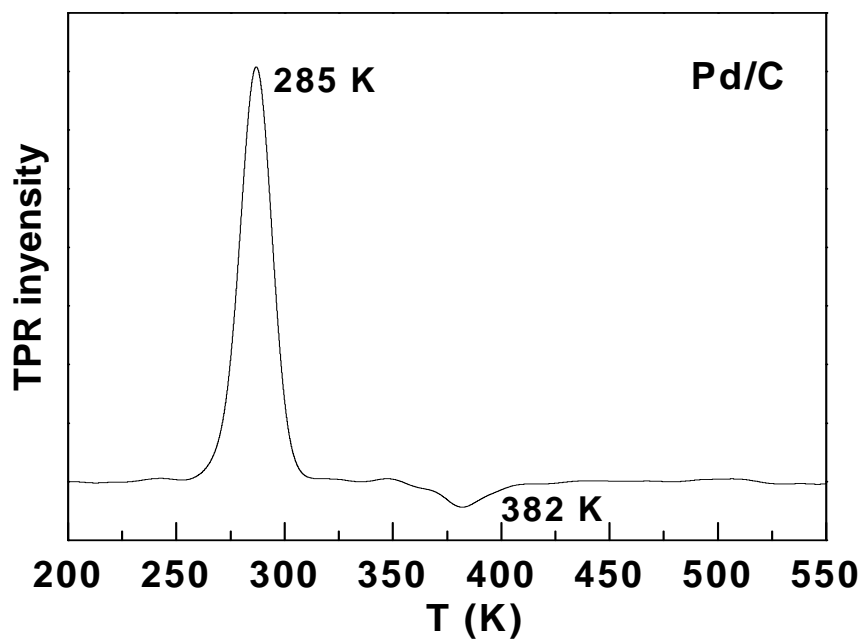


Figure S2 A representative TPR trace of the Pd/C catalysts. Obviously, the temperatures for H₂ consumption and desorption located at 285 and 382 K are assigned to the reduction of surface oxide species (Pd^sO) and the adsorption of H₂ from bulk PdH which is formed in a hydrogen containing environment during the measurement.

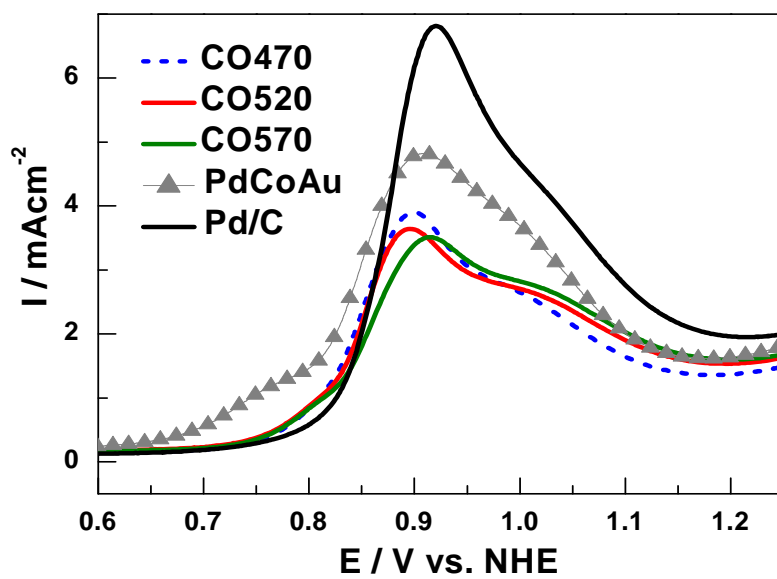


Figure S3 CO stripping profiles of Pd/C, PdCoAu and various CO-treated catalysts.

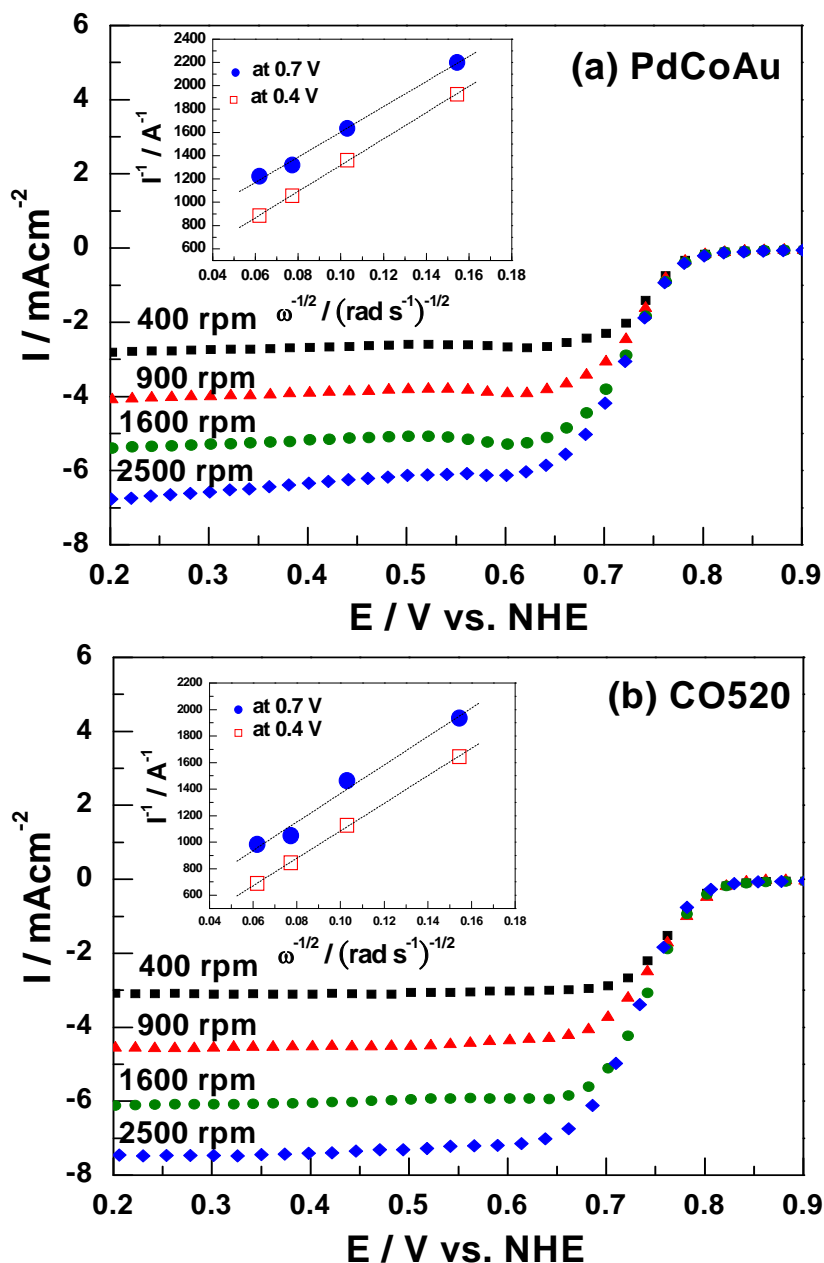


Figure S4 ORR polarization curves of (a) PdCoAu and (b) CO520 alloy catalysts recorded in O_2 -saturated 0.1 M HClO_4 at various rotation speeds. Insets show their corresponding K-L plots obtained at a potential of 0.4 and 0.7 V. Obviously, the straight lines shown in the inset plots suggest the characteristic of first order dependence of O_2 kinetics.^{8,9} Moreover, the calculated n for PdCoAu and CO520 catalysts is about 3.82 and 3.93, respectively, implying that they have similar ORR pathway (i.e. direct four electron pathway) and similar rate-determining step during the ORR.

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