Tweaking Palladium Electronic Structure to Attain Oxygen Reduction Activity Superior to Platinum/C

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Synthesis of catalysts:

Chemicals used:

Following chemicals are used in the synthesis protocol. Palladium acetylacetonate (Pd(acac)₂, Sigma-Aldrich 99.99%), Europium (III) chloride (EuCl₃, Sigma-Aldrich 99.99%), Ytterbium (III) chloride (YbCl₃, Sigma-Aldrich 99.99%), Ethylene Glycol (EG, 99%), Sodium Borohydride (NaBH₄, Sigma-Aldrich 98%), Ethanol (99.9%). All the air-sensitive compounds are handled in glove box.

Synthesis procedure:

In a typical procedure, YbCl₃ (0.1 mmol, 27.9 mg), EuCl₃ (0.1 mmol, 25.8 mg). Pd(acac)₂(0.3 mmol, 97.92 mg) was weighed in stoichiometric quantities in order to prepare the following alloys: $RE_{0.1}Pd_{0.9}$ (RE = Yb & Eu, EuPd-A & YbPd-A). A small amount (~1 to 2 mL) of EG was added to prevent hydrolysis of the added salts. NaBH₄ was added to reduce the Pd salts to their corresponding elemental zero oxidation states. 15 to 16 mL of EG was added to form the reaction solution. The solution turned black due to the reduction of the corresponding Pd²⁺ to its elemental zero oxidation state. The contents were homogeneously mixed using an orbital shaker and heated to 220 °C for 24 h. The precipitate was centrifuged and washed repeatedly with an ethanol. The obtained products were then vacuum dried at 60 °C and used for further characterizations. Quantities were doubled by keeping the solvent volume same for preparing bimetallic *RE*Pd compounds (EuPd-B & YbPd-B).

Characterization:

The PXRD measurements at room temperature were carried out on a Rigaku miniflex X-ray diffractometer with Cu-K α as the X-ray source ($\lambda = 1.5406$ Å). The instrument is equipped with a position sensitive detector in the angular range $20^{\circ} \le 2\theta \le 90^{\circ}$

with the step size 0.02° and scan rate of 1 sec/step calibrated against corundum standard. The experimental patterns were compared to the pattern simulated from the database.

Quantitative microanalyses on all the samples were performed with an Gemini-SEM 500 instrument equipped with an AztecOne (Oxford instruments) instrument. Data were acquired with an accelerating voltage of 5 kV (image acquisition), 20 kV (EDS analysis) and a 100 s accumulation time. The EDS analysis was performed using P/B-ZAF standardless method (where, Z = atomic no. correction factor, A = absorption correction factor, F = fluorescence factor, P/B = peak to background model) on selected spots and points.

TEM images and elemental mapping were collected using a TECHNAI TEM instrument equipped with EDAX®. The samples for these measurements were prepared by sonicating the nanocrystalline powders in ethanol and drop-casting a small volume onto a carbon-coated copper grid.

XPS measurements were carried out using Thermo K-alpha⁺ spectrometer using micro focused and monochromated Al K α radiation with energy 1486.6 eV. The pass energy for spectral acquisition was kept at 50 eV for individual core-levels. The electron flood gun was utilized for providing charge compensation during data acquisition. Further, the individual core-level spectra were checked for charging using C1s at 284.6 eV as standard and corrected if needed. The peak fitting of the individual core-levels were done using Fityk software with a Shirley type background.

Electrochemical measurements:

All the electrochemical measurements were carried out using a CHI760E electrochemical workstation with three electrode channels at room temperature. A conventional RDE and RRDE electrodes are used as a working electrode, graphite rod as a counter electrode and Hg/HgO (MMO) as a reference electrode were used.

Before all the measurements, the electrolyte was de-aerated with continuous purging of nitrogen gas for 30 min. The catalyst ink was prepared by dispersing 2 mg of catalyst in 200 μ L of mixed solvent solution (IPA: H₂O=1:3 v/v). Nafion solution (5 wt%, Sigma Aldrich) is diluted with isopropyl alcohol (IPA) to 0.1 wt%. From the prepared catalyst ink, a 10 µL of the slurry was dropcasted on GC electrode. Upon drying, 2 µL of 0.1 wt% of Nafion solution have been added to the dropcasted electrode and dried overnight in air. The GC electrode was polished with 0.05 μ m alumina slurry and washed several times with distilled water prior to the deposition of catalyst slurry. As-synthesized Pd/C and Pt/C (20 wt%, Sigma Aldrich) (with same Pd/Pt loading on electrode) was used for comparison of activity with same loading as the synthesized catalysts. Linear sweep voltammetry (LSV) was recorded with a sweep rate of 5 mV/s in 0.1 M KOH electrolyte solution under steady state conditions. Tafel plots (TP) were derived from LSV measurement at different rpms. Accelerated degradation test (ADT) was performed with graphite rod (purity >99.9 %, sigma aldrich) to avoid Pt dissolution. Stability tests of were carried out at a scan rate of 100 mVsec⁻¹ and within a potential window of 0.6-0.9 V vs. RHE. Potential window for the stability test was selected based on the previous literatures. Stability of the catalysts were checked using RDE measurements in a 3 mm diameter electrode. LSV graphs were recorded before the accelerated degradation test (ADT), after 1000 cycles and after 5000 electrochemical cycles to check the stability of the catalyst. Assessment of the selectivity towards H₂O, before and after the ADT process, was checked using RRDE electrode with 4 mm diameter and keeping all

other experimental conditions similar. All the electrochemical data, presented in this work, are referenced to RHE scale. All the ORR electrochemical evaluations were performed at 1600 rpm.

Calibration of Hg/HgO w.r.t RHE in 0.1 M KOH and at a scan rate of 5 mV/sec:

The calibration of Hg/HgO electrode was performed in a standard three-electrode system with polished Pt wires as the working and counter electrodes, and the Hg/HgO as the reference electrode. Electrolytes are continuously purged and saturated with high purity H₂. Cyclic voltammetry (CV) is then run at a scan rate of 5 mVsec⁻¹, and the average of the potential, from both the sweeps, at which the current crossed zero is taken to be the thermodynamic potential for the hydrogen electrode reactions. For example, in 0.1 M KOH, the zero current point is at -0.936 V, so E (RHE) = E (Hg/HgO) + 0.936 V.



Derivation of H₂O₂ and H₂O percentage:

 H_2O_2 percentage were derived from the RRDE calculation. The amount of H_2O_2 was then calculated from the ring and disk current using the following formula:

$$\chi_{\rm H2O2} = \frac{2\frac{I_{\rm R}}{N}}{I_{\rm D} + \frac{I_{\rm R}}{N}}$$

where χ_{H2O2} is the number of moles of H_2O_2 formed per mole of O_2 , I_R is the ring (collection electrode) current and I_D is the disc (working electrode) current.

Tables

Table S1. The table shown lists the particle size of the catalysts determined from Scherrer's equation.

				Lattice
Catalyst	FWHM	Theta (in angle)	Crystallite Size (nm)	Strain
YbPd-A	0.3473046	20.0674	24.3	0.009
EuPd-A	0.2892461	20.086685	29.2	0.007
YbPd-B	0.4178431	19.9085	20.2	0.0104
	0.3253861	20.1231	25.9	0.008
EuPd-B	0.2899682	19.835645	29.1	0.007
	0.199047	20.17805	42.4	0.005

Table S2. Relative composition of Pd/PdO as determined from XPS.

Catalysts	Pd/PdO
YbPd-A	1.30
YbPd-B	1.27
EuPd-A	1.51
EuPd-B	1.04

Table S3. The table shown lists the average atomic percentage and average weight percentage of the catalyst obtained from the EDAX measurements.

Catalyst	Average At %	Average Wt%			
YbPd-A	Yb=7.4%, Pd=92.6%	Yb=11.5%, Pd=88.5%			
EuPd-A	Eu=12.6%, Pd=87.4%	Eu=16.1%, Pd=83.9%			

Sl. No.	Elements	<i>RE</i> Pd	REPd (O ₂)	Δ	Pd	Pd (O ₂)	Δ	Pt	Pt (O ₂)	Δ
1.	А	0.070	0.079	0.009	-0.008	0.001	0.009	-0.010	0.003	0.013
2.	В	0.070	0.208	0.138	-0.008	0.001	0.009	-0.010	-0.008	0.002
3.	С	0.070	0.079	0.009	-0.008	0.001	0.009	-0.010	-0.008	0.002
4.	D	-0.123	0.000	0.123	-0.008	0.092	0.1	-0.010	0.003	0.013
5.	Е	-0.123	0.000	0.123	-0.008	0.001	0.009	-0.010	0.022	0.032
6.	F	0.070	0.079	0.009	-0.008	0.091	0.099	-0.010	0.116	0.126
7.	Н	0.070	0.258	0.188	-0.008	0.092	0.1	-0.010	0.116	0.126
8.	Ι	0.070	0.079	0.009	-0.008	0.091	0.099	-0.010	0.022	0.032
9.	J	-0.123	0.000	0.123	-0.008	0.092	0.1	-0.010	0.022	0.032
10.	К	-0.123	0.000	0.123	-0.008	0.001	0.009	-0.010	0.115	0.125
11.	L	0.070	0.079	0.009	-0.008	0.001	0.009	-0.010	0.116	0.126
12.	М	0.070	0.208	0.138	-0.008	0.001	0.009	-0.010	0.022	0.032
13.	Ν	0.070	0.079	0.009	-0.008	0.001	0.009	-0.010	0.003	0.013
14.	0	-	-		-	-		-0.010	-0.008	0.002
15.	Р	-	-		-	-		-0.010	-0.008	0.002
16.	Q	-	-		-	-		-0.010	0.003	0.013

Table S4. Hirshfeld charge analysis of *RE*Pd, Pd and Pt before and after O_2 adsorption. Orange colored column indicates the change in charge before and after the adsorption process.

Figures:



Figure S1. Comparison of zoomed experimental PXRD pattern of EuPd-A, YbPd-A, EuPd-B and YbPd-B.



Figure S2. Comparison of high resolution Pd-*K* edge XPS spectra of *RE*Pd catalysts showing the presence of PdO at 336.2 eV. Blue represents overall fit of the XPS spectra, red and pink color represents the deconvoluted peaks and green represents the residual spectra.



Figure S3. FE-SEM images of EuPd-B (*left*) and YbPd-B (*right*) showing hierarchical nature of the nanoparticles.



Figure S4. SEM images - Elemental mapping of EuPd-B (1a), EuPd-A (2a), YbPd-B (3a) and YbPd-A (4a). Green colour corresponds to Pd, Red corresponds to RE (1c, 2c = Eu & 3c, 4c = Yb) and white corresponds to oxygen.



Figure S5. TEM images - Elemental mapping of YbPd-B (1a), EuPd-B (2a), YbPd-A (3a) and EuPd-A (4a). Green colour corresponds to Pd, Red corresponds to RE (1c, 3c = Yb& 2c, 4c = Eu) and yellow corresponds to oxygen.



Figure S6. Comparison of RRDE polarization curve of Pd/C (20 wt%), Pt/C (20 wt%) and *RE*Pd catalysts recorded at 1600 rpm in O₂-saturated 0.1 M KOH. Disk current (I_D) represents current due to reduction of O₂ to H₂O and H₂O₂ and ring current (I_R) signifies current due to oxidation of H₂O₂.



Figure S7. Trend of onset potential and half-wave potentials extracted from the ORR polarization curves along with the standard deviations.



Figure S8. (*Left*) H_2O_2 percentage and number of electrons and (*right*) mass activity of EuPd-A before and after stability test of 5000 cycles and at a potential of 0.85 V and 0.90 V vs. RHE.



Figure S9. Comparison of Tafel slope of EuPd-A and YbPd-A.



Figure S10. Density of states plot for all the catalyst (Pd, YbPd and EuPd) showing significant amount of DOS at the fermi-level which signifies the metallic behavior of all the catalysts.



Figure S11. (a) PDOS of Eu-*d*, Pd-*d* and O-*p* orbitals showing major contribution of Pd at the valance band and Eu at conduction band and change in LDOS of (b) Eu-*d* and (c) Pd-*d* before and after O_2 adsorption.



Figure S12. Calculated *d*-band center of YbPd, EuPd and Pd showing the shift in the *d*-band center towards the fermi-level after Yb and Eu substitution.



Figure S13. (a) Deconvoluted strain and ligand effect due to *RE* substitution on Pd lattice showing the dominant effect of strain for both YbPd and EuPd and (b) overall effect of electronic contribution and detrimental effect of surface PdO on E_{onset} and $E_{1/2}$ potentials. EuPd-A, due to lower surface PdO and high lying *d*-orbital, has the highest E_{onset} and $E_{1/2}$.



Figure S14. Bonding information in the crystal. 2D-electron localization function mapping of the (100) surface of Pt, YbPd, EuPd and Pd with an isosurface value of 0.8.

References.

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