

Electronic Supporting Information

Climbing with support: Scaling volcano relationship through support-electrocatalyst interactions in electrodeposited RuO₂ for oxygen evolution reactions

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Section S1. Computational Details

All the electronic structure calculations have been carried out within the Density Functional Theory (DFT) approach, utilizing the Vienna Ab Initio Simulation package (VASP) and PBE pseudo-potential.¹⁻³ The bulk lattice constants of RuO₂ are optimized using the 8 x 8 x 12 Monkhorst–Pack type of k-point sampling.⁴ An energy cut-off of 400 eV is used during calculation. Six valence electrons for each O atom (2s² 2p⁴) and fourteen valence electrons for each Ru atom (4p⁶5s²4d⁶) are taken into account while performing calculations.

The bulk lattice constants of RuO₂ are found to be a= 4.55 Å and c=3.14 Å as against experimentally found a=4.49 Å and c=3.10 Å. A periodic stack of asymmetric slabs containing five O-Ru-O layers with adsorption reactions are carried out only on one side of the slab. The structure of the topmost three O-Ru-O trilayers including the adsorbates is allowed to freely relax, while the bottom two O-Ru-O trilayers are kept fixed. A vacuum region of at least 15 Å separates consecutive slabs in the vertical direction. The DFT calculations were restricted to 2 × 1 surface unit cells using a 4× 4 Monkhorst Pack *k*-point mesh for slab calculations. Solvent interaction related corrections are not carried out as they are not too large to be considered (~ 20 meV).⁵

The following assumptions are made to simplify electrochemical reactions:⁶

1. The chemical potential of (H⁺ + e⁻) pair is related to that of 1/2 H₂ in the gas-phase via the normal hydrogen electrode (NHE) at U = 0 V which leads to the relation,

$$G(H^+) = 0.5 G(H_2)$$

2. The free energy of the reaction intermediates are calculated via DFT by also including the zero-point energy (ZPE) and vibrational contributions. The gas-phase molecules are assumed to behave like an ideal gas with the appropriate translation and rotational contribution.

3. The effect of bias on all states involving an electron in the electrode can be included by shifting the reaction step by – eU where U is the applied electrochemical potential.

All the adsorption energies were calculated with respect to gaseous H₂ and H₂O vapor at 298 K and 0.035 bar. The unoccupied Ru_{cus} atoms denoted as (*_{cus}) serve as reference with the neighboring *cus* site occupied by O-adsorbate as O- coverage is found on the surface at the concerned electrochemical OER conditions⁵. We obtain the following equations:

$$\Delta E(\text{O}^*_{\text{cus}}) = E(\text{O}^*_{\text{cus}}) - E(^*_{\text{cus}}) - \text{H}_2\text{O} + \text{H}_2 \cdot$$

$$\Delta E(\text{HO}^*_{\text{cus}}) = E(\text{HO}^*_{\text{cus}}) - E(^*_{\text{cus}}) - \text{H}_2\text{O} + \frac{1}{2} \cdot \text{H}_2$$

$$\Delta E(\text{HOO}^*_{\text{cus}}) = E(\text{HOO}^*_{\text{cus}}) - E(^*_{\text{cus}}) - \text{H}_2\text{O} + \frac{3}{2} \cdot \text{H}_2$$

Section S2. Experimental Section:

Physiochemical Characterizations: XRD analysis were performed using a Siemens D5000 Bragg-Brentano θ - 2θ diffractometer. Step-scan X-ray powder-diffraction data were collected over the 2θ range 15 – 75° with Cu-K α (40 kV, 40 mA) radiation on a diffractometer equipped with a diffracted-beam graphite monochromator crystal, 2 mm (1°) divergence and anti-scatter slits, 0.6 mm receiving slit, and incident beam Sollar slit. The scanning step size was 0.04° with a counting time of 1.5 s step $^{-1}$. Surface morphology was determined by scanning electron micrographs by using an instrument of FESEM - SUPRA 400VP Gemini, Zeiss. The surface elemental composition and chemical state of the components were analysed by XPS studies using PHI *VersaProbe* II Scanning XPS Microprobe. All XPS results are calibrated by setting C1s peak at 284.6 eV.

Electrochemical Characterizations: Electrochemical characterizations were performed using Potentiostat (Autolab 302N, Metrohm India Ltd.). Electrochemical activity of the synthesized electrocatalysts were analyzed in 0.5 M H $_2$ SO $_4$ electrolyte solution with scan rate of 20 mV/s by cyclic voltammetry (CV) measurements in an electrochemical cell with a Pt-mesh as a counter electrode and Ag/AgCl/(sat. KCl) as reference electrode. Linear sweep voltammetry (LSV) measurements were performed at a 5 mV/s scan rate. CV and LSV of the electrodes were performed in a single-compartment cell using potentiostat. All the potentials are with respect to Ag/AgCl if otherwise not mentioned.

To calculate electrochemical surface area (ECSA) of the prepared electrocatalyst, LSV was performed at different scan rates (1, 2, 5, 10, 20, 50, 100 mV/s) within a potential range of 0 - 1.0 V vs Ag/AgCl. The current density is plotted against scan rate at a potential of 0.4 V vs Ag/AgCl. The double-layer charge capacitance measured at non-faradaic regime is a measure of accessible electrochemical surface area (ECSA). This measurement involves calculation of slope of the obtained current density as a function of scan rate at a fixed potential.

$$i = C_{dl} \frac{dv}{dt} \dots\dots\dots (1)$$

Where i is the obtained current density and $\frac{dv}{dt}$ is the scan rate. The obtained C_{dl} (double layer capacitance) can be correlated to ECSA with following relation,⁷

$$ECSA = \frac{C_{dl}}{C_s} \dots\dots\dots (2)$$

Where C_s is the specific capacitance of RuO_2 in 0.5 M H_2SO_4 solution.

The roughness factors of the electrocatalyst are being calculated using following relation,⁷

$$RF = \frac{ECSA}{GSA} \dots\dots\dots (3)$$

Where GSA is the geometrical surface area of the electrode which is 1 cm² in the present case.

The electrochemical porosity is being calculated assuming that total charge (q_t) and outer charge (q_o) of metal oxide can be calculated by integration of voltammograms at different scan rates.⁸ The voltammetric charge corresponding to the total surface area (q_t) can be calculated plotting the reciprocal of q against the square root of the potential scan rate by using the following equation,

$$\frac{1}{q} = \frac{1}{q_t} + kv^{0.5} \dots\dots\dots (4)$$

The total voltammetric charge (q_t) calculated by extrapolation of the linear plots at $v = 0$. The values of outer charge (q_o) can be calculated from the extrapolation to $v \rightarrow \infty$ in the plot of q versus $v^{0.5}$ according to the following equation,

$$q = q_o + k_1 v^{-0.5} \dots\dots\dots (5)$$

where both k and k_1 are constants of proportionality.

The electrochemical porosity is measured as

$$Electrochemical\ porosity = \frac{q_t - q_o}{q_t} \dots\dots\dots (6)$$

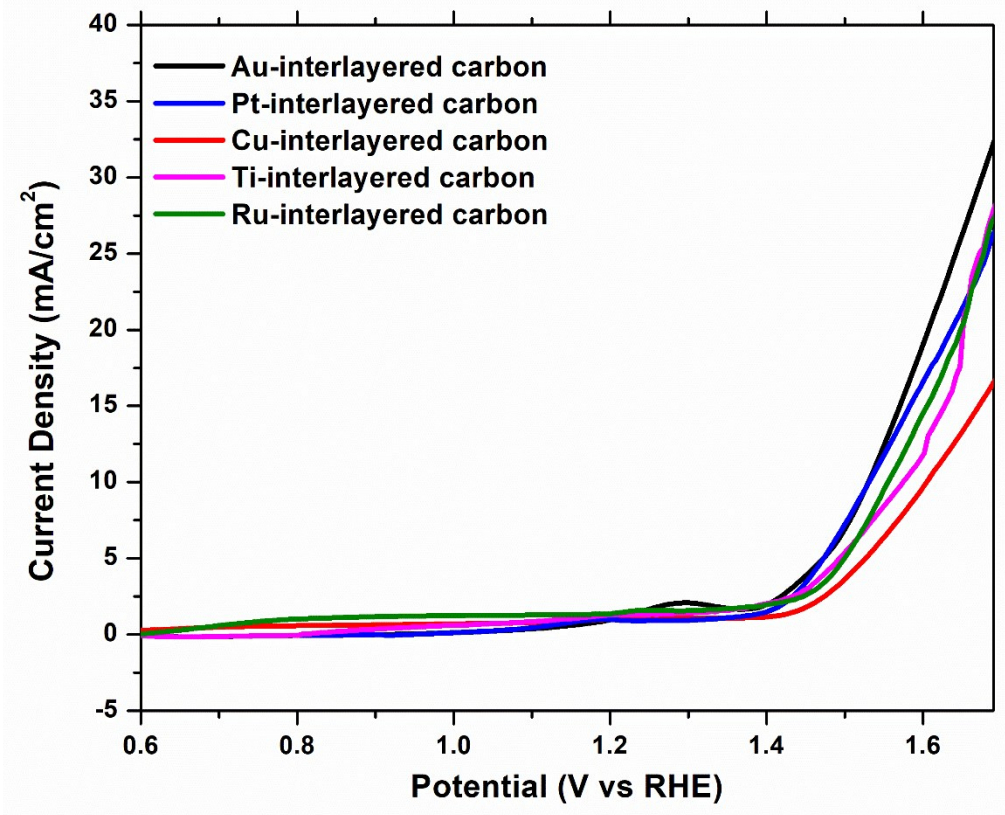


Figure S1. LSV curves of thick film of RuO₂ on different metal-modified carbon supports at a scan rate of 5 mV/s.

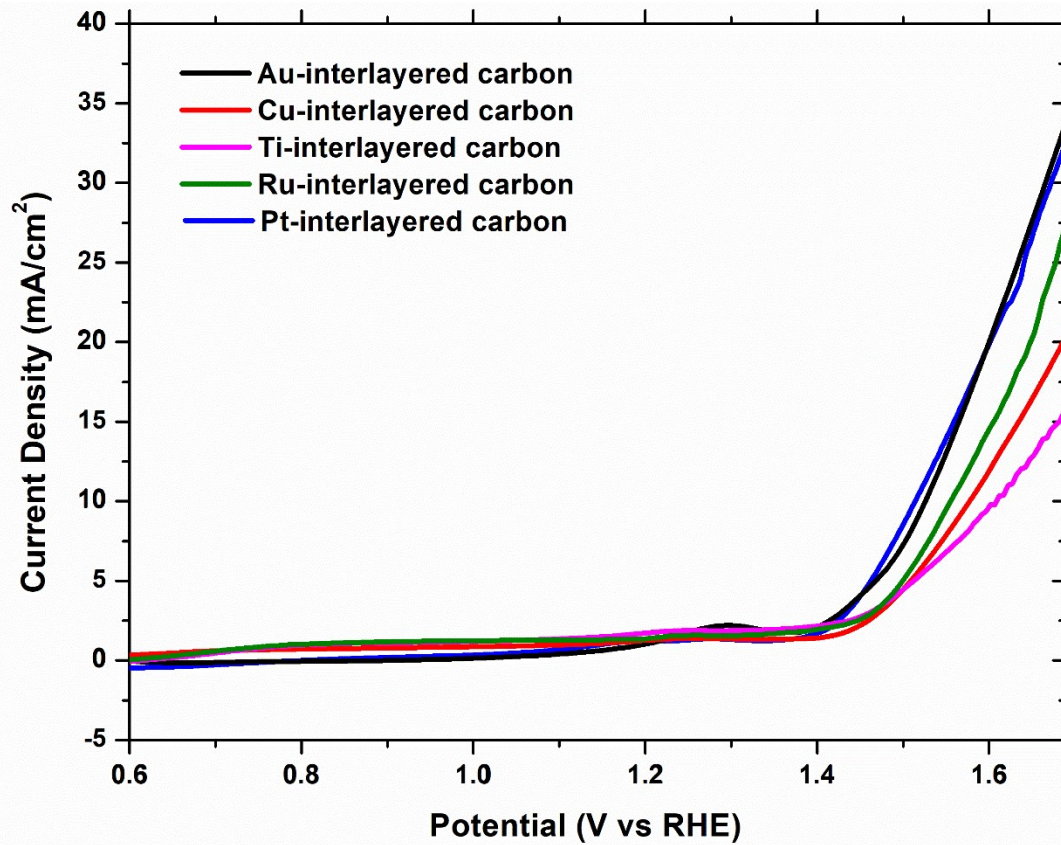


Figure S2. LSV curves of thin film of RuO₂ on different metal-modified carbon supports at a scan rate of 5 mV/s.

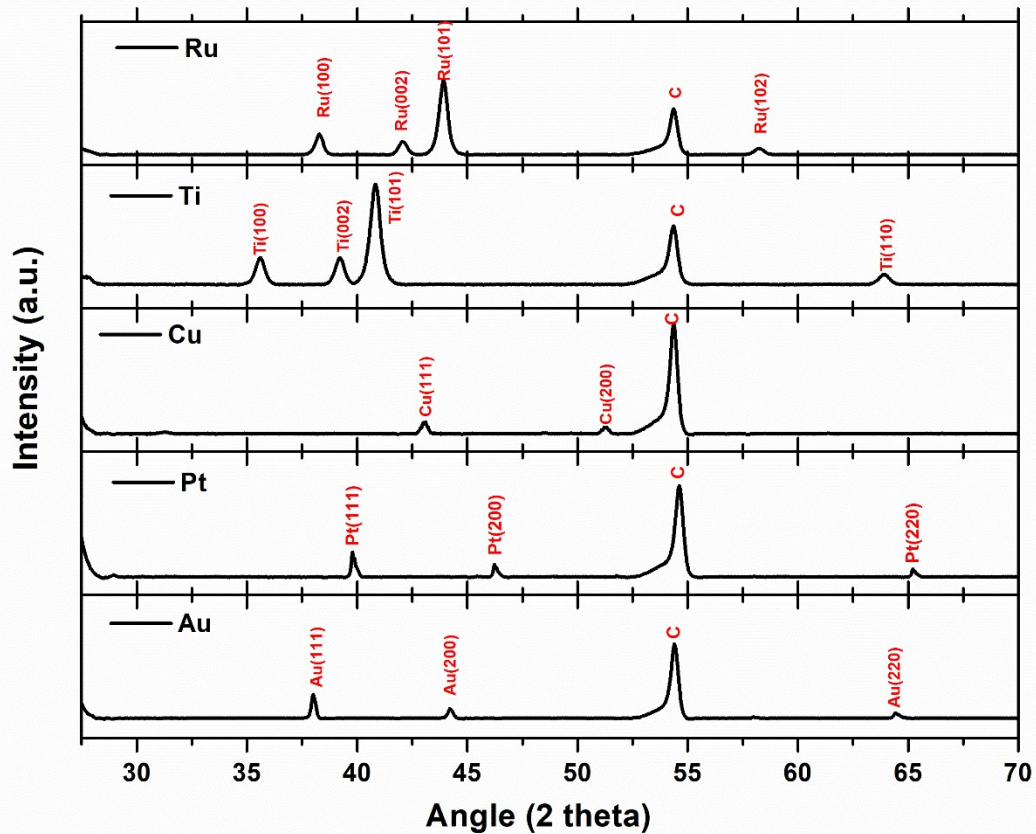


Figure S3. XRD of electrodeposited metallic interlayers on carbon support (Au-, Pt-, Cu, Ti-, Ru).

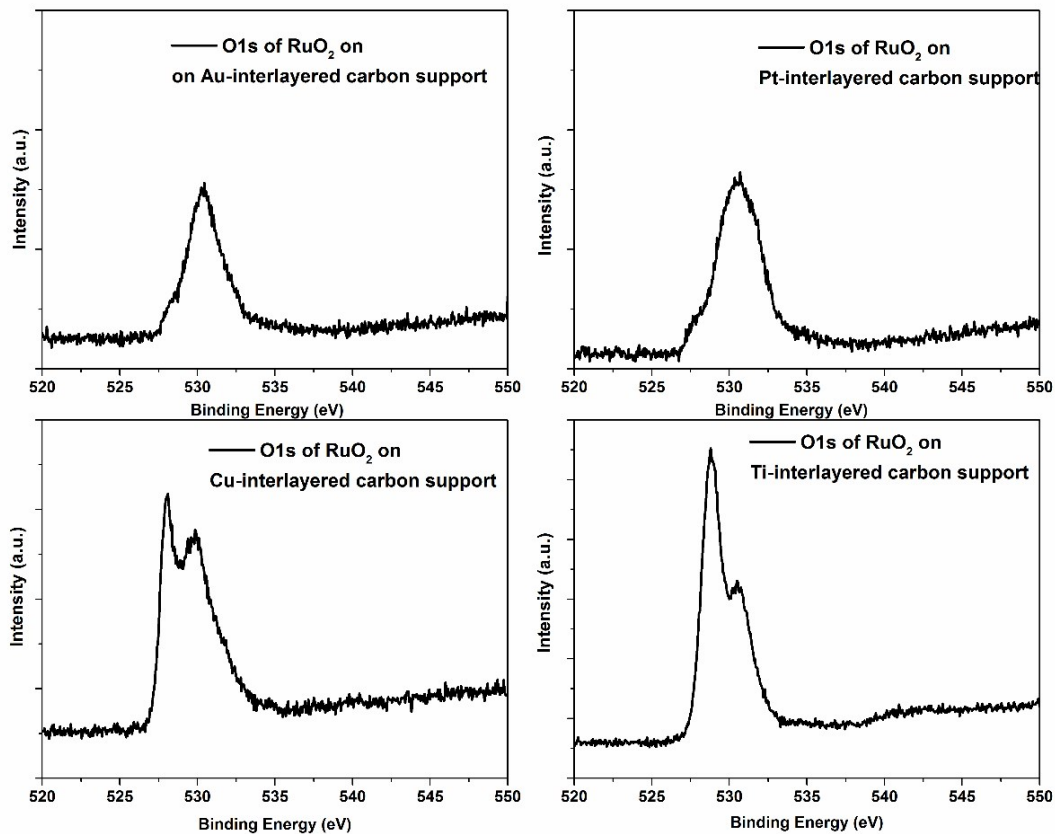


Figure S4. XPS spectra of O-1s (520-550) eV zone at Au-, Pt-, Cu- and Ti-interlayered carbon support.

Table S1: Loading and approximate thickness of thick-RuO₂ on different metal-interlayered carbon supports.

Metal-interlayered carbon support	Weight of electrodeposited Ru on different support ($\mu\text{g cm}^{-2}_{\text{geo}}$)	Monolayer (ML) thickness of the deposited RuO₂ (thickness)
Au	4628	11.2 (3.5 nm)
Pt	5043	10.8 (3.4 nm)
Cu	2274	10 (3.2 nm)
Ti	4663	11 (3.4 nm)

Table S2: Loading and approximate thickness of thin-RuO₂ on different metal-interlayered carbon supports.

Metal-interlayered carbon support	Weight of electrodeposited Ru on different support ($\mu\text{g cm}^{-2}$)	Monolayer (ML) thickness of the deposited RuO₂ (thickness)
Au	962	4.1(1.0 nm)
Pt	3550	4.6 (1.3 nm)
Cu	2000	4.8 (2.2 nm)
Ti	6041	5 (1.6 nm)

*The thickness is calculated taking into account of the plane that has the maximum probability of forming as indicated from interfacial strain calculation (Table 2 in the main manuscript).

Table S3: Electrochemical surface area of electrodeposited thin film RuO₂ and thick film RuO₂ on different metal-modified carbon supports.

Metal-interlayered carbon supports- RuO₂ electrocatalyst system	ECSA (cm²/cm²_{GSA})
Au-thin RuO₂	3997
Au-thick RuO₂	4925
Pt-thin RuO₂	5608
Pt-thick RuO₂	5565
Cu-thin RuO₂	3449
Cu-thick RuO₂	2711
Ti-thin RuO₂	10000
Ti-thick RuO₂	5052
Ru-RuO₂	5224

Table S4: Tafel slope of electrodeposited thin film RuO₂ and thick film RuO₂ on different metal-modified carbon supports.

Metal-interlayered carbon supports- RuO₂ electrocatalyst system	Tafel Slope (mV/dec)	
	Low OER overpotential regime	High OER overpotential regime
Au-thin RuO₂	62	158
Au-thick RuO₂	73	161
Pt-thin RuO₂	60	165
Pt-thick RuO₂	75	171
Cu-thin RuO₂	78	165
Cu-thick RuO₂	71	154
Ti-thin RuO₂	106	172
Ti-thick RuO₂	86	163
Ru-RuO₂	72	145

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