Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information (SI)

The Relationship between Electron-transfer Coefficients of Oxygen Reduction Reaction Estimated from the Gibbs Free Energy of Activation and Butler-Volmer Equation

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1.1 Voltammograms of the Pt electrode before and after recording the ORR polarization curves at various temperatures

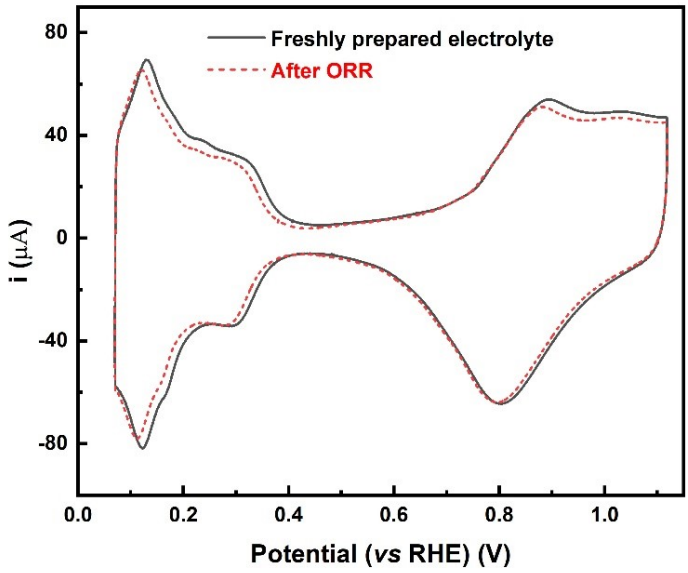

Figure S1 Voltammograms of Pt black (~51 μg cm^{-2}) at room temperature in argon-saturated 0.1 M $HClO_4$ at a scan rate of 20 mV s^{-1}, before and after recording ORR polarization curves at various temperatures (293 – 333 K).

The scan during ORR polarization was limited up to 1.05 V *vs*. RHE, and no prominent effect of temperature was observed on the surface structure or composition. It appears that the deviation in the data for different experiments at a given temperature mainly originates from the film making rather than the change in surface structure or composition. In the experimental temperature, potential and time range, the change in surface structure is negligible.

1.2 Conversion of the potential from *Ag/AgCl* to reversible hydrogen electrode (RHE) scale

All the voltammograms are corrected for the non-zero pH using equation S1.

$$E\ (vs.\ RHE) = E(vs.\ Ag/AgCl) + 0.197\ V\ + 0.059 \times pH \qquad \text{(S1)}$$

1.3 Background voltammogram of Pt-black (0.1 M $HClO_4$) at various temperatures

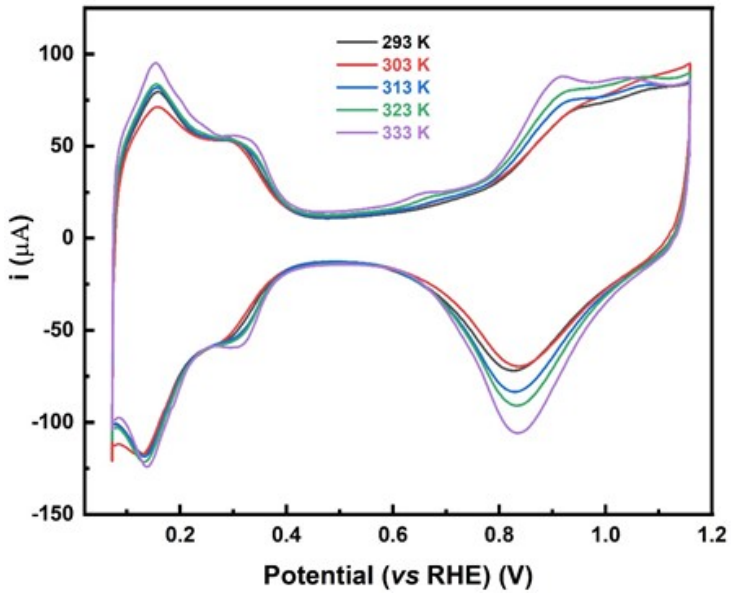

Figure S2 Voltammograms of Pt black (~51 μg cm^{-2}) on a glassy-carbon rotating ring disk electrode (RRDE) in argon-saturated 0.1 M $HClO_4$ electrolyte recorded at a scan rate of 20 mV s^{-1} in the temperature range of 293 – 333 K.

Figure S2 shows the voltammograms of Pt black (~51 μg cm^{-2}) in argon-saturated 0.1 M $HClO_4$ in the temperature range of 293 – 333 K. After conditioning the electrode at room temperature (298 K) for 50 cycles, well-defined hydrogen underpotential adsorption/desorption (H_{upd}) region (0 − 0.35 V), non-faradic double layer region (0.4 − 0.7 V), and oxide formation region (0.7 − 1.1 V) are observed in the voltammogram; these are widely reported typical polycrystalline platinum features.[1–4] With the increase in temperature, the voltammetric features remain almost the same, except for the slight rise in the surface coverage by the oxygenated species (θ) with temperature in the potential range of ~0.4 – 1.1 V.

1.4 Corrections to the ORR voltammogram for the background current, solution resistance, and mass-transport resistance

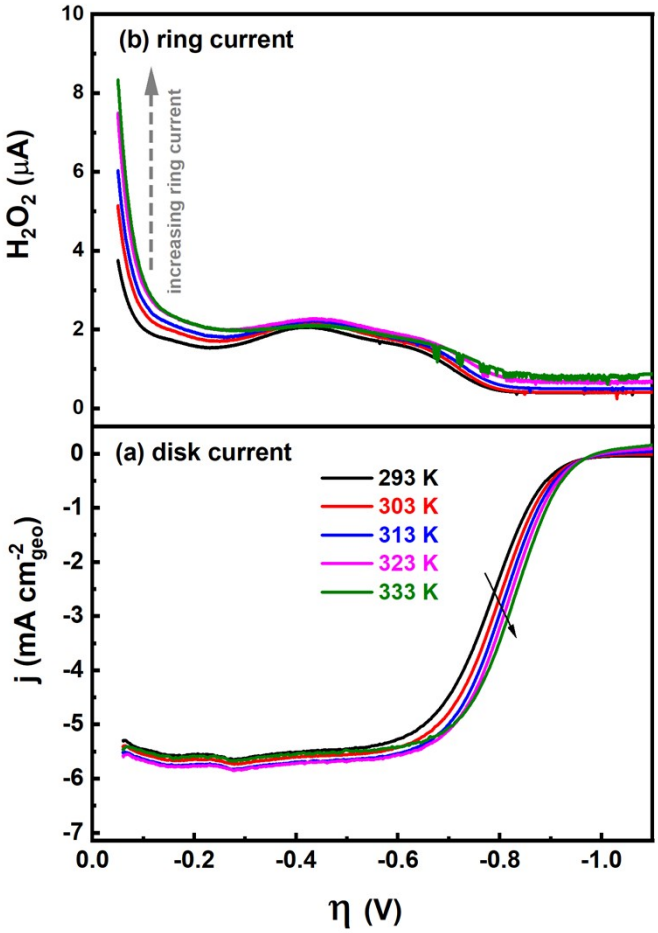

Figure S3 Background corrected ORR voltammograms (disk currents (i_D)) (a) and corresponding ring current (I_R) (H_2O_2 oxidation current) (b) of Pt black (~51 μg cm^{-2}) on RRDE in oxygen-saturated 0.1 M H_2SO_4 at a scan rate of 20 mV s^{-1} in the positive sweep direction with 1600 rpm. The ring electrode potential is 1.23 V, and the collection efficiency is 0.2, in the temperature range of 293 – 333 K.

The ORR polarization curves (**Figure S3**) recorded at various temperatures are corrected for contributions from the background current (CV) and the solution resistance (R_s). The background current correction is done by subtracting the voltammogram recorded in the supporting electrolyte (argon-saturated 0.1 M $HClO_4$) (**Figure S2**) from the ORR voltammogram at the respective temperature. The R_s obtained from the electrochemical impedance spectra of ORR (not shown for convenience) is used to correct for the ohmic drop (iR_s) using the following relation (equation S2).

$$E_{corr.} = E_{mea.} + (R_S \times i_{mea.}) \qquad \text{(S2)}$$

Here, $E_{corr.}$ is the potential corrected for the R_s, $E_{mea.}$ is the measured potential, and $i_{mea.}$ is the measured current.

Koutecky-Levich equation used to correct for the mass-transport resistance is given by equation S3.

$$\frac{1}{i_{mea.}} = \frac{1}{i_k} + \frac{1}{i_d} \tag{S3}$$

Here, i_k is the kinetic current, and i_d is the diffusion-limited current. The i_k obtained from the i_{mea} after correcting for background current, R_s, and mass-transport **(Figure S4)** is used for further analysis.

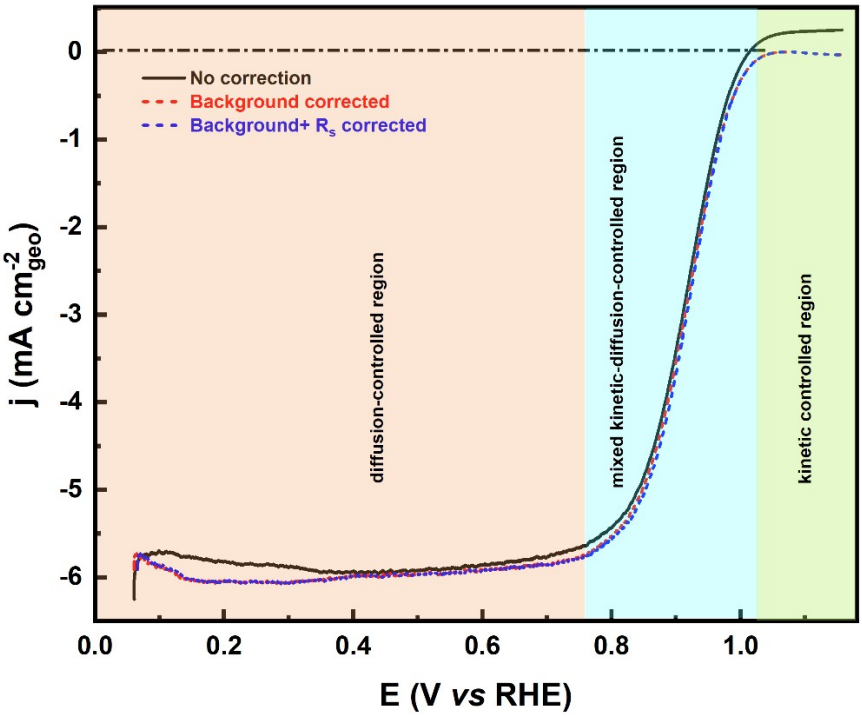

Figure S4 The ORR voltammogram corrected for the background current (red line) and solution resistance (blue line).

2.1 The estimation of α from the B-V fitting

The i_k is analyzed by the B-V relation (equation S4).

$$i_k = i_0(e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}) \tag{S4}$$

This form of the B-V equation accounts for the effect of applied η on both the forward (cathodic) and backward (anodic) reactions; the η range of analysis is high (0.3 – 0.4 V), and the effect of back reaction on the total current is negligible.

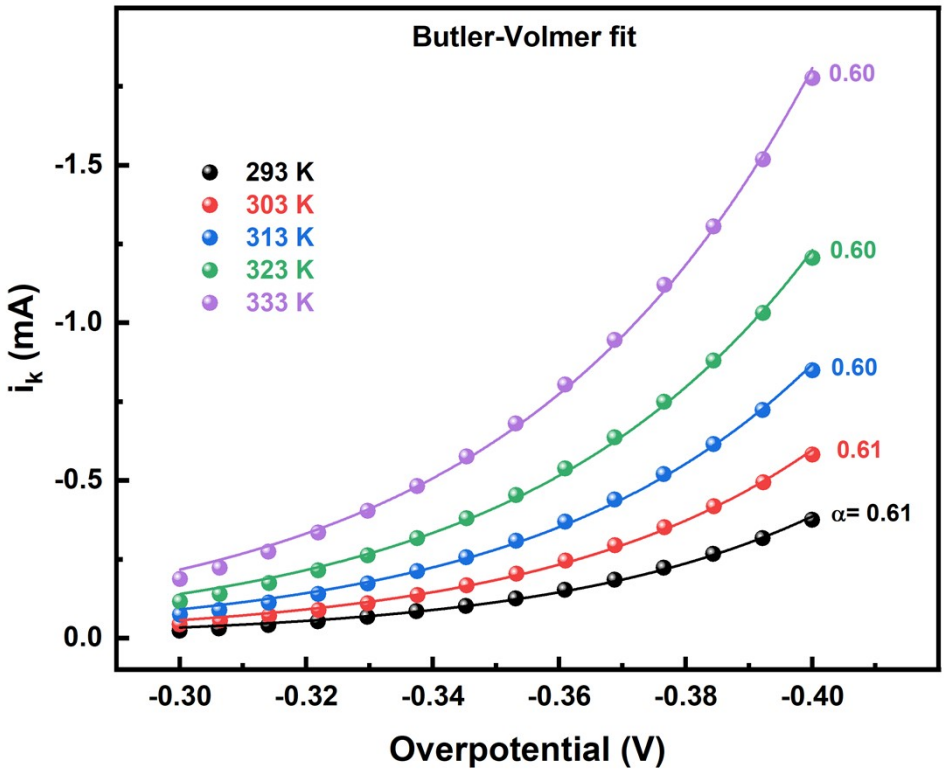

Figure S5 The i_k *vs.* η of ORR of Pt black (~51µg cm^{-2}) in 0.1 M $HClO_4$ in the temperature range of 293 – 333 K. The symbols and solid lines show the experimental and the fitted data, respectively.

α is obtained by fitting the i_k with the B-V equation at various temperatures (**Figure S5**). The α values obtained from the B-V fit are in the range of 0.55±0.03.

Table ST1 α from the Tafel analysis and B-V fit in the temperature range of 293 – 333 K.

Temperature (K)	α (Tafel analysis)	α (B-V fit)
293	0.60±0.03	0.58±0.01
303	0.62±0.02	0.59±0.01
313	0.63±0.04	0.55±0.02
323	0.63±0.04	0.54±0.03
333	0.62±0.04	0.55±0.02

2.2 Estimation of instantaneous Tafel slope and instantaneous cathodic α_C

The cathodic charge-transfer coefficient (α_c) is given by equation S5.[5]

$$\alpha_C = -\frac{RT}{F}\frac{\partial ln(i_k)}{\partial E} \quad \text{(S5)}$$

The α_C calculated from the instantaneous Tafel slope gives scattered values (**Figure S6**) but the average α_C is ~0.7 at all temperatures.

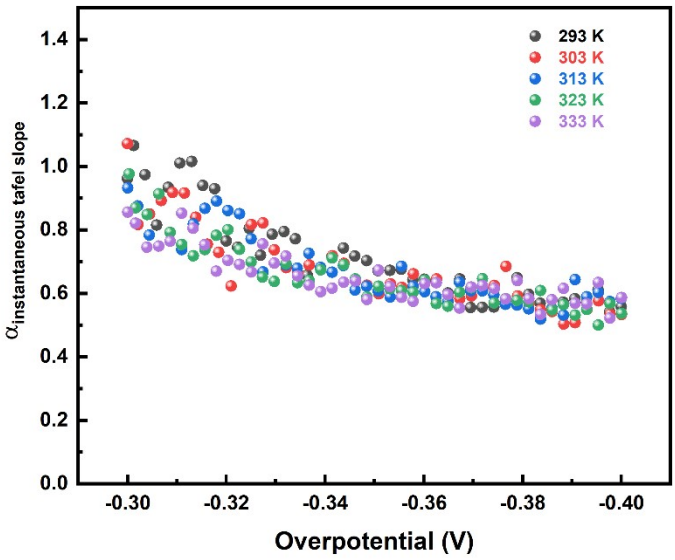

Figure S6 α_C (estimated from the instantaneous Tafel slope) *vs.* η plot at various temperatures.

2.3 Tafel analysis and estimation of the electrochemical charge-transfer coefficient (α)

The relation between the i_k and the applied overpotential (η) is given by the Butler-Volmer (B-V) relation (equation S6).

$$i_k = i_0\left(e^{-\frac{\alpha F\eta}{RT}} - e^{\frac{(1-\alpha)F\eta}{RT}}\right) \quad \text{(S6)}$$

Here, i_0 is the exchange current. At large negative η, the cathodic current contribution in the B-V equation dominates, and the anodic current is negligible; that is $\exp(-\alpha f\eta) >> \exp(1-\alpha)f\eta$. Hence, equation S6 yields equation S7.

$$i_k = i_0 \exp\left(\frac{-\alpha F\eta}{RT}\right) \quad \text{(S7)}$$

Taking log on both the sides and rearranging yields equation S8.

$$\eta = \frac{RT}{\alpha F}\ln(i_0) - \frac{RT}{\alpha F}\ln(i_k) \quad \text{(S8)}$$

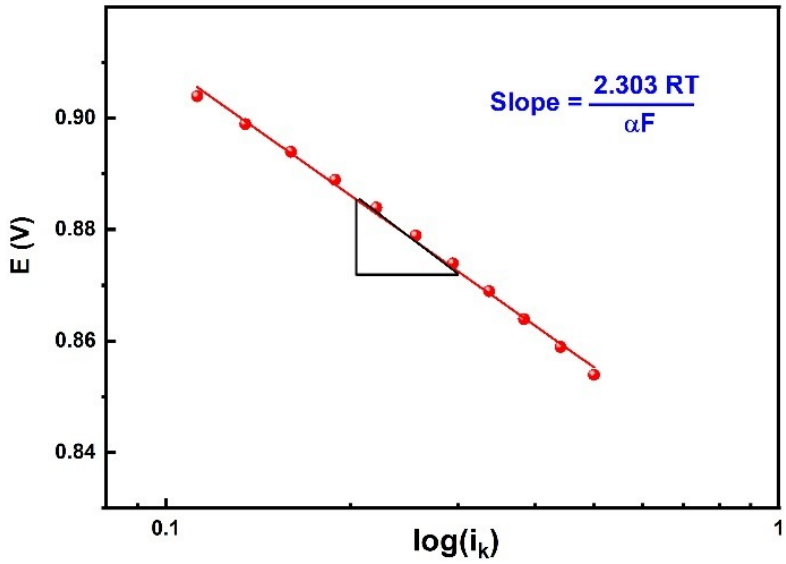

Figure S7 Potential *vs.* log (i_k) plot (Tafel plot).

Hence, plots of η/potential *vs.* log (i_k) (Tafel plots) at various temperatures are used to estimate the α at each temperature (equation S9).

$$\alpha = \frac{2.303 \times R \times T}{slope \times F} \tag{S9}$$

3.1 Estimation of the activation enthalpy ($\Delta H^{\#}$) from the Eyring plot

The rate of any heterogeneous electrochemical reaction is given by equation S10.[6]

$$Rate\ of\ reaction = \frac{dN}{dt} = k[C] = \frac{i_k}{nFA} \tag{S10}$$

$$k = \frac{i_k}{nFAC} \tag{S11}$$

Here *N, k*, C, and A are the number of moles, the heterogeneous rate constant, the concentration of the dissolved reacting species (mol cm^{-3}) and the area of the electrode, respectively.

Rate constant of a heterogeneous reaction is also given by Eyring relation (equation S12).

$$k = \frac{\kappa k_B T}{h} exp\left(-\frac{\Delta G^{\#}}{RT}\right) \tag{S12}$$

Here, $\Delta G^{\#}$ is the Gibbs free energy. Moreover, equation S13 is obtained on accounting for the surface coverage (θ) by the adsorbed species.

$$k = \frac{\kappa k_B T(1-\theta)}{h} exp\left(-\frac{\Delta G^{\#}}{RT}\right) \quad \text{(S13)}$$

Thus, *(1-θ)* is the fraction of the electrode surface available for the electrochemical reaction. Further $\Delta G^{\#}$ is defined by the equation S14.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad \text{(S14)}$$

Here, $\Delta H^{\#}$ and $\Delta S^{\#}$ are the enthalpy of activation and entropy of activation, respectively. On substituting the equation S14 to equation S13 and comparing with equation S11 yields equation S15.

$$\frac{i_k}{T} = \frac{\kappa k_B nFA(1-\theta)C}{h} exp\left(\frac{\Delta S^{\#}}{R}\right) exp\left(-\frac{\Delta H^{\#}}{RT}\right) \quad \text{(S15)}$$

Taking log on both sides yields equation S16.

$$\frac{d\left(log\left(\frac{i_k}{T}\right)\right)}{d(1/T)} = \frac{1}{2.303}\ln\left(\frac{nFAC\kappa k_B(1-\theta)}{h}\right) + \frac{\Delta S^{\#}}{2.303 \times R} + \frac{(-\Delta H^{\#})}{2.303 \times R} \quad \text{(S16)}$$

Thus, $\Delta H^{\#}$ at various overpotentials is estimated from the slope of Eyring plots (log (i_k/T) *vs.* $1/T$) (**Figure S8**). In principle, the intercept of the Eyring plot yields the $\Delta S^{\#}$ values**.**

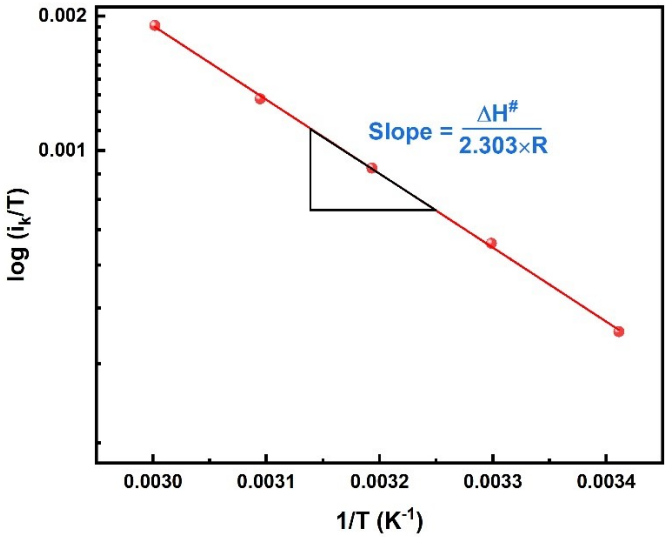

Figure S8 Eyring plot used for the estimation of $\Delta H^{\#}$ (log (i_k/T *vs.* $1/T$)) at a given η.

The following relations (equation S17 and equation S18) are used to estimate the $\Delta H^{\#}$ and $\Delta S^{\#}$ from the Eyring plot.

$$\text{Slope} = \frac{-\Delta H^{\#}}{2.303 \times R} \tag{S17}$$

$$\text{Intercept } (A_f) = \frac{1}{2.303}\ln\left(\frac{nFA(1-\theta)C_{O_2}\kappa k_B}{h}\right) + \frac{\Delta S^{\#}}{2.303 \times R} \tag{S18}$$

3.2 Enthalpic contribution of the charge-transfer coefficient (α_H)

The enthalpic contribution of the α to the total α is obtained from $\Delta H^{\#}$ *vs.* η plot. The slope of $\Delta H^{\#}$ *vs.* η plot is given by the equation S19.

$$slope = \frac{\alpha_H \times F}{1000} \tag{S19}$$

$$\alpha_H = \frac{slope \times 1000}{F} \tag{S20}$$

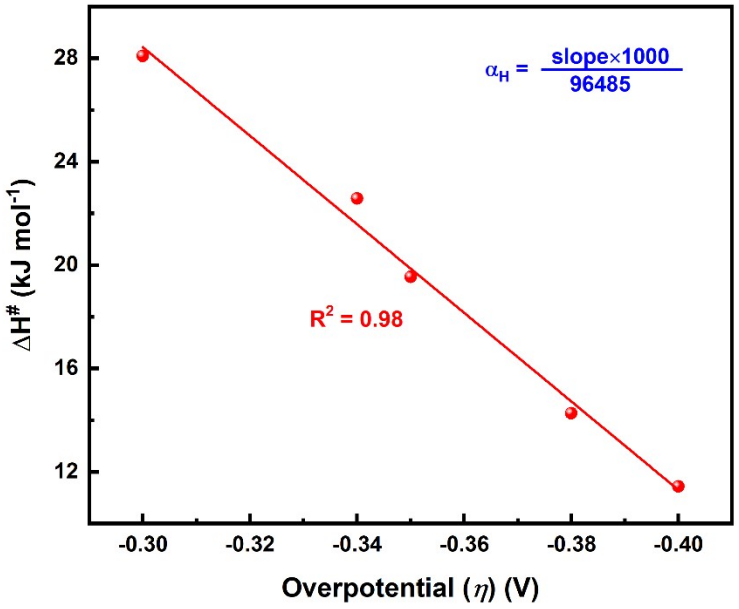

Figure S9 $\Delta H^{\#}$ *vs.* η plot for ORR on Pt black (~51 µg cm^{-2}) in 0.1 M $HClO_4$.

3.3 Entropic contribution of the charge-transfer coefficient (α_S)

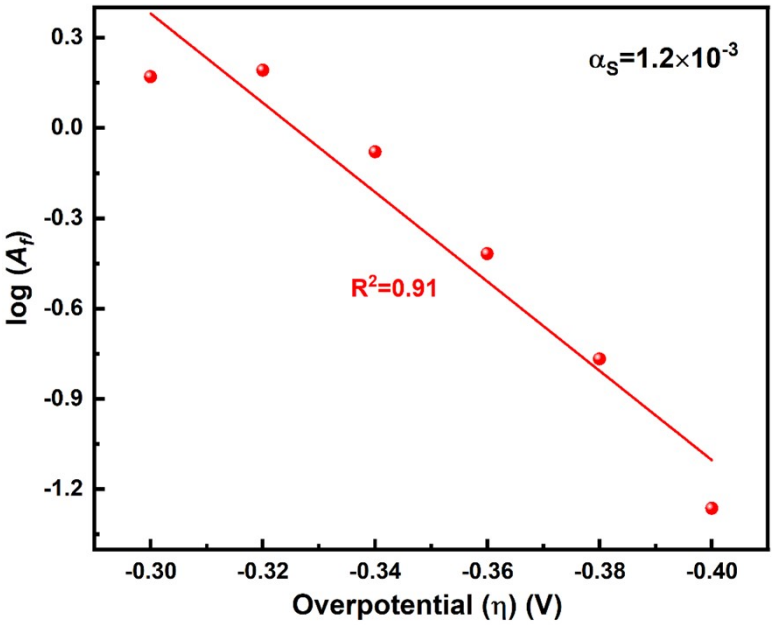

Figure S9 log (A_f) *vs.* η plot for ORR on Pt black (~51 µg cm^{-2}) in 0.1 M $HClO_4$.

Except the $\Delta S^{\#}$ and θ values in the equation S18, all the other quantities remain constant with temperature and potential. Therefore, the plot of intercept of the Eyring plot (A_f) *vs.* η is used to estimate the α_S. As explained in Section 3.4, the slope of the log (A_f) *vs.* η hence α_S does not change much after correcting the A_f for the surface coverage ($1-\theta$). The slope of log (A_f) *vs.* η is given by equation S21.

$$slope = \frac{\alpha_S \times F}{R} \tag{S21}$$

$$\alpha_S = \frac{slope \times R}{F} \tag{S22}$$

The total α of heterogeneous electrochemical reaction is also given by equation S23.

$$\alpha = \alpha_H + T\alpha_S \tag{S23}$$

Table ST2 α_S and Tα_S at 313 K, estimated at various electrodes

Slope	α_S (×10^{-3})	Tα_S	R^2
-17.5	-1.5	-0.47	0.94
-19.4	-1.6	-0.52	0.95
-14.8	-1.2	-0.39	0.91
-21	-1.8	-0.56	0.98
-10.5	-0.9	-0.28	0.85

3.4 Effect of surface coverage on the pre-exponential factor (A_f)

The effect of θ is contained in the pre-exponential term of the Eyring relation (equation S24).

$$\frac{i_k}{T} = \frac{\kappa k_B n F A (1-\theta) C_{O_2}}{h} exp\left(\frac{\Delta S^{\#}}{R}\right) exp\left(-\frac{\Delta H^{\#}}{RT}\right) \quad \text{(S24)}$$

$$\frac{d\left(log\left(\frac{i_k}{T}\right)\right)}{d(1/T)} = \frac{1}{2.303}\ln\left(\frac{nFAC_{O_2}\kappa k_B}{h}\right) + \frac{1}{2.303}\ln(1-\theta) + \frac{\Delta S^{\#}}{2.303 \times R} + \frac{(-\Delta H^{\#})}{2.303 \times R} \quad \text{(S25)}$$

Since the θ is estimated from the voltammograms at various temperatures, equation S25 is used to account for the θ. The A_f *vs.* η slope does not change after accounting for the θ (**Fig. S11**).

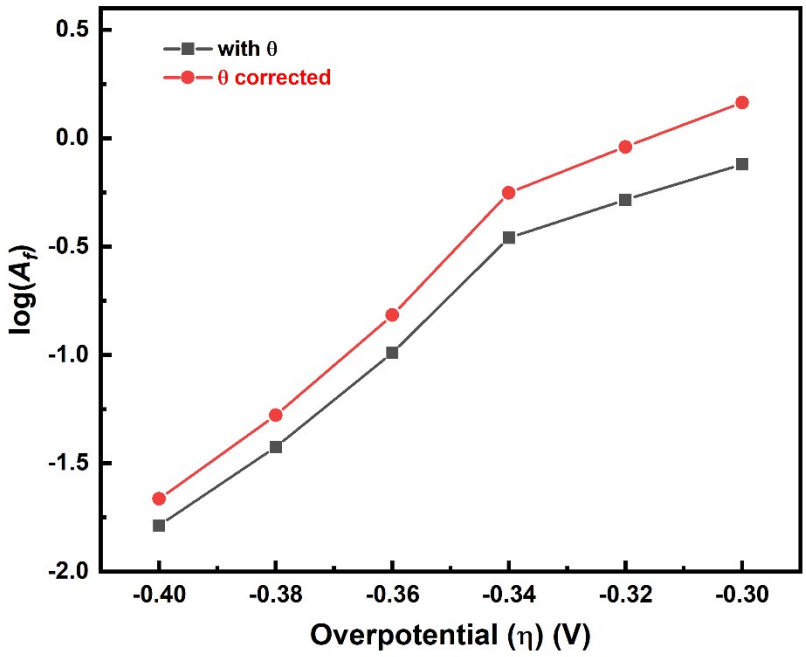

Figure S10 log (A_f) *vs.* η plot for ORR on Pt black (~51 µg cm^{-2}) in 0.1 M $HClO_4$, red line represents the data corrected for θ.

3.5 Illustration of electrochemical and electrocatalytic processes by Eyring plots at various overpotentials

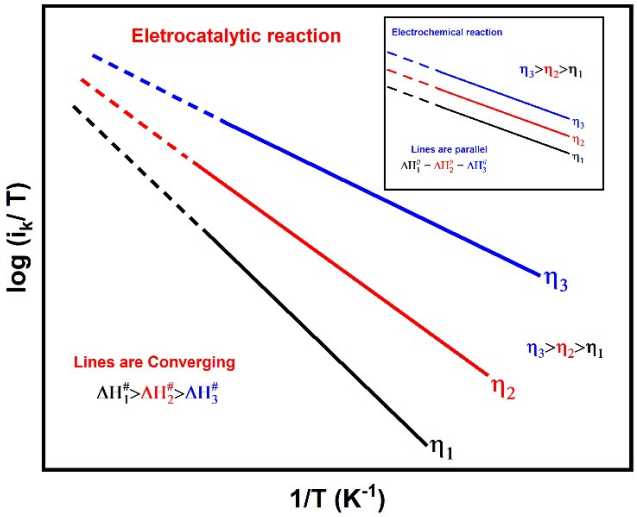

Figure S11 Schematic of the Eyring plots at various overpotentials for electrochemical (inset) and electrocatalytic reactions.

3.6 Theoretical limiting current density at rotating disk electrode (RDE)

Diffusion-limited current density (j_d) of the reaction in a rotating disk electrode (RDE) configuration is given by the Levich relation (equation S26).

$$j_{d,RDE} = 0.62nFC_0D^{2/3}\upsilon^{-1/6}\omega^{1/2} \quad \text{(S26)}$$

For ORR at 293 K, *n (4), F (96485 C mol^{-1}), C_0 (1.26×10^{-6} mol cm^{-3}), D (1.93×10^5 cm^2 s^{-1}), υ (0.01009 cm^2 s^{-1}), ω (1600 rpm=167.5 rps)* are the number of electrons transferred, Faraday constant, concentration of the dissolved oxygen, diffusion coefficient of the oxygen, kinematic viscosity, and angular velocity, respectively.

Putting these values in equation S26.

$$j_{d,RDE} = 0.62 \times 4 \times 96485 \times 1.26 \times 10^{-6} \times (1.93 \times 10^5)^{2/3} \times (0.01009)^{-1/6} \times (167.5)^{1/2}$$

$$j_{d,RDE} = 6.034\ mA\ cm^{-2}$$

3.7 Temperature dependence of the j_d

j_d of an electrochemical reaction in a RDE configuration is given by Levich relation (equation S26). It is decided by the temperature-dependent diffusion coefficient of O_2 (D_{O2}) in the electrolyte and kinematic viscosity (υ).

Temperature-dependence of the D_{O2} in the aqueous electrolyte is given by equation S27.

$$D_{O_2} \propto \frac{T}{\eta} \tag{S27}$$

The relation between the ratio of dynamic viscosity (η) and the electrolyte density (ρ) is given by equation S28.

$$\nu = \frac{\eta}{\rho} \tag{S28}$$

Also, for an open system, the sum of the partial pressures is the total pressure of 1 bar (equation S29).

$$P_{O_2} + P_{H_2O} = 1 \tag{S29}$$

Using equations S26, S27, S28, and S29, then rearranging yields equation S30[2].

$$J_{d,T} \propto \frac{T^{2/3}\,\rho^{1/6}}{\eta^{5/6}} C_{O_2}\left(1 - P_{H_2O}\right) = P_T C_{O_2}\left(1 - P_{H_2O}\right) \tag{S30}$$

Normalizing the temperature-dependent j_d with j_d at 20°C temperature gives equation S31.

$$\frac{j_{d,T}}{j_{d,20}} = \frac{P_T C_T\left(1 - P_{H_2O(T)}\right)}{P_{(20^oC)} C_{(20^oC)}\left(1 - P_{H_2O(20^oC)}\right)} \tag{S31}$$

Here, C_T is the total pressure of dissolved oxygen at temperature T, and P_T is the total pressure. It is assumed that the temperature dependence of viscosity, solubility of O_2, and acid density are the same as those for pure water.

Based on the above relations, the j_d up to 318 K is predicted to be constant; and then it decreases with increase in temperature[2]. At higher temperatures, such decrease in j_d is attributed to a significant rise in the electrolyte partial pressure.

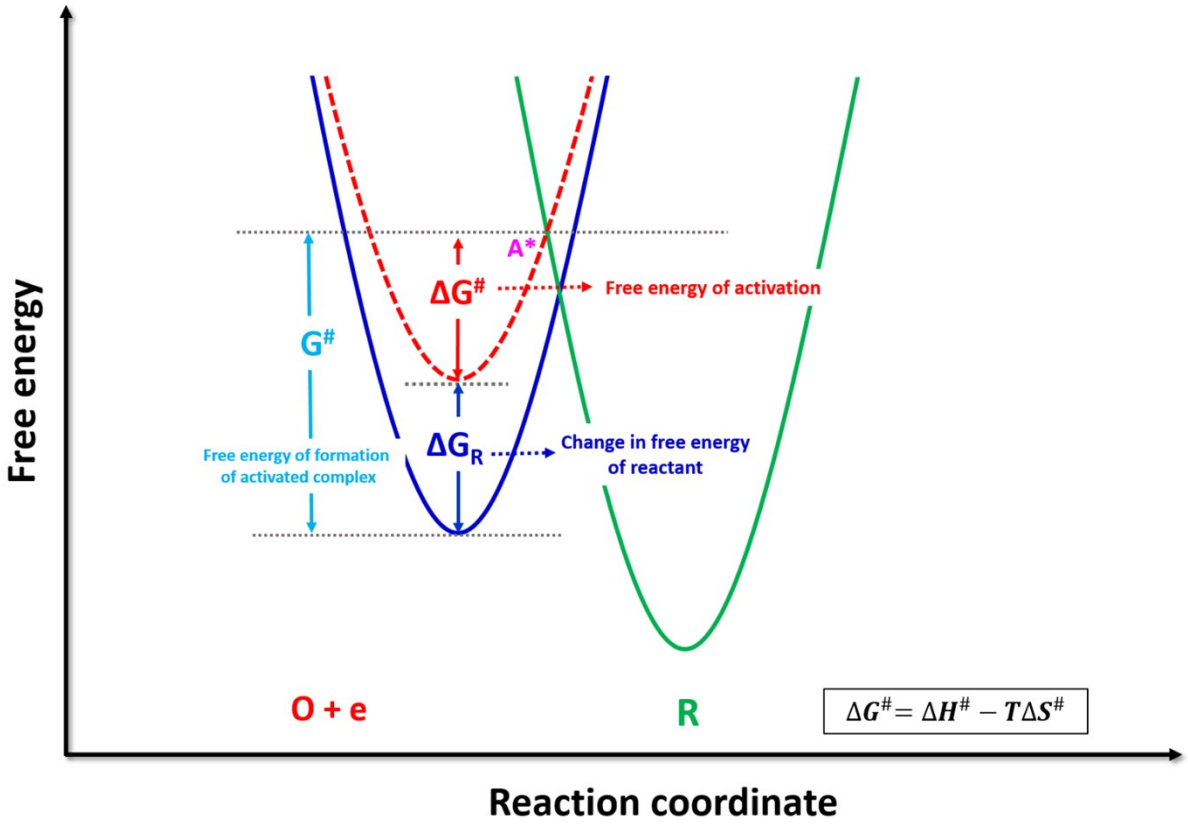

Figure S12 Schematic of energy surface diagram for Gibbs Free Energy/activation enthalpies referred in the main manuscript.

References

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