The Impact of Overpotential on the Enthalpy of Activation and Pre-1 exponential Factor of Electrochemical Redox Reactions 2 Anand Kumar Tripathi¹, Divya Priyadarshani², Miji E Joy¹, Rajan Maurya¹ and Manoj 3 4 Neergat*1 5 ¹Department of Energy Science and Engineering ²Centre for Research in Nanotechnology & Science 6 Indian Institute of Technology Bombay, Powai, Mumbai-400076, India 7 8 9 *Corresponding author:

- 10 Tel.: +91 22 2576 7893
- 11 Fax: +91 22 2576 4890
- 12 E-mail address: nmanoj@iitb.ac.in



Supporting Information (SI)



14

15 Figure S1. The calculation for $\Delta H^{\#}$ and pre-exponential factor from the slope and intercept

16 of the Eyring plot, respectively.



1

Figure S2. Electrochemical impedance spectra (EIS) of V⁵⁺/V⁴⁺ redox reaction at various 2 temperatures. Symbols and solid lines represent experimental and fitted data, respectively. 3 The impedance spectra are fitted using complex non-linear least square (CNLS) method with 4 5 "ZSimpWin" software from Solartron. All the EIS measurements are conducted at OCP with 10 mV sinusoidal amplitude in the frequency range of 100 kHz to 50 mHz (with 10 points per 6 7 decade). Modified Randle's circuit, shown in the inset, is used for fitting all the EIS data, where Q_1 and Q_2 are constant phase element for charge-transfer and mass-transfer processes, 8 respectively, and R_S , R_I and R_2 are the solution resistance, charge-transfer and mass-transfer 9 resistance, respectively. The values of solution resistance (R_s) obtained are 2.55, 2.43, 2.36 10 and 2.25 ohm at 25, 30, 35 and 40 °C, respectively. 11



1

Figure S3. LSVs of equimolar (0.5 M each) V^{5+}/V^{4+} solution recorded at 25 °C at a scan rate of 20 mV s⁻¹ and 1600 RPM. The location 1 is the position at which measured current at overpotential 295 mV (1.23 and -1.03 mA cm⁻² for anodic and cathodic reactions, respectively) used for j_l . The location 2 is the position of the assumed j_l (1.25 and -1.06 mA cm⁻² for anodic and cathodic reaction, respectively).



8 **Figure S4**. Differential Tafel plot (DTP) using j_l as the measured current at 9 overpotential 295 mV (black circle; 1) and the same calculated using the assumed value 10 of j_l (red circle; 2).

1 S1. Estimation of wetted surface area of Vulcan XC-72 modified glassy carbon electrode

2 For the kinetic analysis, Vulcan XC-72 modified glassy carbon rotating disk electrode is used. Since electrode is porous, the real surface area is different from the geometrical surface 3 area. Therefore, an active surface area of the electrode must be estimated. Geometric surface 4 area of smooth glassy carbon electrode can be approximated as an active surface area.¹⁻³ 5 Specific surface area of the porous electrode is estimated using BET theory⁴⁻⁶ and sometime, 6 porous electrode material can be made inaccessible for the electrolyte by filling it with 7 lacquer or epoxy.⁷ Friedl *et al.* proposed a method to estimate the wetted surface area (A_{wet}) 8 for the multiwalled carbon nanotubes (MWCNTs).8 Similar method is used to estimate the 9 wetted surface area of Vulcan XC-72 as well as nitrogen-doped carbon in alkaline medium.9 10 Therefore, A_{wet} is calculated in a similar way using C_{DL} derived from the EIS and it is used to 11 normalize the current throughout this study. For cylindrical capacitor, A_{wet} is determined from 12 the double layer capacitance (C_{DL}) using equation S1.⁸ 13

$$C_{DL} = \epsilon_0 \epsilon_r \frac{A_{wet}}{t_{DL}}$$
(S1)

14 Here, $\in_{0^{p}} \in_{r}$ and t_{DL} are permittivity of free space, relative dielectric permittivity and 15 thickness of double layer, respectively.

16 Equation S1 can be simplified for a plate capacitor, if radius of one MWCNT is much larger 17 than the t_{DL} . In other words, it is applicable to all porous materials where the particle diameter 18 is much higher than the double layer thickness. The double layer thickness is considered as an 19 innermost water layer (~2 A)¹⁰ and dielectric constant chosen within first layer of water is 20 ~7.¹¹ The value of *Awet* obtained using C_{DL} is ~10 cm².



Figure S5. Eyring plots derived from *i-V* curve for anodic (a) and cathodic (b) reactions at 60
mV of overpotential with equimolar (0.5 M each) V⁵⁺/V⁴⁺ solution. Symbols and solid lines
show the experimental and fitted data, respectively.

5 The R²-values of the lines for both the anodic and cathodic reactions, reported in the Figure 3
6 in the revised manuscript, are ~0.98. Figure S5 shows the Eyring plots with an error bar for
7 both the anodic and cathodic reactions at 60 mV of overpotential.

8 The scale of y-axis of Figure S5 is changed (compared to the scale of y-axis of Figure 3
9 shown in the revised manuscript) to show the error bar clearly.

10 At 60 mV of overpotential, the R²-values of the fitted lines for both anodic and cathodic

- 11 reactions are ~0.98. The 95% two-sided confidence interval for $\Delta H^{\#}$ is (21 kJ mol⁻¹, 26.66 kJ
- 12 mol⁻¹) and (23.64 kJ mol⁻¹, 31.83 kJ mol⁻¹) for anodic and cathodic reactions, respectively.







2

Figure S7. Variation of the ΔH[#] (a) and pre-exponential factor (b) with overpotential using
equimolar concentration (0.5 M each) of V⁵⁺/V⁴⁺ solution.

5 **Table S1.** Charge-transfer coefficients estimated from the Tafel plots for anodic 6 and cathodic reactions at various overpotential ranges at 298 K. LSV recorded in a three-7 electrode configuration on Vulcan XC-72 modified glassy carbon rotating disk electrode is 8 corrected for solution resistance and mass-transfer resistance.

Overpotential	$\alpha_{\rm a}$ (calculated from	Tafel slope	$\alpha_{\rm a}$ (calculated from	Tafel slope
regions	the anodic current)	(mV dec ⁻¹)	the cathodic current)	(mV dec ⁻¹)
Region 1	0.72	82	0.51	115
(10 -80 mV)				
Region 2	0.4	149	0.34	172
(90 -140 mV)				
Region 3	0.35	170	0.38	154
(150 -200 mV))			



2 Figure S8. Chronoamperometry responses of equimolar (0.5 M each) V⁵⁺/V⁴⁺ solution at
3 various overpotentials for anodic (a) and cathodic (b) reactions.



4

5 Figure S9. Steady-state polarization curves (Tafel plots) constructed using the current 6 densities sampled from chronoamperometry responses. The *i-V* curve was corrected for iR_s , 7 and mass-transfer. Symbols and solid lines show the experimental and fitted data, 8 respectively. The R²-values of the fitted lines are ~0.99.

Table S2. Charge-transfer coefficients obtained using the Tafel plots constructed from the
 current densities sampled using chronoamperometry responses for anodic and cathodic
 reactions at 25 °C. The value shown in bracket is obtained from the linear-sweep
 voltammogram (LSV).

Temperature (K)	α_a	α_c
(13)	(calculated from anodic current)	(calculated from cathodic current)
298	0.76 (0.72)	0.55 (0.51)

5

6 References

- 7 1. G. Oriji, Y. Katayama and T. Miura, J. Power Sources, 2005, **139**, 321-324.
- 8 2. E. Sum and M. Skyllas-Kazacos, *J. Power Sources*, 1985, **15**, 179-190.
- 9 3. E. Sum, M. Rychcik and M. Skyllas-Kazacos, J. Power Sources, 1985, 16, 85-90.
- X. W. Wu, T. Yamamura, S. Ohta, Q. X. Zhang, F. C. Lv, C. M. Liu, K. Shirasaki, I.
 Satoh, T. Shikama, D. Lu and S. Q. Liu, *J. Appl. Electrochem.*, 2011, 41, 1183-1190.
- D. Aaron, C.-N. Sun, M. Bright, A. B. Papandrew, M. M. Mench and T. A.
 Zawodzinski, *ECS Electrochem. Lett.*, 2013, 2(3), A29-A31.
- 14 6. R. Schweiss, J. Power Sources, 2015, **278**, 308-313.
- A. Bourke, M. A. Miller, R. P. Lynch, X. Gao, J. Landon, J. S. Wainright, R. F.
 Savinell and D. N. Buckley, *J. Electrochem. Soc.*, 2016, 163, A5097-A5105.
- 17 8. J. Friedl and U. Stimming, *Electrochim. Acta*, 2017, **227**, 235245.
- A. Chakraborty, R. Devivaraprasad, B. Bera and M. Neergat, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25414-25422.
- 20 10. J. Friedl, C. M. Bauer, A. Rinaldi and U. Stimming, *Carbon*, 2013, **63**, 228-239.
- 21 11. J. O. Bockris, M. A. V. Devanathan and K. Mueller, Proc. R. Soc. Lond. A. Math.
- 22 Phys. Sci., 1963, **274**, 55-79.