Revisiting Ammonia Oxidation Reaction on Polycrystalline Pt: A Rotating Ring Disk Electrode-based Investigation

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S1. Cyclic voltammograms of Pt-black electrodes in acidic and alkaline medium

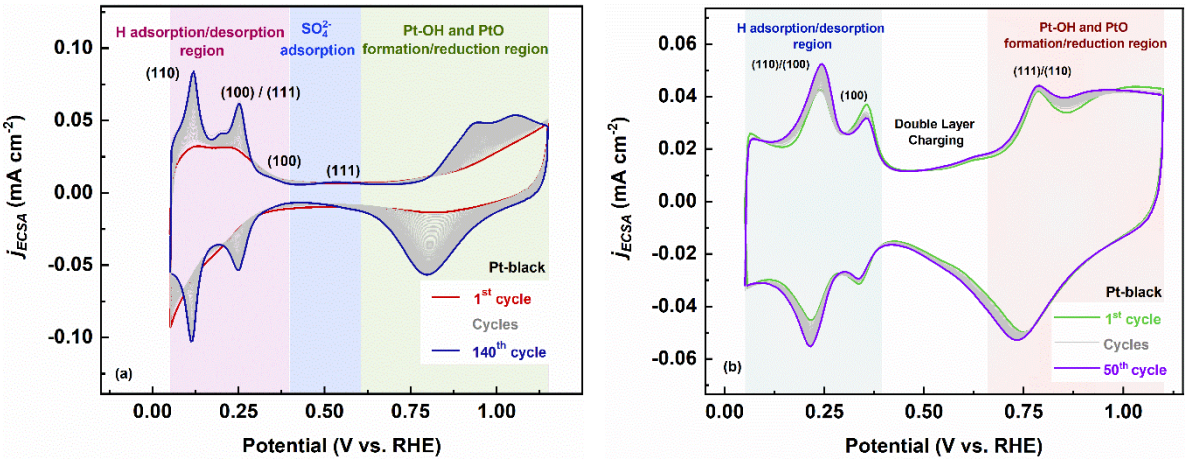


Figure S1. CVs of Pt-black (51 μg_{Pt} cm^{-2}) electrodes in argon-saturated (a) 0.5 M H_2SO_4 and (b) 0.1 M KOH supporting electrolyte. CVs were recorded in the potential range of 0.05–1.15 V and 0.05–1.1 V in 0.5 M H_2SO_4 and 0.1 M KOH, respectively, at a scan rate of 50 mV s^{-1}.

The cyclic voltammograms (CV) of Pt-black in 0.5 M H_2SO_4 and 0.1 M KOH are shown in **Figure 4.1.1. (a) and (b)**. The CVs can be bifurcated into three distinct regions- H adsorption and desorption at potentials less than 0.4 V, double layer charging in between 0.4-0.65 V and Pt-O formation at potentials greater than 0.65 V.[1–3] The voltammograms of Pt-black were first recorded in 0.5 M H_2SO_4 to activate the sites followed by potential cycling in 0.1 M KOH until the CVs saturated. The potential range for CVs in Figure 4.1.1. (b) was chosen such that the surface oxides at higher potentials could undergo reduction and there was minimal irreversible adsorption of OH^- species.[4]

S2. Procedure for preparing NH_3 solution in 0.1 M KOH

For most of the experiments reported in this study, the AOR voltammograms were recorded in an aqueous argon-saturated 0.1 M KOH + 1 M NH_3. The electrolyte solution was prepared by injecting 6.75 mL of NH_3 (28 wt %) into 100 mL of 0.1 M KOH, already purged with Ar for 30 min. The electrode was rotated at 1600 rpm for 10 s after adding the NH_3 solution to ensure uniform distribution of NH_3 in the electrolyte. For experiments involving various other concentrations of NH_3, the required volume of NH_3 was calculated using Equation S1.

$$\boldsymbol{Volume\ of\ NH_3 = \frac{M \times V \times MW}{\rho \times wt\ \%}} \qquad \textbf{(S1)}$$

S3. NH_3 concentration dependence profile of Pt-disk and Pt-black

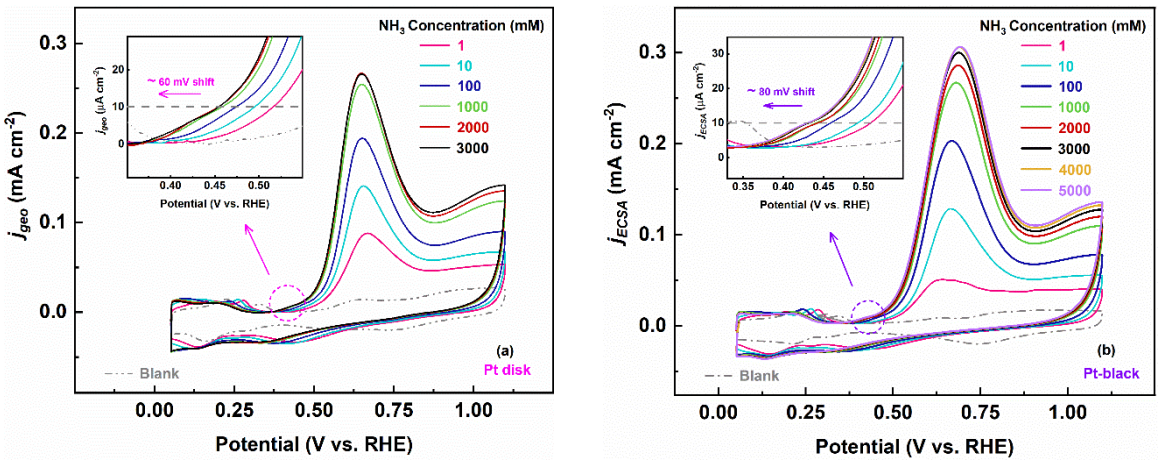


Figure S3. Cyclic voltammograms of (a) Pt-disk and (b) Pt-black in argon-saturated 0.1 M KOH with various concentrations of NH_3 at a scan rate of 20 mV s^{-1}. The inset shows the shift in the potential at a fixed current density of 10 µA cm^{-2} with increasing NH_3 concentration.

The effect of concentration on AOR was investigated by varying the NH_3 concentration till the AOR peak currents attained saturation. The AOR peak currents begin saturating at concentrations of 1 M, and hence, all experiments were performed using that concentration.

S4. Electrochemical active surface area measurements (ECSA)

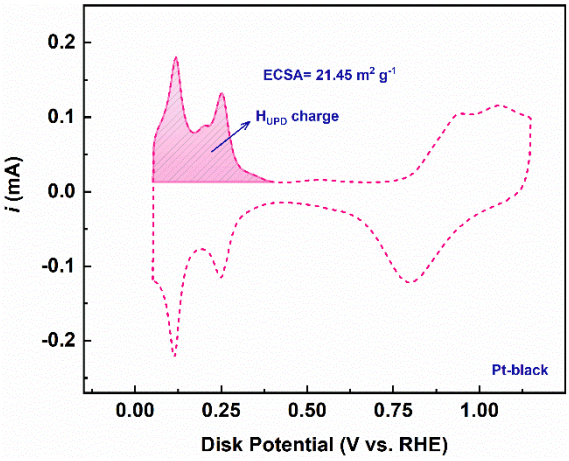


Figure S4. Voltammogram of Pt-black in argon-saturated 0.5 M H_2SO_4 solution at a scan rate of 50 mV s^{-1}. The shaded region refers to hydrogen desorption.

The Pt ECSA can be estimated using **Equation S2**.

$$\boldsymbol{ECSA_{Pt}\left(cm_{Pt}^{2}\,g^{-1}\right) = \frac{H_{upd}\ charge\ (C)}{Charge\ density\ (\mu C\ cm^{-2}) \times n \times m_{Pt}\ (g)}} \qquad \textbf{(S2)}$$

Here, H_{upd} charge corresponds to the charge under the H_{des} region in the CV (shaded region), n refers to the number of electrons involved in the charge transfer, and m_{Pt} is the mass of the catalyst drop-casted on to the GCD. For a smooth Pt surface, 210 µC cm^{-2} is a widely accepted value as the average charge density of (100), (110 and (111) planes.[5]

S5. Effect of cycling of AOR on Pt-black

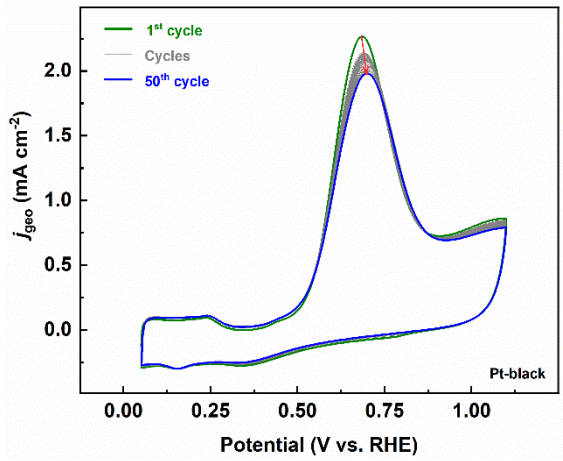


Figure S5. CVs of AOR on Pt-black up to 50 cycles in Ar-saturated 0.1 M KOH containing 1 M NH_3 at a scan rate of 20 mV s^{-1}.

S6. Mass transport dependence of AOR at different NH_3 concentrations

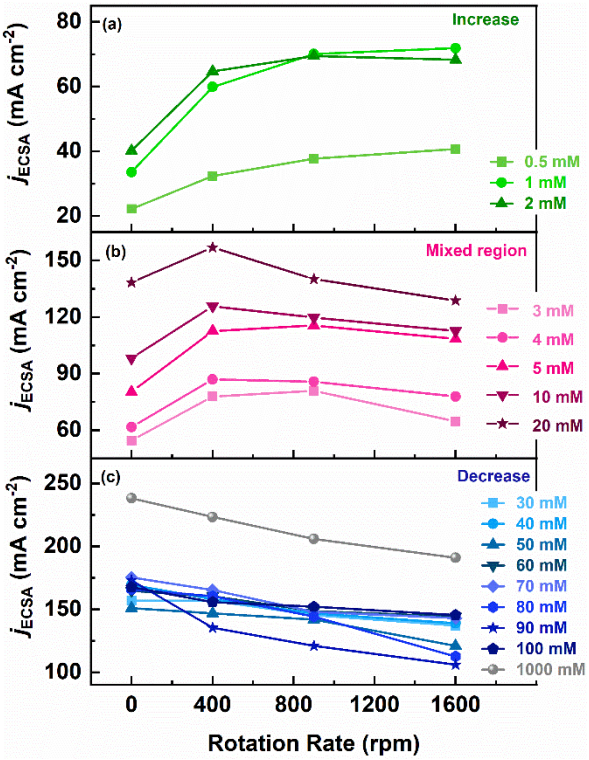


Figure S6. The trend in AOR currents on Pt-black with varying rates of rotations at different concentrations of NH_3 in 0.1 M KOH at 20 mV s^{-1}. (a) corresponds to experiments in the NH_3 concentration range from 0.5 mM to 2 mM, (b) corresponds to 3 mM to 20 mM and (c) refers to 30 mM to 1 M.

The influence of mass transport on AOR was investigated using a Pt-black electrode in different concentration ranges. At low concentrations of NH_3 (Figure S6a), the j_{peak}^{AOR} increases as the rotation rate is varied from 0.0 rpm to 1600.0 rpm. In the concentration range of 3 mM to 20 mM NH_3 (Figure S6b), no consistent trend is observed in the j_{peak}^{AOR} with rotation rate and is termed the mixed region. At concentrations higher than 20 mM, however, a consistent decrease in the j_{peak}^{AOR} mass transport is observed (Figure S6c).

S7. Recovery of H_{upd} area in 0.5 M H_2SO_4 after cycling in ammonia-containing supporting electrolyte up to different upper potentials

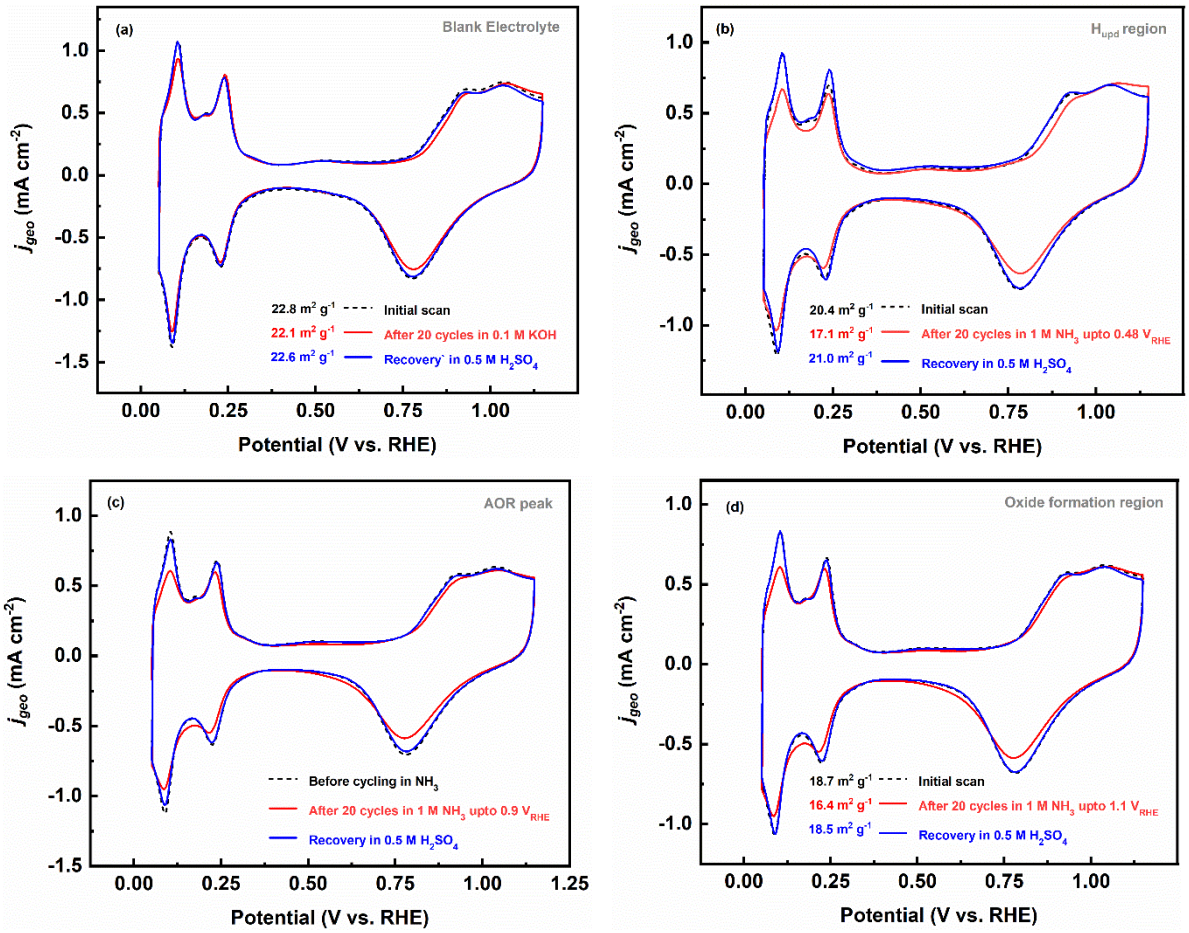


Figure S7. Voltammograms of Pt-black in 0.5 M H_2SO_4 before and immediately after recording 20 cycles in Ar-purged (a) 0.1 M KOH up to 1.1 V, (b) 1 M NH_3 in 0.1 M KOH up to 0.48 V, (c) 1 M NH_3 in 0.1 M KOH up to 0.9 V and (d) 1 M NH_3 in 0.1 M KOH up to 1.1 V.

Voltammograms of Pt-black were recorded in 0.5 M H_2SO_4 to estimate the ECSA using the method described in S4.

S8. Chronoamperograms under different experimental conditions

To clarify the origin of the step response, chronoamperograms of Pt-black were recorded in four different experimental conditions in NH_3-free and NH_3-containing solutions (**Figures S9**):

1. Case A: O_2-saturated 0.1 M KOH
2. Case B: 0.1 M KOH (not subjected to any method of purging or de-oxygenation)
3. Case C: Ar-saturated 0.1 M KOH (Figure 6c and 6c' presented in main manuscript)
4. Case D: Ar-saturated 0.1 M KOH post-electrochemical de-oxygenation (by holding the disk electrode at 0.45 V for 30 mins at 1600 rpm with continuous Ar purging)

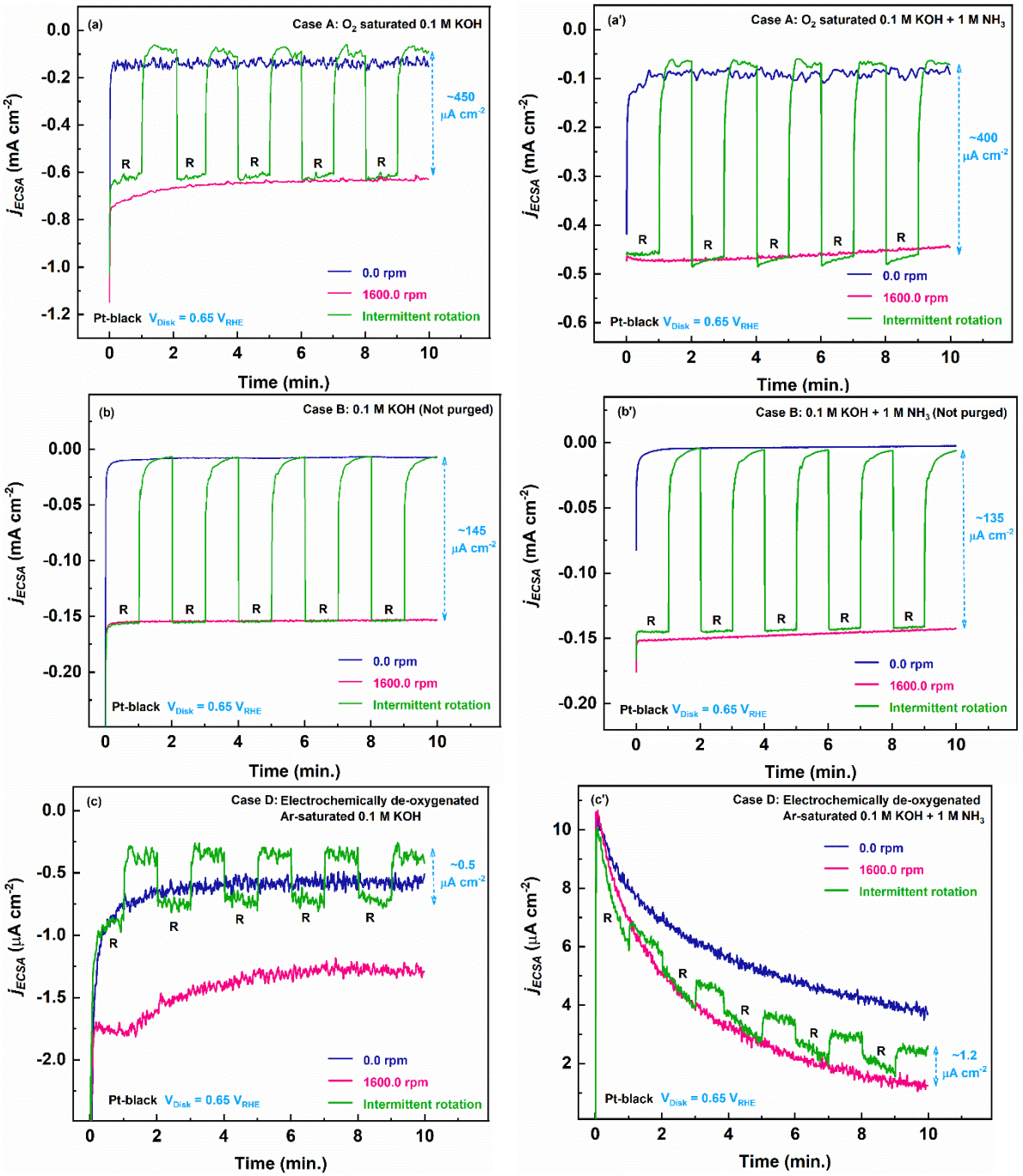


Figure S8. CAs on Pt-black at 0.65 V_{RHE} depicting the effect of intermittent rotation and convective mass transport in the (a) absence and (a') presence of 1 M NH_3 in O_2-saturated 0.1 M KOH. (b) and (b') correspond to the CAs recorded in absence and presence of 1 M NH_3, respectively, in 0.1 M KOH. (c) and (c') contain the CAs recorded in absence and presence of 1 M NH_3, respectively, in Ar-saturated 0.1 M KOH after electrochemical de-oxygenation. Figures (b), (b'), (c) and (c') present a magnified view highlighting the effect of intermittent rotation in 0.1 M KOH. The label 'R' denotes the period of rotation (1600.0 rpm) of the Pt-black electrode during intermittent rotation.

To establish a direct comparison, the step amplitudes of the chronoamperograms are tabulated (Table R1) under various experimental conditions (with and without NH_3 in O_2 purged, Ar-purged, electrochemically deoxygenated Ar-purged electrolytes by holding the disk electrode at 0.45 V for 30 mins at 1600 rpm with continuous Ar purging).

Table S1. Step amplitudes of the chronoamperograms under intermittent rotation with and without NH_3 under various experimental conditions

Conditions	**Step Amplitude**	
	Without NH_3 ($\mu A\ cm^{-2}$)	**With 1 M NH_3 ($\mu A\ cm^{-2}$)**
Case A (O_2-purged)	~450	~400
Case B (No purging)	~145	~135
Case C (Ar-purged) (from the manuscript)	~1.15	~1.06
Case D (Electrochemically deoxygenated and Ar-purged)	~0.5	~1.2

As evident from Table R1 and **Figure R4**, the step response reduces systematically with decrease in the dissolved O_2 content (440, 145, 1.15, 0.5 $\mu A\ cm^{-2}$) in NH_3-free electrolytes. This strongly indicates that the step response is a result of the reduction in the unintentionally dissolved oxygen content, i.e., ORR.

S9. Increased solubility of O_2 in NH_3

To experimentally verify the contribution of the dissolved O_2 content in the NH_3 stock solution to ORR, CAs were recorded in deoxygenated Ar-purged NH_3 solution in 0.1 M KOH electrolyte. **Figure R5** presents the step amplitudes obtained in Ar-purged NH_3. The decrease in the step amplitudes from ~1.06 $\mu A\ cm^{-2}$ (Figure R5) to ~0.6 $\mu A\ cm^{-2}$ (Figure 6b), indicates that the inherently dissolved O_2 content in the NH_3 solution contributes to ORR and leads to the step response.

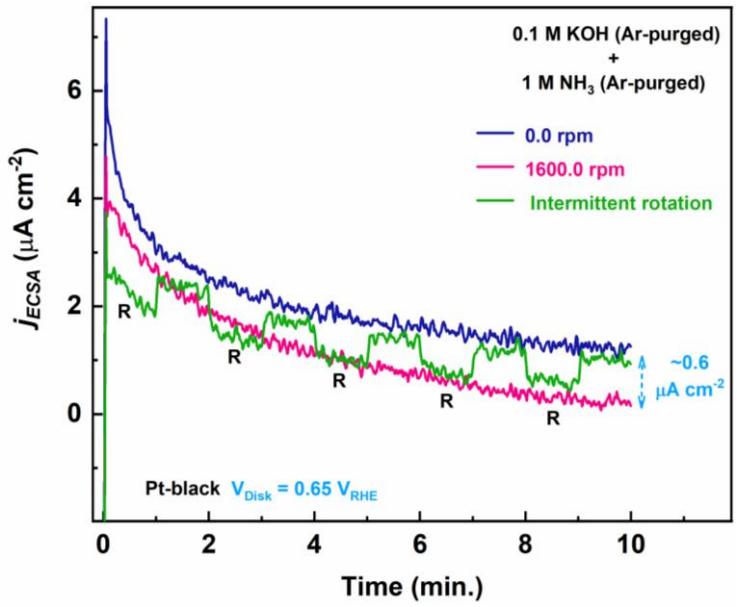


Figure S9. CAs on Pt-black at 0.65 V_{RHE} depicting the effect of intermittent rotation and convective mass transport in in Ar-purged 1 M NH_3 in Ar-purged 0.1 M KOH. Figures presents a magnified view highlighting the effect of intermittent rotation in 0.1 M KOH. The label 'R' denotes the period of rotation (1600.0 rpm) of the Pt-black electrode during intermittent rotation.

S10. RRDE data in NH_3-free supporting electrolyte

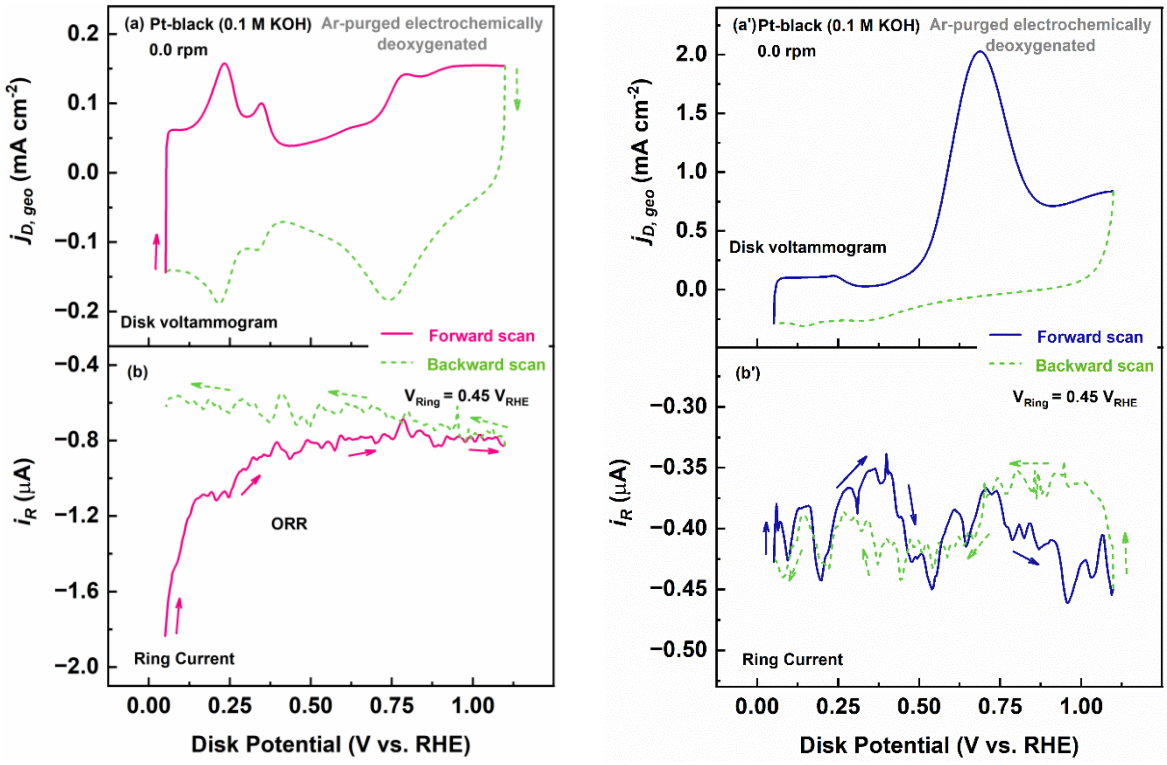


Figure S10. (a) and (a') CVs of Pt-black in (a) NH_3-free and (a') NH_3-containing solutions under static conditions. Frames (b) and (b') present the i_R recorded at 0.0 rpm in NH_3-free and NH_3-containing solutions, respectively. Solid and dotted lines correspond to forward and backward scan, respectively and arrows depict the direction of scan. All the data were recorded in electrochemically deoxygenated Ar-saturated 0.1 M KOH electrolyte as a function of the disk potential at a scan rate of 20 mV s^{-1}.

References

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