Supporting Information

Mechanism of hydrazine oxidation at Palladium electrodes: Long-lived radical di-cation formation

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Section 1 Palladium oxide voltammetry

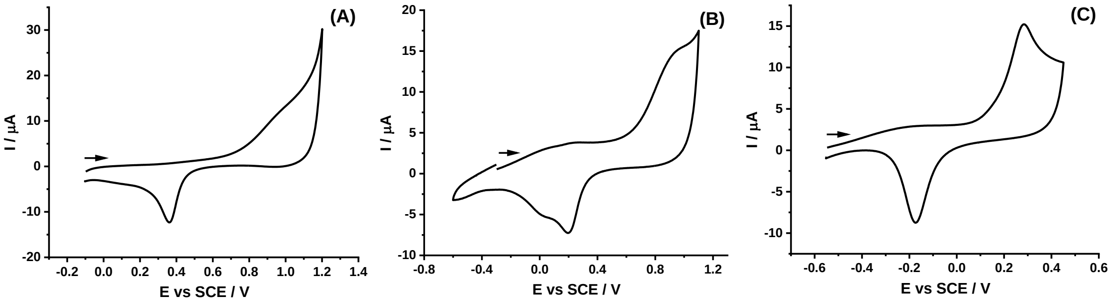

Fig. S1. Voltammograms recorded at a Pd electrode at 50 mV/s in (A) 0.1 M KNO_3 of pH 2, (B) 0.1 M KNO_3 of pH 7 and (C) 0.1 M PBS of pH 11. The transverse arrows indicate the start potentials and directions of the voltametric scans.

Section 2 Calculation of the effective dissociation constant

It is argued in the main text that in Fig. 3, Peak 1 corresponds to the direct oxidation of N_2H_4 and Peak 2 to the coupled pair of reactions consisting of a chemical dissociation reaction of $N_2H_5^+$ to N_2H_4 and then the following oxidation of the produced N_2H_4. Their mechanisms are as below:

Peak 1: $N_2H_4 \xrightarrow[slow]{-e} N_2H_4^{\bullet +} \xrightarrow[fast]{-3e} N_2 + 4H^+$

Peak 2: $N_2H_5^+ \rightleftarrows N_2H_4 + H^+$; $N_2H_4 \xrightarrow[slow]{-e} N_2H_4^{\bullet +} \xrightarrow[fast]{-3e} N_2 + 4H^+$

The peak potential shift between Peaks 1 and 2 is thus attributed to the preceding chemical equilibrium. Hence this separation can be used to describe the energetics of the equilibrium.

$$\Delta E = E_{Peak\,2} - E_{Peak\,1} = -\frac{RT}{\beta F}\ln K_{a,eff}$$

where $E_{Peak\,1}$ and $E_{Peak\,2}$ are the peak potentials of Peaks 1 and 2 respectively, ΔE the peak potential separation between both peaks, R the gas constant of 8.314 J mol^{-1} K^{-1}, T the temperature of 298.15 K, β the anodic transfer coefficient of N_2H_4 oxidation with a value of 0.42 from Tafel analysis (main text), F the Faraday constant of 96,485 C mol^{-1}, and $K_{a,eff}$ is the effective dissociation constant for $N_2H_5^+$ to N_2H_4 which is the product of the true K_a divided by the local proton concentration $K_{a,eff} = K_a / \left[H^+\right]_{local}$. Note that the local proton concentration is closely related to the progress of the oxidation of hydrazine with a value of *ca.* 10^{-3} M in the vicinity of the peak position where the exact value reflects not only the oxidation of hydrazine releasing four protons but also the high diffusion coefficient of the latter in aqueous media.

ΔE was estimated from Fig. 3 (main text) to be *ca.* 0.38 to 0.49 V where the uncertainty arises from the overlapping of Peaks 2 and 3. Hence, $K_{a,eff}$ is calculated to be 3.3×10^{-4} M to 2.0×10^{-3} M, which when corrected for the estimated local pH is consistent with the literature theoretical value of K_a (8.5×10^{-7} M) [1, 2]. This value signifies the significant effect of the preceding chemical equilibrium and local pH change as reported in our previous work [3].

References

[1] F. Cardulla, Hydrazine, J. Chem. Educ., 60 (1983) 505.
[2] L.J. Vieland, R.P. Seward, The Electrical Conductance of Weak Acids in Anhydrous Hydrazine, J. Phys. Chem., 59 (1955) 466-469.
[3] R. Miao, R.G. Compton, The Electro-Oxidation of Hydrazine: A Self-Inhibiting Reaction, J. Phys. Chem. Lett., 12 (2021) 1601-1605.