Electronic Supplementary Material

Single entity electrochemistry and the electron transfer kinetics of hydrazine oxidation

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Section S1: Chemical compositions of the solutions from pH 2 - 11

Table S1 Chemical compositions of the solutions from pH 2 - 11

pH	$[H^+]$ / M	$[H_2PO_4^-]$ / mM	$[HPO_4^{2-}]$ / mM	$[N_2H_4]$ / mM	$[N_2H_5^+]$ / mM
2	1.0E-02	/	/	0	1.500
7	1.0E-07	61.3	38.7	0.110	1.390
8.1	7.9E-09	11.2	88.8	0.750	0.750
8.3	5.0E-09	7.4	92.6	0.920	0.580
8.5	3.2E-09	4.8	95.2	1.073	0.427
8.8	1.6E-09	2.5	97.5	1.250	0.250
11	1.0E-11	0.0	100.0	1.498	0.002

Section S2: Mass transport corrected Tafel analysis

The Tafel slopes were calculated to be 0.41 ± 0.05 for the direct oxidation of $N_2H_5^+$ at pH 2 and 0.45 ± 0.08 for the direct oxidation of N_2H_4 at pH from mass transport corrected Tafel analysis of the nano-impact data (see the main text).

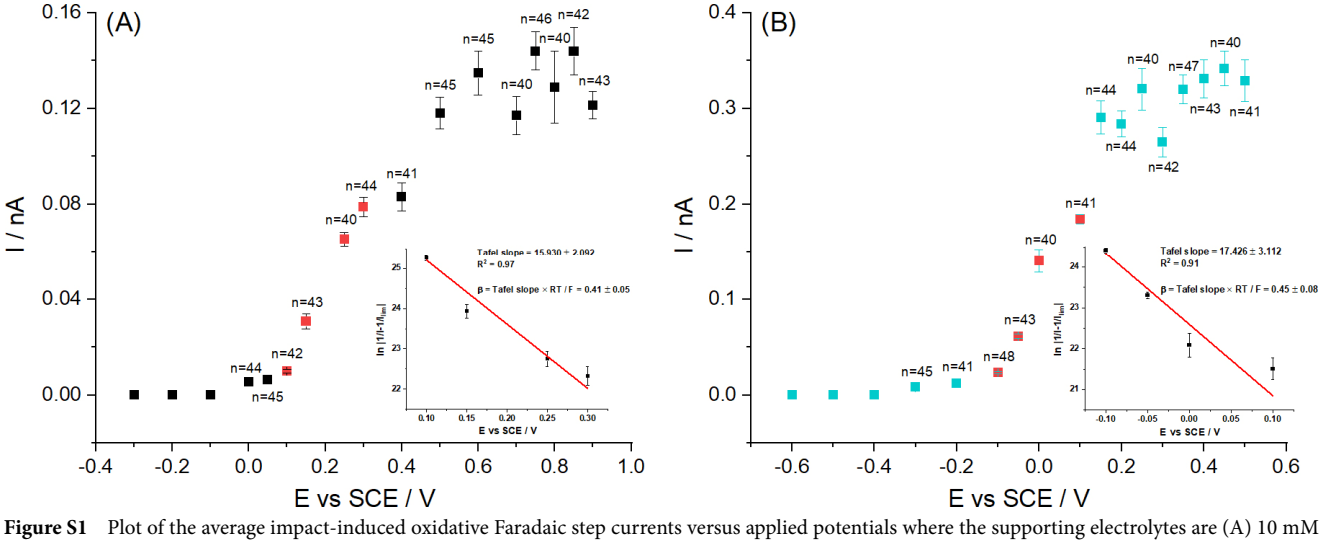

Figure S1 Plot of the average impact-induced oxidative Faradaic step currents versus applied potentials where the supporting electrolytes are (A) 10 mM HNO_3 and 0.1 M KNO_3 of pH 2 and (B) 0.1 M PBS of pH 11. n is the number of the steps analysed. The error bar is the standard error of the mean.

Section 3: Calculation of the diffusion coefficients

The chronoamperometric transient of a microband electrode is given by

$$i(t) = nFDclf(\tau)$$

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with

$$f(\tau)=1.004+\frac{1}{\sqrt{\pi\tau}}+1.3\exp(-2.53x)+\left(-1.133+\frac{0.59}{1+3\exp\left(\frac{x-1}{0.3415}\right)}\right)$$
$$\times\exp\left(\frac{-9.85}{\left(\ln\left[\tau\left(17.22-\frac{18.04}{1+\exp\left(\frac{x-1.113}{0.367}\right)}\right)\right]\right)^2}\right)$$

$$\tau=\frac{Dt}{w^2}$$

$$x=\log_{10}\frac{l}{w}$$

where n is the number of electrons transferred (assumed to be 4 [1-3]), D the diffusion coefficient, c the concentration of the analyte, l the length of the microband, w the width of the microband and t the time in seconds.

The limiting current is 0.13 ± 0.02 nA for the direct oxidation of $N_2H_5^+$, thus giving the $D_{N_2H_5^+}$ value of (2.8 ± 0.3) × 10^{-6} cm^2/s, whist that for N_2H_4 is 0.31 ± 0.04 nA giving the $D_{N_2H_4}$ value of (7.1 ± 0.8) × 10^{-6} cm^2/s.

Section 4: Details of the DIGISIM simulation

Table S2 DIGISIM simulation parameters

pH	$\beta_{N_2H_5^+}$	$k_{N_2H_5^+}$ (cm/s)	$D_{N_2H_5^+}$ (cm^2/s)	$\beta_{N_2H_4}$	$k_{N_2H_4}$ (cm/s)	$D_{N_2H_4}$ (cm^2/s)	$K_{eq,eff}$	k_f (s^{-1})
2	0.41	0.06	2.8×10^{-6}	/	/	/	/	/
7				0.45	3.3	7.1×10^{-6}	0.08	variable
8.1							1.0	
8.3							1.6	
8.5							2.5	
8.8							5.0	
11	/	/	/				/	/

The parameters used in the following simulation are summarised in Table S2. $\beta_{N_2H_5^+}$ and $\beta_{N_2H_4}$ are the transfer coefficients of $N_2H_5^+$ and N_2H_4 respectively; $D_{N_2H_5^+}$ and $D_{N_2H_4}$ are the diffusion coefficients of $N_2H_5^+$ and N_2H_4 respectively. Note that because the processes are fully electrochemically irreversible it is not possible to obtain unique values of the formal potentials and the electrochemical rate constants. Rather a single composite rate constant, $k=k^0e^{-\beta FE_f^0/RT}$ ($k_{N_2H_5^+}$ for $N_2H_5^+$ oxidation and $k_{N_2H_4}$ for N_2H_4 oxidation), is inferred with the implications that the simulation data are consistent with any pairs of standard electrochemical rate constant and formal potential values which fit the composite relationship.

Simulation for hydrazine oxidation at pH 2

As hydrazine oxidation involves four electrons transferred of which the first is rate-determining [1, 4, 5] and the homogeneous interconversion between N_2H_4 and $N_2H_5^+$ is negligible at pH 2, the mechanism of $N_2H_5^+$ oxidation was:

$$N_2H_5^+\xrightarrow{rds}N_2H_{5-a}^{2-a}+aH^++e$$

$$N_2H_{5-a}^{2-a}\xrightarrow{fast}N_2+(5-a)H^++3e$$

where a is the number of the protons released in the rate determining step. The rate constant for the fast step was set as 1 × 10^4 cm/s so to be fully driven. The formal potential E_f^0 for the rate determining step and the electrochemical rate constants were set arbitrarily as they cannot be determined independently for a fully irreversible process, rather an infinite range of pairs of these values are possible but subject to a composite electrochemical rate constant dependent on both parameters. Given the values of $\beta_{N_2H_5^+}$ = 0.41 and $D_{N_2H_5^+}$ = 2.8 × 10^{-6} cm^2/s as above, the experimental voltammogram-like characteristic from nanoimpacts of single Pd/GO in Figure 5A (black squares) was fitted well by the numerical simulation as depicted in Figure 5B (black line), yielding a composite electrochemical rate constant of $k^0_{N_2H_5^+}e^{-\beta_{N_2H_5^+}FE^0_{f,N_2H_5^+}/RT}$ = 0.06 ± 0.02 cm/s.

Simulation for hydrazine oxidation at pH 11

For pH 11, the mechanism of N_2H_4 oxidation was proposed as:

$$N_2H_4 \xrightarrow{rds} N_2H_{4-b}^{1-b} + bH^+ + e$$

$$N_2H_{4-b}^{1-b} \xrightarrow{fast} N_2 + (4-b)H^+ + 3e$$

where c is the number of the protons released in the rate determining step. Setting the formal potential arbitrarily with the known parameters $\beta_{N_2H_4} = 0.45$ and $D_{N_2H_4} = 7.1 \times 10^{-6}$ cm^2/s, the simulated result in Figure 5B (aquamarine line) is in accordance with the experimental data (aquamarine squares), from which the composite parameter $k^0_{N_2H_4} e^{-\beta_{N_2H_4} F E^0_{f,N_2H_4}/RT}$ for the direct oxidation of N_2H_4 was derived to be 3.3 $\pm$ 0.2 cm/s.

Simulation for hydrazine oxidation at pH 7 - 8.8

For the intermediate pHs from 7 - 8.8 where both N_2H_4 and $N_2H_5^+$ contribute to the electrochemical signals, a mechanism for the configurative oxidation of $N_2H_5^+$ and N_2H_4 was proposed:

$$N_2H_5^+ \rightleftharpoons N_2H_4 + H^+$$

$$N_2H_5^+ \xrightarrow{rds} N_2H_{5-a}^{2-a} + aH^+ + e$$

$$N_2H_{5-a}^{2-a} \xrightarrow{fast} N_2 + (5-a)H^+ + 3e$$

$$N_2H_4 \xrightarrow{rds} N_2H_{4-b}^{1-b} + bH^+ + e$$

$$N_2H_{4-b}^{1-b} \xrightarrow{fast} N_2 + (4-b)H^+ + 3e$$

Note that the *effective* equilibrium constant between $N_2H_5^+$ and N_2H_4 is pH-dependent as $K_{eq,eff} = K_{eq}/[H^+]$. The simulation was conducted based on the kinetic parameters inferred from pH 2 and 11. The simulated result (lines) is presented in Figure 5D, consistent with the experimental data (squares). Figure 2S demonstrates that the simulation is almost independent of the forward and back rate constant k_f of the homogeneous reaction. This is likely ascribed to the ultrashort voltammetric timescale for the oxidation reactions occurring at the individual Pd/GO particle refraining from the interconversion between $N_2H_5^+$ and N_2H_4.

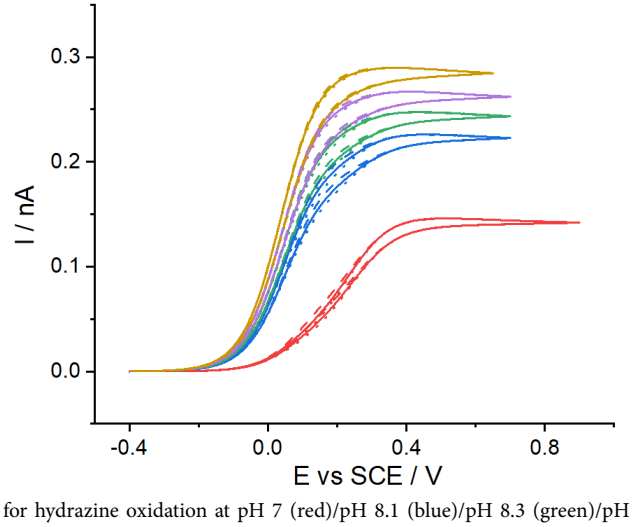

Figure S2 DIGISIM-simulated curves for hydrazine oxidation at pH 7 (red)/pH 8.1 (blue)/pH 8.3 (green)/pH 8.5 (purple)/pH 8.8 (yellow) using the parameters derived from pH 2 and pH 11. The forward rate constants k_f are 2 s^{-1} (dotted), 200 s^{-1} (solid) and 2×10^4 s^{-1} (dashed).

Section 5: pH dependency of the electrochemical rate constant within a Butler-Volmer perspective

We consider an electrochemical one-electron oxidation process:

$$A = B + mH^+ + e \tag{S1}$$

and note that the equilibrium potential is given via the Nernst equation

$$E = E^0_{f,A/B/mH^+} + \frac{RT}{F} \ln\left(\frac{[B][H^+]^m}{[A]}\right)$$

where E^0_f is the formal potential of reaction (S1).

We can alternatively write

$$E = E^0_{f,A/B} + \frac{RT}{F}\ln\frac{[B]}{[A]}$$

where

$$E^0_{f,A/B} = E^0_{f,A/B/H^+} + m\frac{RT}{F}\ln[H^+] = E^0_{f,A/B/H^+} - 2.303\frac{mRT}{F}\times pH$$

Thus,

$$E^0_{f,A/B/H^+} = E^0_{f,A/B} + 2.303\frac{mRT}{F}\times pH$$

where $E^0_{f,A/B}$ is the formal potential of the A/B couple if the reaction is analysed simply as the basis of the reaction

$$A = B + e \tag{S2}$$

For reaction (S1), the Butler-Volmer kinetic equation is

$$j = k^0 e^{\frac{\beta F}{RT}\left(E - E^0_{f,A/B/H^+}\right)} = k^0 e^{\frac{\beta F}{RT}\left(E - E^0_{f,A/B}\right)} e^{-m\beta\ln[H^+]} = \frac{k^0}{[H^+]^{m\beta}} e^{\frac{\beta F}{RT}\left(E - E^0_{f,A/B}\right)}$$

where j is the flux and k^0 the standard electrochemical standard rate constant. Hence, j increases as $[H^+]$ decreases corresponding to an enhanced thermodynamic "driving force" for reaction (S1). It follows that if $[H^+]$ is modelled as a simple one-electron concentration of A to B that the effective standard electrochemical rate constant is shown to be pH-dependent given by

$$k^0_{eff} = \frac{k^0}{[H^+]^{m\beta}}$$

In the case of the four-electron oxidation of hydrazine or protonated hydrazine,

$$j = \frac{4k^0}{[H^+]^{m\beta}} e^{\frac{\beta F}{RT}\left(E - E^0_f\right)}$$

where E^0_f is the formal potential of the first rate determining electron transfer as

$$N_2H_4 \xrightarrow{rds} X + e$$

$$X \xrightarrow{fast} N_2 + 4H^+ + 3e$$

In the main text the effective standard electrochemical rate constant for the oxidation of $N_2H_5^+$ and N_2H_4 are shown to be pH-insensitive, showing, on the voltammetric timescale (see main text) that $m \simeq 0$ and no protons are released in the first electron transfer, namely $a = 0$ and $b = 0$ in the SI Section 4. Thus, the realistic mechanism of hydrazine oxidation is given by

$$N_2H_5^+ \rightleftharpoons N_2H_4 + H^+$$

$$N_2H_5^+ \xrightarrow{rds} N_2H_5^{2+} + e$$

$$N_2H_5^{2+} \xrightarrow{fast} N_2 + 5H^+ + 3e$$

$$N_2H_4 \xrightarrow{rds} N_2H_4^+ + e$$

$$N_2H_4^+ \xrightarrow{fast} N_2 + 4H^+ + 3e$$

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