

Supporting Information for

How changes in interfacial pH lead to new voltammetric waves: The case of the electrochemical oxidation of hydrazine

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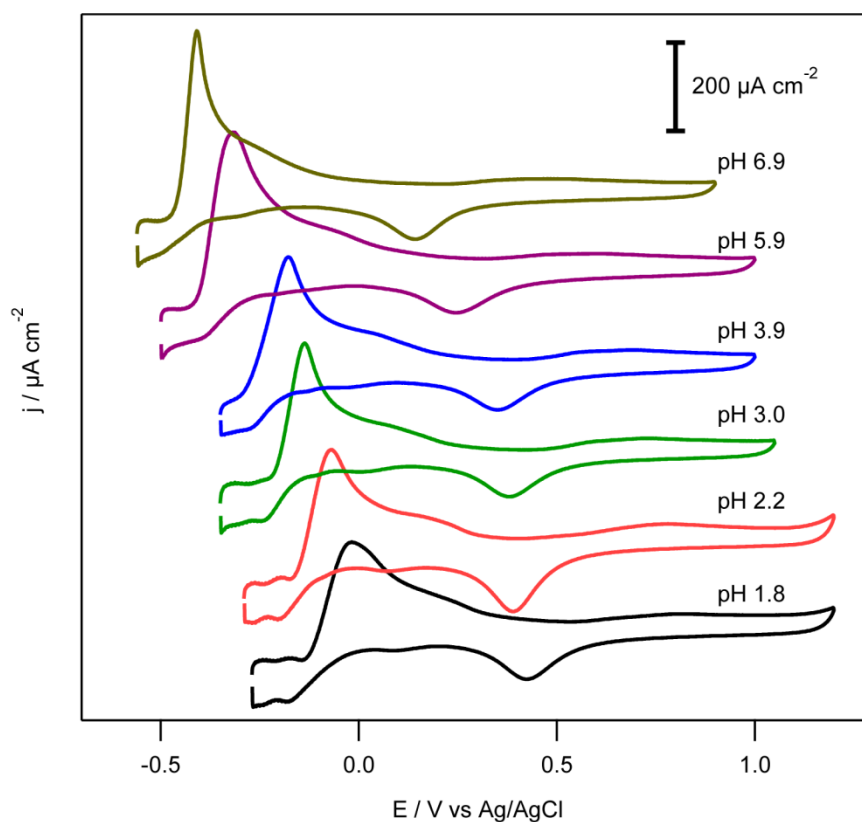
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SI-1. Cyclic voltammograms (CVs) of hydrazine oxidation at a macroscopic platinum electrode in phosphate buffer solutions as a function of pH

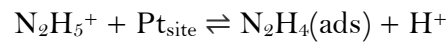


Cyclic voltammograms (CVs) for the oxidation of 0.5 mM hydrazine in 50 mM phosphate buffer solutions of varying pH. The CVs have been vertically offset for clarity. First voltammetric cycles, scan rate 20 mV s^{-1} .

SI-2. Finite element method model for proton-electron transfer reactions in buffered media

Description of the hydrazine oxidation reaction:

The pH-dependent cyclic voltammograms of hydrazine oxidation on macroscopic electrodes and ultramicroelectrodes (UMEs) were simulated using a commercial finite-element software (COMSOL v5.1). One dimensional and two dimensional-axial geometries were used for the macroscopic electrode and the UME, respectively. The irreversible oxidation of hydrazine on platinum is described by two sequential reactions:



The first reaction represents the reversible adsorption of (protonated) hydrazine on Pt (two adjacent atoms), releasing a proton in the process. This adsorption equilibrium is described with a Langmuir isotherm.

$$K_{ads} = \frac{[\text{N}_2\text{H}_4][\text{H}^+]}{[\text{N}_2\text{H}_5^+][\text{Pt}]} \quad \text{S1}$$

Here $[\text{N}_2\text{H}_4]$ and $[\text{Pt}]$ are surface concentration while $[\text{N}_2\text{H}_5^+]$ and $[\text{H}^+]$ are volume concentrations.

The second reaction describes the irreversible oxidation of N_2H_4 , releasing 4 electrons and 4 protons. The kinetics for this electrochemical reaction were described empirically with the Butler-Volmer-like equation

$$i = n * F * D * S * k_0 e^{\frac{(1-\alpha)n_{app}F(E(t)-E^{0'})}{RT}} [\text{N}_2\text{H}_4] \quad \text{S2}$$

, where i is the current, n the total number of electrons transferred ($n=4$), F is Faraday's constant ($F = 96,485 \text{ C mol}^{-1}$), D is the diffusion coefficient of hydrazine, S is the electrode surface area, k_0 is the electron transfer rate constant (here in s^{-1} , as the redox species is immobilized on the surface), α is the transfer coefficient, n_{app} describes the number of electron exchanged in the elementary step ($n_{app} \approx 2$), $E^{0'}$ is the formal potential for the adsorbed species N_2H_4 , and R and T are the gas constant and temperature, respectively. From the equations S1 and S2, a pH-dependence of the current is obvious. As the pH change of the solution at the interface, the current in equation S2 is convoluted by the diffusion of the various species, and simulations are needed to validate this model.

For a macro-electrode the current $i(t)$ is calculated using the equation:

$$i(t) = nFAD_{N_2H_5} \left(\frac{\partial C_{N_2H_5}(t)}{\partial x} \right)_{x=0} \quad S3$$

where A is the surface of the electrode, $D_{N_2H_5}$ is the diffusion coefficient of hydrazine and $C_{N_2H_5}(t)$ is the concentration of hydrazine. For a UME, the current is integrated over the surface of the electrode using the equation:

$$i(t) = nFD_{N_2H_5} \int_0^a \left(\frac{\partial C_{N_2H_5}(t)}{\partial z} \right)_{z=0} r dr \quad S4$$

where a is the radius of the micro-electrode and z is the axial symmetry axis, perpendicular to the electrode surface.

The diffusion of the i^{th} species is described by the second Fick's law:

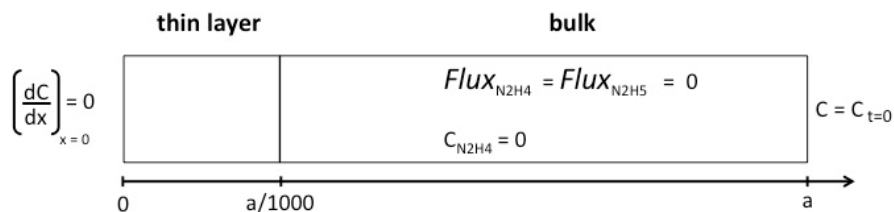
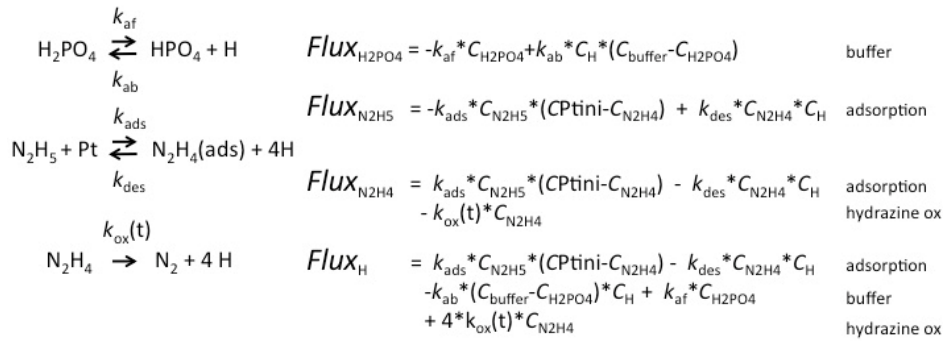
$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 C_i \quad S7$$

Description of the simulation:

For computational efficiency, the adsorbed species are represented by a very thin layer at the electrode surface (1/1000 of the size of the electrode in 2D/cell in 1D) where the adsorbed species have a very low (essentially zero) diffusion coefficient. The concentration of adsorbed species is set to zero out of this thin layer. Diffusion of the freely diffusing species in the thin layer is extremely fast compared to the time scale of the experiment (i.e. homogeneous concentration in the thin layer).

Furthermore, we have set the diffusion coefficients of $H_2PO_4^-$ and HPO_4^{2-} to be the same. This allows the total concentration of phosphate species ($H_2PO_4^- + HPO_4^{2-}$) to be set at the constant value throughout the simulated space, reducing the number of species to be simulated to 4 ($N_2H_5^+$, N_2H_4 , H^+ and $H_2PO_4^-$).

The flux of all the species in the two domains (thin layer and bulk) and the boundary conditions are provided in the following figure.



The tables below show the values of the parameters used in the simulations

Variable	Expression	Description
α	0.5	Transfer coefficient
k_o	$1 \times 10^{-6} \text{ s}^{-1}$	Heterogeneous electron transfer rate constant
E^o	-0.1 V	Formal potential for N_2H_4 oxidation (vs. Ag/AgCl in 3 M NaCl)
K_{ads}	1×10^{-10}	Adsorption equilibrium constant
k_{des}	$1 \times 10^{15} \text{ l mol}^{-1} \text{ s}^{-1}$	Desorption rate constant
G_{Pt}	$1 \times 10^{-9} \text{ mol cm}^{-2}$	Surface concentration of Pt sites
K_a	$1.259 \times 10^{-7} (\text{mol l}^{-1})$	Acid-base equilibrium constant ^[1] for H_2PO_4^- / HPO_4^{2-}
k_{ab}	$1 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$	Protonation rate constant
k_{af}	$k_{ab} \times K_a$	Deprotonation rate constant
$C(\text{buffer})$	$50 \times 10^{-3} \text{ mol l}^{-1}$	Total buffer concentration
$C(\text{H})_{mi}$	$10^{-(\text{pH}_{mi})} \times 1000 \times C_0$	Initial proton concentration
$C(\text{H}_2\text{PO}_4)_{mi}$	$C(\text{H})_{mi} \times C(\text{buffer}) / (K_a + C(\text{H})_{mi})$	Initial concentration of H_2PO_4^-
$C(\text{N}_2\text{H}_4)_{mi}$	$(K_{ads} \times G_{Pt} \times C(\text{N}_2\text{H}_5)_{mi}) / (C(\text{H})_{mi})$	Initial concentration of adsorbed hydrazine
n_{app}	2	number of electron exchange in elementary step
v	0.02 V s^{-1}	Voltammetric scan rate
D_{H^+}	$9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient ^[2] of H^+
$D_{\text{H}_2\text{PO}_4}$	$8.46 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient ^[2] of H_2PO_4^-
D_{HPO_4}	$= D_{\text{H}_2\text{PO}_4}$	Diffusion coefficient of HPO_4^{2-}

References

- [1] CRC Handbook of Chemistry and Physics, **1982**.
- [2] L. Yuan-Hui, S. Gregory *Geochim. Cosmochim. Acta.* **1974**, 38, 703-714.