OSCILLATING OXIDATION OF FORMIC ACID
Part 1: The Model & Solution Strategy
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Following is how the process looks:
1. Formic acid moves towards the Platinum electrode
2. At the electrode, formic acid decomposes to CO and H_2O
3. CO starts blocking the electrode
4. After a critical number of sites are blocked, the electrode starts oxidising all the CO
5. CO is oxidised to CO_2
6. The electrode is free and the cycle repeats.

This is how the reactions look like:
1. $HCOOH \leftrightarrow$ CO (adsorbed) + H_2O
2. $CO + H_2O \rightarrow CO_2 + H_2 + 2e^-$ (only after reaching a critical concentration)

Variables:

Symbol	Meaning	Units
C	Concentration of Formic Acid	mol/m^3
D	Diffusivity of Formic Acid	m^2/s
ρ	Surface Density of total active sites	mol/m^2
θ	Fraction of Active sites blocked by CO	-
k_1	First order surface reaction rate constant	m/s
j	Current Flux	A/m^2
F	Faraday's Constant	C/mol
j_0	Exchange Current Density	A/m^2
Y	Hysteresis Function	-
α	Charge Transfer Coefficient	-
η	Overpotential	V
k_2	Zeroth-order rate constant for CO oxidation	$mol/m^2/s$
S	Sigmoidal function	-
H	Heaveside function	-
C*	Bulk concentration of Formic Acid	mol/m^3

Let's model the system

1. *Bulk Diffusion of Formic Acid*

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \; (0 < x < \delta) \tag{1}$$

2. *Surface Coverage of CO*

$$\rho\frac{d\theta}{dt} \;=\; k_1 * C(0,t) * (1-\theta) \;-\; \frac{j}{nF} \tag{2}$$

3. *Butler Volmer Kineitcs with hysteresis*

$$j \;=\; j_0 * Y * \left[exp\left(\frac{\alpha nF}{RT}\eta\right) - exp\left(\frac{(\alpha-1)nF}{RT}\eta\right) \right] \tag{3}$$

$$j_0 \;=\; nFk_2\theta \tag{4}$$

$$Y \;=\; S(\theta - \theta_{on}) * H\left(\frac{d\theta}{dt}\right) + S(\theta - \theta_{off}) * H\left(-\frac{d\theta}{dt}\right) \tag{5}$$

4. *Boundary Conditions*

$$C \;=\; C^* \quad (x \;=\; \delta) \tag{6}$$

$$D\frac{\partial C}{\partial x} \;=\; k_1 * C(0,t) * (1-\theta) \quad (x \;=\; 0) \tag{7}$$

5. *Initial Conditions*

$$C \;=\; C^* \tag{8}$$

$$\theta \;=\; 0 \tag{9}$$

Key Assumptions:
1. Negligible side reactions
2. All parameters like k_1, D etc are constant during the experiments
3. δ is constant due to constant mixing

Checks performed:
1. Sanity Check: All equations are physically reasonable
2. Dimension Check: All terms are dimensionally homogeneous
3. Sign Check: All the signs are checked multiple times to make sure they are correct

Key Attributes:
1. Deposition and oxidation of CO are surface phenomena, hence k_1 has the unit m/s while k_2 has the unit $mol/m^2/s$.
2. The physical phenomena of starting the oxidation when a critical coverage is reached and stopping it when the entire eletrode is cleaned is perfectly modelled by the mentioned hysterisis function. As far as the author is aware, there is **no literature** that uses this model for the formic acid oxidation process.
3. Note that the j and η are considered positive when oxidising

Solution Steps

After modelling the system, let's attempt to solve it.

For this purpose, the solution is divided into 5 parts:

1. $\dfrac{\partial C}{\partial t} = 0$; Constant potential : This case will create a foundation for the system

2. $\dfrac{\partial C}{\partial t} \neq 0$; Constant potential: This is the base case on which analysis will be established

3. $\dfrac{\partial C}{\partial t} \neq 0$; Step change in potential: This is the first layer of complication

4. $\dfrac{\partial C}{\partial t} \neq 0$; Cyclic Voltametry: This is where effect of frequency of potential change is found

5. $\dfrac{\partial C}{\partial t} \neq 0$; Sinusoidal Voltage: This is the final stage where we try to find resonance

Each of these cases is solved in a different code and their explanations and code can be found in this directory.