

OSCILLATING OXIDATION OF FORMIC ACID

PART 2: Case 1

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In this case, we assume that the Diffusion is much faster than the rate of Surface adsorption. This means, as soon as the surface coverage changes a little, the diffusion makes up for it. This means that in the longer term, there is no apparent change in the concentration over time. In other words, $\frac{\partial C}{\partial t} = 0$. This changes our system to a simpler one. Let's analyse this simpler system.

Modified Model

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \Rightarrow D \frac{\partial^2 C}{\partial x^2} = 0 \Rightarrow C = a \cdot x + b \quad (1)$$

From the Boundary conditions,

$$C = C^* \quad (x = \delta) \quad (2)$$

$$D \frac{\partial C}{\partial x} = k_1 * C(0, t) * (1 - \theta) \quad (x = 0) \quad (3)$$

Eq (1) and (2) tell us :

$$a \cdot \delta + b = C^* \quad (4)$$

And Eq (1) with Eq (3) gives us :

$$D * a = k_1 * b * (1 - \theta) \quad (5)$$

Solving (4) and (5) simultaneously, we get :

$$a = \frac{k_1 * C^* * (1 - \theta)}{D + k_1 * \delta * (1 - \theta)}; b = \frac{D * C^*}{D + k_1 * \delta * (1 - \theta)} \quad (6)$$

Now, we can use these coefficients to fit in our 2nd model equation :

$$\rho \frac{d\theta}{dt} = k_1 * C(0, t) * (1 - \theta) - \frac{j}{nF} \quad (7)$$

to give

$$\rho \frac{d\theta}{dt} = k_1 * \frac{D * C^*}{D + k_1 * \delta * (1 - \theta)} * (1 - \theta) - \frac{j}{nF} \quad (8)$$

Next, we can insert the equation for j from the model equation to get :

$$\rho \frac{d\theta}{dt} = k_1 * \frac{D * C^*}{D + k_1 * \delta * (1 - \theta)} * (1 - \theta) - k_2 * \theta * Y(\theta) * p \quad (9)$$

where p is a constant and $p = \left[\exp\left(\frac{\alpha n F}{RT} \eta\right) - \exp\left(\frac{(\alpha - 1)n F}{RT} \eta\right) \right]$

Which means that equation (9) is now an uncoupled ODE

However, it can't be solved analytically due to its highly non – linear nature, thus, we use MATLAB to numerically solve it.

The logic used is a simple method of lines.

Results and Discussions

$\alpha. \theta$ v/s time as η changes

There are various different regimes of the results found when observe how θ changes over time for different over potential values.

(Note that $\theta_{on} = 0.5$ and $\theta_{off} = 0.1$)

Regime 1: Complete Saturation ($\eta = 0$)

This happens for zero over potential. Which means that the deposition is completed without any restrictions. This is a trivial case.

Regime 2: Partial Saturation ($0 < \eta \leq 0.11$)

This happens because after reaching a certain degree of saturation, the rate of deposition is equal to that of oxidation. This is a non – trivial but simple case.

Regime 3: Bounded Oscillations ($0.12 \leq \eta \leq 0.21$)

This regime happens when the overpotential can take the surface coverage to the off value but can also stop there. Note that as η increases, the rate of oxidation increases and thus, the frequency of cycles goes up.

Regime 4: Overshooting Oscillations ($0.22 \leq \eta < 0.3$)

These are the cases when the overpotential is so high that it can't stop at the θ_{stop} . This is due to the quantized dt values. That is why there are some combination in which a certain rate fits and we don't see any over shooting.

Regime 5: Boundary Oscillations ($0.3 \leq \eta$)

This is when the overpotential simply brings down the surface coverage to zero in one dt interval. The only reason that it is not going negative is you can't oxidise CO that's not absorbed yet.

The attached Bifurcation diagram clearly shows these regimes.

β . C v/s x as time changes

We then consider an overshooting case ($\eta = 0.25$) and observe how concentration and θ vary with time. The surface coverage (θ) has already been discussed before.

Let's observe the value of C as time changes. If you see the equations,

$$C' = \frac{k_1 * C^* * (1 - \theta)}{D + k_1 * \delta * (1 - \theta)} \quad (10)$$

*For the given values of the parameters, $k_1 * \delta \ll D$*

Thus, we can estimate :

$$C' \approx \frac{k_1}{D} * C^* * (1 - \theta) \quad (11)$$

or

$$C' \propto (1 - \theta) \text{ (approximately)} \quad (12)$$

Now if you observe the clip, when θ decreases, $(1 - \theta)$ increases and the slope increases too

Key point

We considered $\frac{\partial C}{\partial t} = 0$ however, it clearly changes with time.

This approximation could only be made based on the argument that Diffusion is faster than Surface deposition. However, this is still an approximation and will be dropped in subsequent cases.