

OSCILLATORY BEHAVIOR OF NI-S ELECTRODES

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This paper shows that for an anodic polarization of the sulphur-doped nickel electrode the active and pre-passive zones correspond to greater current values than for pure nickel electrodes. It was also pointed out that there exists a oscillatory range ΔE_{OSC} of the time-dependent current. It was shown that this range varies significantly with the sulphuric acid and sodium sulphate concentrations and the potential.¹

The electrode surface is subject to successive phases. First, the electrode presents a glittery metallic aspect until the oscillatory domain on the $I = f(\eta)$ curve is reached. Within this domain the electrode achieves the typical behavior of an anodic oscillatory phenomenon. A blackening of the electrode is first noted, accompanied by a marked decrease of the current supported by the system. The black film appeared on the electrode surface begins to be penetrated and then cracked by nickel ions moving towards the bulk electrolyte. The increase of the current is accompanied by an increase of the cracks in the black film on the electrode, followed by its detachment and fall in the electrolyte solution. The film detachment has as immediate consequence a sudden increase of the current up to its maximum value. The phenomenon described above continues periodically until the total electrode dissolution.

The comparison between the experimental results associated with the S class electrodes in sulphuric acid solutions allows the formulation of some conclusions:

- ✓ forced periodic oscillations are characteristic to the 1N sulphuric acid solution only;
- ✓ Na_2SO_4 , NiSO_4 additions and the pH increase have a destructive effect on the oscillation periodicity and even on the oscillatory phenomenon;
- ✓ the oscillation amplitude decreases with potential increase.
- ✓ the decrease in amplitude is compensated by the frequency increase when the overvoltage is increased;
- ✓ the oscillations disappear at large overvoltage values.

The mathematical model consists of a two-dimensional ODE system. Non-Langmuir isotherm was found to be essential for producing the limit cycle. Only local fit between experiment and theory is obtained. The occurrence of oscillations is possible only in systems with positive feedback. In practice, as in the other area of chemical oscillations, the widely used mechanism's elements, which make possible the existence of the electrochemical oscillations, are the third order autocatalytic step and without Langmuir adsorption-desorption mechanism. With the model used in this paper only a local description of the phenomena occurring at the anodic polarization of Ni-S electrode was obtained. The same affirmation is also valid for the models used by Talbot J.B et. al.²⁻⁴. The mass balance equations [1] for the Ni^{2+} and the electrode surface coverage, considered as process variables are:

$$\frac{d[\text{Ni}^{2+}]}{dt} = k_e^*(1-\theta) - k_r[\text{Ni}^{2+}] \quad [1]$$

$$\frac{d\theta}{dt} = k_a[\text{Ni}^{2+}](1-\theta) - k_d \cdot \theta \cdot g(\theta)$$

with $g(\theta) = \exp(-\beta\theta)$ and

$$k_e^* = k_e \exp(2\alpha FE / RT).$$

Using the dimensionless variables and after the solving of the ODE system we found the kinetic values parameters k_e , k_d , k_r , and K . The existence of the multiplicity implies $\beta > 5.8$. The value chosen for β is 6. The theoretical curves $I - t$ calculated with these kinetic parameters are given in Fig. 2. As can be seen from Figs. 1 and 2 a good agreement between theory and experiment was obtained. The Ni-S dissolution in sulfuric acid solution is a complex, which involve a continuous modification of the metal/solution interface. Even when the corrosion process is initiated under common (usual) condition, the black sulfur film modifies the corrosion phenomenon. Within such condition determination of the corrosion rate becomes quite a problem. The proposed model correctly reproduces the oscillatory shape over the range of applied potentials, and amplitude versus potential is in good agreement with experimental data.

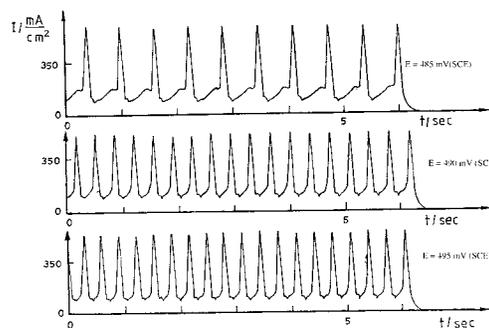


Figure 1. Current experimental oscillations obtained on Ni electrode in 1M H_2SO_4 on NiS 0.0743% w.g.

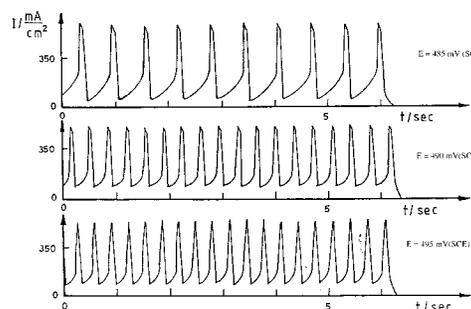


Figure 2. Theoretical oscillations predicted by the model

References

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