

Electrochemical Nucleation and Growth of Uranium and Plutonium on Tungsten Electrode from Molten Salts

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Outline

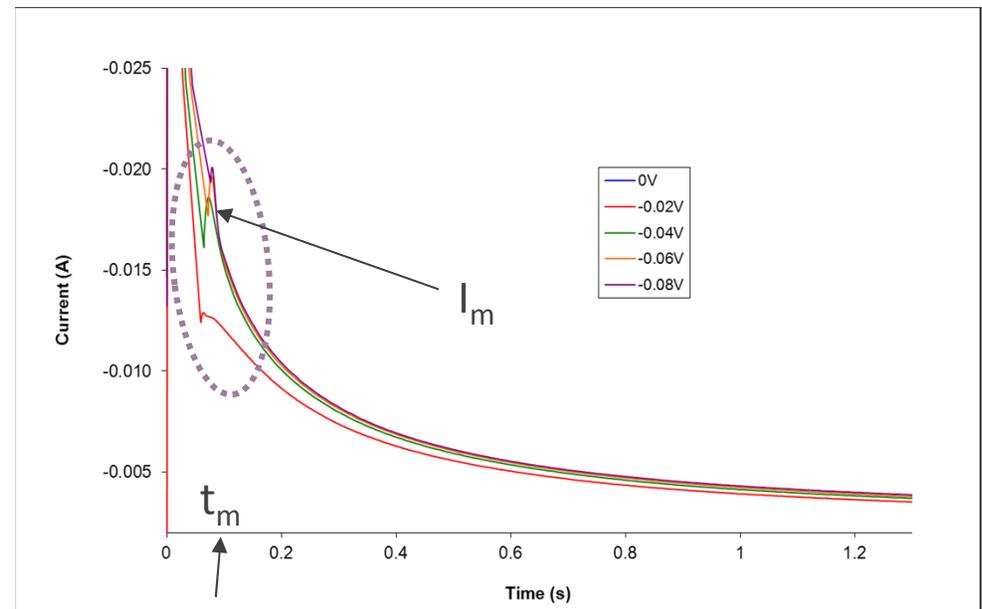
- Chronoamperometry studies provide insight into the nature of the nucleation.
 - The time resolution of the data has to be sufficiently high
- Current transients are used to analyze the data
- Theoretical models : progressive and instantaneous nucleation modes
- Nucleation studied at several salt concentration:
 - Three U^{3+} concentrations (0.45wt%, 0.95wt%, and 1.73wt%)
 - 1.3wt% Pu^{3+}
 - 0.5wt% U^{3+} and 1.3wt% Pu^{3+}
- Estimation of the number of nuclei during electrochemical deposition
- Calculation of additional parameters:
 - Nucleation rate for instantaneous mode
 - Nuclei density for progressive mode



Potentiostatic Current Transients

- Chronoamperometry data provide insight into the nature of the nucleation.
- The current transient can be divided into three time intervals:
 - 1st: current sharply decreases after charging a double layer which corresponds to the formation of first deposition nuclei on the electrode surface.
 - 2nd: current increases due to an increase in the active surface area of the electrode caused by the growth of crystals on the electrode.
 - 3rd: a slow decrease of the current as the diffusion layer at the electrode/electrolyte interface increases according to the Cottrell equation where $I=f(t^{1/2})$.

Current vs. time plot for different potential steps at 0.46 wt% U^{3+} in LiCl-KCl eutectic

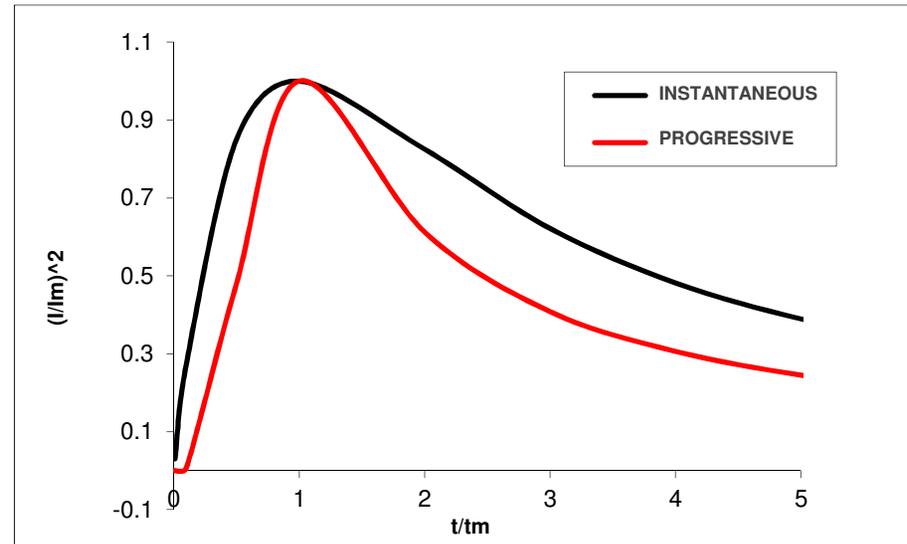


The two phenomena associated with the first and second time intervals are in competition and result in a current maximum (I_m) at time, t equals t_m in the second time interval.



Theoretical Models

- Nucleation can be described in terms of two limiting cases
 - In the *instantaneous* case, the rate of nucleation is rapid in comparison with the rate of crystal growth. Nuclei are formed at all possible growth sites within very short times.
 - In the *progressive* case, the rate of nucleation is slow and continues to take place at the surface while other clusters are growing.
- The analytical expression most widely used in the literature for the current transient is the equation derived by Sharfker and Mostany.³
- Plots of $(I/I_m)^2$ vs. t/t_m generate two distinct theoretical curves



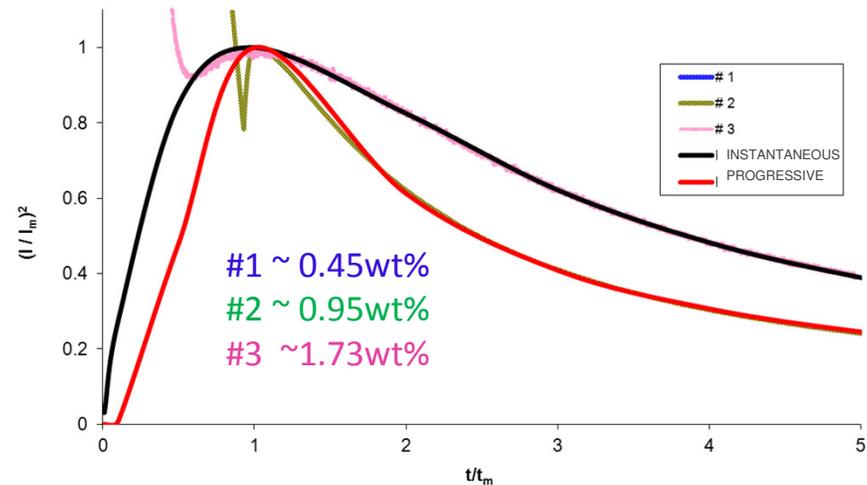
$$\left(\frac{I}{I_m}\right)^2 = \frac{1.9542}{t/t_m} \left\{ 1 - \exp\left[-1.2564\left(\frac{t}{t_m}\right)^2\right] \right\}^2 \quad \text{Instantaneous Nucleation}$$

$$\left(\frac{I}{I_m}\right)^2 = \frac{1.2254}{t/t_m} \left\{ 1 - \exp\left[-2.3367\left(\frac{t}{t_m}\right)^2\right] \right\}^2 \quad \text{Progressive Nucleation}$$



Electrochemical Nucleation of Uranium in LiCl-KCl on W electrode.

- Three different U^{3+} concentration were investigated:
 $\sim 0.46\text{wt}\%$, $\sim 0.95\text{wt}\%$, $\sim 1.73\text{wt}\%$
- In order to identify the uranium nucleation mode (instantaneous or progressive), obtained current transients are compared with the dimensionless theoretical curves for each mode of nucleation
- The experimental data for compositions #1 and #2 correlates with the progressive nucleation model while the experimental data for composition #3 correlates with the instantaneous nucleation model.

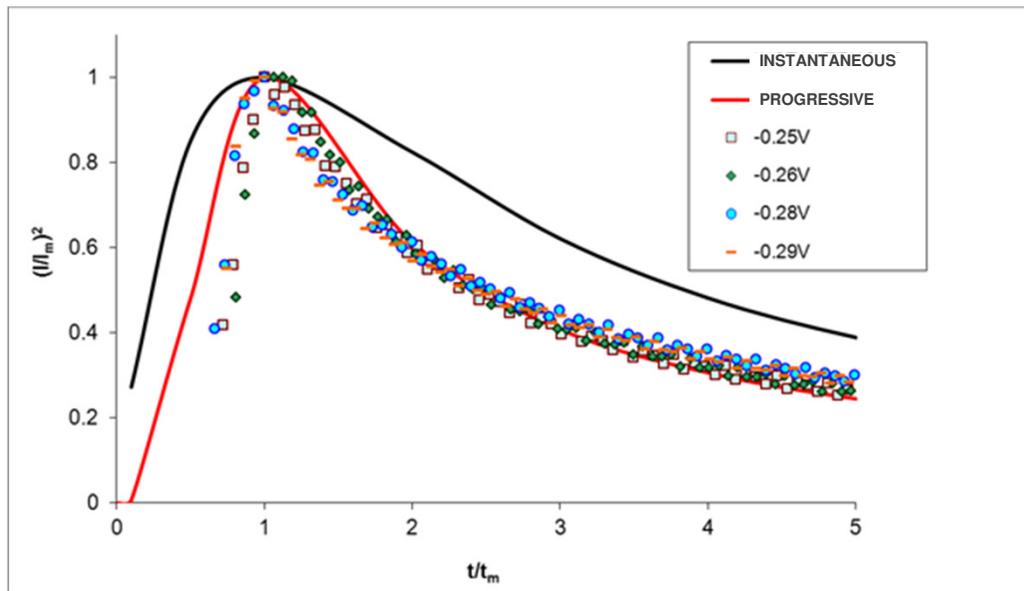


The mode of nucleation is apparently dependent on the salt concentration with a change from progressive to instantaneous nucleation occurring between 0.90 and 1.73wt% U^{3+} .



Nucleation of Pu^{3+} in LiCl-KCl on W electrode

- Salt containing $\sim 1.3\text{wt}\%$ of Pu in LiCl-KCl was tested and the current transients for various potentials were recorded.
- The type of nucleation occurring during electrodeposition of Pu on tungsten electrode was investigated.

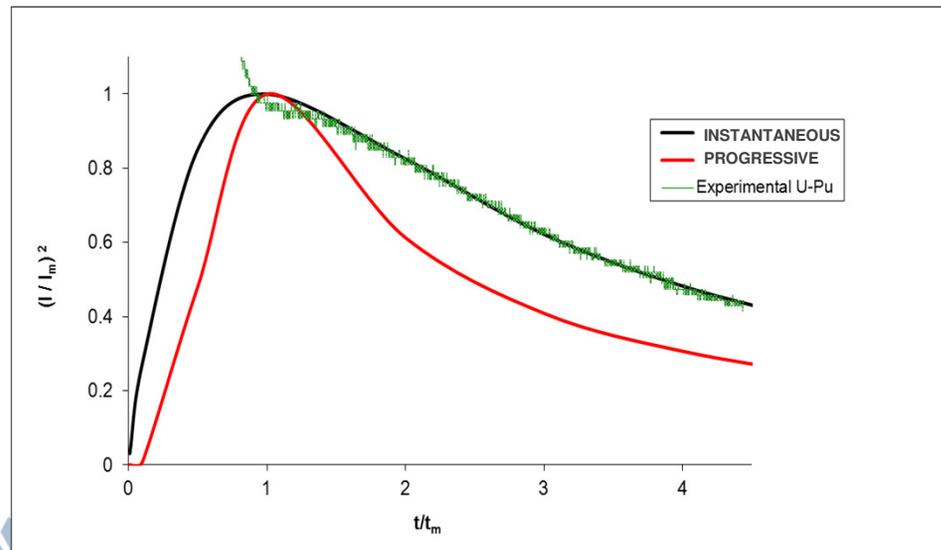


Nucleation of Pu^{3+} at $1.3\text{wt}\%$ clearly correlates with the progressive nucleation model - similar to the lower U^{3+} concentrations.



Nucleation During Codeposition of U-Pu

- Salt containing $\sim 1.3\text{wt}\%$ Pu and $\sim 0.5\text{wt}\%$ U was tested.
- Current transients for various potential pulses were used to obtain information about the type of the nucleation observed during codeposition of U-Pu.
- As was done in the U and Pu experiments, the chronoamperograms obtained at different overvoltages were compared to the theoretical curves corresponding to both nucleation modes: instantaneous and progressive.
- The experimental data indicates an instantaneous nucleation mode at this concentration.



Nucleation is progressive for individual salts: 1.33wt% Pu and 0.5wt%.
Nucleation switches to instantaneous for 1.33wt%Pu+0.5wt%U combined.

Variation in the Number of Nuclei During Uranium Electrodeposition

- The variation in the number of nuclei created over time obeys the following general law:

$$N = N_0 (1 - \exp(-At))$$

- Using the equations, additional parameters can be calculated:
 - The number of nuclei for different overvoltage values.
 - Influence of the concentration on the density of created nuclei
 - Minimum number of atoms required to form a stable (critical) nucleus.
 - Diffusion coefficient from the product of $I_m^2 t_m$ - only if its value is constant at different overvoltages.

For instantaneous nucleation: $N=N_0$

$$t_m = \frac{1.2564}{N\pi k D} \quad I_m = 0.6382nFD C_o (kN)^{1/2}$$

For progressive nucleation: $N=N_0At$

$$t_m = \frac{4.6733}{AN_0\pi k D} \quad I_m = 0.4615nFD^{3/4} C_o (kAN_0)^{1/4}$$

Symbol	Unit	
A	s ⁻¹	nucleation rate constant per site
M	g mol ⁻¹	molar weight
No	cm ⁻²	total number of favorable sites
N	cm ⁻²	density of nuclei created
S	cm ²	surface area of the working electrode
ρ	g cm ⁻³	density of the deposit

$$k = \frac{4}{3} \left(\frac{8\pi C_o M}{\rho} \right)$$

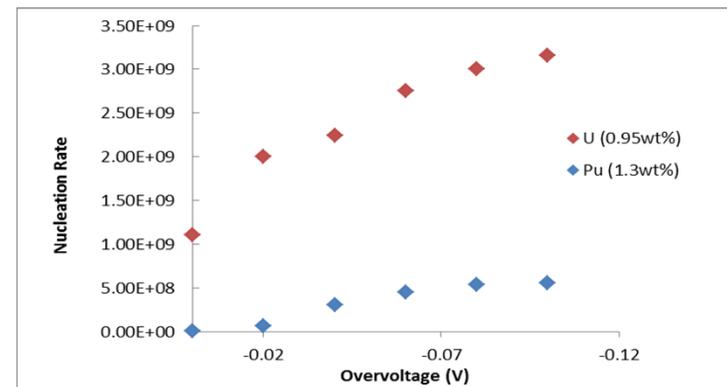

Progressive Nucleation Rates (AN_0)

- In progressive nucleation the new crystals are continuously created throughout electrolysis.
- The nucleation rates (AN_0) were calculated for U^{3+} (~0.95wt%) and Pu^{3+} (~1.3wt%) as a function of overvoltage and the results were compared.
- The individual nuclei of the completed surface can be approximated as having a two-dimensional circular geometry on the electrode surface with a radius r

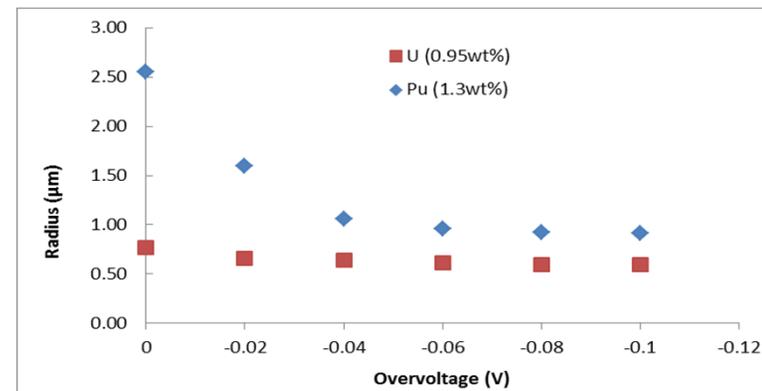
$$r = \left(\frac{2^{0.5} k^{0.5} D^{0.5}}{\pi A^{0.5} N_o^{0.5}} \right)^{0.5}$$

Overvoltage	0.95wt%U	r (μm)	1.33wt% Pu	r (μm)
V	AN_0 (cm ⁻² s ⁻¹)		AN_0 (cm ⁻² s ⁻¹)	
0	1.10E+09	0.77	9.06E+06	2.55
-0.02	2.00E+09	0.66	5.93E+07	1.60
-0.04	2.24E+09	0.64	3.02E+08	1.06
-0.06	2.75E+09	0.61	4.49E+08	0.96
-0.08	3.01E+09	0.60	5.33E+08	0.92
-0.1	3.16E+09	0.59	5.58E+08	0.91

Nucleation rates increase at more negative overvoltages. U^{3+} nucleates faster than Pu^{3+} .



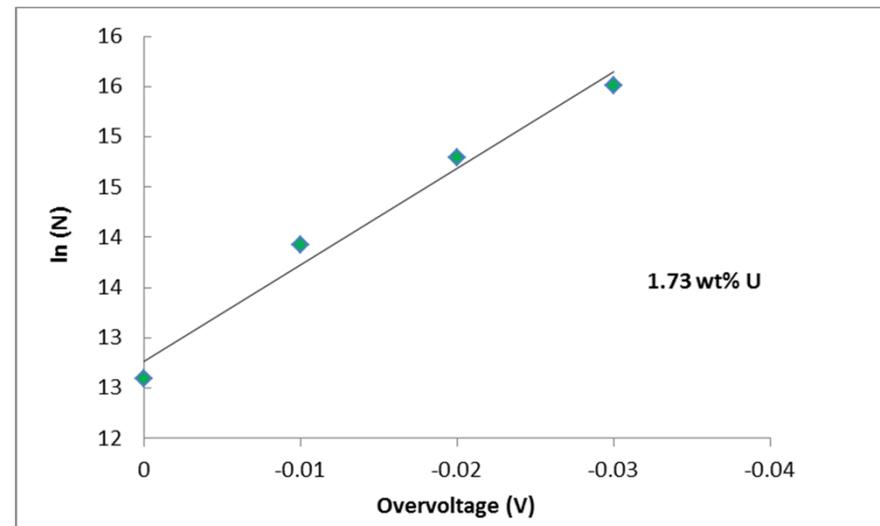
The radius of Pu^{3+} nuclei are larger than U^{3+} and their size decreases with increasing overpotential



Density of Nuclei Created During Instantaneous Nucleation

- In the instantaneous nucleation all clusters are created at the same moment at the beginning of the electrolysis.
- The number of nuclei (density of nuclei) for different overvoltages can be calculated from the expressions of I_m and t_m
- The density of nuclei for instantaneous nucleation of U^{3+} (1.73wt% U) was calculated and it is shown that it increases significantly as the overvoltage increases.
- A linear relationship between $\ln(N)$ and overvoltage suggests that the nucleation is three-dimensional and controlled by diffusion.

Overvoltage	1.73wt% U
V	$N \text{ cm}^{-2}$
0	2.95E+05
-0.01	1.11E+06
-0.02	2.66E+06
-0.03	5.46E+06



Concluding Remarks

- Analysis of the potential step data was used to characterize the type of nucleation (progressive or instantaneous) for deposition of uranium and plutonium as well as U/Pu codeposition.
- It was found that the nucleation mode is a function of concentration.
- At low concentrations, the nucleation data fits the model for progressive nucleation. However, at higher concentrations the nucleation data fits the model for instantaneous nucleation.
- The type of nucleation has implications for the morphology of the deposited metal with instantaneous nucleation resulting perhaps in fewer and larger crystals than those formed under progressive nucleation conditions.
- From the current maximum of the potentiostatic experiment, additional parameters were obtained:
 - Nucleation rates for progressive nucleation
 - Density of nuclei for instantaneous nucleation.



Acknowledgements

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