Investigation & Modeling Of Anodic Behavior During Electrorefining Of U-10Mo Fuels For Uranium Recovery

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Outline

- Motivation
- Brief description of electrorefining
- Development of electrorefining model
  - Application of corrosion theory
- Experiments showing film development
- Progress of film investigation
- Film's anticipated effect on the model
- Planned experiments
- Summary

Motivation

Background

- Reduced Enrichment for Research and Test Reactors is an international program sponsored by NNSA with the goal to convert research and test reactors from HEU to LEU fuel
  - Inspired a new fuel type: monolithic U-Mo alloy, Zr bonded, Al clad
- Five U.S. high performance research reactors to be converted to LEU fuel
  - 17 international reactors could also use this fuel

The Problem

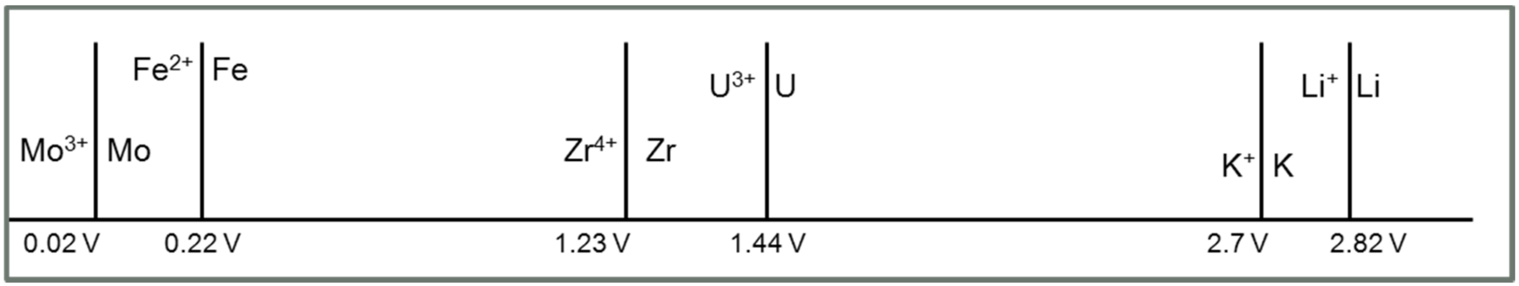
- New fuel needs a waste management procedure to recycle uranium
  - Approx. 2400Kg/year of scrap would be produced in the manufacture of this fuel
  - Recovery of uranium from the scrap improves resource utilization
- Pyroprocessing is one option to recover uranium from that scrap

The Goal

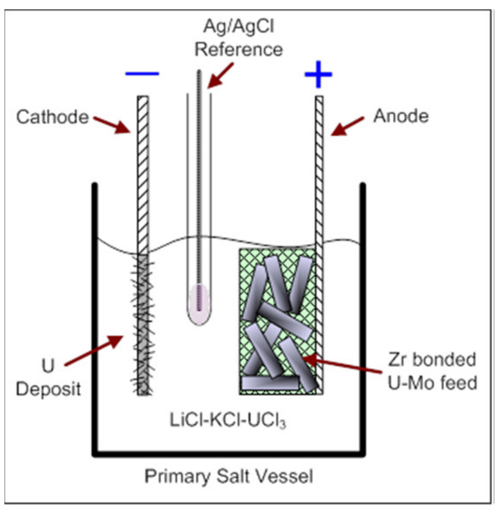
- Produce an integrated process model for the pyrochemical recovery of uranium from scrap U-Mo alloy
  - Why pyroprocessing?
    - Metal fuel to metal product
    - Less waste than an aqueous process
    - No concerns with Zr-based chemistry
  - Include the following steps in the model:
    - Fuel Processing
    - Electrorefining
    - Cathode processing
- R&D efforts to date have focused on:
  - Developing an electrorefiner model using corrosion theory
  - Investigating and analyzing anodic behavior due to a film formation

Electrorefining: Exploitation of Standard Potential

Every species has its own standard oxidation/reduction potential



Standard Potential Line With Respect to Ag/AgCl Reference Electrode



Schematic of an Electrorefining Cell

Basic Process

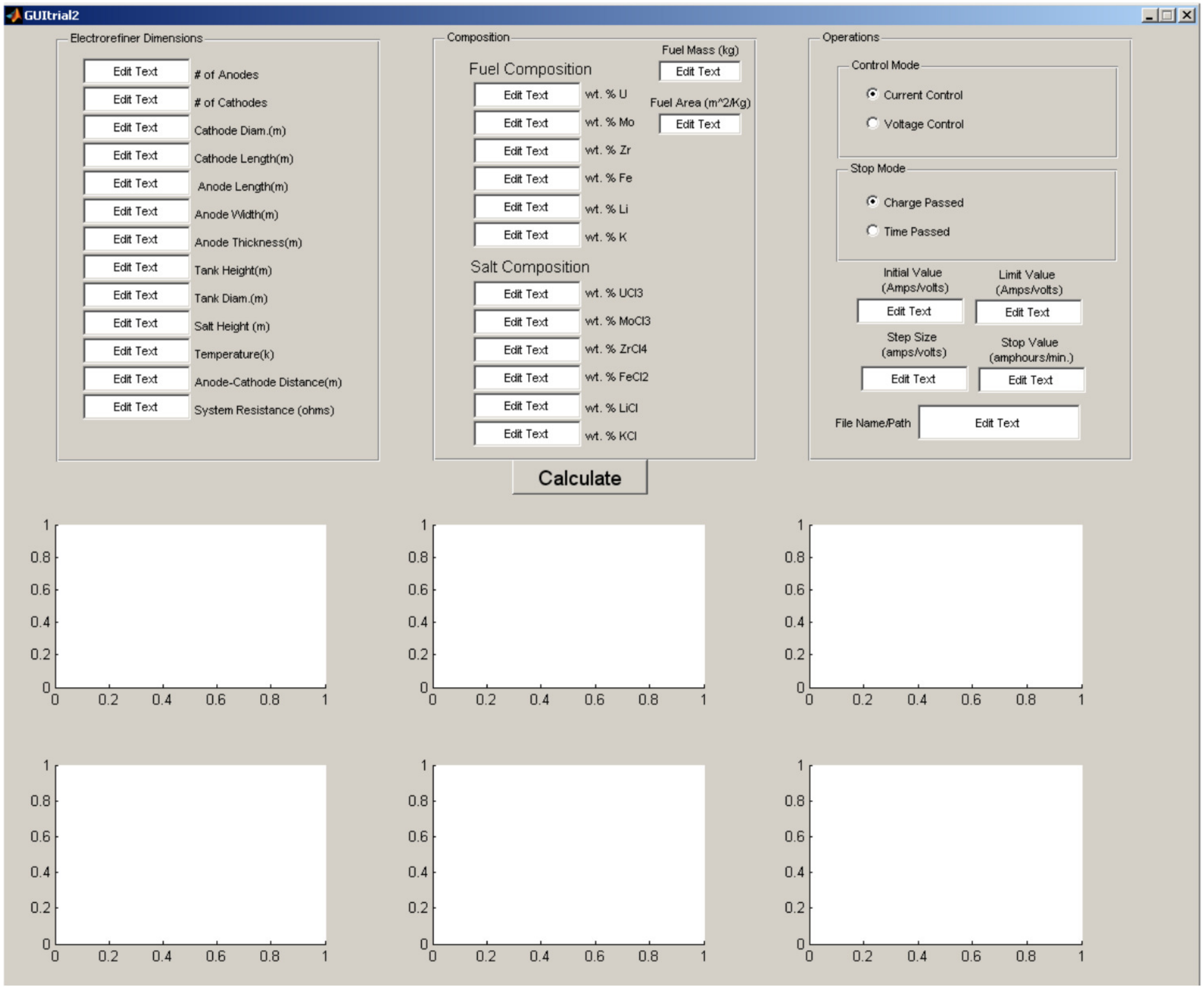
- Two electrodes are immersed in a molten salt electrolyte
- Current is passed causing transport of material from one electrode (anode) to the other (cathode)
- By setting the electrode potentials advantageously in relation to the reaction's individual oxidation/reduction potentials, desired materials can be oxidized at the anode and reduced at the cathode

Model Construction

- Model is intended as an engineering tool
  - Non-Intensive computation is desired
    - Neglected 3-D fluid dynamics
  - Dynamic prediction of deposit, fuel loss, concentration, voltage, and/or current
  - Uses corrosion theory to predict operating conditions
    - Empirically developed polarization curves
    - Tafel behavior is assumed when no curves are available
- Assumptions
  - Bulk salt phase concentration assumed constant
  - Constant fuel surface area
  - No stirring and isothermal conditions eliminate the need for a convective driving force
- Model is constructed in MatLab with a user interface

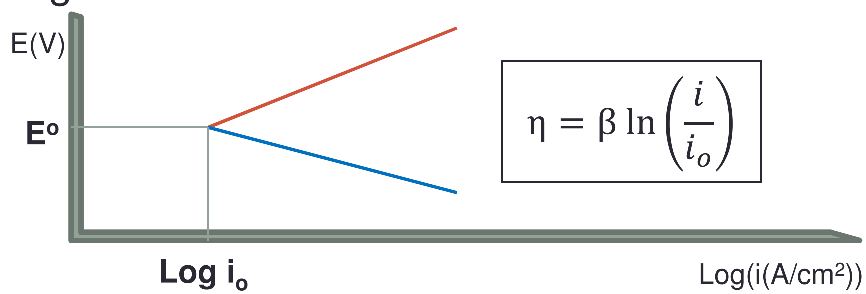
Model Input

- The GUI allows the user to input:
  - Size and shape of ER
  - Composition and amount of fuel
  - Average surface area per kg of fuel
  - Salt composition
  - Operating mode and cut off points
- It outputs the operating data and concentration profiles into the plots



Corrosion Theory

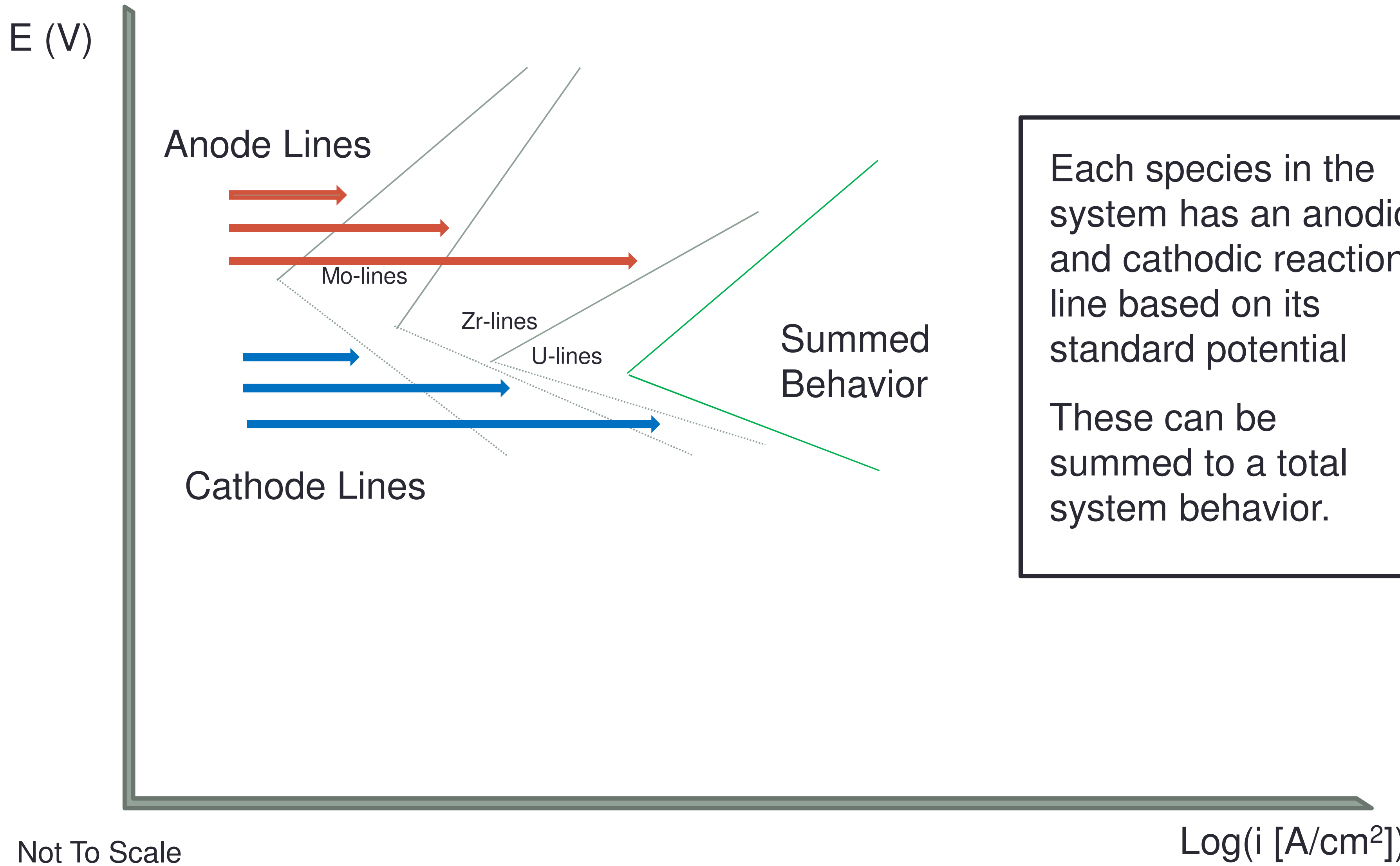
- Electrorefining is the electrically induced corrosion (oxidation) of impure metal from an anode combined with electrodeposition (reduction) of pure metal at a cathode
  - Tafel plots show the relationship between overpotential and current at an interface
  - Exchange current is determined by the activation energy for the reaction (ΔG_f^*) at a ground state.



$$\eta = \beta \ln\left(\frac{i}{i_o}\right)$$

- Tafel behavior is applicable where interfacial electron transfer kinetics play a larger role than mass transfer
- As mass transfer becomes significant it has the following effects:
  - Limiting currents will alter cathodic behavior in the presence of a dilute electrolyte
  - Anodic behavior will be altered by passivation or changes in the electrode surface composition

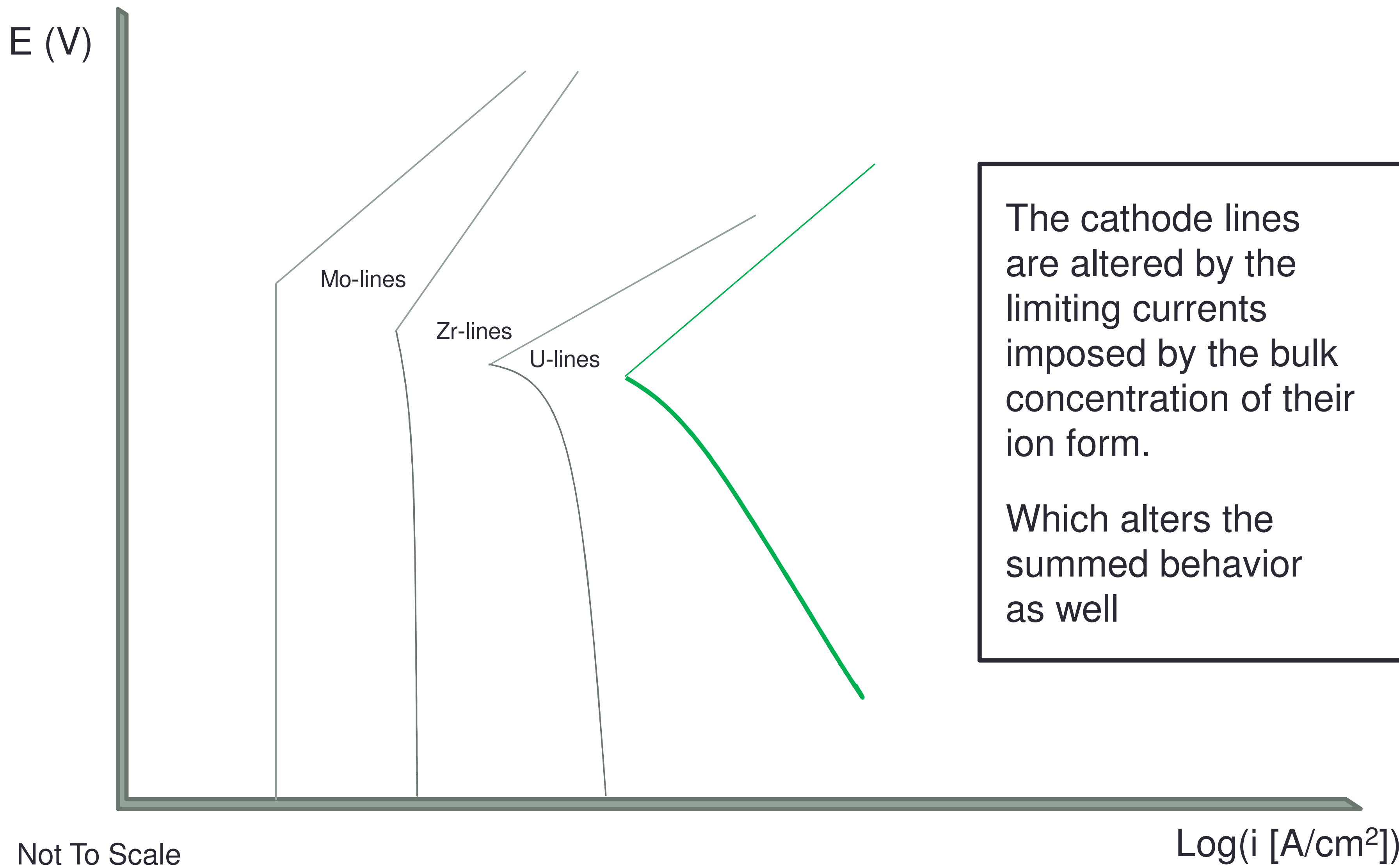
Operating Parameter Prediction



Each species in the system has an anodic and cathodic reaction line based on its standard potential

These can be summed to a total system behavior.

Mass Transport Effects

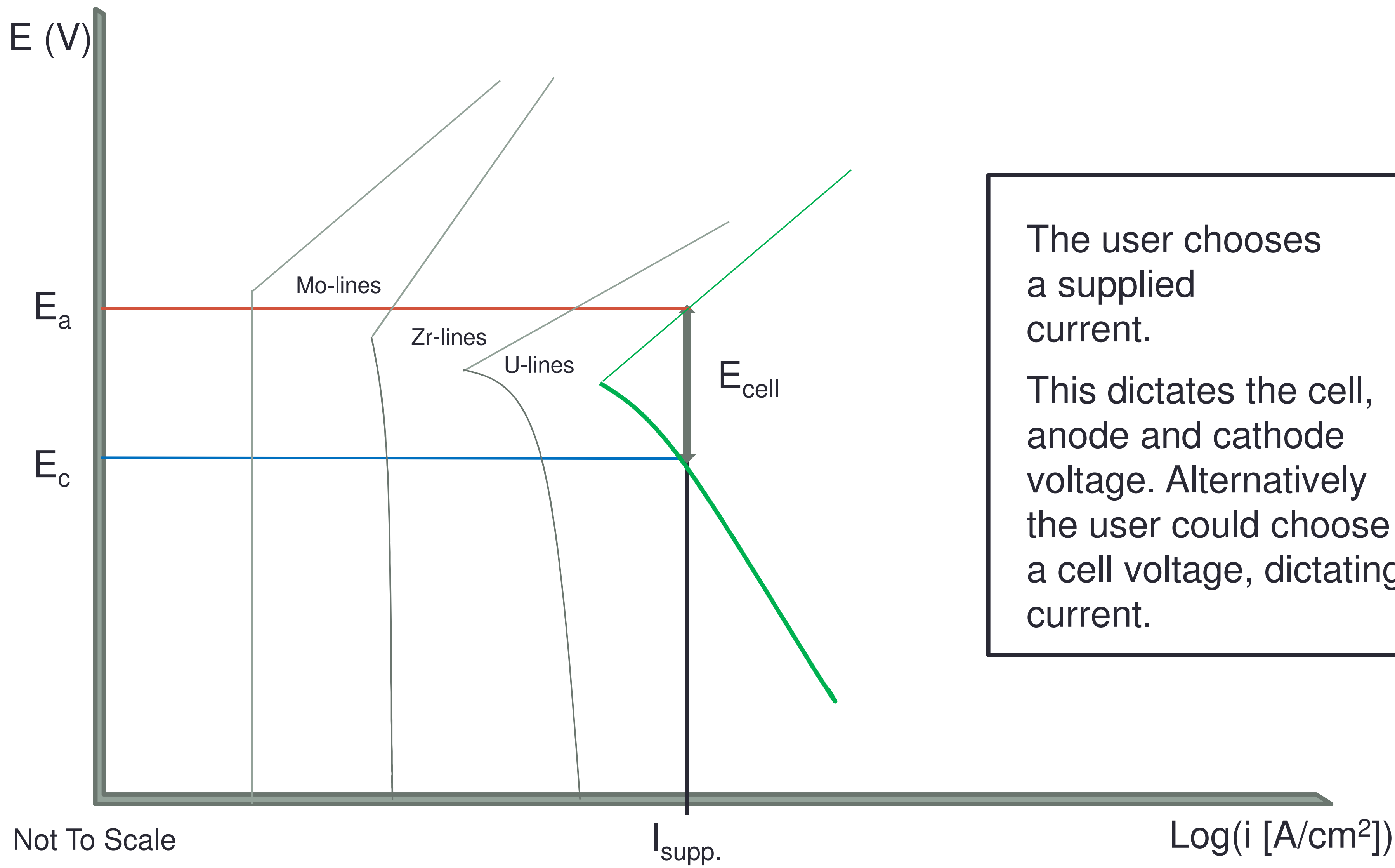


The cathode lines are altered by the limiting currents imposed by the bulk concentration of their ion form.

Which alters the summed behavior as well

Not To Scale

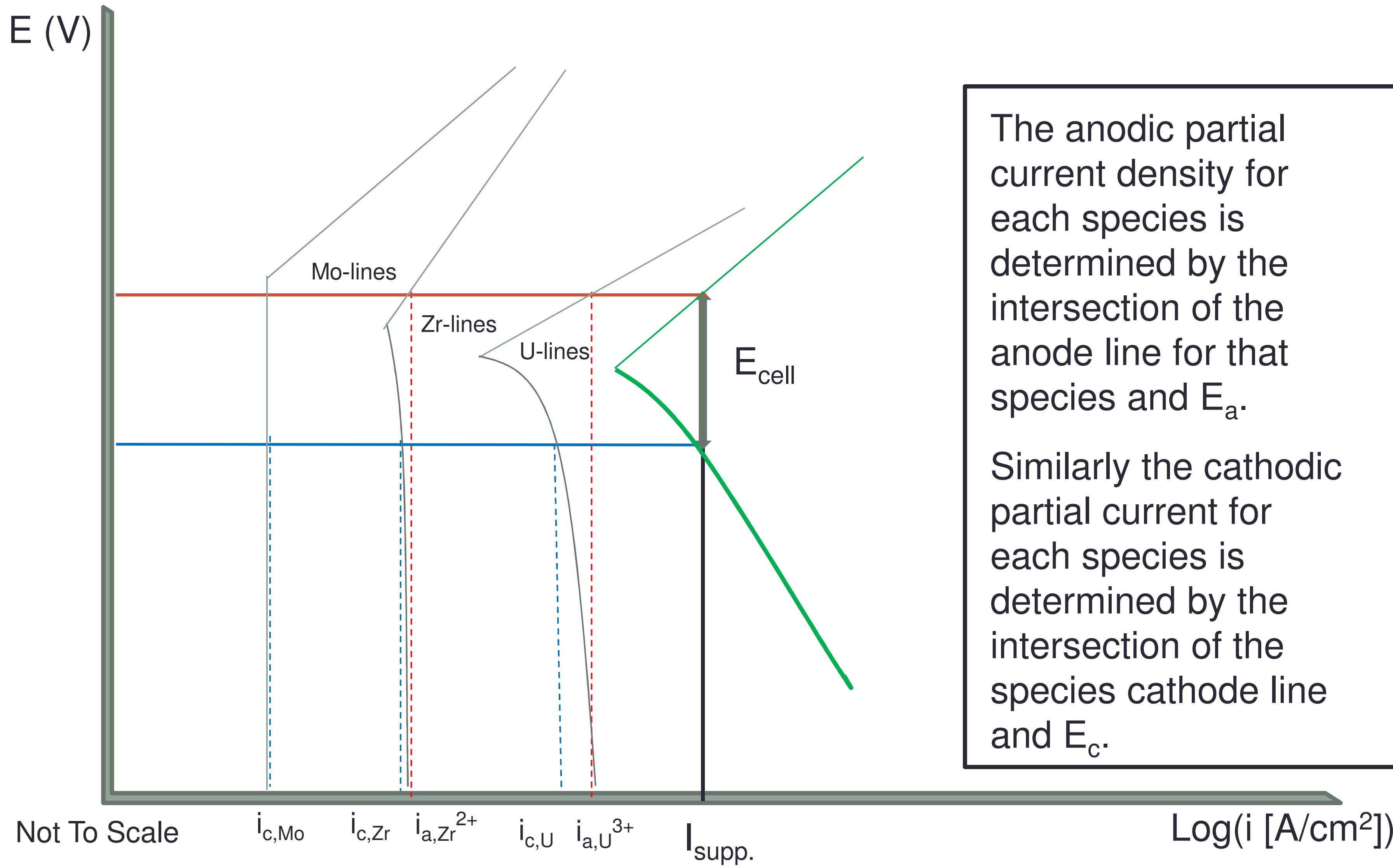
Operating Current / Voltage



The user chooses a supplied current.

This dictates the cell, anode and cathode voltage. Alternatively the user could choose a cell voltage, dictating current.

Partial Currents For Each Species



The anodic partial current density for each species is determined by the intersection of the anode line for that species and E_a.

Similarly the cathodic partial current for each species is determined by the intersection of the species cathode line and E_c.

Finding Concentration

Partial currents for both anodic and cathodic reactions are used to determine corrosion and deposition rates for each species(k) using the following formula derived from the Nernst equation:

$$\dot{r}_k = \frac{i_k \, MW_k}{n_k F}$$

The accumulated concentration of ion k at the anode surface is:

$$C_{a,k} = (\dot{r}_{a,k} - J_k)\delta$$

And at the cathode surface is:

$$C_{c,k} = (J_k - \dot{r}_{c,k})\delta$$

Flux has a three-part driving force:

- First term is due to electric migration
- Second term is Fick's law of diffusion
- Third term is due to convection (neglected in this case)

$$J_k = -n_k \left(\frac{D_k}{RT} \right) F C_{kn+} \nabla E - D_k \nabla C_{kn+} + C_{kn+} v$$

Concentration Profile

Calculation of concentration rise or fall due to the passage of current produces a concentration profile, which can be plotted by the model

- Concentrations calculated using the Nernst equation give the electrode surface concentrations by subtracting or adding their effect to the bulk concentration
  - Diffusion theory states that there is a thin layer near each electrode within which a concentration gradient drives the transfer of material

Predicting Deposit

- The rates of corrosion, deposition and flux are all iterated with time to create the dynamic aspect of the model

- Summing these iterations gives:
  - Anode material loss
  - Accumulated cathodic deposit

- Because the partial currents are current densities, the areas of the electrodes have a large impact on the calculation of accumulated deposit and total anode loss
  - The anode area is currently approximated as constant
    - Focus of future model improvement
  - The cathode area is approximated by Shibuta's relation for dendrite growth:

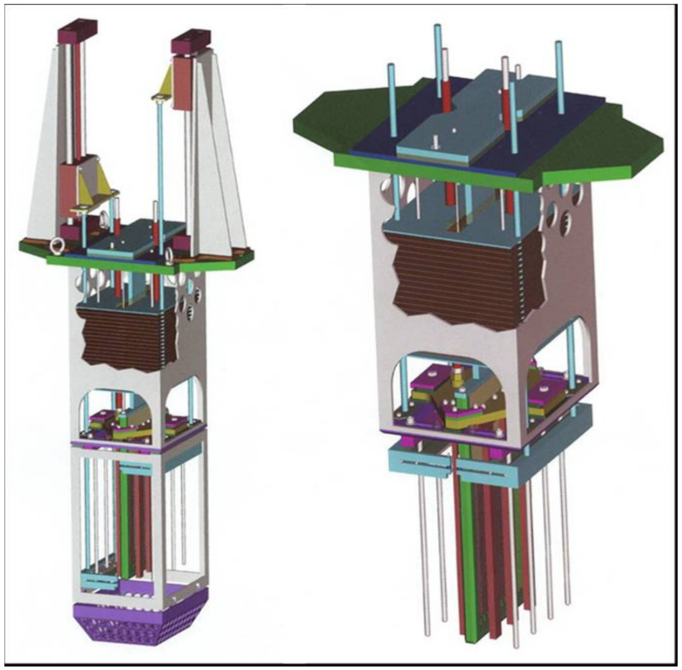
$$i = \frac{FZ}{V_m}\left(\frac{\Delta A}{L\Delta t}\right)$$

Model Output

- Operating conditions
  - Cell voltage or current, whichever was not specified by the user
  - Partial current associated with each component of the system
    - Anodic and cathodic for each species
- Mass balance
  - Concentration profile
  - Anode fuel loss (oxidized mass)
  - Cathodic deposit (reduced mass)
    - Product composition and yield
- Plots are shown on the user interface for these outputs, and the data is exported to an Excel file for further analysis

U-10Mo Experiments

- Planar electrode electrorefiner at ANL (PEER)
  - 500℃, inert atmosphere
  - Rectangular frame
  - LiCl/KCl eutectic salt
  - Planar anode
  - Eight cathodes
  - No stirring
  - Fuel: U-10Mo
- Experimental results will be used to validate model mathematics

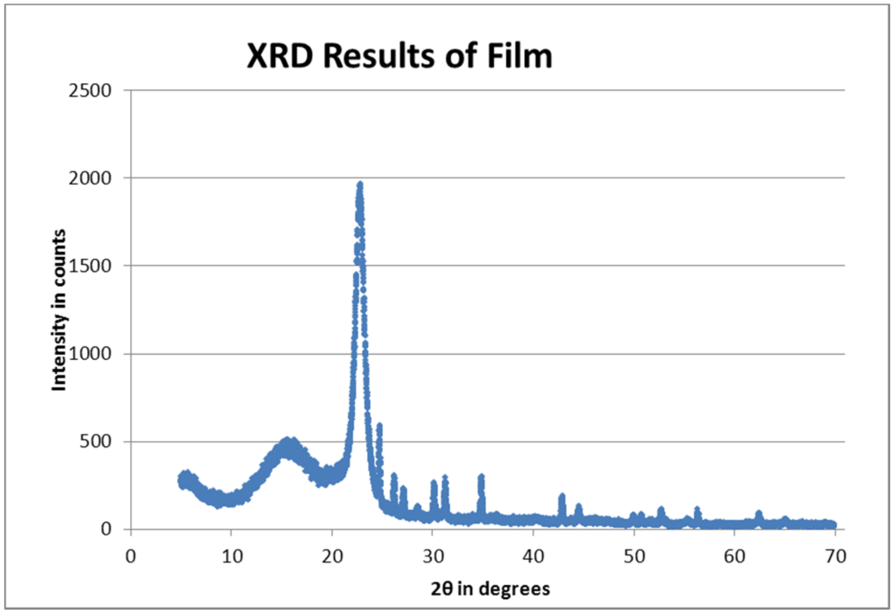


Anodic Film Formation and Composition

- Film has been produced on:
  - U-10Mo at engineering scale
  - U at lab scale and engineering scale
- Analysis of sample by mass spectrometry gave a 3:1 ratio between U and K
- Film melting point was initially found to be 530℃ using calorimetry
  - Slurry at the electrorefining temperature of 500℃

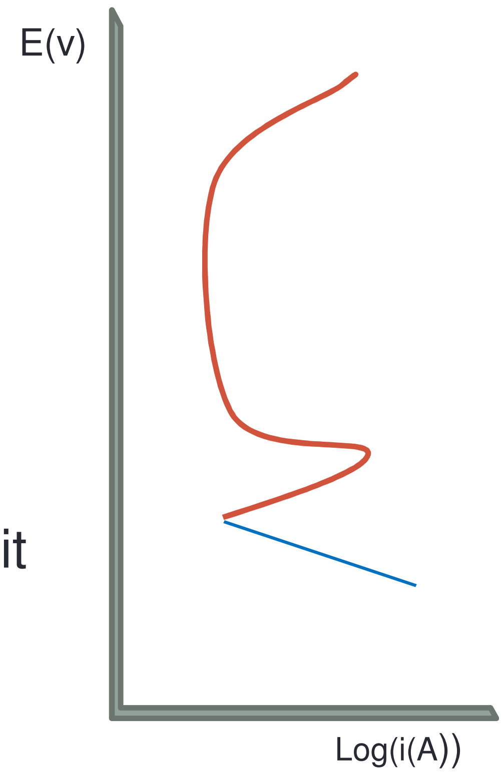
XRD data suggests

- $K_3U_5Cl_{18}$ with some LiCl/KCl eutectic present, $K_3La_5Cl_{18}$ and $K_3Ce_5Cl_{18}$ have major peaks between 22.7& 22.8 degrees 2θ
- K_3UCl_6 is also possible but standard diffraction data was not available for comparison



Anodic Film's Anticipated Effect

- The data suggests that the film is a slurry of dense salt mixture, in which a complex of potassium and uranium chloride may have formed
  - This film presents a barrier to diffusion or a rate controlling step in the diffusion process
  - It is anticipated that polarization data will reveal it as a passivating film
    - This will alter the anodic line of the U/U^{3+} couple



Typical passivated surface anodic polarization curve

Future Work

- Anodic polarization curves will be developed using polarography
- Cathodic curves will be approximated by Tafel behavior moderated by a limiting current
  - Tafel slopes and exchange currents will be found empirically
- Anodic film will be further investigated to determine its effect on the system and character
  - A quasi-diffusion coefficient will be identified from experiments
  - AC Impedance may be used to further characterize the film

Summary

- A mathematical model is being developed for electrorefining using corrosion theory
  - Assumes constant anodic area
  - Need to obtain Tafel slopes and exchange currents
  - Anodic polarization behavior needs investigation
- Formation of U-rich salt film on anode is being experimentally explored
  - May be a dense, U rich, potassium uranium chloride layer, which appears to be a slurry
  - Potential significant impact on dynamic modeling of electrorefining

QUESTIONS?

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