

2012 IPRC

Investigation of Kinetic Parameters Determination Using CFD-based Electrochemo-hydrodynamics Simulation



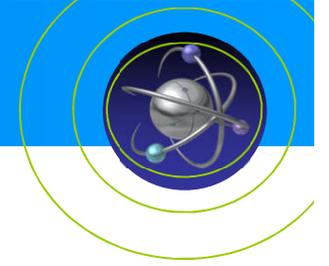
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Korea Atomic Energy Research Institute



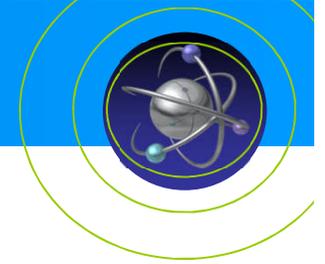
한국원자력연구원
Korea Atomic Energy Research Institute

Outline



- Motivation & challenges
- Theory & approach
- Results & discussion
- Summary

Motivation & challenges



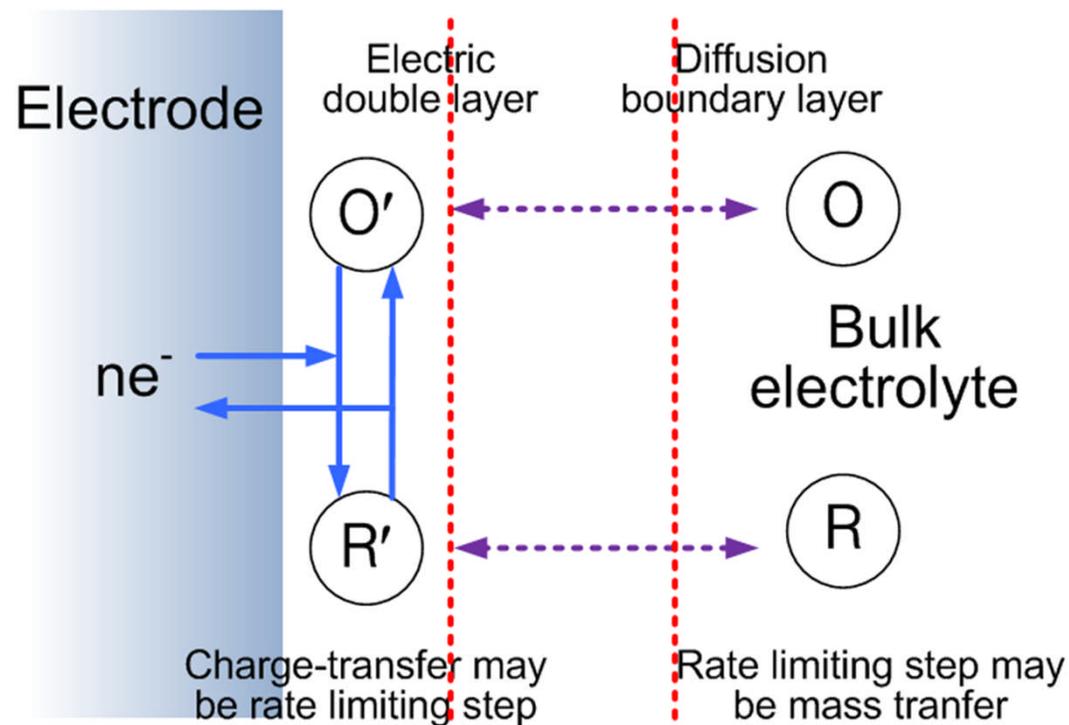
- Electrodeposition steps are the main unit process to achieve a separation using difference in the reduction potentials of metal ions in the molten-salt electrolysis.
- Kinetic properties of the molten-salt electrode reaction is essential for design and operational analysis of advanced electrochemical processors
- Despite a lot of research in this area, these properties are still lacking and have not been thoroughly investigated yet.
- Relatively few kinetic data such as exchange current density and transfer coefficient have been reported for molten-salt electrodeposition system.

Motivation & challenges

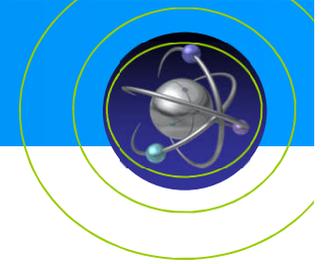


■ Mixed kinetics: possible steps in charge transfer & mass transport process

- Charge transfer: exchange current density (or transfer rate)
- Mass transport : diffusion coefficient



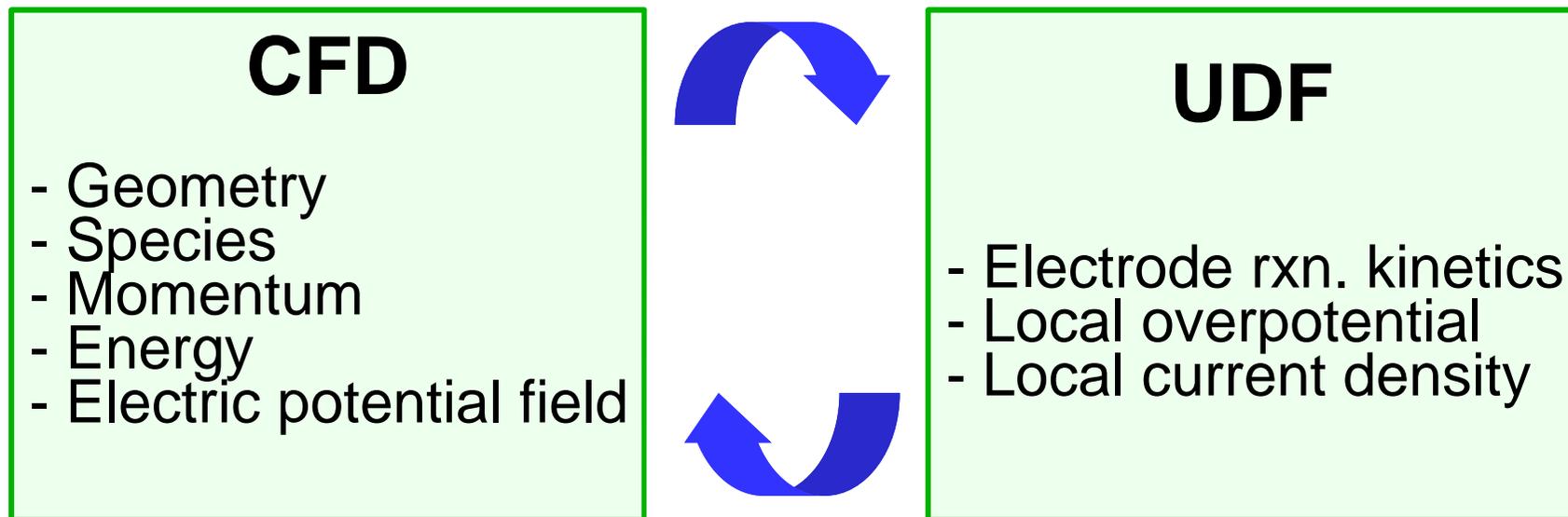
Motivation & challenges



■ Why CFD (Computational Fluid Dynamics) coupled electrochemical model?

- More complexity can be introduced in to electrochemical cell geometry.
- More real polarization can be simulated by using CFD.

Local species concentration



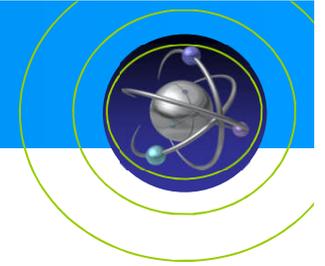
Local species flux at the boundary

Motivation & challenges



- Linear sweep voltammetry (LSV) is frequently used as a reliable method and the theory for their application to reversible reactions well understood.
- The analytical expressions for the shape of linear sweep voltammogram are known only for the special case of Nernstian reversibility with fast electron transfer kinetics in a specific cell geometry.
- In this study, a computational fluid dynamics (CFD) based electrochemo-hydrodynamics model has demonstrated for predicting the shapes of linear-potential sweep voltammograms under irreversible circumstances depending on the cell geometry.

Theory & approach

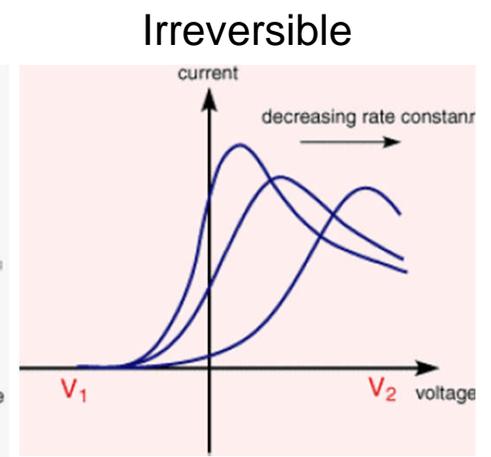
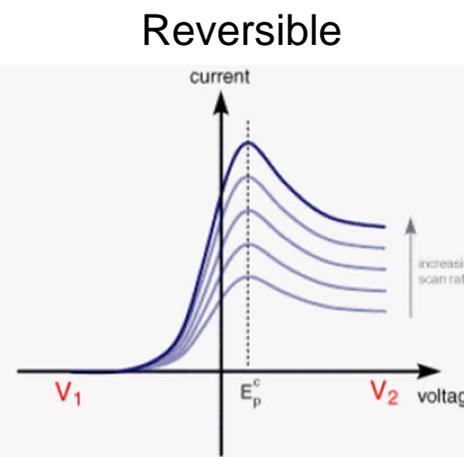
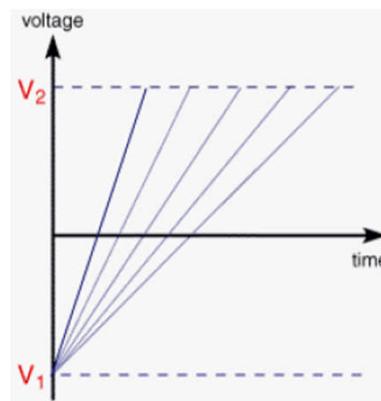


Linear sweep voltammetry (LSV)

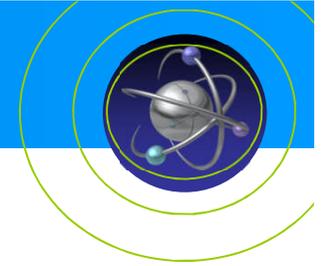
- Potential sweep method: LSV is useful analytical technique for insoluble deposition system.
- The electrode potential is made to increase linearly with time.
- The cathodic current increases as the potential reaches the reduction potential of the reducible species.
 - The rate of the electron transfer reaction
 - The chemical reactivity of the electroactive species
 - The voltage scan rate

$$E^e = E^0 + (RT/nF)\ln(\gamma) + (RT/nF)\ln(c)$$
$$= E^{0'} + (RT/nF)\ln(c)$$

$$\eta = E^e - vt$$

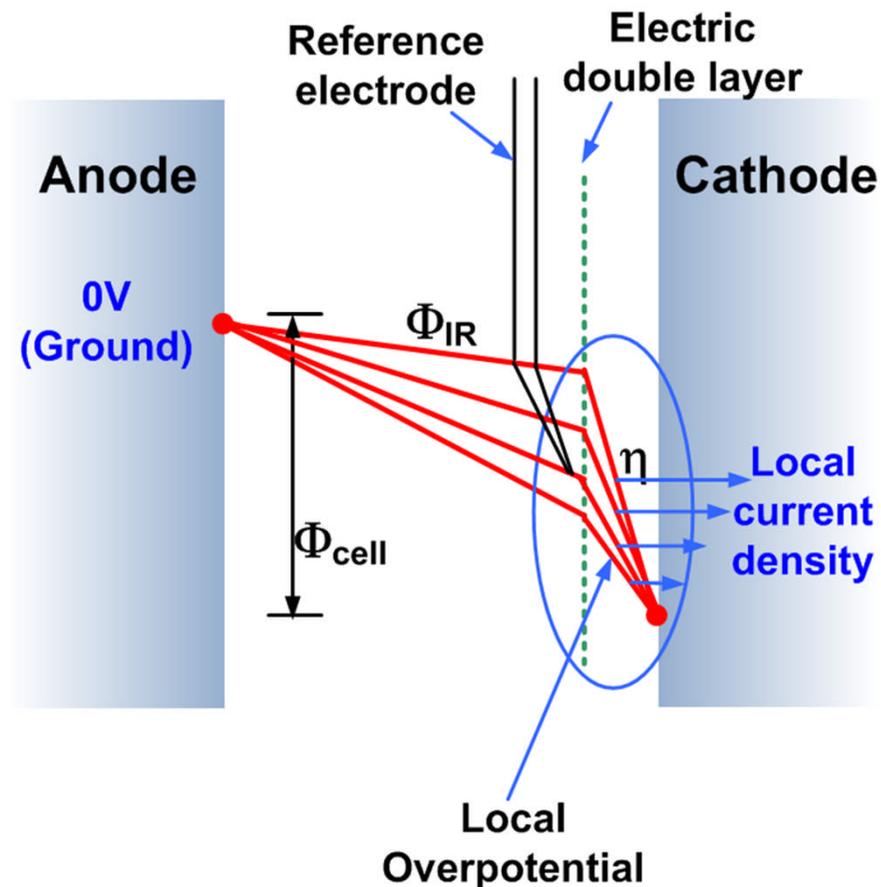


Theory & approach

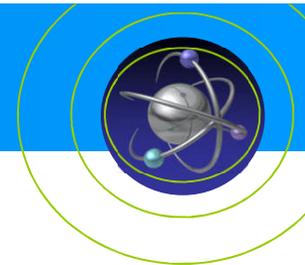


■ Focused on cathode deposition

- Not uniform potential drop over the electrode surface
- Local current density \propto local deposition rate
- Local electrode overpotential: activation & concentration polarization

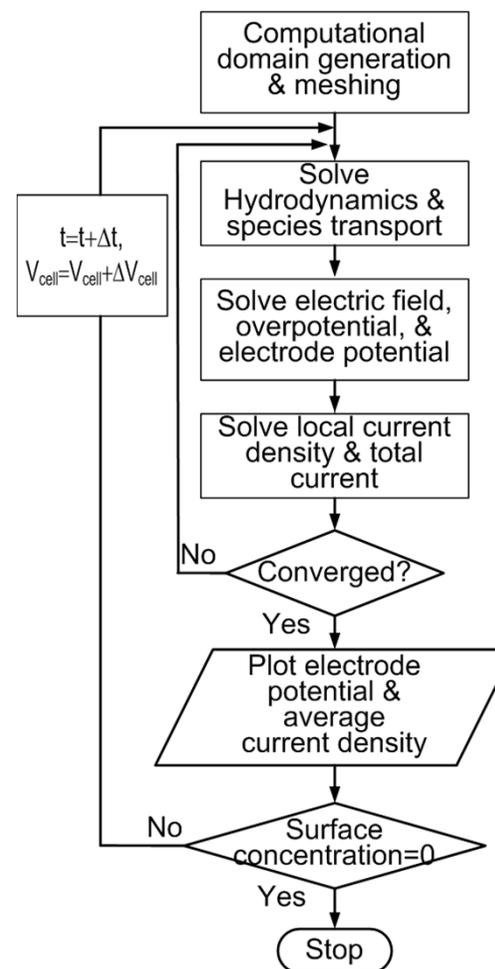
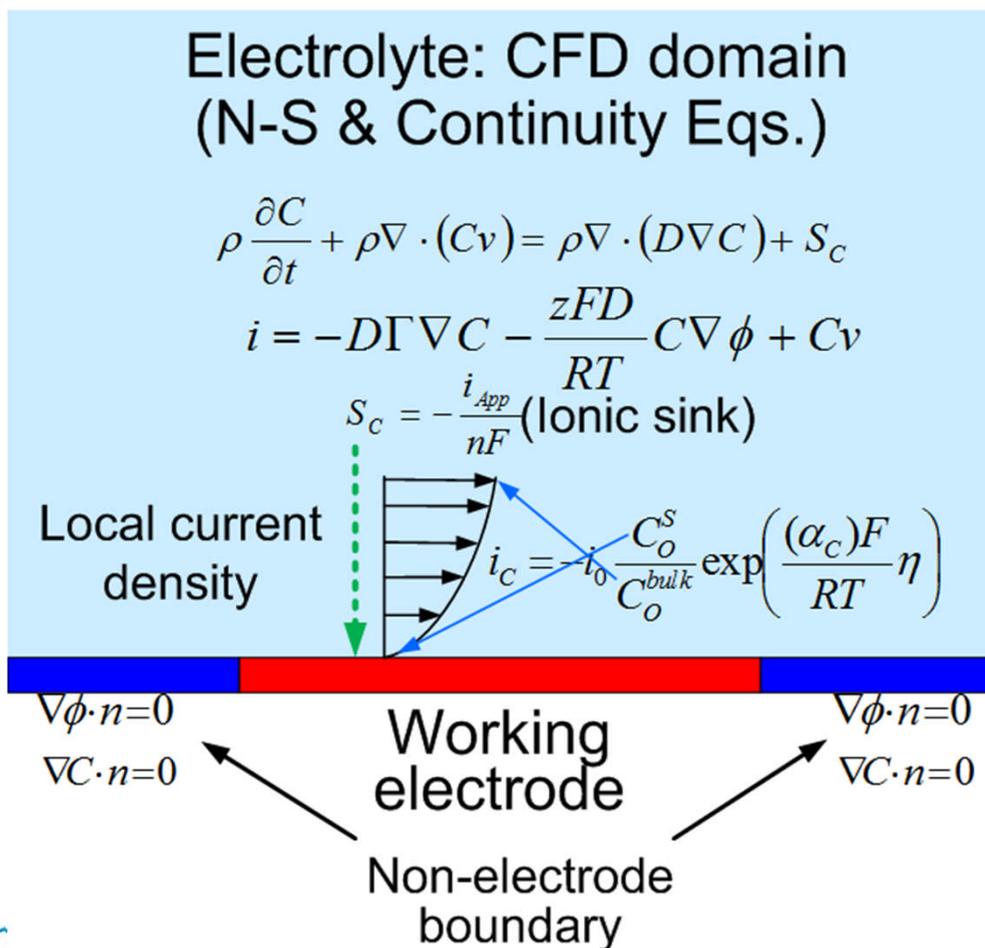


Theory & approach



Voltage to current (VTC) algorithms

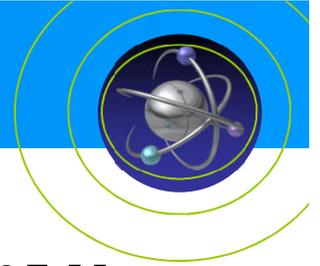
- Iterative VTC algorithm: capability for accurate calculation of the local overpotentials & current density distribution over the electrode



Total current on the working electrode can be obtained by integrating the local flux of ions at the electrode surface:

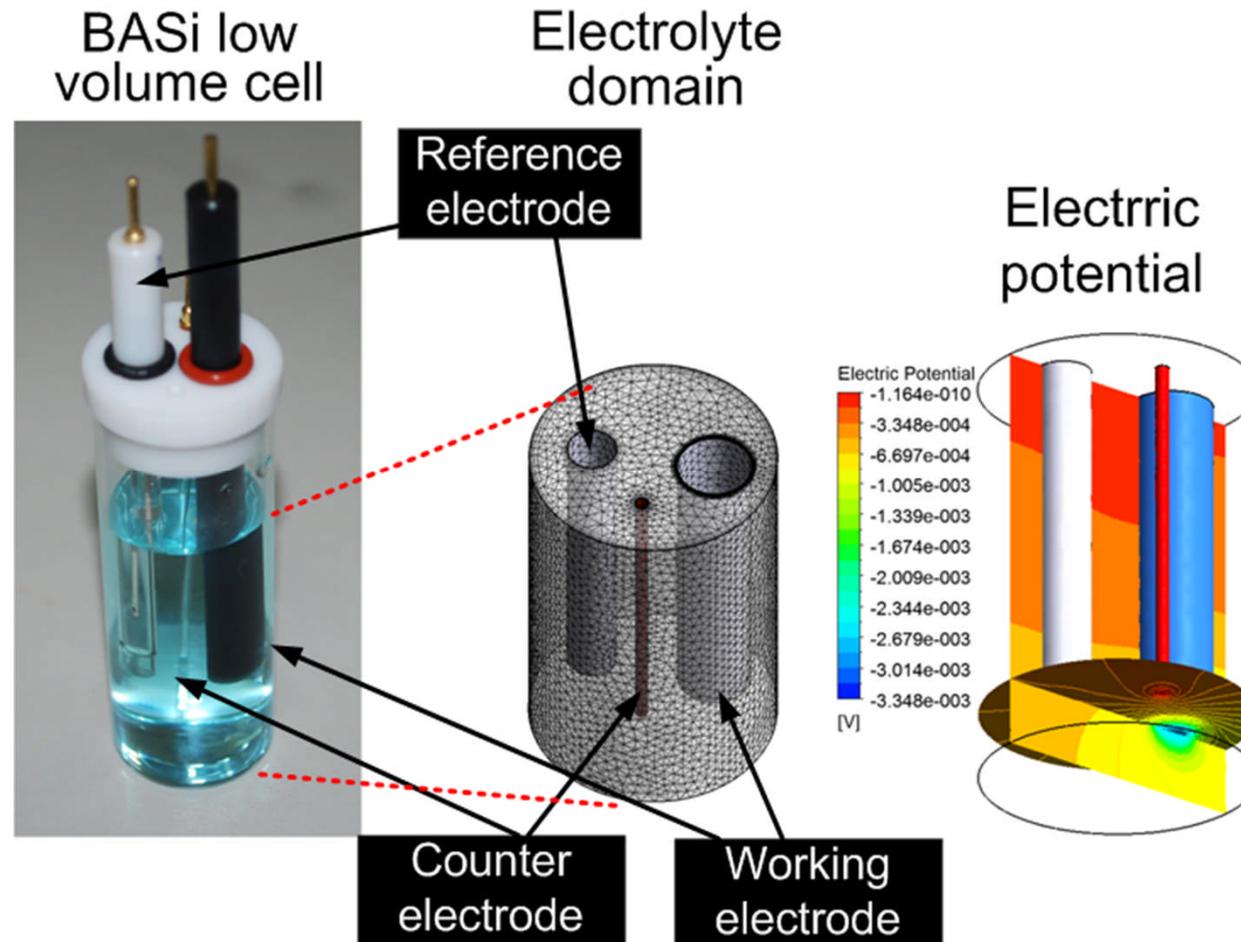
$$i_{ave} = \frac{I}{A} = \frac{\int i dA}{A}$$

Cu²⁺ in aqueous sulfate system

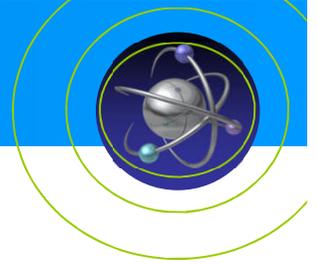


■ Benchmark simulation of Cu electrodeposition

- Computational fluid domain: aqueous sulfate electrolyte (0.05 M CuSO₄, 0.5 M Na₂SO₄)
- WE(gassy carbon), CE(Pt) & RE(Ag/AgCl)

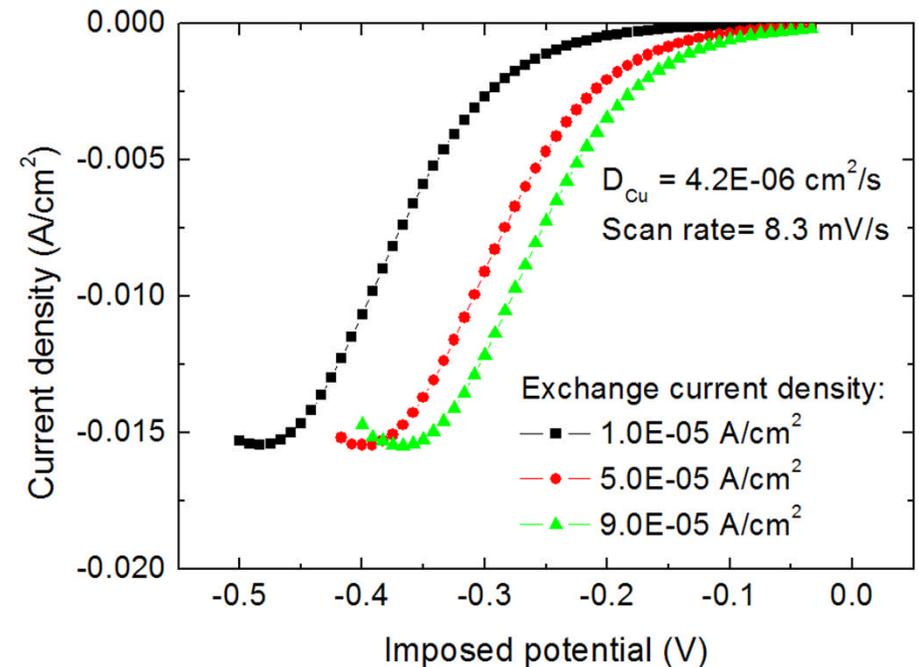
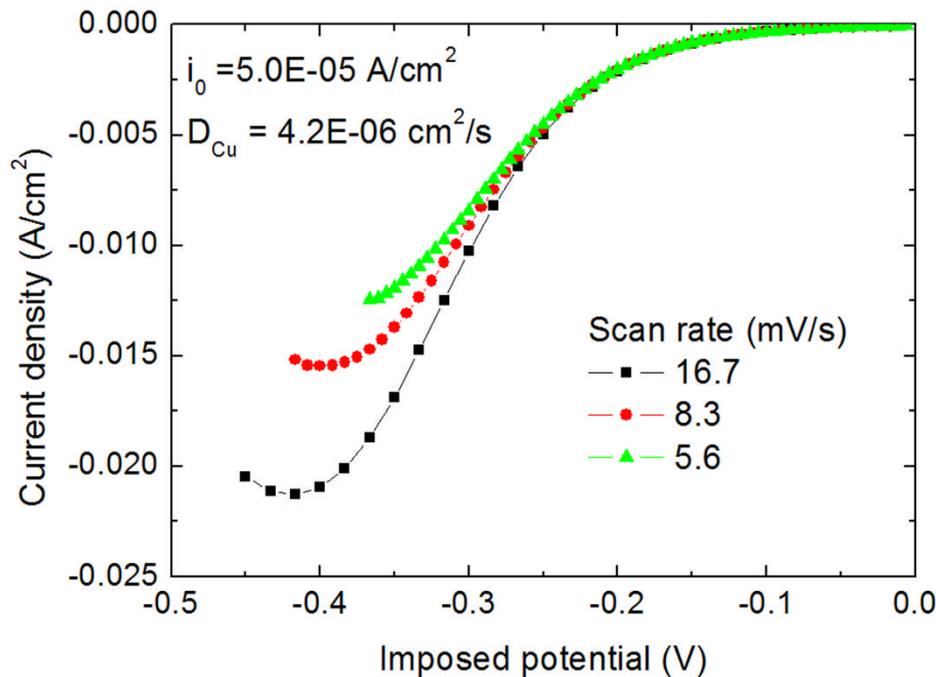


Cu²⁺ in aqueous sulfate system



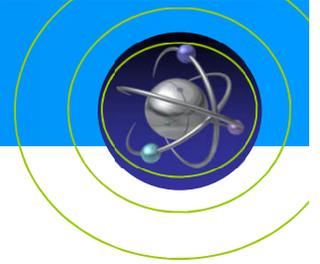
Linear sweep voltammetry simulation

- Peak current increases with scan rate, but potential where peak occurs change due to controlled charge transfer rate (irreversible electrode reaction system).
- Higher exchange current density → decreased polarization

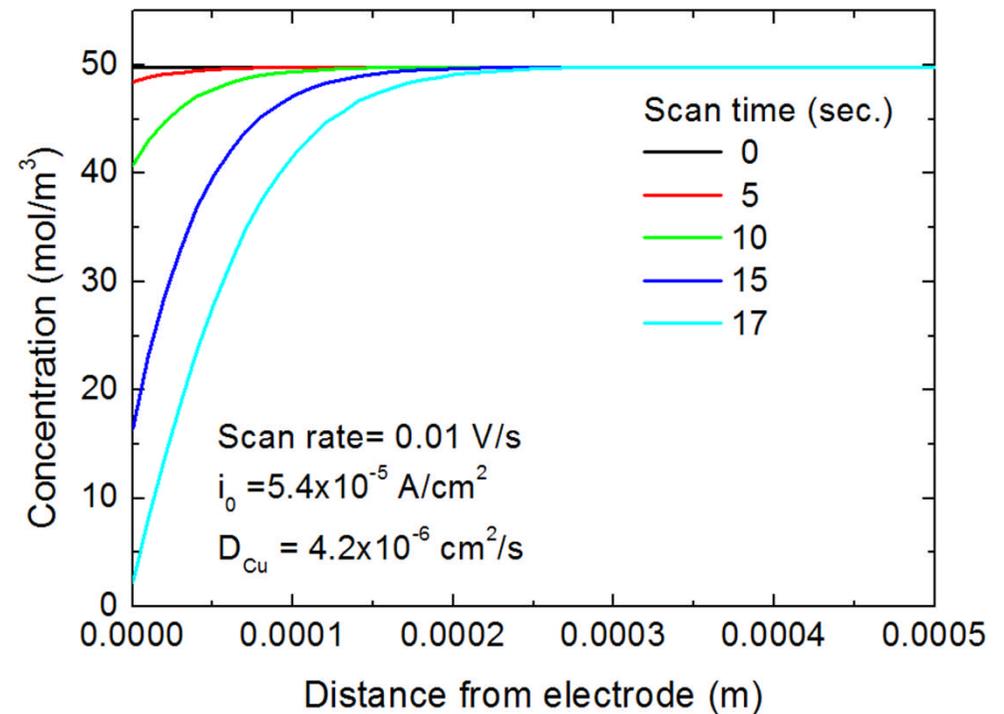
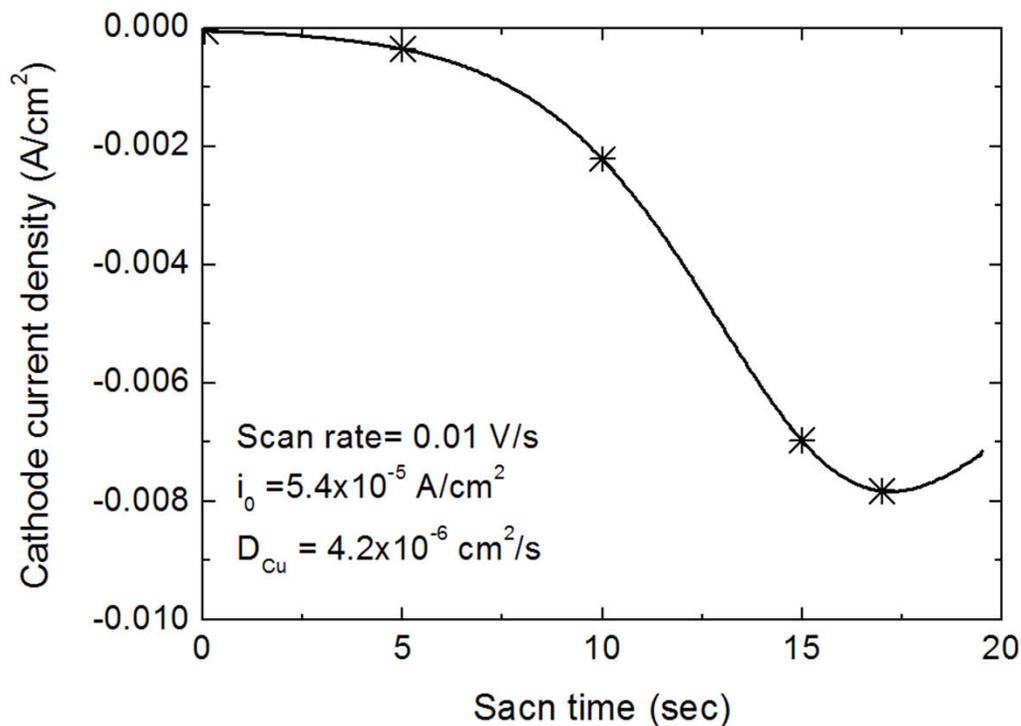


LSV range = 0 to -0.5 V

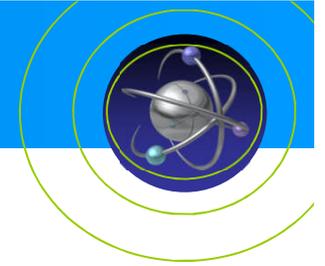
Cu²⁺ in aqueous sulfate system



- Concentration profile at the cathode during the LSV
 - Time dependent polarized current densities & corresponding concentration-distance profiles
 - Mass transport limited at the decreased concentration condition at the electrode surface

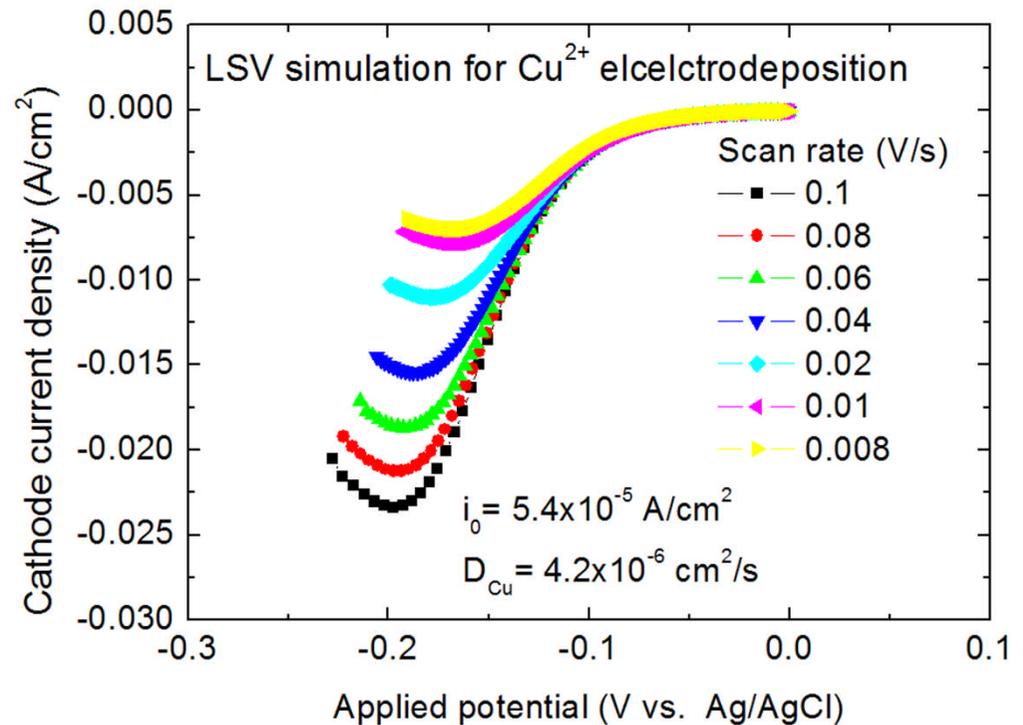
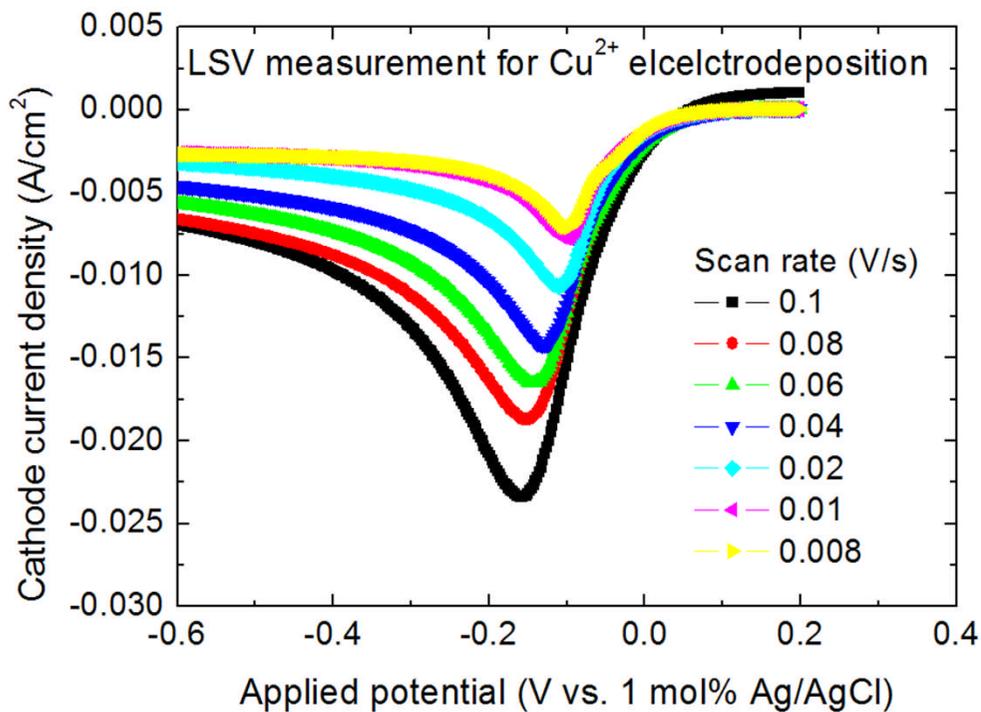


Cu²⁺ in aqueous sulfate system

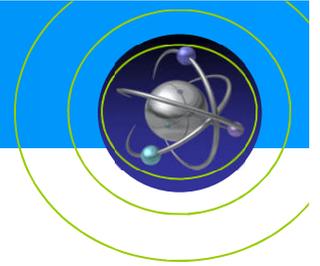


Linear sweep voltammetry (LSV) approach

- Peak current increases with scan rate, but potential where peak occurs changes → irreversible process.
- Simulations for cathodic polarization of Cu deposition could give a reasonable approach for determination of kinetic parameters.

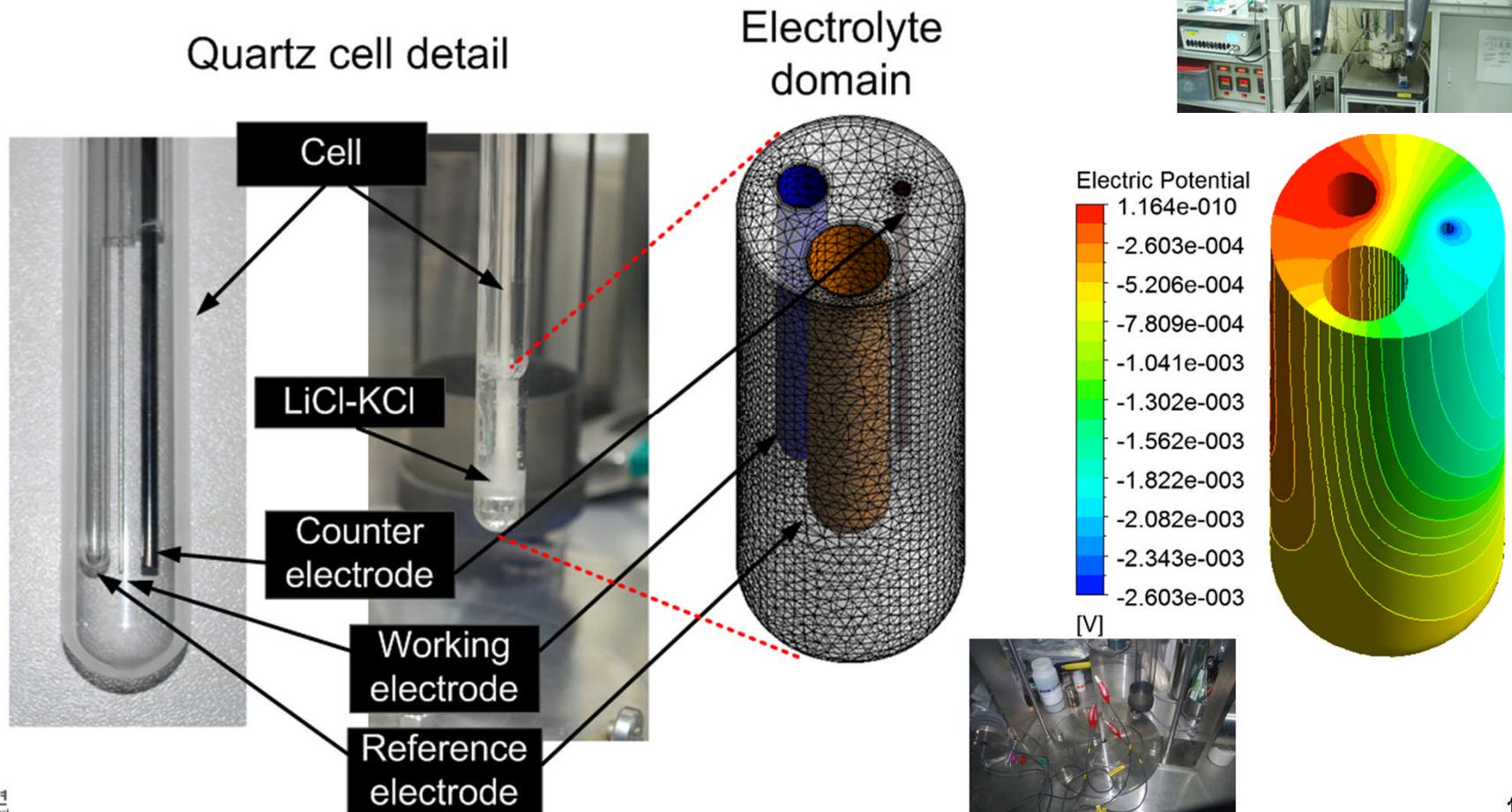


LiCl-KCl-LaCl₃ System

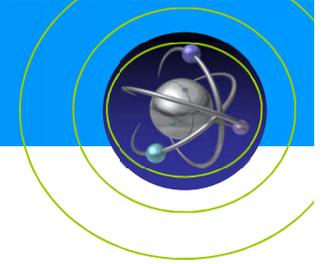


■ Computational domain for molten-salt cell

- Computational fluid domain: molten-salt electrolyte (1.51×10^{-4} mol/cm³ of LaCl₃ in LiCl-KCl) at 500°C
- WE(tungsten), CE(glassy carbon) & RE(1 mol% Ag/AgCl)

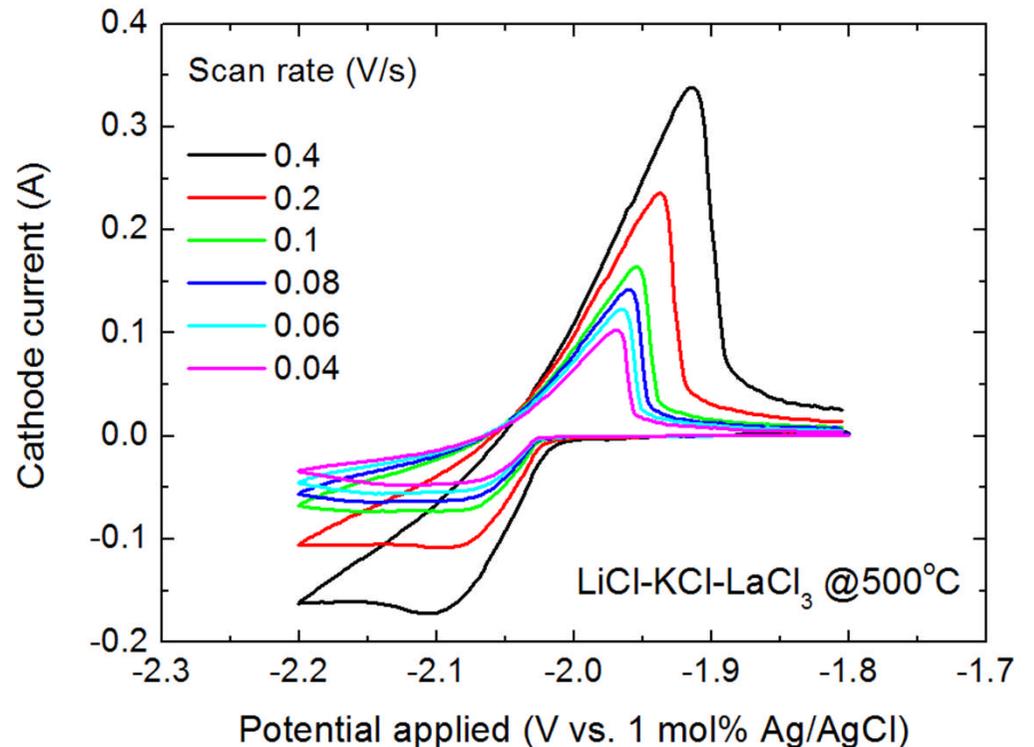
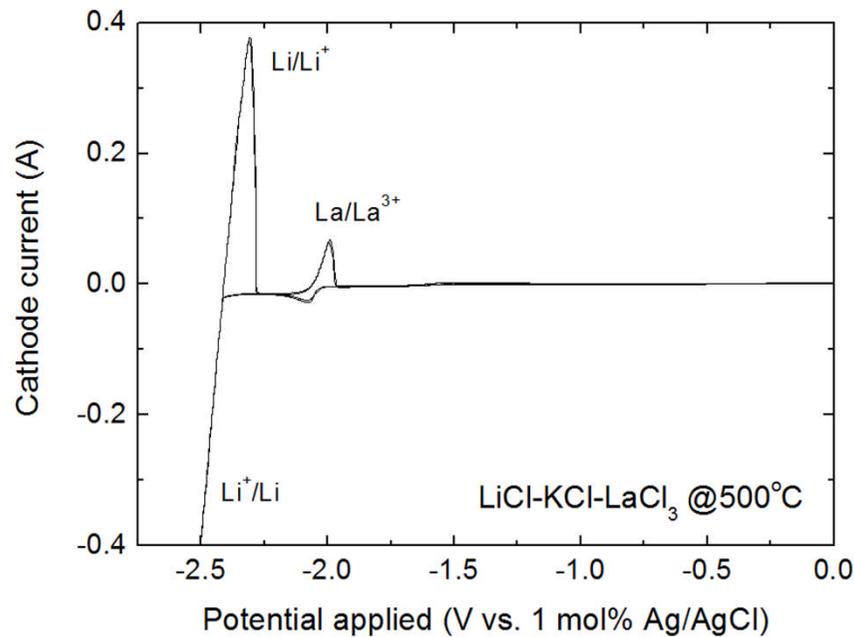


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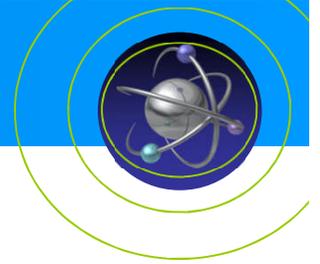


Cyclic voltammograms of LiCl-KCl-LaCl₃

- As the sweep rate is increased, irreversible cyclic voltammogram is recorded.
- Anodic & cathodic peak currents show irreversible in charge transfer.
- Soluble-insoluble exchange peaks

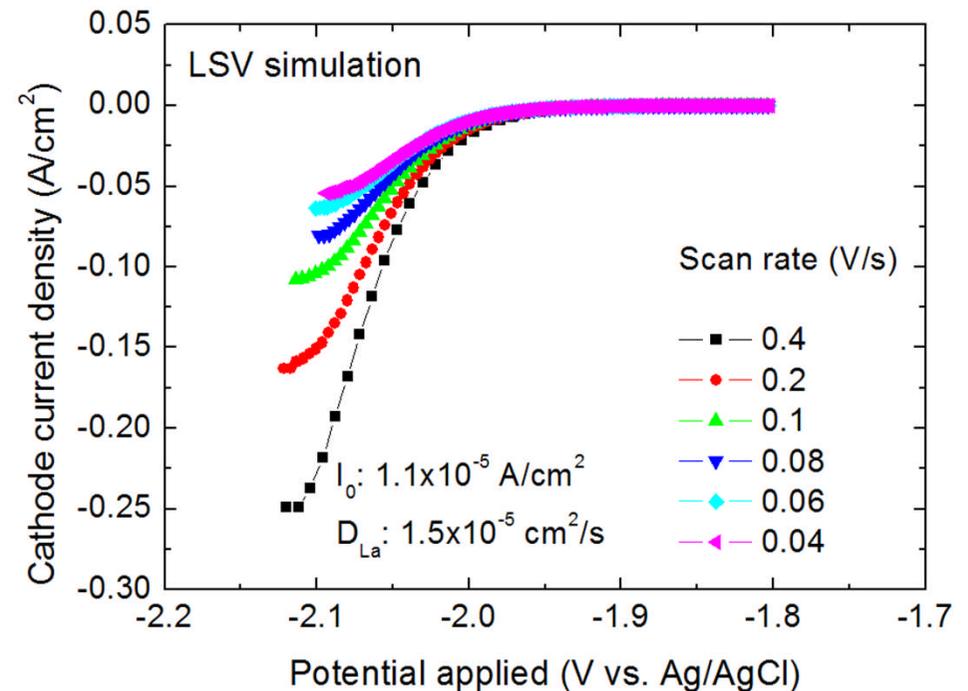
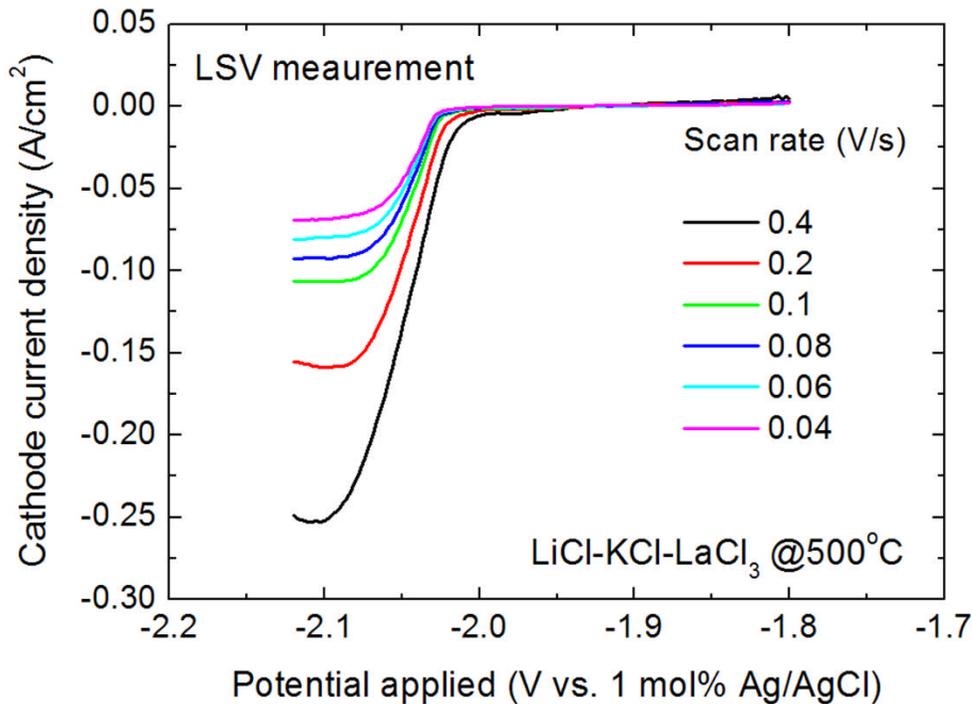


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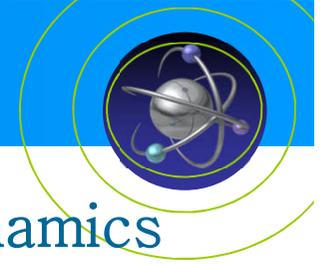


Linear sweep voltammetry (LSV) approach

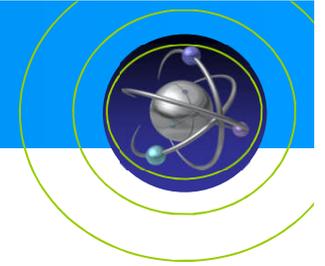
- Cathodic polarization measurement & simulation at various scan rates.
- Simulations for cathodic polarization of La deposition could give a reasonable approach for determination of kinetic parameters.



Summary



- A model using the CFD-based electrochemo-hydrodynamics simulation has been developed to investigate the determination of the kinetic parameters for the metal electrodeposition.
- The mass and charge transfer limited current density on the electrochemically irreversible reaction was simulated for linear sweep voltammetry
- This modeling approach gives us one of the solutions of predicting the kinetic parameters by adjusting to give the best fit of voltammogram in a real irreversible situation of the given geometry cell.
- This model could provide quantitative information about the electrochemical kinetic properties.



Thank you for your attention!