

Spatio-temporal evolution of charge transfer current in an Li-ion battery

Charge Transfer Current

- Drives battery charge/discharge process
- Involves two parallel phenomena
 - Dissolution of Li_+ ions into electrolyte
 - Conduction of electrons through electrode material and carbon fillers

Representation

- Commonly used method: Butler-Volmer current
- Hypothesis:
 - Activation energy = weighted average of oxidized and reduced states

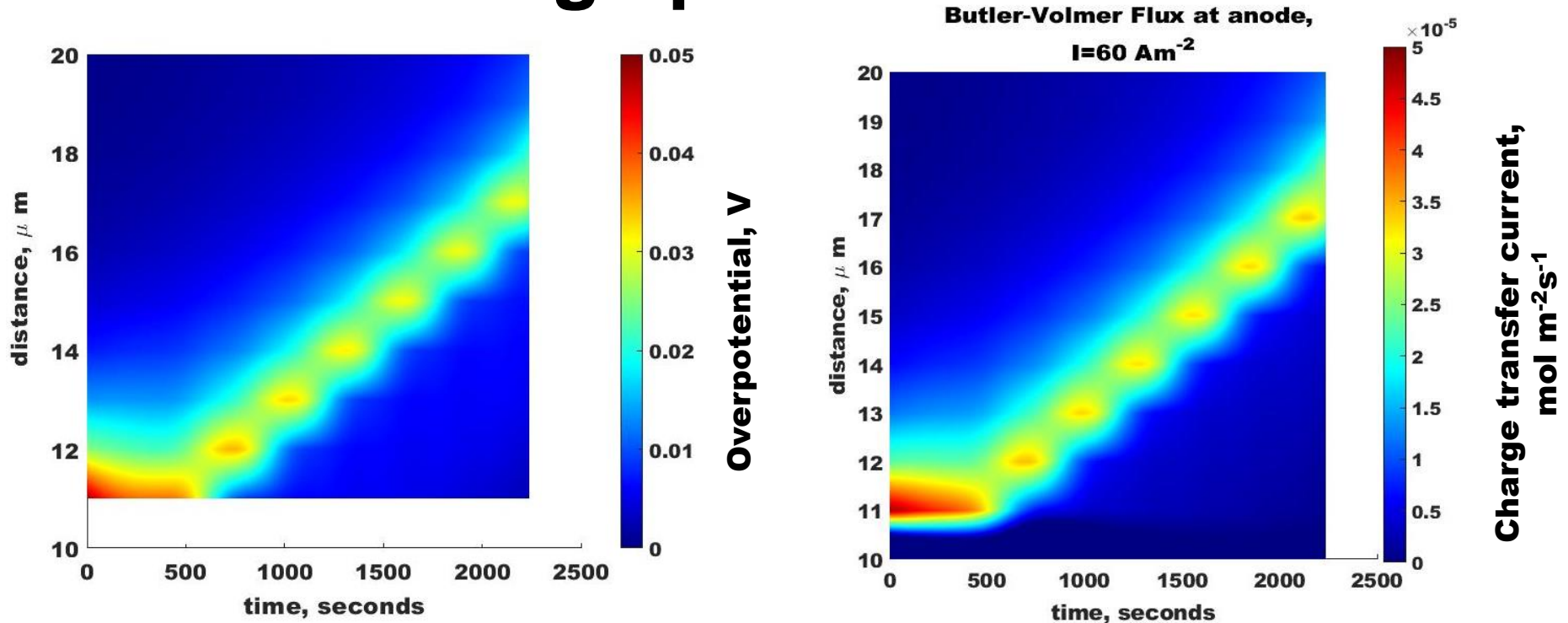
The diagram shows the Butler-Volmer current equation with red arrows pointing from descriptive labels to specific parts of the equation:

$$j(x, t) = 2k_{\text{eff},i} \sqrt{c_e(x, t)(c_{s,i}^{\text{max}} - c_s^*(x, t))c_s^*(x, t)} \sinh \left[\frac{0.5R}{FT(x, t)} \eta_i(x, t) \right]$$

Labels and their corresponding parts in the equation:

- Butler-Volmer current**: Points to $j(x, t)$
- Rate constant**: Points to $k_{\text{eff},i}$
- Electrode capacity**: Points to $c_e(x, t)$
- Electrolyte Li concentration**: Points to $c_{s,i}^{\text{max}}$
- Surface Li concentration**: Points to $c_s^*(x, t)$
- Overpotential**: Points to $\eta_i(x, t)$

Factors driving spatio-temporal evolution



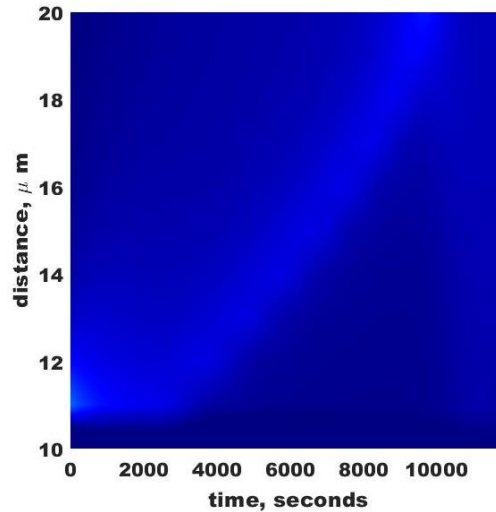
- LION-SIMBA 1-D P2D multiphysics model
 - Input current 60 A m^{-2}
 - $T=298\text{K}$
 - Graphite anode, LiCoO_2 cathode
- Marked correlation between Butler-Volmer flux and overpotential (η)

Spatio-temporal evolution of overpotential

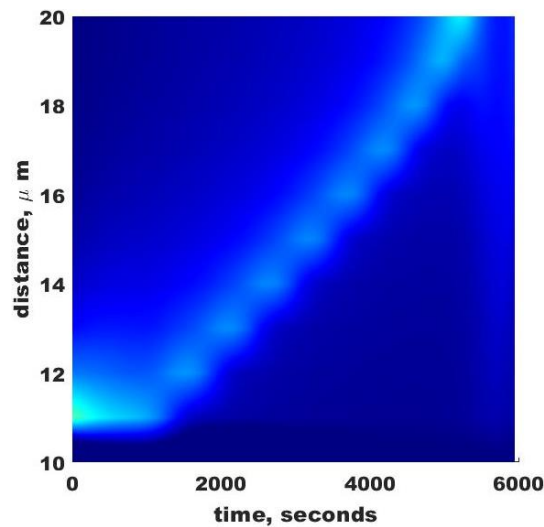
- ▶ Beginning of discharge: concentration polarization due to instantaneous charge transfer at the outermost layer (#10)
 - ▶ Lithium atoms from inner layers move in to fill in outermost layer
 - ▶ Surface lithium concentration, and hence potential, relaxes to its steady state, open circuit value
 - ▶ Outermost layer closest to separator, first to empty
- ▶ Phenomenon repeated over inner layers

How does applied current affect overpotential and charge transfer dynamics?

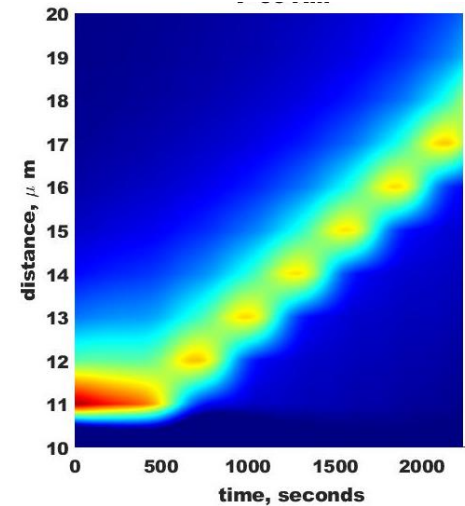
15 A m⁻²



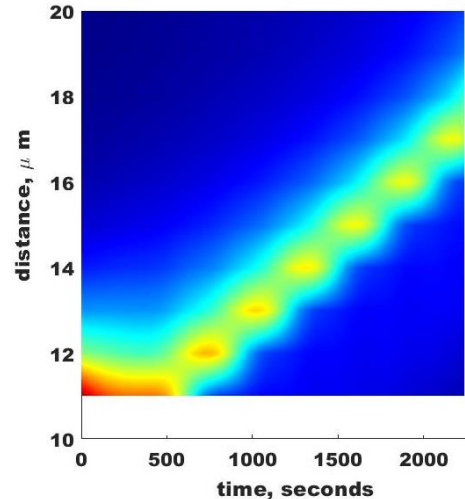
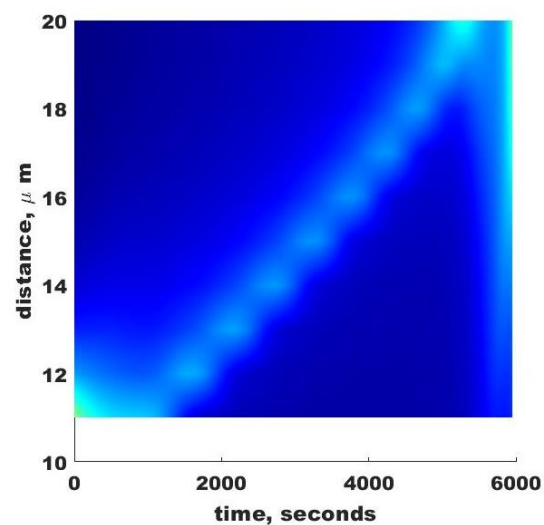
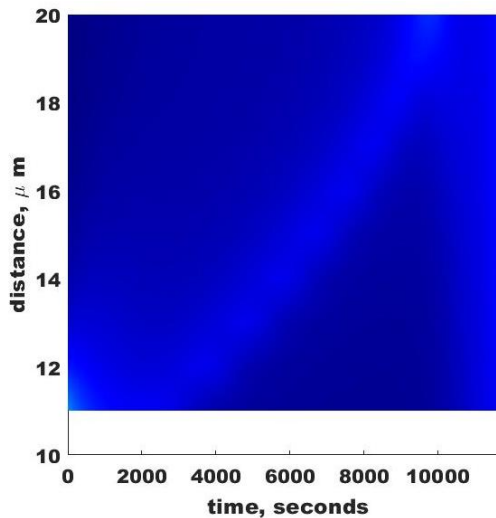
30 A m⁻²



60 A m⁻²



Charge transfer current,
mol m⁻²s⁻¹



Overpotential, V

Key takeaways

- Overpotential hotspots and consequently Butler-Volmer flux increase with applied current
- Highest overpotentials and fluxes for 60 A m^{-2}
 - Higher currents provide lesser relaxation time
- Lowest overpotentials and fluxes at 15 A m^{-2}
 - Attributed to ability to relax to open circuit value
- System for most of the time is at open circuit voltage for all 3 input currents