Phase-field Modeling of Graphite Single Particles And Porous Electrodes

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Abstract

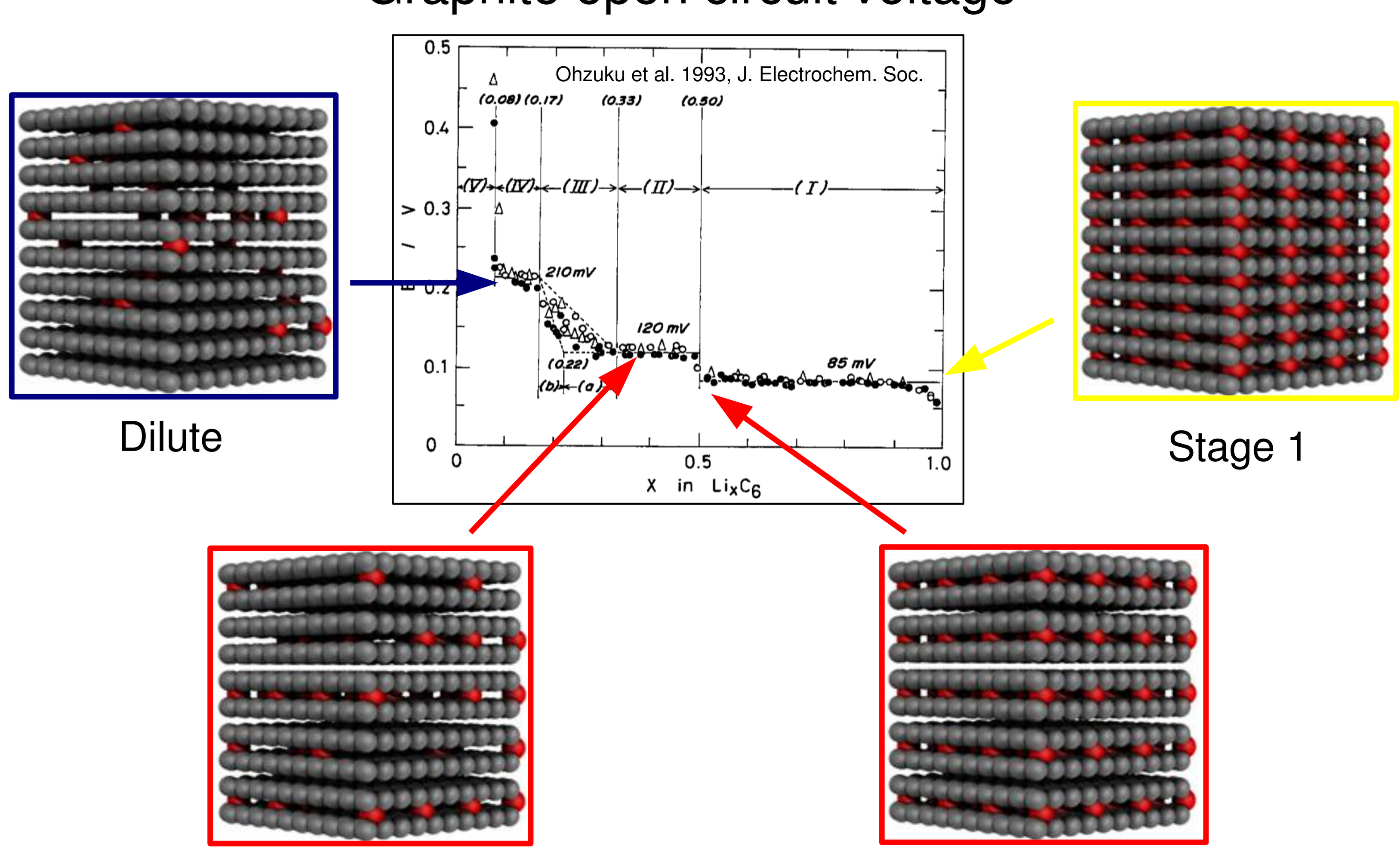
Graphite is the most commonly used anode material in lithium-ion batteries because of excellent stability and electrochemical properties.

It has been well studied as an intercalation compound because of its characteristic "staging" behavior which leads to a staircase open circuit voltage profile. Lithium intercalation is also associated with color changes, which allow for direct experimental probing of spatial and temporal concentration profiles to resolve widely ranging reported values of diffusivities.

Here, we develop a 2-conserved-parameter phase field model to capture the dynamic behavior of the layered graphite material. We use the same model to fit both single-particle experimental data as well as full-electrode scale data by using a modified porous electrode theory.

Graphite Staging

Graphite open circuit voltage

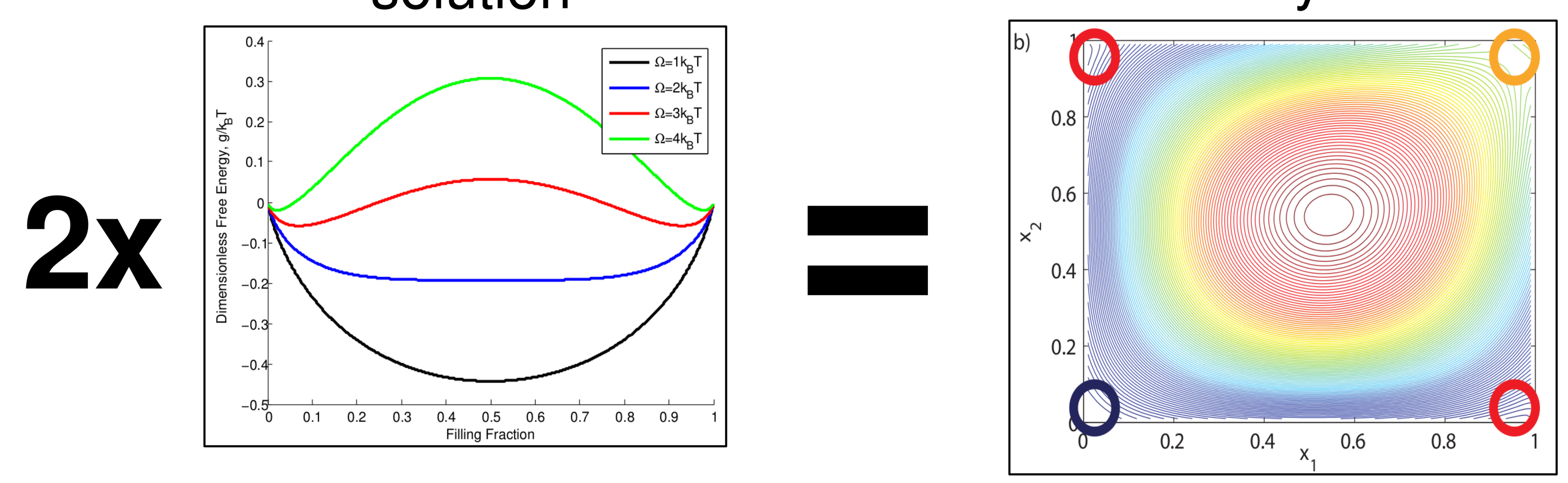


Goals:

- Develop a model to capture staging and transport of Li within a single particle, which affects rate performance.
- Simplify model for electrode-scale simulations to capture voltage curves and electrolyte interactions.

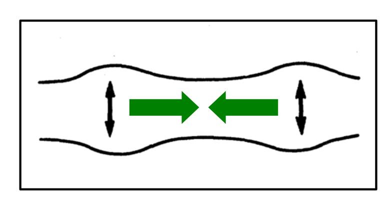
Thermodynamic Model

Single-layer regular solution | Coupled 2-layer thermodynamics



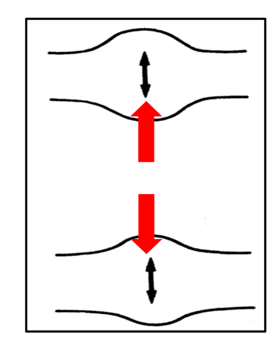
$$g_i = kT[x_i \ln(x_i) + (1 - x_i)\ln(1 - x_i)] + \Omega_a x_i(1 - x_i) + \frac{1}{2}\kappa(\nabla x_i)^2$$

$$g = g_1 + g_2 + \Omega_b x_1 x_2 + \Omega_c x_1(1 - x_1)x_2(1 - x_2)$$



In-plane attraction

Safran and Hamann 1979 Phys. Rev. Lett.

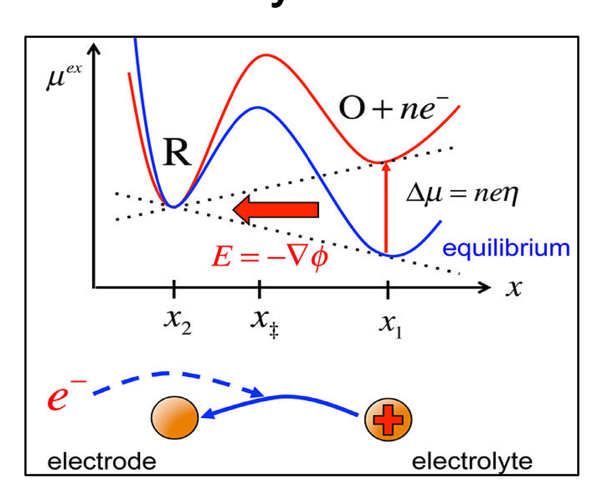


Out-of-plane repulsion

Safran and Hamann 1979 Phys. Rev. Lett.

Reaction Model and Geometry

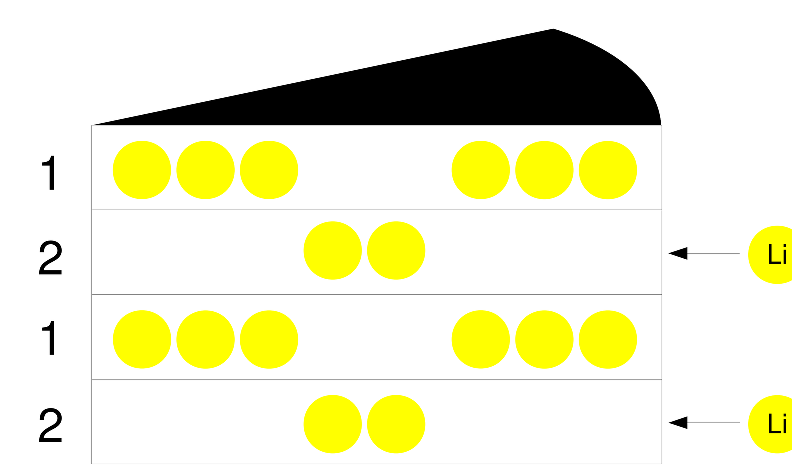
Consistent reaction boundary condition



Bazant 2013, Acc. Chem. Res.

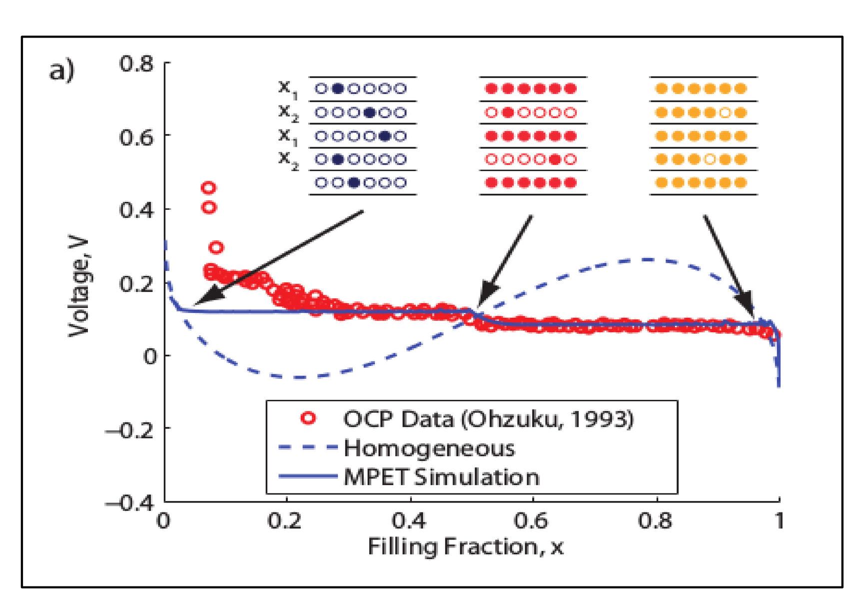
$$R = k_0\left(e^{(\mu_\ddagger^{ex} - \mu_1)/k_BT} - e^{(\mu_\ddagger^{ex} - \mu_2)/k_BT}\right)$$

Schematic of cylindrical graphite model



- Cahn-Hilliard dynamics within each layer
- Reaction boundary condition for each layer

Model Validation: Open Circuit Voltage

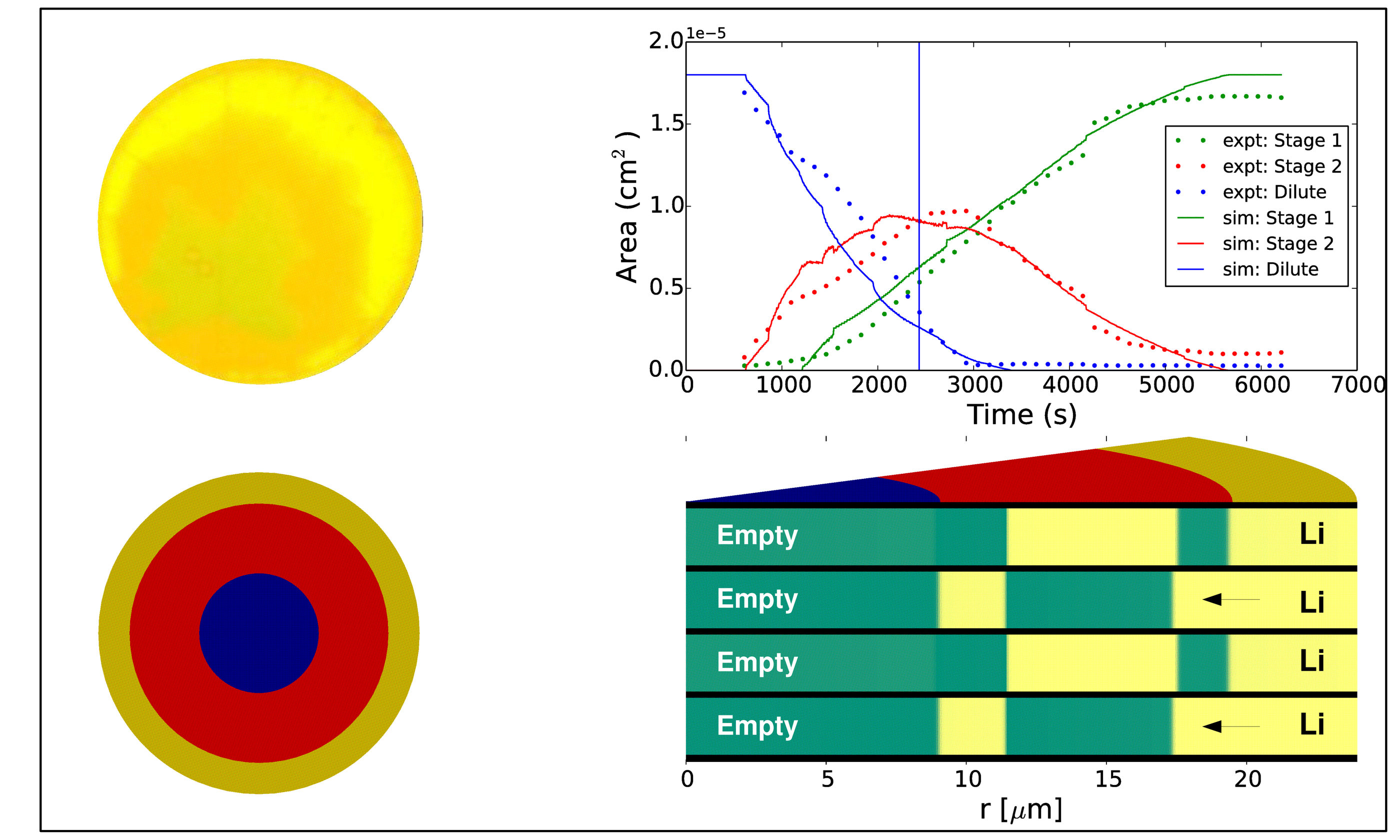


Ferguson and Bazant, submitted

Assumptions:

- Ensemble of particles
- Fast particle filling compared to experimental discharge (homogeneous layers)
- Parameters (fit): $\Omega_a, \Omega_b, \Omega_c$

Single Particle Model and Experiments

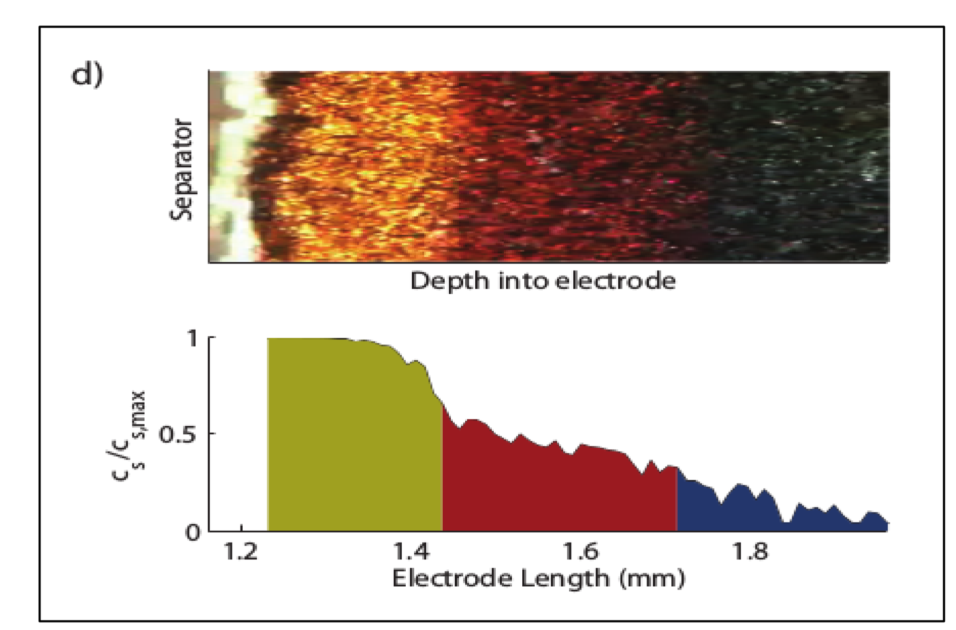


Assumptions:

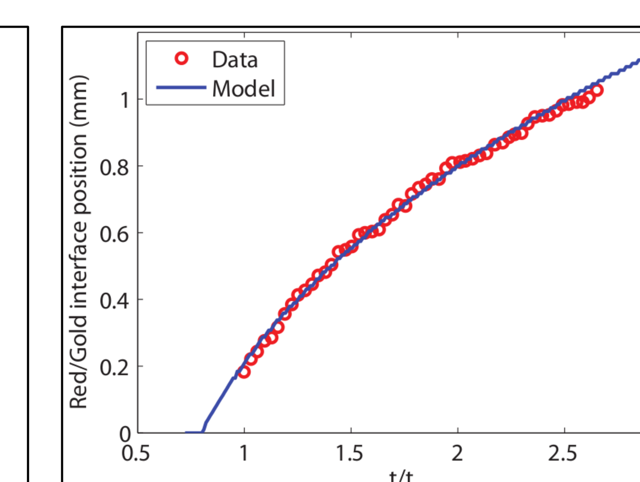
- Reaction activity coefficient: $\gamma_{\ddagger,i} = e^{\mu_{\ddagger,i}^{ex}/k_BT} = \frac{1}{x_i(1 - x_i)}$
- Two new parameters (fit):
  Dilute tracer diffusivity (agrees with *ab initio*), applied voltage

Model Scale-up to porous Electrodes

Porous electrode simulations require simulation of many particles, coupled to electrolyte transport, requiring particle model reduction.



Ferguson and Bazant, submitted;
Data/movies from Harris et al. 2010, Chem. Phys. Lett.



Assumptions:

- Homogeneous layers
- One new parameters (fit):
  Porosity

Conclusions

- With few free parameters, our model captures (1) electrode open circuit voltage, (2) microscopic reaction and transport, and (3) electrode-scale filling behavior.
- Single particle behavior shows strong reaction/transport competition, allowing refinement of reaction model.

Acknowledgements

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