Mechanistic Modeling of Sodium-Ion Adsorption and Pore Filling in Hard Carbon Anodes

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Not for Review

Project Profile

Topic: Sodium Batteries
Vertical: Materials and Systems Innovation
Strategic Pathway: Grow
Project start and finish: FY26-FY27

Problem

- Due to the global abundance of sodium, sodium-ion (Na-ion) batteries offer a potentially lower-cost alternative to lithium-ion batteries for grid-scale energy storage.
- Na-ion batteries utilizing hard carbon anodes have demonstrated high rate capability and promising cycle life:
  - 95% capacity retention after 1000 cycles at 3C – 8C [1]
  - 83% capacity retention after 3000 cycles at 6.5C [2]
- Some studies suggest the high rate capability arises from the adsorption- and pore-filling-based ion storage mechanisms. [2, 3]
- A physics-based model is needed to understand how adsorption and pore-filling influence sodium-ion battery rate capability and degradation.

Fig. 1. Illustration of Na-ion adsorption, intercalation, and pore filling storage mechanisms in a hard carbon anode material

Approach

A pseudo-two-dimensional (P2D) Doyle–Fuller–Newman (DFN) model is extended to include coupled adsorption and pore filling storage mechanisms.

Adsorption to defects and edges in the carbon structure

$$j_{adp}[\frac{A}{m^3}] = \frac{c_{\theta,max}F}{a} k_{ads} [\theta e^{\frac{F}{2RT}(\phi_s-\phi_e-U_{ads})} - \frac{c_e}{c_e^0}(1-\theta)e^{\frac{-F}{2RT}(\phi_s-\phi_e-U_{ads})}]$$

$$U_{ads} = U_{ads,0} + \frac{RT}{zF}\ln\left(\frac{\theta}{1-\theta}\right) + \frac{RT}{zF} g\theta - \frac{RT}{zF}\ln(\frac{c_e}{c_e^0})$$

Pore filling

$$j_{pore}[\frac{A}{m^3}] = -\frac{FD_{pore}c_{mi}}{dRT}(\phi_e + \frac{RT}{F}\ln(\frac{c_e}{c_e^0}) - \Psi_{pore})$$

$$\Psi_{pore} = \frac{RT}{F}(E_{pore,0} + \ln\left(\frac{\frac{c_{mi}}{c_{mi,max}}}{1-\frac{c_{mi}}{c_{mi,max}}}\right) + g_1(\frac{c_{mi}}{c_{mi,max}}) + g_2(\frac{c_{mi}}{c_{mi,max}})^{\frac{3}{2}})$$

Fig. 2. Modeled concentration of Na-ions stored in the anode through intercalation, adsorption, and pore filling over three continuous full equivalent cycles (FECs). Each FEC consists of a constant-current charge to 4.1 V, a constant-voltage hold at 4.1 V for 1800 s, a 600 s rest, a constant-current discharge to 1.5 V, and a final 600 s rest.

Results

Fig. 3. Charge and discharge voltage profiles at C/2, 1C, 2C, and 5C.

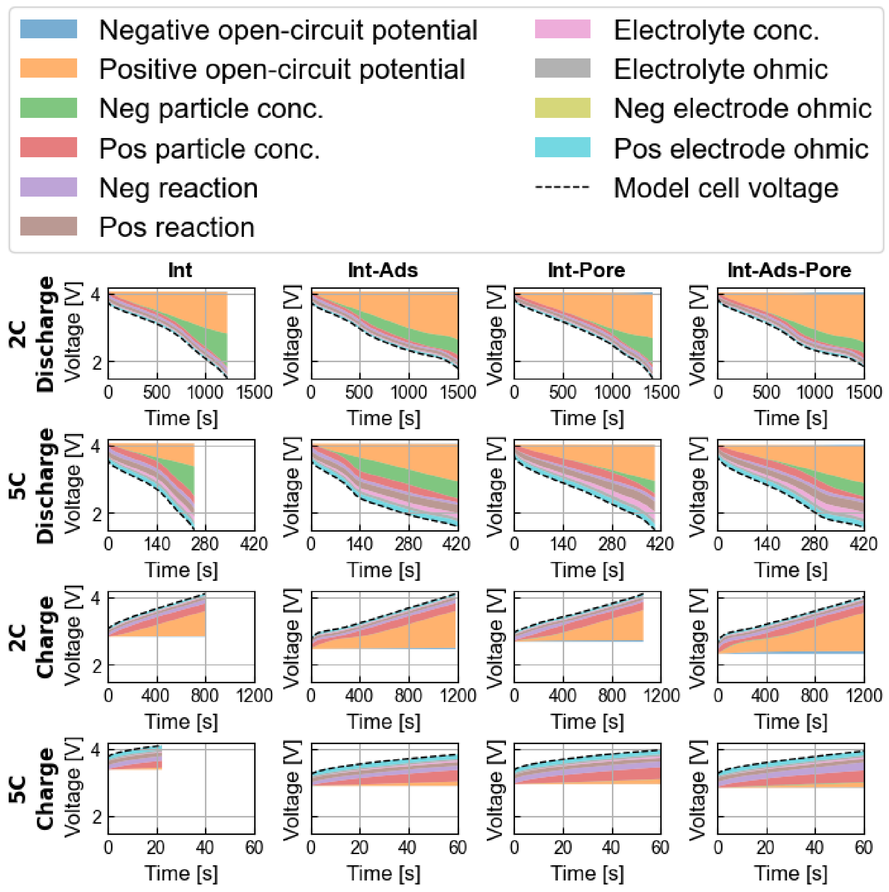

Fig. 4. Overpotential contributions from diffusions, kinetics, and conductions for the charge and discharge models at 2C and 5C.

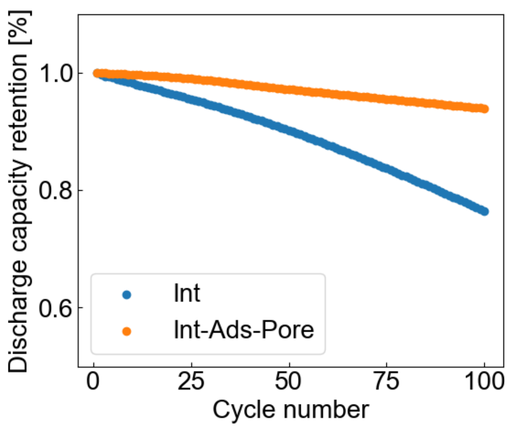

Fig. 5. Capacity retention over 100 FECs at C/2, modeled with SEI growth and sodium plating.

Conclusions & Impact

- Adsorption and pore filling improve rate capability by reducing concentration gradient within anode particles.
- The model incorporating adsorption and pore filling predicts longer cycle life despite SEI growth and sodium plating.

Future Directions

- Integrate with the experimental team at the material scale to validate model predictions.
- Incorporate the developed model into system-level analysis for grid-scale applications.

References

[1] Laufen, Hendrik, et al. "Multi-method characterization of a commercial 1.2 Ah sodium-ion battery cell indicates drop-in potential." Cell Reports Physical Science 5.5 (2024).
[2] Li, Yuqi, et al. "Origin of fast charging in hard carbon anodes." Nature Energy 9.2 (2024): 134-142.
[3] Qi, Yuruo, et al. "Slope-dominated carbon anode with high specific capacity and superior rate capability for high safety Na-ion batteries." Angewandte Chemie International Edition 58.13 (2019): 4361-4365.

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