Model analysis of silicon-based electrodes for lithium ion batteries

Electrochemical Science and Engineering

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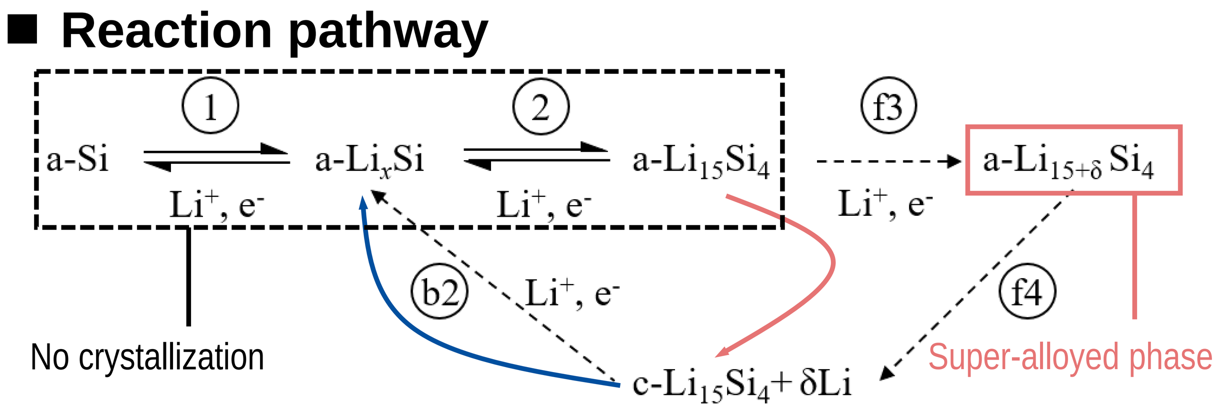
Introduction

Silicon is an attractive anode material in lithium ion batteries. Here we build a mechanistic model of silicon electrodes and correlate their voltage hysteresis to the underlying multi-phase electrochemical reactions, crystallization and amorphization processes. The effects of the voltage hysteresis on (de)lithiation behaviors of composite silicon/graphite electrodes are further studied. The model provides a necessary tool for future design and development of longer-life silicon-based batteries.

Voltage hysteresis model

■ **Reaction pathway**



■ **Electrochemical reactions (1, 2, f3, b2)**

$$i_{(j)} = -2 i_{(j),0} \sinh\left(\frac{f\eta_{(j)}}{2}\right)$$

■ **Homogeneous crystallization (f4)**

$$\frac{dx_{cryst}}{dt} = k_{cryst}\left(\frac{x_{(f3)}}{\Delta x_{(f3)}} - x_{cryst}\right) x_{cryst}$$

■ **Heterogeneous amorphization (b2)**

Amorphization results in elevated voltage

$$E_{(b2),0} = \frac{\Delta G_{(2b),0}}{(3.75-x)e} = \frac{\Delta G_{(2),0} + \boxed{\Delta G^*}}{(3.75-x)e} = E_{(2),0} + \boxed{E^*}$$

Si/Gr composite electrode model

A pseudo-two-dimensional (P2D) multi-material model for Si/Gr electrode is developed, considering different properties and electrochemical kinetics of Si and Gr. The voltage hysteresis of Si is included in the model.

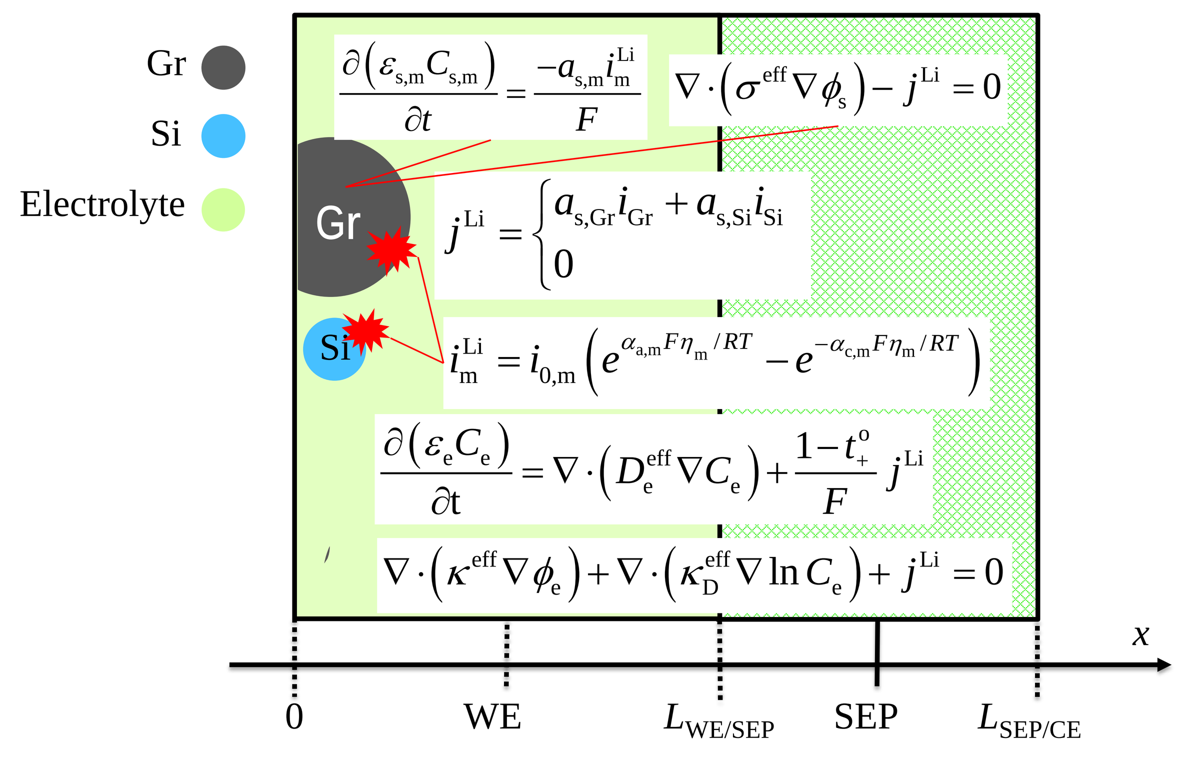


Figure 1: Schematic configuration of the P2D multi-material porous electrode model

Result 0 - Validation

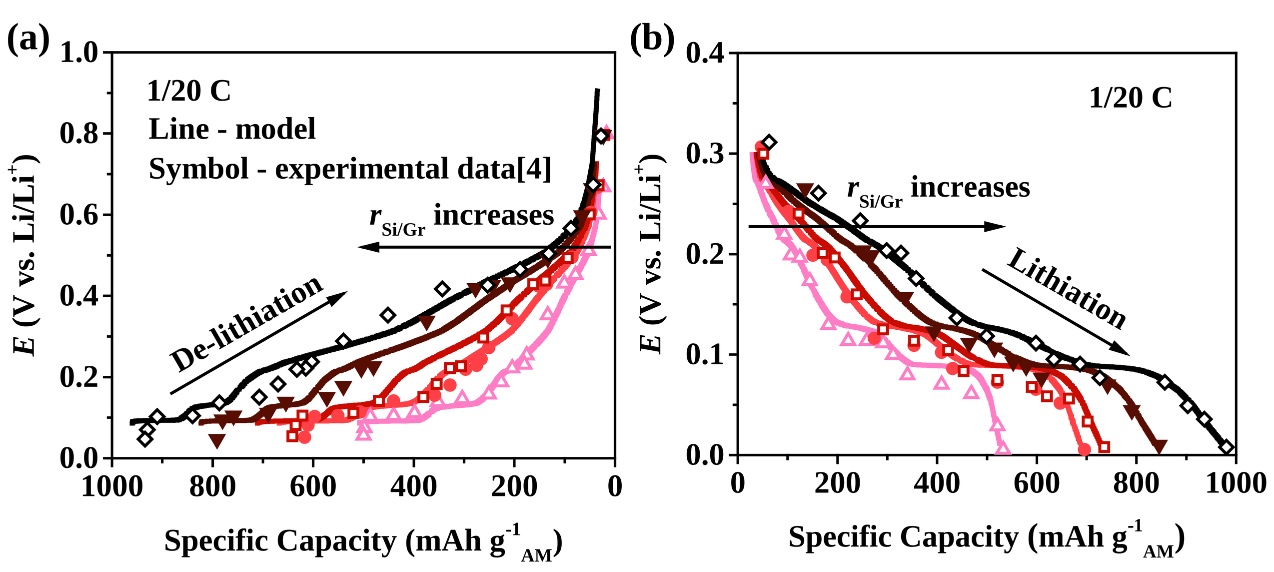


Figure 2: Comparison of simulated and experimental voltage curves of Si/Gr blended electrodes with different Si/Gr mass ratios ($r_{Si/Gr}$) in (a) delithiation and (b) lithiation.

Result 1 – Voltage hysteresis of Si

When the voltage falls to 0 V, the silicon electrode undergoes two phase transformation stages I and II. After the current is reversed, a distinct plateau V occurs suggesting the amorphization process b4. When $V > 0.05$ V, no crystallization occurs and two sloping plateaus (III and IV) in delithiation voltage curves are observed.

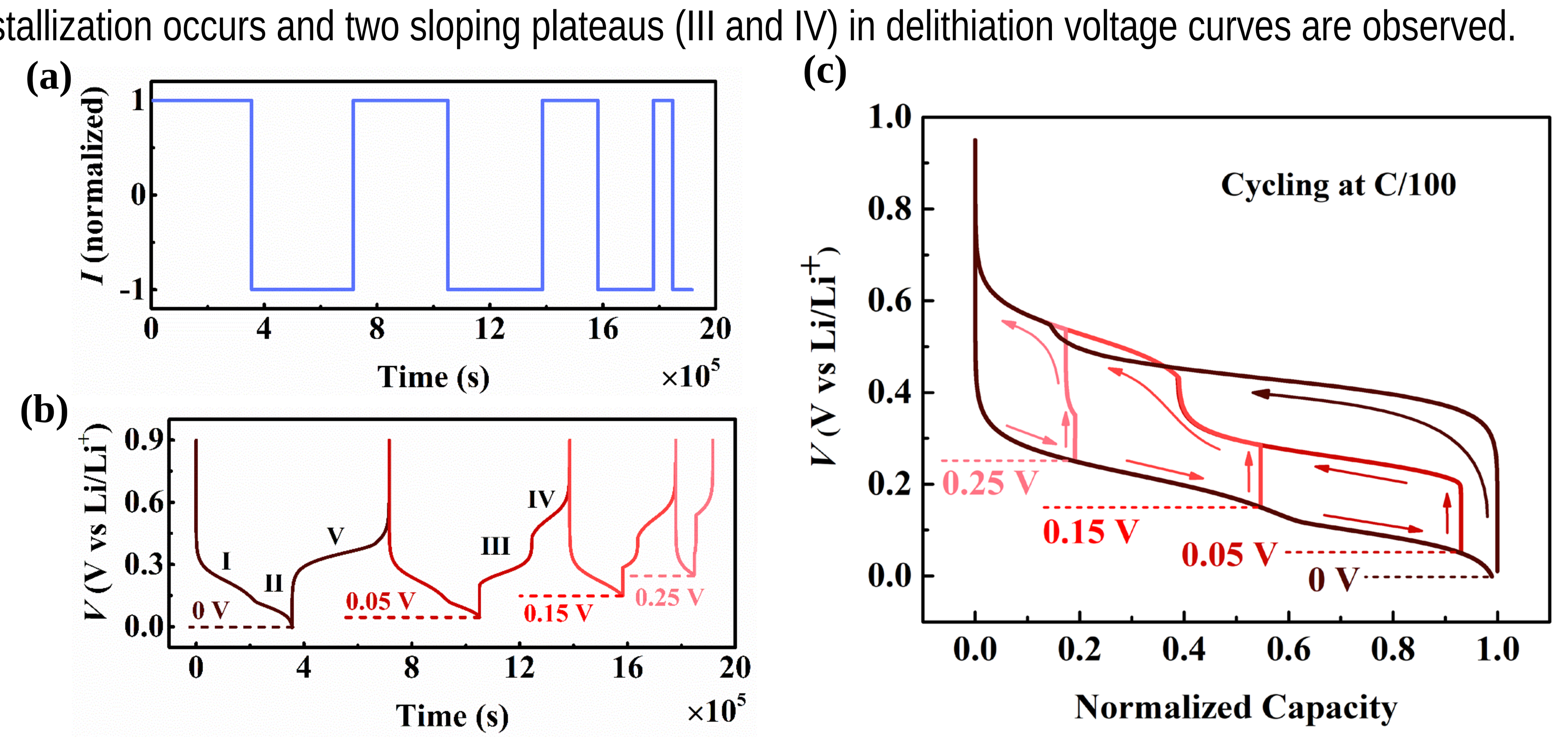


Figure 3: Electrochemical behaviors of silicon cycled between different voltage limits: (a) current density vs time; (b) voltage vs time; (c) voltage loops.

Result 2 – Variation of crystalline Li-Si phase

The predicted composition change during deep cycling is compared with the XRD results in [3]. Fig. 4(a) shows a sudden formation of c-$Li_{15}Si_4$ due to homogeneous crystallization process f4 at the end of charge process. Fig. 4(b) shows the linear decrease of c-$Li_{15}Si_4$ through discharge process.

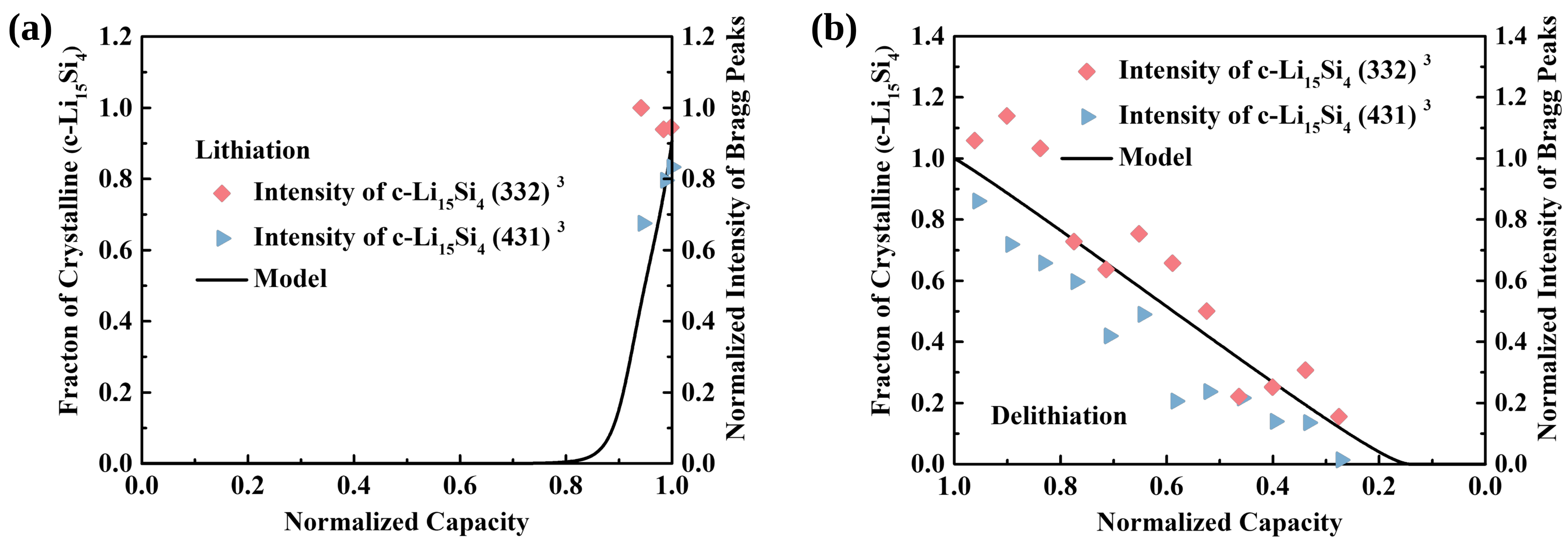


Figure 4: Concentration variation of c-$Li_{15}Si_4$ during (a) charge and (b) discharge.

Result 3 –(De)Lithiation competition between Si and Gr

■ Voltage hysteresis of Si results in asymmetric (de)lithiation competition in a composite electrode. Lithiation starts with Si, and then the lithiation rate of Gr is comparable to Si at high SOC levels. Delithiation occurs preferentially from Gr at high SOC levels, while Si at lower SOC levels.

■ A dimensionless competing factor χ_m is proposed to quantify the active range of each active material, Fig. 5(c) shows limiting the electrode potential below 0.24V can reduce the excessive use of Si.

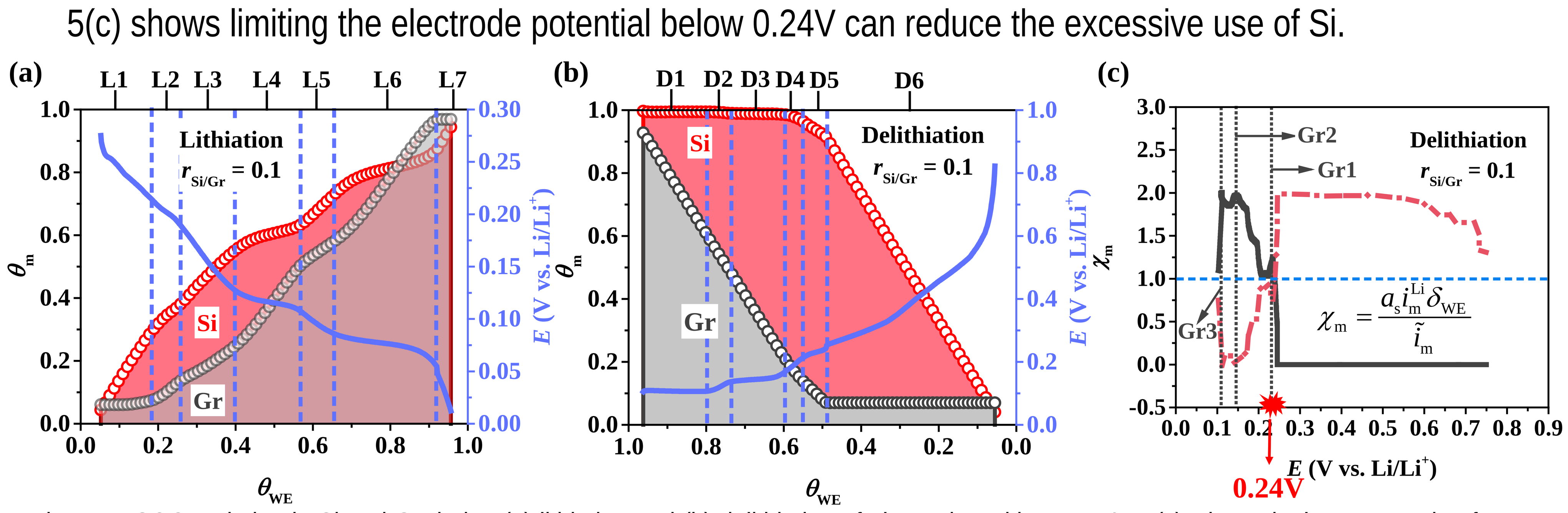


Figure 5: SOC variation in Si and Gr during (a) lithiation and (b) delithiation of electrodes with $r_{Si/Gr} = 0.1$. (c) Dimensionless competing factor χ_m during delithiation: $\chi_m > 1$ means the electrochemical reaction of active material m dominants.

Conclusions

- Voltage hysteresis model for Si-based lithium ion batteries.
- The abrupt appearance of the crystalline Li-Si phase in lithiation and its gradual disappearance in de-lithiation are retrieved.
- A multi-material model is developed for Si/Gr electrodes
- A derived dimensionless competing factor is used for design of cycling protocol for Si/Gr electrodes

References

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