Li^+ Crosstalk-driven Calendar Aging in Si/C Composite Anodes

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Introduction

Cells with silicon/graphite (Si/C) composite anodes hold the advantages of high energy density (>500 Wh kg^{-1}), quickly attracting attention from both academia and industry [1].

Although Si shows a super high specific capacity (3579 mAh g^{-1} for $Li_{3.75}Si$) [2], it readily undergoes side reactions with the electrolyte, resulting in capacity loss [3]. To improve the stability of Si/C composite anodes, significant efforts have been made from material design to electrode preparation, such as employing nano-Si, modifying material structures, and changing binders and electrolytes [4-6].

Although the cycling performance has been improved effectively, the performance decay during storage, i.e. calendar aging, has been habitually overlooked [7]. During the storage, the high reactivity of Si leads to remarkable performance decay, while the inner processes have not yet been thoroughly examined.

In this work, the Li^+ transfer process were specified by combining cross-scale characterization with multi-dimensional simulation models. Li^+ crosstalk was identified as a key factor in calendar aging, which the transfer of Li^+ from graphite to Si compromises the stability of graphite. By adjusting Li^+ crosstalk process, the improved cells demonstrated an increase of 20% in calendar life after 24 h of storage. We emphasize the significant impact of Li^+ crosstalk on calendar aging, and this effect offers guidance for investigating degradation mechanisms in other composite electrode systems.

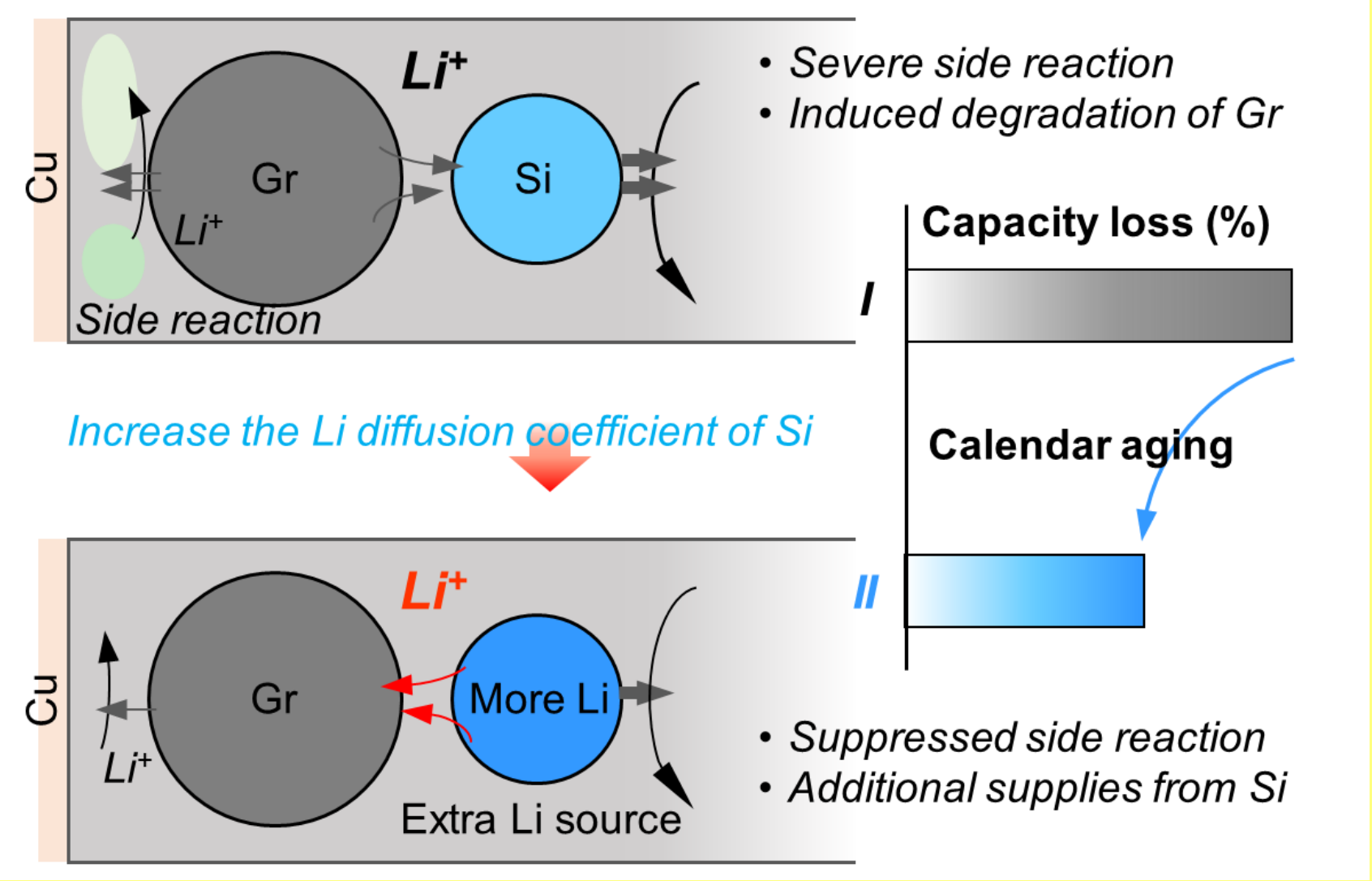

Fig. 1. Scheme of the Li^+ crosstalk effect.

Experiment

CELLS PREPARATION

1. Positive electrode: $LiNi_{0.8}Co_{0.1}M_{n0.1}O_2$ (NCM811, 3.5 μm of D50) electrode was purchased from Canrd Ltd., with an areal capacity of 1.60 mAh cm^{-2}.

2. Negative electrodes: Pure graphite electrode with 1.88 mAh cm^{-2} areal capacity was from Canrd Ltd., and various Si content composite electrodes were prepared in laboratory, with the same areal capacity of graphite electrode.

3. Electrolyte: 1 M $LiPF_6$ in ethylene carbonate/ ethyl methyl carbonate/ diethyl carbonate (EC/EMC/DEC = 3:4:2 in volume) plus 10 wt% fluoroethylene carbonate (FEC) purchased from Canrd Ltd.

ELECTROCHEMICAL TEST

1. Formation: 0.1 mA (~0.06 C) constant current-constant voltage (CC-CV) charging to 4.2 V, 0.05 mA, and 0.1 mA CC discharging to 2.5 V for twice.

2. Storage: Cells were 0.1 C (0.18 mA) CC-CV charged to 4.2 V and 0.05 C, then stored at RT for hours, 0.1 C discharged to 2.5 V at last.

3. Electrochemical impedance spectra(EIS) test: A frequency range of 10^{-1}-10^6 Hz and an applied signal amplitude of 5 mV.

4. Galvanostatic intermittent titration technique (GITT) test: Cells were charged at 0.1C with a 30-minute pulse and a 2-hour rest period to 4.3 V.

Results

THE NEGATIVE ELECTRODE INDUCED AGING MECHANISM

Fig. 2 depicts the performance decay for different Si content batteries after 24 h of storage. As Si content increases, the open circuit voltage (OCV) drops increases from 78 mV to 123 mV, and the capacity retention decreases from 92.4 to 77.7% (Figs. 2a and 2b). Fig. 2c demonstrates the interface products evolution, a surge of Li_2CO_3 and decomposition of F-containing intermediates are discovered on higher Si content electrode. In F 1s spectra, the $Li_xPO_yF_z$ peak at 686.9 eV demonstrates an inverse relationship with Si content, where the $Li_xPO_yF_z$ peak decreases as the Si content increases (Fig. 2d). To reveal the real-time kinetic process during calendar aging, side reaction-mass transfer coupled models are developed. The simulation results show good consistency with the experimental data, demonstrating a high accuracy of the models (Figs 2e and 2f).

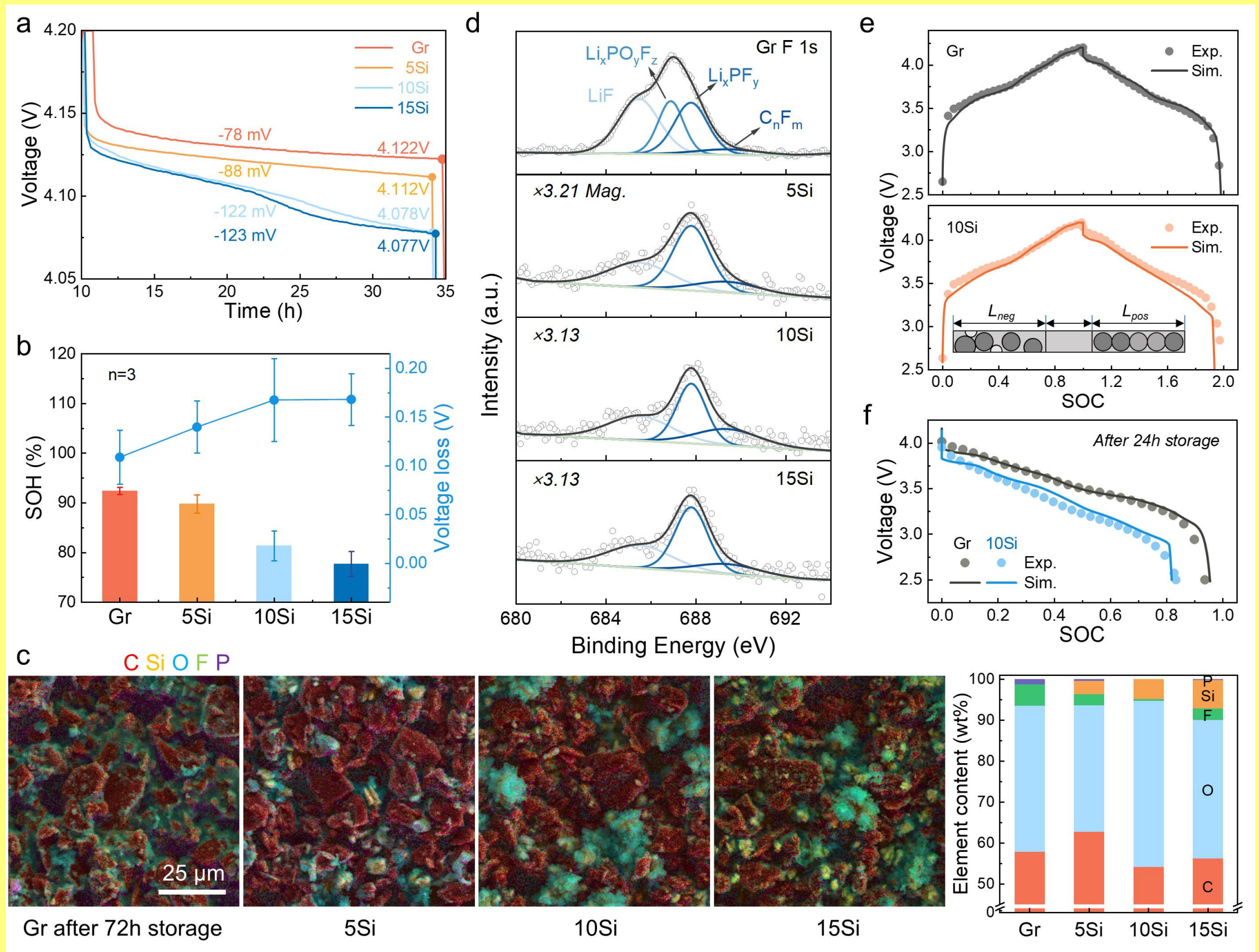

Fig. 2. Negative electrode evolution process and simulation introduction.

EXTRA LOSS OF GRAPHITE IN COMPOSITE ELECTRODES

Fig. 3a shows that the Li loss of the 10Si anode is much faster than that of the graphite anode, causing a nearly 3-fold increase in attenuation (8.7% vs. 2.3% in 24 h).

Further analysing the Li content in active materials, the SOC of graphite dropped rapidly from 0.874 to 0.739, while the SOC of Si decreased slowly from 0.842 to 0.771 (Fig. 3b). Besides, the Li loss of graphite in Si-containing electrode is higher than that in pure graphite electrode. The potential of Si increased rapidly with an increase of 18.8 mV during 24 h of storage, and the potential jump of graphite particles was faster than the one in graphite anode (3.7 mV vs. 2.1 mV, Fig. 3c). All results demonstrate that the addition of Si accelerate the decay of graphite.

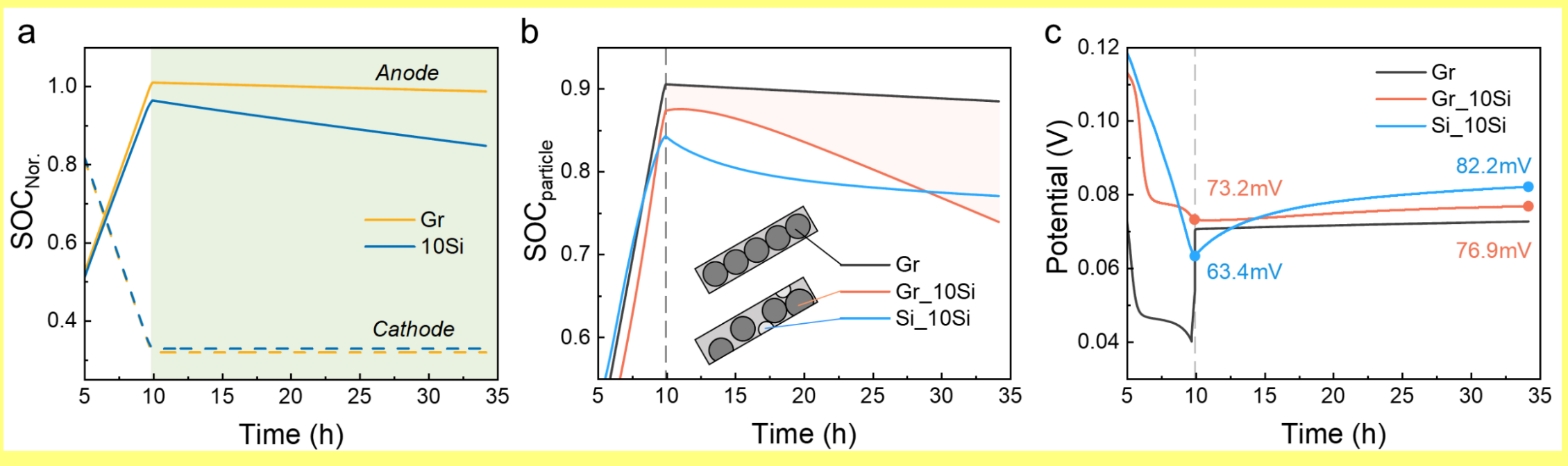

Fig. 3. The lithiation state comparisons between full cells with 10% Si content electrode and cells with graphite electrode during 24 h of storage by simulating.

THE LI^+ CROSSTALK EFFECT

Fig. 4a displays the Li^+ distribution and mass transfer process. Once the charging process stopped, the Li^+ transferred from graphite to Si with a current density (I) around 100 mA m^{-2} (Figs. 4a and 4b) . During the storage time, Si displays a higher potential than graphite, thus a micro-loop is formed between Si and graphite, in which lithiated graphite is treated as a Li source. Driven by the overpotential, the Li^+ ions in graphite particles are forced to supply to Si, leading an extra Li loss in graphite.

This crosstalk effect leads to a local high liquid current density and electrolyte consumption near the Si (Figs 4f-4n).

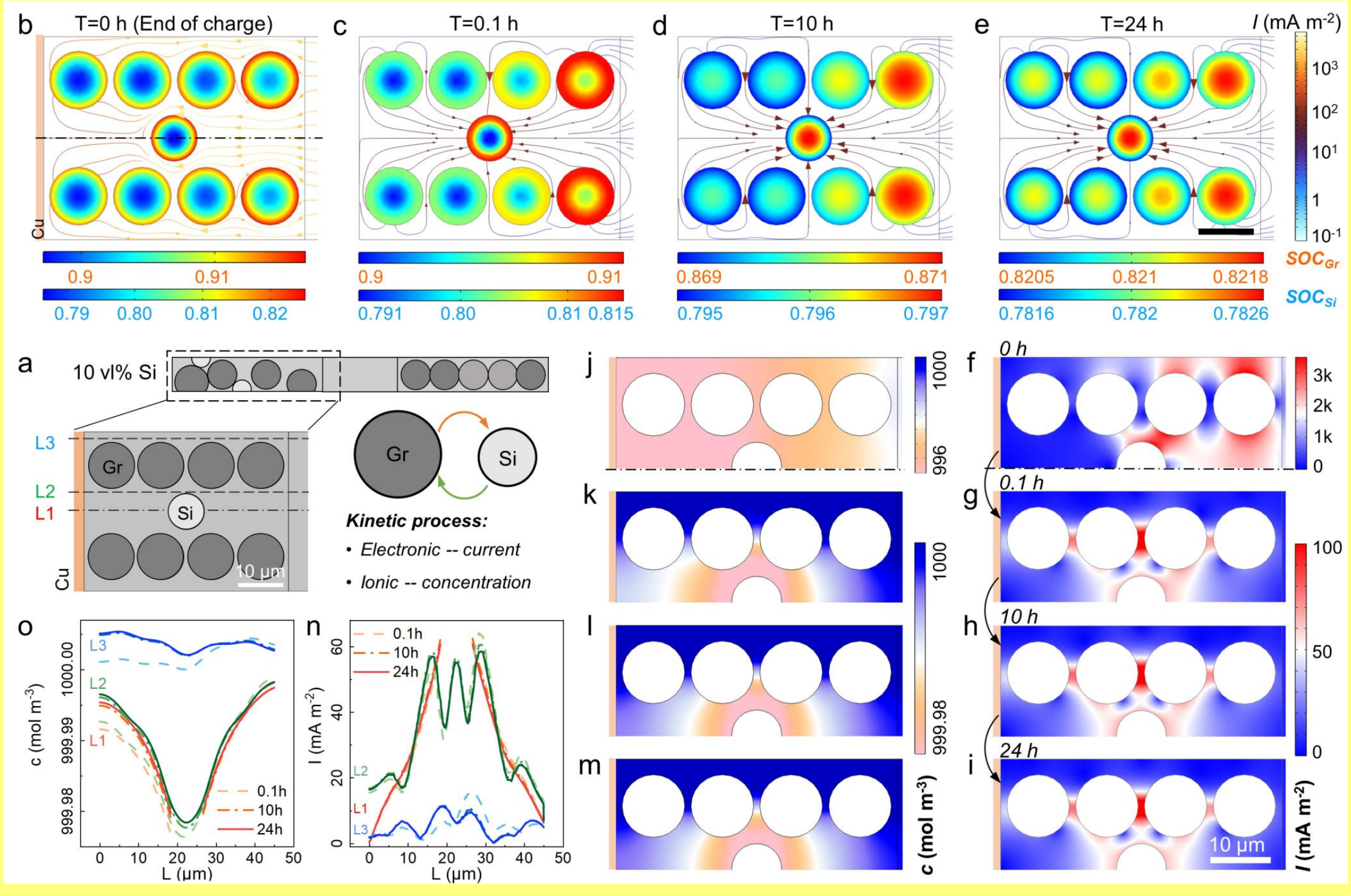

Fig. 4. The Li^+ crosstalk between graphite and Si particles during calendar aging.

A SELF-DISCHARGE SUPPRESSION METHOD BY ADJUSTING LI^+ CROSSTALK

It is revealed that adjusting the Li^+ transfer direction could inhibit the capacity loss. Thus, nano-Si deposited in porous carbon (marked as "Si@C") is prepared by chemical vapor deposition (CVD) to improve the lithiation kinetic of Si (Figs. 5a-5c). The Li diffusion coefficient (D_{Li^+}) of Si@C is found highe than the original Si by EIS and GITT test (Figs. 5d-5f). And the improved cells show a higher OCV and a 20% capacity retention after 24 h storage (Figs. 5g and 5h).

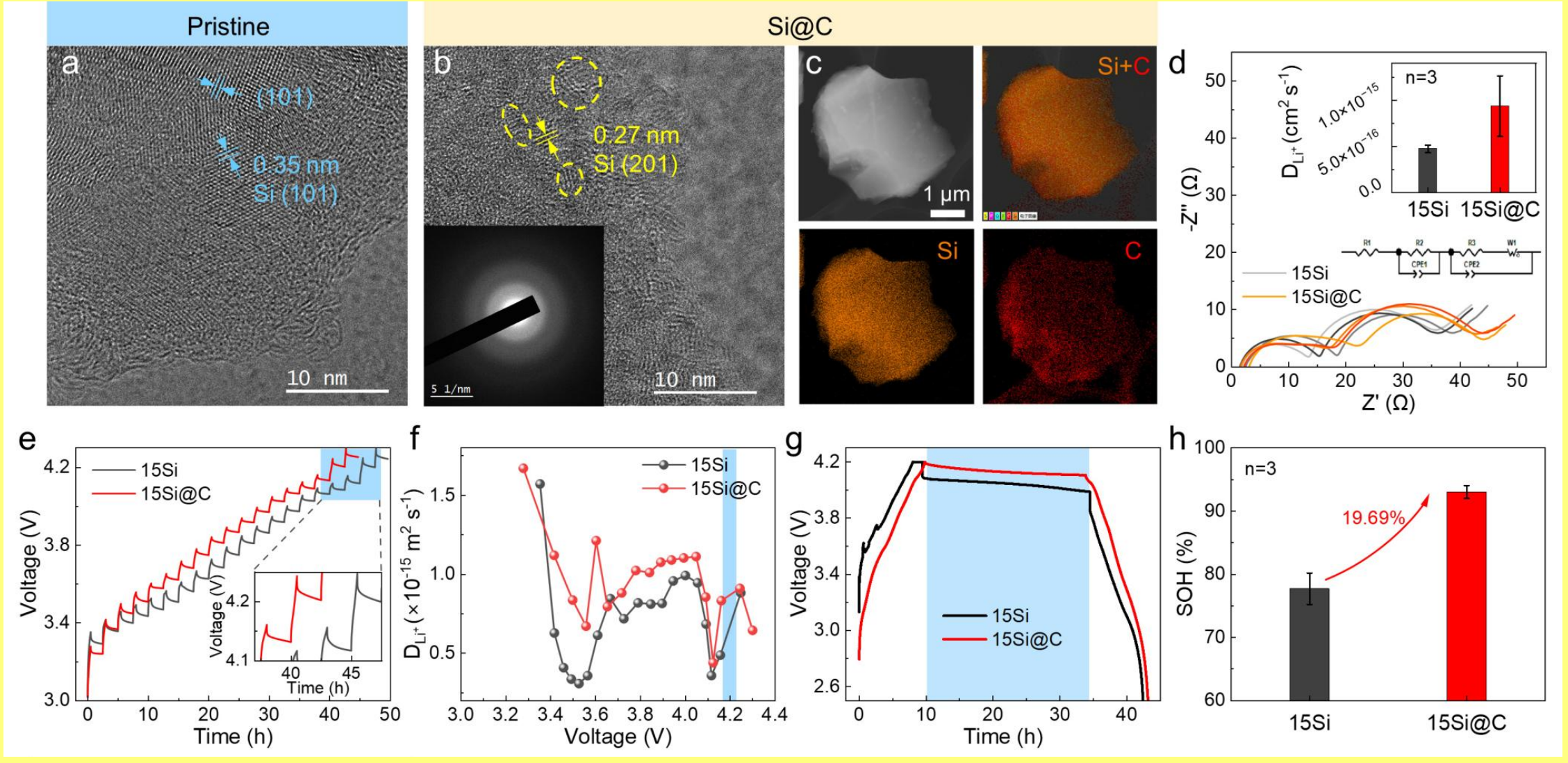

Fig. 5. Improved calendar life by increasing the D_{Li^+} of Si.

Conclusions

The main conclusions drawn from all these work are:

- The unstable Si induced more severe Li loss, causing extra Li loss of graphite;
- Adjusting the Li transfer direction to "Si → graphite" would inhibit the extra Li loss of graphite;
- Increasing the D_{Li} of Si would change the Li transfer direction. And the improved Si-containing cells with a doubled D_{Li} indeed causing a 20% capacity retention increase after 24 h storage.

References

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