



Constant voltage lithiation for effective activation of lithium sulfur battery

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Introduction

Lithium-sulfur batteries (LSBs) are recognized as promising next-generation energy storage systems owing to their high gravimetric energy density, making them suitable for applications such as drones and high-altitude platform stations (HAPS). Unlike conventional cathodes in lithium-ion batteries, the sulfur cathode operates at lower potentials, where carbonate-based electrolytes undergo reductive decomposition, leading to the formation of a cathode-electrolyte interphase (CEI) analogous to the solid-electrolyte interphase (SEI). This CEI formation strongly influences LSB performance and polysulfide dissolution during lithiation. Previously, we reported a potentiostatic approach to fabricate Li_2S cathodes for LSBs with lithium-free anodes.^[1] In this study, we investigate the effect of activating LSBs by applying a potentiostatic method during the first lithiation.

[1] Y. Wu, T. Jin, T. Momma, T. Yokoshima, H. Nara, T. Osaka, J. Power Sources, 399 (2018) 287-293.

Constant-voltage and constant-current lithiation and Charge-discharge properties

Lithiation condition

Constant-voltage lithiation: 1.0 V for 20 hours
Constant-current lithiation: 0.1 C 1.0 V cut-off

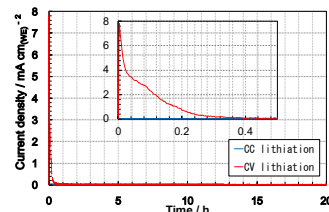


Fig. 1 Current density profiles during CC and CV lithiation.

Charge-discharge condition

Constant-current: 0.1 C
Voltage range: 1.0 – 3.0V

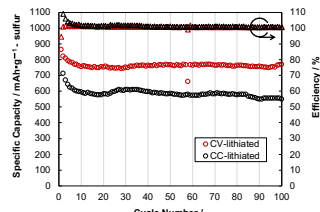


Fig. 2 Cycle durability of LSBs of CC-lithiated and CV-lithiated cathode.

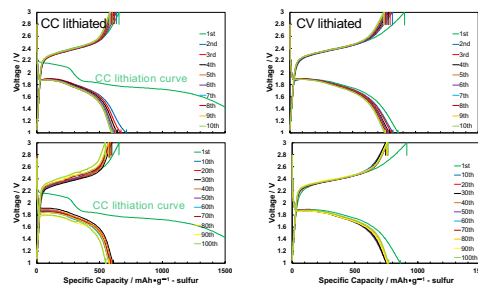


Fig. 3 Charge-discharge profiles of LSBs of CC-lithiated and CV-lithiated cathode.

(mAh/g-S)	CC lithiation	CV lithiation
Capacity for lithiation	2107	2481
First charge capacity	526	912
Irreversible capacity	1581	1569

During constant-current (CC) lithiation, a steady current was maintained, resulting in a lithiation capacity of 2107 mAh g^{-1} . In contrast, during constant-voltage (CV) lithiation, a large current flowed at the initial stage, yielding a total lithiation capacity of 2481 mAh g^{-1} .

Both CC- and CV-lithiated sulfur cathodes exhibited stable cycling, delivering discharge capacities of approximately 600 and 800 mAh g^{-1} , respectively.

Characterization of S/KB cathodes lithiated by constant-current and constant-voltage

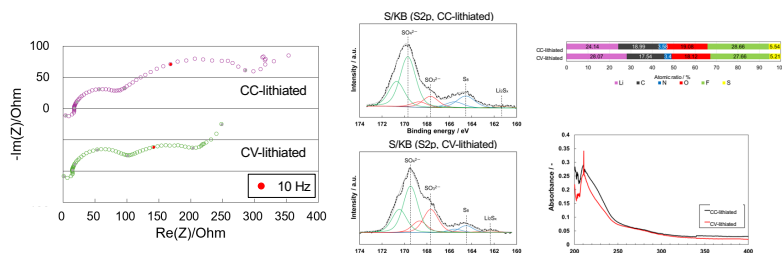


Fig. 4 Nyquist plots of LSBs of CC-lithiated and CV-lithiated sulfur cathode after 1 charge-discharge

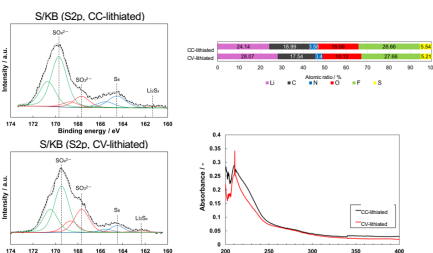


Fig. 5 XPS spectra of CC-lithiated and CV-lithiated sulfur cathodes, atomic ratios derived from the XPS results, and UV-vis spectra of the electrolytes after lithiation.

The Nyquist plots of both LSBs with CC-lithiated and CV-lithiated sulfur cathodes exhibited two semicircles: one appearing in the frequency region above ~ 100 Hz and the other below 100 Hz. The semicircles observed above ~ 100 Hz were nearly identical, whereas those below ~ 100 Hz differed; the semicircle for the CC-lithiated cathode was larger than that for the CV-lithiated cathode. The semicircle observed above ~ 100 Hz is considered to correspond to the CEI resistance, while the one below ~ 100 Hz represents the charge-transfer resistance. XPS data indicate that the CEI compositions on the surfaces of CC-lithiated and CV-lithiated sulfur cathodes are nearly identical, showing no significant difference between the two lithiation methods. The UV-vis spectra also showed no difference between the electrolytes from CC-lithiated and CV-lithiated sulfur cathodes, suggesting that the degree of dissolution was nearly identical.

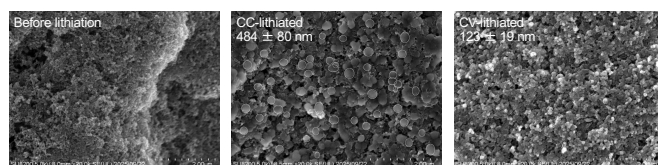


Fig. 5 SEM images of the sulfur cathode before lithiation and after CC and CV lithiation.

The SEM images clearly indicated a difference between the CC- and CV-lithiated sulfur cathodes. After CC lithiation, large particles with an average size of 484 ± 80 nm, considered to be Li_2S , were observed. In contrast, after CV lithiation, much smaller particles with an average size of 123 ± 19 nm were observed.

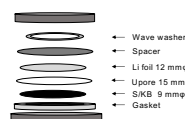
In summary, EIS, XPS, and irreversible capacity measurements during lithiation revealed that CC and CV lithiation do not affect the CEI formation process. UV-vis analysis also suggested that the degree of polysulfide dissolution was nearly identical for both conditions. In contrast, SEM observations indicated that the Li_2S particles formed by CV lithiation were much smaller than those formed by CC lithiation.

Lithium-sulfur battery fabrication

- S/KB composite**
 - Mixing S : KB (50 : 50 wt.%)
 - Heating @ 155°C under N_2 / 12 hours
- Cathode slurry**
 - S/KB (5/5) : PVdF = 90 : 10 wt. %
 - NMP solvent

Cathode: S/KB composite (~ 0.33 mg/cm²)
Anode: Li metal
Separator: UBE Upore3085
Electrolyte: 1 M LiTFSI in FEC/HFE (1:1 vol.)
KB: Ketjenblack
LiTFSI: Lithium Bis(trifluoromethanesulfonyl)imide
FEC: Fluoroethylene carbonate
HFE: 1,1,2,2-Tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether

2032-coin type cell



Conclusion

- In situ* constant-voltage lithiation of the sulfur cathode effectively enhanced the charge-discharge capacity. (Charge-discharge test)
- The characteristics of the CEI formed during constant-current and constant-voltage lithiation were nearly identical. (EIS, XPS, Irreversible cap.)
- The degree of active-material loss due to polysulfide dissolution during lithiation could not be clearly determined. (UV-vis)
- Li_2S particles formed by CV lithiation were finer than those formed by CC lithiation. (SEM)
- The finer Li_2S particles are considered to reduce solid-state lithium-ion diffusion, increase the electrochemically active surface area, and facilitate lithium-ion transport into the deeper regions of the cathode layer.

Acknowledgement

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GteX Green Technologies of Excellence

