Nanoscale Sulfide Coatings for High-performance Ni-rich Cathodes

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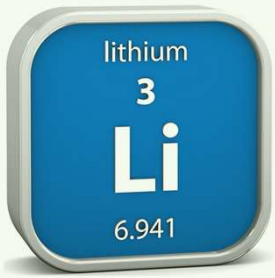
Outline

- Research motivation
- Tackle issues of NMC811 cathodes by sulfide coatings via ALD
- Conclusions
- Acknowledgements

Research motivation

High-energy lithium metal batteries (LMBs)

Anode



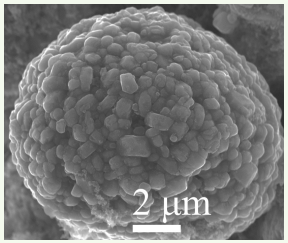
3860 mAh/g

> 300 Wh/kg; < $100/kWh

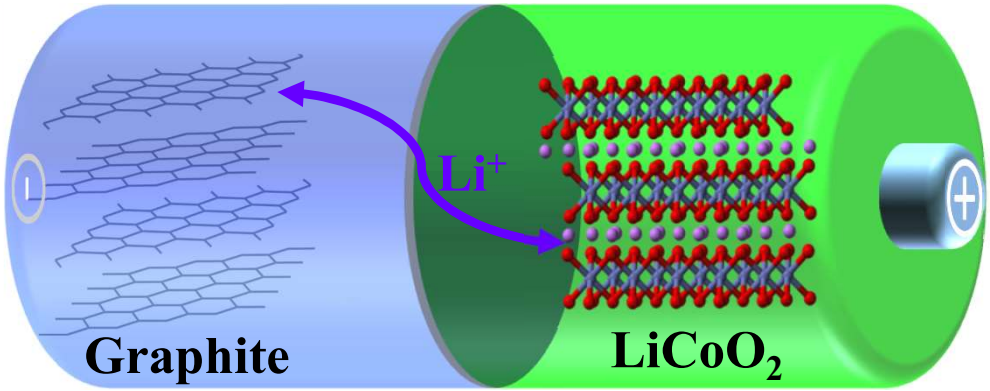
$250/kWh
200 – 250 Wh/kg

Cathode

$LiNi_xMn_yCo_zO_2$ (NMCs)



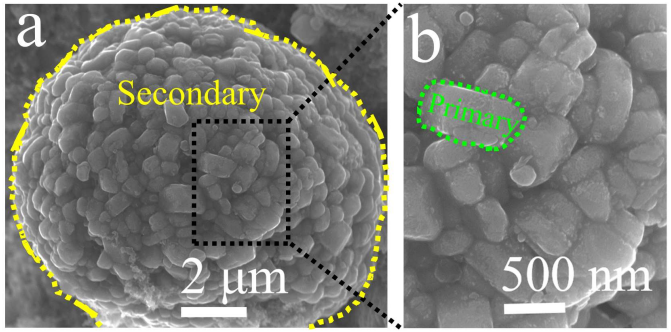
~200 mAh/g

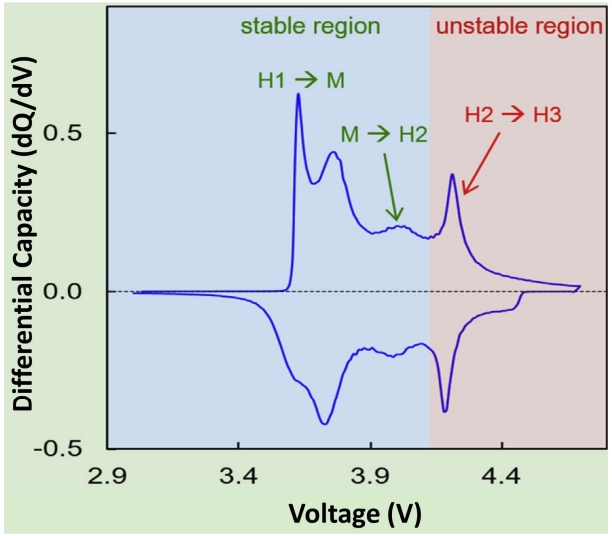


372 mAh/g

140 mAh/g

NMC cathodes





Cost-effective; higher capacity

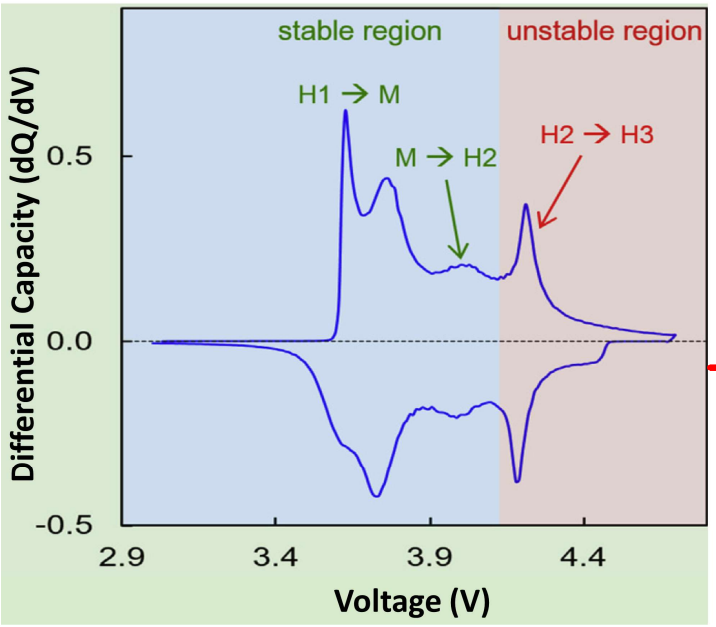
NMC111, NMC442, NMC532, NMC622, NMC811

More challenging

Hexagonal (H1) to monoclinic (M) and hexagonal (H2 and H3) phases

The voltage for the H2→H3 phase transition decreases with increased Ni contents, which is ~4.7 V (all voltages in this proposal are against Li/Li^+) for NMCs of $x \leq 0.6$ (e.g., NMC622 and NMC532), but is ~4.3 V for NMC811

Structural and interface instability of NMC



Hexagonal (H1) to monoclinic (M) and hexagonal (H2 and H3) phases

Oxygen release

Occurred near the onset of H2 → H3

- ❑ **Oxidization of electrolyte solvents** with generation of gases and H_2O
- ❑ **Ni/Li cationic mixing**
- ❑ **Irreversible layered-spinel-rocksalt phase transition**
- ❑ **Transition metal ion dissolution**
- ❑ **Microcracking**

Residual lithium compounds

(RLCs: Li_2CO_3 and LiOH)

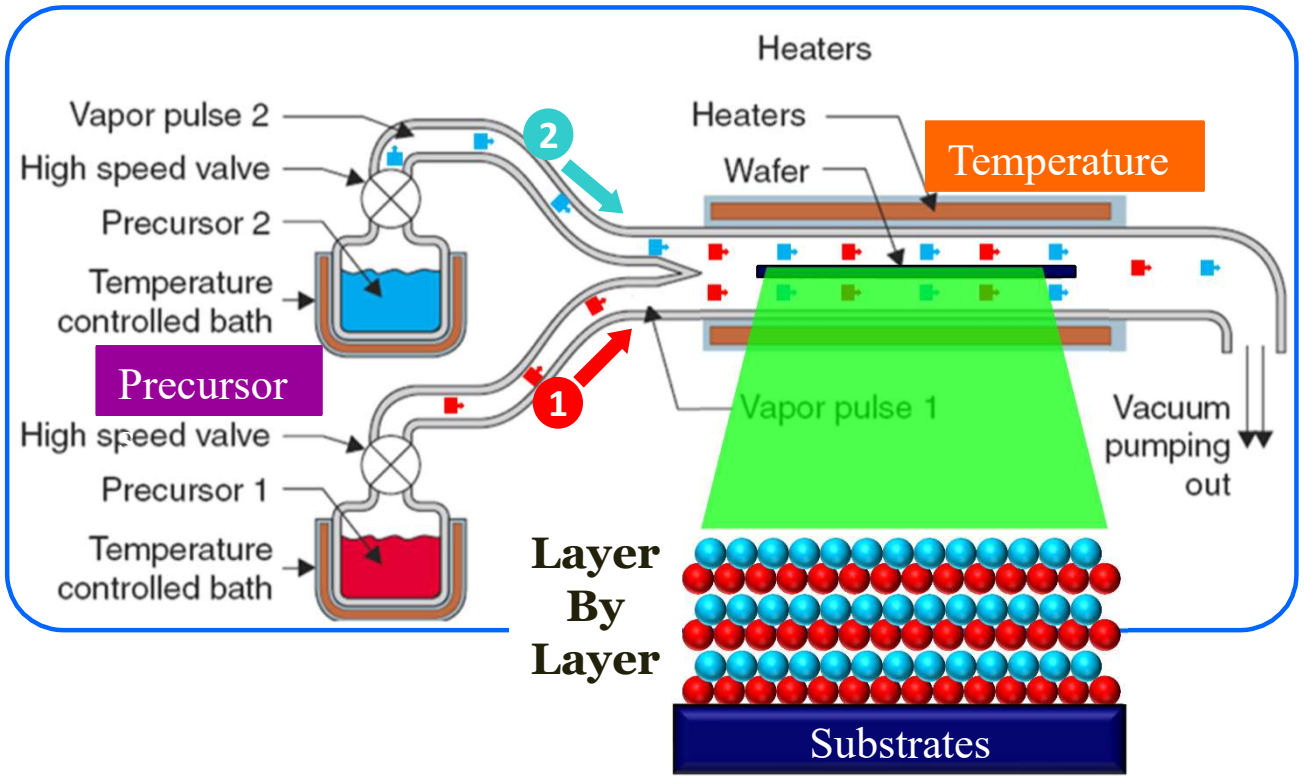
- ❑ **Battery gassing**
- ❑ **Electrode structural degradation**

How to tackle these issues?

Atomic layer deposition (ALD)

Atomic and Molecular Layer Deposition (ALD/MLD)

A *surface-controlled* chemical vapor deposition process enabling conformal and uniform films



- ALD for inorganic materials
- MLD for polymeric materials

Unique capabilities of ALD/MLD

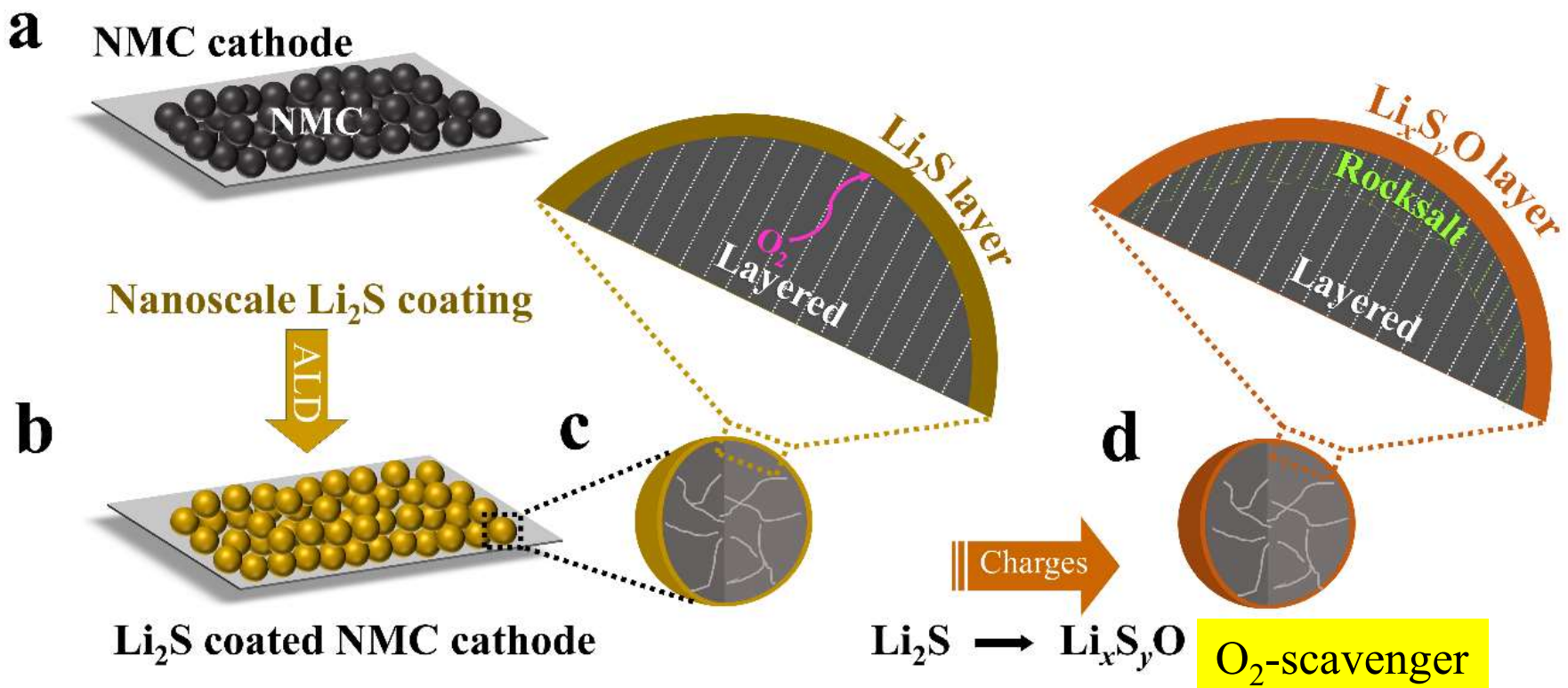
- A surface-controlled process proceeded with self-terminating surface reactions
- Atomic/molecular-scale control over materials growth:
  1 -2 Å /cycle for ALD; several Å /cycle for MLD
- Uniform and conformal coating
- Highly tunability in composition and crystallinity
- Low growth temperature: **< 300 °C**
- Nearly any materials, ranging from inorganic to organic materials

Exceptional NMC Cathodes by Novel Sulfide Coatings via ALD

1. ALD Sulfides – Li_2S on NMC811 electrodes

J. Energy Chem. 2022, 69, 531 – 540

We **for the first time** revealed that sulfides are an unexplored class of coating materials having some unique benefits!



Effects of ALD Li_2S on NMC811 electrodes

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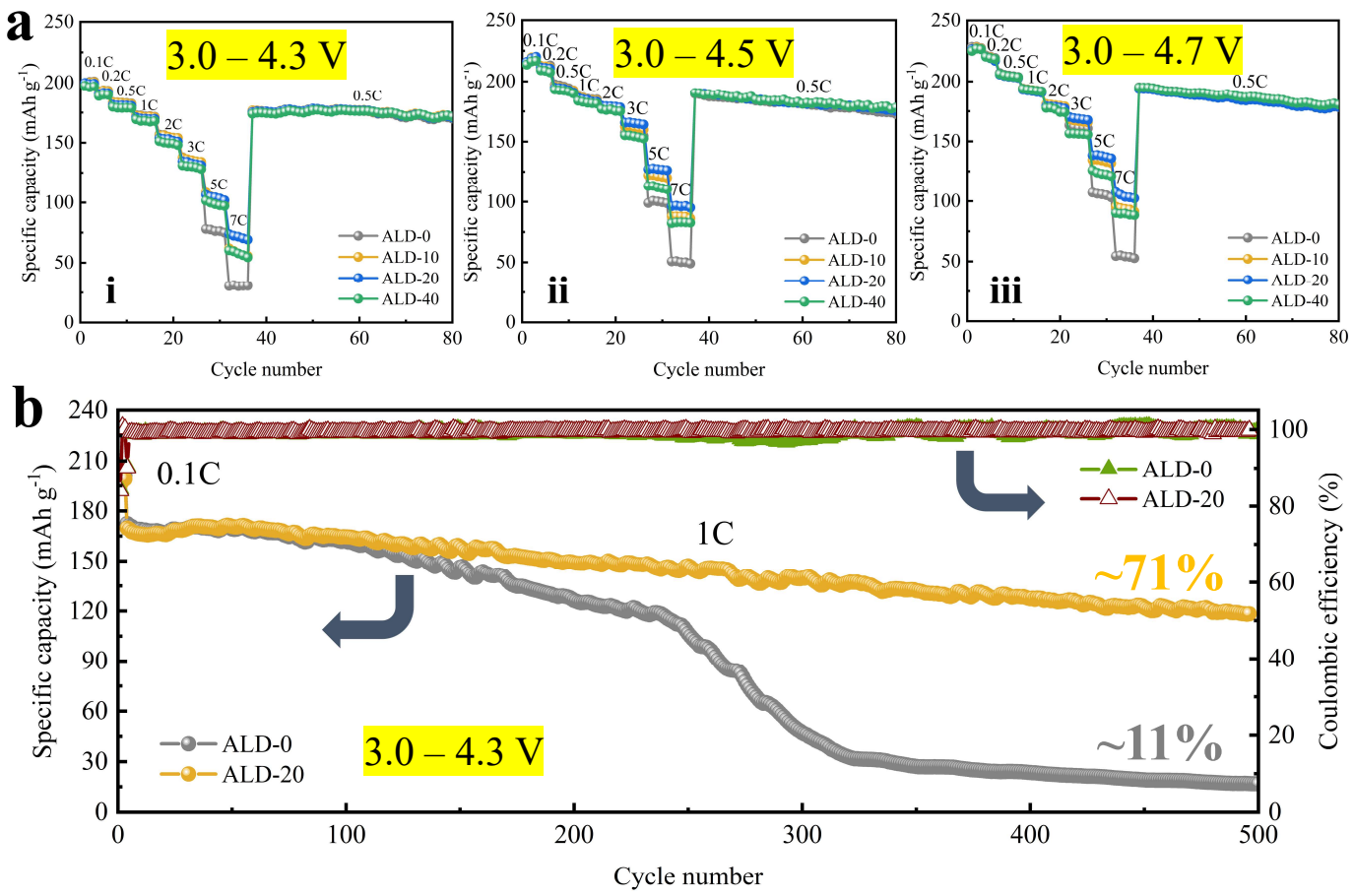

Effects of ALD Li_2S on NMC811

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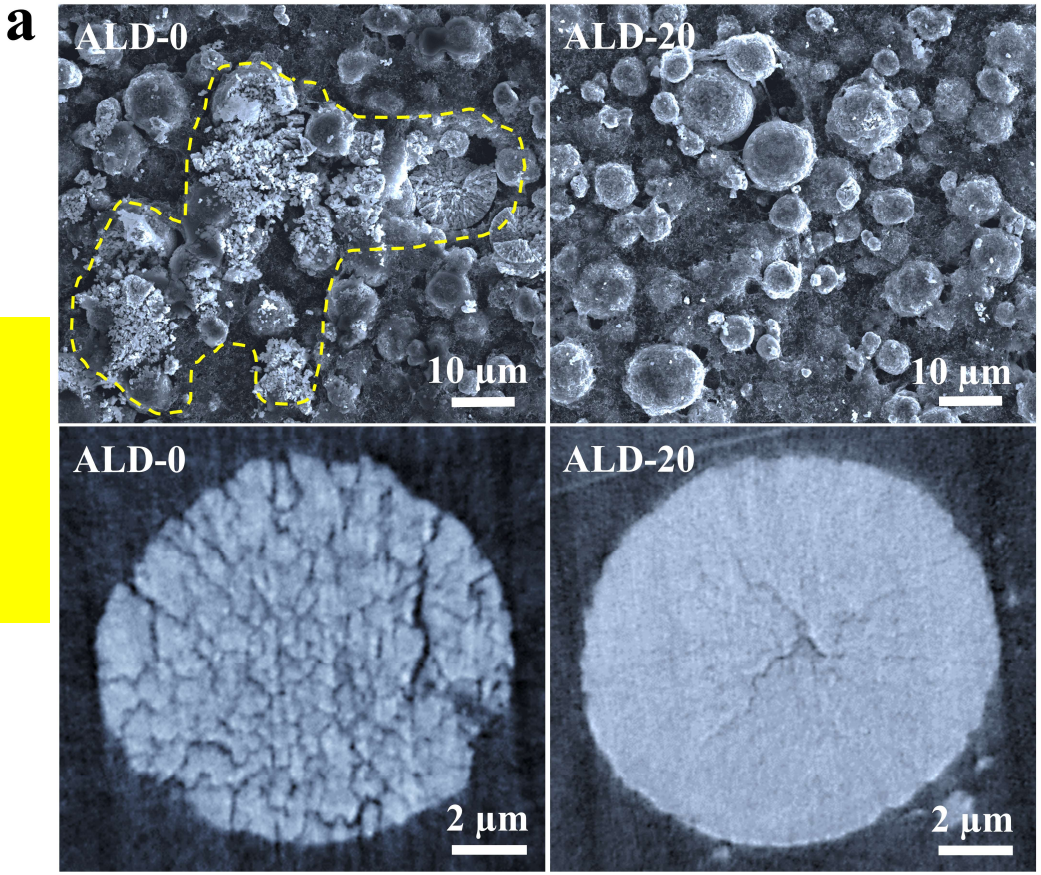
NMC811 suffer from serious cracking during cycling



ALD Li_2S coating well protected NMC811 from cracking

Effects of ALD Li_2S on NMC811 electrodes

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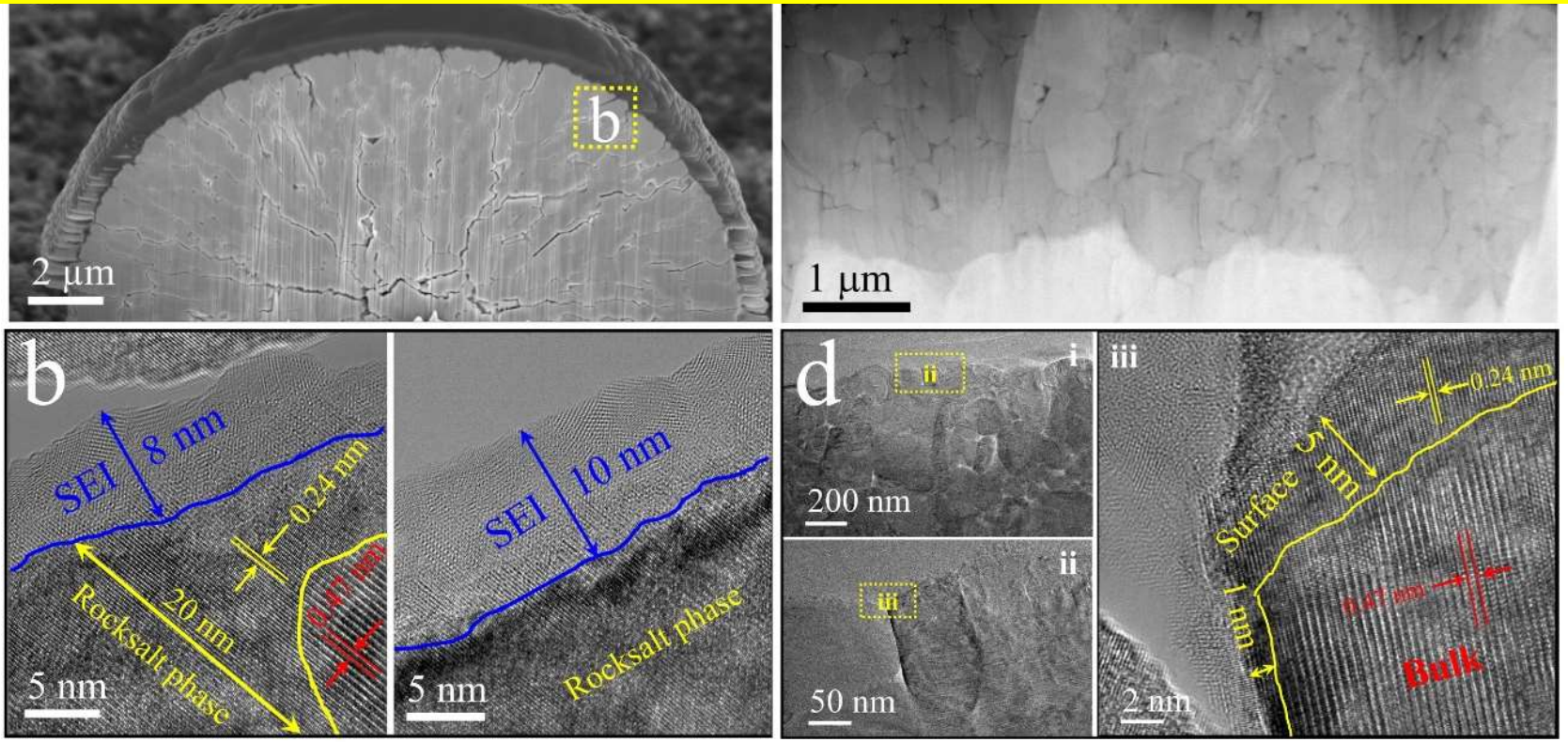
ALD Li_2S coating protected NMC cathodes from structural degradation.



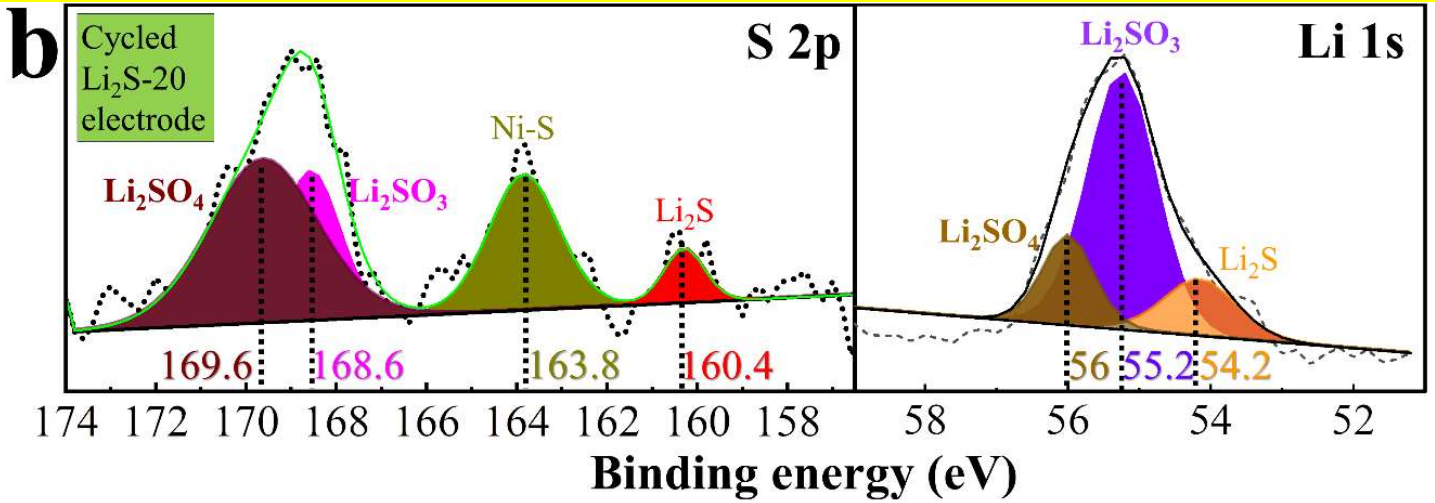
In-situ conversion of the ALD Li_2S coating

J. Energy Chem. 2022, 69, 531 – 540

ALD Li_2S coating protected electrolytes from oxidation and any further side reactions:

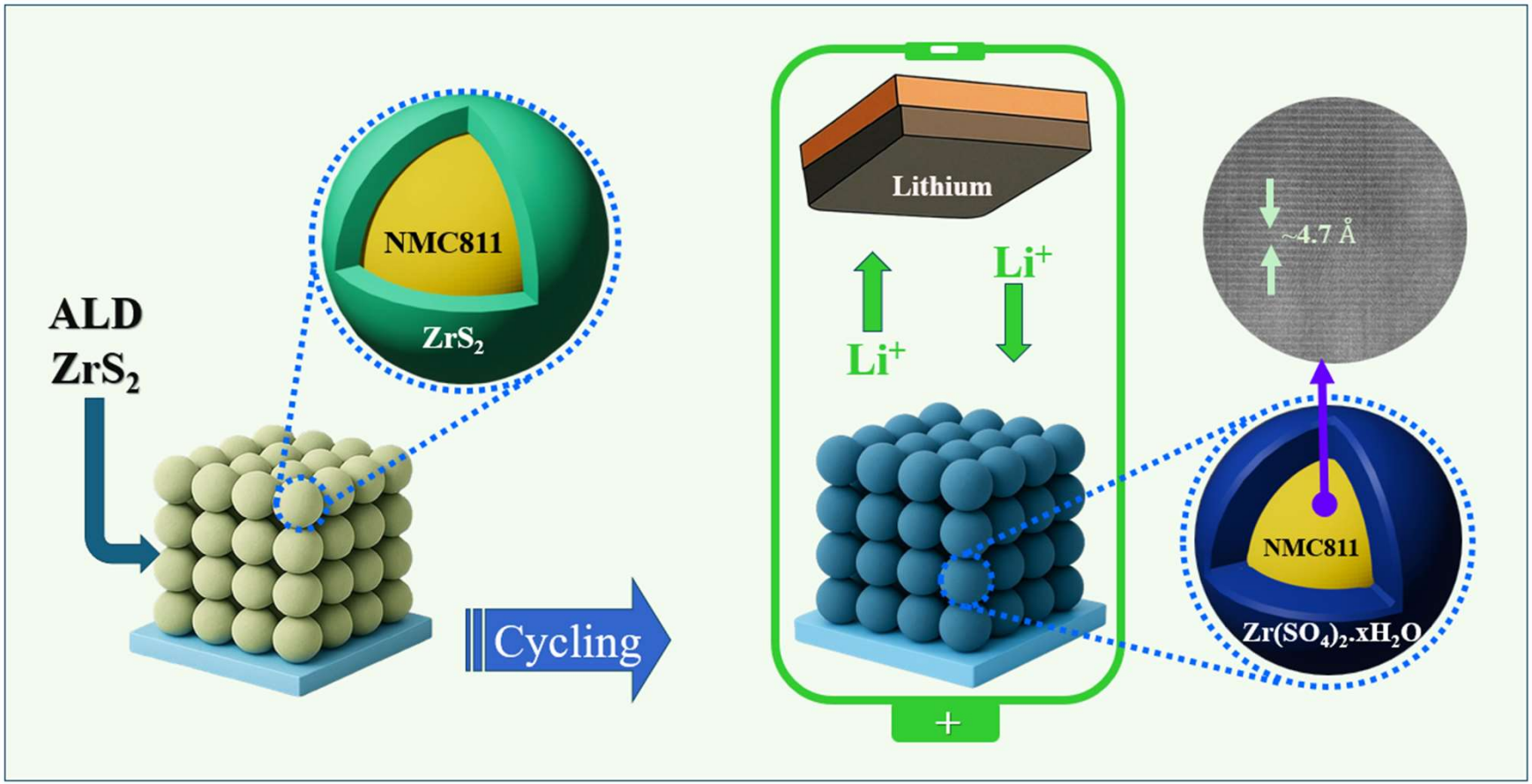
$2Li_2S + 3O_2 \rightarrow 2Li_2SO_3$ (lithium sulfite)

$2Li_2SO_3 + O_2 \rightarrow 2Li_2SO_4$ (lithium sulfate)



2. ALD Sulfides – ZrS_2 on NMC811 electrodes

Small 2025, DOI: 10.1002/smll.202509789



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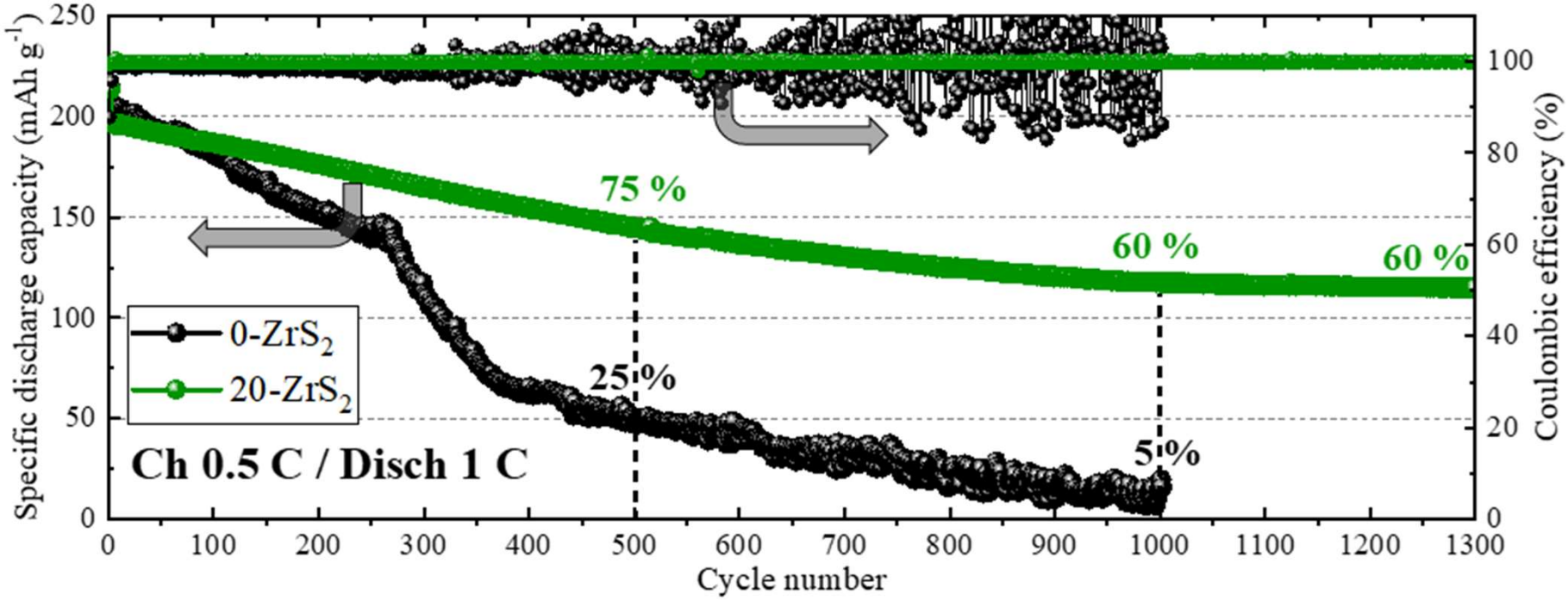

1.2 M $LiPF_6$ in 3:7 EC/EMC

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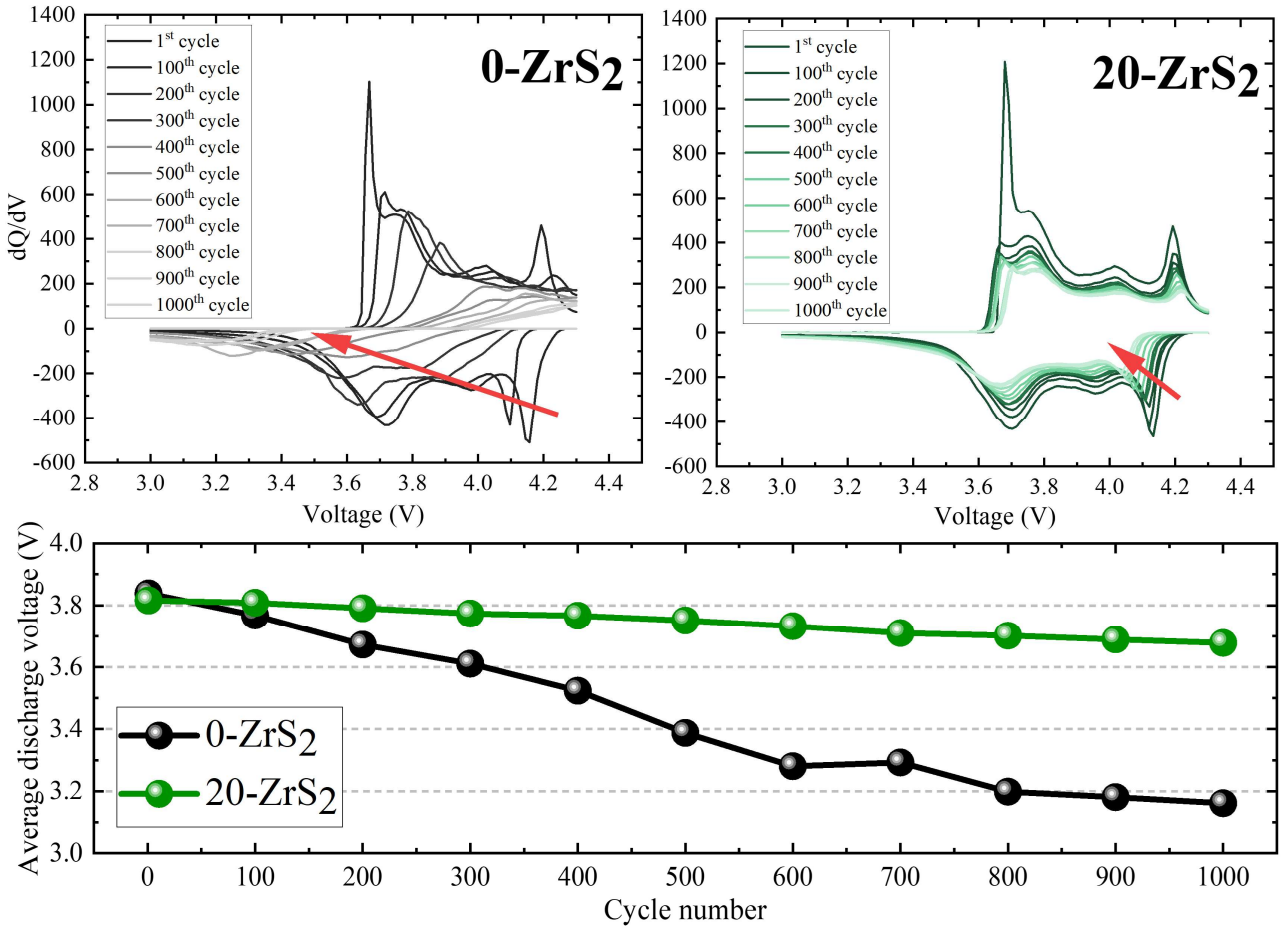

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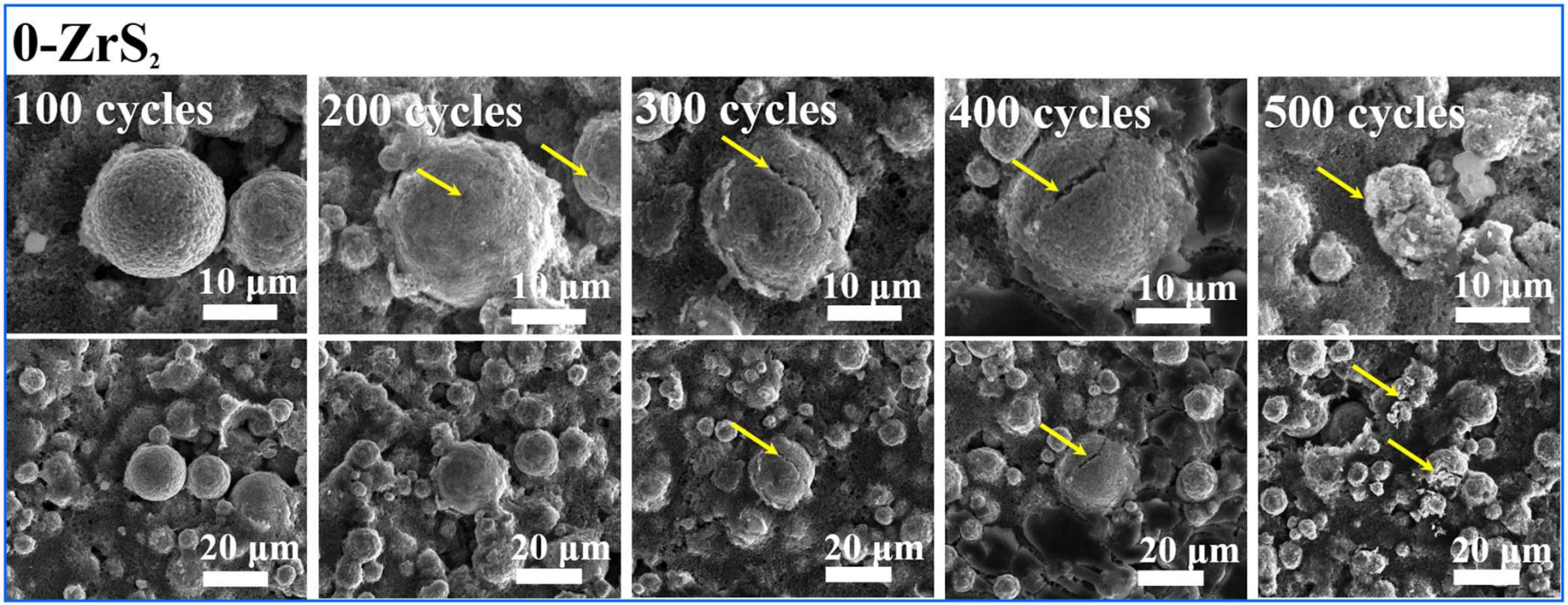

Microcracking becomes more and more serious with increased cycles!

Effects of ALD ZrS_2 on NMC811

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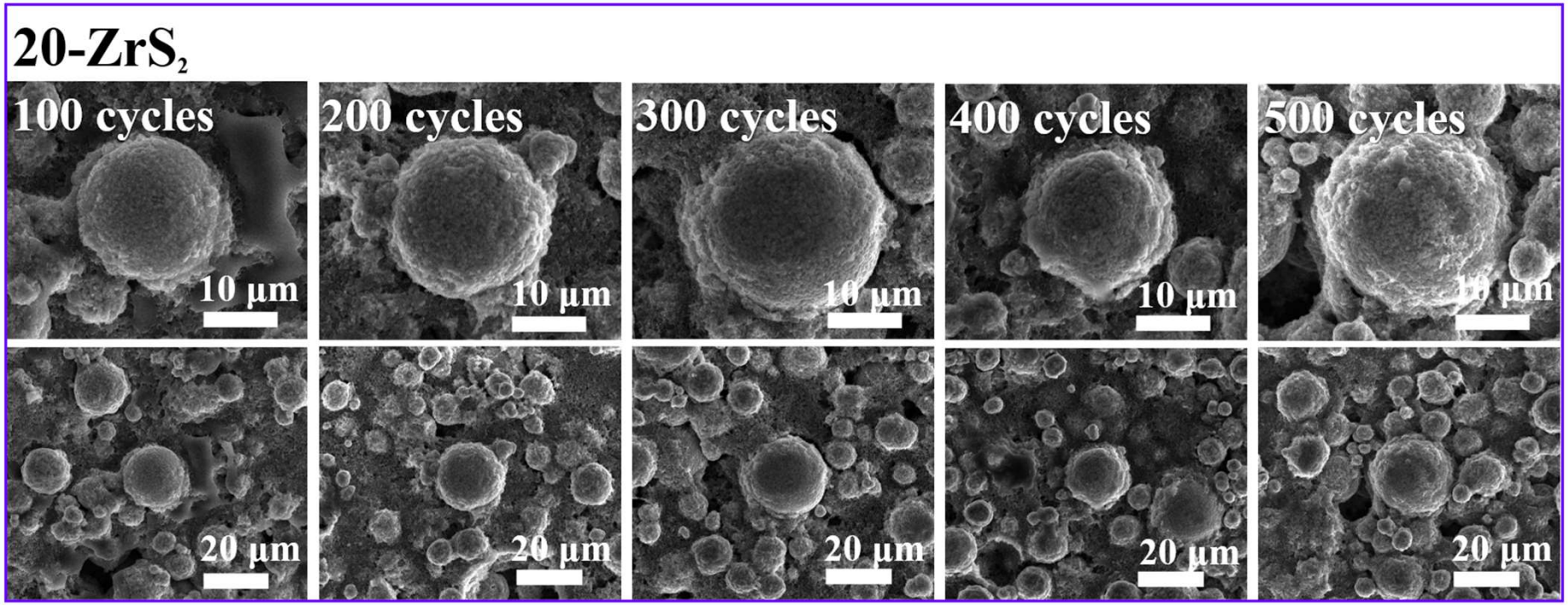

No microcracking is observed!

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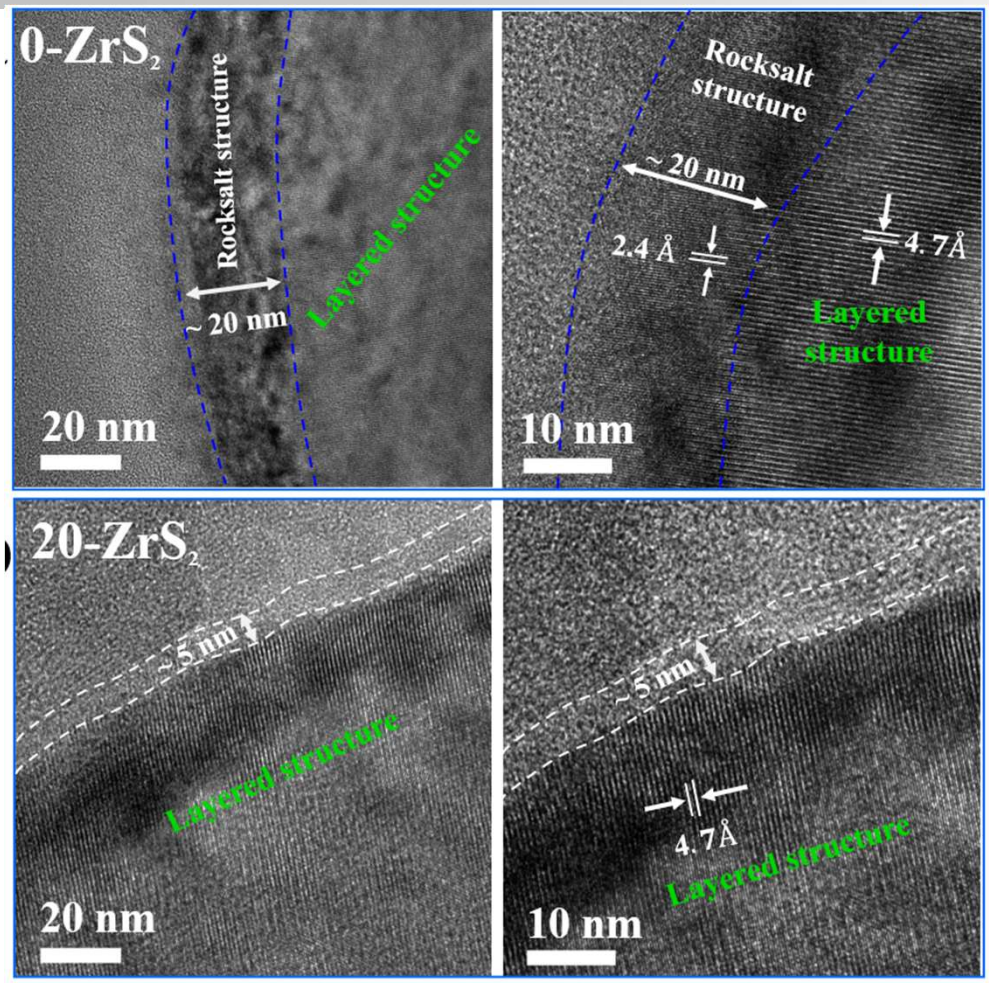

Evidently irreversible phase transition from layered structure to rocksalt structure.

No phase transition observed.

Effects of ALD ZrS_2 on NMC811

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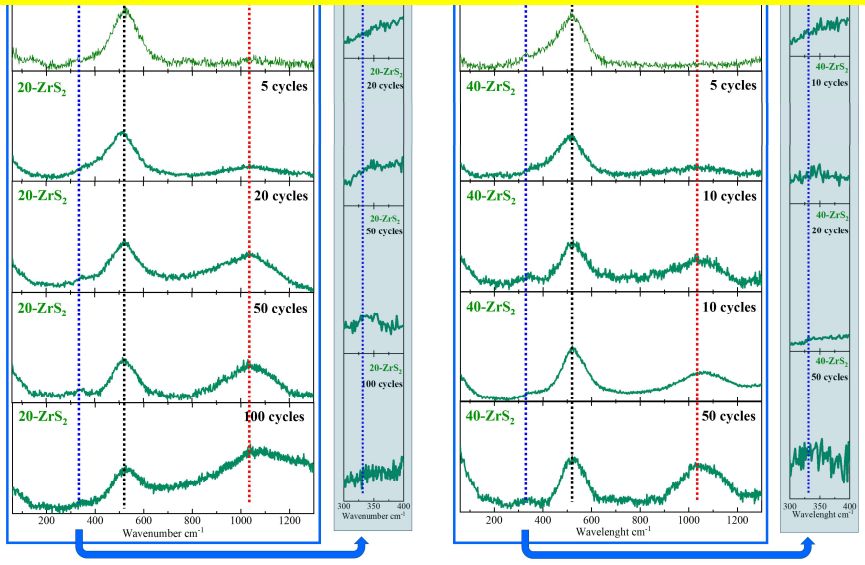
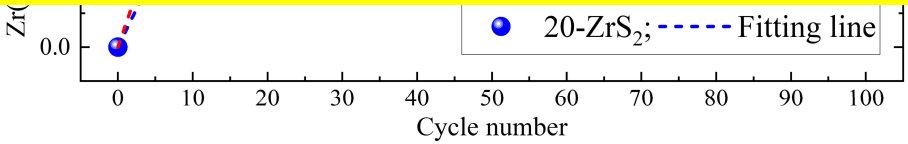
ALD ZrS_2 coating protected electrolytes from oxidation and any further side reactions:

$ZrS_2 + 4O_2 \rightarrow Zr(SO_4)_2$ (zirconium sulfate)

$Zr(SO_4)_2 + 4H_2O \rightarrow Zr(SO_4)_2.4H_2O$ (zirconium sulfate hydrate)





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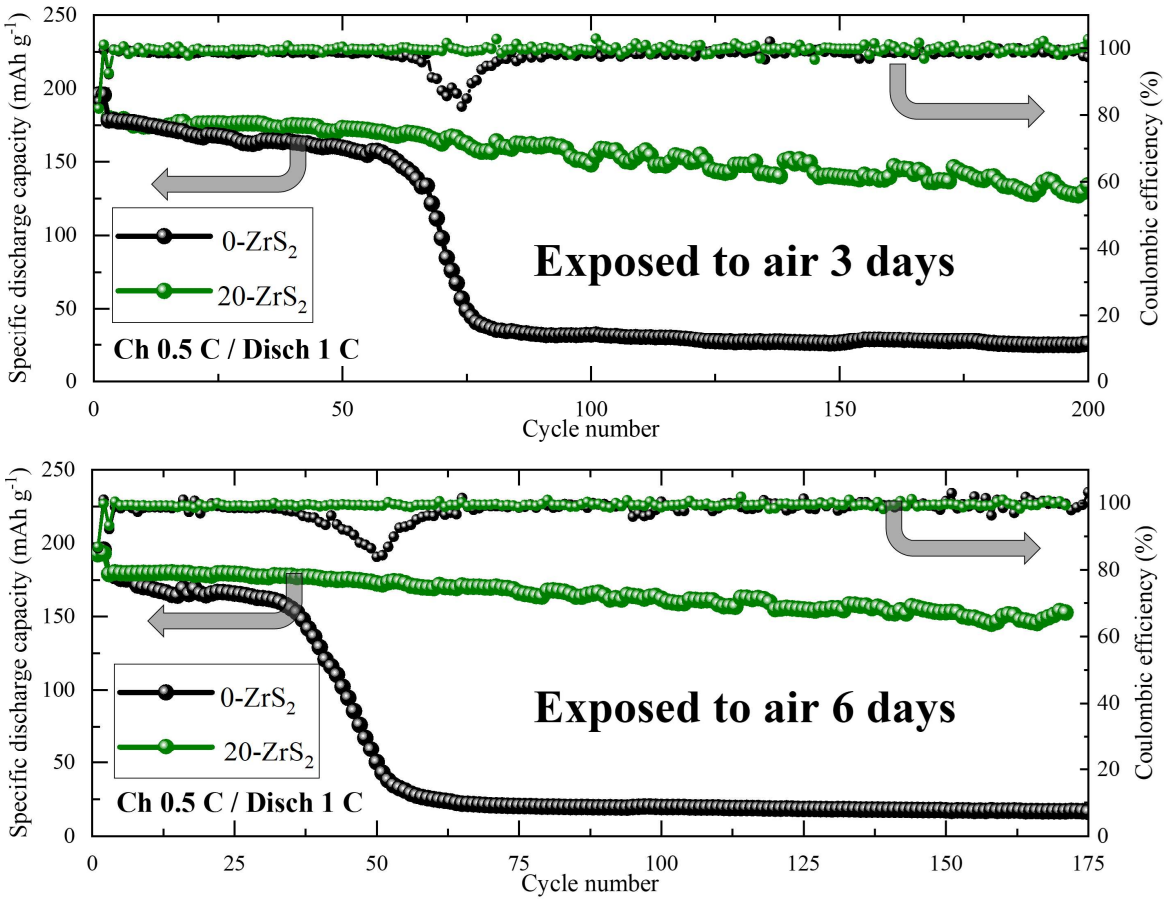
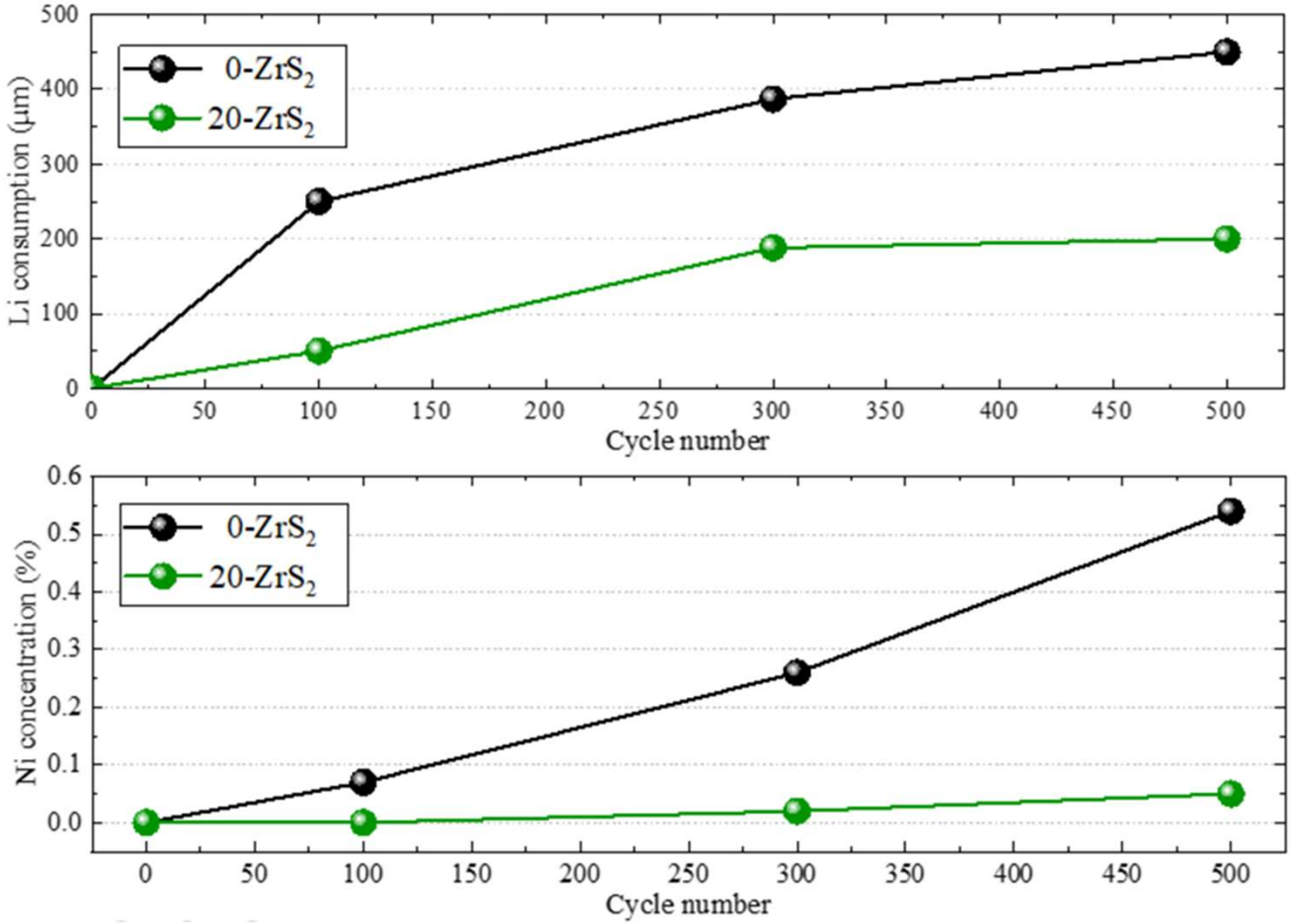


ZrS_2 coating is air-stable and can protect the NMC cathodes from degradation.

Effects of ALD ZrS_2 on Li anodes

Small 2025, DOI: 10.1002/smll.202509789



SEM observations disclosed that the ZrS_2 coating remarkably helped mitigate the consumption of Li metal anodes.

EDS revealed that the ZrS_2 coating considerably reduce transition metal dissolution.

Benefits of sulfide coatings

- O_2-scavengers via sulfide-sulfate conversion: $MS_x + 2xO_2 \rightarrow M(SO_4)_x$
- Remove water via hydration process: $M(SO_4)x + yH_2O \rightarrow M(SO_4)_x.yH_2O$
- Significantly reduce interfacial reactions
- Protect electrolytes from oxidation
- Remarkably mitigate irreversible structural transition
- Greatly enhance the mechanical integrity of electrodes
- Tremendously alleviate microcracking
- Considerably decrease transition metal dissolution
- Notably improve air stability of NMC electrodes
- Visibly protect Li anodes from consumption.

Conclusions

- ALD is a powerful techniques for novel high-quality coatings.

- Novel sulfide coatings via ALD exhibited promising protection effects over NMC cathodes.

Acknowledgements

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NATIONAL LABORATORY OF THE ROCKIES

Ford

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