

Understanding the Appropriate Depth of Discharge of a Sulfurized Polyacrylonitrile Positive Electrode Applied to Ether-based Room Temperature Sodium-Sulfur Batteries

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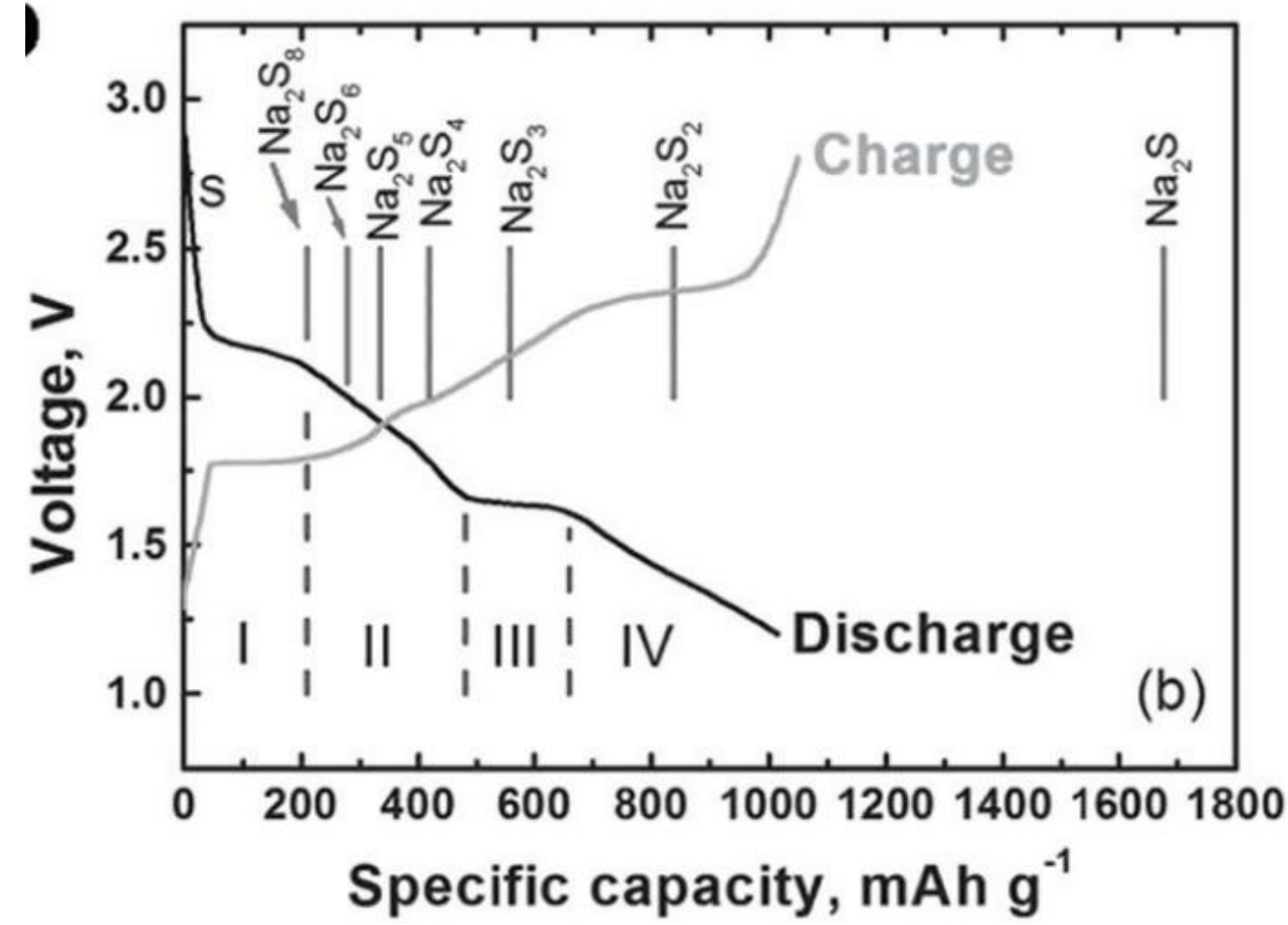
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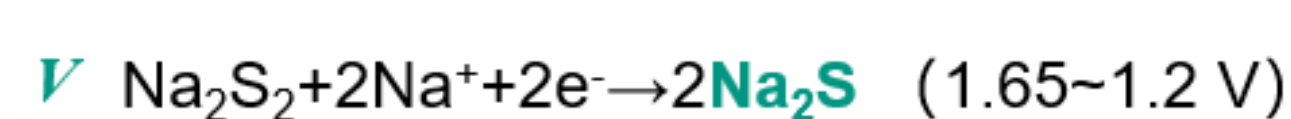
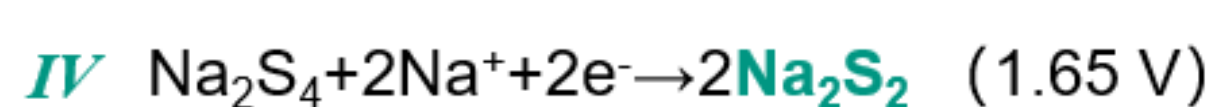
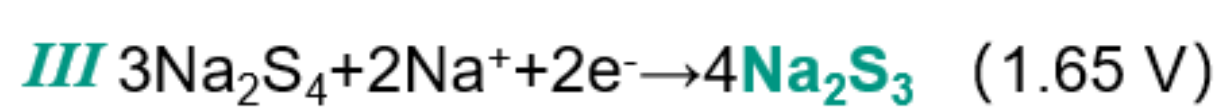
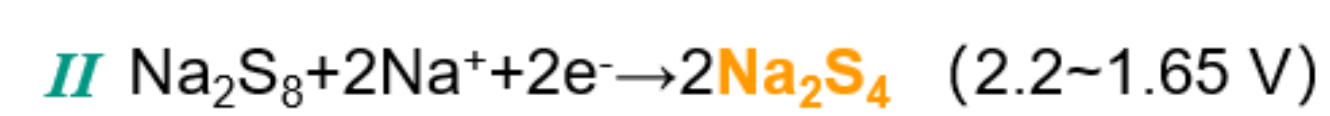
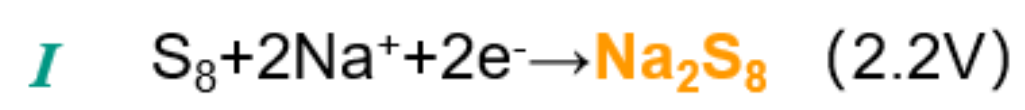
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Sodium-Sulfur Battery (Na-S Battery)

Working mechanism



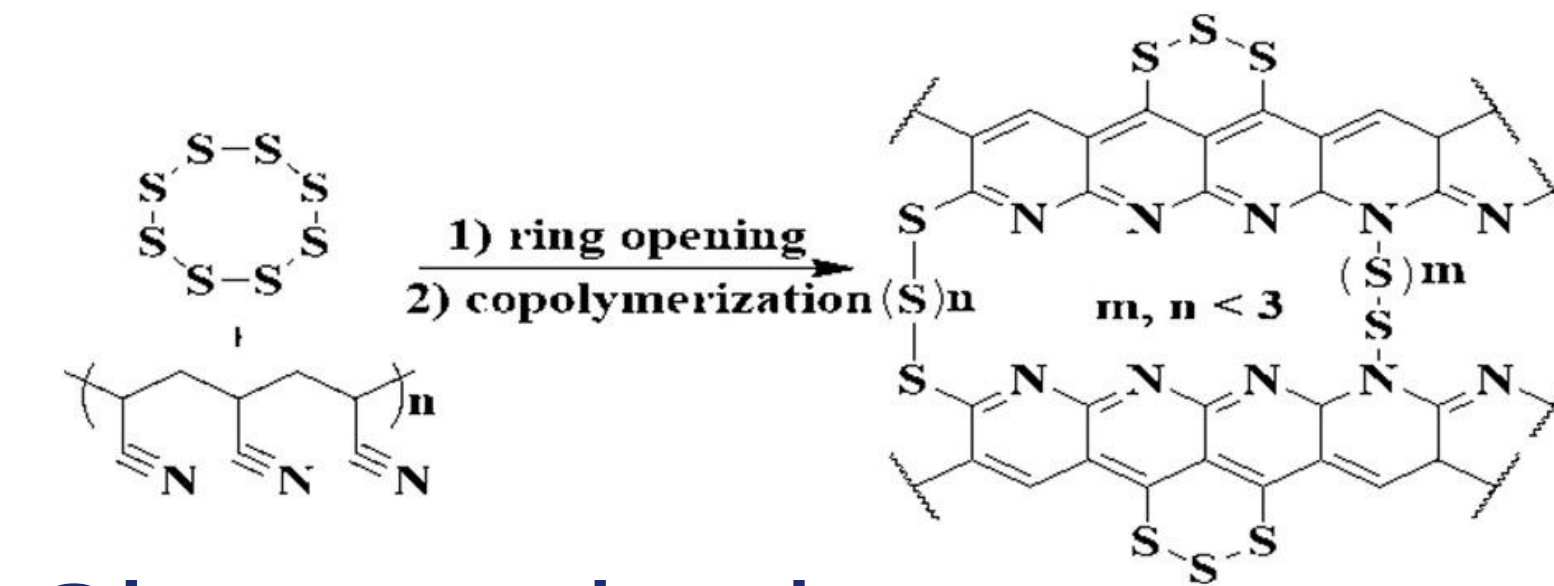
solid-liquid-solid



Challenges of Na-S Battery

- **Electronic insulation:** Hinder charge conduction
- **Shuttle effect:** loss of sulfur, capacity attenuation, degradation of sodium anode
- **Volume change effect:** electrode degradation
- **Sodium dendrites:** short circuit, potential safety hazard

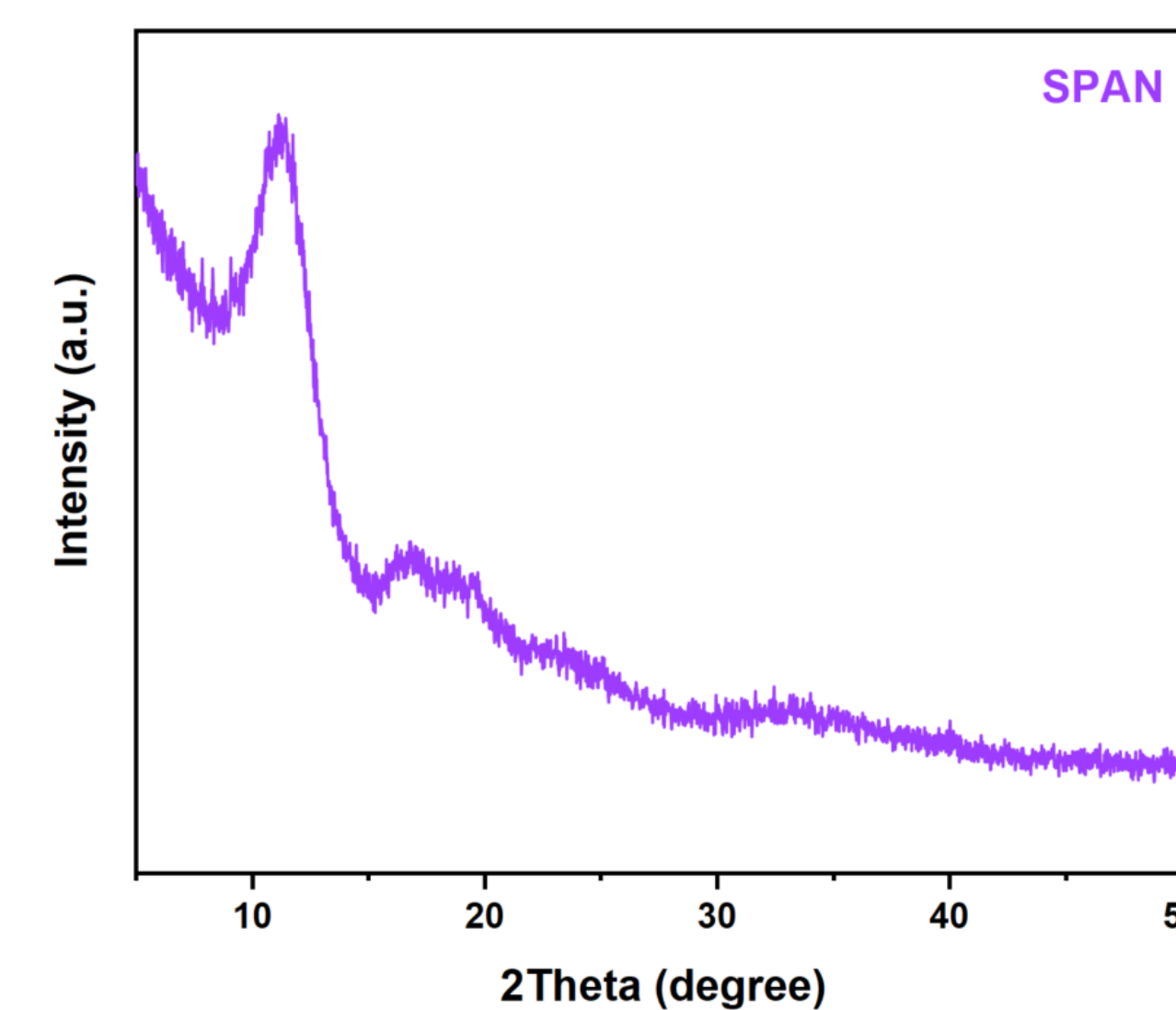
Solve Challenges by Sulfurized polyacrylonitrile (SPAN)



- Conjugated backbone
- Polymer chain network
- Short sulfur chain

Characterization

- XRD

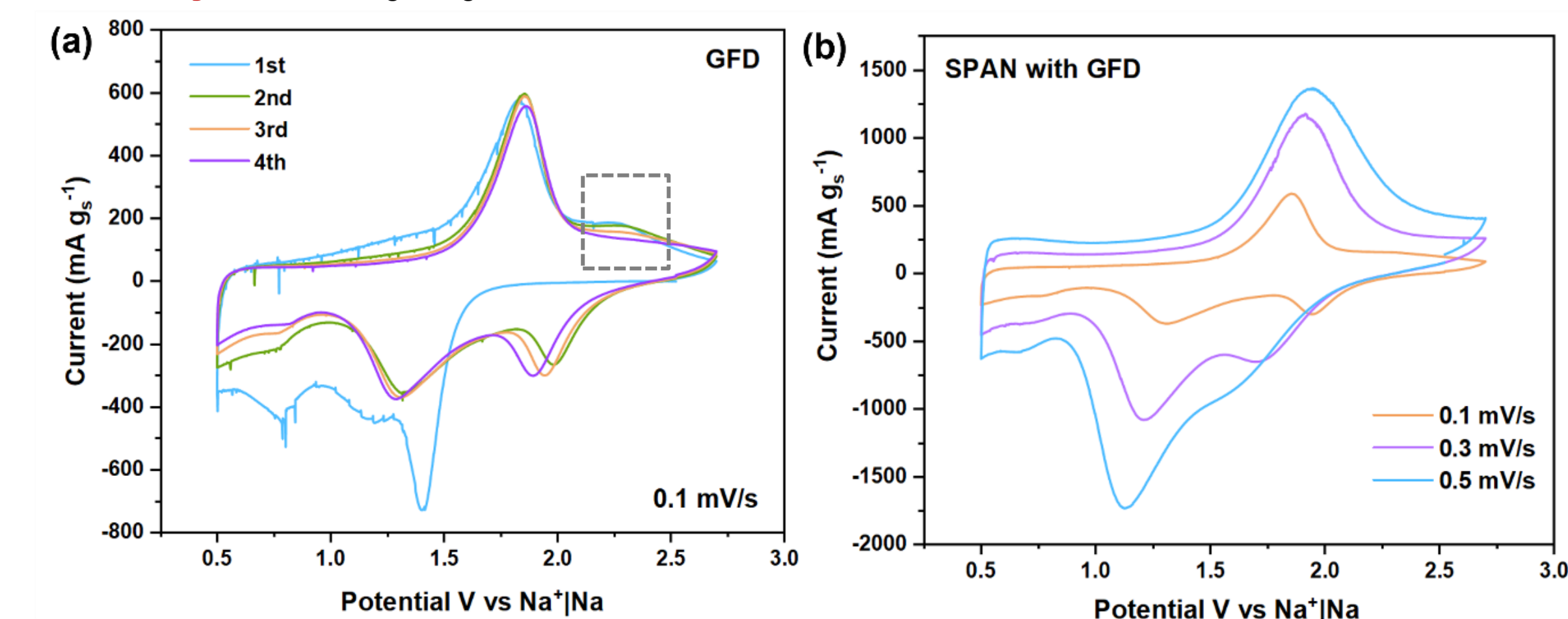


- Elemental analysis

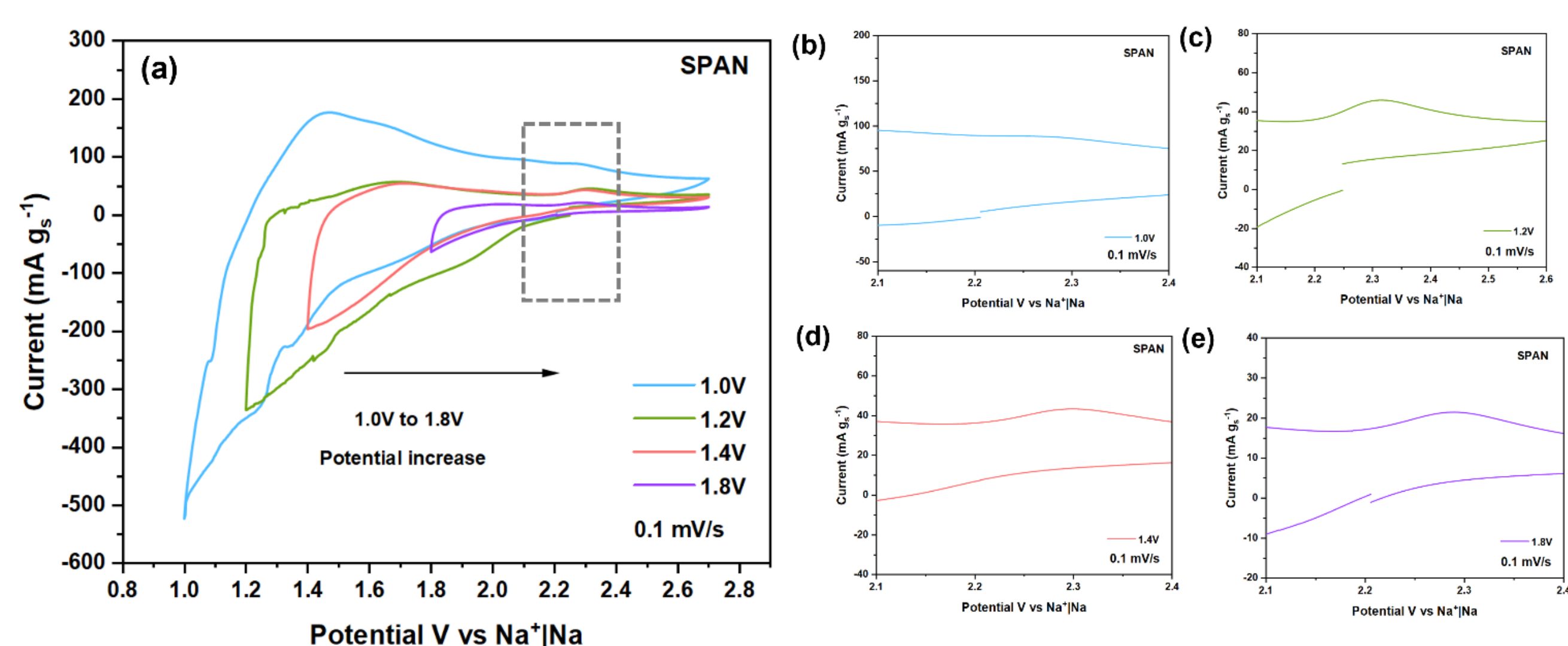
Element	Content
N%	15.4
C%	42.8
H%	1.158
S%	44.340

Electrochemical Behavior

Working electrode: SPAN: C65:LA133=6:3:1 (wt.%) **Separator:** glass fiber
Electrolyte: NaCF₃SO₃ in TEGDME **Counter/Reference electrode:** Sodium

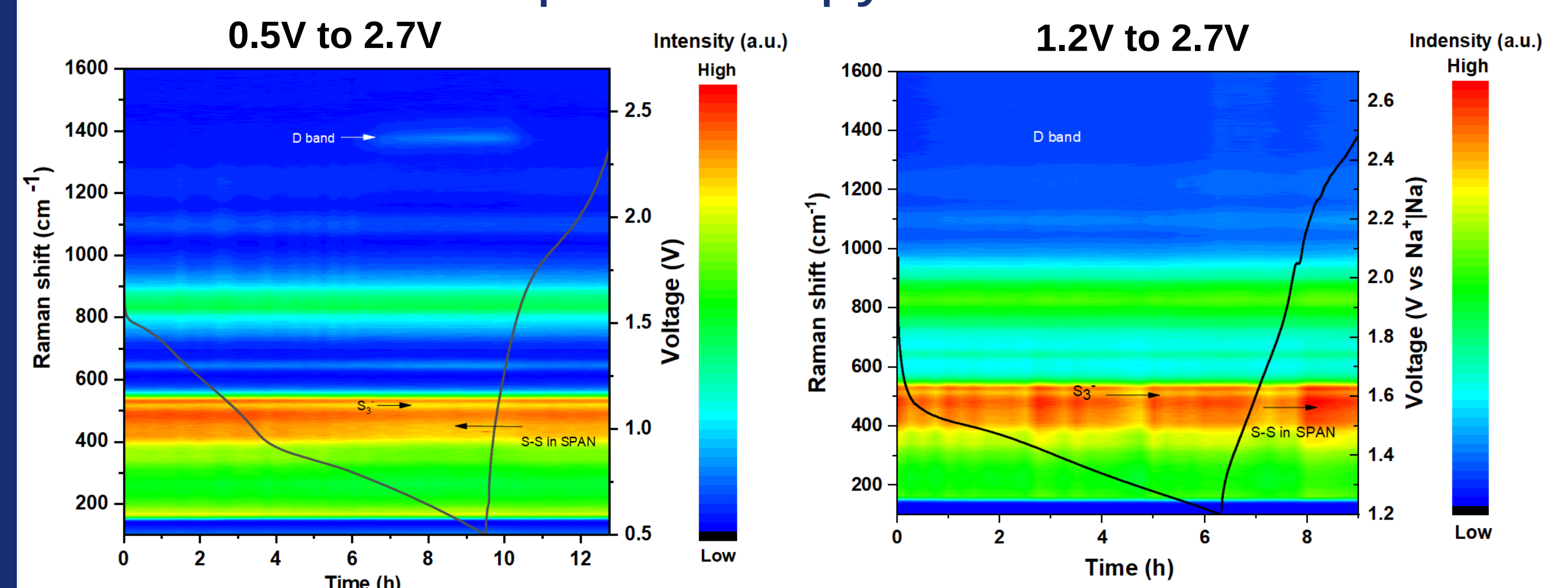


- Small peak at 2.2V-2.4V disappear at 4th cycle in 0.5V-2.7V



- Small peak at 2.2V-2.4V become border with increase discharge depth

In-Situ Raman Spectroscopy



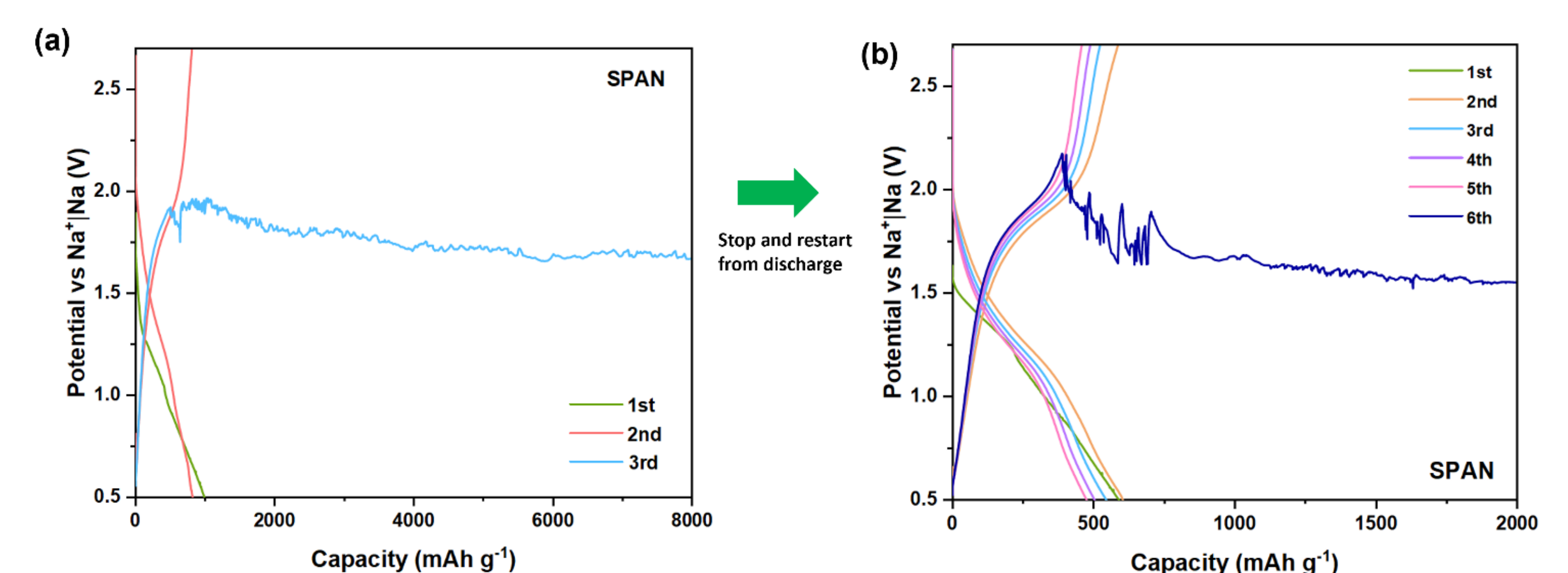
<1.0V: D-band change, S₃⁻ ion react with PAN

Charge: S-S chain cannot reform

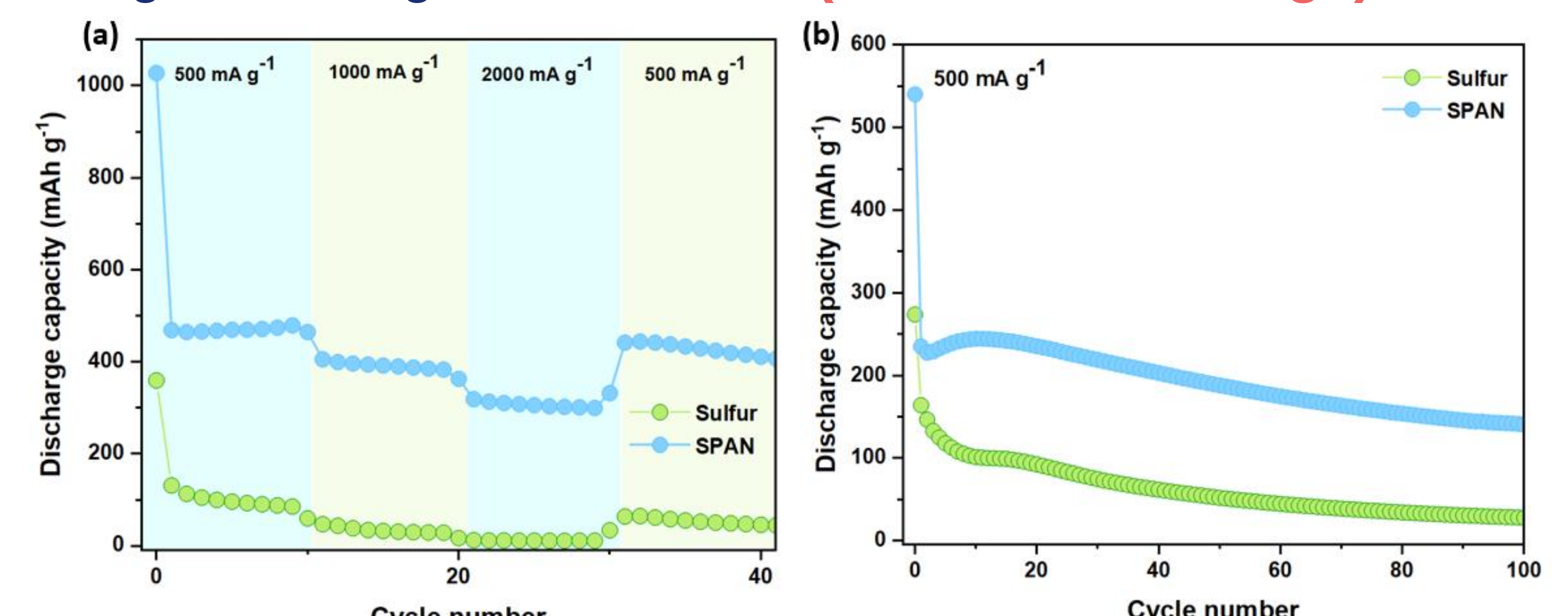
1.2V: D-band signal no change

Charge: S-S chain can reform

➤ Charge-discharge in 0.5V-2.7V (micro short circuits will happen)



➤ Charge-discharge in 1.2V-2.7V (Reasonable Range)



- Higher capacity and stability than elemental sulfur

Conclusion

- In ether-based electrolytes, deep discharge (e.g., down to 0.5 V) can lead to difficulties in restructuring polymer structures and to accumulation of polysulfides in the electrolyte.
- This accumulation exacerbates the shuttle effect and the generation of non-active sites on the sodium negative electrode, which leads to uneven current distribution at the negative electrode interface. Uneven current distribution can lead to easier growth of sodium dendrites, resulting in the occurrence of micro short circuits in the battery.
- Excessively high cut-off voltage (such as 1.4V) can lead to incomplete sulfur-sodium reaction. The most suitable discharge cut-off voltage is 1.2V, which can avoid micro short circuits and the generation of a large amount of polysulfides.