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# New insight into the working mechanism of lithium-sulfur batteries: in situ and operando x-ray diffraction characterization

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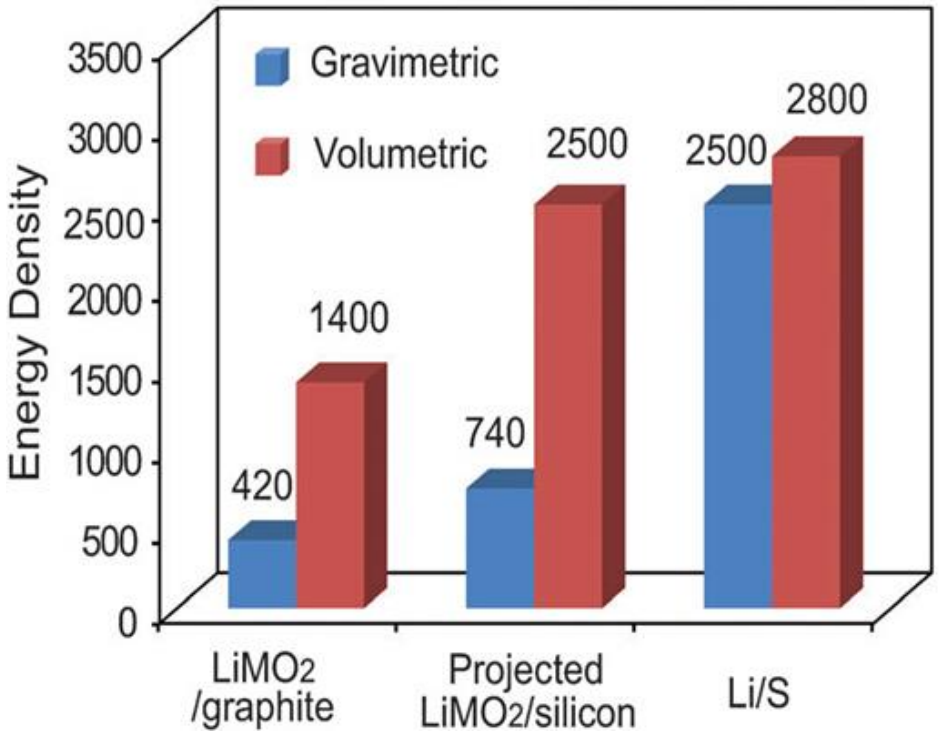
# Rechargeable Batteries

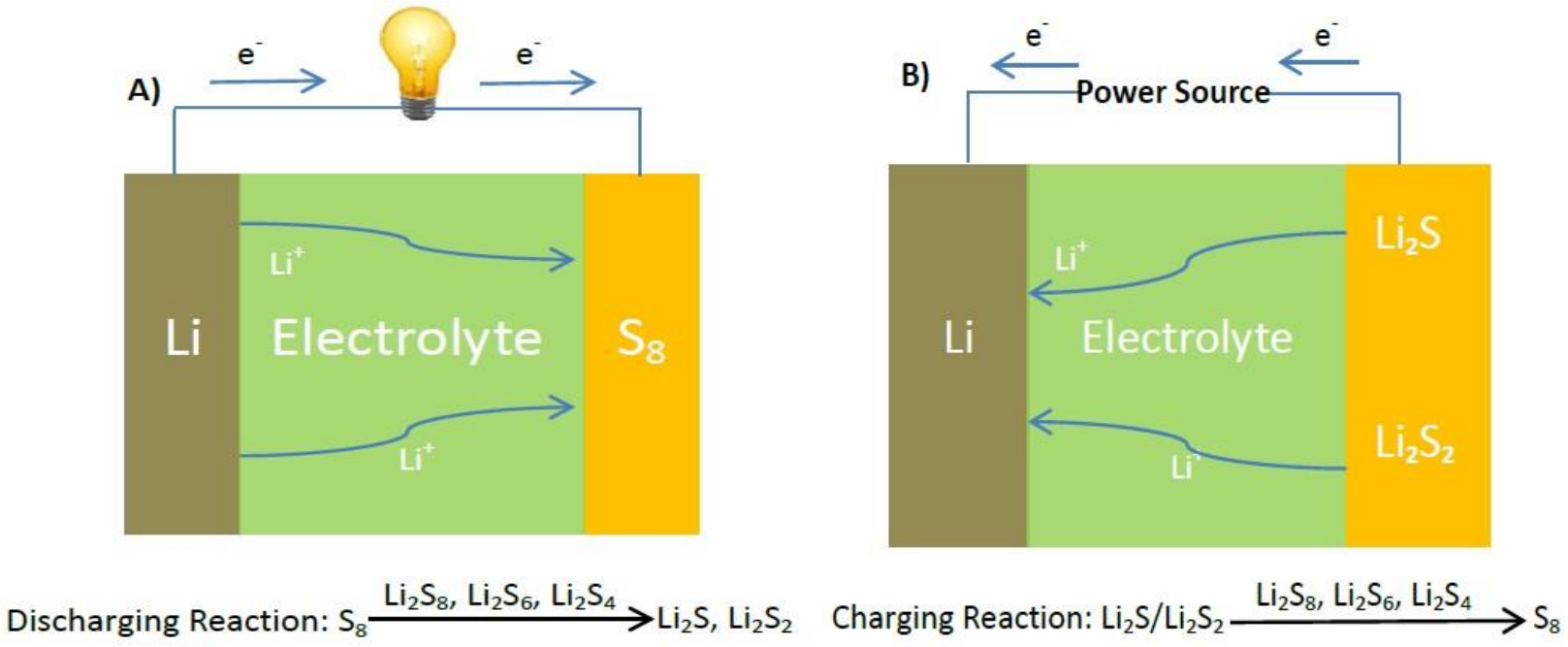
# Background




The theoretical energy density of different systems

Y. Yang, G. Zheng and Y. Cui, Chem. Soc. Rev., 2013, 42, 3018-3032.

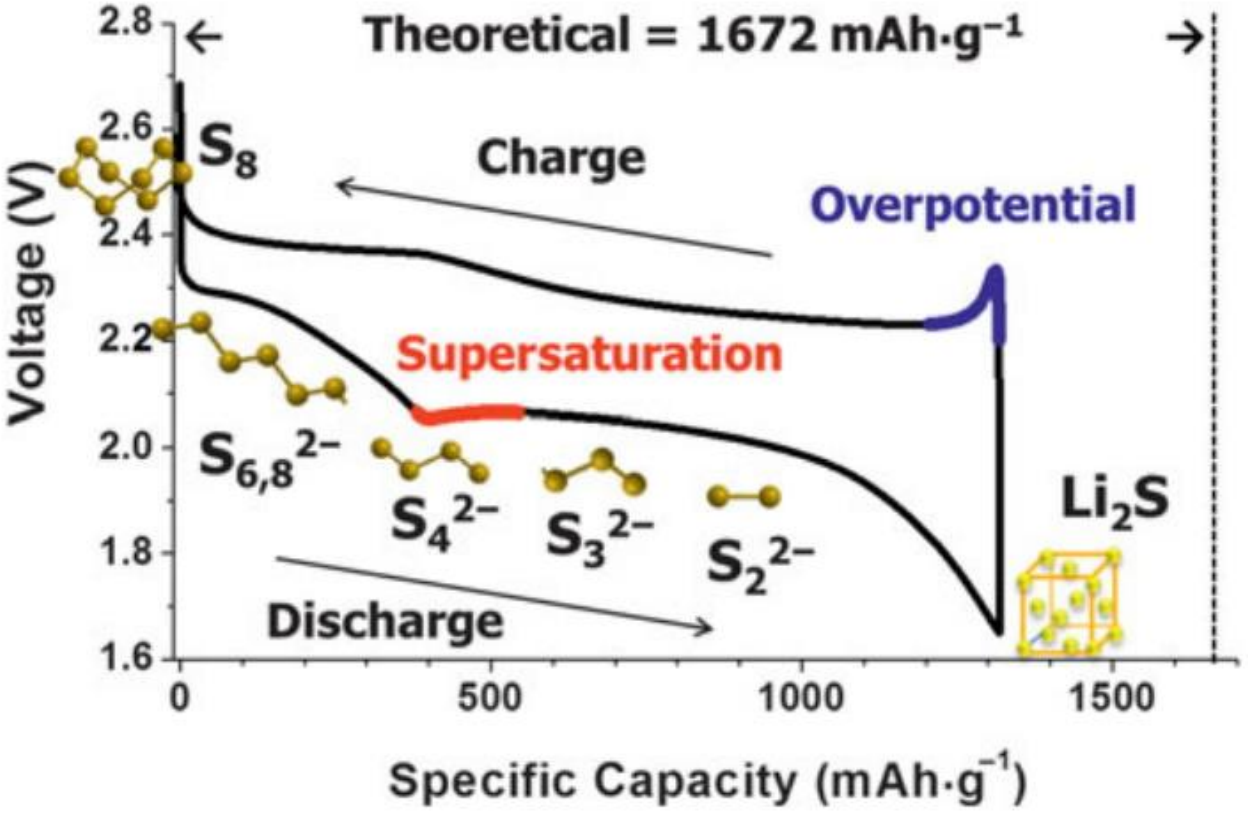
# Li-S Batteries




Schematic presentation of a lithium-sulfur battery with the anode (metallic lithium) and cathode (sulfur-containing material), separated by a non-aqueous liquid electrolyte. A) discharging process and B) charging process.

L. Chen and L. Shaw, J. Power Sources, 2014, 267, 770-783.

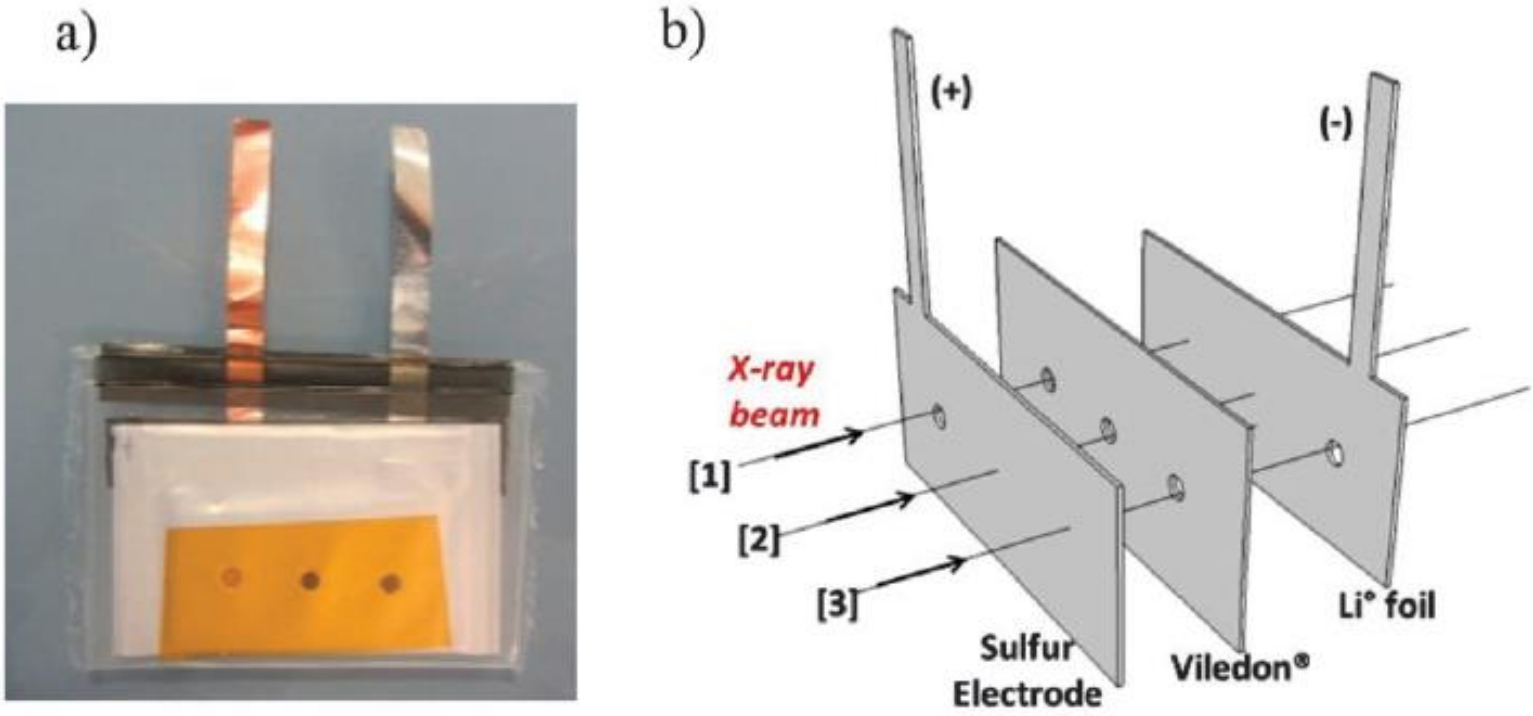
# Electrochemical Reactions




Schematic presentation of reactions in lithium sulfur batteries

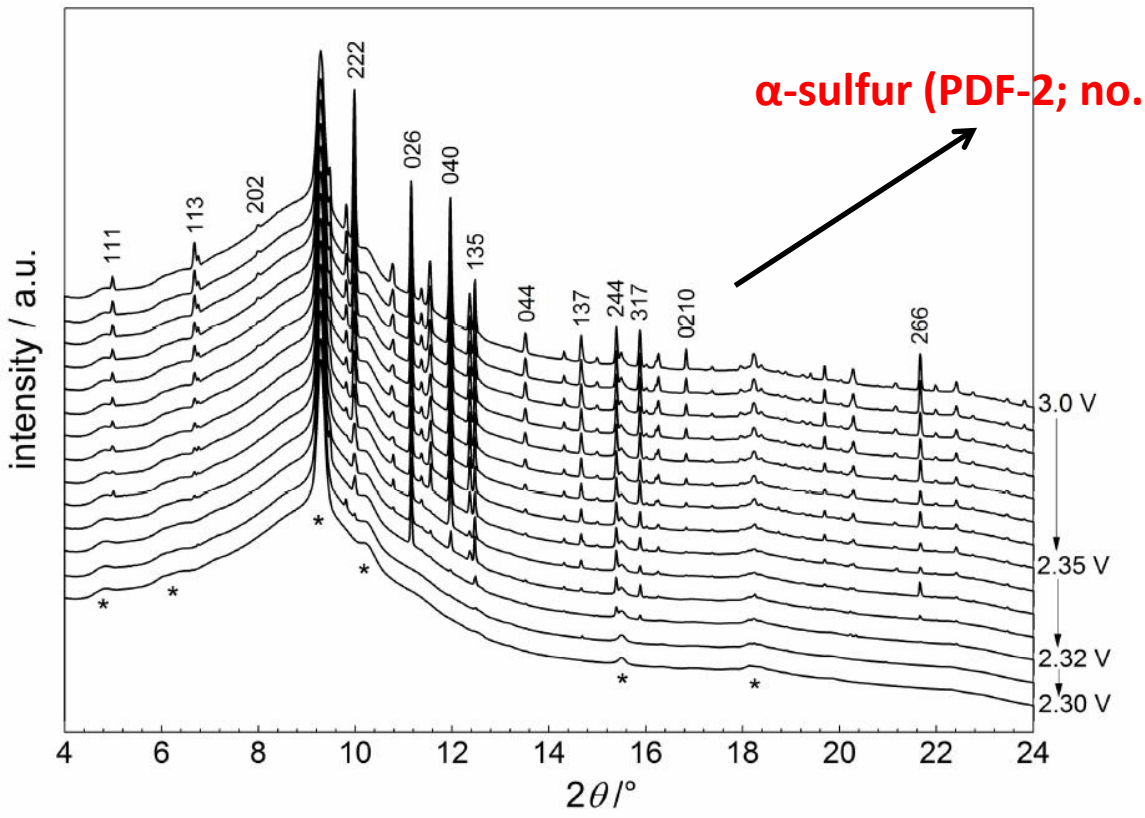
L. Nazar, M. Cuisinier and Q. Pang, MRS Bulletin, 2014, 39, 436-442.

# Cells for In-situ XRD




In situ XRD pouch cell (a); schematic illustration (b) of the cell components, with indicated beam positions at which XRD of the total cell [2], the sulfur electrode [3] and metallic $Li^o$ [1] were recorded.

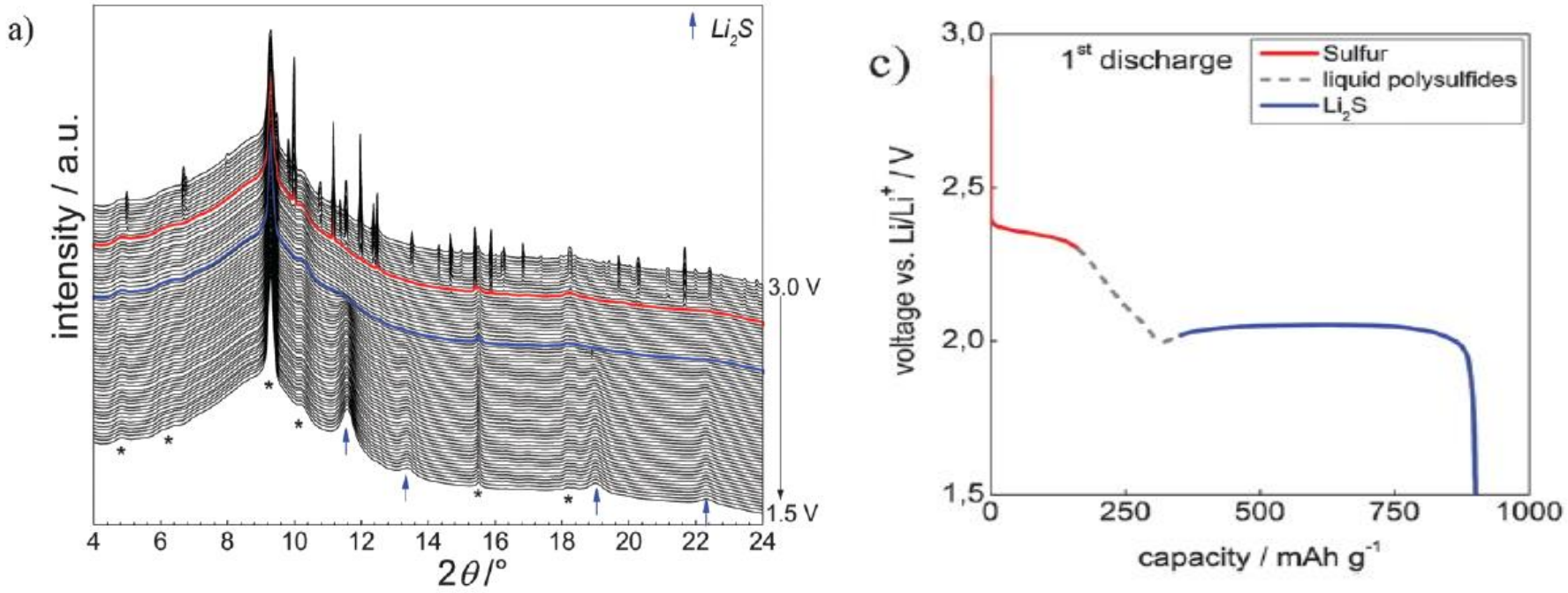
# In-situ XRD for Discharge




In situ XRD patterns evolution (zoomed image) indicating disappearance of solid sulfur during initial discharge. Peaks attribution according to orthorhombic a-Sulfur, PDF-2 no. 00-008-0247. * marks peaks coming from packaging.

# In-situ XRD for Discharge

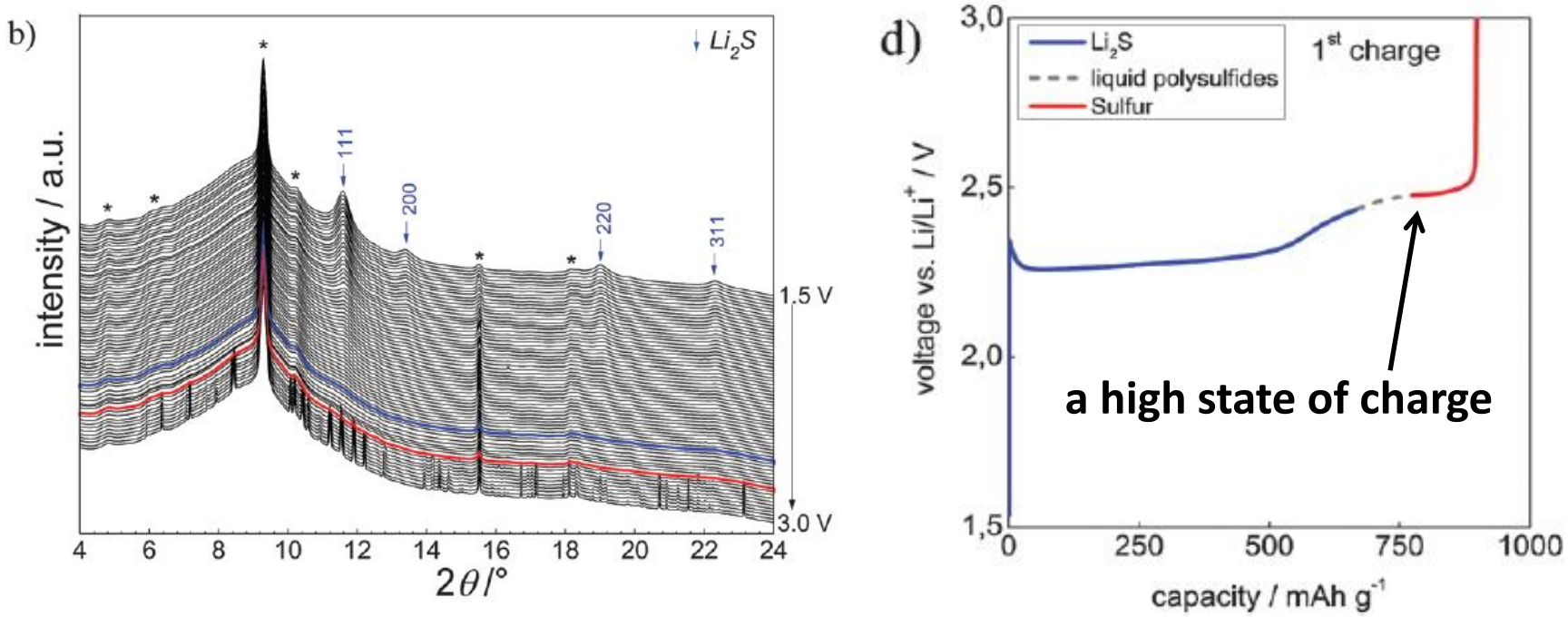
**$Li_2S$ is formed not successively but rather simultaneously**




In situ XRD patterns of the complete cell (position [2]) during 1st discharge (a); corresponding electrochemical plots c. Peaks associated with packaging are marked by *. Bold lines indicate moments of solid phase appearance–disappearance.

# In-situ XRD for Charge

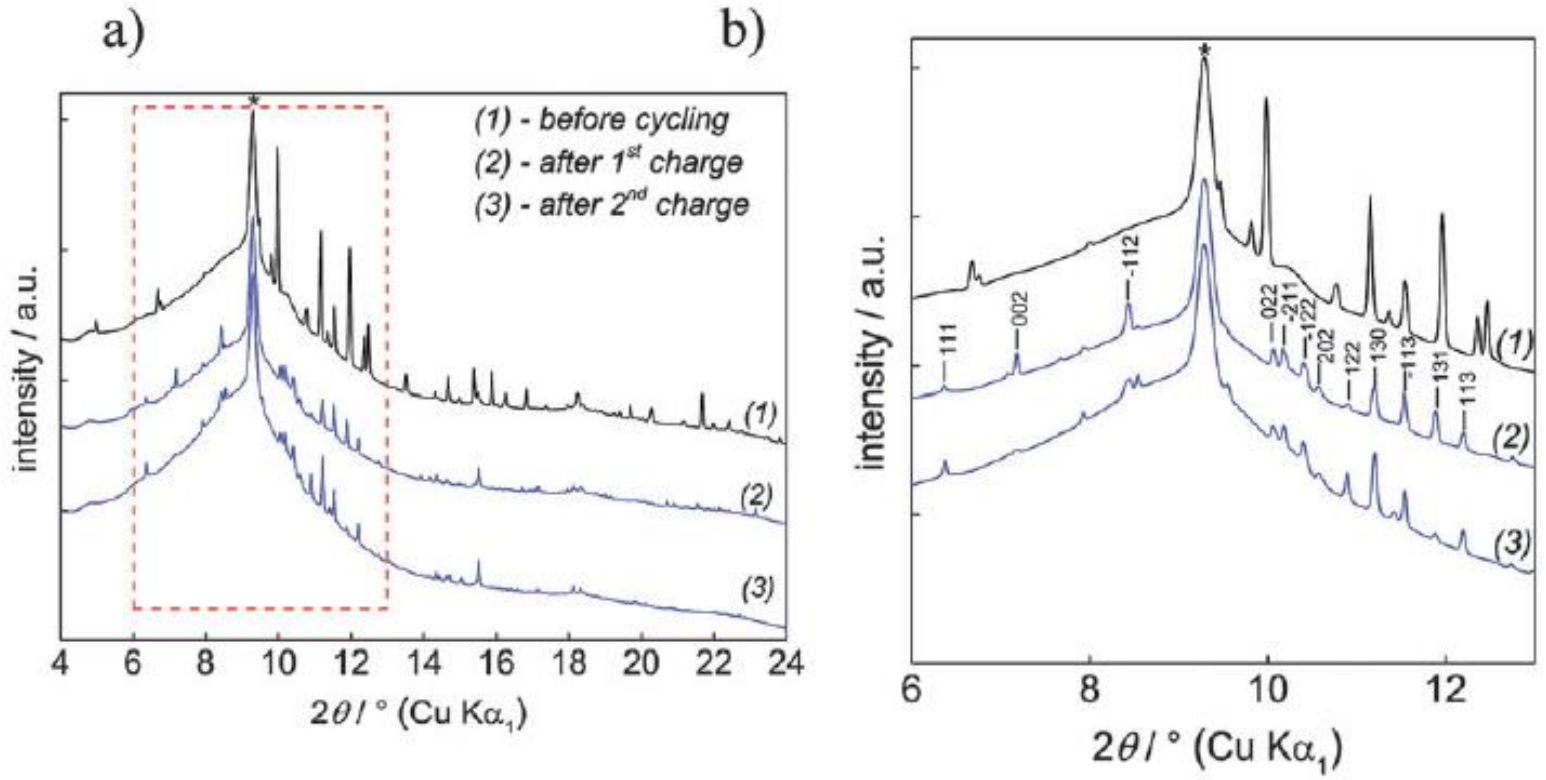
**β-sulfur (PDF-2; no. 01-071-0137) is formed during recrystallization**




In situ XRD patterns of the complete cell (position [2]) during charge (b); corresponding electrochemical plots d. Peaks associated with packaging are marked by *. Bold lines indicate moments of solid phase appearance–disappearance.

# High Resolution XRD Data

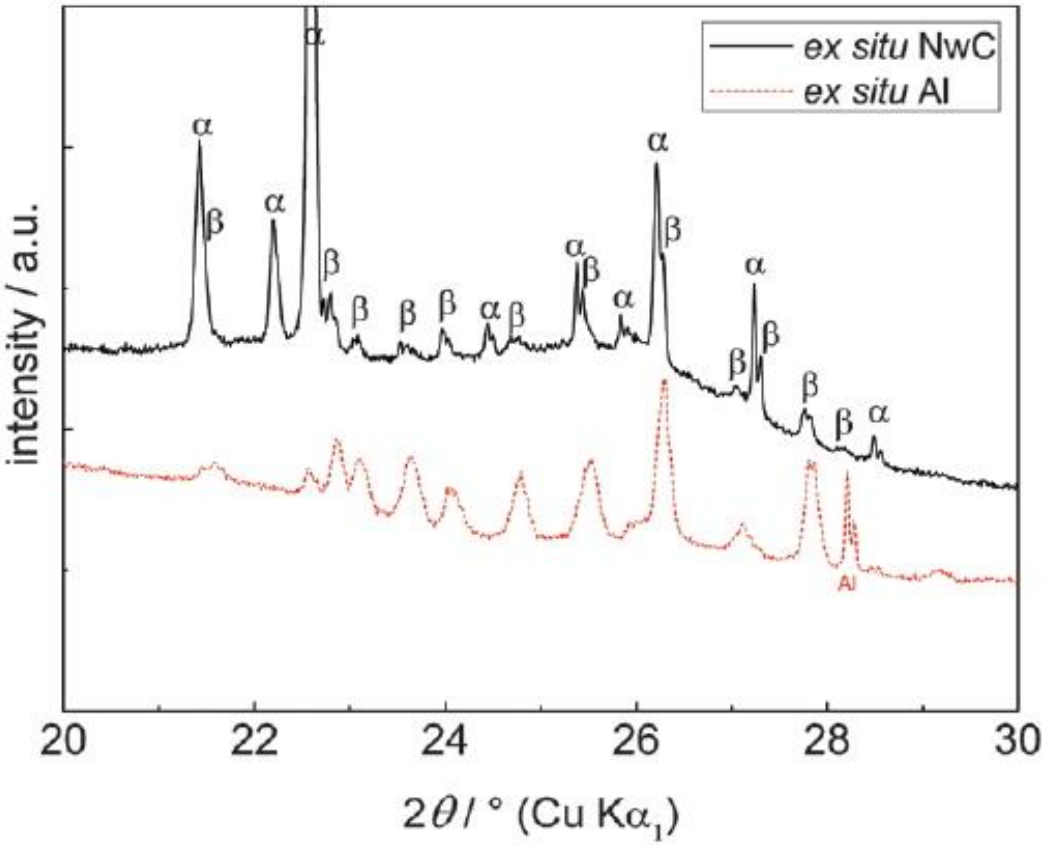
**The formation of β-sulfur (PDF-2; no. 01-071-0137) is confirmed**




XRD patterns of the complete cell recorded before cycling (1), where α-S is present and at the end of 1st and 2nd charge (2 and 3), where peaks of β-S can be identified (a); the zoomed image of the region marked by the red box (b).

# Ex-situ XRD for Charge

**Not X-ray radiation, but energy liberated in the electrochemical reaction may induce the formation of β-S**




Ex situ XRD data of charged sulfur electrodes on different collectors: a nonwoven carbon tissue (NwC) and Al foil. Peaks were attributed to coexisting α- and β-S phases.

# Conclusion

1. Crystalline $Li_2S$ on cathodes are formed at the very beginning of the lower discharge plateau and its complete consumption during following charge.

2. After recrystallization, sulfur does not come back to its pristine structure, but it appears to be another allotrope: monoclinic β-sulfur.

3. In-situ XRD study is one of the most accurate methods for the analysis of structural changes, bringing new information for the working mechanism of Li–S batteries.

***Thanks for your attention!***