



High-Performing Lithium-Sulfur Cathode Development Through Rationally Incorporated Graphene-Derived Carbon Materials

JULEN CASTILLO

29/11/22

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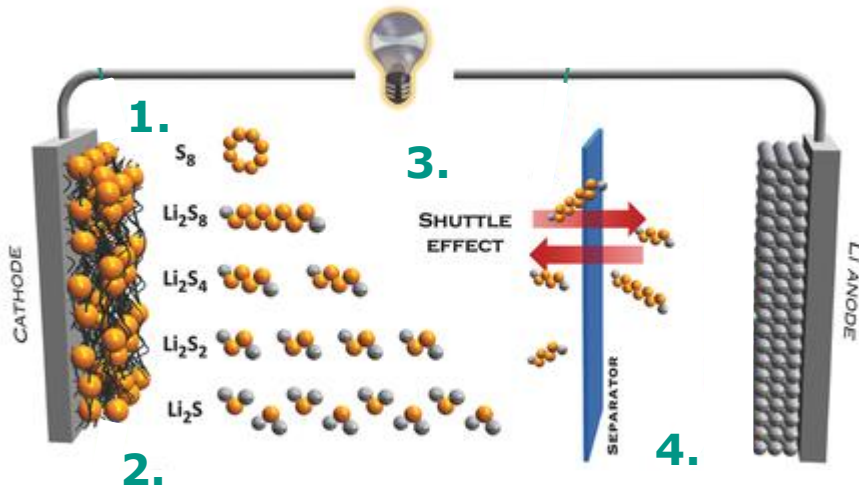
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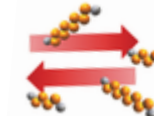
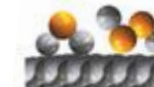
MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE

> INTRODUCTION

CHALLENGES OF LSB FOR REAL APPLICATION

Inherent challenges



1.  Insulating nature of S₈ and Li₂S
2.  Severe volume expansion of S cath.
3.  "Shuttle effect"
4.  Li⁰ anode corrosion

Most of the challenges come from the cathode

Yang et al., *Ionics*, **26**, (2020) 5299–5318

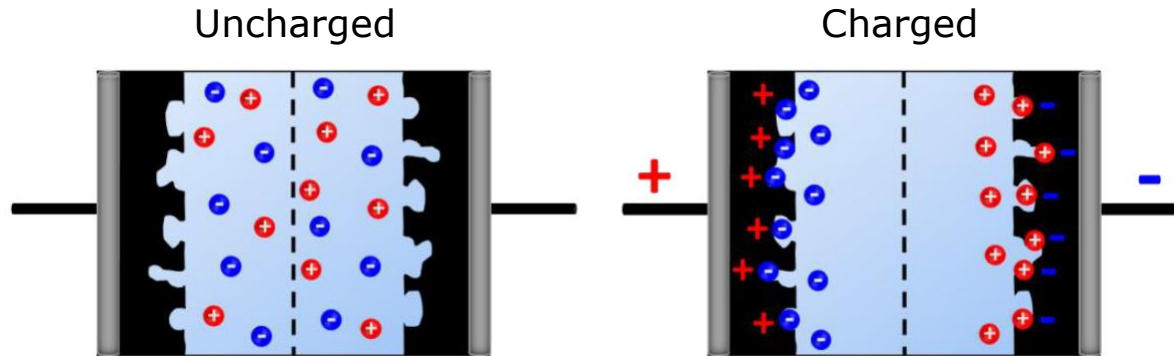


Selecting a suitable S carbon host

- ✓ High electronic conductivity
- ✓ Suitable textural properties
- ✓ Good LiPS affinity

> INTRODUCTION

GRAPHENE-BASED ACTIVATED CARBONS



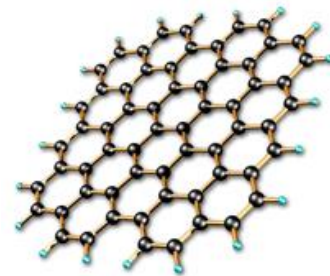
Electric double-layer capacitors (EDLCs)

$$E = \frac{1}{2} C \cdot V^2$$

$$C_e = \epsilon_0 \epsilon_r \frac{S}{d}$$

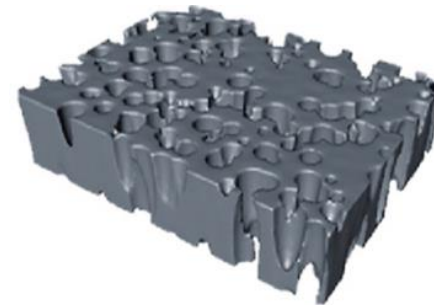
High surface porous carbon
to **maximize** the capacitance,
and thus **energy**

- ✓ Electronic conductivity
- ✓ High theoretical specific surface
- ✗ Stacking issues



Graphene

+



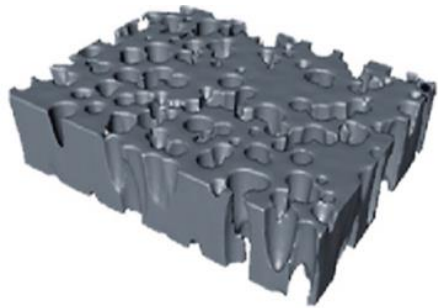
Activated carbons

- ✓ High specific surface area
- ✓ High porosity
- ✗ Electronic conductivity

Graphene-based activated carbons

> OUR SCOPE

GRAPHENE-BASED ACTIVATED CARBONS

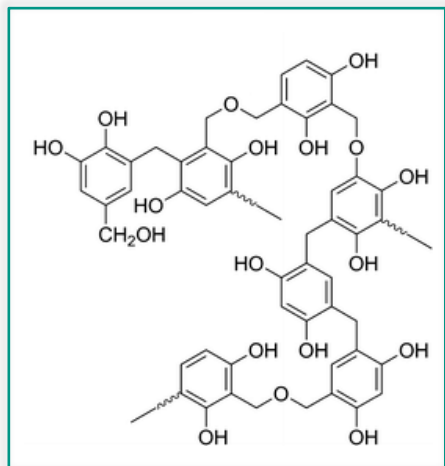


Activated carbons



Natural wastes

- ✓ High abundance/sustainable
- ✓ Low cost
- ✗ High impurity content
- ✗ Porosity dependent on the nature



Phenolic resins

**High-purity
polymer
pyrolysis**

- ✓ Well-constructed structure
- ✓ Tunable porosity

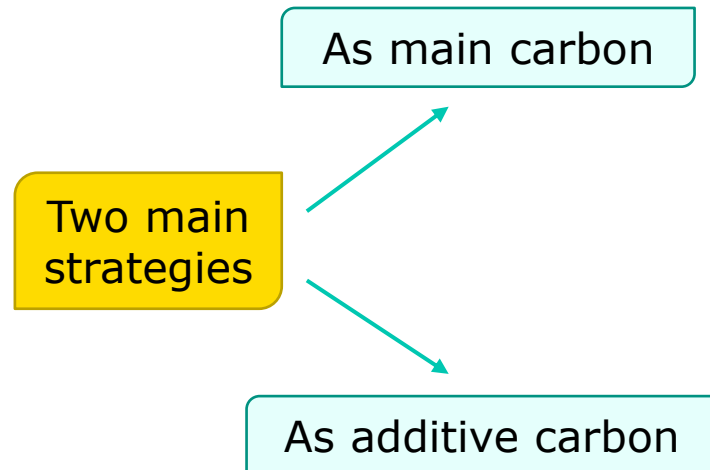
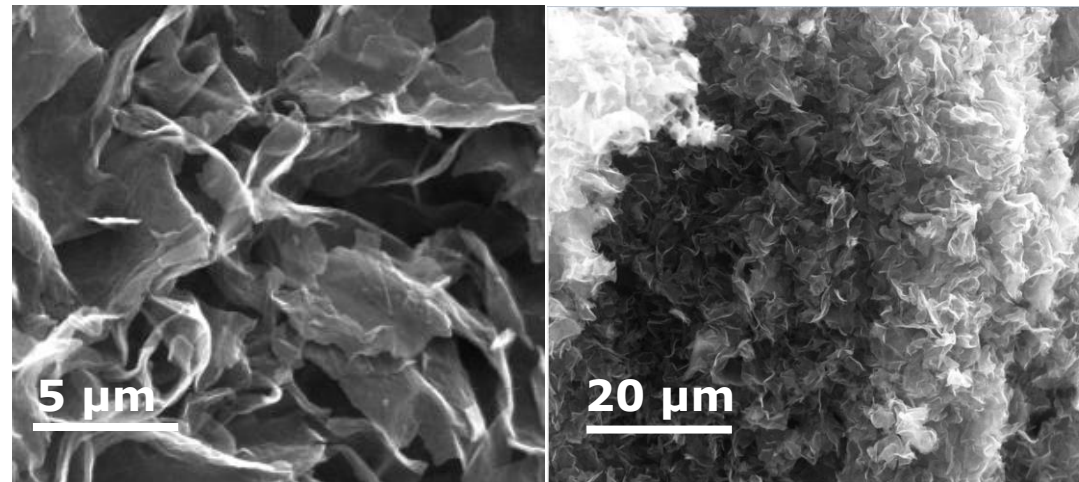
> EXPERIMENTAL

ResFArGO PREPARATION ROUTE

ResFArGO: Use of high purity resin



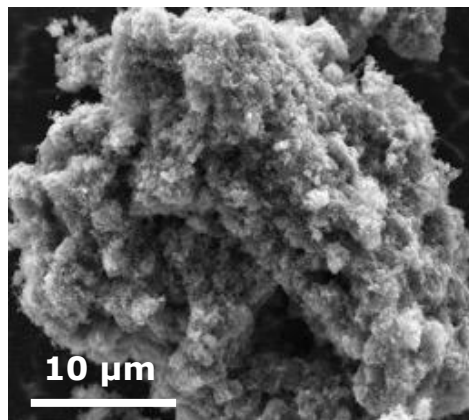
Open and uniform 2D
flat-shape particles



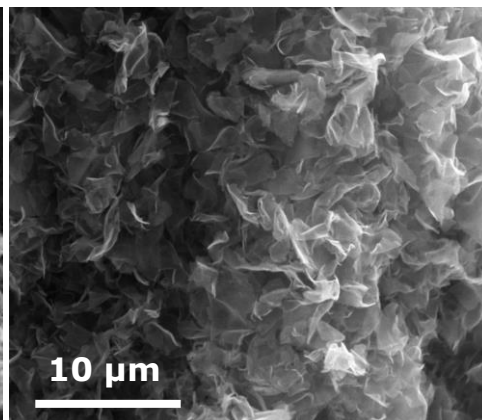
> MATERIAL CHARACTERIZATION

INDIVIDUAL PROPERTIES OF ResFARGO MATERIAL

KJ600

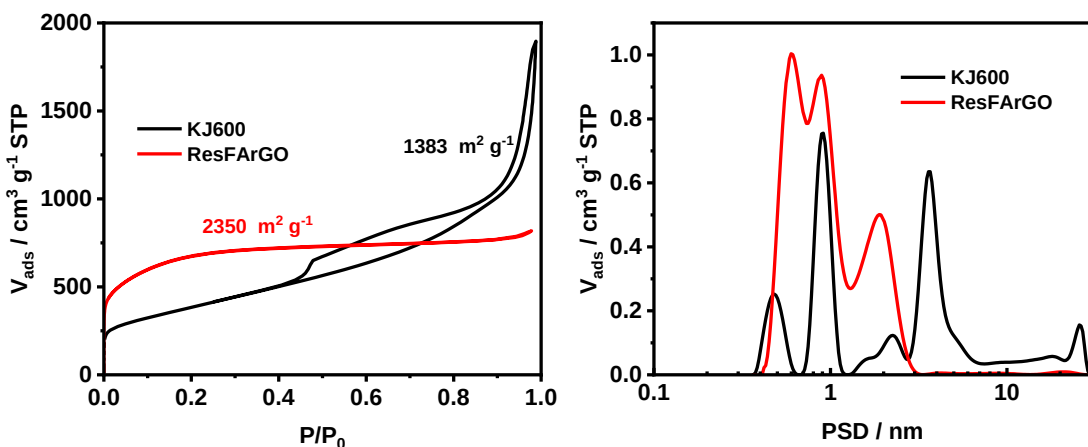


ResFARGO



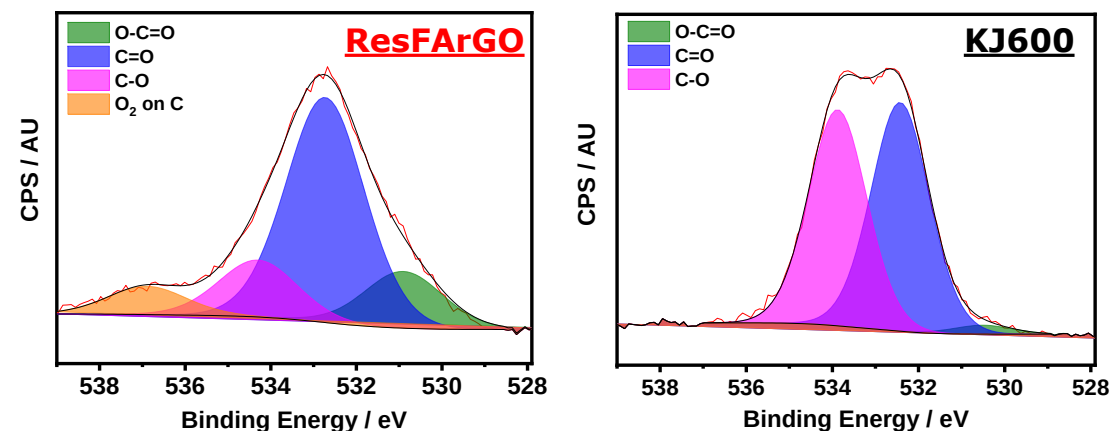
- ✓ High specific surface area of the proposed material ($> 2300 \text{ m}^2 \text{ g}^{-1}$)
- ✓ Highly microporous material (ResFARGO $< 0.7 \text{ nm}$)
- ✓ High amount of polar-based oxygen species in ResFARGO surface
- ✓ ResFARGO presents excellent retention of LiPSs

N_2 adsorption/desorption



Suitable Textural properties

XPS

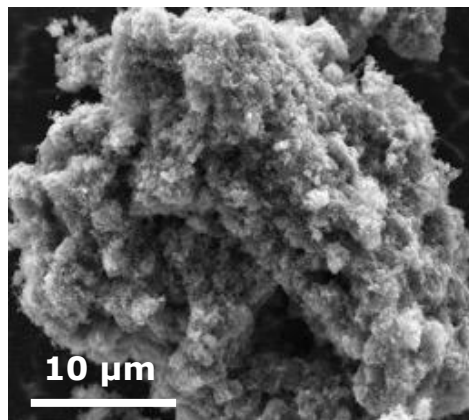


Good Surface chemistry

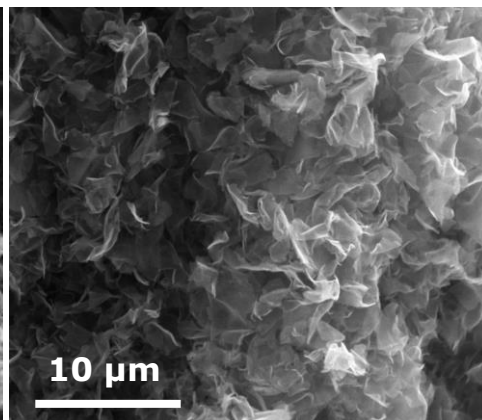
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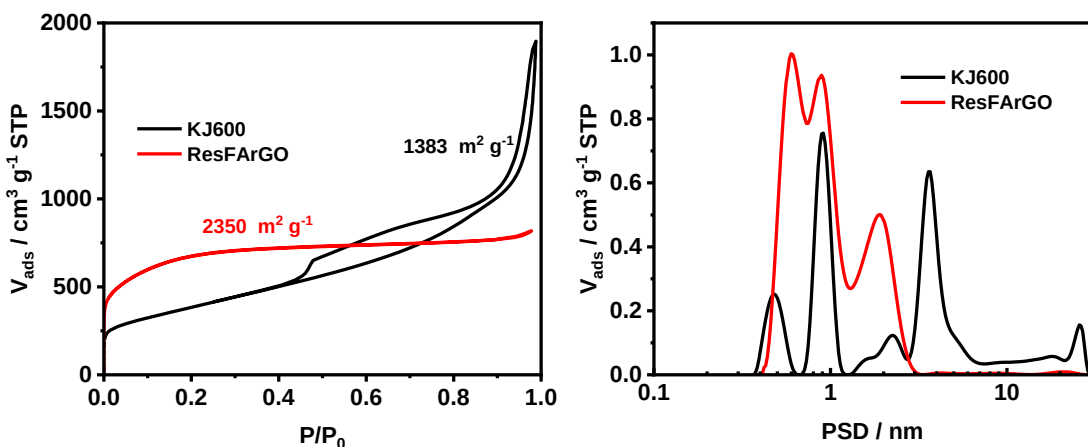


ResFARGO



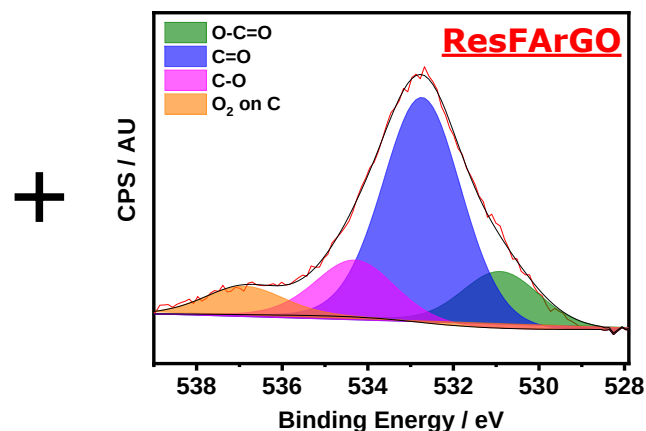
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N₂ adsorption/desorption



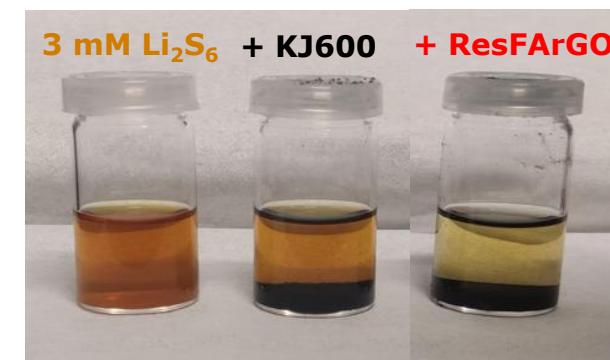
Suitable Textural properties

XPS



Good Surface chemistry

Lithium polysulfides test



Strong LiPS affinity

> S CATHODE CHARACTERIZATION

Composition - 64 wt.% S₈ + 26 wt.% carbon + 10 wt.% binder

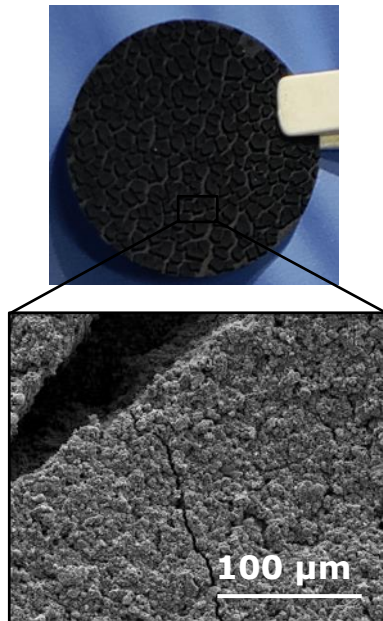
ML ($\approx 3 \text{ mg S cm}^{-2}$) →

Power cells

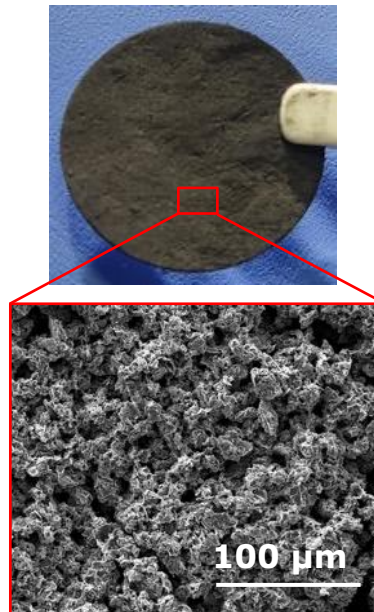
HL ($\approx 4 \text{ mg S cm}^{-2}$) →

Energy cells

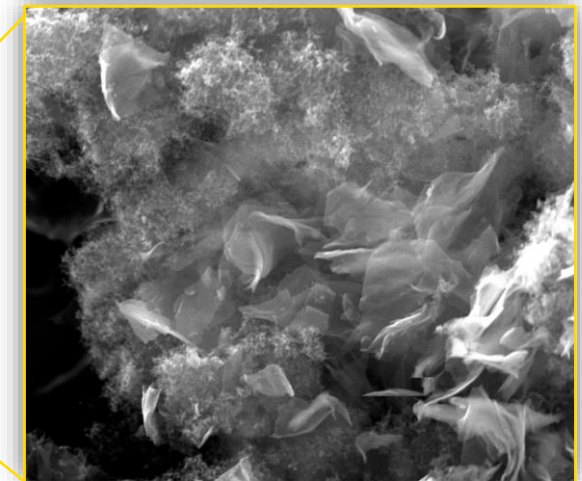
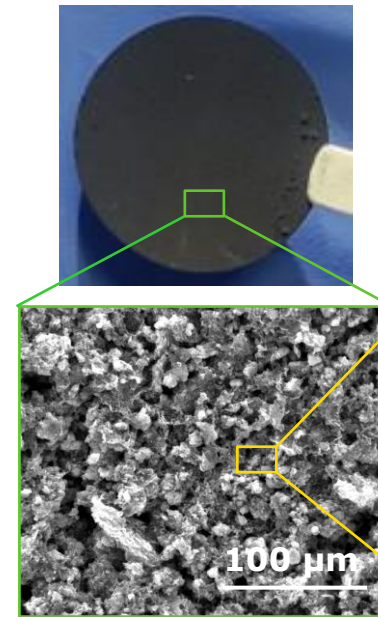
S@KJ600



S@ResFArGO₂₆



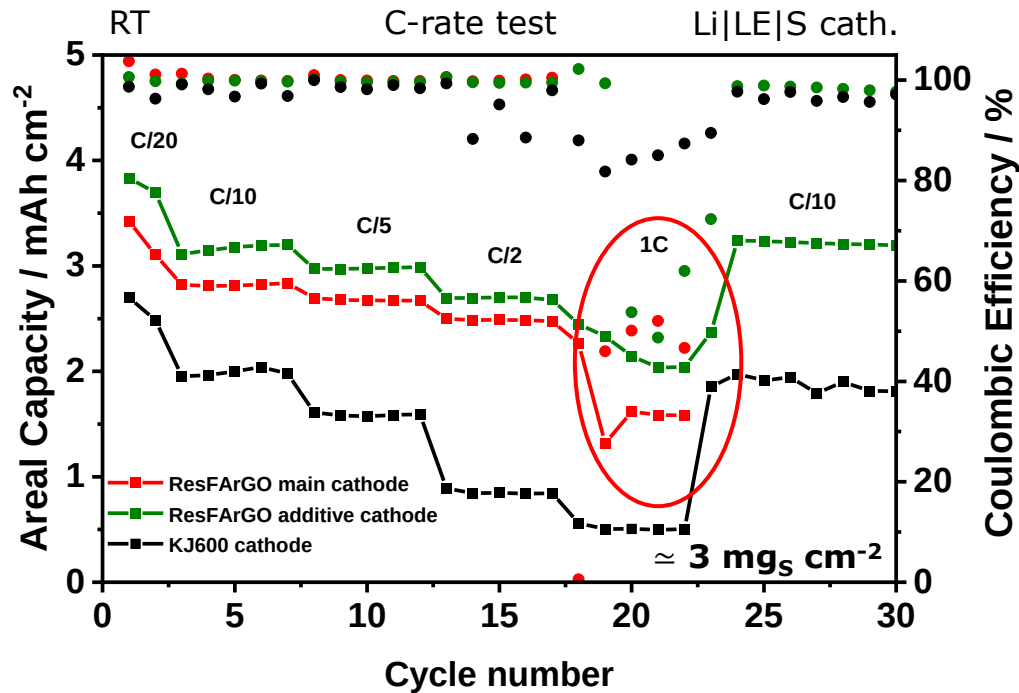
S@KJ600₁₆ + ResFArGO₁₀



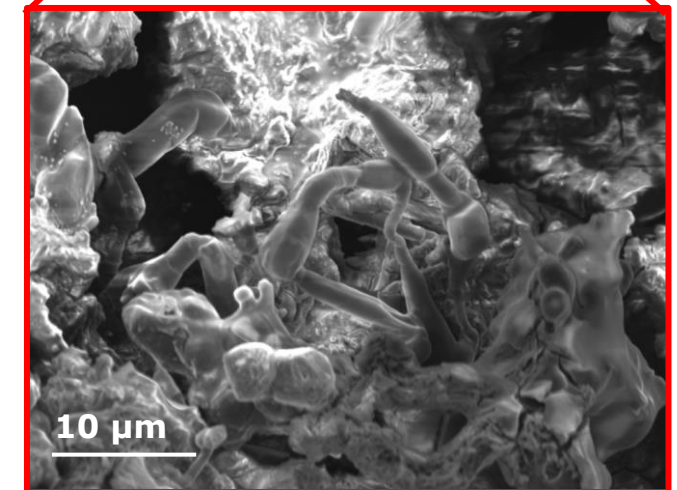
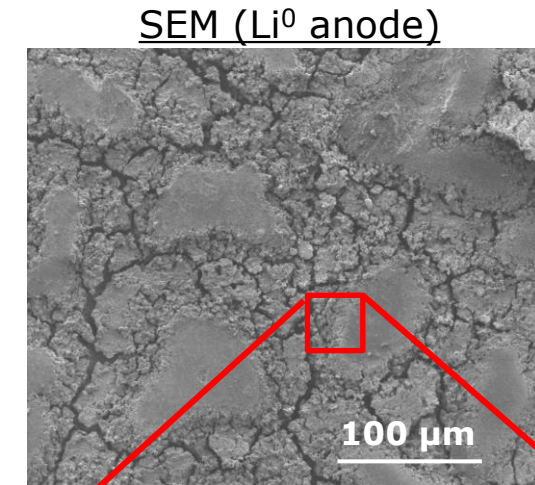
- ✓ Crack-free and highly compact high S loading electrodes using ResFArGO (both main as additive)
- ✓ Excellent combination between the 2D structure of ResFArGO and the carbon black particles

> ELECTROCHEMICAL POWER CELLS

$E/S = 7 \mu\text{l/mg}_s$ SoA electrolyte 0.5 M LiTFSI + 0.5 M LiNO₃ in DME/DOL (1:1 in vol.)



Post-mortem analysis



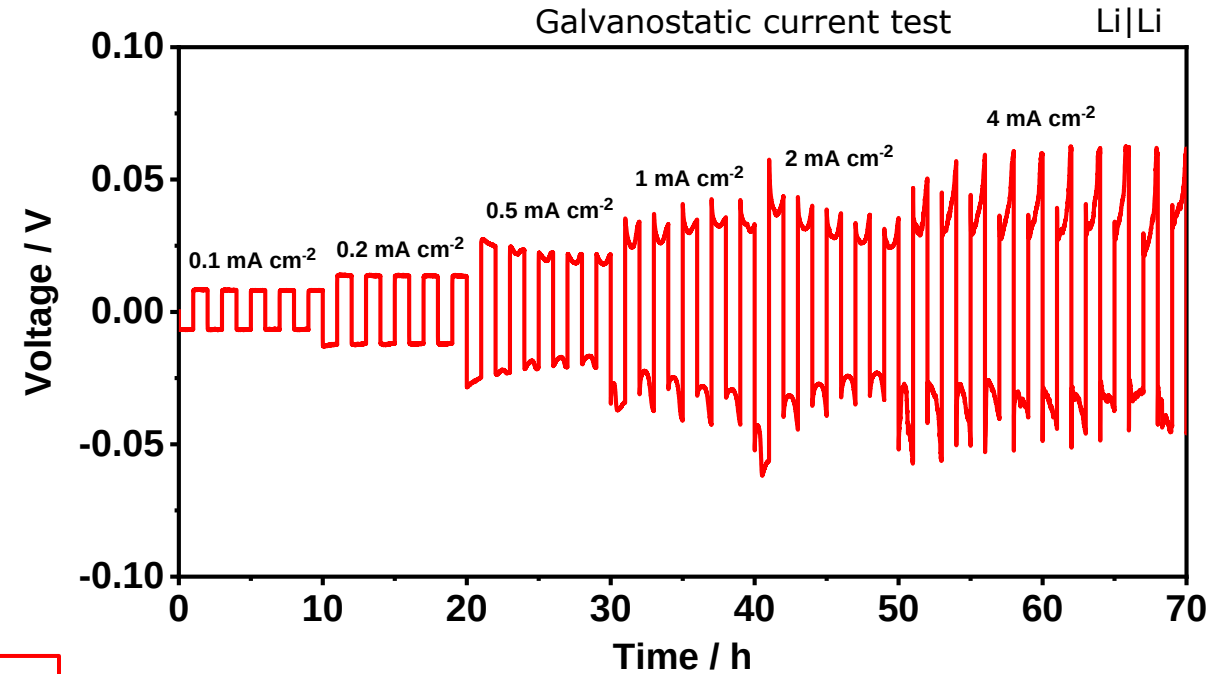
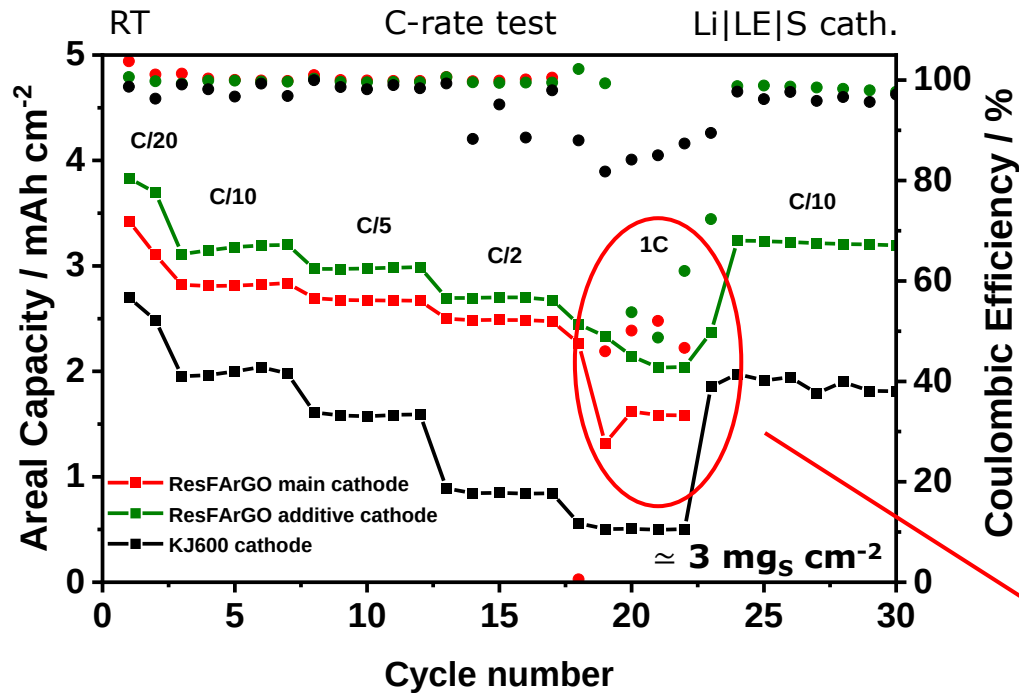
✓ Remarkable rate capability of ResFARGO-containing electrodes

✗ Poor CE at high C-rates (at 1C)

Instability issues of Li anode side (Li powdering and dendrite growth)

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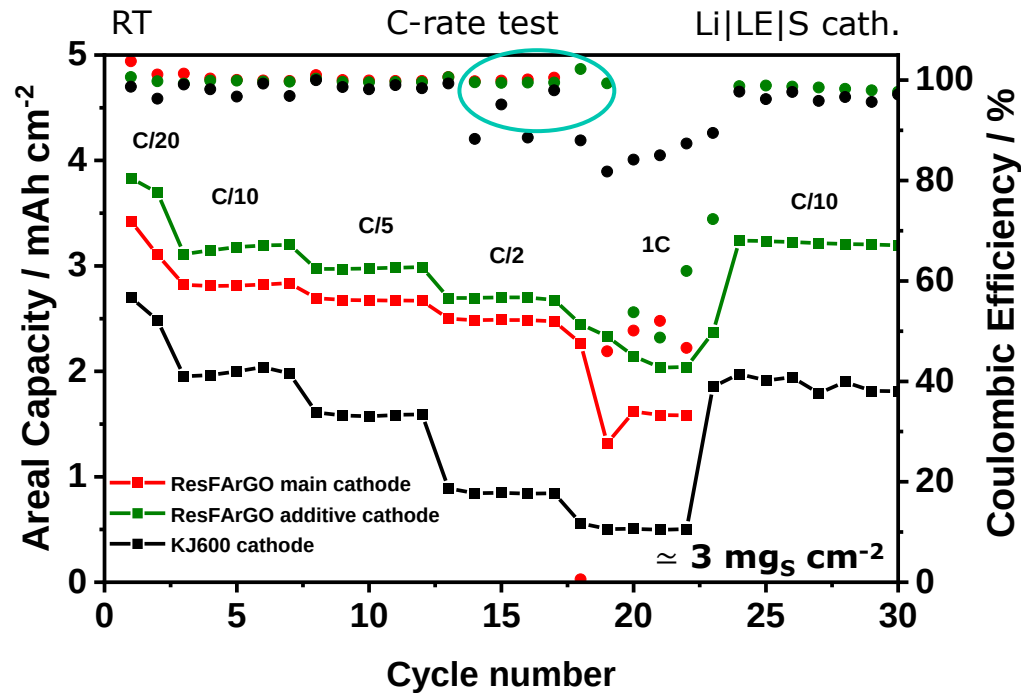
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Instability issues of Li anode side (Li powdering and dendrite growth)

Unsuitable compatibility of the SoA electrolyte with Li anode

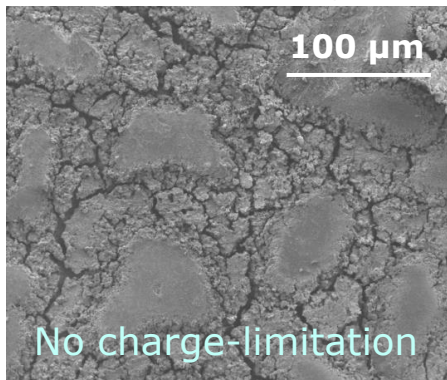
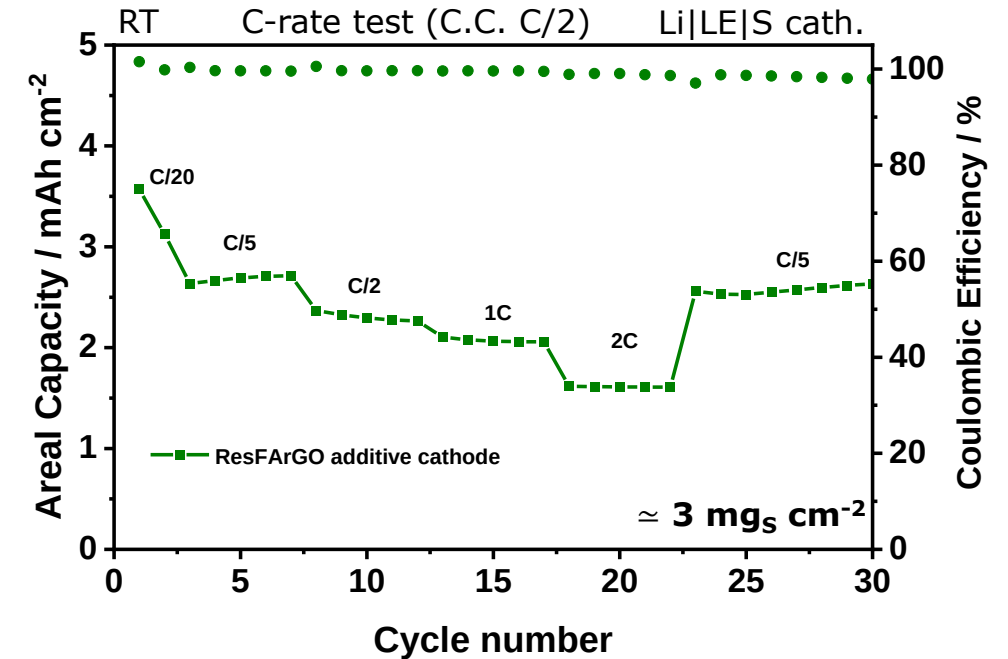
> ELECTROCHEMICAL PERFORMANCE POWER CELLS

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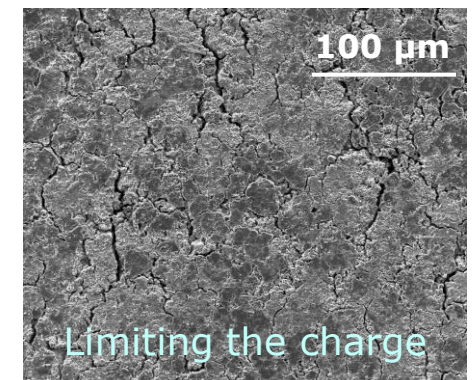


Limiting the charge

C/2

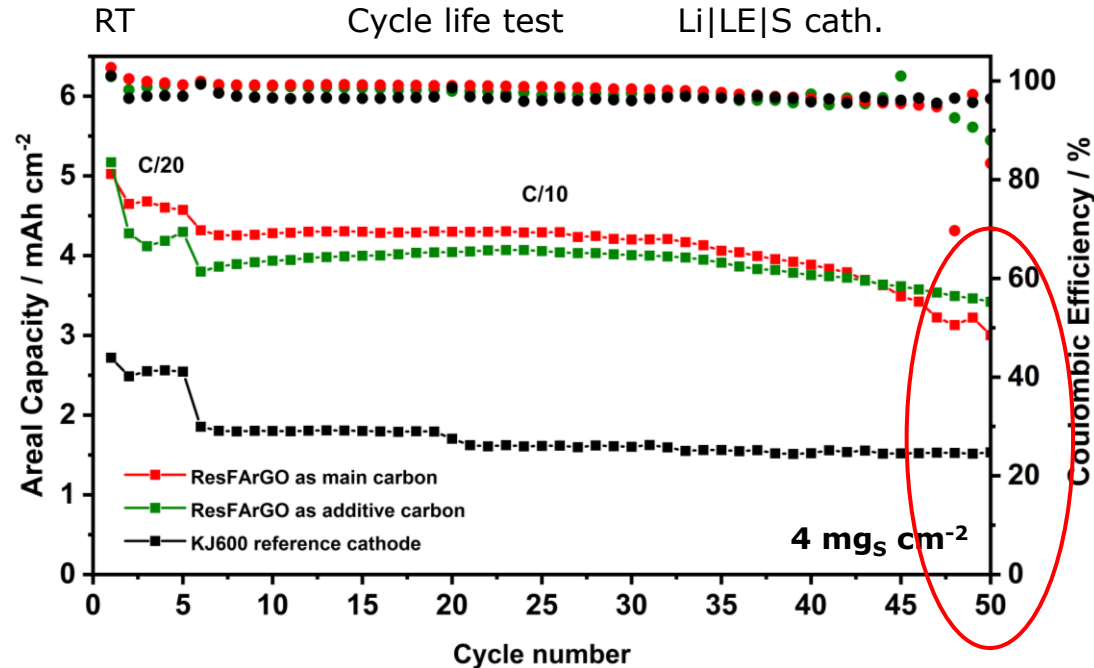


- ✓ Outstanding discharge capacity at high C-rates (ca. 1.7 mAh cm⁻² at 2C)
- ✓ Li anode issues are avoided at a C.C. of C/2
- ✓ Clearly a more compact and smoother deposition of Li



> ELECTROCHEMICAL PERFORMANCE OF ENERGY CELLS

$E/S = 7 \mu\text{l/mg}_S$ SoA electrolyte 0.5 M LiTFSI + 0.5 M LiNO₃ in DME/DOL (1:1 in vol.)



Post-mortem
analysis



Li⁰ anode

- ✓ High areal capacities ($> 4 \text{ mAh cm}^{-2}$) in both ResFARGO-containing cathodes
- ✓ Greatly improved sulfur utilization



Long-cycling life maintaining these
high-areal capacities

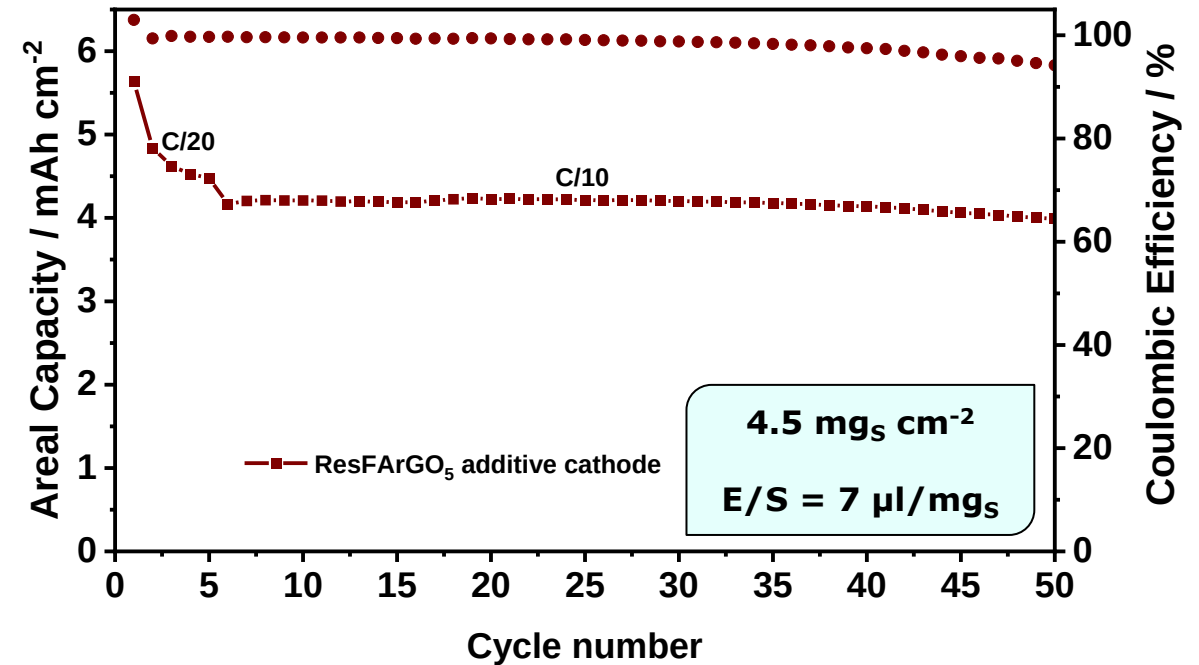
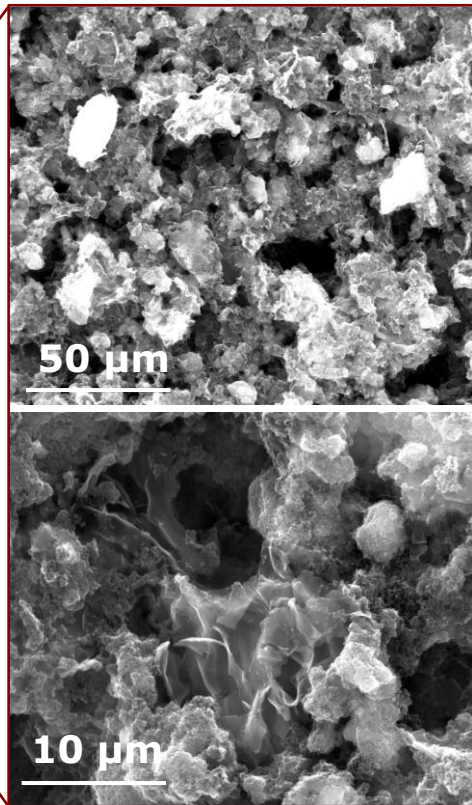
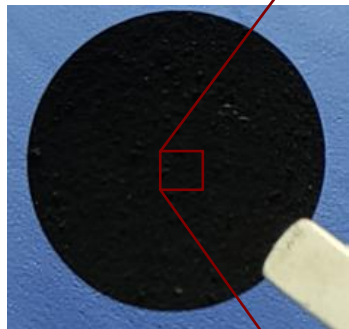
Unsuitable compatibility of the
SoA electrolyte with Li anode

> ELECTROCHEMICAL PERFORMANCE OF ENERGY CELLS

Composition - 69 wt% S₈ + 21 wt% carbon + 10% binder

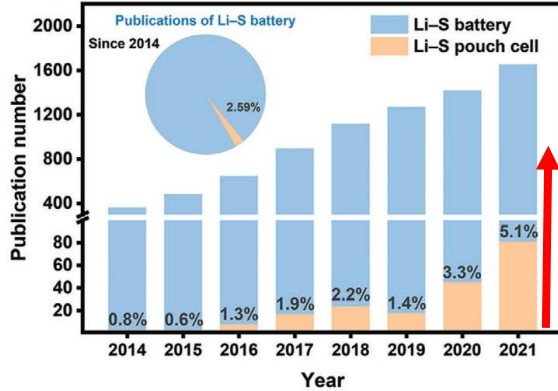
SoA electrolyte 0.5 M LiTFSI + 0.5 M LiNO₃ in DME/DOL (1:1 in vol.)

S@KJ600₁₆ + ResFArGO₅



- ✓ Allows increasing the active material content while reducing the cost of the electrode
- ✓ Outstanding areal capacity and S utilization with a minimal amount of ResFArGO

> PROTOTYPE CELL RESULTS



Still few Li-S pouch cell works

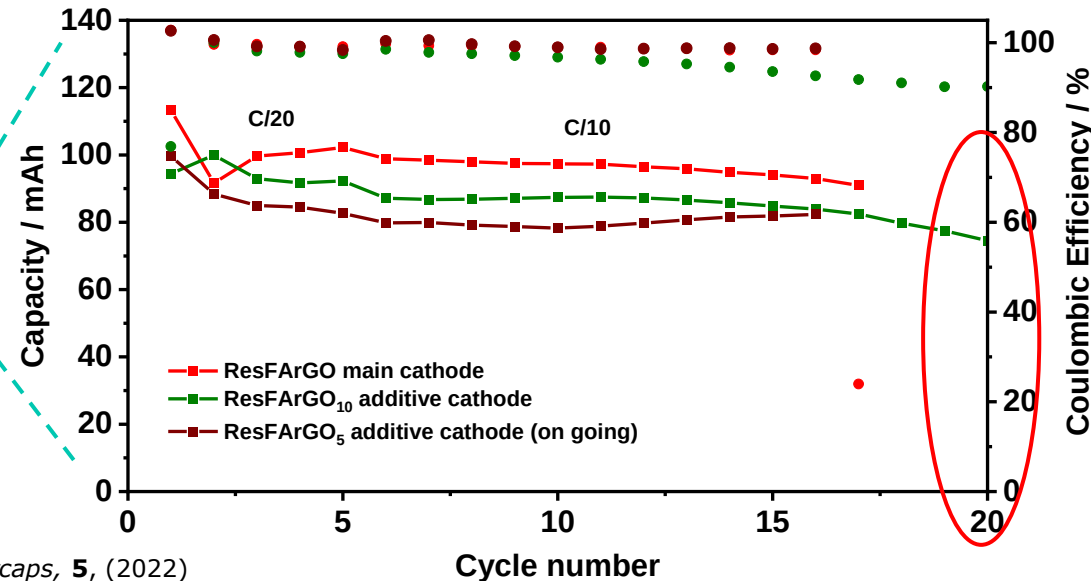
Unsuitable compatibility of the SoA electrolyte with Li anode



Severe anode degradation

Chen et al., *Adv. Mater.*, **34** (2022) 2201555

$E/S = 7 \mu\text{l}/\text{mg}_S$ SoA electrolyte 0.5 M LiTFSI + 0.5 M LiNO_3 in DME/DOL (1:1 in vol.)



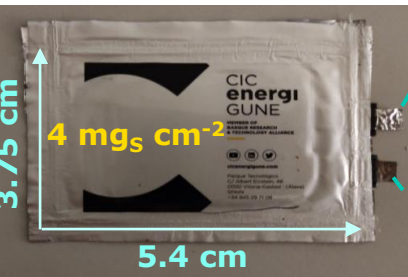
× Poor cycle life



✓ Proven scalability of these S cathodes

✓ Outstanding sulfur utilization

✓ Incredibly high total capacities

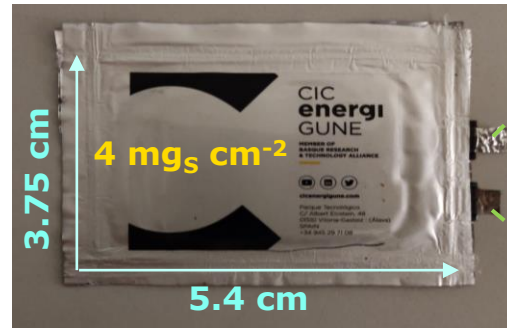


Jimenez-Martin et al., *Batter. supercaps*, **5**, (2022)

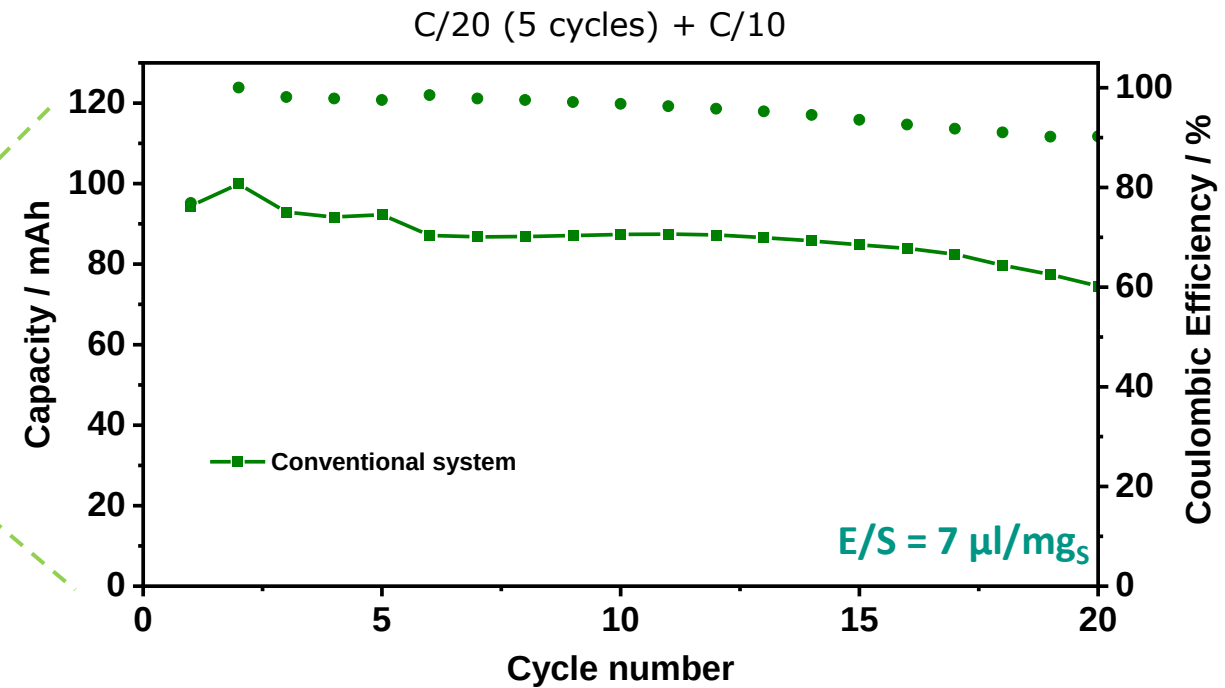
Castillo et al., *J. Power Sources*, (submitted)

> PROTOTYPE CELL RESULTS

NEW PROMISING RESULTS



S@KJ600₁₆ + ResFArGO₁₀



> PROTOTYPE CELL RESULTS

NEW PROMISING RESULTS

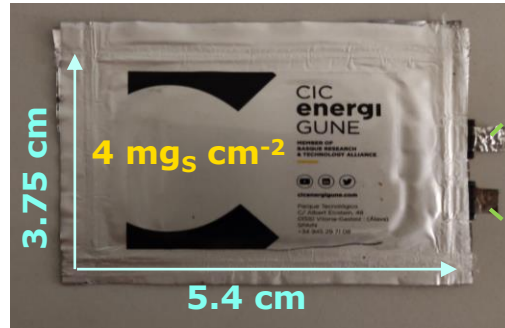


New promising results – **CONFIDENTIAL** – Patent in process

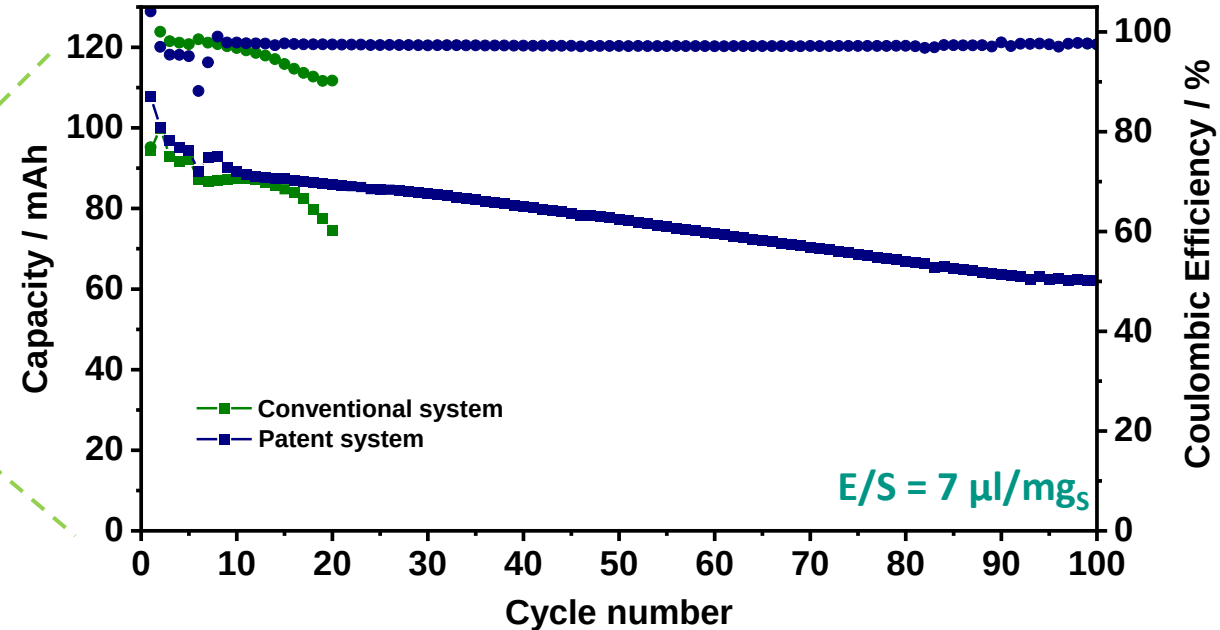


EP22383131.4

C/20 (5 cycles) + C/10



$S@KJ600_{16} + ResFArGO_{10}$



- 5-fold increased stability of the pouch cells
- 67% of capacity retention after 100 cycles
- Substantially improved lithium anode stability (highly stable CE)

> CONCLUSION AND FURTHER STEPS

S-positive electrodes have been successfully developed overcoming the main inherent challenges of Li-S while obtaining high-energy cells

- ❑ The identification of commonalities with supercapacitors gives rise to ResFARGO composite material
- ❑ S cathodes with excellent rate capability and outstanding sulfur utilization have been developed
- ❑ Scalability of the electrodes has been demonstrated by obtaining prototype cells that deliver high total capacities
- ❑ The excellent results obtained with the optimized system are highly promising, but ...

... there is a lot to do toward potential commercialization

> ACKNOWLEDGMENTS



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GOBIERNO VASCO**



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European Union Funding
for Research & Innovation**



GRACIAS · THANK YOU · ESKERRIK ASKO

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