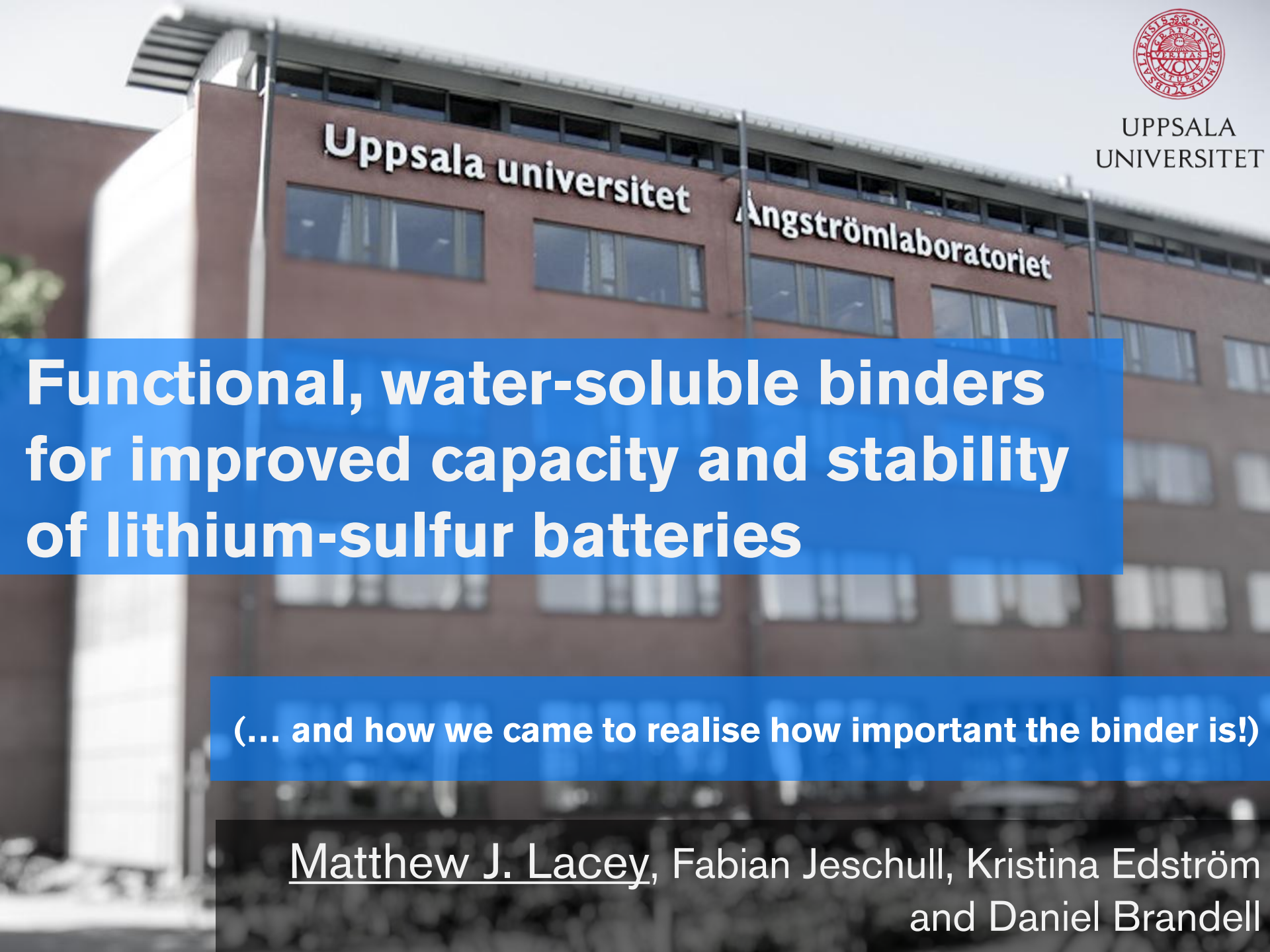

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Functional, water-soluble binders for improved capacity and stability of lithium-sulfur batteries

(… and how we came to realise how important the binder is!)

Matthew J. Lacey, Fabian Jeschull, Kristina Edström and Daniel Brandell

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Overview

Compared to Li-ion, the choice of binder in a Li-S electrode can be significant in the following ways:

The effect of pore blocking by the binder

New study – how the binder can limit cathode energy density

Functional capacity and stability enhancement

Continuing work – how functional binders can enhance performance

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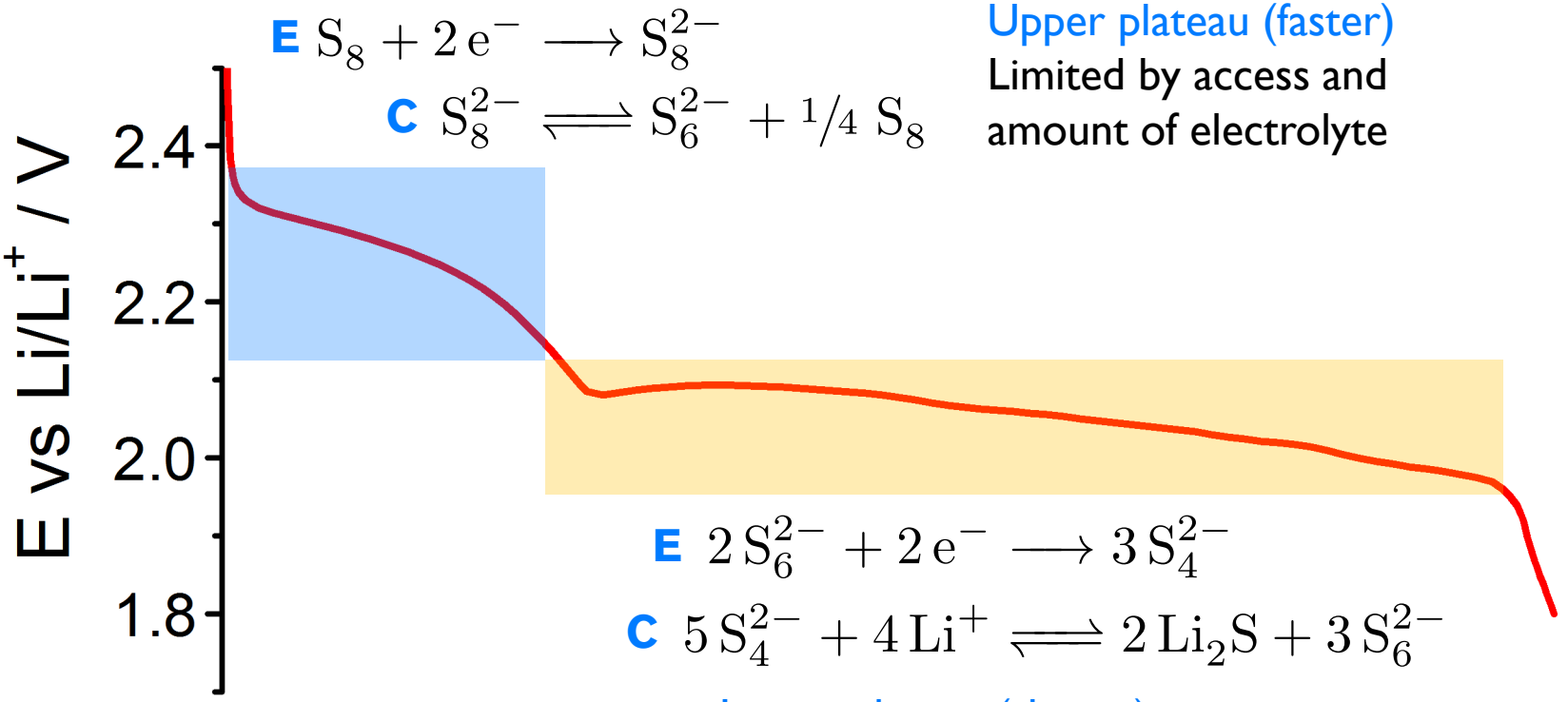
Simple recipe for high discharge capacity:
surface area and pore volume

In DME:DOL-based electrolytes…



Pore volume
for maximum sulfur loading

Surface area
for greatest utilisation, electron transfer…

Lacey et al, Electrochem. Comm. 46, 91 (2014)
Cuisinier et al, J. Phys. Chem. Letts. 4, 3227 (2014)
Lu et al, J. Phys. Chem. C 118, 5733 (2014)

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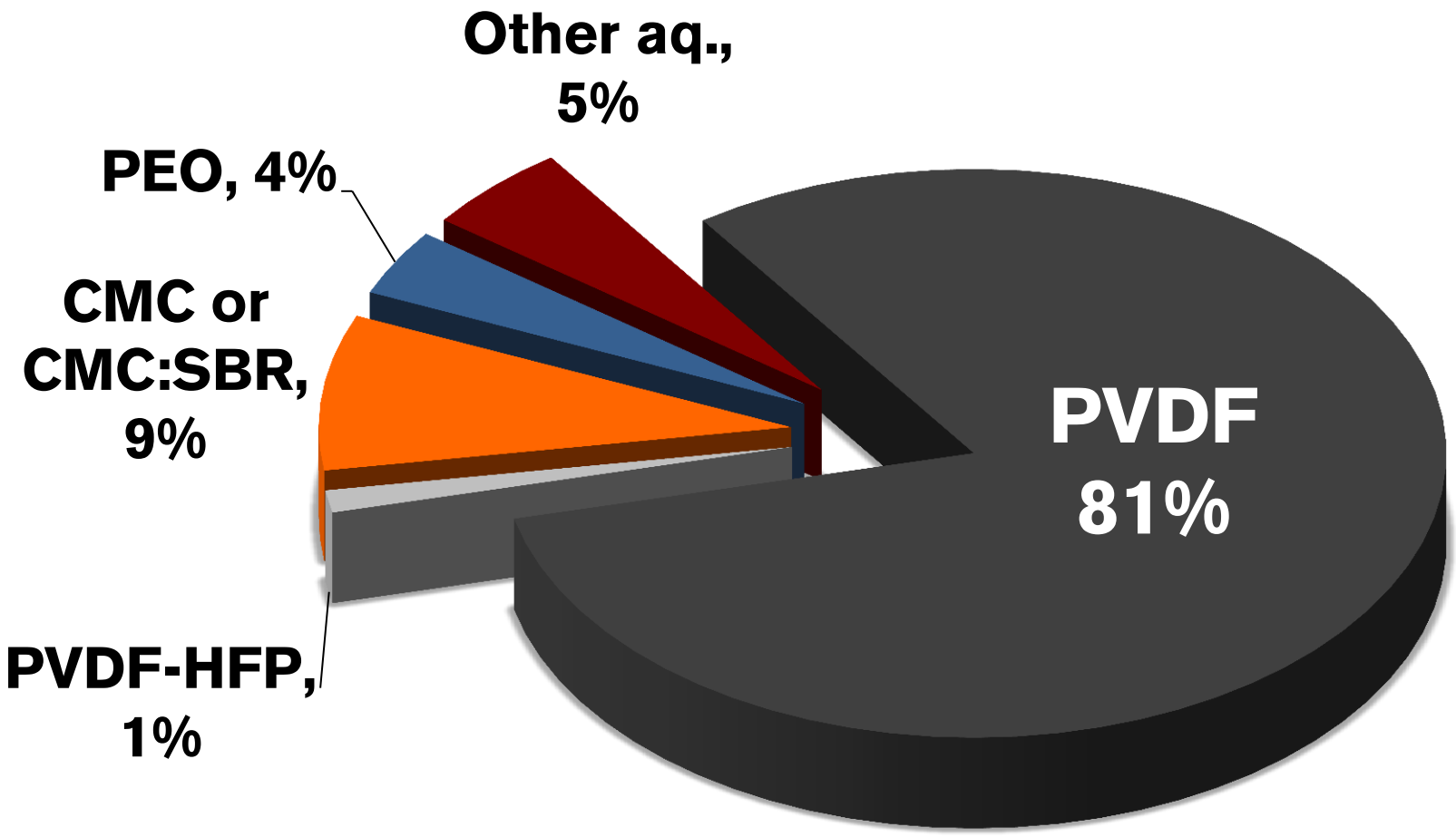
Favoured binders for Li-S



…according to 79 recent publications (2013-2014) where electrodes were casted from slurries

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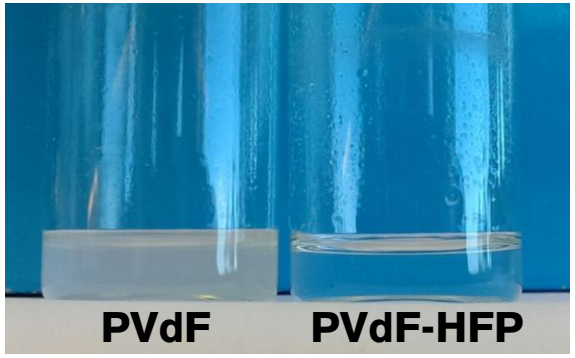
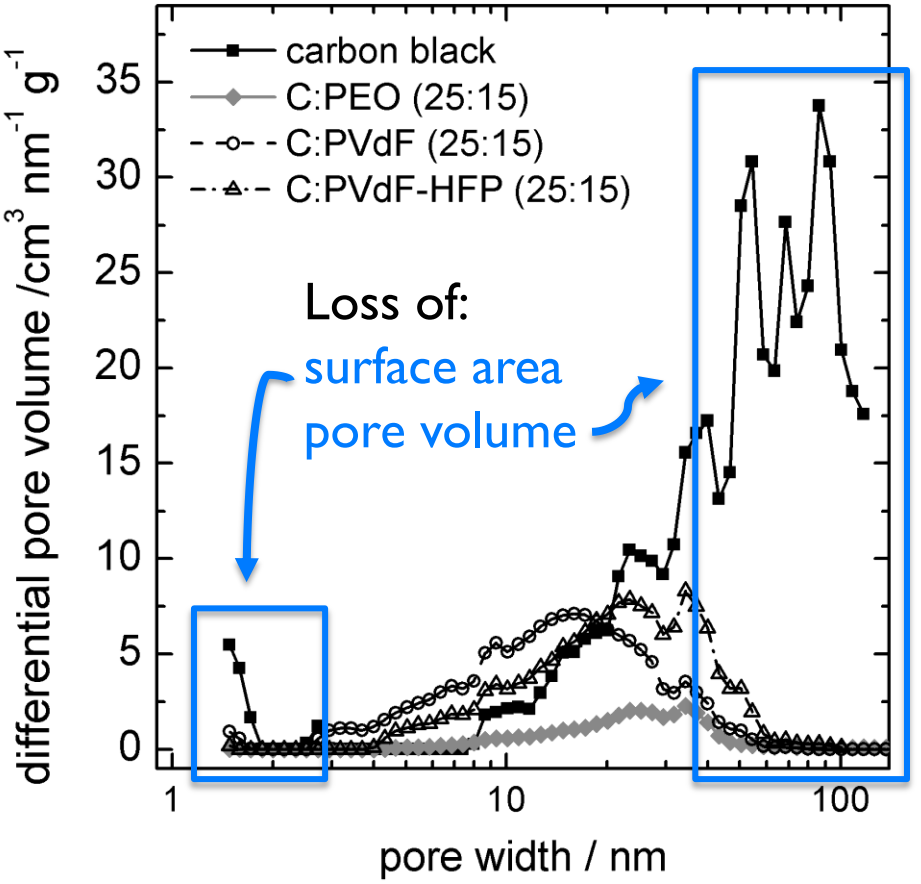
Porosity blocking in carbon black



Comparison of PVdF and PVdF-HFP in a cathode with high S.A. carbon black – only binder solubility in the electrolyte differs.

In NMP	S.A. m^2/g	pore vol $cm^3\ g^{-1}$	μpore S.A.	μpore vol
CB	1100	2.07	376	0.16
C:PVdF	175	0.53	0	0.00
C:(-HFP)	119	0.55	0	0.00
C:PEO	17	0.11	0	0.00



Pores of all sizes filled between 1.7 and 100 nm, significant reduction of S.A. and pore volume

Lacey et al, submitted

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Trend in binder "swellability"

Exaggerated cathode composition:
60% S, 25% C, 15% binder ~ 1 mg cm^{-2}
6 µL mg^{-1} (S) electrolyte, C/20 rate

1 M LiTFSI, 0.25 M $LiNO_3$, 1:1 DME:DOL
same electrolyte for all experiments

"Swellability series":

- PEO > PVdF-HFP > PVdF

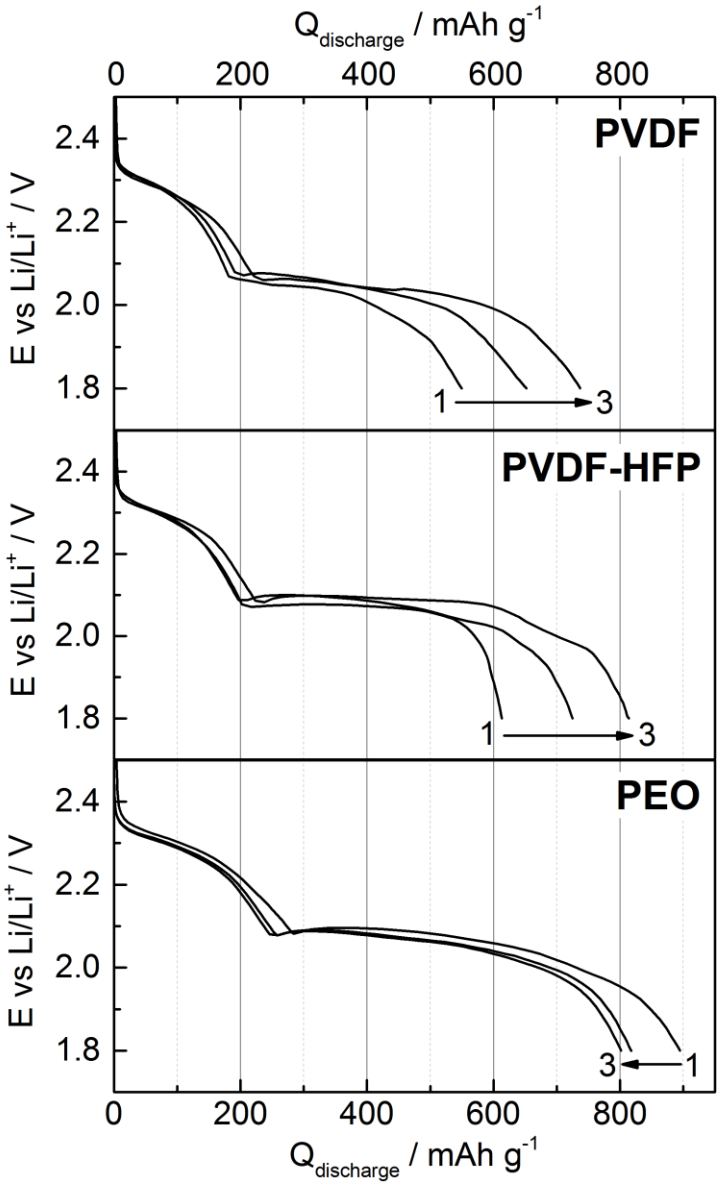
Unusual increasing capacity over first few cycles because of swelling

No observable trend in capacity with quality of coating

- Note: PVdF-HFP = Kynar Flex 2801

2025 coin cell

Lacey et al, submitted



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Effect is even more pronounced

with pre-infiltration of sulfur

Pre-infiltration of S by mixing with C and heating to 155 °C

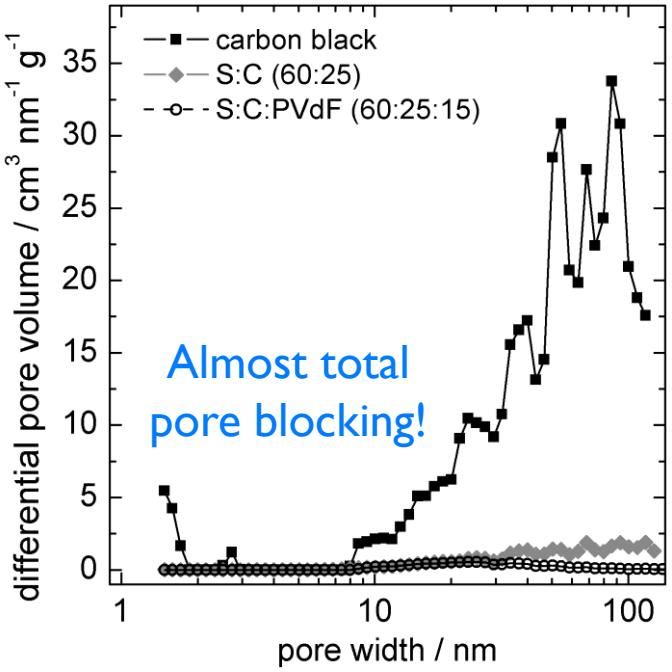
Binder fills remaining pores

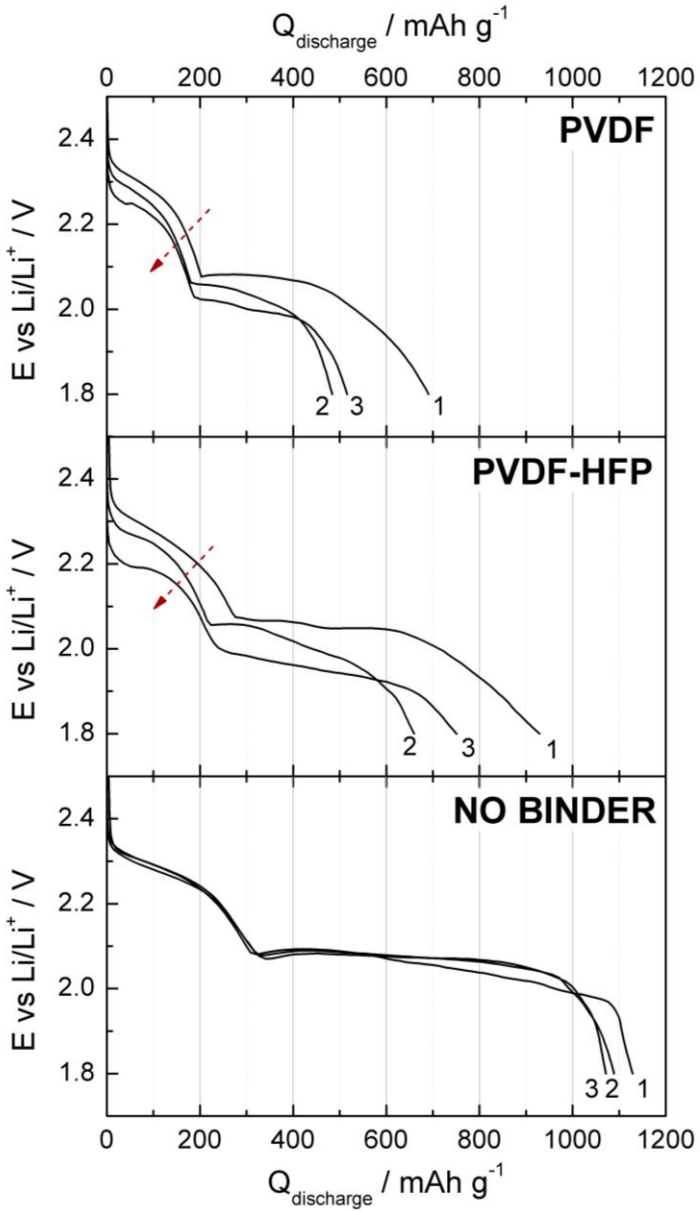
Electrochemistry even worse, except if binder is not included at all!

~1100 mAh g^{-1} with 70.6% S in cathode – extremely high!

Lacey et al, submitted

2025 coin cell





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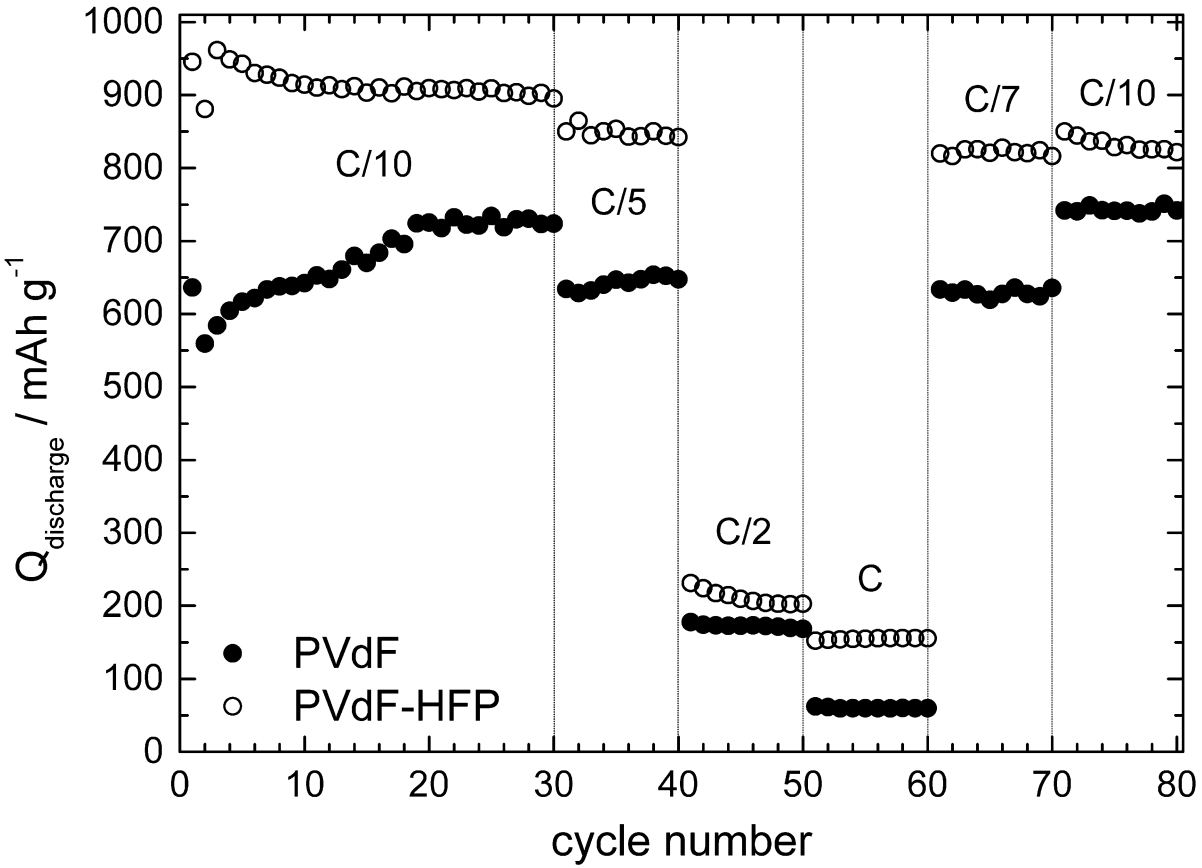
PVdF* is not a good binder for Li-S

*** Disclaimer: only guaranteed for homopolymer PVdF in DME:DOL electrolytes with high S-loading into highly porous carbon hosts prepared from slurries in NMP!**



2025 coin cell

"Realistic" composition:

86% (2:1 S:C, melt infiltr.)

7% Super P

7% binder (from NMP)

→ 57.3% w/w S in cathode

PVdF homopolymer shows consistently poorer performance compared to PVdF-HFP over extended period and over a range of rates

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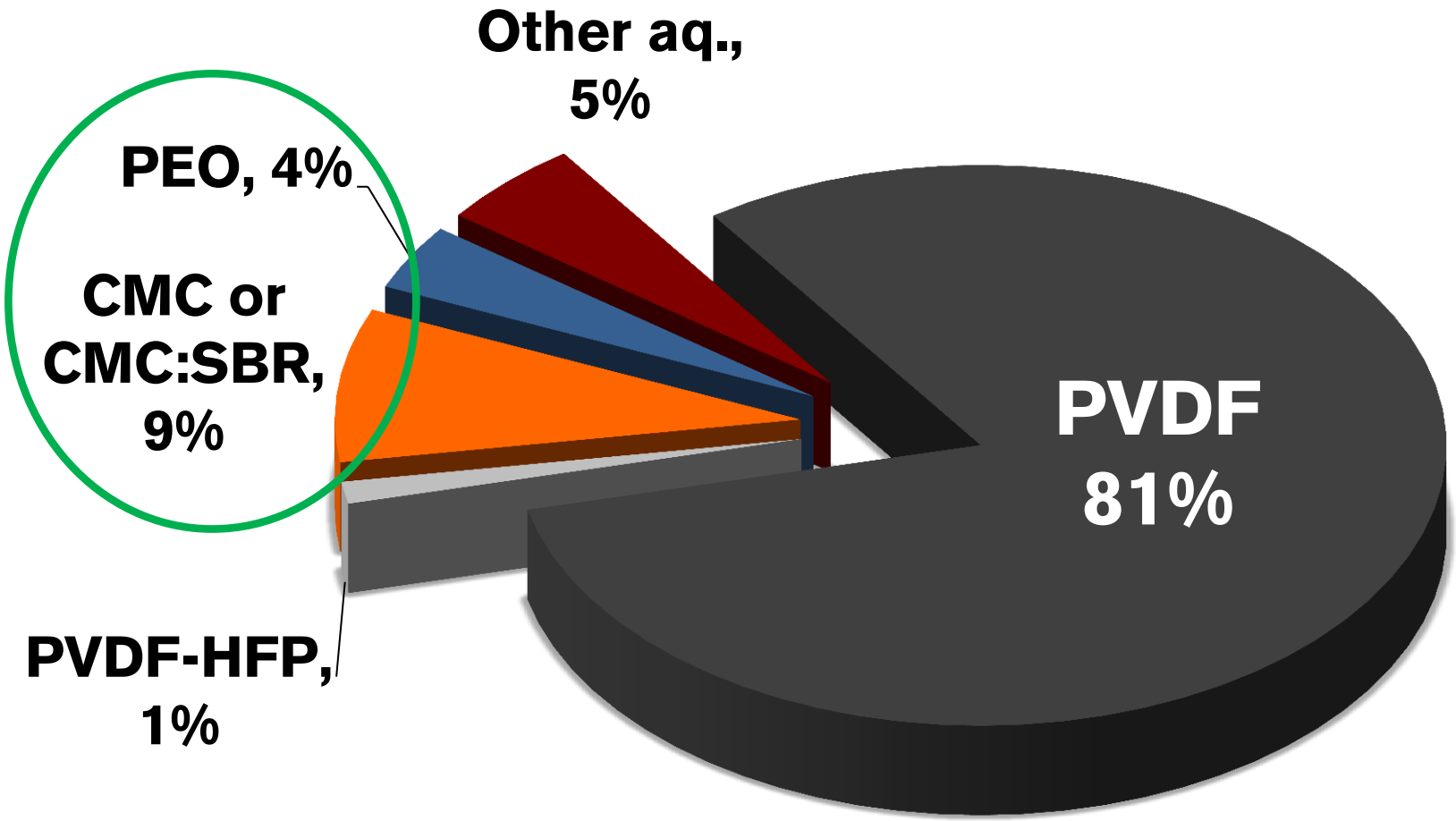
Reminder…



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CMC:SBR and PEO

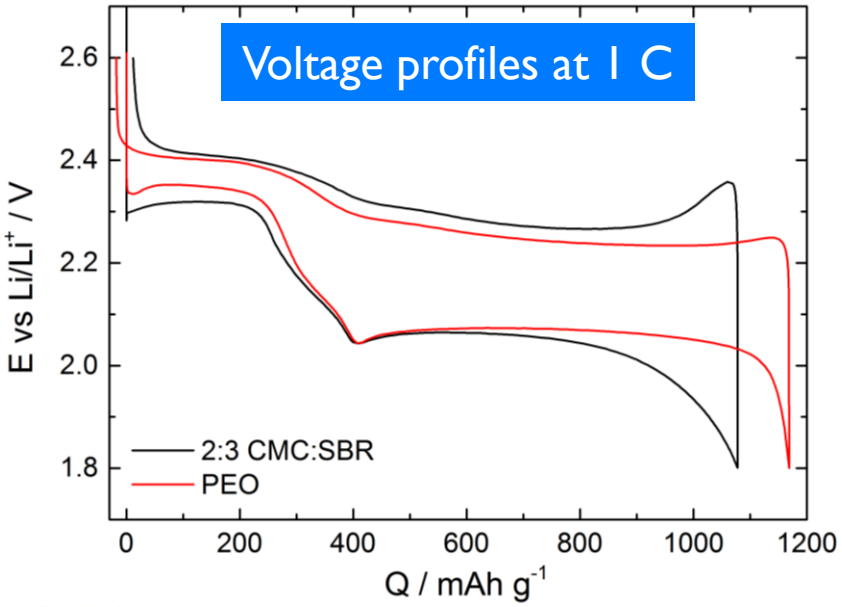
CMC:SBR is a decent alternative to PVdF

Stable binder system with reduced degree of microporosity blocking from water-based slurries

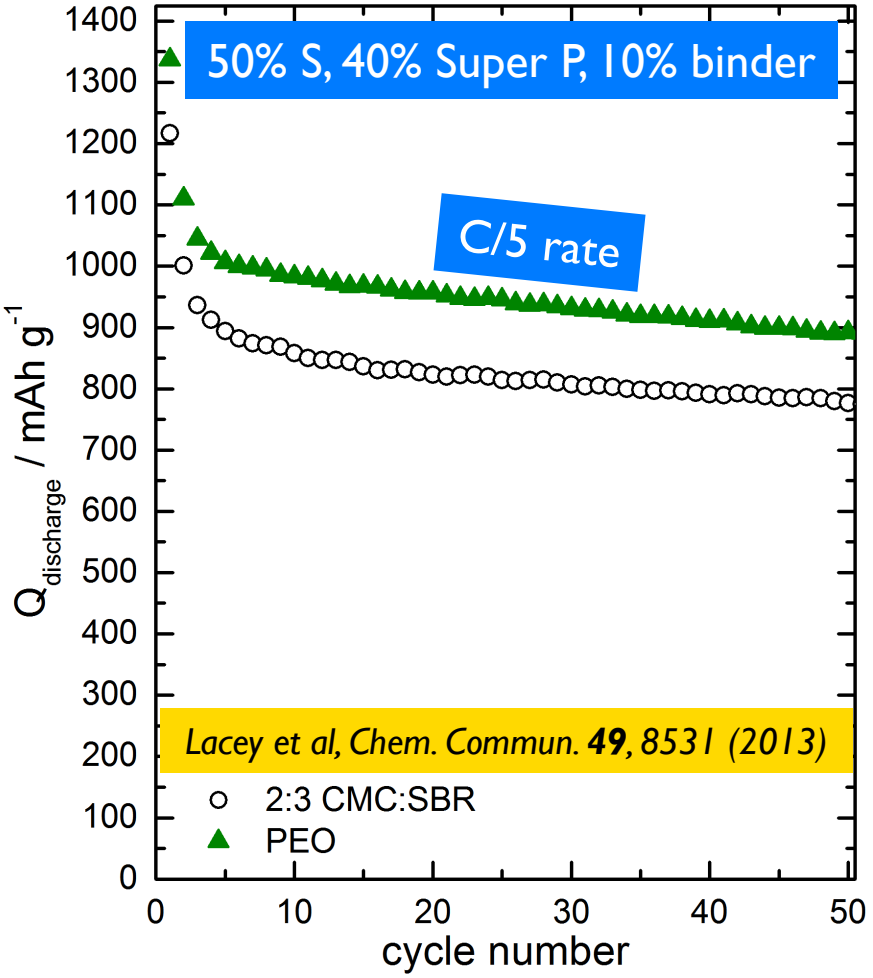
Note! Older results with different cathode composition and cell construction. Capacities and capacity fade cannot be compared between coin cell and coffee-bag cells

PEO shows better performance

Higher capacity, reduced hysteresis, lower impedance at charge/discharge limits



"Coffee-bag" cell
20 mm dia. cathodes
100 µL/mg (S) electrolyte



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Local electrolyte additive effect of PEO

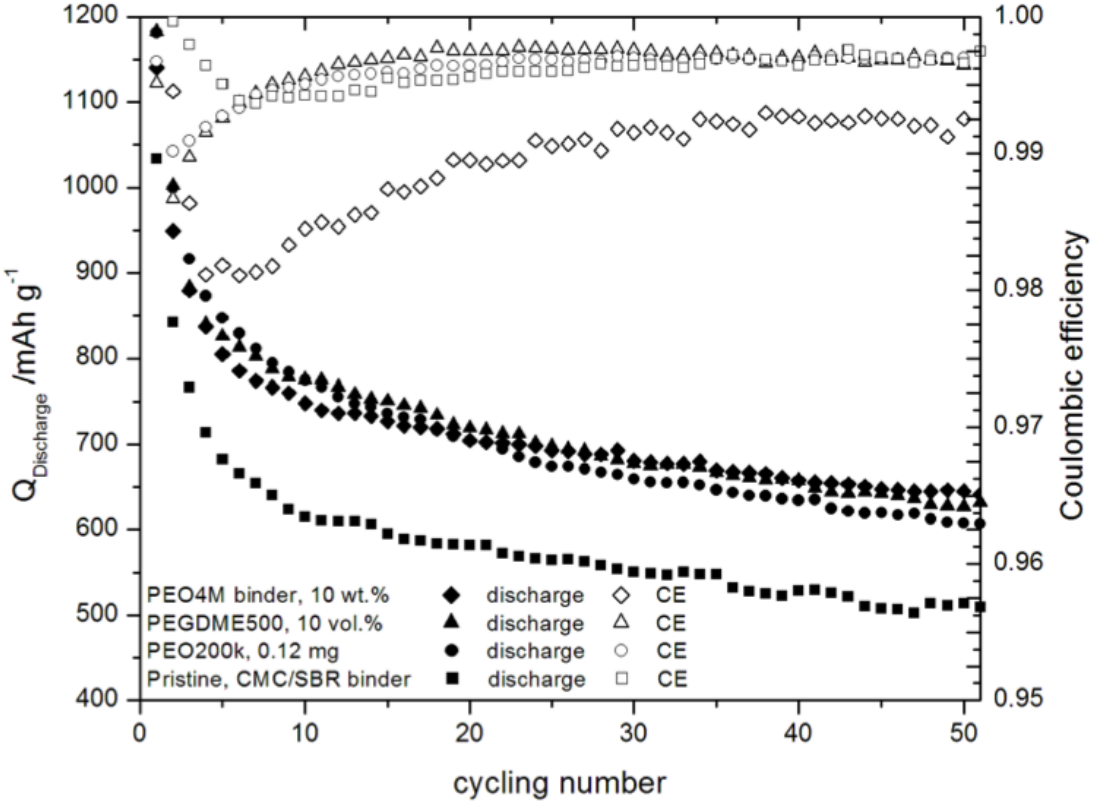
*Lacey et al, Chem. Commun. **49**, 8531 (2013) – Hot article for Aug 2014!*

Motivated by reports of PEO/PEG-based cathode "barriers" or "polysulfide traps"

Unification of several literature studies

Common beneficial effect of polyethers – as a binder, a cathode coating, or electrolyte additive

Higher capacity (sulfur utilisation) and reduced hysteresis



"Coffee-bag" cell

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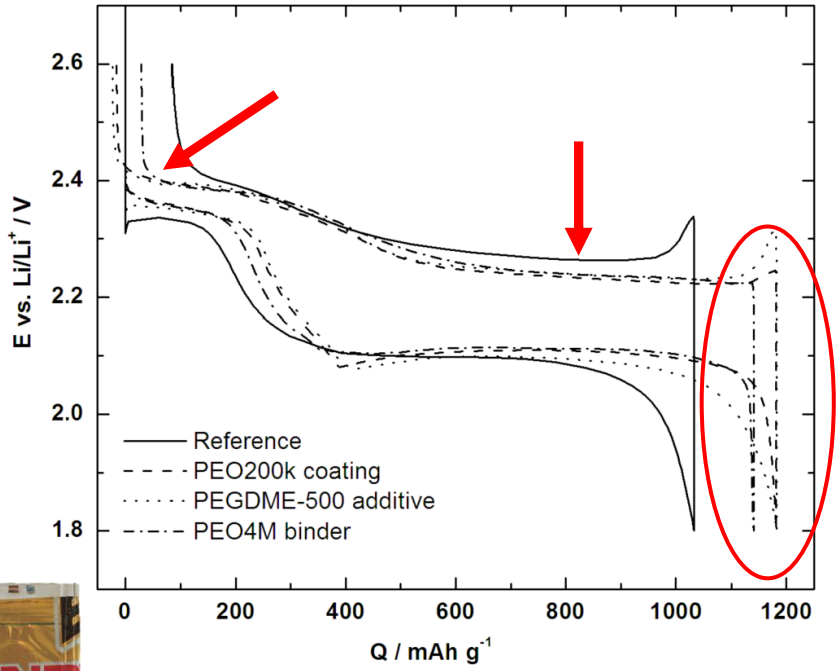
PEO as a binder: best performance

Reduced overpotential at charge/discharge limits

→ Reduced passivation of electrode surface (e.g., effect of Li^+ softening)?

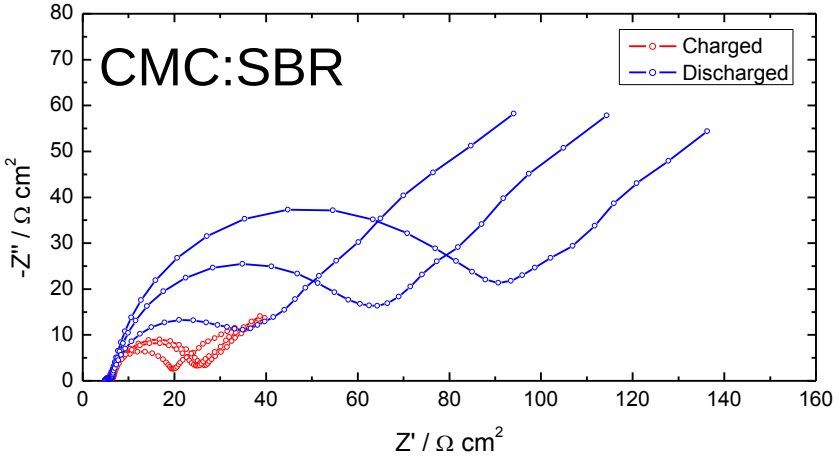
Lacey et al, Chem. Commun. ***49****, 8531 (2013)*

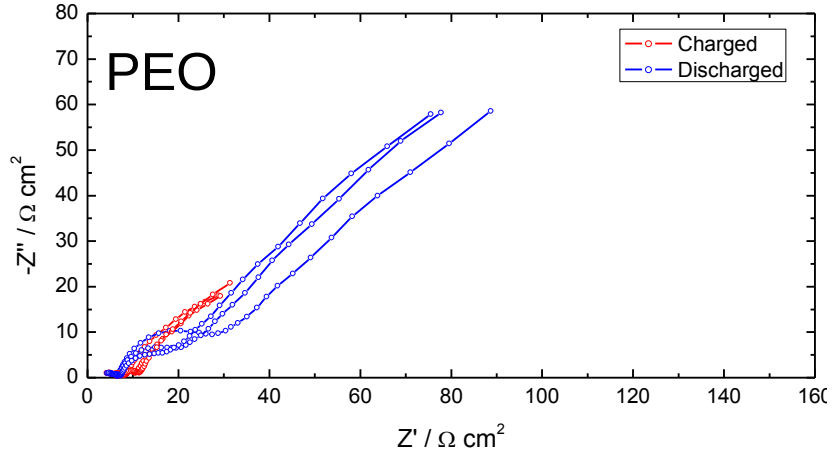


"Coffee-bag" cell

Lower impedance with PEO binder

Lacey et al, J. Power Sources ***264****, 8–14 (2014)*





However: PEO is actually not a very good binder... difficult to coat from water, poor adhesion

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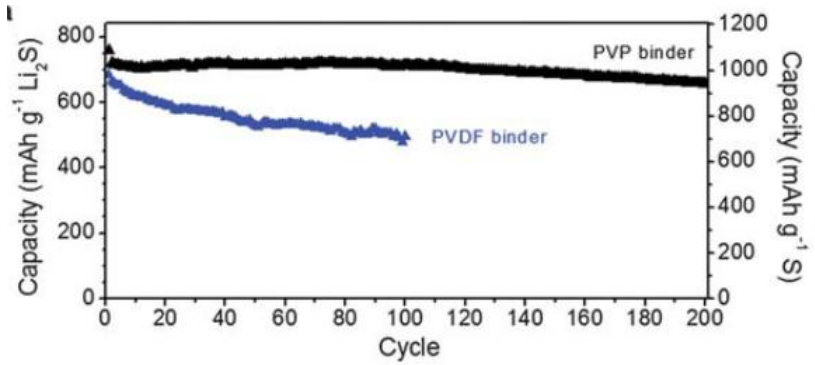
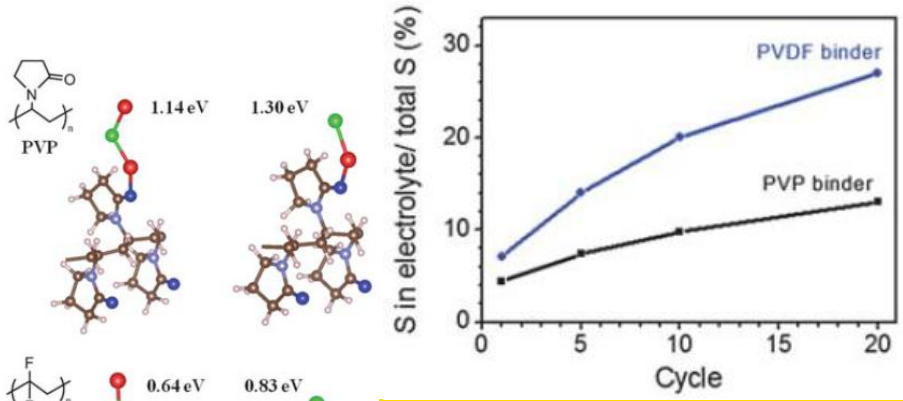
Amides/lactams

strong interactions with PS! Can it be a real barrier?

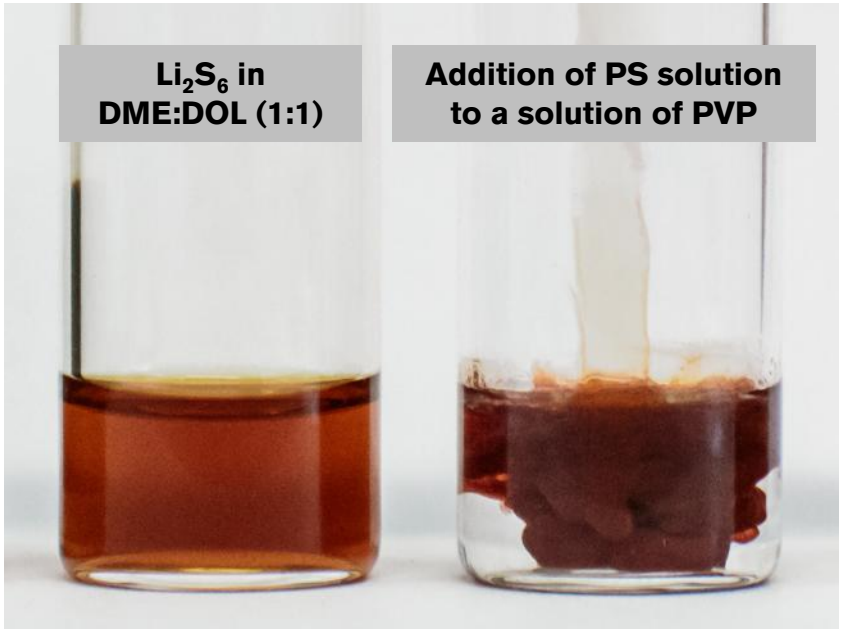




*Seh et al, Chem. Sci. **4**, 3673 (2013)*

Increased stability of Li_2S-based cathodes with PVP binder – less PS in electrolyte, therefore less active mass loss to the anode

*Lacey et al, J. Power Sources **264**, 8–14 (2014)*



Our observation – dark red, insoluble, stable complex formed between Li_2S_6 and PVP

Is the effect retained with S-based cathodes?

Can we pair it with PEO for increased capacity and stability?

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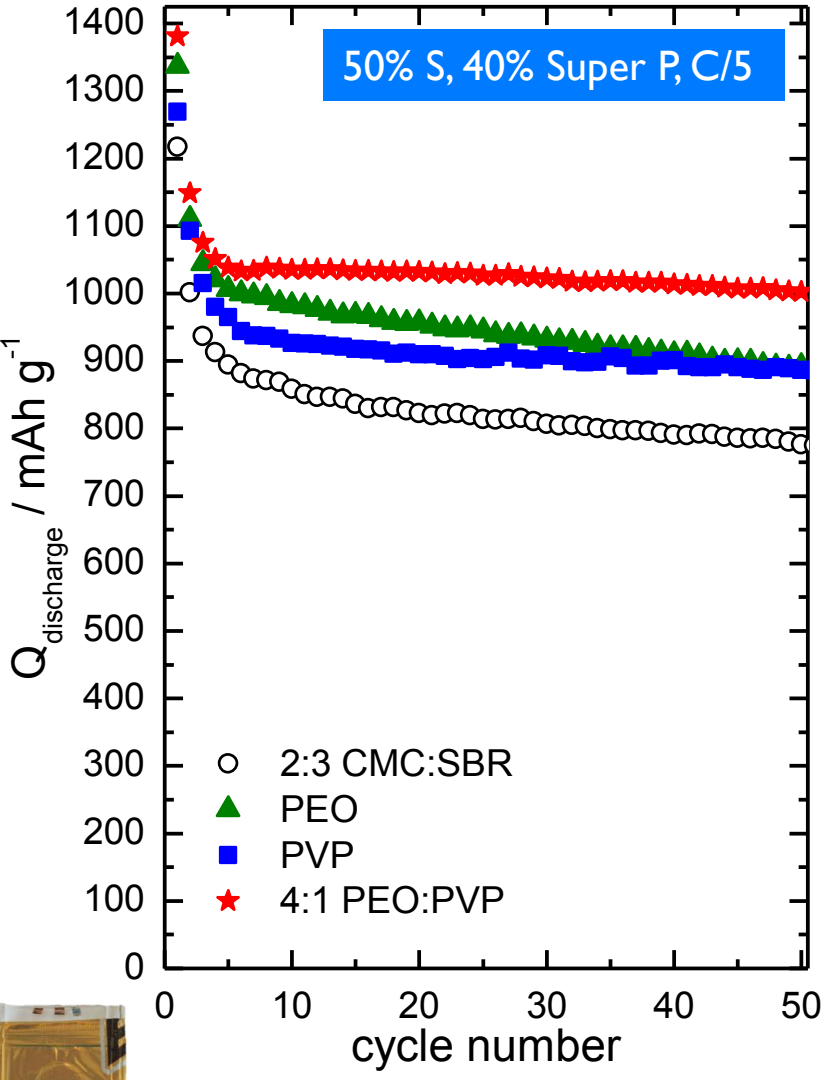
PEO:PVP

a functional, cooperative binder system



"Coffee-bag" cell

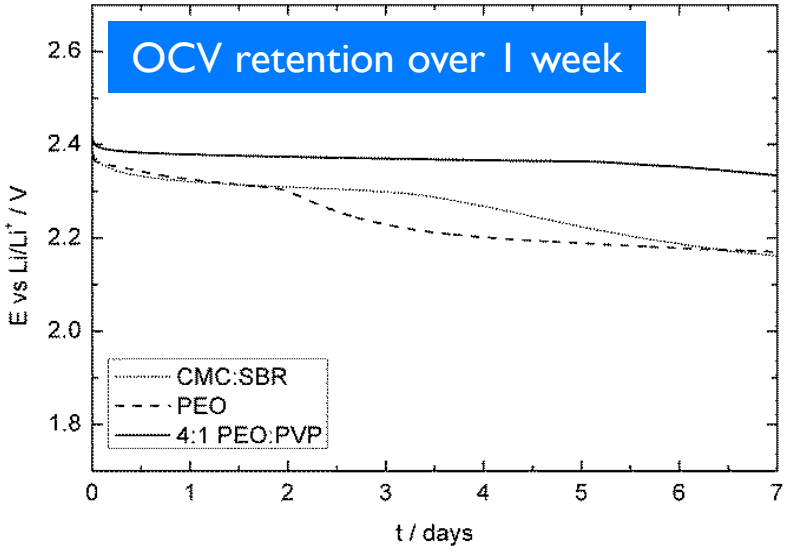
Lacey et al, J. Power Sources ***264****, 8–14 (2014)*

1000 mAh g^{-1} after 50 cycles

Optimal 4:1 mixture outperforms individual components

PEO increases capacity, PVP stabilises

PVP reduces slurry viscosity enabling water-based cathode preparation



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Very promising results with optimised PVP-based binders

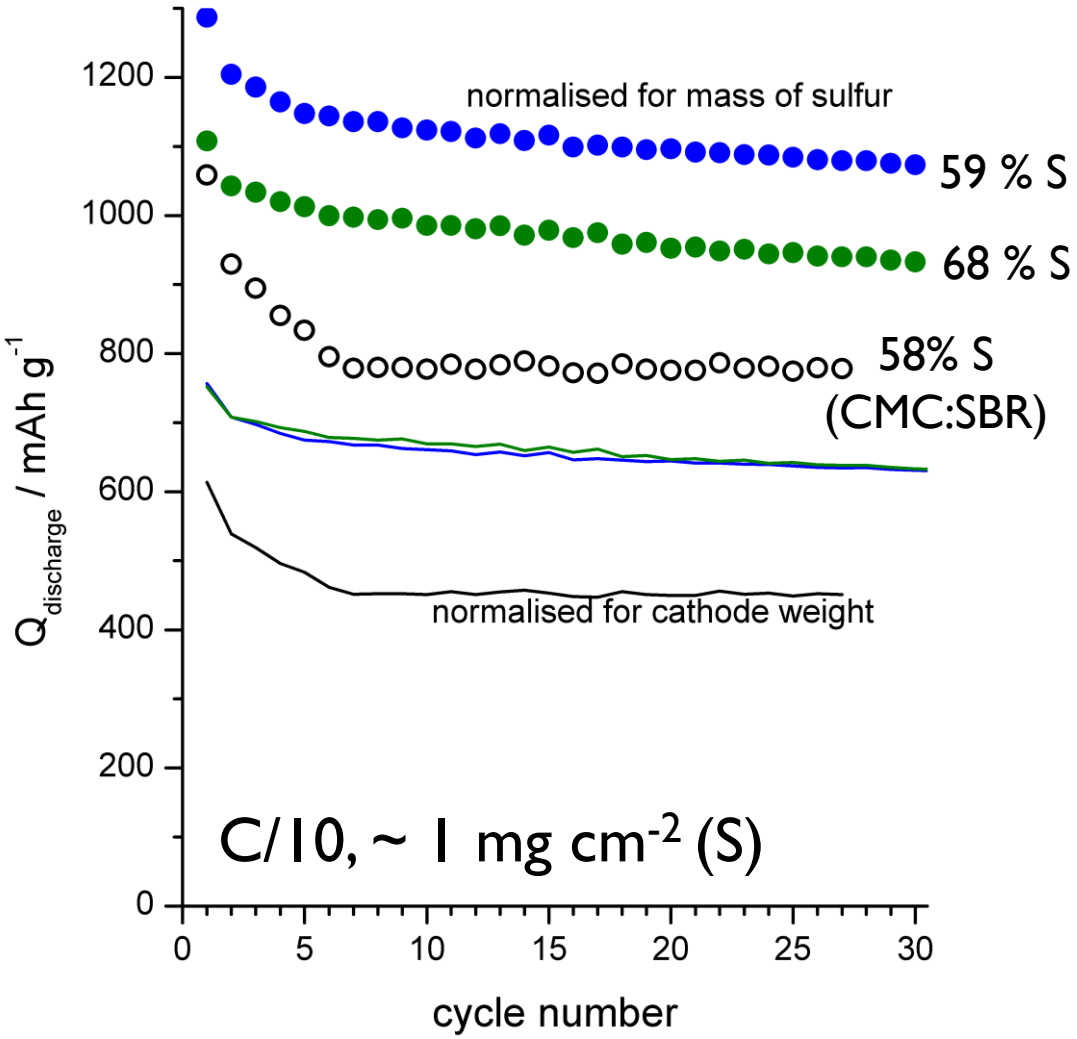
1100 mAh g^{-1}, 59% S in cathode, commercial materials only!

PVP-based binder mixtures

High capacity @ high S loading, water solubility, compatible with high S.A. carbons

No exotic materials or techniques

Optimised binder in this case matched to optimised carbon with slightly higher S.A. and pore volume



2025 coin cell

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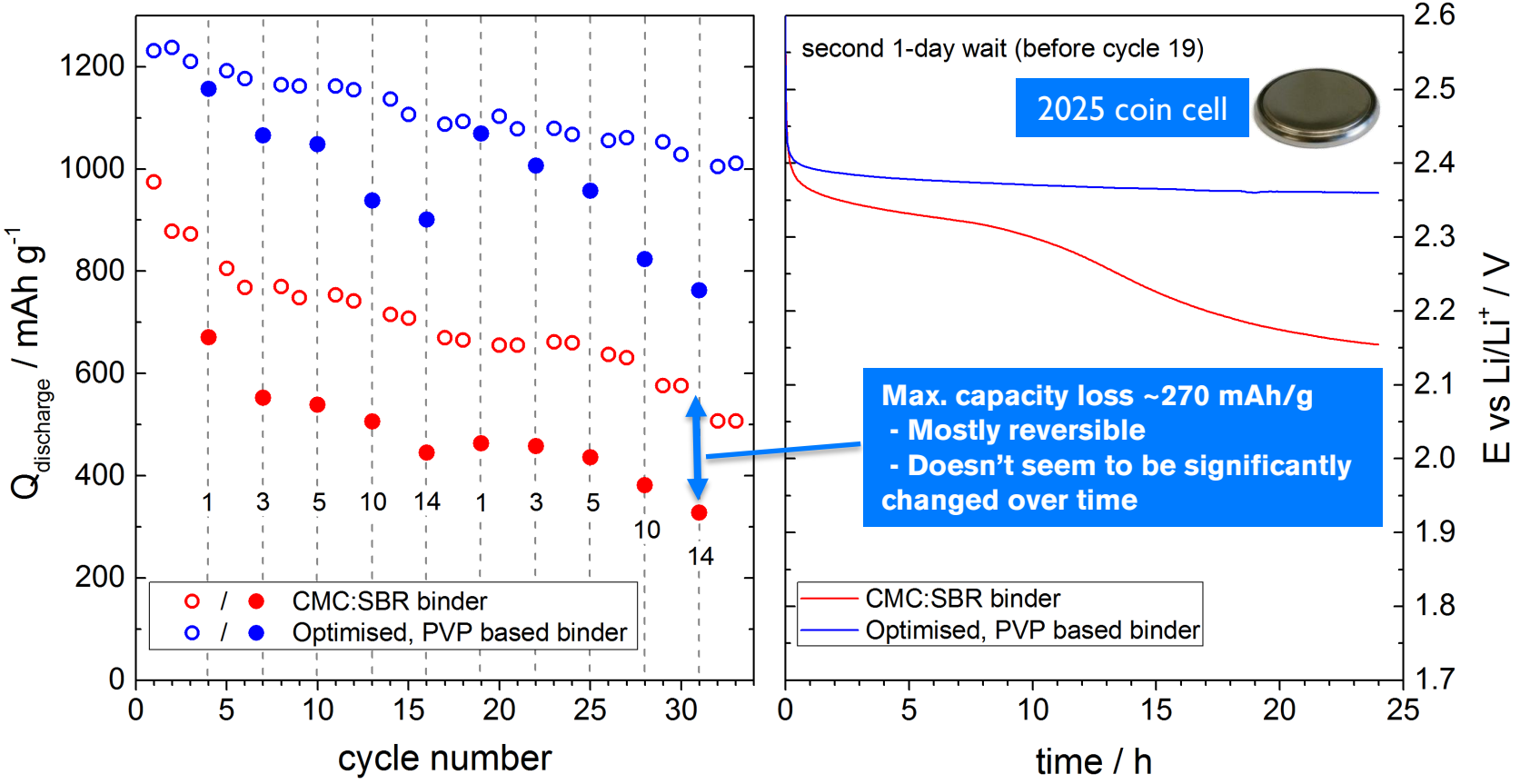
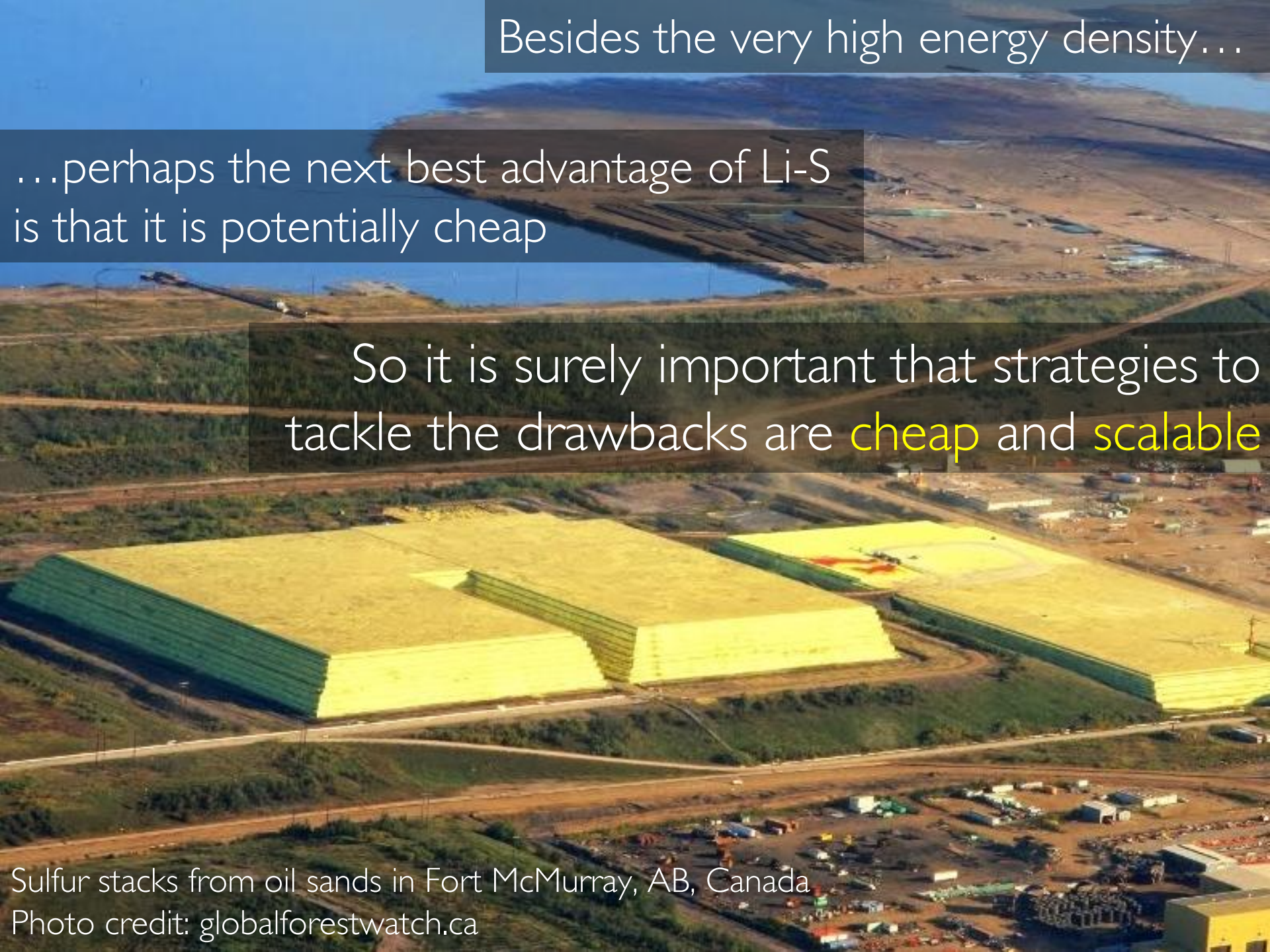
Very promising results with optimised PVP-based binders



Filled points – cycle begins after a wait at OCV – number of days indicated by number

Rate of self-discharge clearly slowed by PVP binder

With optimised carbon/binder – double capacity after 3 months!



Sulfur stacks from oil sands in Fort McMurray, AB, Canada
Photo credit: globalforestwatch.ca

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Conclusions

- The binder can be considered as a functional, local electrolyte additive
- Polyethers can be used to increase capacity, PVP can be used to stabilise capacity
  - Can investigate cooperative and water-soluble binder combinations based on this concept
- Certain binder/solvent combinations can be detrimental to performance – PVdF/NMP is a notable example
- Self-discharge is still a considerable problem with this system which deserves more attention

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Thank you for your attention!

Kind acknowledgements:

- *Martin Oschatz, TU Dresden*
- *Dr Martin Cadek, Orion Engineered Carbons GmbH*
- *Era Net Transport project "MaLiSu"*
- *Vinnova, Sweden*

For further information:

The effect of PEO:

Lacey et al, Chem Commun. 49, 8531 (2013)

PEO:PVP binder:

Lacey et al, J. Power Sources 264C, 8 (2014)

Porosity blocking:

Lacey et al, in submission

Our poster – a Li anode study (s05-054)

Before it gets taken down this evening!

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