



## Choosing the cathode binder:

### How much difference can it make?

#### Matthew J. Lacey

Fabian Jeschull, Kristina Edström and Daniel Brandell

Department of Chemistry – Ångström Laboratory, Uppsala University

matthew.lacey@kemi.uu.se





http://www.iws.fraunhofer.de/malisu



#### The target:

Optimisation of carbon structure for energy density and stability

Polymer materials/electrolyte additives for redox shuttle/self-discharge suppression

Anode stabilisation, cell balancing

Prototype cell of 400 Wh/kg (3 mg (S) cm<sup>-2</sup>, 60% S in cathode, 1 Ah g<sup>-1</sup> (S))



### Why binder? Why would it matter?

Slurry casting: convenient existing process using active material, binder and other additives for making stable composite electrodes

But, compared to Li-ion, we think the binder in a Li-S electrode can be significant in the following ways:

Pore blocking: i.e., inaccessibility of surface area/pore volume → reduced capacity, rate capability

Functionality: beneficial interactions with intermediates (or even end products?)



## **Experimental overview**

 $R = H \text{ or } CH_2CO_2H$ 

**Binders:** 

PVdF (Aldrich)

PVdF-HFP (Kynar FLEX 2801)

PEO

(Aldrich, M<sub>w</sub>~4M)

(Leclanché, Targray)

PVP (Aldrich, M<sub>w</sub> ~360k)

'n

:SBR

Two types of cell:



2025 coin cell

"Coffee-bag" pouch cell

**Electrolyte:** 

1 M LITFSI, 0.25 M LINO<sub>3</sub>, DME:DOL 1:1

### Simple recipe for high capacity: surface area, pore volume





Surface area for kinetics, delayed passivation

**Pore volume** space for discharge products

...and some sort of strategy to minimise capacity loss

# Optimised host structures are well-investigated



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## Pore filling in carbon black





	S.A. m²/g	pore vol cm <sup>3</sup> g <sup>-1</sup>	μpore S.A.	µpore vol
СВ	1100	1.76	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 surface area and pore volume.

N.B. pore volume measured up to ~75 nm pore width



# "Swellability series"

**PEO > PVdF-HFP > PVdF-HFP** 

## Exaggerated cathode composition: 60% S, 25% C, 15% binder

6 μL/mg (S) electrolyte, C/20 rate

Unusual increase in capacity in first few cycles because of swelling

No observable trend in capacity with quality of coating









# Even more pronounced effect 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<sup>-1</sup> with 70.6% S in cathode – extremely high!

Lacey et al, J. Phys. Chem. C, in press







### 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!







# **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

#### PEO shows better performance

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



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





### Background: PEO as a polysulfide trap?

Functionalised mesoporous carbon surface with PEG-250



"We believe that the effect of the PEG-functionalized surface is twofold. First, it serves to **trap the polysulphide species** by providing a highly hydrophilic surface chemical gradient that preferentially solubilizes them in relation to the electrolyte. Second, by limiting the concentration of the polysulphide anions in the electrolyte, the **redox shuttle mechanism is curtailed to a large degree**. Spin-coated PEG-20000 "barrier"







## **Alternative interpretation?**

Ji et al: "the kinetics of the last reaction step has a role in capacity limitation...There is progressively more limited accessibility of Li<sup>+</sup> ions and electrolyte to the sulphur mass towards the end of discharge because the pores become filled with insoluble  $Li_xS$  (x = 1-2)"



Fig. 6. First cycle profile and capacity fading of a sulfur electrode in ether-based electrolytes (1 mol L<sup>-1</sup> LiTFSI), with a varying glyme chain length. All solvents were mixed with DIOX in a 50/50 volume ratio. The capacities are given in mAh g<sup>-1</sup> of sulfur material.

C. Barchasz, J.-C. Leprêtre, S. Patoux, F. Alloin, Electrochim. Acta 89 (2013) 737.



Barchasz et al: "PEGDME solvents proved to be key components for Li/S electrolytes, as **preventing the fast electrode passivation** and extending the length of the second discharge plateau."



Ji et al: "Deposition of insoluble sulphur species on the surface of the Li electrode and formation of irreversible  $Li_2S$  on the [PEG-modified] cathode surface are strongly inhibited"



### Local electrolyte additive effect of PEO

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



Motivated by reports of PEO/PEGbased 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



### PEO as a binder: best performance

Reduced overpotential at charge/ discharge limits

→ Reduced passivation of electrode surface (e.g., effect of Li<sup>+</sup> softening)?



Lower impedance with PEO binder



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

## **Amides/lactams**

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



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

Increased stability of Li<sub>2</sub>S-based cathodes with PVP binder – less PS in electrolyte, therefore less active mass loss to the anode Is the effect retained with S-based cathodes? Can we pair it with PEO for increased capacity and stability?

## Lacey et al, J. Power Sources 264, 8–14 (2014) PEO:PVP

#### a functional, co-operative binder system



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1000 mAh g<sup>-1</sup> after 50 cycles Optimal 4:1 mixture outperforms individual components PEO increases capacity, PVP stabilises PVP reduces slurry viscosity enabling water-based cathode preparation





# PVP – high impedance on its own, kept low in combination with PEO



# To answer a question from earlier: self-discharge reduced, rate capability preserved



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# Very promising results with optimised PVP-based binders

1100 mAh g<sup>-1</sup>, 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





# 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!

#### Besides the very high energy density...

...perhaps the next best advantage of Li-S is that it is potentially cheap

# So it is surely important that strategies to tackle the drawbacks are cheap and scalable

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



## 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



## Thank you!

#### 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, J. Phys. Chem. C, DOI: 10.1021/jp508137m

#### Correspondence to: matthew.lacey@kemi.uu.se