A robust, water-based, functional binder framework for high-energy Li-S batteries

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Binders: properties → function

**“Inswellable”**

- The binder is either not swollen or only very slightly by the electrolyte
- E.g., PAA, CMC, conducting polymers
- Layer covering the electrode surface?* Or fibres holding particles together

**“Swellable”**

- The binder is swollen, maybe significantly, by the electrolyte
- E.g., PVdF(-HFP)**, PEO, PVA
- Is at the electrolyte-electrode interface, but also becomes a part of the electrolyte system

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* Sulfur | LiTFSI, DME:DOL | Graphite cell with PAA-protected graphite electrode
Jeschull, Brandell, Lacey, *Chem. Commun.* 2015, 51, 17100

** Porosity blocking by PVdF(-HFP) in porous carbons for Li-S
Lacey, Jeschull, Edström, Brandell, *J. Phys. Chem. C* 2014, 118, 25890
Many common binders (e.g. PVdF, PVdF-HFP block pores in carbon black and affect sulfur utilisation according to the solubility/swellability of the binder.

Lacey, Jeschull, Edström, Brandell, J. Phys. Chem. C 2014, 118, 25890
4:1 PEO:PVP

improved capacity and capacity retention, and reduced self-discharge

PEO

\[ \text{M}_w \sim 4 \text{M} \]

Swells, locally changes solvent system to the benefit of PS solubility/kinetics

PVP

\[ \text{M}_w \sim 360 \text{k} \]

Is soluble, but forms an insoluble complex with \( \text{Li}_2\text{S}_x \) – improves capacity stability, reduces self-discharge

Lacey, Jeschull, Edström, Brandell, Chem. Commun. 2013, 49, 8531
J. Power. Sources 2014, 264, 8
Our progress with the PEO:PVP binder system between 2013 and 2015

Electrolyte: LiTFSI/LiNO₃/DME:DOL

17 Wh kg⁻¹
236 Wh kg⁻¹ (projected cell-level energy density based on materials ratios)

2013
~0.5 - 0.8 mg_S cm⁻², 50% S,
Super P carbon black, 100 µL mg_S⁻¹

2015
~2 - 4 mg_S cm⁻², 65% S,
Ketjen Black EC-600JD, 6 µL mg_S⁻¹,
<200% anode excess
4:1 PEO:PVP

a suitable binder for water-based casting of highly porous carbon black-based electrodes (with some small modifications)

- 65:21 S:Ketjen Black, melt-infiltrated
- + 3.5% CNF, + 3.5% Super C65, 7% binder
- 5-10% EtOH in slurry
- Graphite-coated Al foil

Typical electrode at 2 mg_s cm^{-2}. Cracking begins to appear ~3 mg_s cm^{-2}

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, submitted.
Electrodes with CMC:SBR binder at 2 mg S cm\(^{-2}\) are **outperformed** by PEO:PVP electrodes up to at least 5.3 mg S cm\(^{-2}\)

*Rate: 167.2 mA g\(_S\)\(^{-1}\) (“C/10”)*

**Grey points: CMC:SBR**

- Capacity up to 4.5 mAh cm\(^{-2}\)
- Coulombic efficiency increased, stability much improved
- Cycle life problematic at high loading because of the Li metal negative

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, *submitted.*
Lower electrode resistance with PEO:PVP

Internal resistance here is sum of ohmic + kinetic resistances, for both electrodes

ICI method for following resistance in batteries: Lacey, ChemElectroChem 2017, in press
The “framework”

- PEO
- PVP
- PDMA
- PNIPAM
- POZ

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, submitted.
Substitution of PEO or PVP for another polymer bearing the same functional group very closely preserves the electrochemical performance.

\[
\text{\begin{align*}
PPEGMA & \quad \quad \text{POZ} \\
PDMA & \quad \quad \text{PNIPAM}
\end{align*}}
\]

...Despite differences in physical properties! (PPEGMA is a liquid, amide alternatives gave more brittle electrodes)

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, submitted.
Cycle life should be interpreted carefully - limited to 100-120 cycles in these experiments

+ effect of Li electrode*, LiNO₃ consumption…

Lacey, ChemElectroChem 2017, in press

* Lacey, Edström, Brandell, Chem. Commun. 2015, 51, 16502
Mechanical integrity of electrodes certainly is a factor in cycle stability – but one of many

**Effect of calendering**

- Electrodes calendered from ~0.6 g cm\(^{-3}\) to ~0.9 g cm\(^{-3}\) (sulfur loading ~2 mg\(S\) cm\(^{-2}\))

See also: Kim, C.-S., et al. *J. Power Sources*, 2013, 241, 554–559
• ~1 mg_S cm^{-2}, no S melt-infiltration for functionalised carbon

• HEP-KB w/ PEO binder shows very similar electrochemical performance to “blank” KB with PEO:PVP binder

• Supports existing evidence that PVP adsorbs at C surface and promotes

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, submitted.
Directions for future development: Wide scope for co-polymer synthesis!

Huge number of monomers and scope for copolymer synthesis

2-oxazolines

Several routes to 2-oxazolines from carboxylic acids or nitriles with various R-groups
Conclusions

- **PEO:PVP** is a suitable *water-based binder* for electrodes based on *highly porous carbon black*

- Electrochemical performance *preserved* if one polymer is swapped for a *functionally similar* one

- **Chemical functionality** more influential than electrode integrity for *sulfur utilisation & coulombic efficiency* - but mechanical integrity important on extended cycling

- Plenty of scope for future exploration in this area!
Experimental contributions

Viking Österlund
Andreas Bergfelt
Fabian Jeschull

Finance

Era-Net Transport Project “MaLiSu”
Vetenskapsrådet
Energimyndigheten
Extras
The image shows a chemical reaction involving the conversion of a molecule containing an alcohol group (OH) to a molecule with an ester group (O=O). The reaction sequence is represented by the following transformations:

1. OH group is replaced by an acetyl group (O-C=O).
2. The resulting molecule undergoes an additional reaction resulting in a fully esterified molecule.

The graph below illustrates the discharge capacity (Qdischarge) over cycle number for two different systems:

- PEO:PVP
- PEO:PNAEP

The data shows a consistent discharge capacity with slight fluctuations over multiple cycles.
Self-discharge rate is roughly halved for PEO:PVP compared to CMC:SBR.

*Cycle/wait test:* discharge capacity following an OCV period with a duration of the indicated number of days.