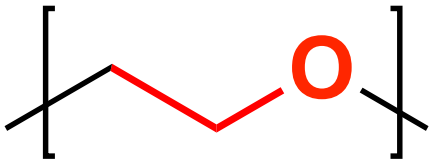
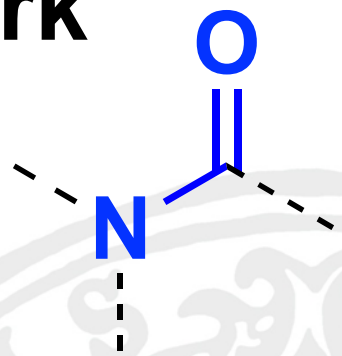
A robust,
water-based,
functional binder framework
for high-energy
Li-S batteries





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Viking Österlund, Andreas Bergfelt, Fabian Jeschull, Tim Bowden, Daniel Brandell

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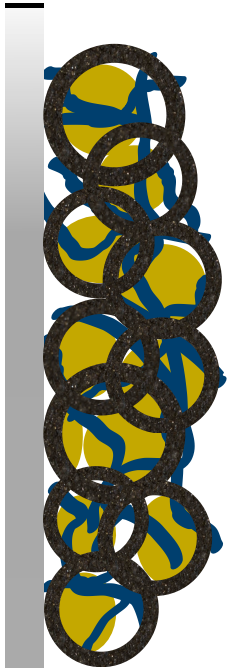
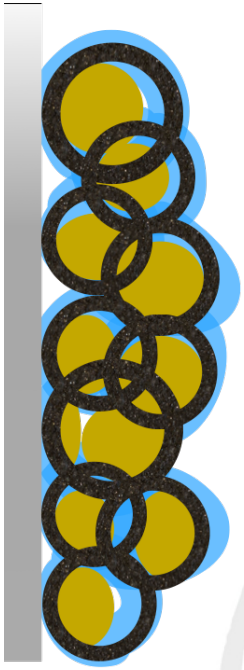
Binders: **properties → function**

"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"



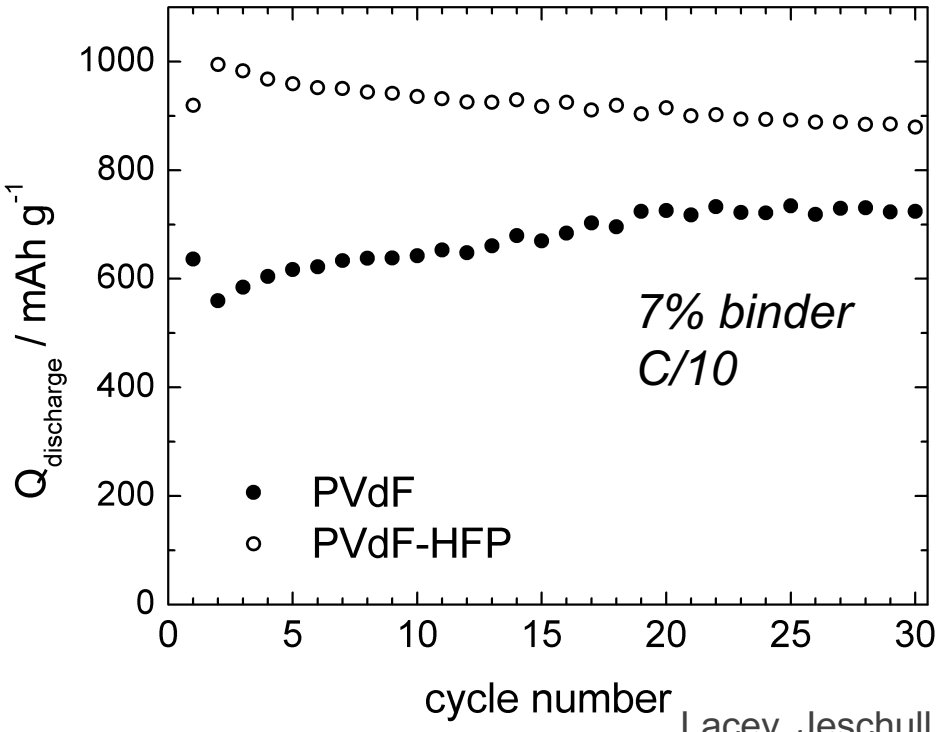
- The binder is swollen, maybe significantly, by the electrolyte
- E.g., PVdF(-HFP)**, PEO, PVA
- Is at the electrolyte-electrode interface, but also becomes *a part of the electrolyte system*

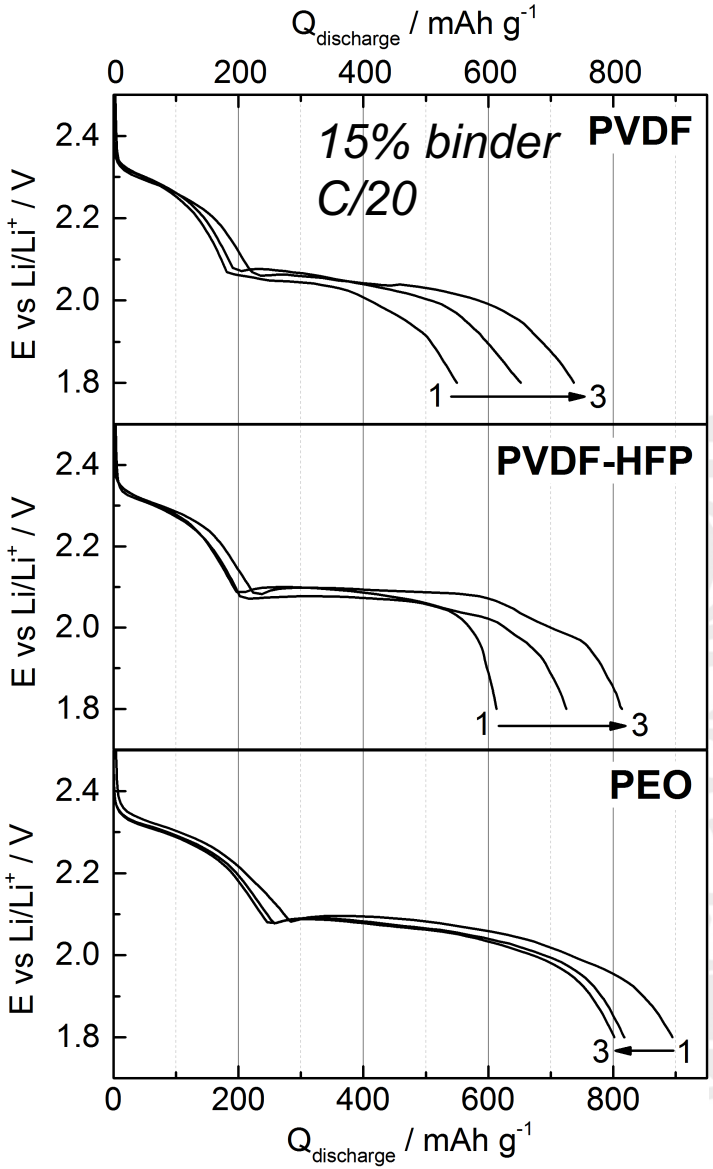
*** Sulfur | LiTFSI, DME:DOL | Graphite cell with PAA-protected graphite electrode**
Jeschull, Brandell, Lacey, *Chem. Commun.* 2015, 51, 17100
Fabian Jeschull, PhD Thesis, 2017 (diva-portal.org)

** **Porosity blocking by PVdF(-HFP) in porous carbons for Li-S**
Lacey, Jeschull, Edström, Brandell, *J. Phys. Chem. C* 2014, 118, 25890

The binder can be very important!

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

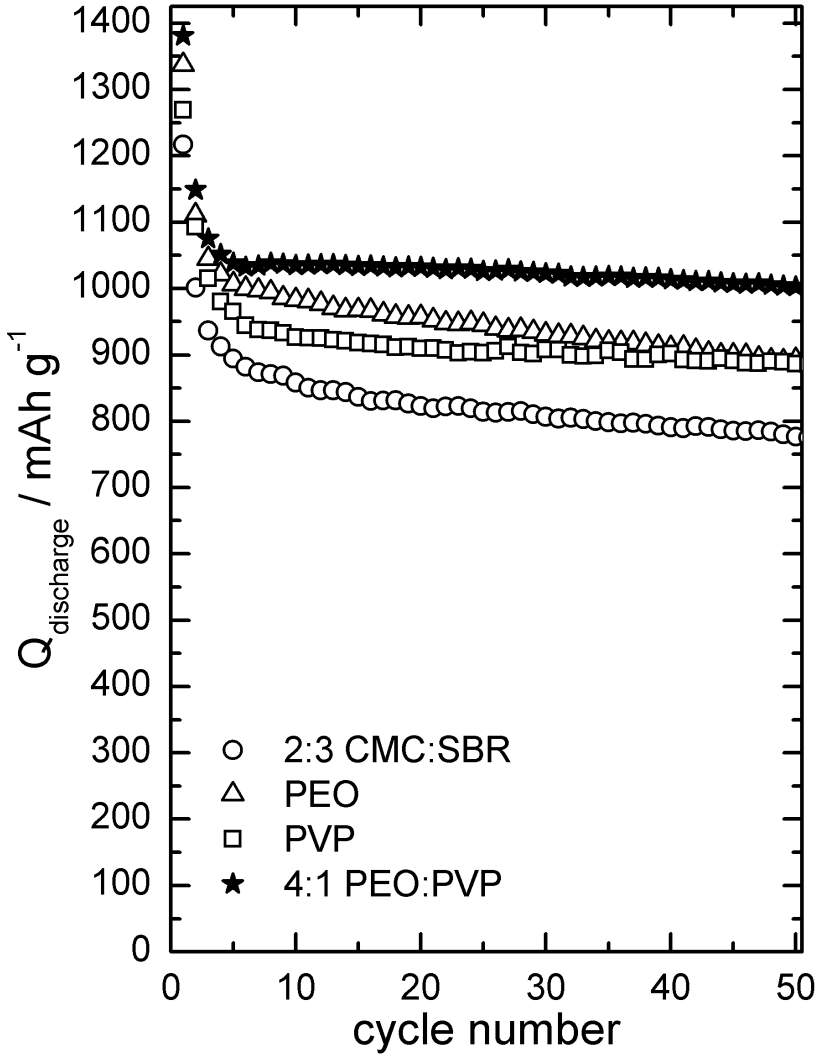


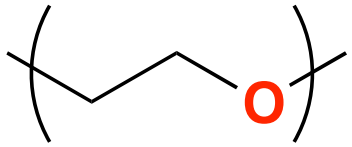


Lacey, Jeschull, Edström, Brandell, *J. Phys. Chem. C* 2014, 118, 25890

4:1 PEO:PVP

improved capacity and capacity retention, and reduced self-discharge

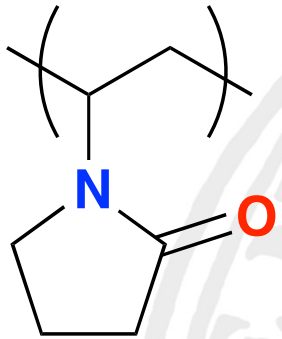




PEO

M_w ~ 4M

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



PVP

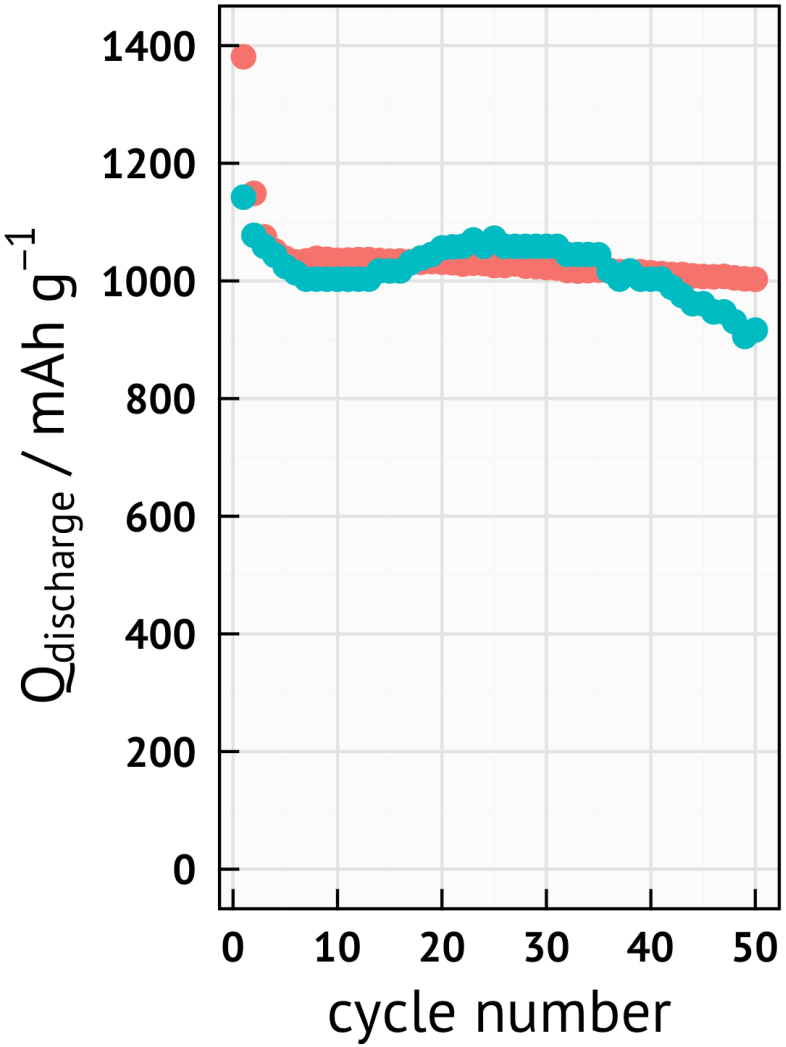
M_w ~ 360k

Is soluble, but forms an insoluble complex with Li_2S_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/$LiNO_3$/DME:DOL

17 Wh kg^{-1}
236 Wh kg^{-1}

(projected cell-level energy density based on materials ratios)

2013

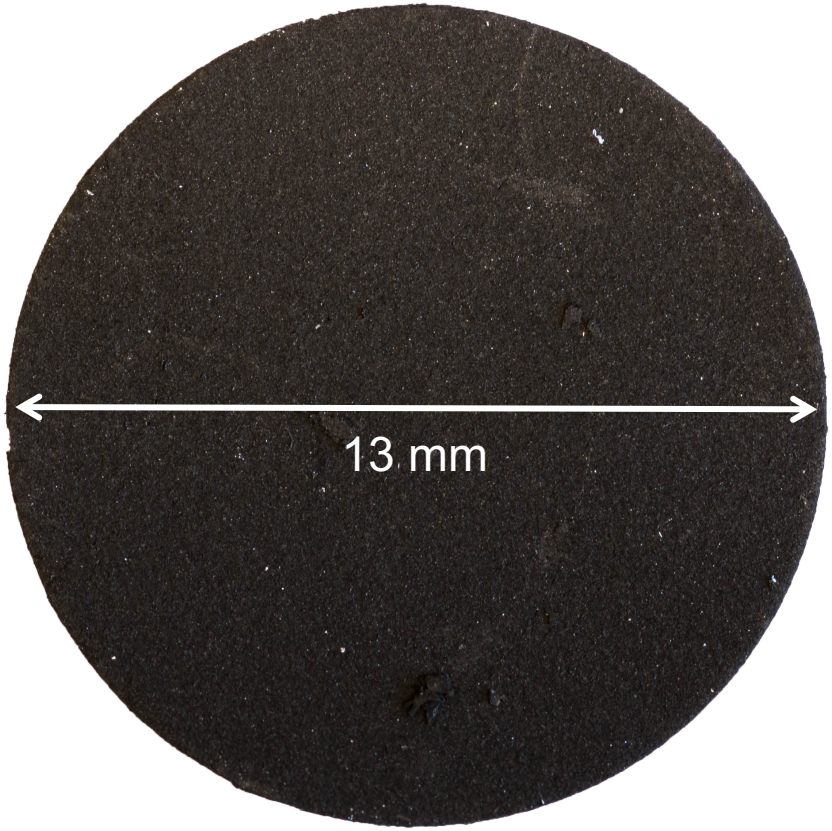
~0.5 - 0.8 mg_S cm^{-2}, 50% S,
Super P carbon black, 100 µL mg_S^{-1}

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)

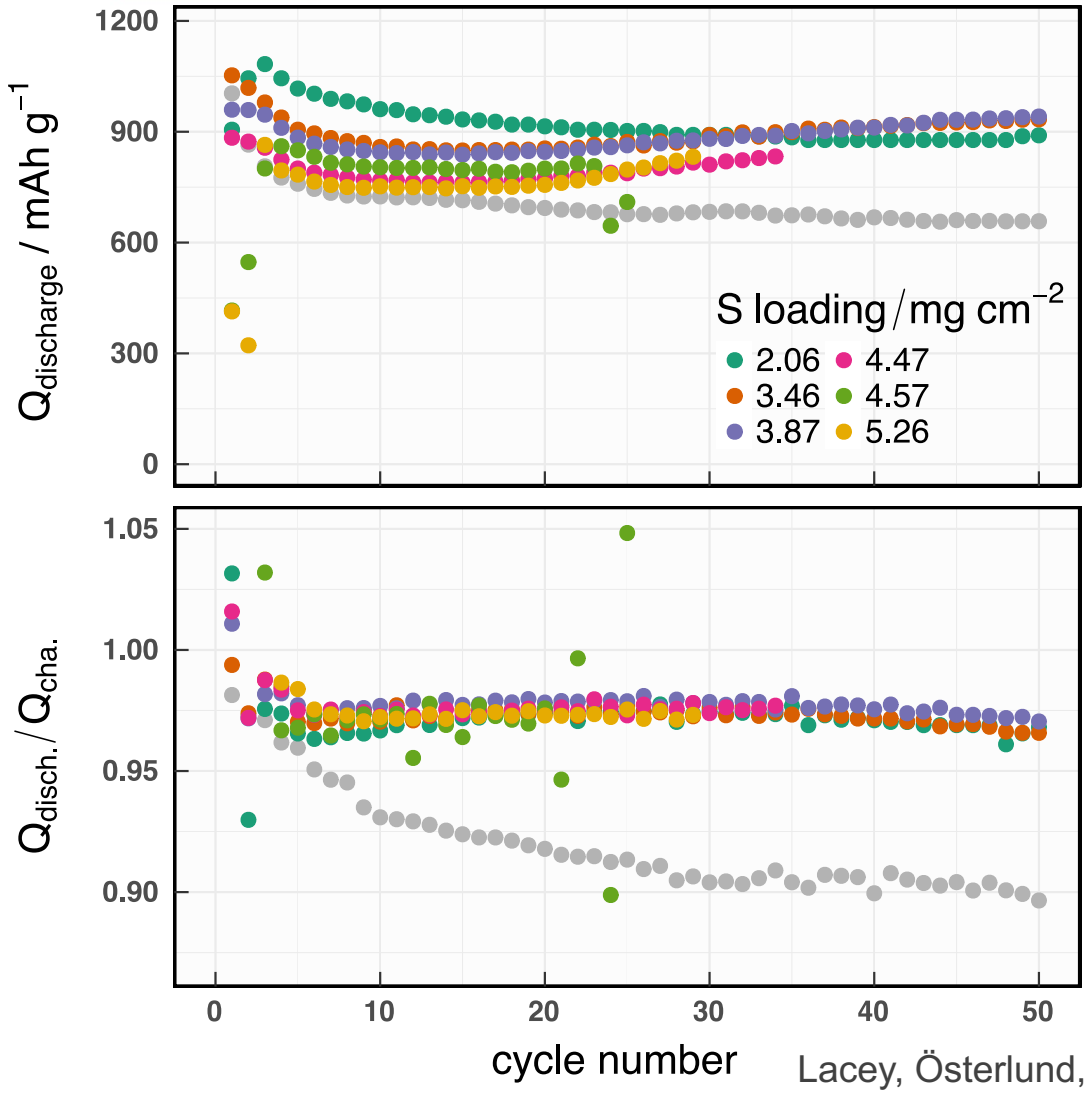


Typical electrode at 2 mg_S cm^{-2}.
Cracking begins to appear ~3 mg_S cm^{-2}

- 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

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")

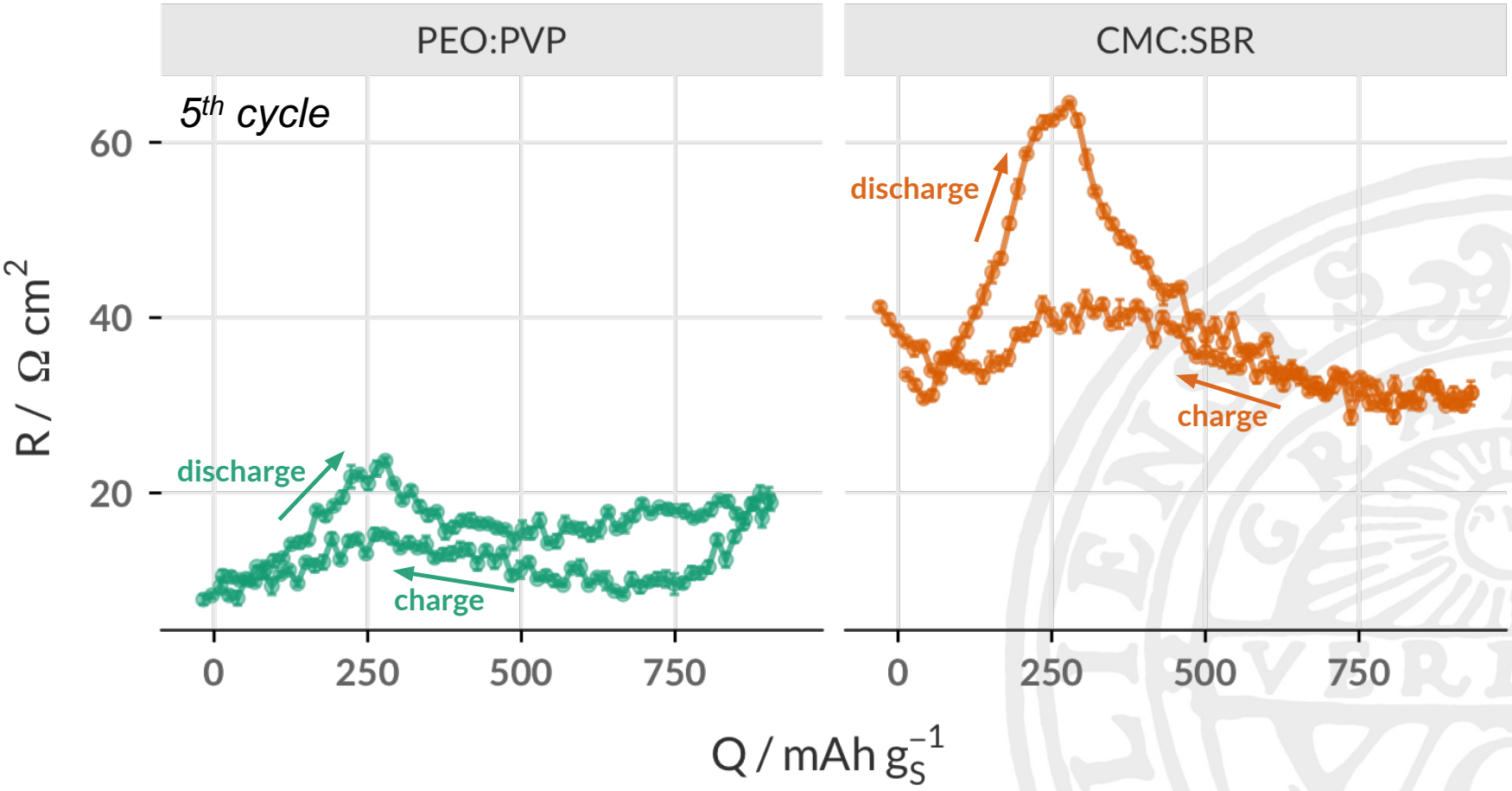
Grey points: CMC:SBR

- 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.*

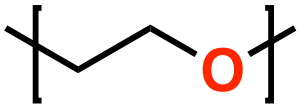
Lower electrode resistance with PEO:PVP

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

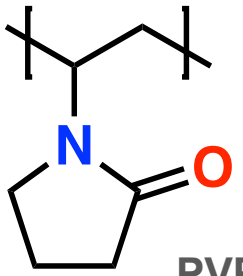


ICI method for following resistance in batteries: Lacey, *ChemElectroChem* 2017, in press

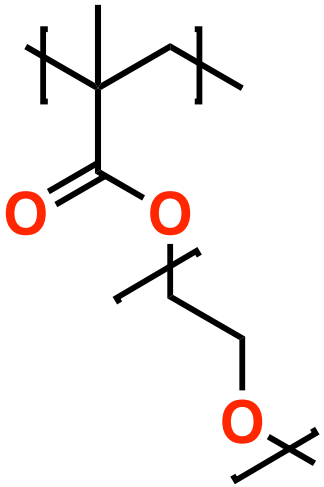
The “framework”



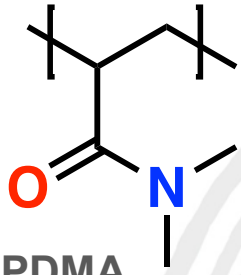
PEO



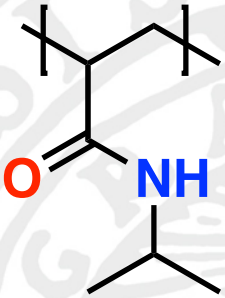
PVP



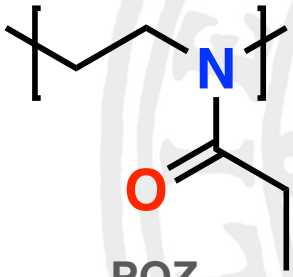
PPEGMA



PDMA



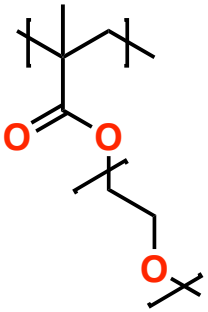
PNIPAM



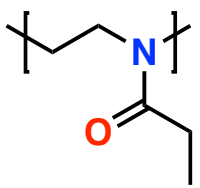
POZ

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, *submitted.*

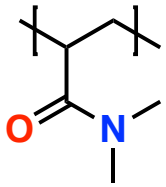
Substitution of PEO or PVP for another polymer bearing the same functional group very closely preserves the electrochemical performance



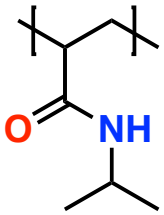
PPEGMA



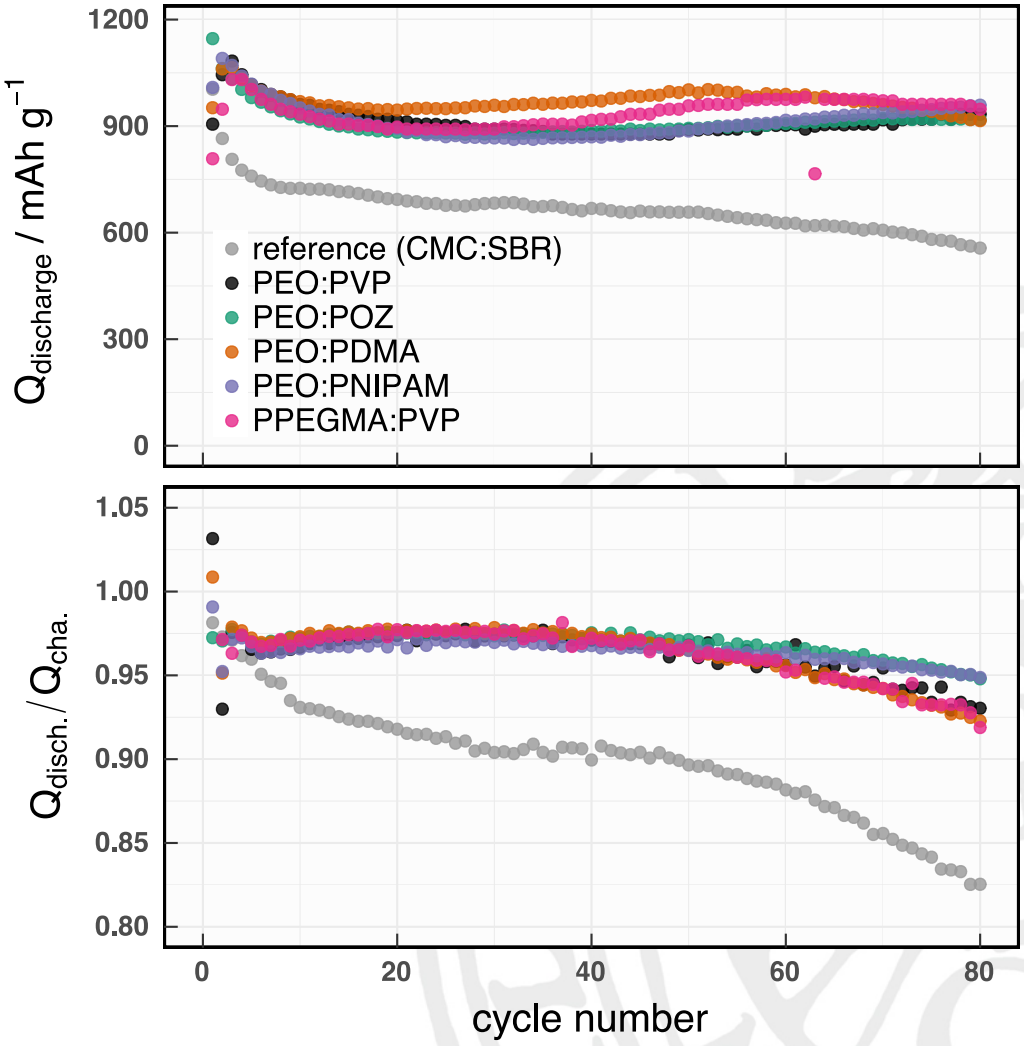
POZ



PDMA



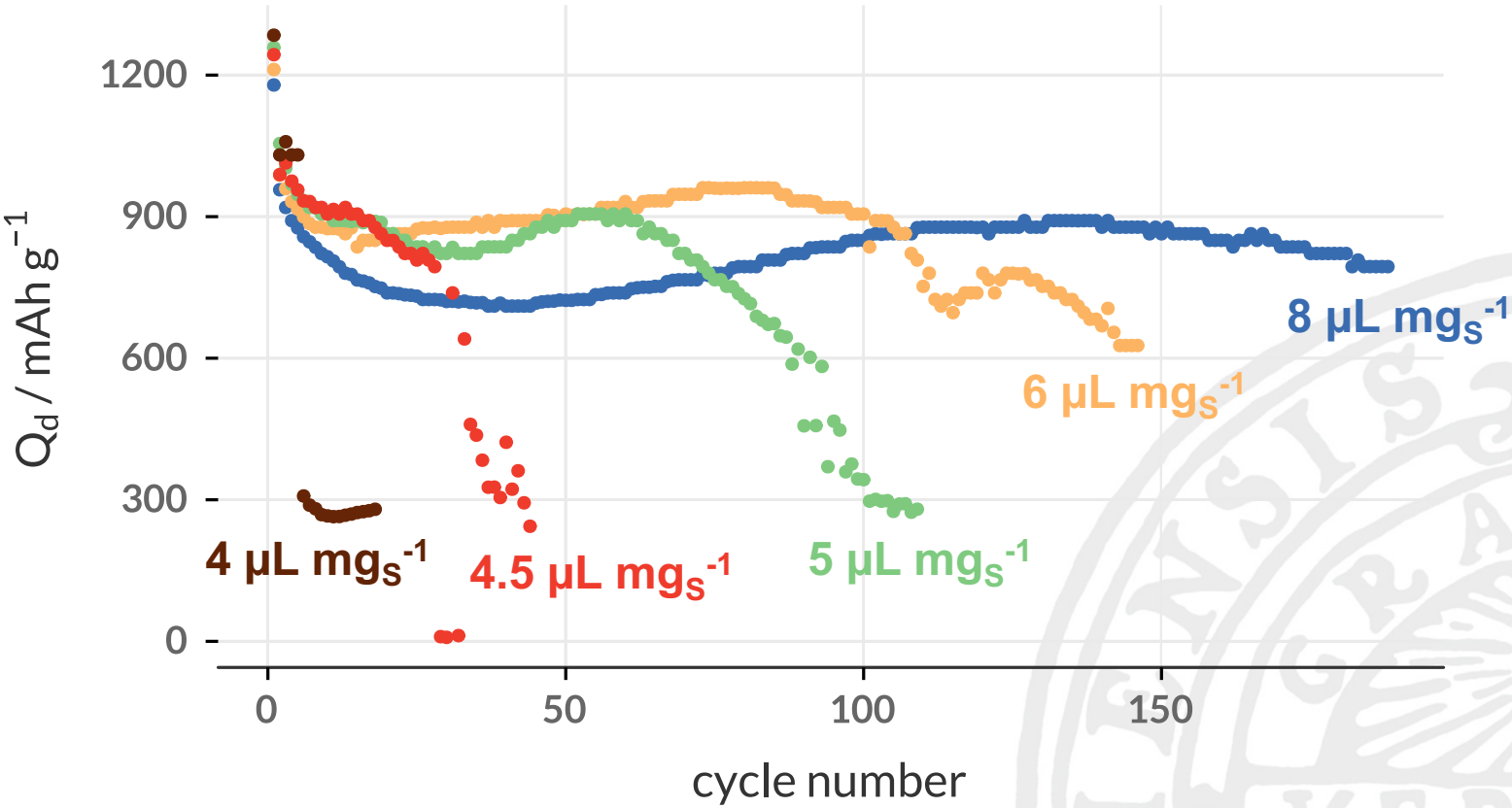
PNIPAM



…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

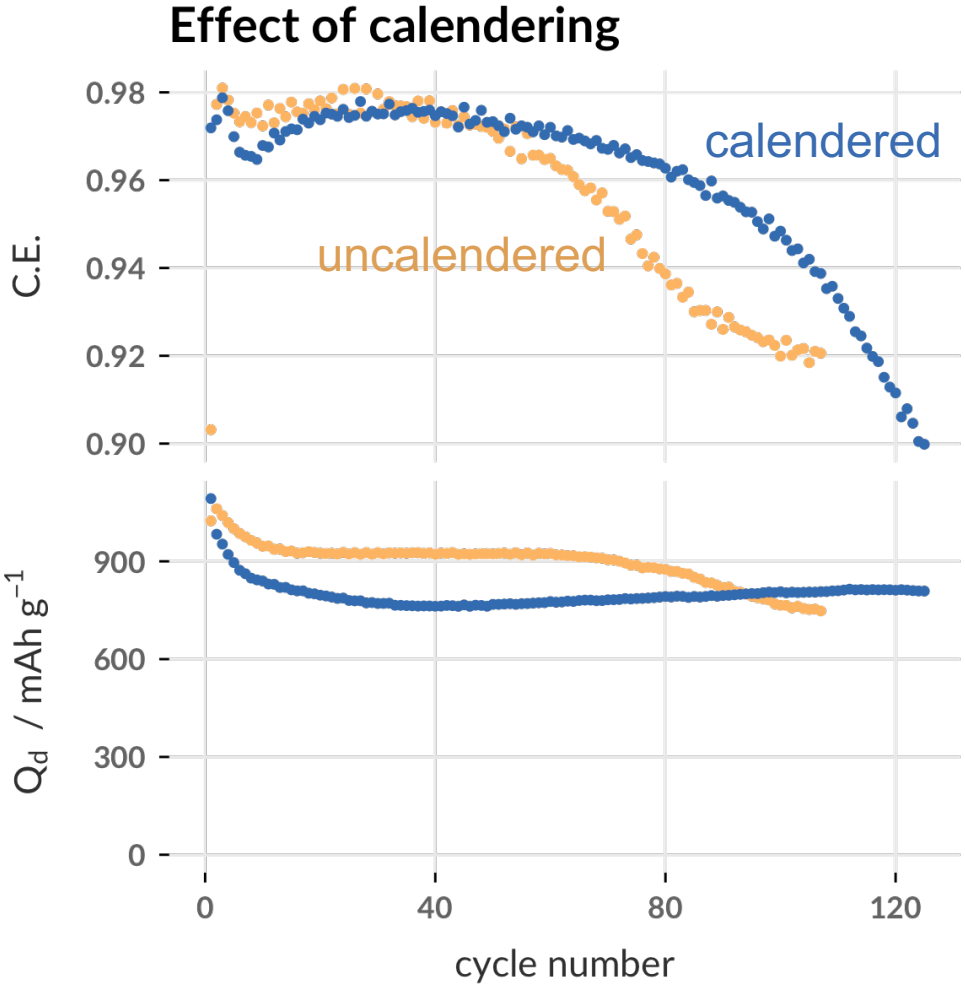


+ effect of Li electrode*, $LiNO_3$ consumption…

Lacey, *ChemElectroChem* 2017, in press

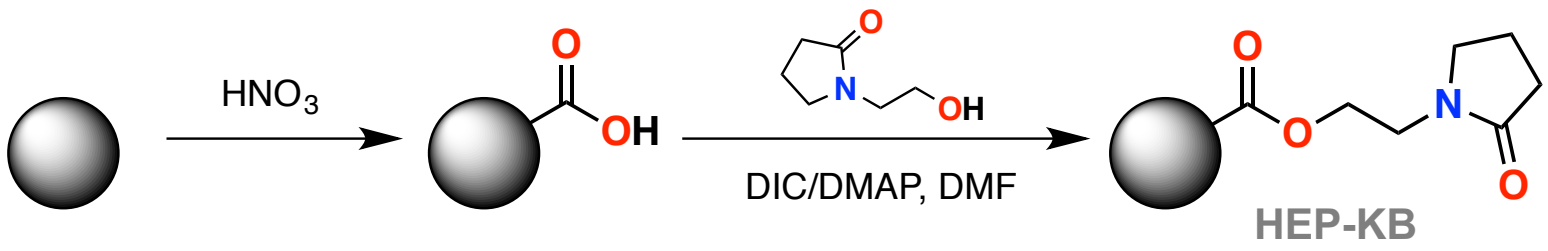
* Lacey, Edström, Brandell, *Chem. Commun.* 2015, 51, 16502

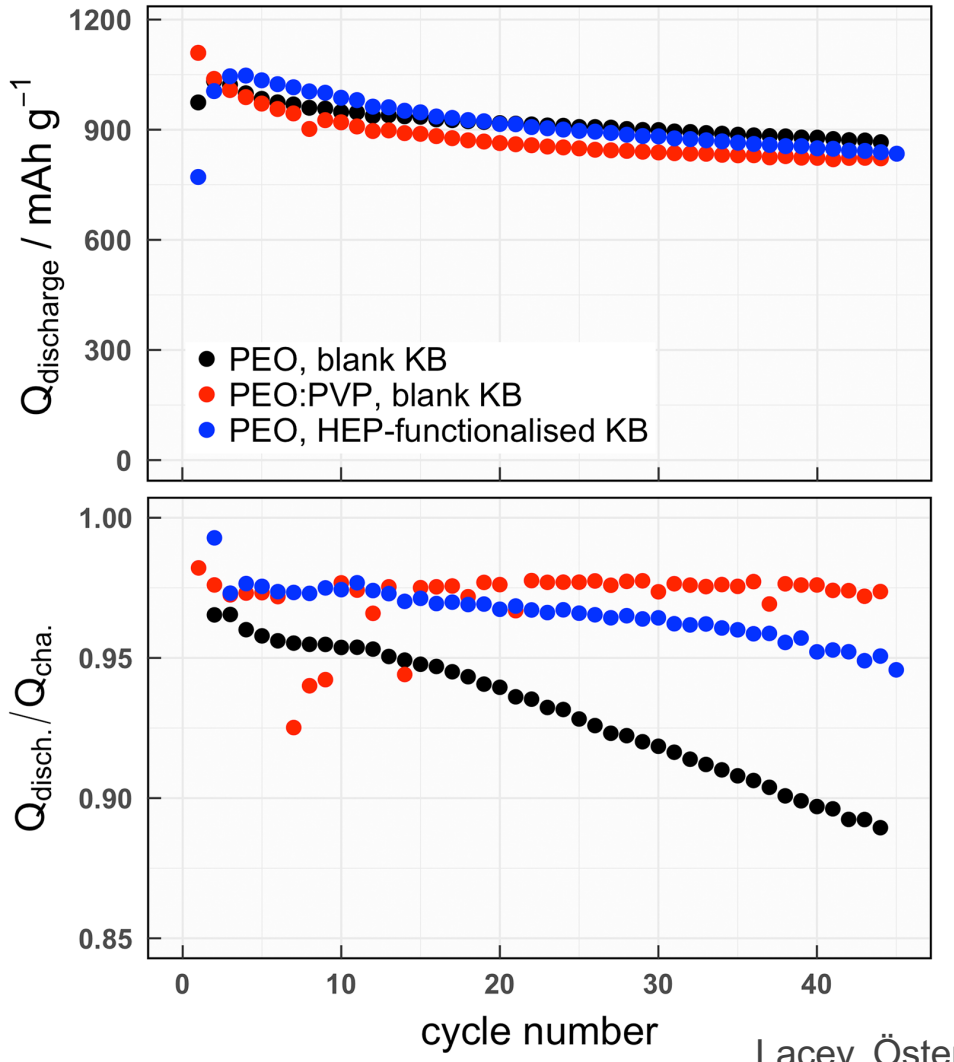
Mechanical integrity of electrodes certainly is a factor in cycle stability – but one of many



- 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

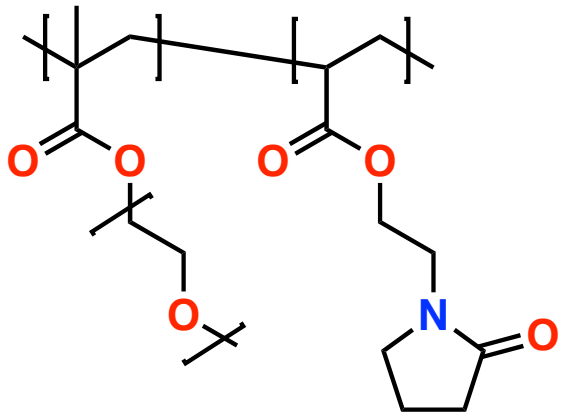




- ~1 mg_S cm^{-2}, no S melt-infiltration for functionalised carbon
- HEP-KB w/ PEO binder shows very similar electrochemical performance to “blank” KB with PEO:PVP binder
- Supports existing evidence that PVP adsorbs at C surface and promotes

Lacey, Österlund, Bergfelt, Jeschull, Bowden, Brandell, *submitted.*

Directions for future development: Wide scope for co-polymer synthesis!

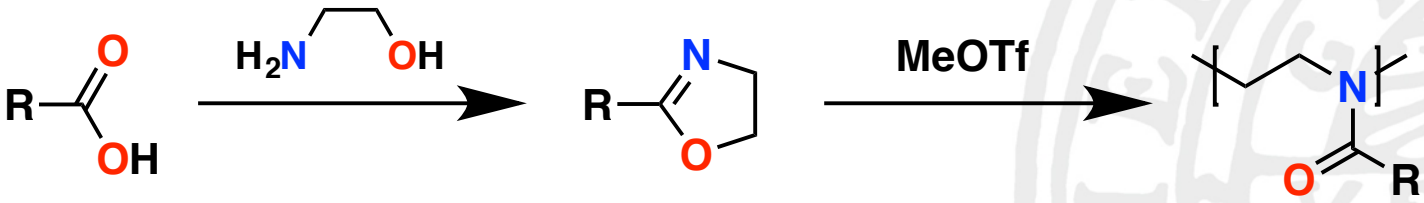


Acrylates

← synthesised, but not tested (liquid!)

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

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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!

Acknowledgements

Experimental contributions

Viking Österlund

Andreas Bergfelt

Fabian Jeschull

Finance

Era-Net Transport Project “MaLiSu”

Vetenskapsrådet

Energimyndigheten

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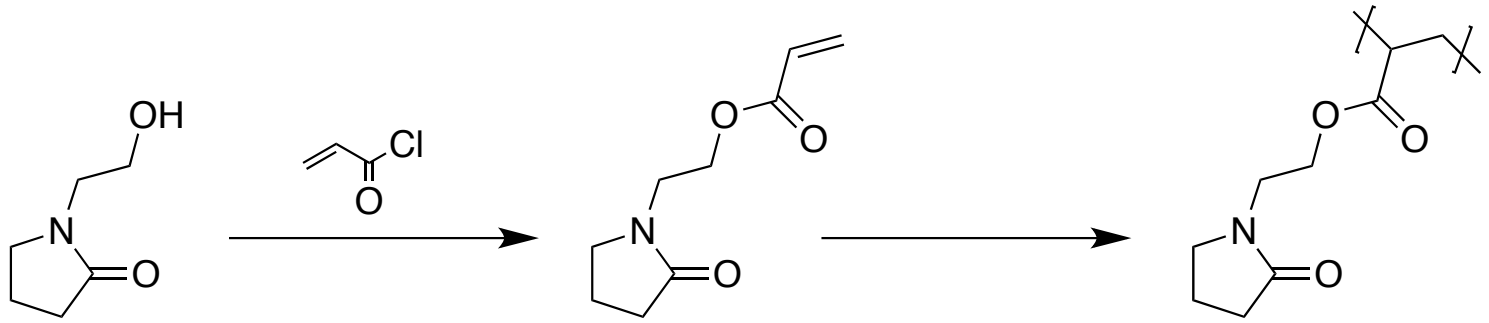
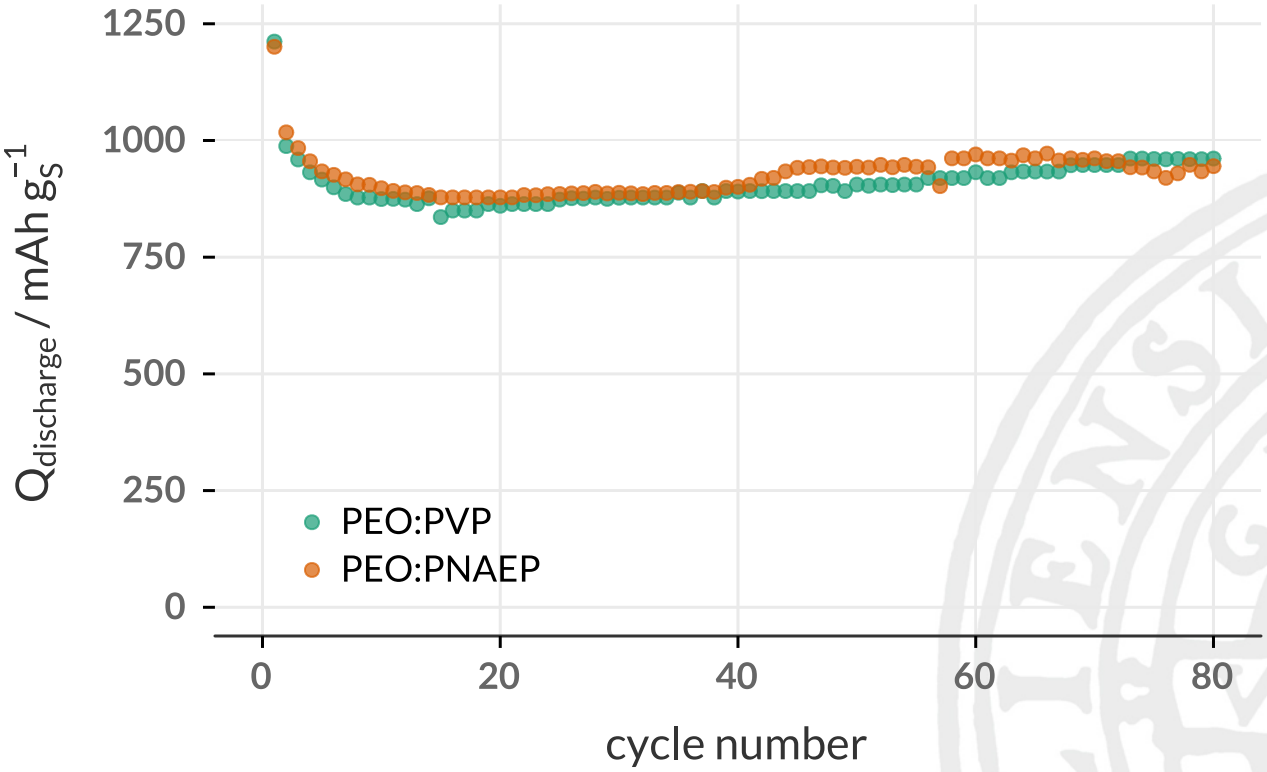
Extras


OH
N
O
Cl
O
O
O
N
O
O
O
O
N
O


1250
1000
750
500
250
0
$Q_{discharge}$ / mAh g_S^{-1}
PEO:PVP
PEO:PNAEP
0
20
40
60
80
cycle number

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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