

Towards high-energy Li-S batteries based on commercial materials and water-soluble functional binders

Matthew J. Lacey, Viking Österlund, Andreas Bergfelt, Fabian Jeschull, Tim Bowden, Kristina Edström and Daniel Brandell

Department of Chemistry – Ångström Laboratory, Uppsala University, Sweden

✉ matthew.lacey@kemi.uu.se

Summary

The functional, mixed binder system of poly(ethylene oxide) and poly(vinylpyrrolidone) (PEO:PVP) is applied here in the water-based preparation of sulfur positive electrodes of moderate-to-high loadings (2 – 4 mAh/cm²) bearing a high fraction of sulfur in the electrode (65%) and using only commercially available carbon materials as the conductive host. Use of this binder system results in higher capacities, efficiencies, cycle life, and lower internal resistance compared to the reference water-based binder, CMC:SBR.

Exchange of either binder component (PEO or PVP) for a different polymer with similar functionality preserved electrochemical behaviour independent of observed differences in the mechanical integrity of electrodes.

These results demonstrate the robustness and practical relevance of this straightforward approach, as well as the considerable scope for designing new binders with targeted properties.

Why water-based functional binders?

- Use of water for electrode slurries is preferable to the organic solvent NMP
- PVdF (in NMP) and other 'unswellable' binders may block pores in host materials and reduce capacity[1]
- PEO and PVP are two examples of polymers previously demonstrated to be beneficial for the electrochemistry of the positive electrode[2]

Electrode composition and characterisation

- 65% w/w sulfur, 21% w/w Ketjenblack carbon (melt-infiltrated at 155 °C)
- 3.5% w/w Super C65 carbon, 3.5% w/w carbon nanofibres (CNF)
- 7% binder (4:1 PEO:PVP)

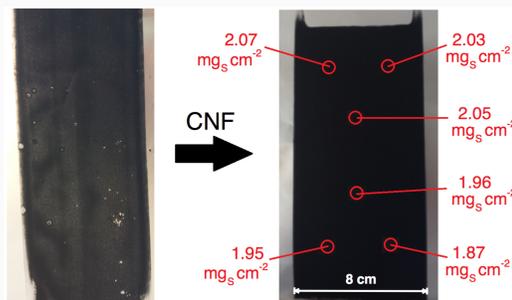


Figure 1: photographs of electrode sheets prepared from slurries with and without 3.5 wt% CNF.

Electrodes coated onto graphite-coated Al foil (graphite loading 0.075 mg cm⁻²) from 90:10 H₂O/EtOH and dried at 55 °C under vacuum. Electrodes tested in CR2025 coin cells at C/10 (167.2 mA g⁻¹) between 1.8 and 2.6 V vs Li/Li⁺. Electrolyte: 1 M LiTFSI, 0.25 M LiNO₃, 1:1 DME:DOL @ 6 μL mg_S⁻¹.

High reversible capacity at >5 mg_S cm⁻²

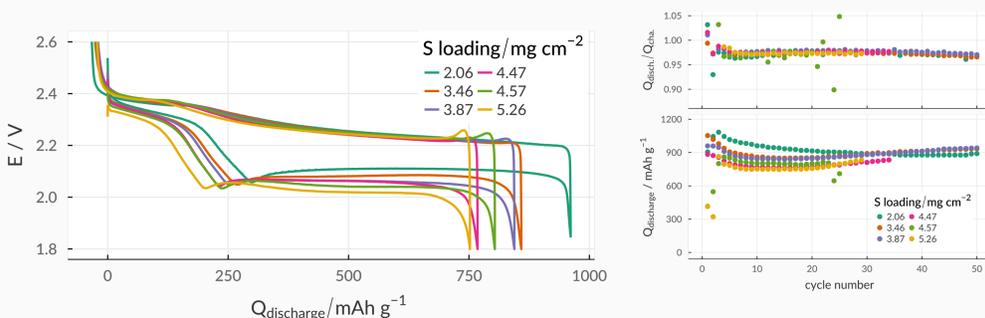


Figure 2: left) voltage profiles of electrodes with loadings between 2.1 and 5.3 mg_S cm⁻² at C/10. right) discharge capacity and coulombic efficiency over the first 50 cycles.

Electrodes >4 mg_S cm⁻² showed short cycle life because of short-circuit from the negative electrode.

PVP addition enhances coulombic efficiency

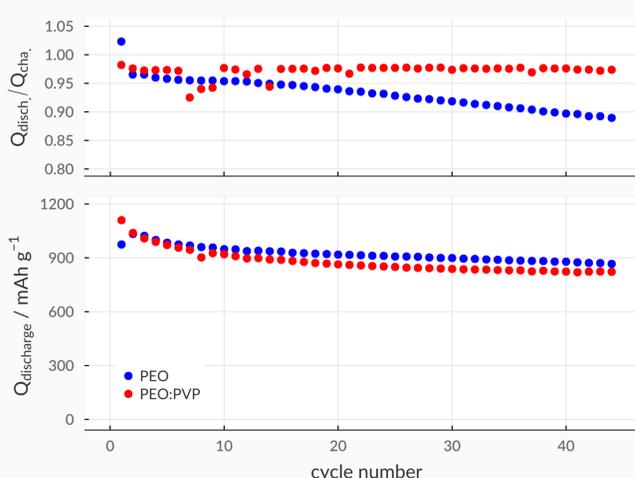


Figure 3: Comparison of electrodes with either a PEO or 4:1 PEO:PVP binder system. Discharge capacity (bottom) and coulombic efficiency (top) given over the first 45 cycles.

Presence of PVP in the binder system (even at 1.4% of the total electrode) maintains coulombic efficiency at 97-98% over extended cycling.

PVP is thought to be preferentially adsorbed on carbon surfaces and slows diffusion of PS from the electrode.

In this comparison, electrode composition is kept the same but loading is relatively low (~1.2 mg_S cm⁻²) due to the difficulty of coating electrodes from slurries where PEO is the sole binder.

Alternative amide-containing binders

PVP (M_w ~ 360,000) and poly(2-ethylloxazoline) (POZ, M_w ~ 500,000) were obtained from Aldrich. Poly(N,N-dimethylacrylamide) (PDMA) and poly(N-isopropylacrylamide) (PNIPAM) were synthesised by a simple free radical polymerisation.

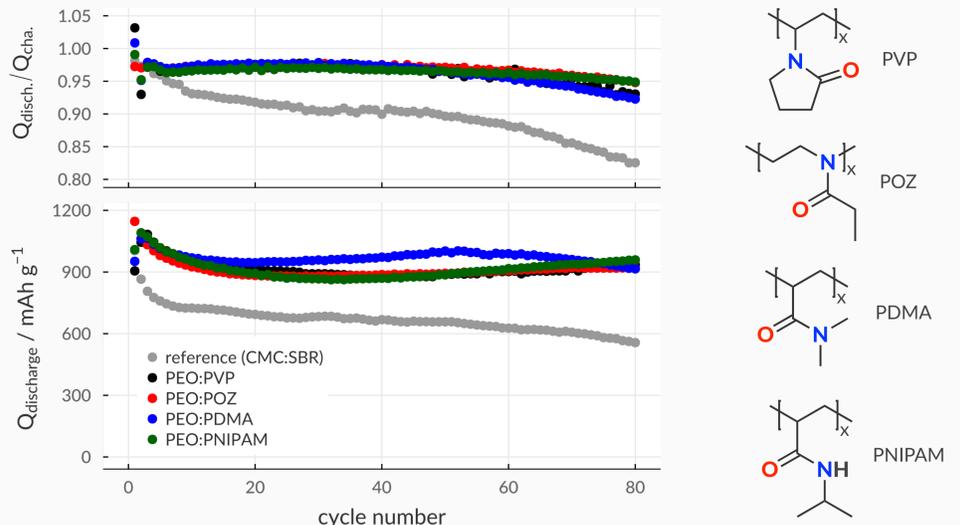


Figure 4: left) Comparison of electrodes with a 4:1 PEO:[amide] binder system with the 2:3 CMC:SBR and 4:1 PEO:PVP reference binder systems by galvanostatic cycling at C/10 rate. Discharge capacity (bottom) and coulombic efficiency (top) given over the first 80 cycles. Right) structures of the four amide components tested.

Alternative polyether-containing binders

PEO (M_w ~ 4,000,000) was obtained from Aldrich. Poly(poly(ethylene glycol methyl ether methacrylate)) was synthesised by a reversible addition-fragmentation chain-transfer (RAFT) polymerisation method.

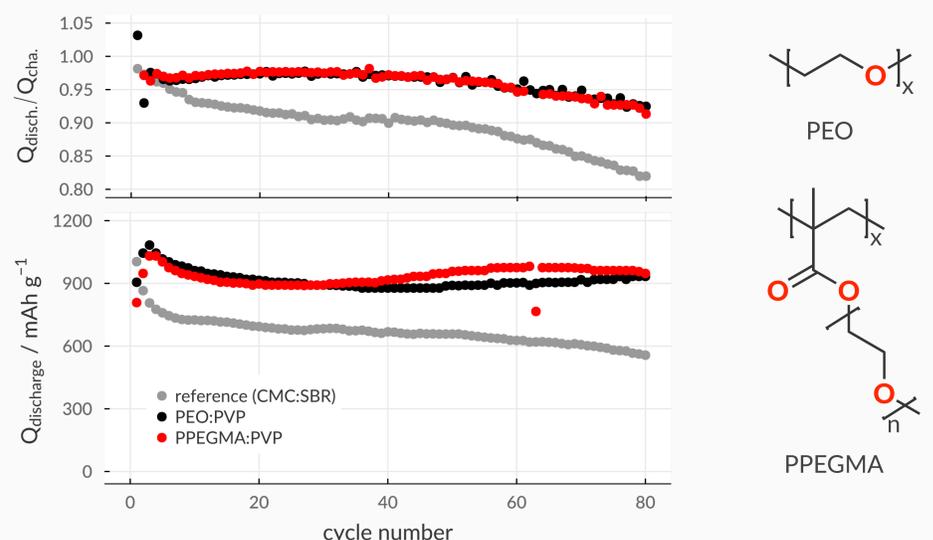


Figure 5: left) Comparison of electrodes with a 4:1 PPEGMA:PVP binder system with the 2:3 CMC:SBR and 4:1 PEO:PVP reference binder systems by galvanostatic cycling at C/10 rate. Discharge capacity (bottom) and coulombic efficiency (top) given over the first 80 cycles. Right) structures of PPEGMA and PEO.

Projecting gravimetric energy density

Energy densities comparable to existing Li-ion batteries are predicted for scaled-up cells. This is based *not only* on electrode parameters but also *electrolyte amount* and *negative electrode thickness* used in this work.

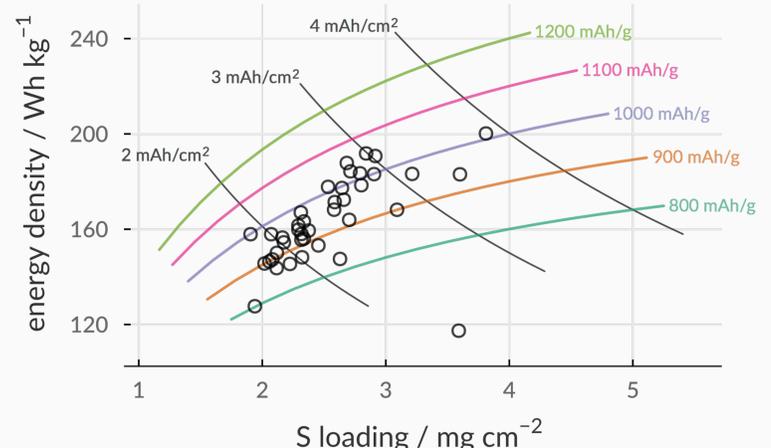


Figure 6: energy densities predicted based on the 50th cycle capacity of 41 cells using electrodes of the type described in this work, tested between Jul 2015 and Apr 2016.

>300 Wh/kg is considered realistic if the electrolyte/sulfur ratio can be halved, and the negative electrode thickness can be reduced to 30 μm (6.3 mAh/cm²). Further work to improve energy density should also target higher utilisation of sulfur in the electrode, since this has a greater influence on cell energy density than loading or fraction of sulfur in the electrode, if other parameters remain unchanged.

References

- [1] M. J. Lacey *et al.*, J. Phys. Chem. C 118 (45), 25890-25898 (2014).
- [2] M. J. Lacey *et al.*, J. Power Sources 264C, 8-14 (2014).