Functional, water-soluble binders for improved capacity and stability of Li-S batteries

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1. Introduction

Besides the considerably higher theoretical energy density compared to Li-ion, perhaps the greatest potential advantage of the Li-S system is in the extremely low cost of the active material: sulfur is abundant and a major waste product from the oil industry.

Figure 1: Stacks of sulfur extracted from oil sands at Fort McMurray, Canada. If assembled into Li-S batteries, the sulfur shown in this photo alone could theoretically power hundreds of millions of electric vehicles.

However, sulfur only remains a cheap active material if the techniques used to convert it into functioning cells are also cheap. It is therefore important to investigate strategies which are easily scaled up to the level required for the envisaged application of this system, e.g., electric vehicles.

Our group has recently explored the effect of PEO and related materials on the performance of Li-S cells, and conclude that, when used as a binder, PEO enhances capacity in much the same manner as short-chain PEG used as an electrolyte additive[1]. Possible reasons for this are enhanced wetting of the electrode surface and/or improved reaction kinetics.

Until very recently, the binder has only been considered as a means to control mechanical stability of the composite electrode and to efficiently disperse particles, thereby maximising active material utilisation. In this work, we aim to demonstrate that the binder should be considered as a functional component of the electrolyte system, which can influence the reaction kinetics of polysulfide intermediates in solution.
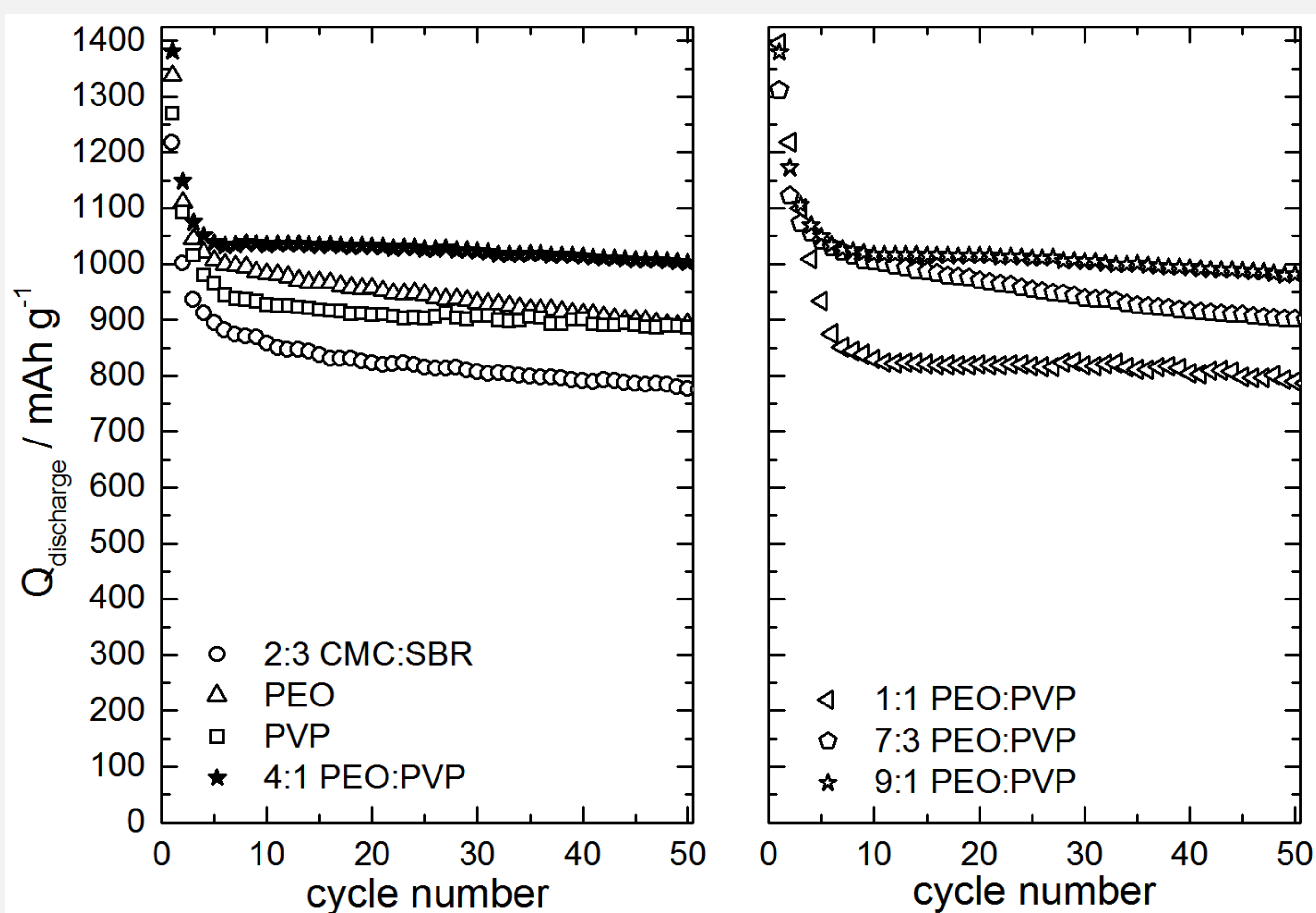
2. Results and discussion

Figure 2: Discharge capacity at C/5 for Li-S cells containing different binders[3]. Electrode composition: 50:40:10 sulfur:Super P:binder, coated onto Al from water-based slurry. Electrolyte: 1 M LiTFSI, 0.25 M LiNO$_3$ in 1:1 DME:DOL.

Following the identification of PVP as a good binder for Li$_2$S cathodes by Seh *et al*[2], we observe that the inclusion of a small amount of PVP in a binder where PEO is the major component results in a further increase in capacity: 1000 mAh/g after 50 cycles for a binder composed of 4:1 PEO:PVP. This value is over 200 mAh/g higher than for the CMC:SBR reference system and is extremely high considering the lack of an optimised carbon host structure.

References and acknowledgements

[1] M. Lacey, F. Jeschull, K. Edström, D. Brandell, *Chem. Commun.* 49, 76, 8531 (2013)

[2] Z. Seh, Q. Zhang, W. Li., G. Zheng, H. Yao, Y. Cui, *Chem. Sci.* 4, 9, 3673 (2013)

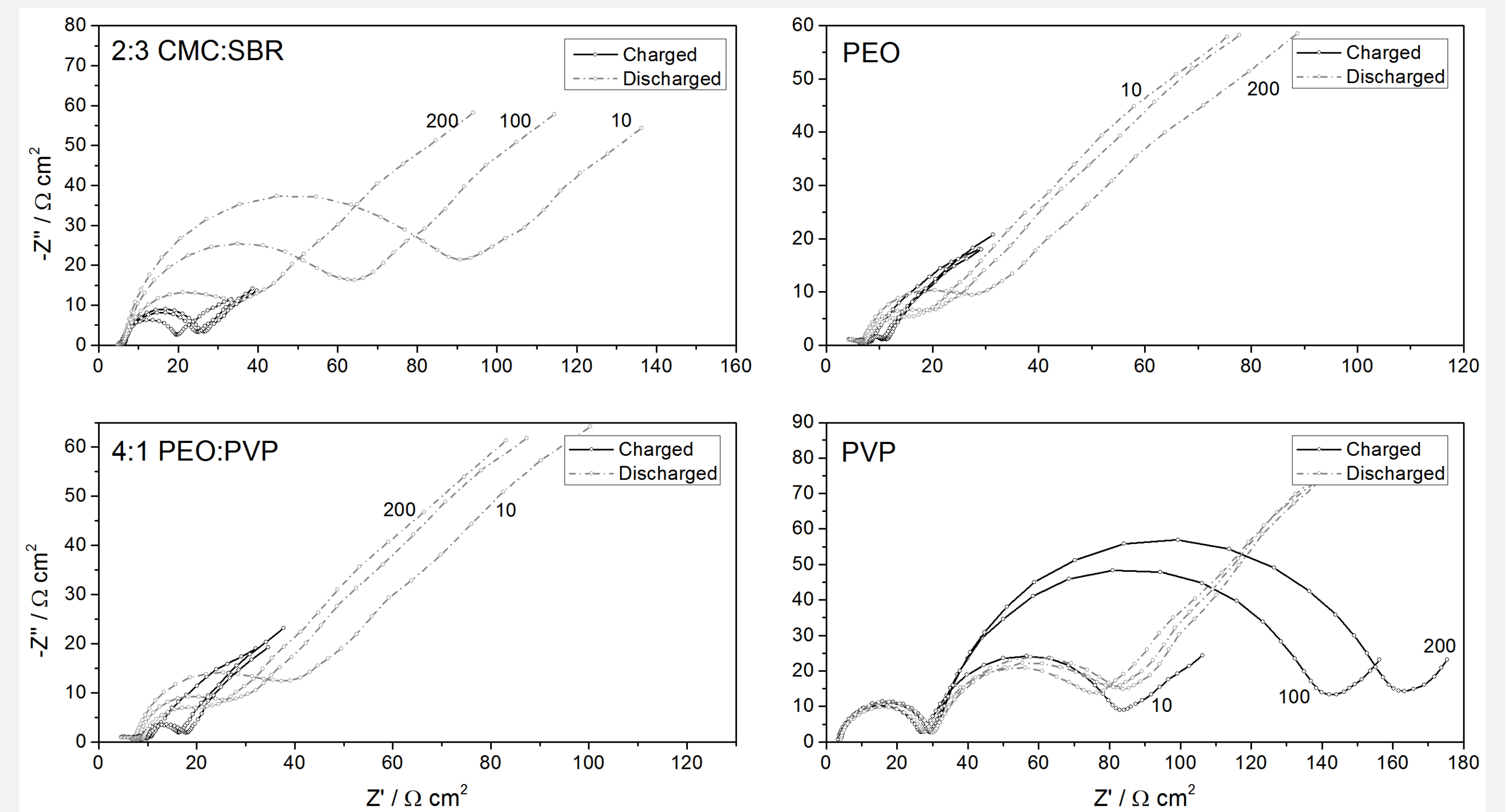[3] M. Lacey, F. Jeschull, K. Edström, D. Brandell, *J. Power Sources 264C*, 8-14 (2014)

Figure 3: Nyquist plots for Li-S cells containing different binders in the charged and discharged states following 10, 100 and 200 charge-discharge cycles at 1C.

AC impedance analysis of Li-S cells with different binders in the charged and discharged states reveals lower R$_{ct}$ for the cathode reaction (major semicircle) for PEO-based binders. However, R$_{ct}$ alone may be a misleading indicator of electrochemical kinetics for a porous electrode since the true electrochemical surface area may change depending on passivation or wetting. Analysis of the relaxation frequency f^* (maximum in $-Z''$ for the semicircle) may give a less ambiguous picture. Assuming the fastest reactions are those of soluble polysulfide intermediates, starting from a linear approximation of the Butler-Volmer equation we can derive the relationship[3]:

$$\tau = \frac{1}{2\pi f^*} \propto \frac{1}{[PS]k_s}$$

	τ, discharged [ms]	τ, charged [ms]
CMC:SBR	66 ± 19	19 ± 2
PEO	34 ± 6	4 ± 1
PVP	46 ± 5	92 ± 23
4:1 PEO:PVP	35 ± 5	8 ± 2

where *[PS]* represents the solubility of polysulfides and k_s is a pseudo-rate constant representing electron transfer kinetics. The relaxation time τ is independent of surface area and only reflects polysulfide chemistry (concentration and kinetics). From this we can see a clear differences between binders, notably the shorter relaxation times for PEO-containing systems. PVP is unique in that the relaxation time in the discharged state is shorter than in the charged state, possibly suggesting some stabilisation of discharge products.
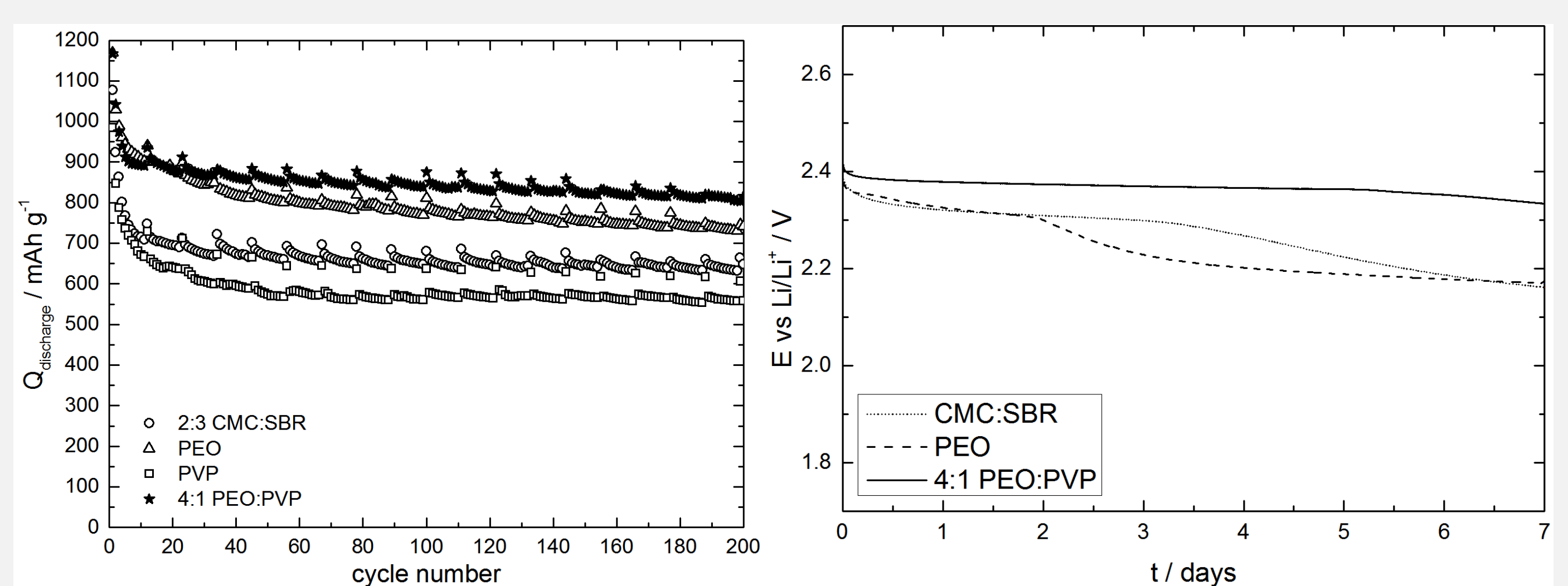

Figure 4: left) Discharge capacity vs cycle number at 1C for the combined IS/cycling experiment indicated in Fig. 3. Right) OCV following five charge/discharge cycles at C/5.

The trend in τ is largely reflected in the cycling behaviour at higher rate. The combination of PEO:PVP retains capacity better in spite of slower kinetics; indicating that the effect of PVP is most likely not related to kinetics. Stability at rest is also vastly improved with the inclusion of PVP in the system.

The stabilising effect of PVP is likely to be related to a complexation of Li$_2$S$_x$ by PVP into an insoluble component in the binder (a precipitate can be clearly observed by mixing of the two in DME:DOL). Further characterisation is necessary to establish the true capacity-stabilising mechanism.

These results demonstrate the important role of the binder in the Li-S system, in that it can be considered as an active material, rather than simply ensuring mechanical stability and efficient dispersion of particles.

3. Conclusions

A binder combination of 4:1 PEO:PVP significantly improves capacity, rate capability and stability with respect to conventional alternatives. The two components contribute to very different but complementary beneficial effects in the system. The use of such functional binders may be a potentially important step towards commercially viable large-scale Li-S systems.