



# A study of the anode in the lithium-sulfur system and its influence on cycle life

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## 1. Introduction

The lithium-sulfur (Li-S) system, with a theoretical energy density of  $2,600 \text{ Wh kg}^{-1}$ , is a promising future energy storage system for transport applications with the possibility of fully-assembled battery packs boasting an energy density two to three times larger than that of current Li-ion. However, the system suffers from short cycle life and a high degree of self-discharge, attributable in part to the well-documented polysulfide shuttle.

As for all secondary lithium metal battery systems, the inefficiency of the anode reaction is a significant barrier to realizing the full potential of the system. The continuous consumption of active material and electrolyte components, coupled with the deposition of dendritic or “mossy” lithium on charge, at least severely shortens the cycle life of the battery if not causing premature cell death by internal short circuit. Despite the importance of this phenomenon and its notoriety in the field, relatively little study has been devoted to the lithium-sulfur system in this respect in recent years.

This poster aims to give an overview of our research on the study of Li metal as the anode for this system, and how it can influence cycle life and charge storage.

## 2. Results and discussion

### a. SEM and XPS study on Li | Li symmetrical cells

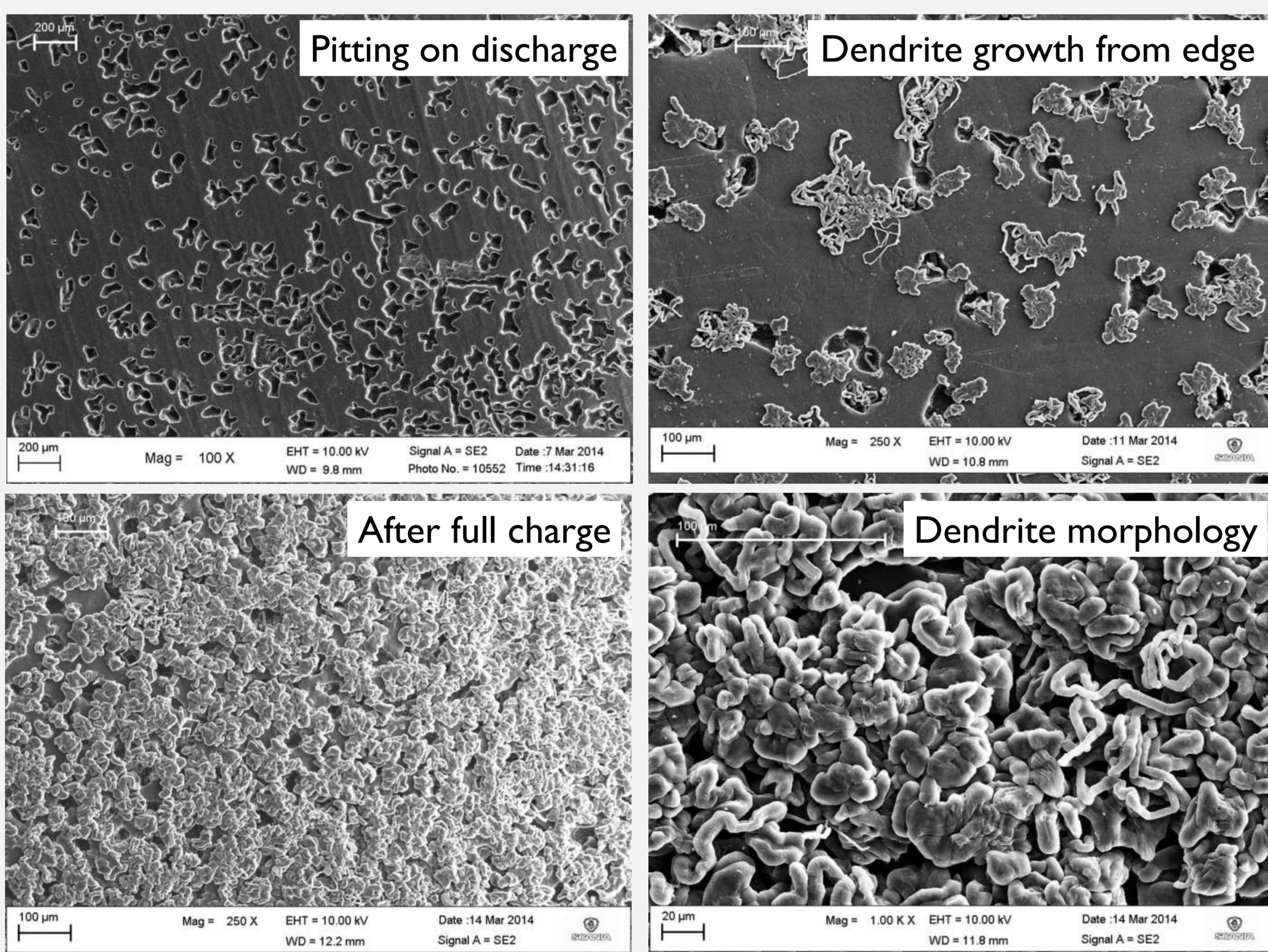


Figure 1: SEM images of Li metal foil. Top left) discharge of  $2.4 \text{ mAh cm}^{-2}$ , top right) discharge of  $2.4 \text{ mAh cm}^{-2}$ , charge of  $1.2 \text{ mAh cm}^{-2}$ , bottom left) discharge  $2.4 \text{ mAh cm}^{-2}$ , charge of  $2.4 \text{ mAh cm}^{-2}$ . For all samples:  $0.4 \text{ mA cm}^{-2}$ , electrolyte:  $1 \text{ M LiClO}_4$ ,  $0.25 \text{ M LiNO}_3$ , sat.  $\text{Li}_2\text{S}_8$ , 1:1 DME:DOL

Symmetrical cells with electrolyte pre-saturated with lithium polysulfide (PS) to mimic chemistry of Li-S in operation are convenient and easily reproducible for studying changes in anode morphology. For investigations of SEI composition, the use of  $\text{LiClO}_4$  electrolyte allows for clearer interpretation of XPS spectra.

### b. Probing self-discharge – SEM/XPS

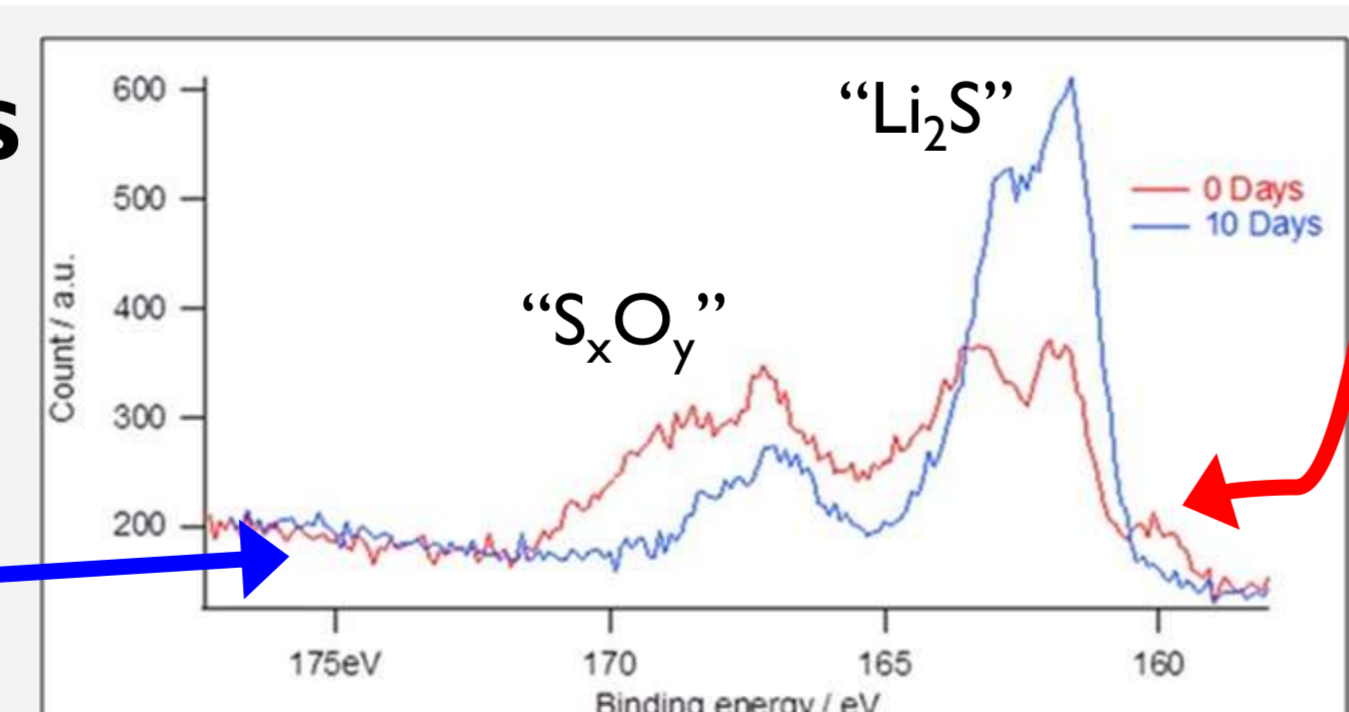
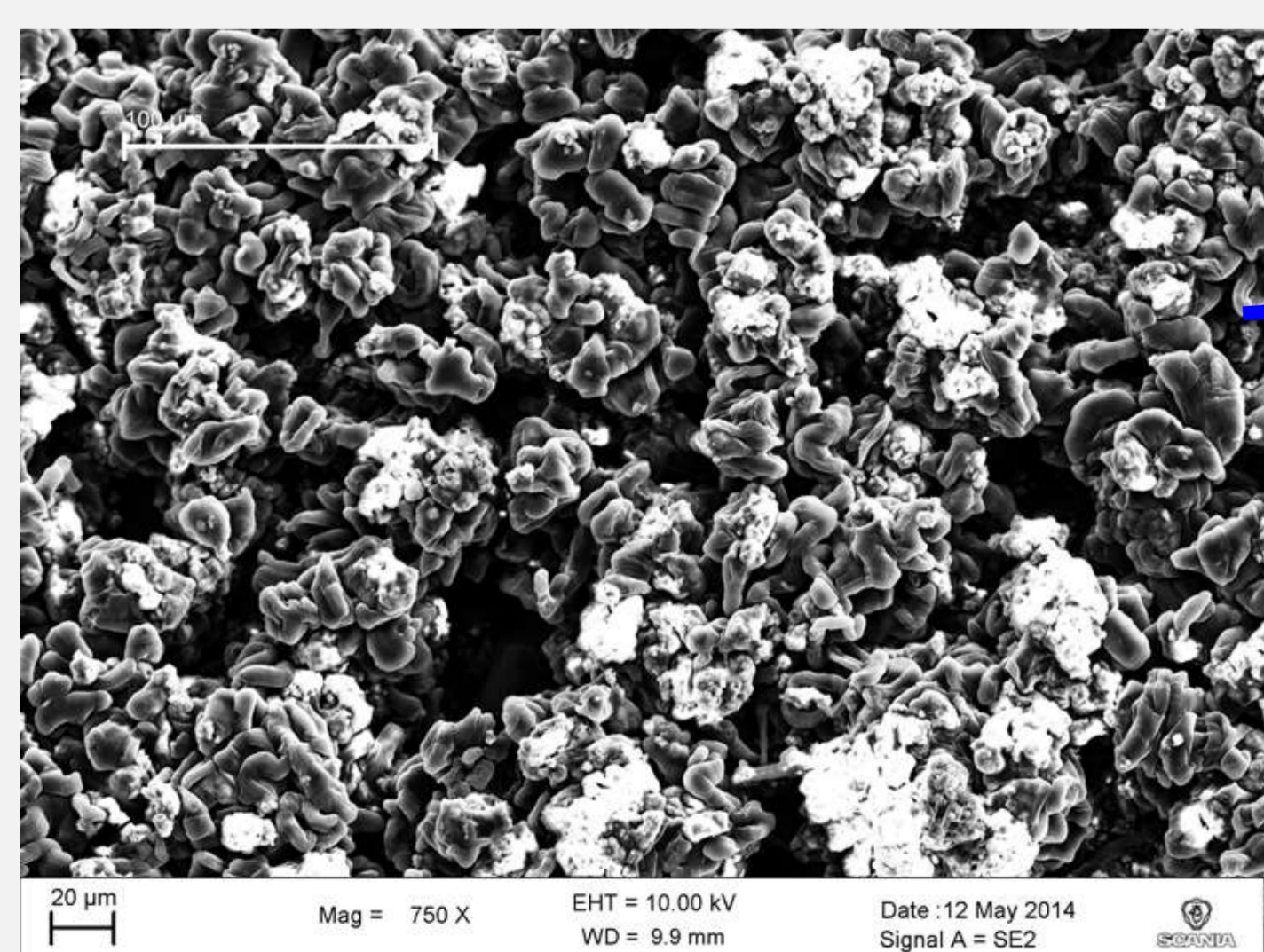


Figure 2: left) SEM image of discharge and charged ( $2.4/2.4 \text{ mAh cm}^{-2}$ ) Li sample and then left in the cell for 10 days before disassembly. Above) S2p XPS spectra for the left) sample compared with the equivalent immediately disassembled sample (Section a.)

Initial XPS studies indicate gradual reaction of PS with Li to form deposits of  $\text{Li}_2\text{S}$  on the surface, even in the presence of  $\text{LiNO}_3$ .

The peaks at low binding energy are significantly increased after 10 days additional exposure of the anode to the electrolyte. This is most likely due to be reduced S species, e.g.,  $\text{Li}_2\text{S}$ . However, the shape of the peak indicates more than one environment for S. This may be evidence for compounds such as  $\text{Li}_2\text{S}_2$ , which has been proposed but as yet unproven.

## References and acknowledgements

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

### c. Cycle/wait testing of Li-S cells

Electrochemical characterisation of Li-S cells by including relaxation periods provides useful information about the rate of self-discharge. This is especially useful for evaluation of cathode modification strategies targeted at control of PS migration to the anode.

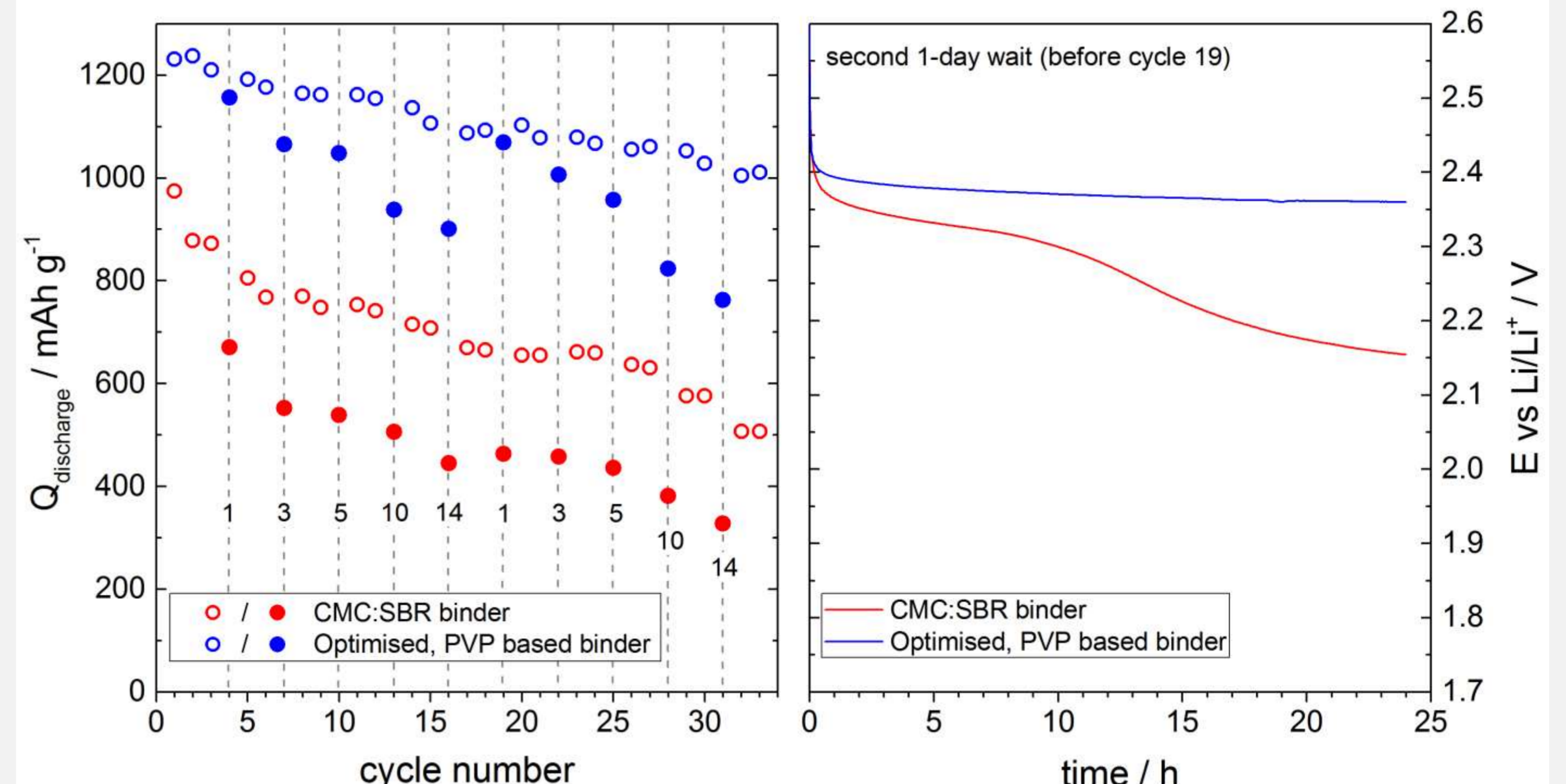


Figure 3: Left) galvanostatic cycling of Li-S cells with different cathode compositions (S content 58%) at C/10 rate. Filled data points indicate discharge following a fixed relaxation period at OCV following previous charge; time is given as a number below in days. Right) voltage profiles for one relaxation period (before cycle 19 discharge). Electrolyte:  $1 \text{ M LiTFSI}$ ,  $0.25 \text{ M LiNO}_3$ , 1:1 DME:DOL. Electrode mass  $\sim 0.8 \text{ mg S cm}^{-2}$

Relaxation at OCV for up to 2 weeks following charge demonstrates that maximum capacity loss is  $\sim 265 \text{ mAh g}^{-1} (\text{S})$  – almost the theoretical capacity of  $278 \text{ mAh g}^{-1}$  for the reaction  $3 \text{S}_8 + 8 \text{e}^- \rightarrow 4 \text{S}_6^{2-}$  which governs the upper plateau in the voltage profile. In this case we have used this test to demonstrate the effect of reduced self-discharge from optimised PVP-based binders, which we are currently investigating[1].

### d. Impedance spectroscopy

Impedance spectroscopy of three-electrode Li-S cells can be used to study the anode/electrolyte interface in isolation. Separating the contribution of the anode from the highly complex cathode environment greatly simplifies analysis.

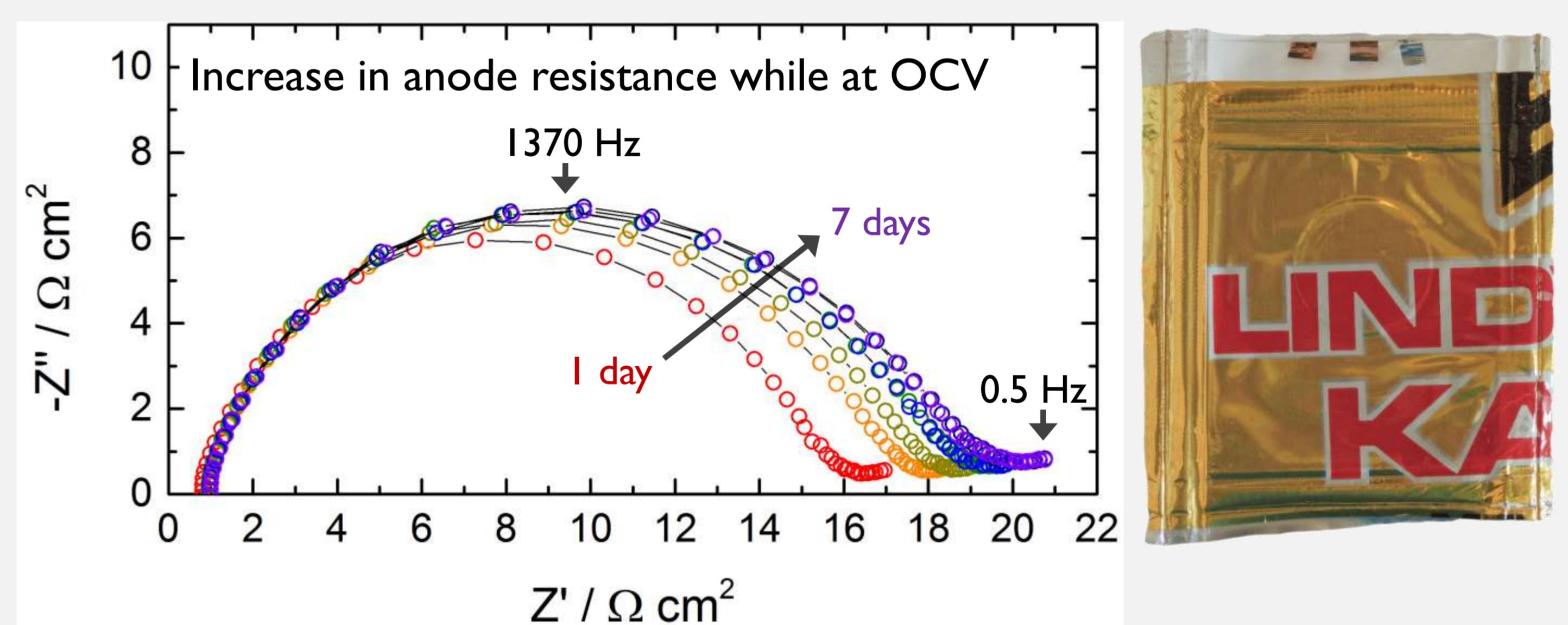


Figure 4: Left) Nyquist plots of Li-S cells, assembled in a three-electrode pouch cell configuration with the anode as the working electrode, and a Li reference. Cathode: 58/35/7 S/C/CMC:SBR, electrolyte  $1 \text{ M LiTFSI}$ ,  $0.25 \text{ M LiNO}_3$ , 1:1 DME:DOL. After 6 cycles at C/5, IS was measured at 24 hour intervals with  $V_{pp} = 5 \text{ mV}$ . The cell was kept at OCV for a period of 1 week. Right) typical 3-electrode pouch cell used in this experiment.

### e. Thin Li anodes

Li-S cathodes tend to be cycled against Li foil of thicknesses far in excess of what would be acceptable – this hides the effect of anode efficiency on the true cycle life of the system. Extending practical cyclability beyond  $\sim 80$  cycles is still limited by the anode.

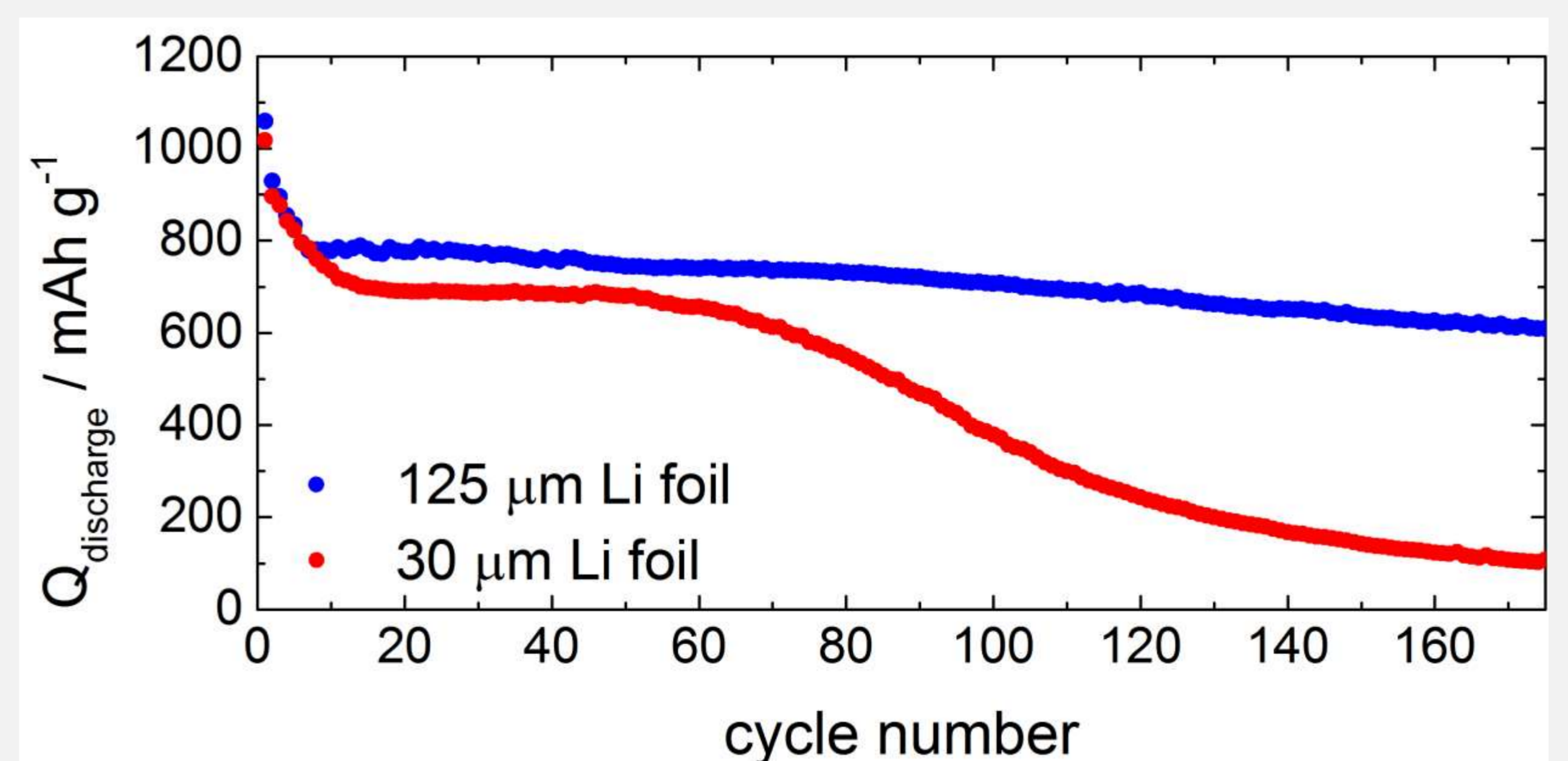


Figure 5: Galvanostatic cycling of Li-S cells with different thicknesses of Li foil as the anode. Cathode: 58/35/7 S/C/CMC:SBR,  $\sim 0.8 \text{ mg S cm}^{-2}$ ; electrolyte:  $1 \text{ M LiTFSI}$ ,  $0.25 \text{ M LiNO}_3$ , 1:1 DME:DOL,  $6 \mu\text{L/mg (S)}$ , 2025 coin cell format. Constant rate of C/10.

## 3. Conclusions

Our initial results demonstrate that, even with the use of  $\text{LiNO}_3$ , self-discharge is still a problem which contributes to capacity fade and rapid loss of  $>25\%$  of stored charge. This can be slowed through approaches such as optimised functional binders. However, the intrinsic inefficiency of the anode is still a major obstacle to long-term cycling of cells of realistic specification. It is unlikely this can be remedied by cathode optimisation alone.