Can paper waste be used to make anode-free lithium-sulfur batteries?

Naturally-derived lignin current collectors as a lithium anode substitute

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Abstract

A porous carbon fibre (CF850) current collector with a high Coulombic efficiency (CE) has been fabricated using Organosolv Lignin, a byproduct of papermaking. CF850 has potential as a replacement for the Li metal anode in conventional Li-S cells, due to its lower Li inventory losses & improved safety.

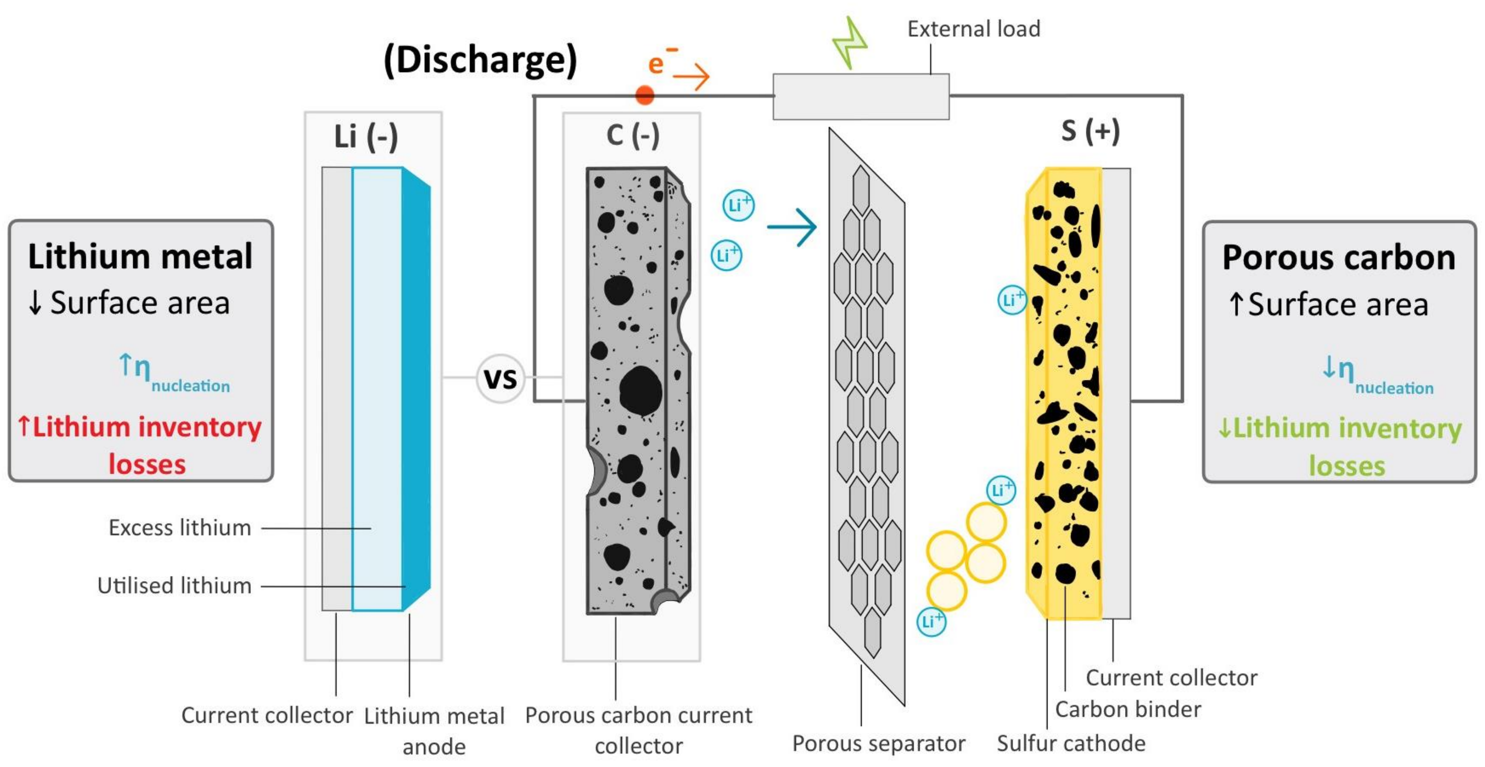

Figure 1. Schematic showing discharge of a proposed anode-less Li-S cell and advantages over a conventional lithium anode.

Motivation

- Li-S batteries offer advantages over commercial Li-ion batteries, but lithium inventory losses can create problems [1], [2], [3].
- Lignin-based carbon can replace lithium anodes to overcome this.

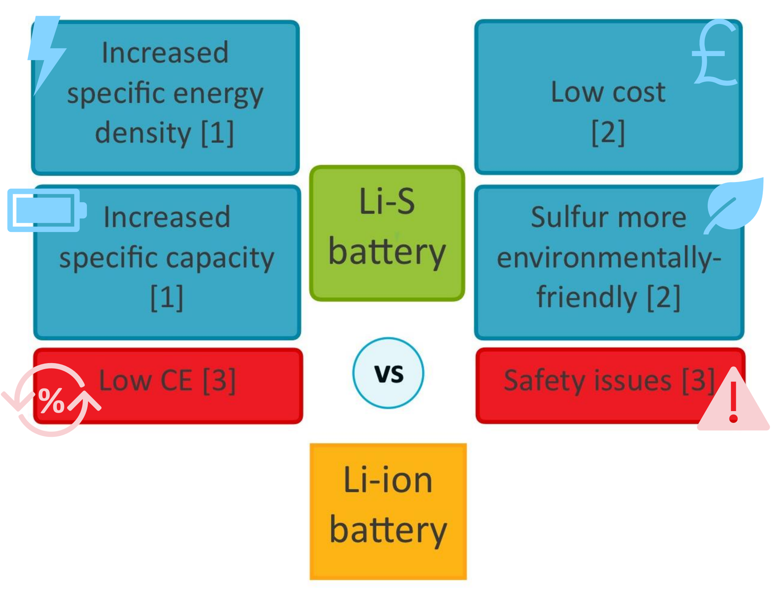

Figure 2. Illustration of the advantages and disadvantages of lithium-sulfur batteries compared to lithium-ion batteries.

Methods

- 8ml precursor solutions of NaOH, PEO and Organosolv Lignin were electrospun at 20kV into a mat.
- The mat was carbonised in sections at 700, 850 and 1000°C for 2 hours in a furnace.
- Electrodes were cut from the sections and used to make coin cells, which were cycled at a current density of 1mA.cm^{-2}.
- The section morphology was analysed by Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) methods.
- Fibre diameters were sampled from SEM images using ImageJ.

Results & Discussion

The average Coulombic efficiency was 98.78 ± 0.43% for the mat section carbonised at 850°C, the highest and most consistent of all electrodes tested as seen in **Figure 3**.

BET pore size distributions (**Figure 4**) show that CF850 also has the largest total pore volume (0.216 cm^3.g^{-1}) and the largest mesopore volume (0.061 cm^3.g^{-1}) compared to CF700 and CF1000.

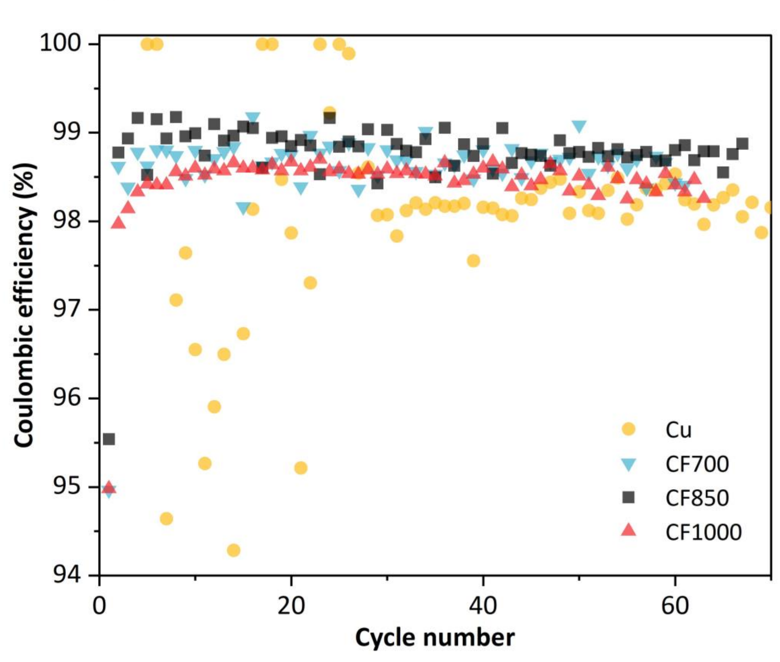

Figure 3. Coulombic efficiency of coin cells with current collectors made of copper and carbon fibres carbonised at 700, 850 and 1000°C.

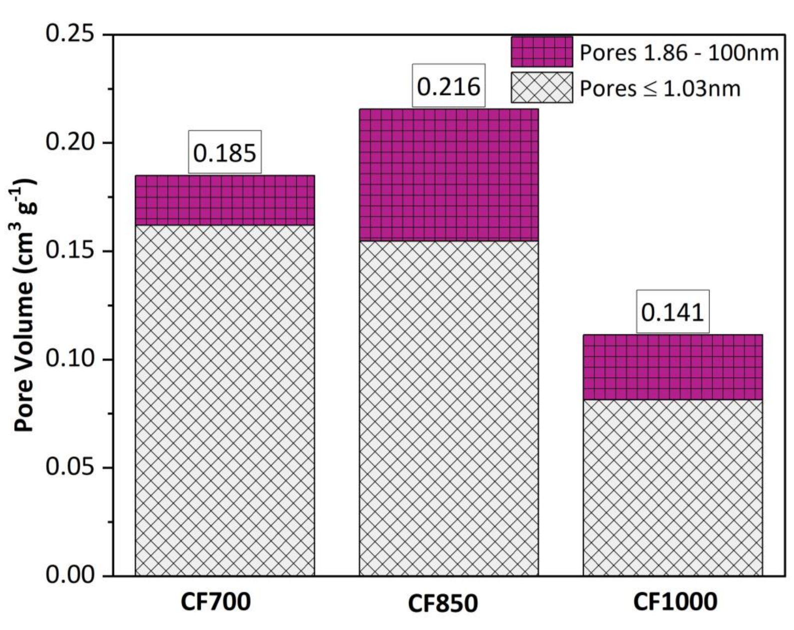

Figure 4. Summary of BET pore size distributions within 3 carbon fibre mats carbonised at 700, 850 and 1000°C.

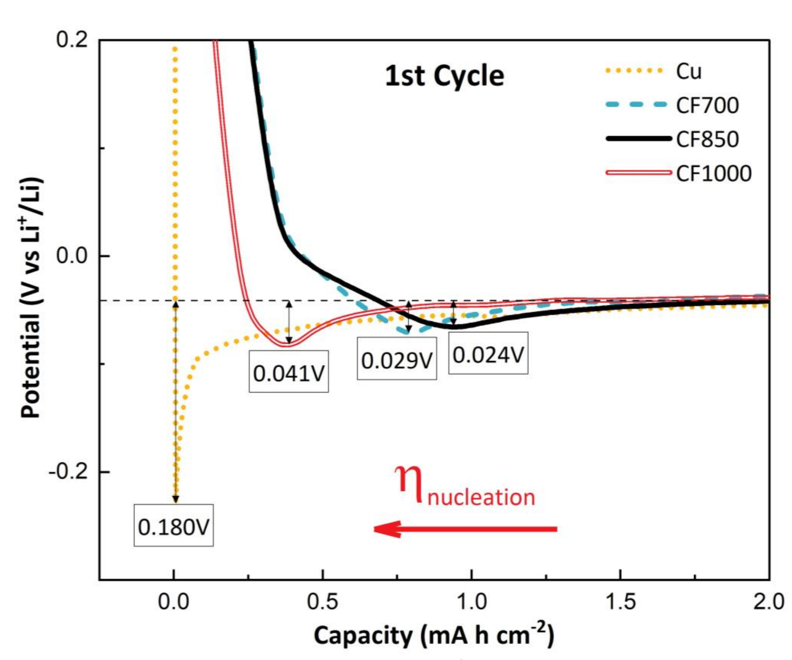

Figure 5. Capacity vs. potential (V vs. Li$^+$/Li) of coin cells with current collectors made of copper and carbon fibre mats carbonised at 700, 850 and 1000°C. Nucleation overpotentials ($\eta_{nucleation}$) are shown in the boxes.

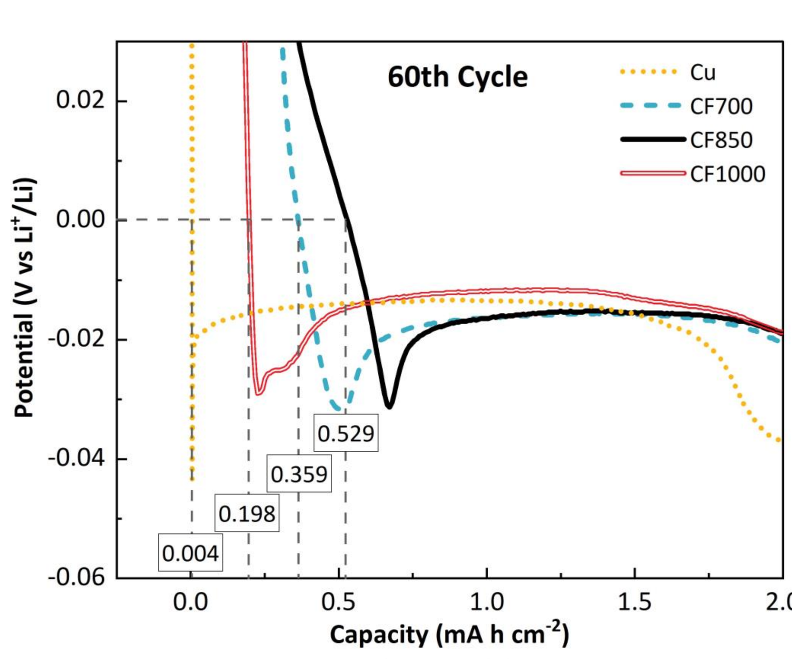

Figure 6. Capacity vs. potential (V vs. Li$^+$/Li) of coin cells with current collectors made of copper and carbon fibre mats carbonised at 700, 850 and 1000°C. (Pre-plating) Capacities at 0V are shown in the boxes.

The results imply that carbonising at 850°C enhances porosity. The resulting high surface area can dissipate large local current densities and promote smooth Li deposition on the collector [4]. Thus, lower overpotential losses via activation polarisation are expected when cycling, which could improve CE [5].

CF850 has the lowest lithium nucleation overpotential in the 1st discharge cycle at 0.024V (**Figure 5**), supporting the above. **Figure 6** shows that its capacity at 0V stays the highest at 0.529mAh.cm^{-2} after 60 cycles. A possibility is that high porosity helps to adsorb/intercalate more Li ions, raising CE [6].

Most of the fibre diameters sampled from SEM of CF850 (**Figures 7 & 8**) were 550-650nm. The effect on porosity, if any, remains to be elucidated.

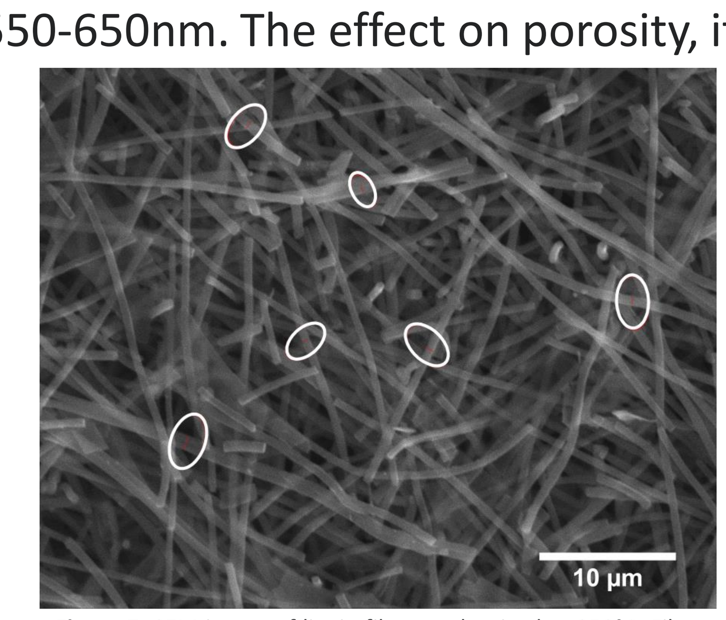

Figure 7. SEM image of lignin fibres carbonised at 850°C. Fibre diameters were sampled from regions bound by white ellipses.

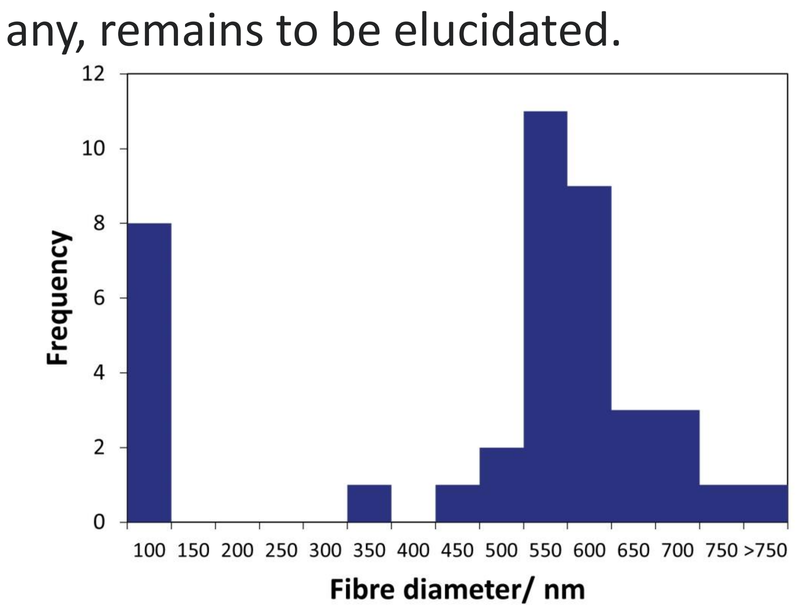

Figure 8. Histogram containing 40 carbon fibre diameters in the 100-750nm range for an Organosolv Lignin mat carbonized at 850°C.

Conclusions

It has been shown that increasing porosity in lignin-based carbon fibre current collectors is key to improving their Coulombic efficiency, likely due to its effect in mitigating cell polarisation losses from activation polarisation, minimising the nucleation overpotential for lithium and aiding smooth deposition. The porosity may also alter/enhance lithium storage mechanisms, for example by adsorbing or intercalating additional Li ions. Fibre diameter as a potential variable in maximising porosity has also been briefly introduced.

Impact / Next steps

- The work done has demonstrated one factor in the improvement of the low Coulombic efficiency of anode-less Li-S batteries.
- If this weakness can be overcome, Li-S batteries become a cheaper, cleaner prospect to replace Li-ion in portable/mobile applications [2].
- In future, carbonisation temperatures of 800 & 900°C should be applied to lignin mats.
- Orienting fibres using a rotating drum at varying RPM while electrospinning will allow for easier control and investigation of diameter.
- Compression of aligned and unaligned fibres in stacks could further impact porosity.

References

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Intern bio

Peter Akinshin is a final-year MEng undergraduate studying Materials Science & Engineering at Imperial College London. He is a strong proponent of innovative new ways in which sustainable energy can be generated and stored, aiming to make novel materials for energy devices. From synthesising biodegradable packaging films in eliminating plastic waste to designing battery packs for Hyperloop transport, Peter is drawn to cutting-edge projects for the improvement of people's quality of life.

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