UNIVERSITY OF Southampton

sse Solid State Electrochemistry group

Electrodeposition of polymer electrolytes for 3D Li-ion microbatteries

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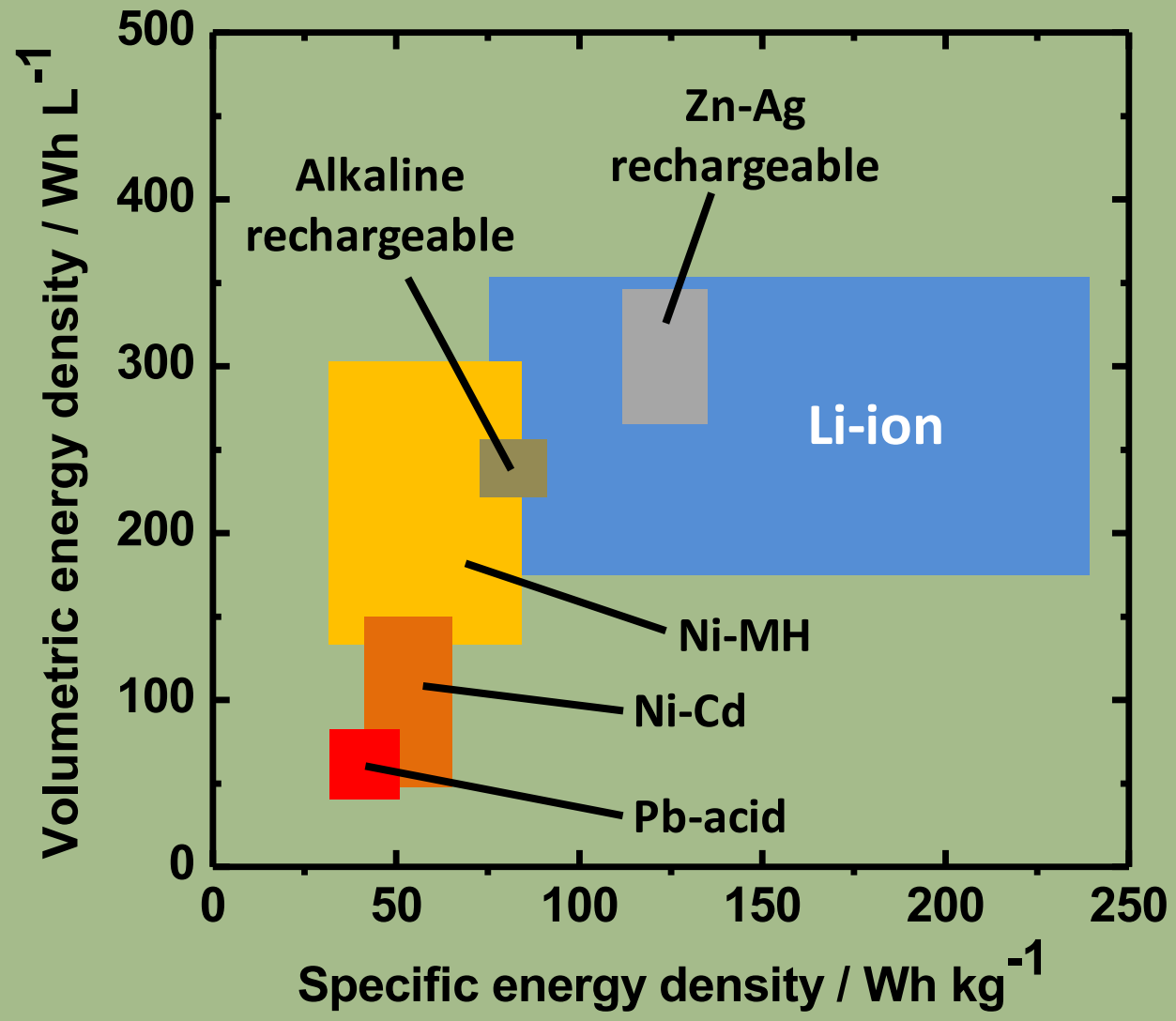
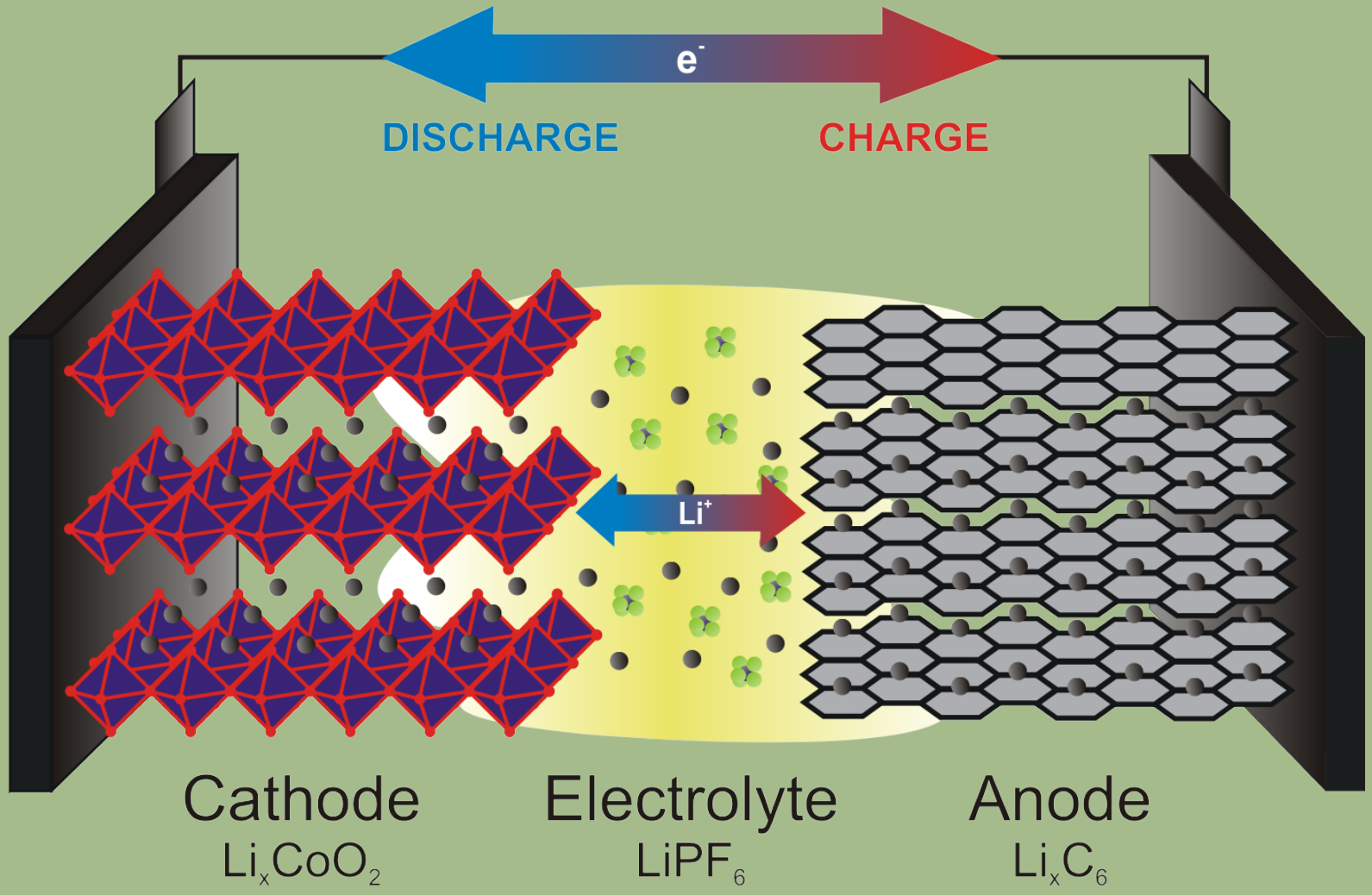
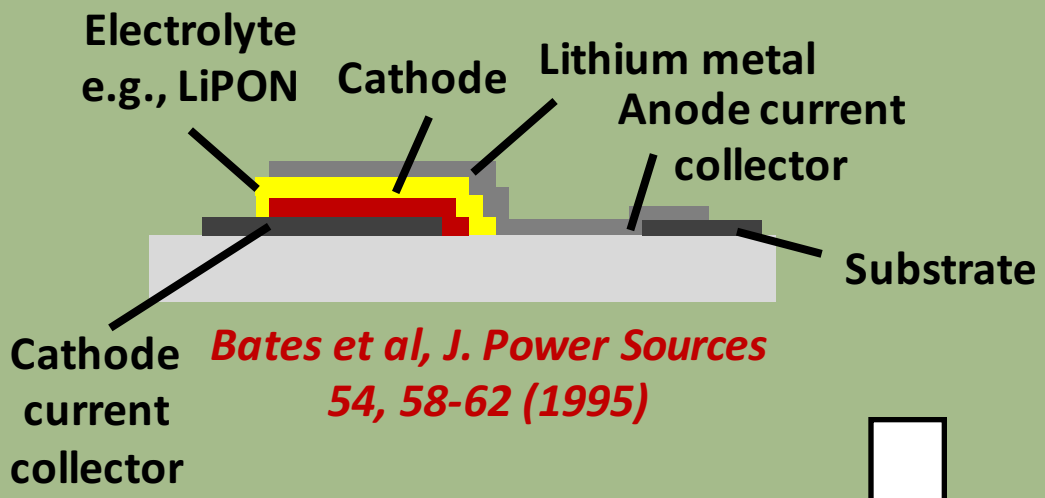
Rechargeable batteries



Li-ion batteries



Planar thin film → 3D



Bates et al, J. Power Sources 54, 58-62 (1995)

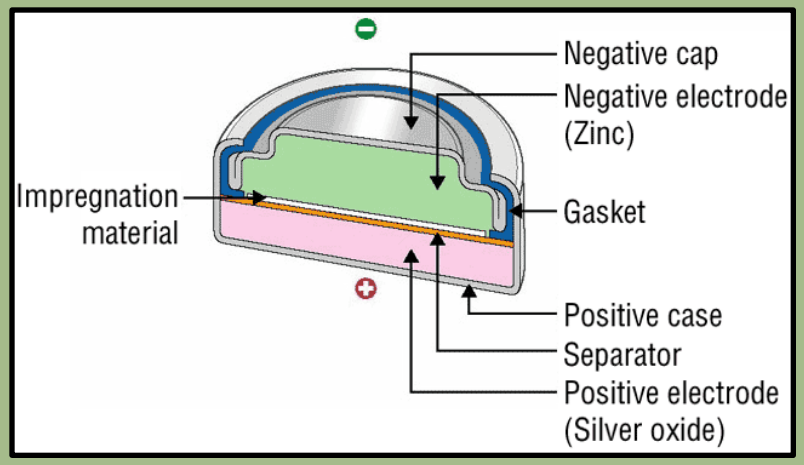
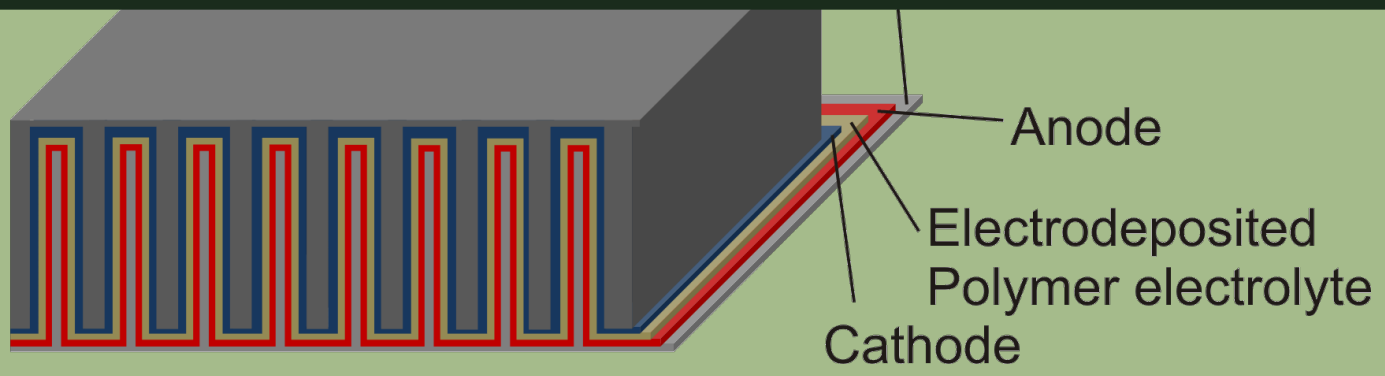
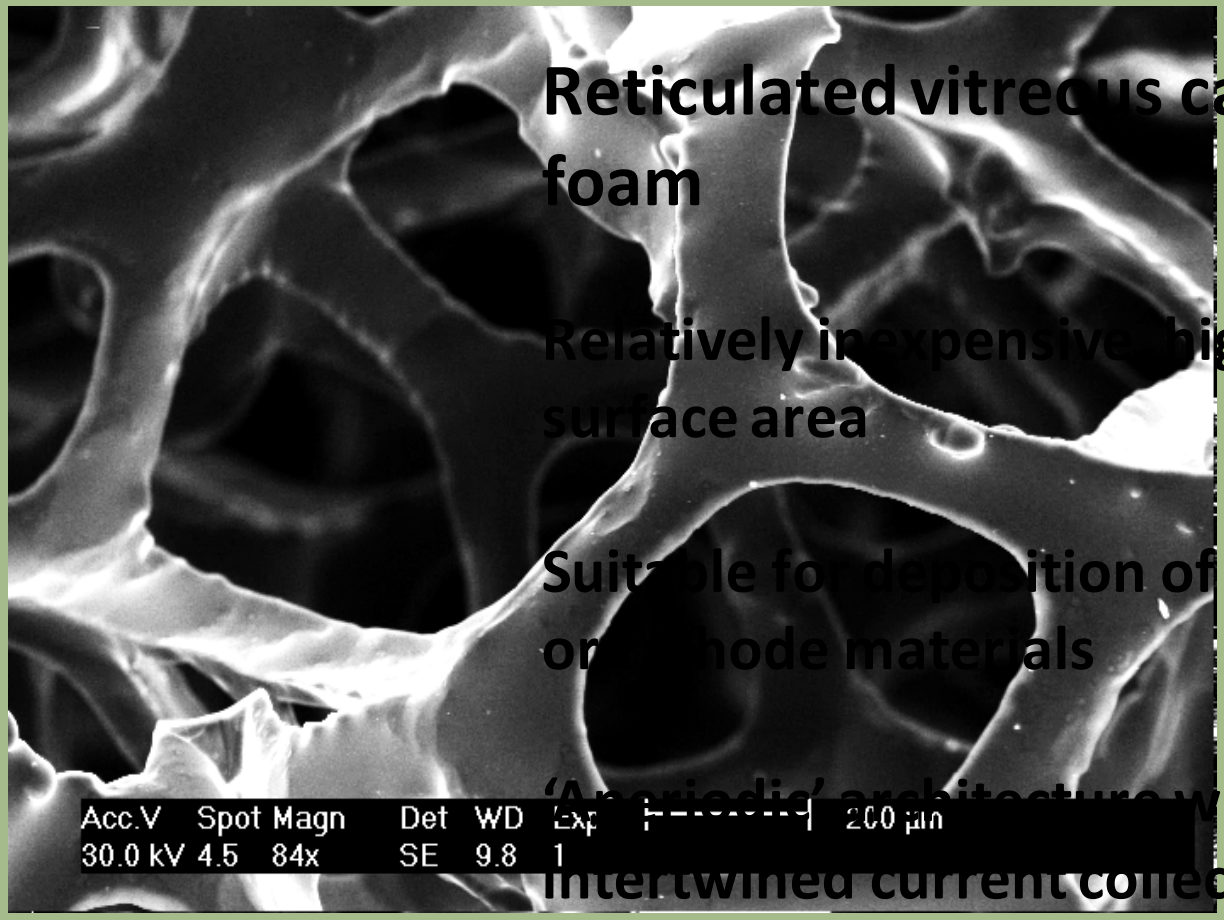


Image from baj.or.jp

Higher energy, capacity and power *per footprint area*



3D-MB by electrodeposition



Reticulated vitreous carbon foam

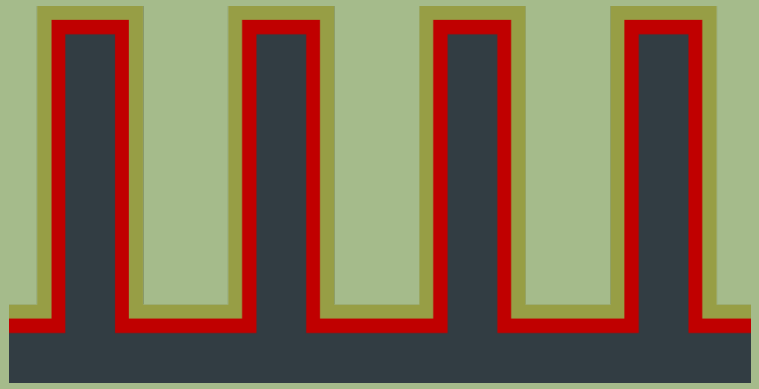
Relatively inexpensive, high surface area

Suitable for deposition of anode or cathode materials

'Aperiodic' architecture with intertwined current collectors

Polymer electrolytes for 3D-MBs

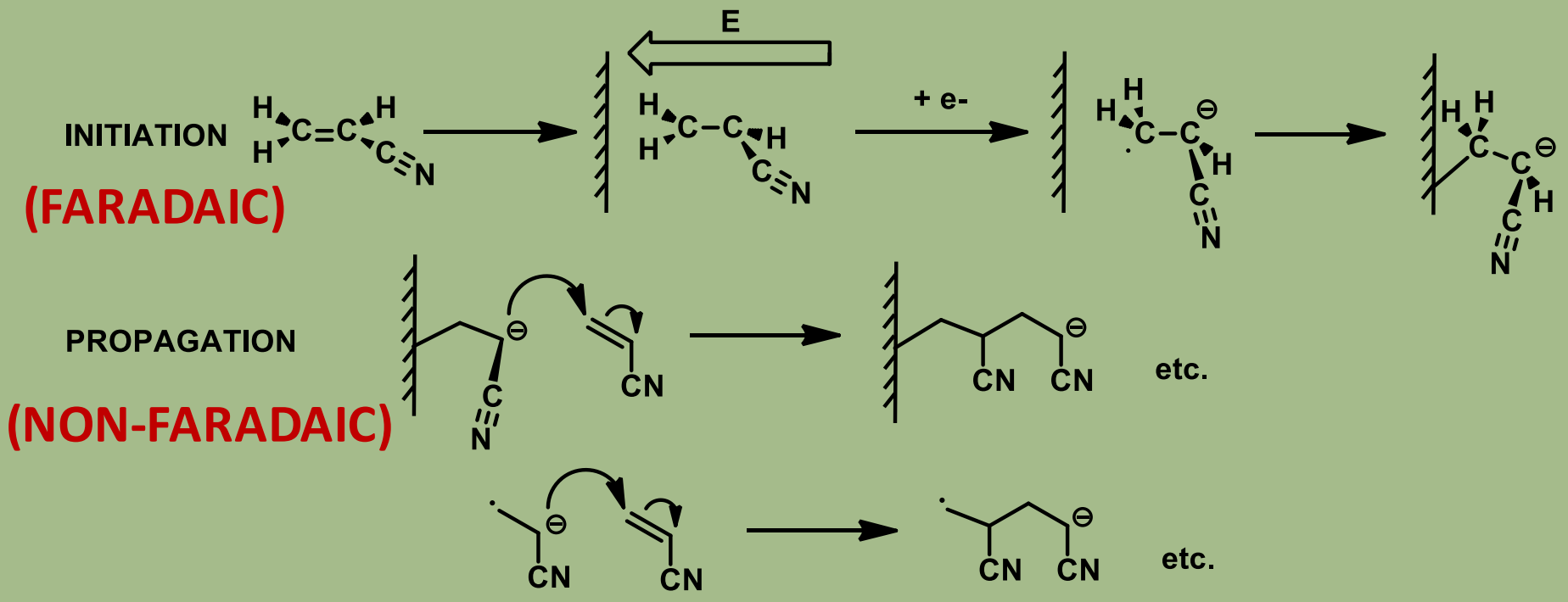
Requirements!



- Thin: 1-5 μm
- Conformal to the surface
- Pinhole-free
- Electronically insulating
- Li^+ conductivity (10^{-3} – 10^{-5} S cm^{-1})
- Mechanically robust

In principle, an electrodeposited polymer electrolyte should satisfy all of these requirements

How do you electrodeposit a polymer electrolyte?



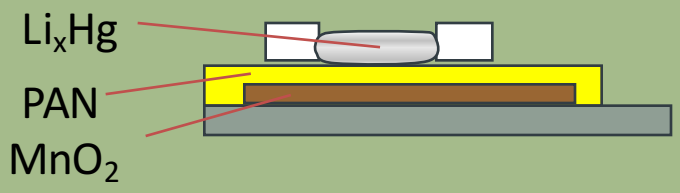
Lécayon et al, *Chem. Phys. Lett.* 1982, *91*, 506-510

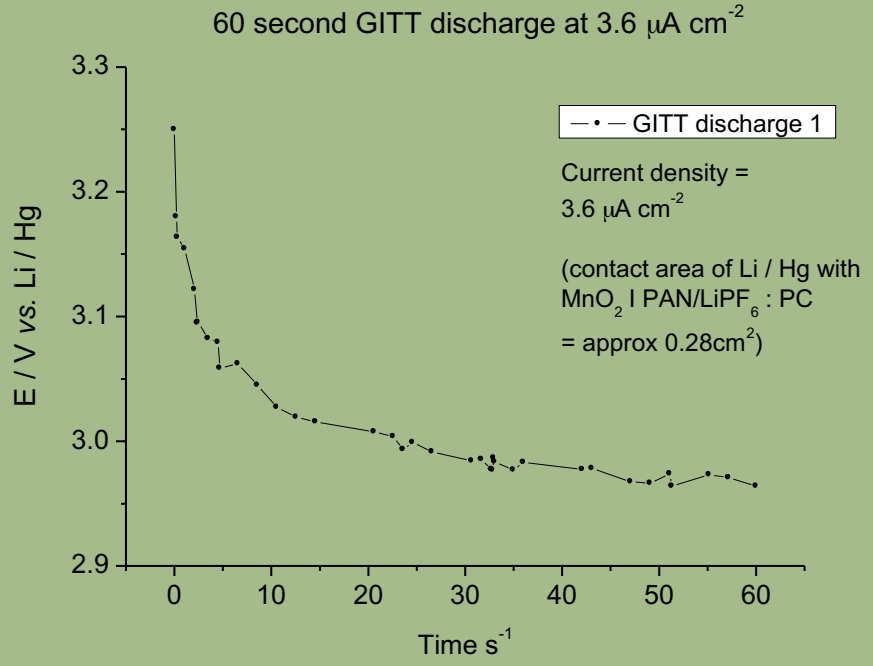
Depends on solvent, monomer and surface

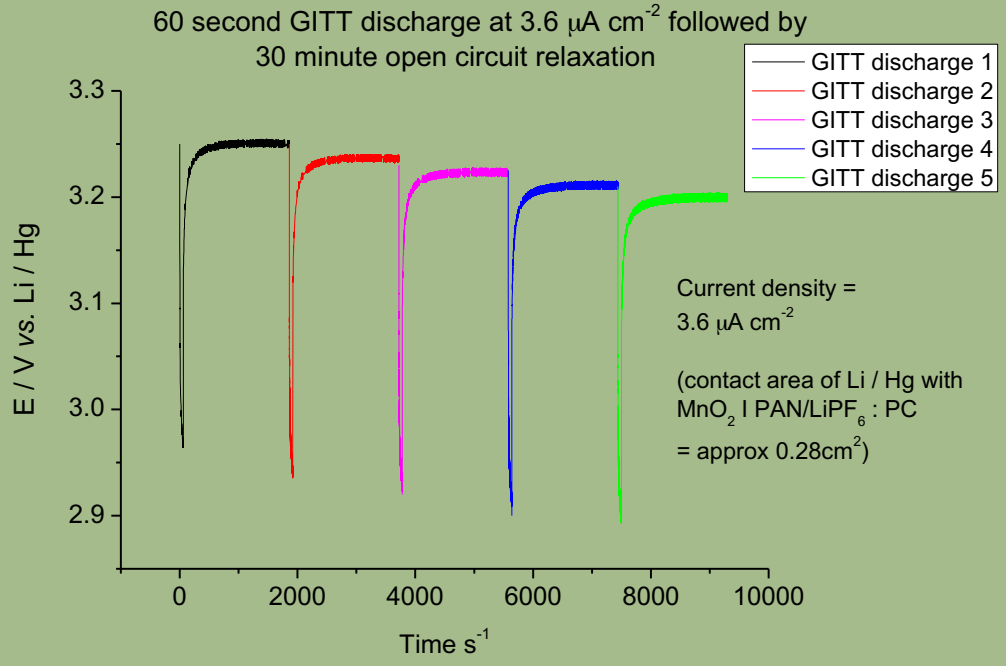
Electrodeposited PAN as an electrolyte

Films soaked with 1 M $LiPF_6$ in 1:1 EC:DMC

GITT – 60 s pulses at 3.6 μA cm^{-2}

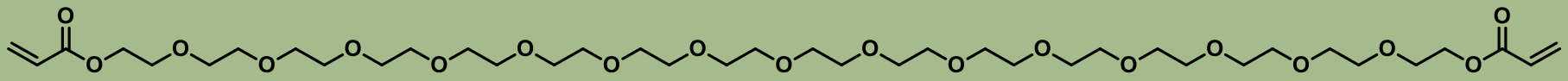


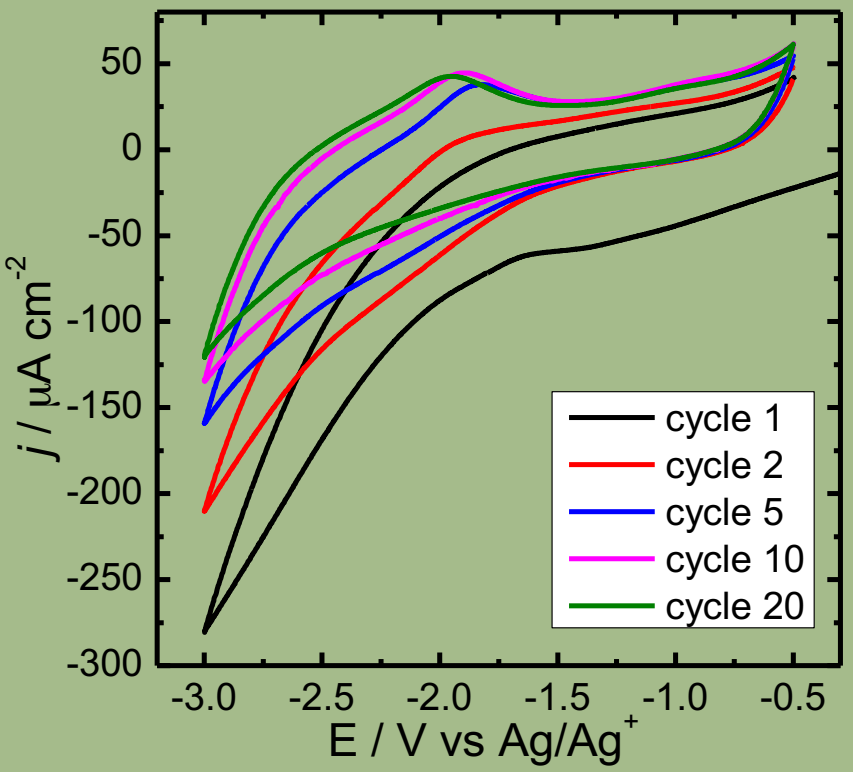


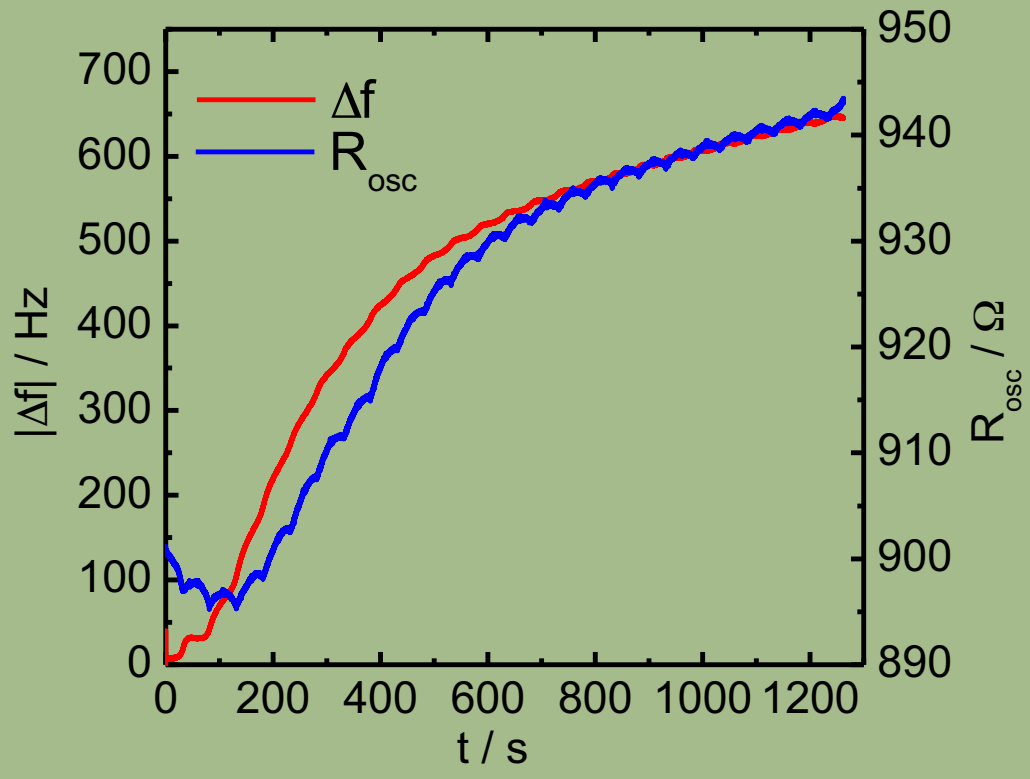


G. El-Enany, M.J. Lacey, P.A. Johns, J.R. Owen, Electrochem. Comm. 11 (2009) 2320-2323

Poly(ethylene glycol) diacrylate (PEGDA)



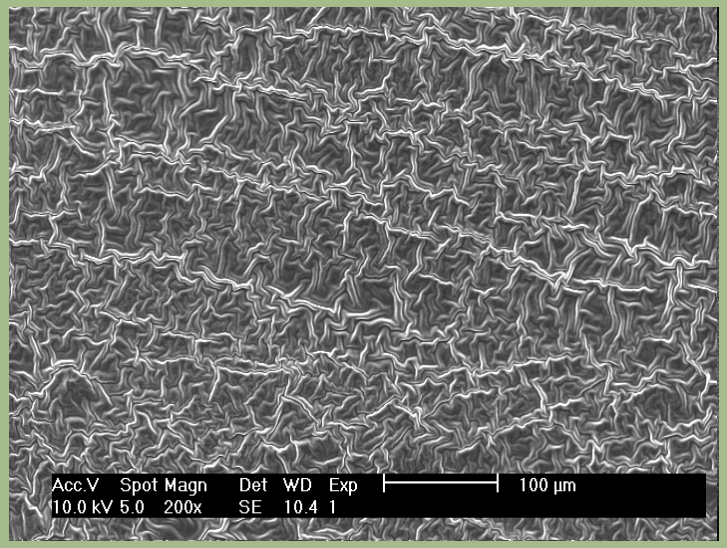


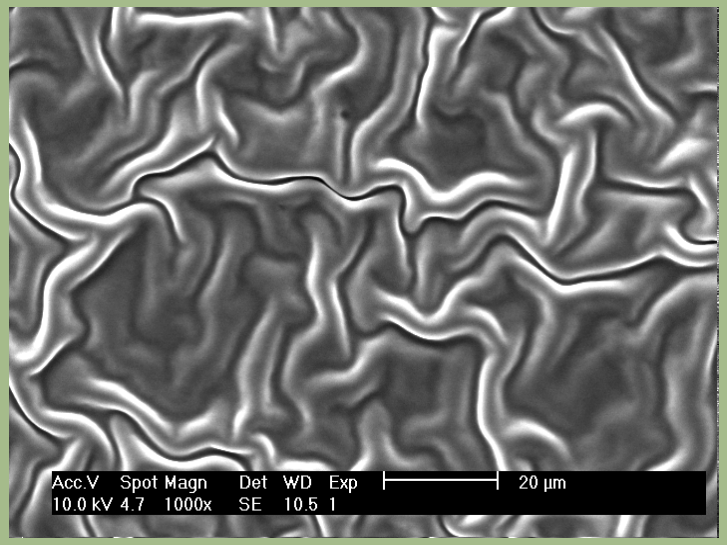


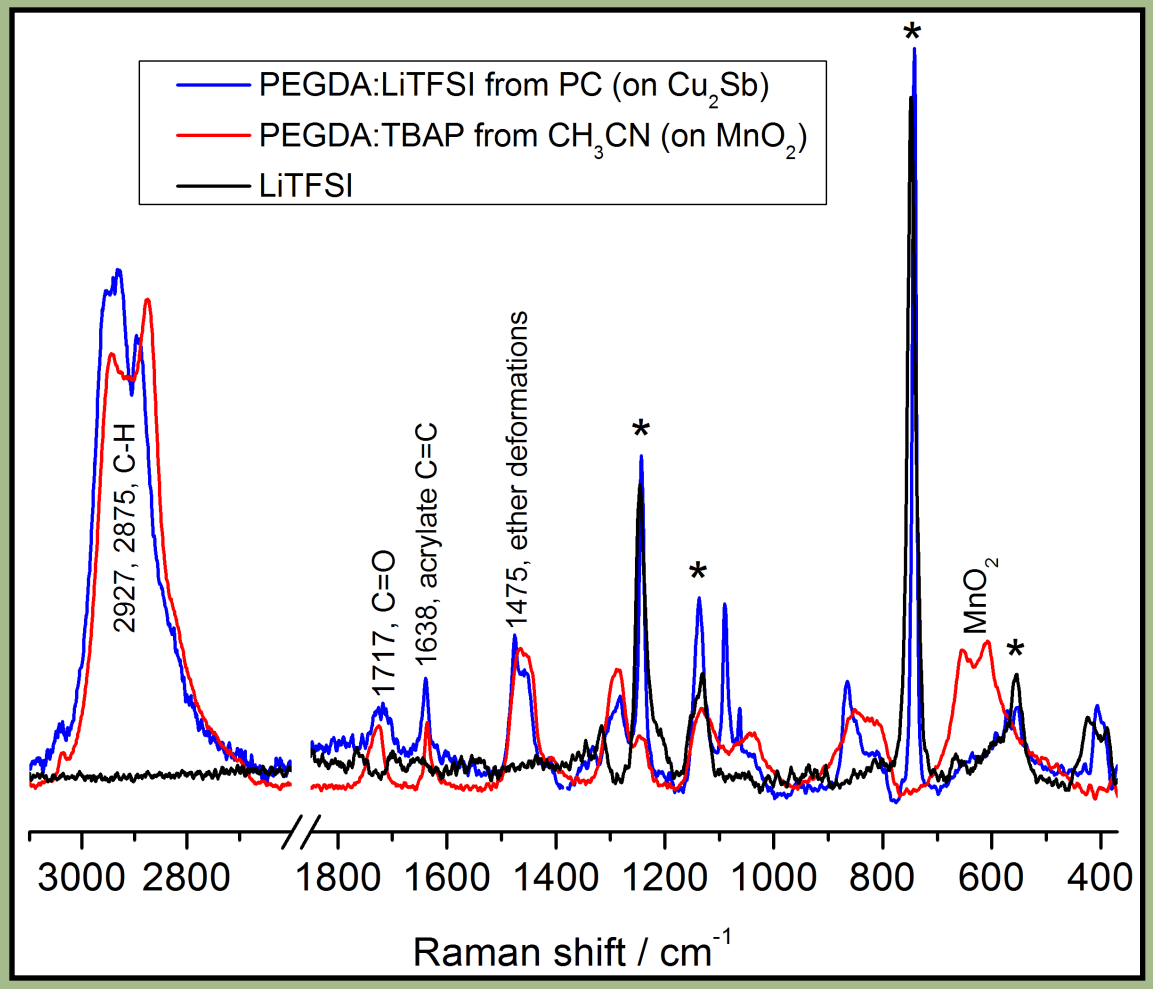
15% v/v PEGDA (M_n ~700) in PC, 0.5 M LiTFSI supporting electrolyte

Deposited on Cu_2Sb on Au/Cr EQCM substrate at 100 mV s^{-1} between -0.5 V and -3.0 V vs Ag wire over 25 cycles

PPEGDA deposition on Cu_2Sb

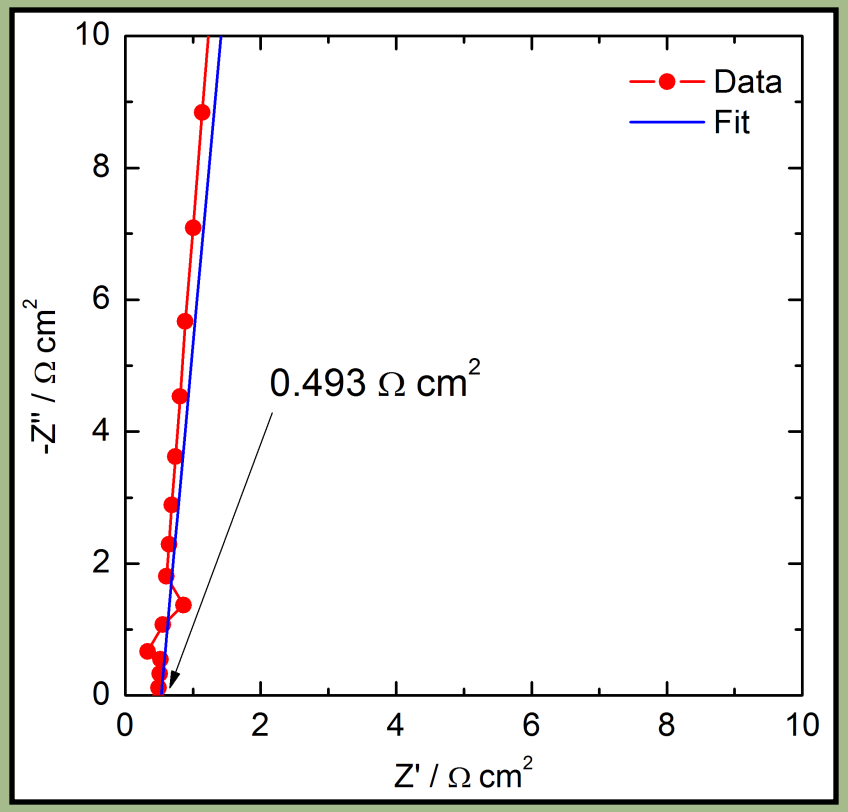


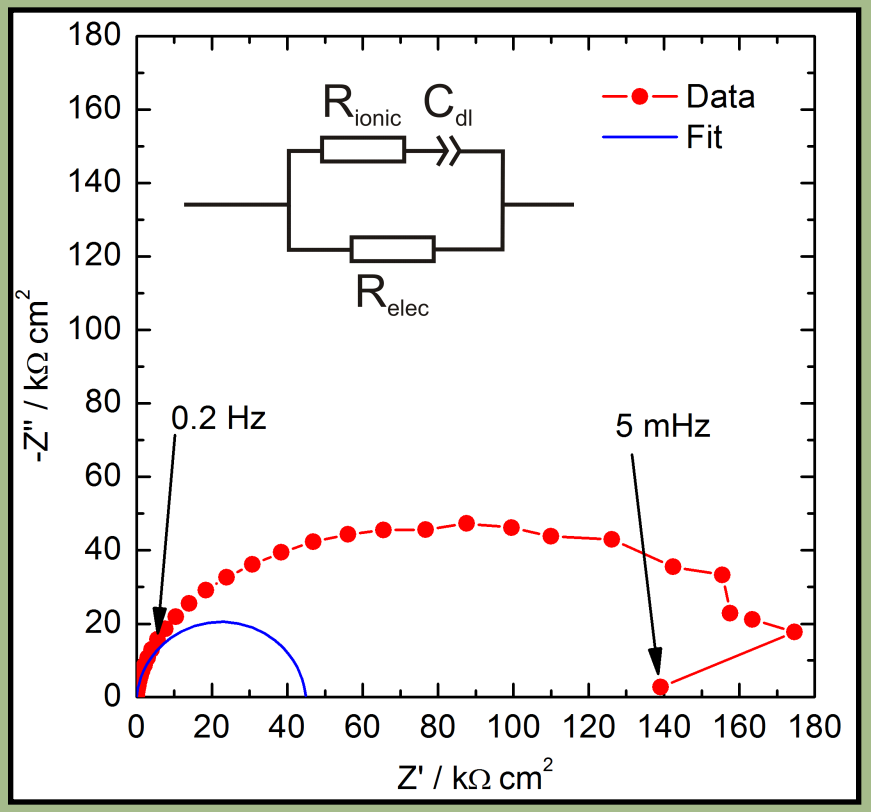




AC Impedance

Cu_2Sb | PPEGDA:LiTFSI | Hg





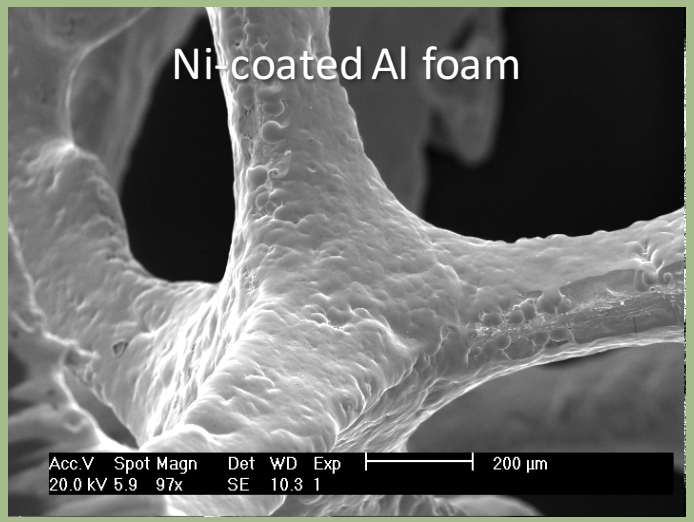
Assuming film thickness = 5 ±2.5 m;

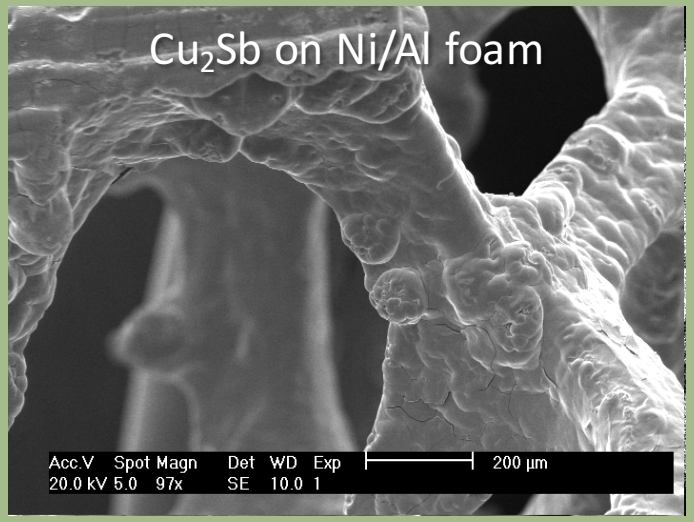
$\sigma_{ionic} = (1 \pm 0.5) \times 10^{-3}$ S cm^{-1}

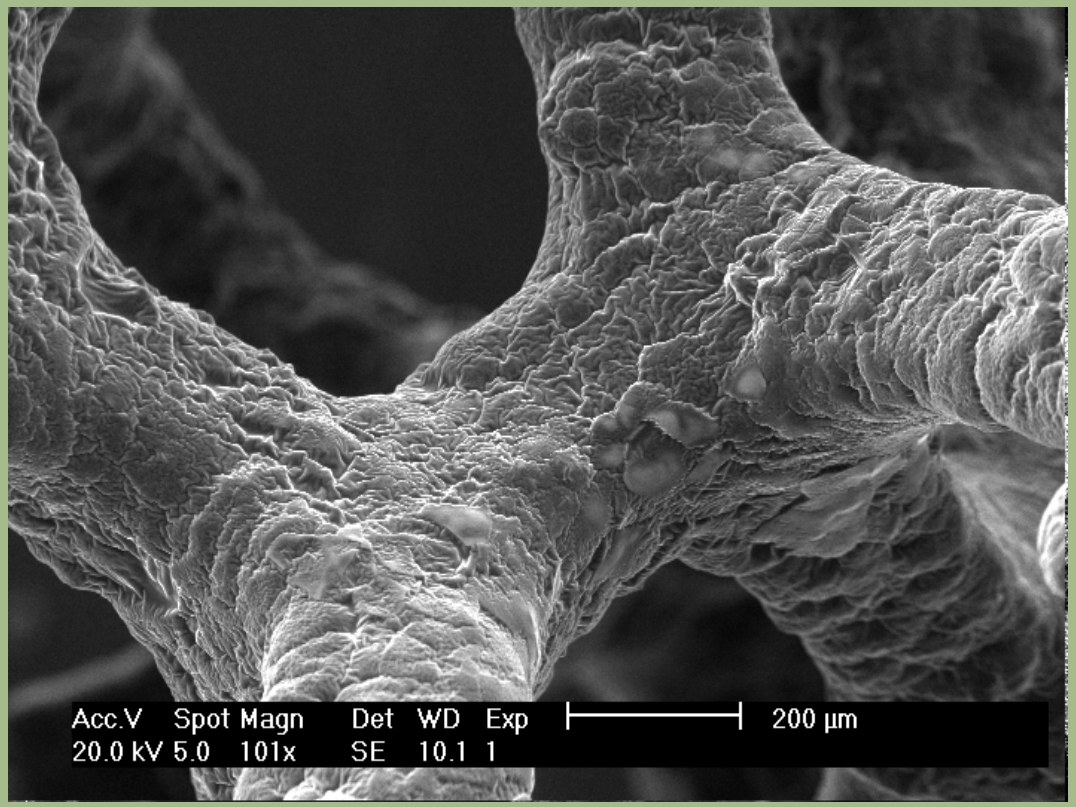
$\sigma_{elec} < (1.1 \pm 0.6) \times 10^{-8}$ S cm^{-1}

PPEGDA in 3D

Deposition onto Cu_2Sb on Ni-coated Al foam, 45 ppi



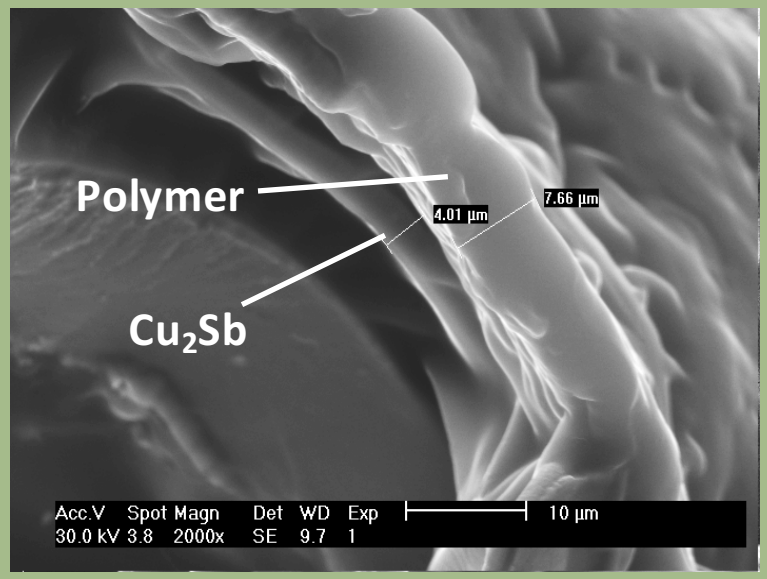


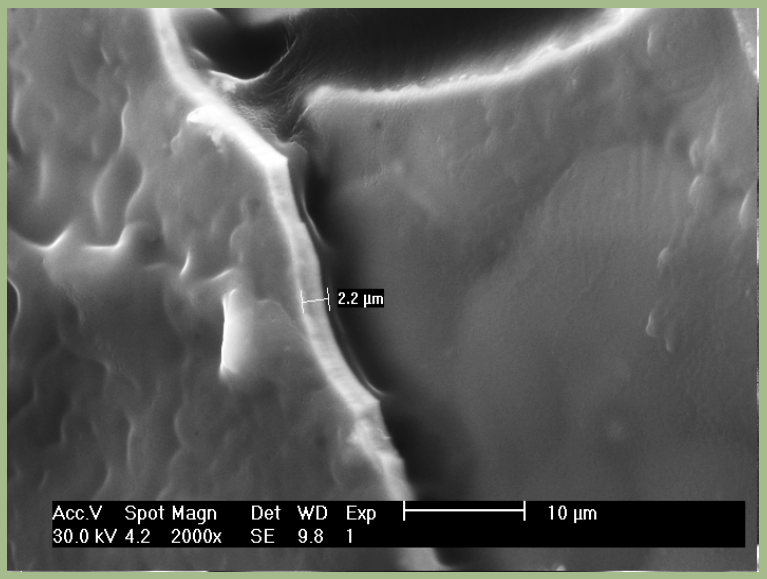


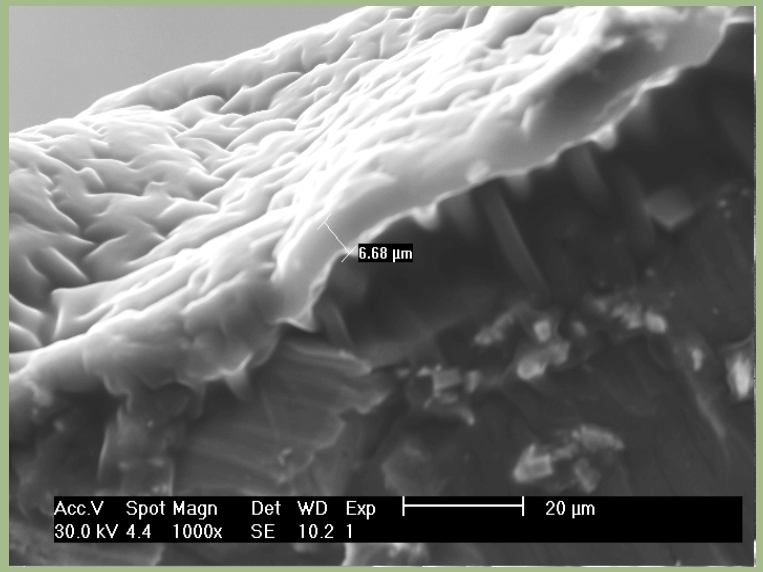
PPEGDA:LiTFSI on Cu_2Sb on Ni/Al foam

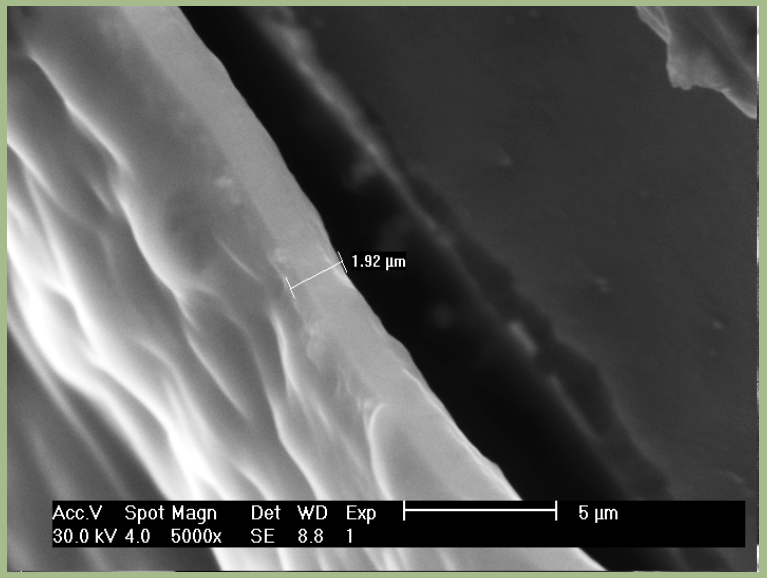
Cross-sectional view

OUTSIDE



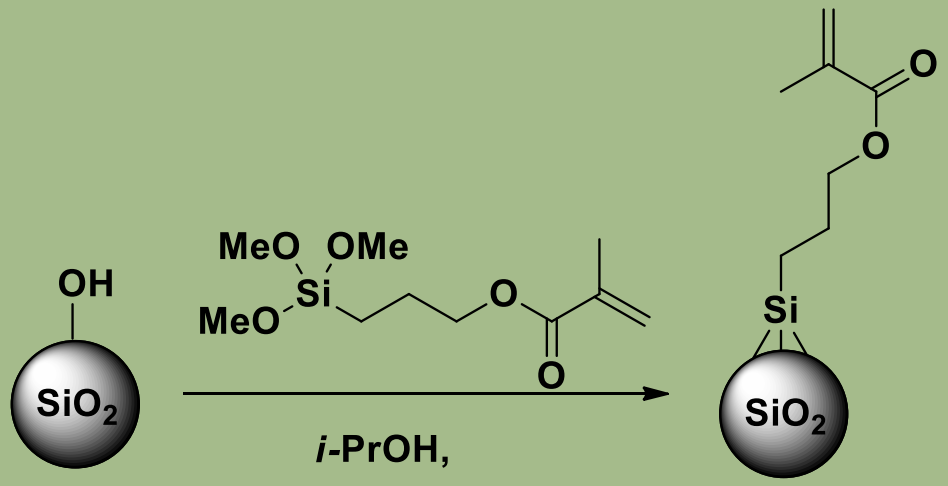




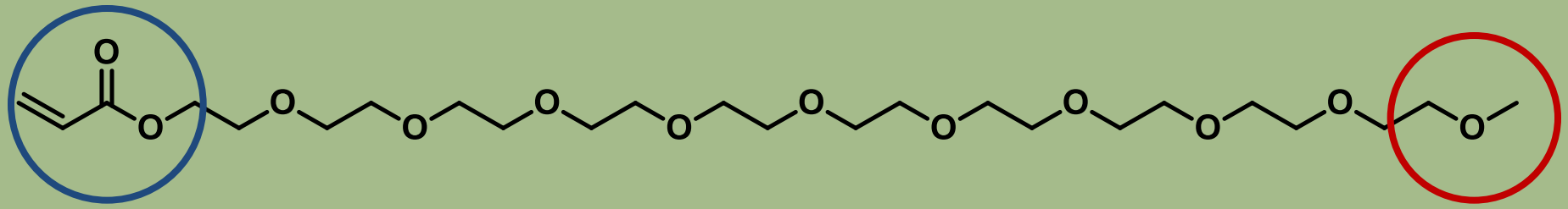


DOWN A PORE

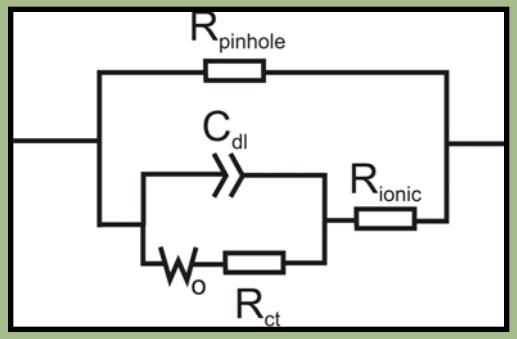
Modifying PPEGDA (2 approaches)



Major improvements in mechanical stability but lower ionic conductivity (lower electrolyte volume?)



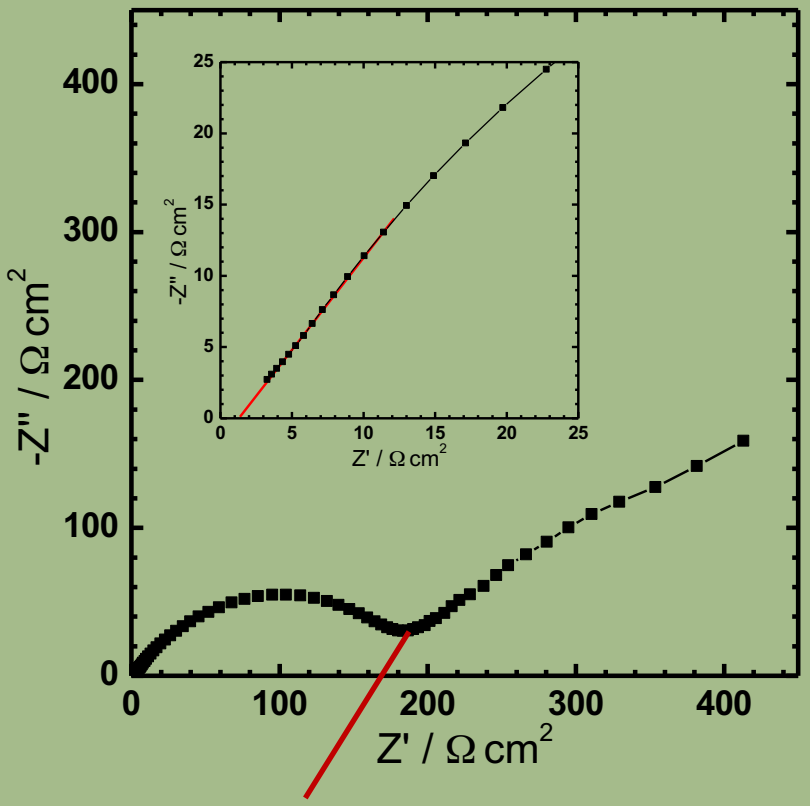
"Internal plasticiser" improves film flexibility and ionic conductivity – works at room temperature

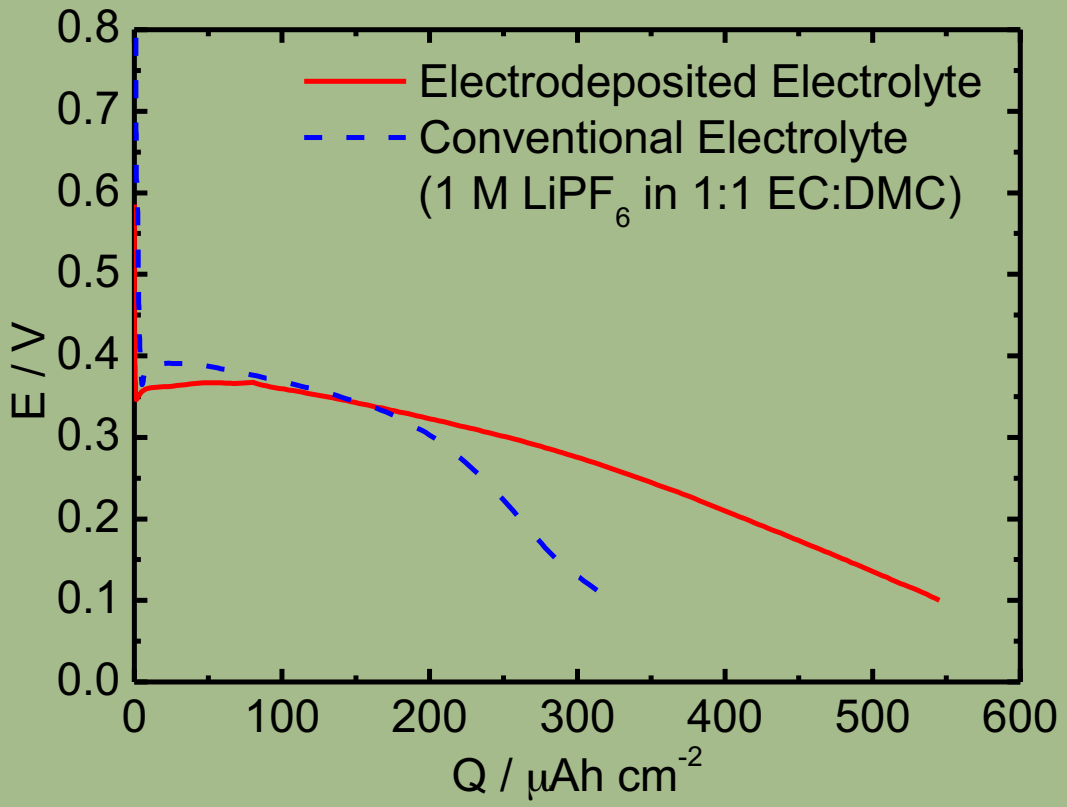


Half cell discharge

Deposition solution: 0.5 M LiTFSI in: 15% v/v PEGDA (containing 10% w/w nano-SiO_2), 4% v/v PEGMEA in PC

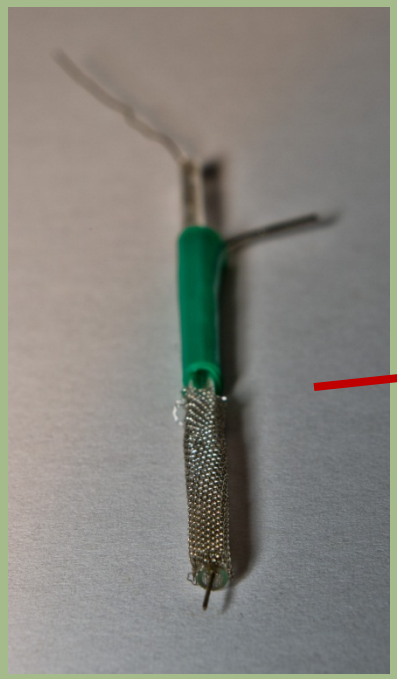
NiSn | polymer | Li



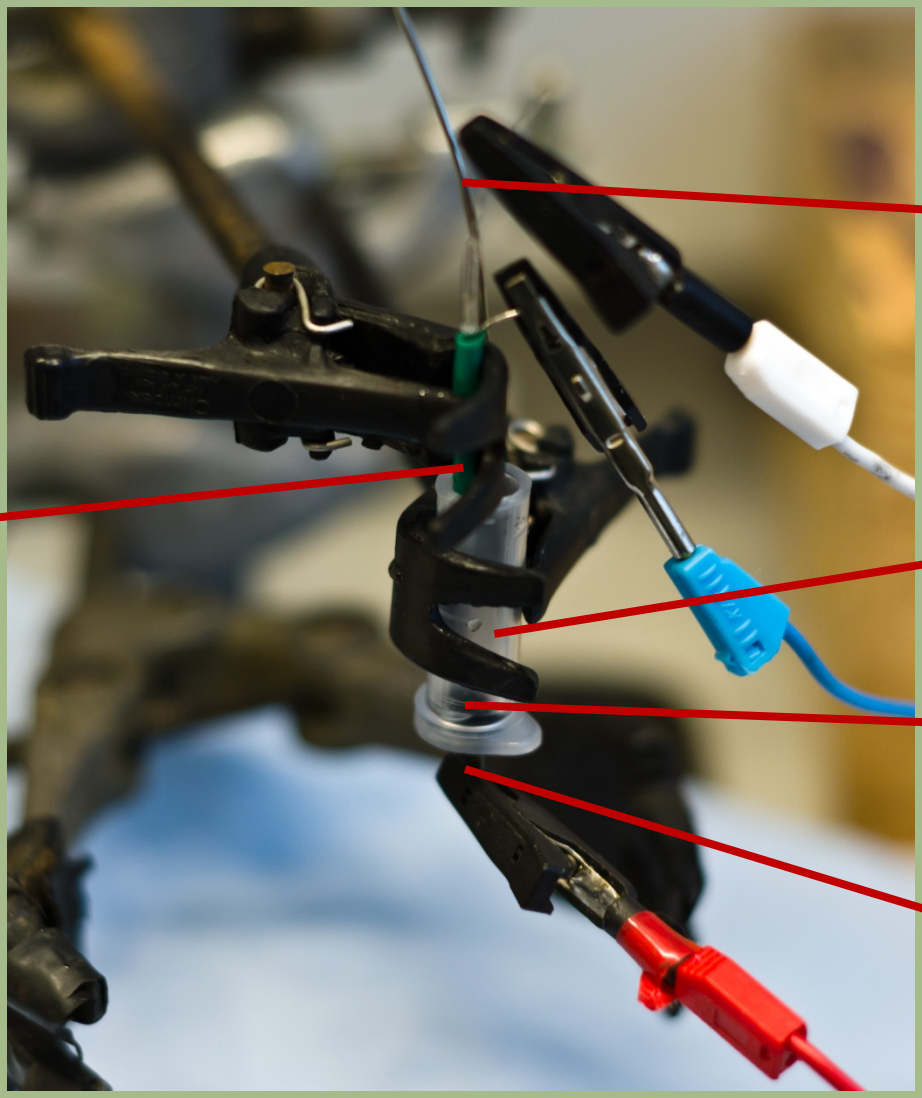


"Charge transfer resistance" – probably due to SEI on NiSn surface

Deposition onto high surface area RVC substrates (100 ppi)



Combined Ag wire reference & Pt mesh counter electrode (2 mm diameter)



Syringe needle to Ar gas supply

~ 1 mL deposition solution

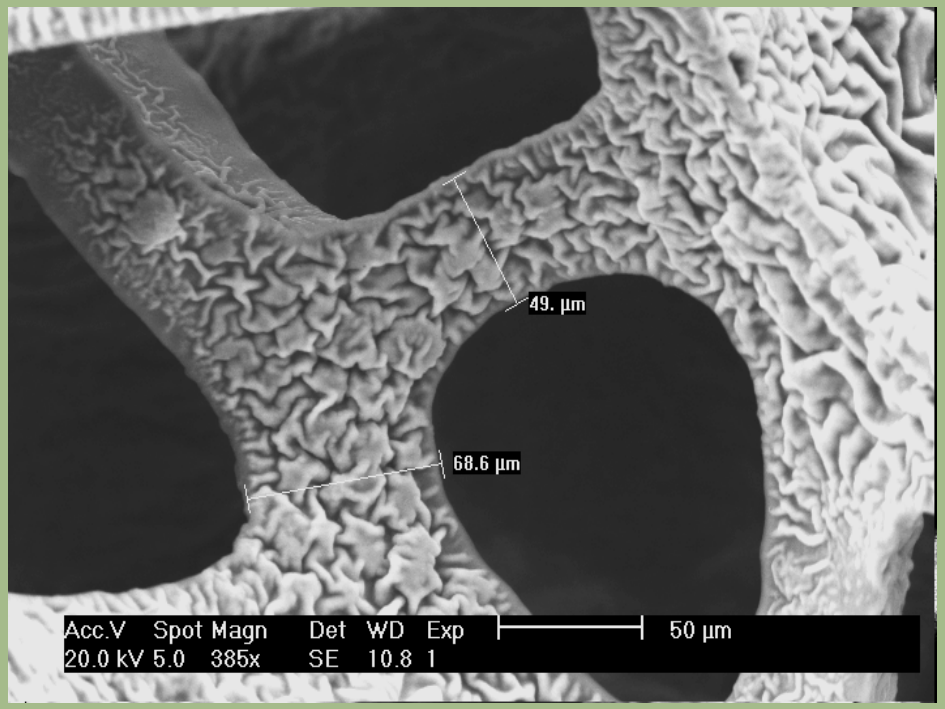
RVC substrate fixed by epoxy resin

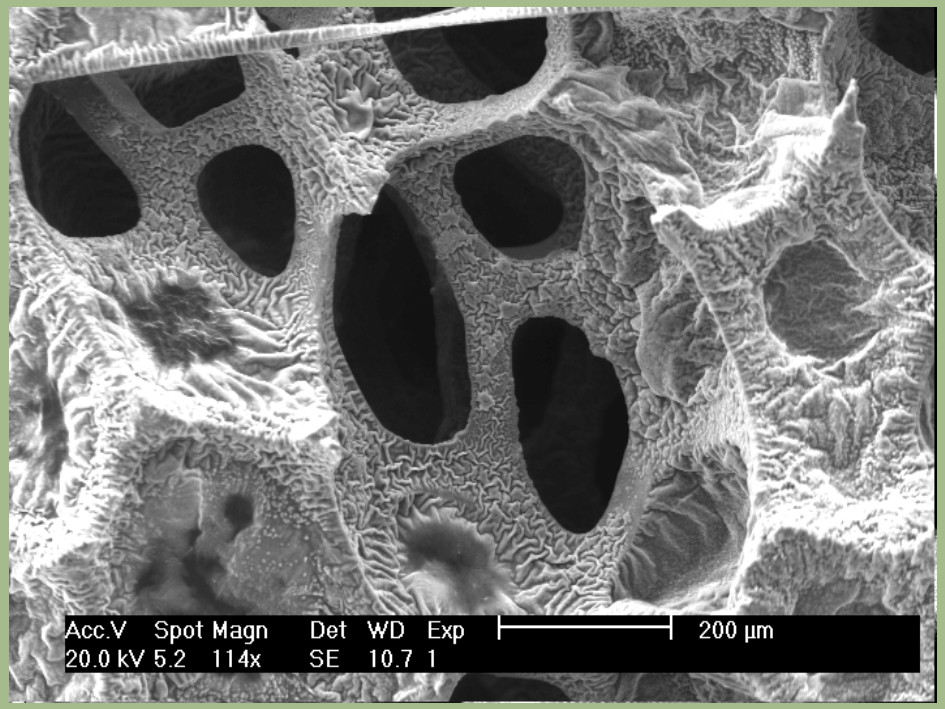
Ti foil contact to substrate

SEM

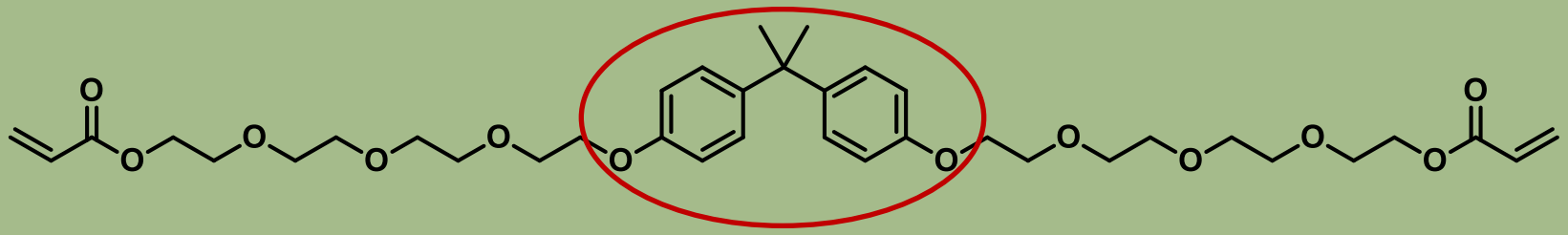
Same polymer electrolyte composition as shown on Slide 16

Deposition onto $LiFePO_4$ film (from ink) on 100 ppi RVC

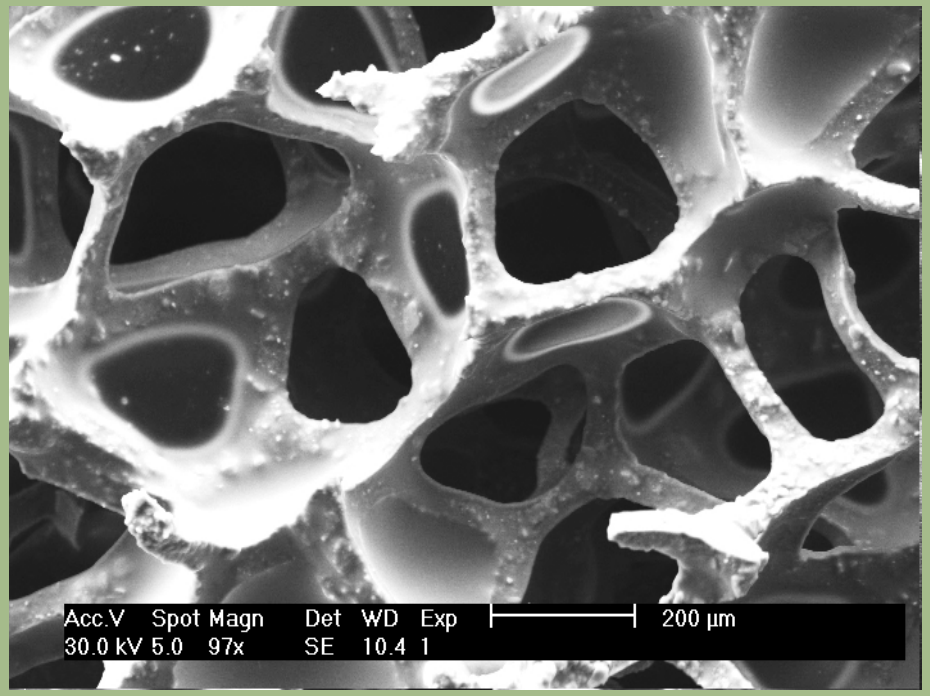


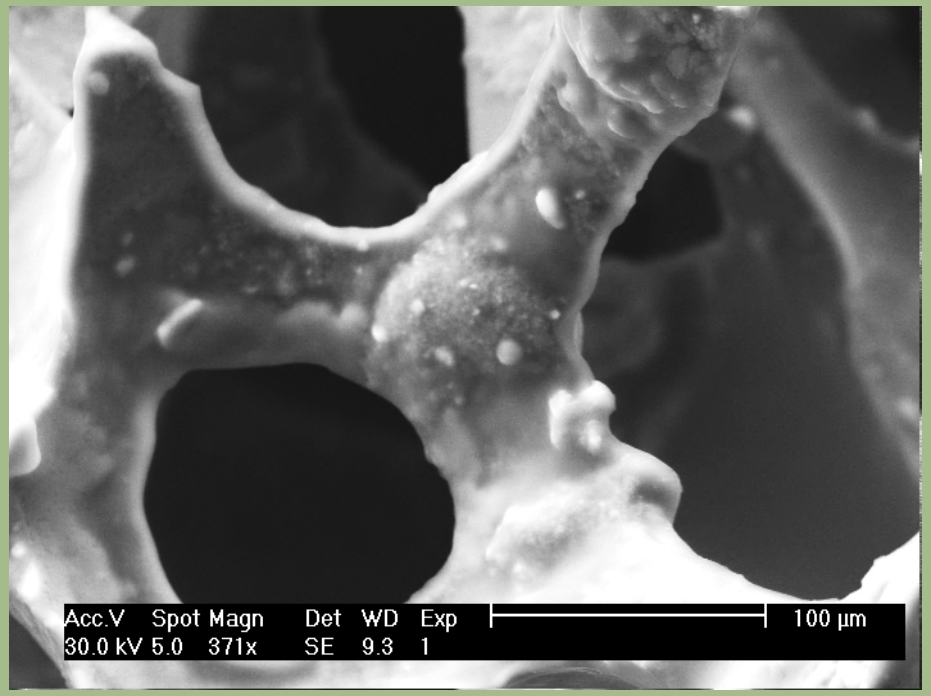


Different polymer electrolytes



Bisphenol A ethoxylate diacrylate (BEDA) instead of PEGDA





Summary

1. Vinyl electropolymerisation reaction is applicable to electrodeposition of polymer electrolytes
2. Electrodeposition of PAN and PPEGDA has been demonstrated on both cathode and anode materials on planar and 3D substrates
3. PPEGDA is modifiable through internal plasticisation and addition of inorganic fillers to give a polymer electrolyte of acceptable mechanical strength and ionic conductivity
4. Full cell testing is a work in progress but a realistic objective

Acknowledgements

- Dr Maciej Sosna
- Robert Johnson
- EPSRC
- EU FP7 NMP “SUPERLION”