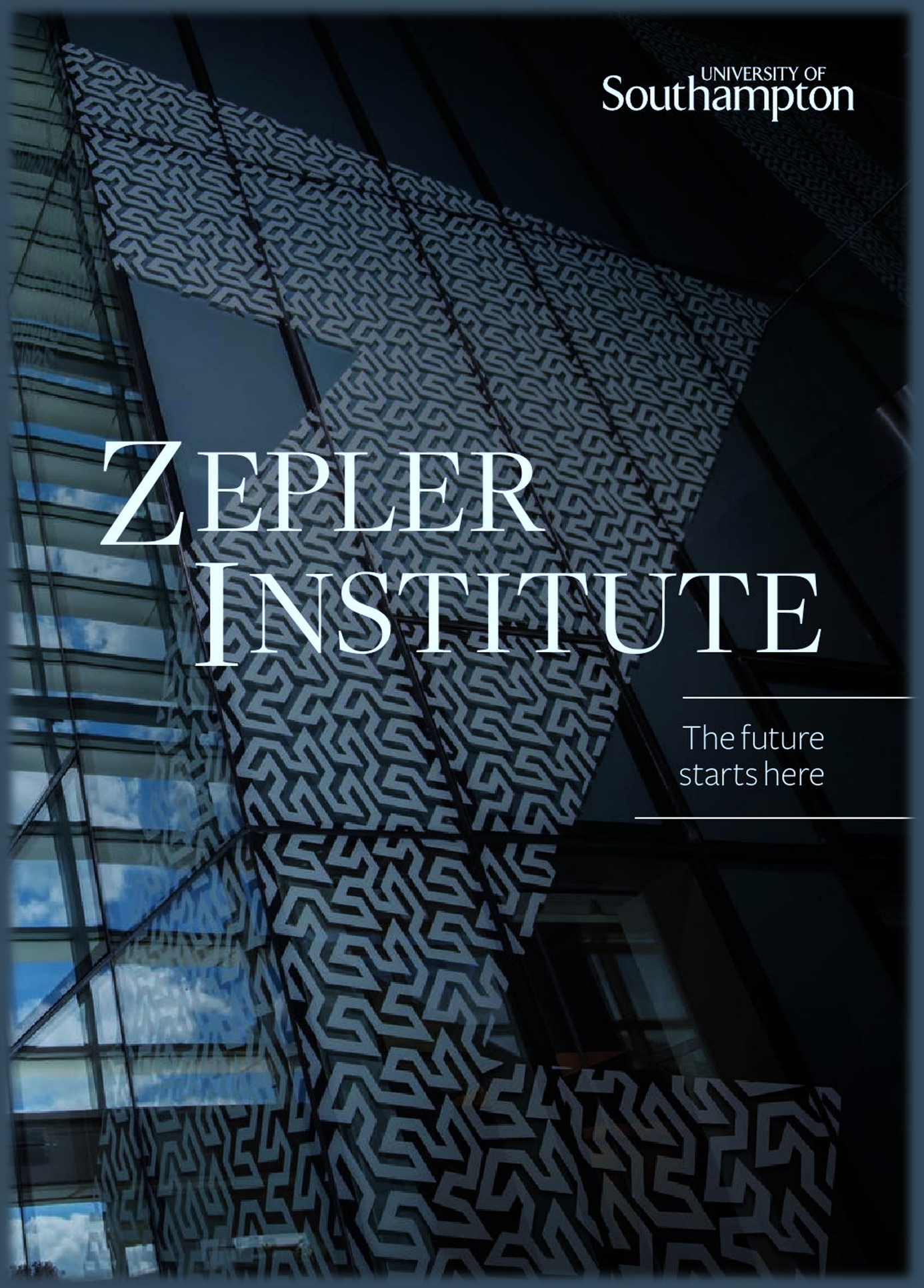


Conductive Polymers as Battery Cathodes for Future Safe and Sustainable Energy Storage

NASA Aerospace Battery Workshop

November 21, 2019

Dr Theresa Schoetz
Zepler Institute
University of Southampton
Mountbatten Building
SO17 1BJ | UK
+44 (0) 23 8059 8931
T.Schoetz@soton.ac.uk

Development of novel energy storage materials:

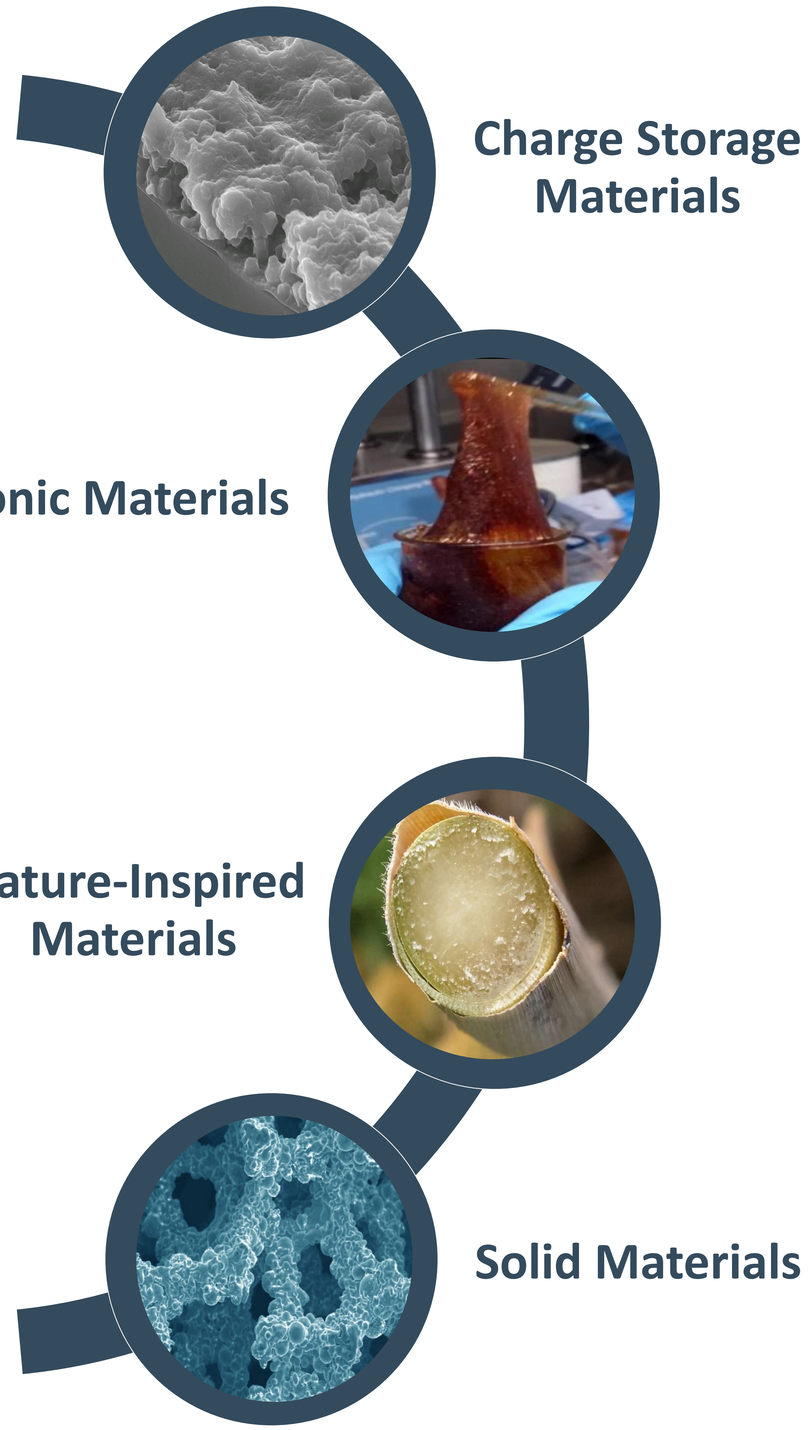
- Performance (≥200 Wh kg^{-1} and 300 W kg^{-1})
- Economically and ethically available raw materials
- Safe cell reactions
- Low weight
- High active surface
- Long cycle life
- Low-cost production and recycling
- Size and shape adaptable

= safe, sustainable and smart Energy Storage Materials (3sESM)

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Modern Batteries

Combination of…

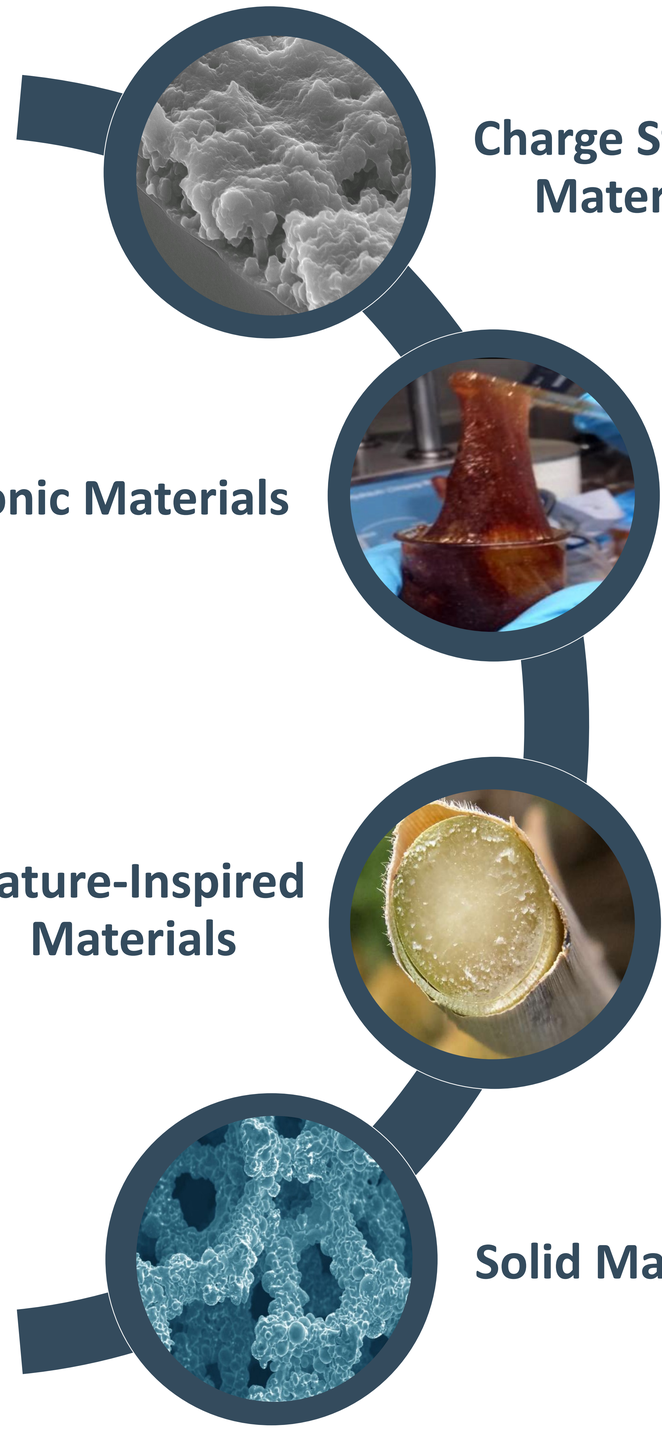


Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Energy Storage Materials

Modern Batteries

Combination of…



Charge Storage Materials

- Conductive polymers
- 3D Carbon materials
- Zeolites

Ionic Materials

- Ionic liquids
- Ionogels
- Deep eutectic solvents

Nature-Inspired Materials

- Natural fibres and tissues
- Engineered microorganisms

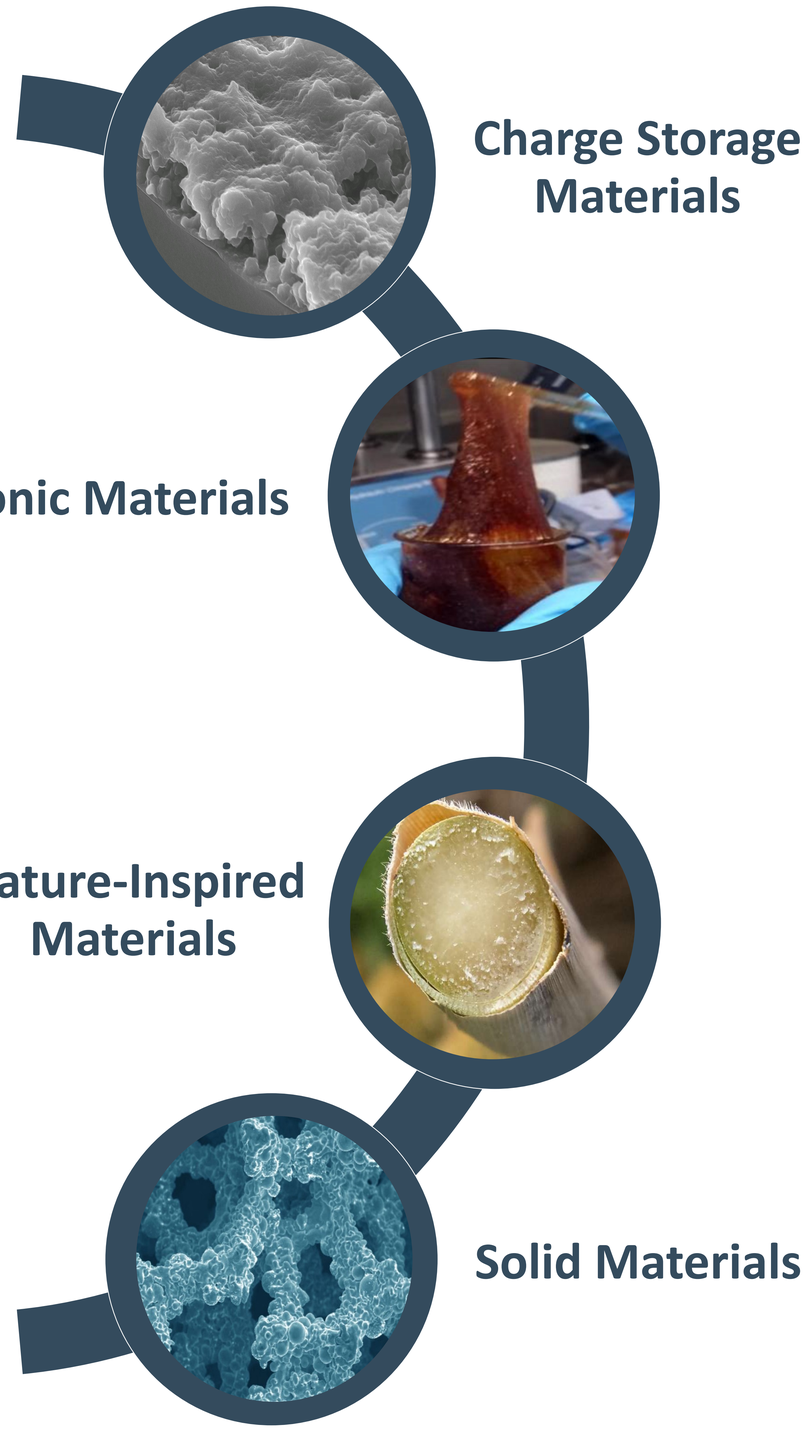
Solid Materials

- Al, Mg, Na, Zn, Si
- Metal oxides
- Conductive glass

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Modern Batteries

Combination of…



Conductive polymers
3D Carbon materials
Zeolites

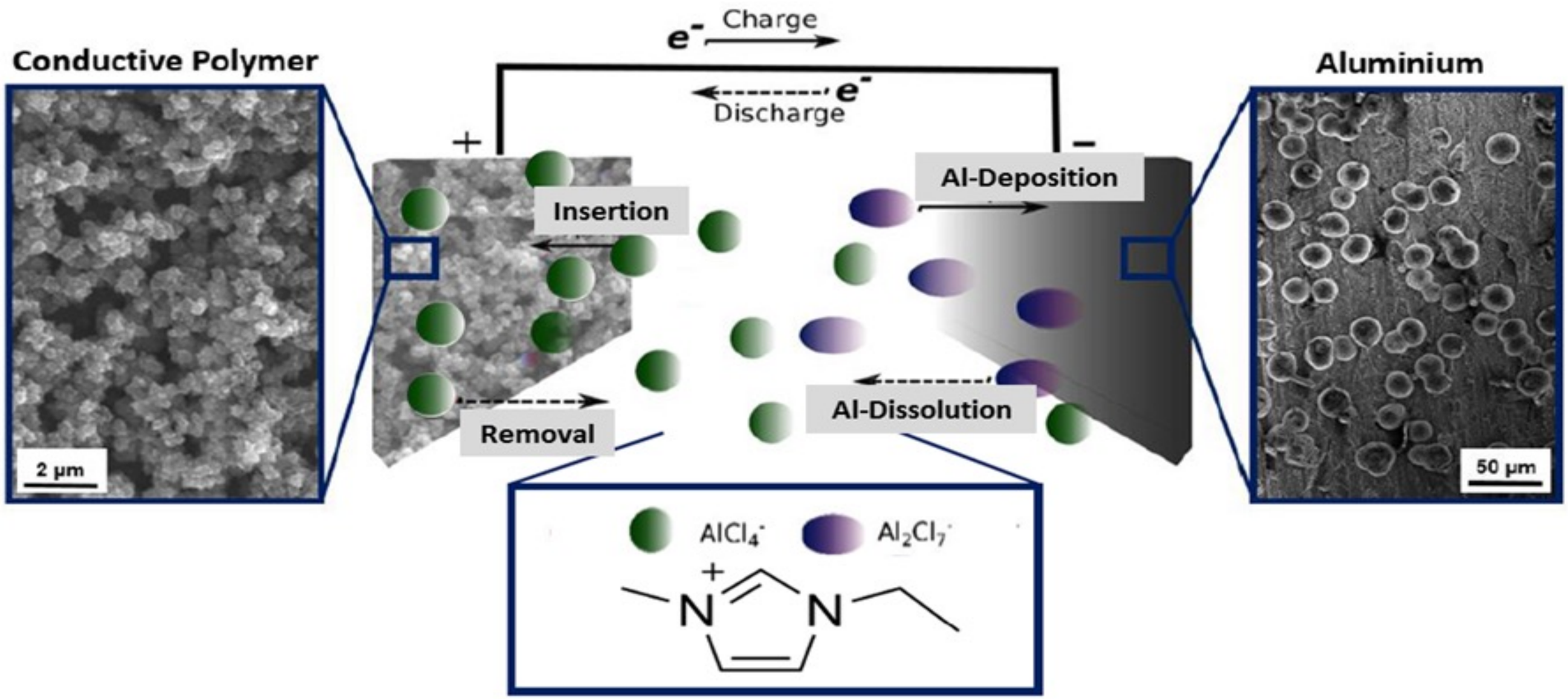
Ionic liquids
Ionogels
Deep eutectic solvents

Natural fibres and tissues
Engineered microorganisms

Al, Mg, Na, Zn, Si
Metal oxides
Conductive glass

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer-Aluminium Battery



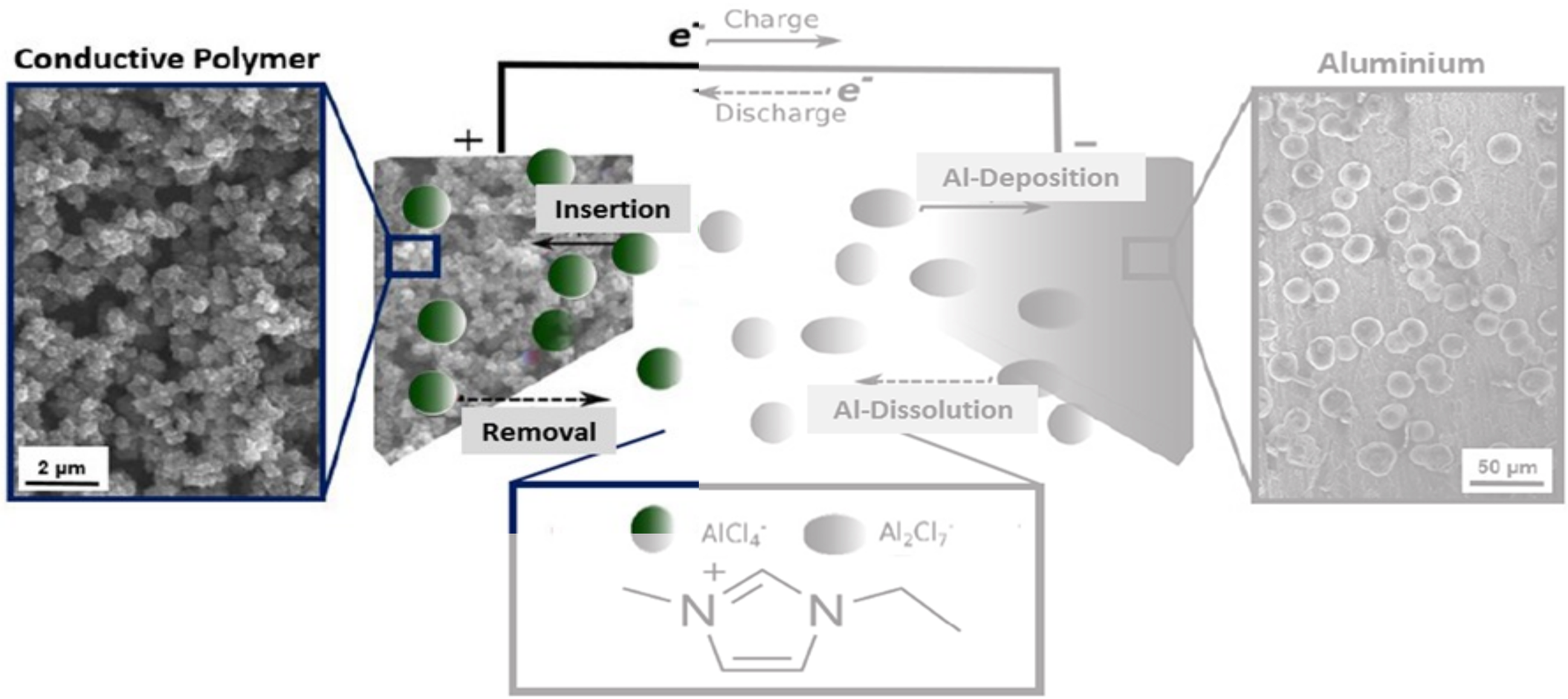
1-Ethyl-3-methylimidazolium chloride – Aluminium chloride

$$3\mathrm{MonomerUnit}_{\alpha}+3X^{-}+4Al_2Cl_7^{-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 3[\mathrm{MonomerUnit}]_{\alpha}X+Al+7AlCl_4^{-}$$

T. Schoetz et al. Journal of Solid State Electrochemistry 21, 3237–3246, 2017.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer Cathode

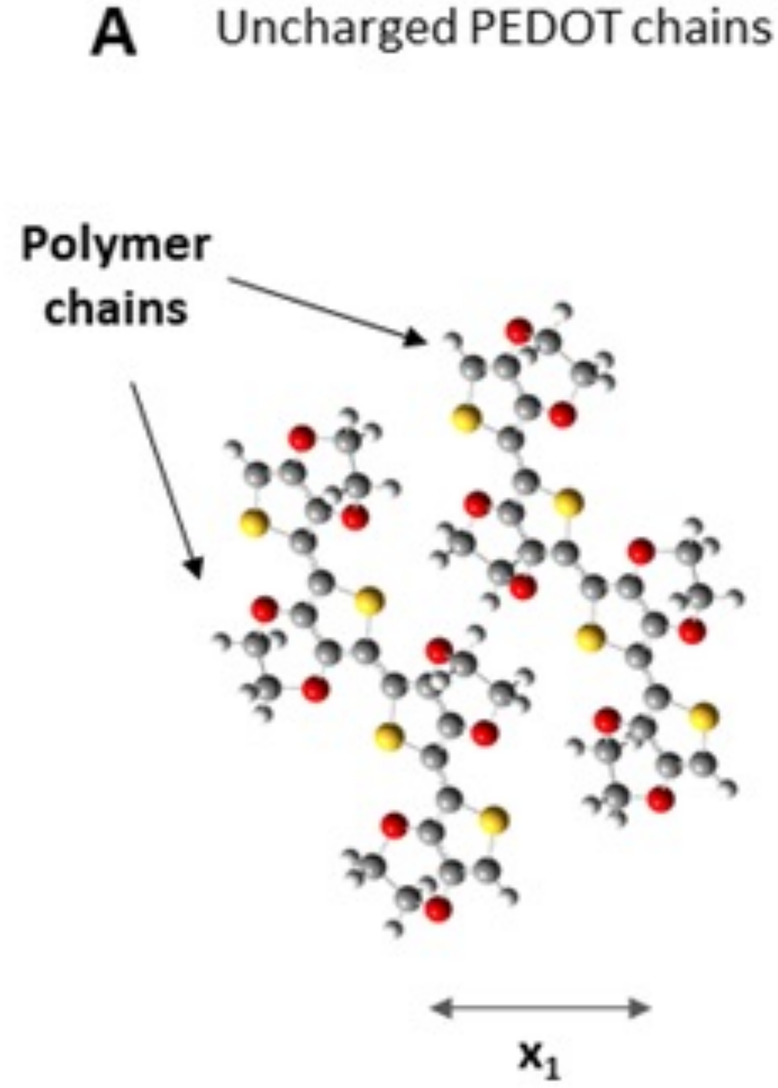


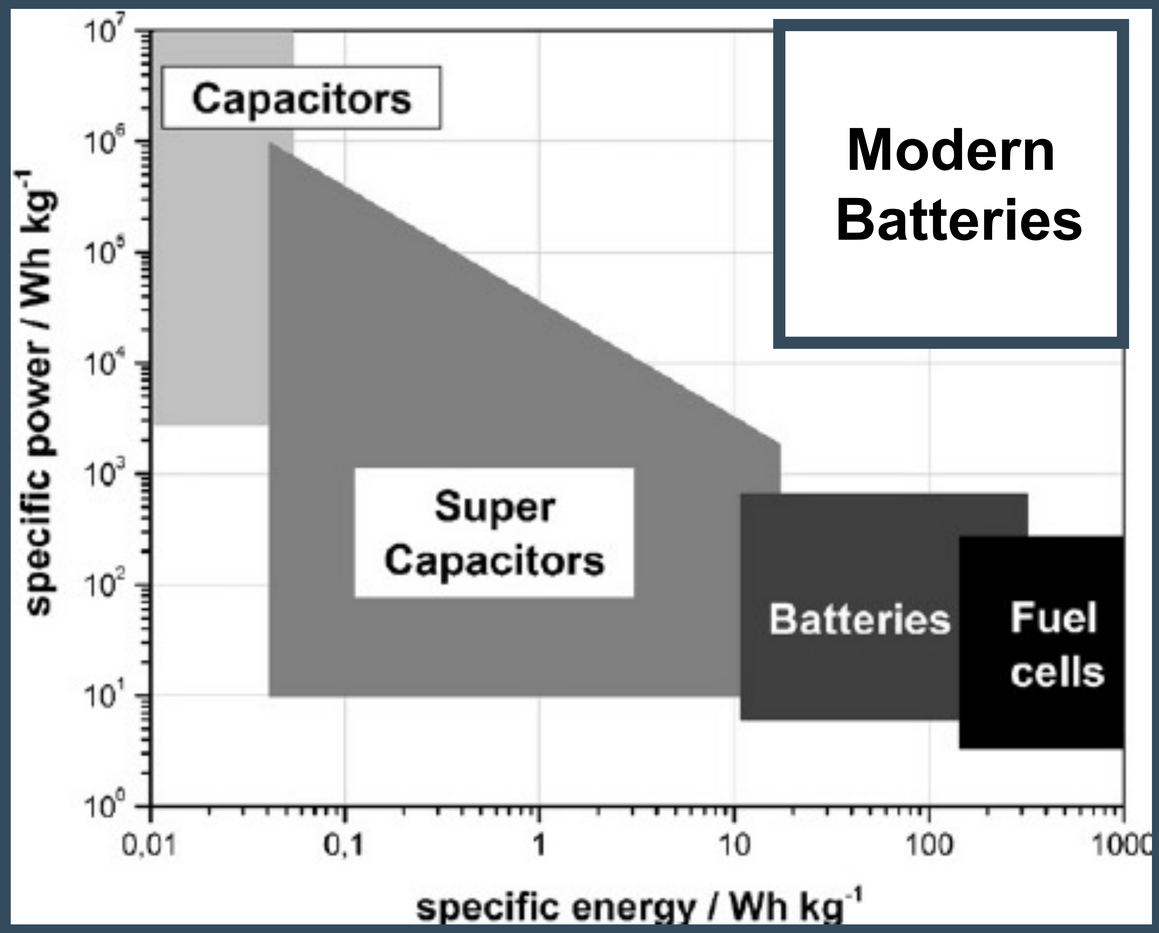
$$\mathrm{MonomerUnit}_{\alpha} + X^{-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} [\mathrm{MonomerUnit}]_{\alpha}X + e^{-}$$

T. Schoetz et al. Journal of Solid State Electrochemistry 21, 3237–3246, 2017.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

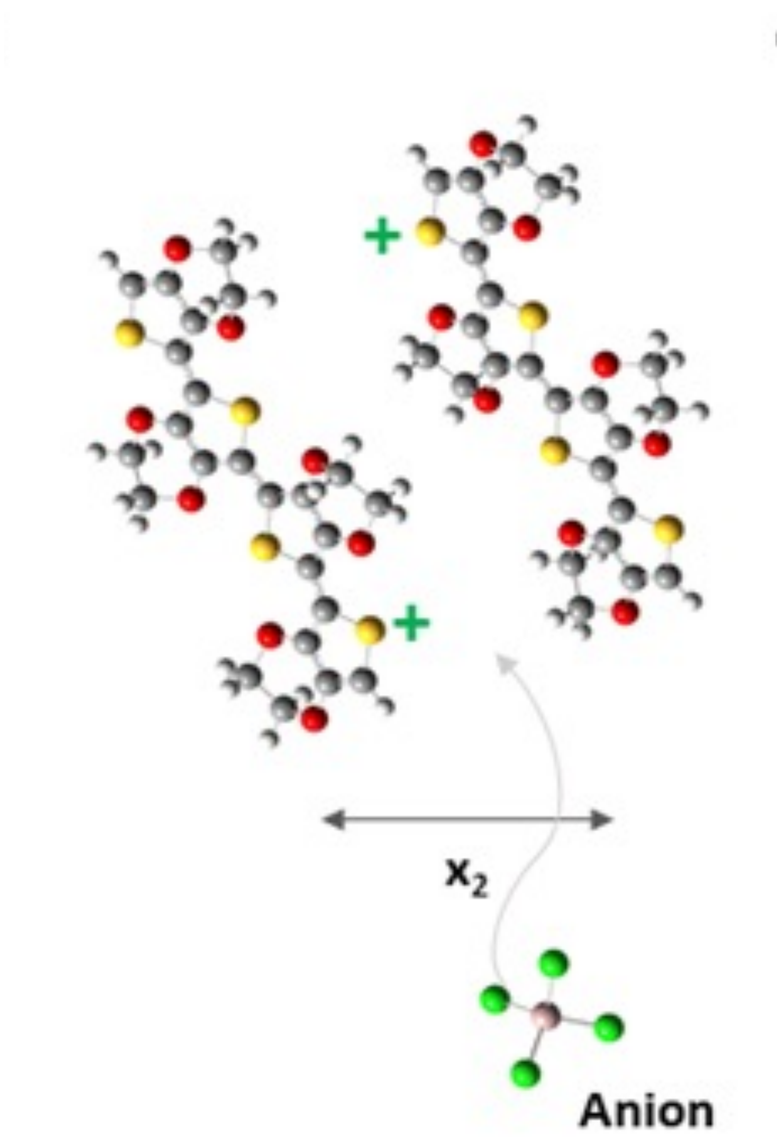
Conductive Polymer Cathode

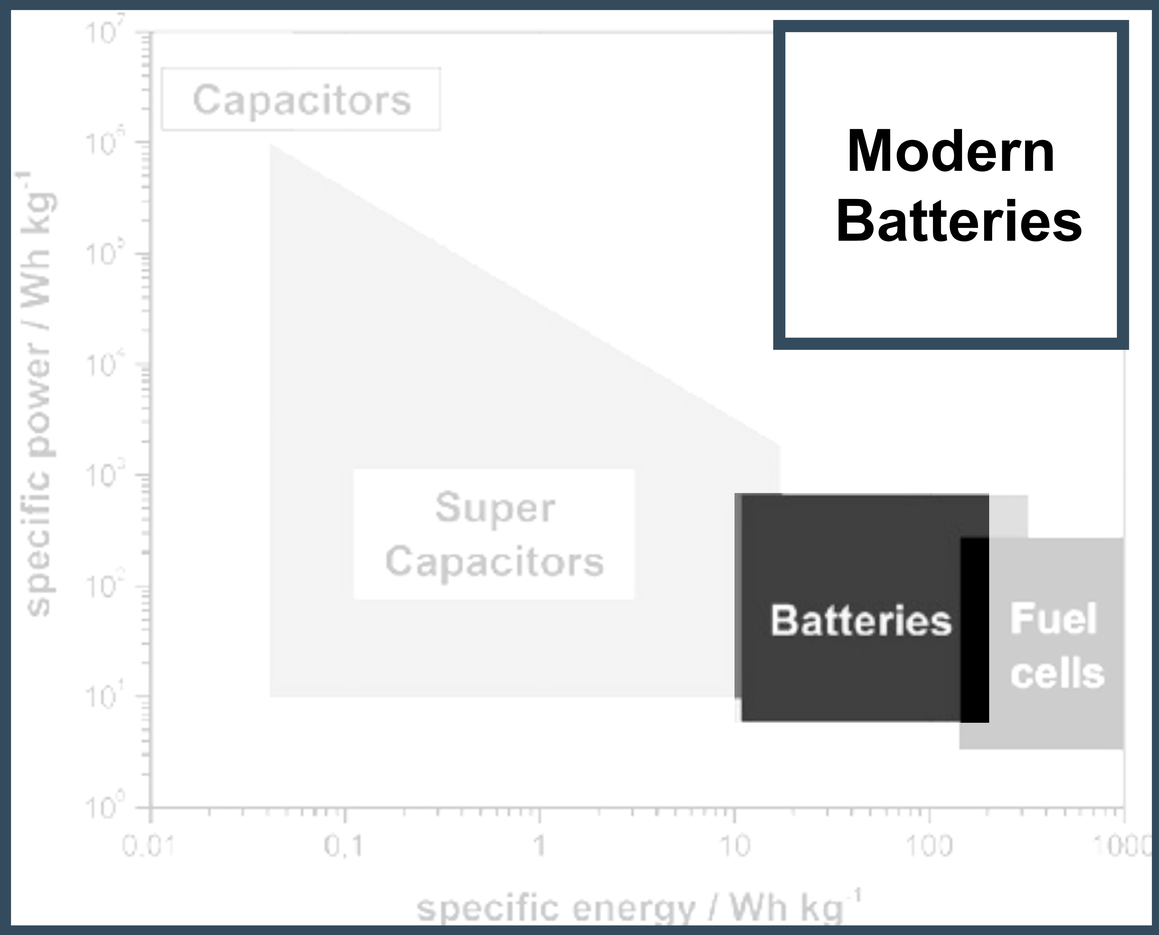




Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

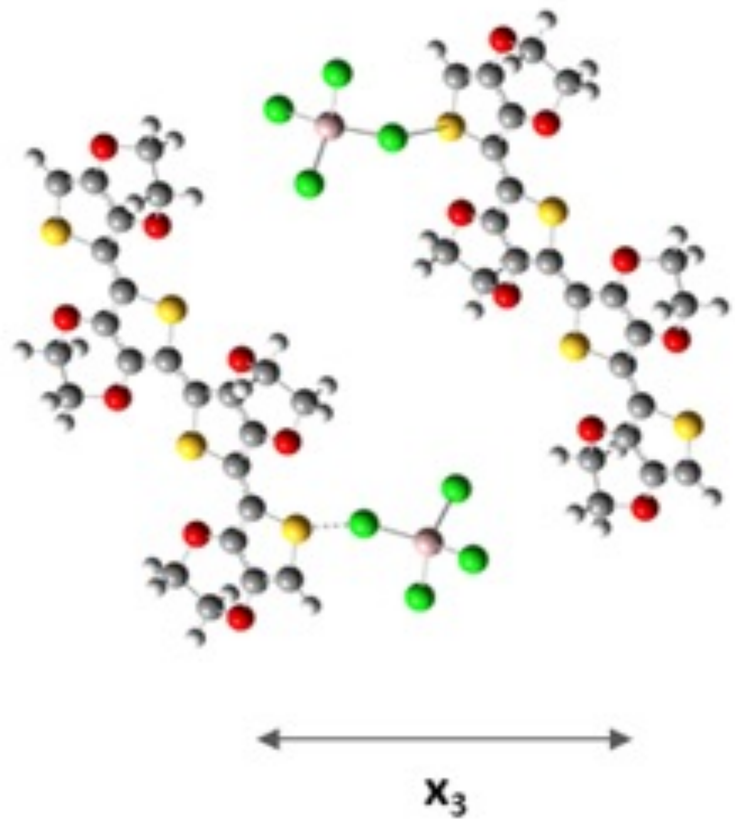
B Charging PEDOT chains: faradaic charge transfer



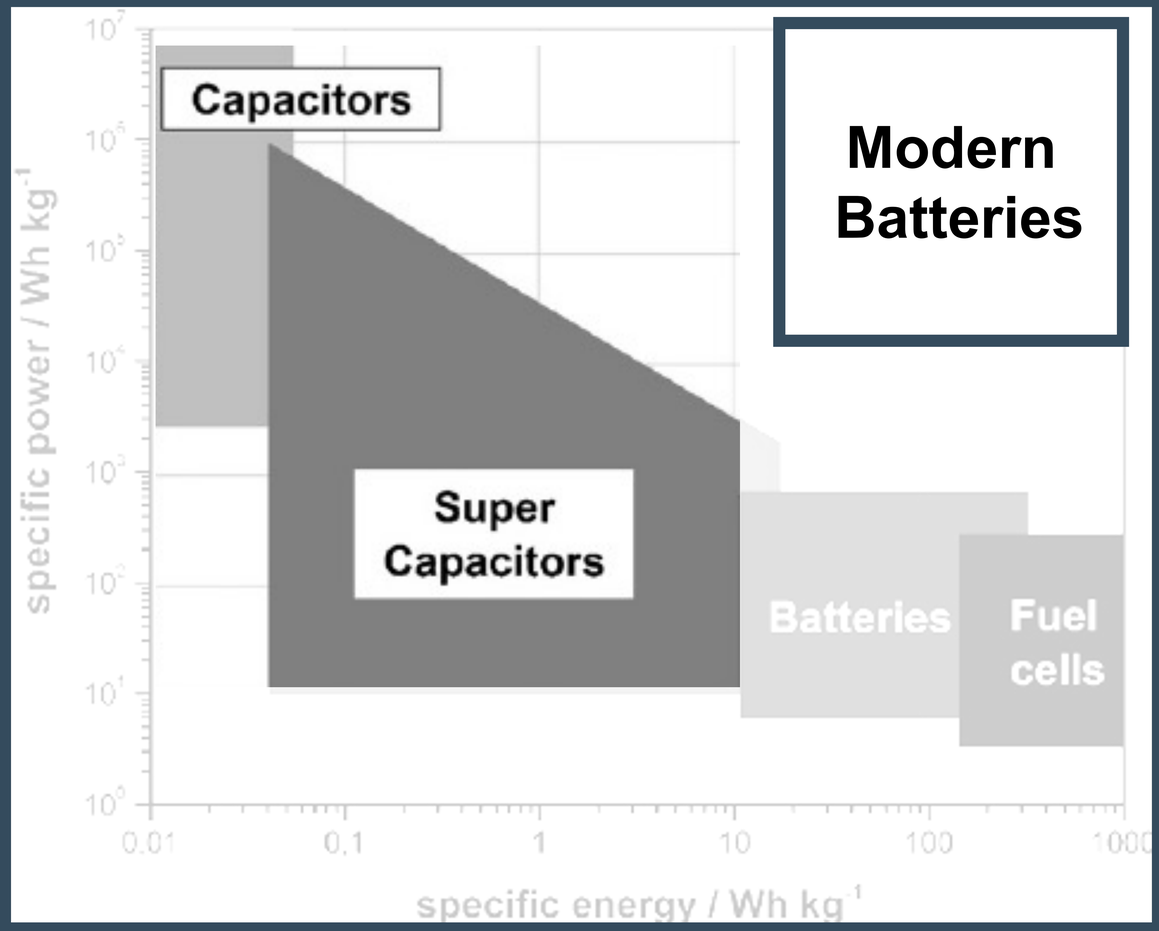


Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

C Insertion anions between PEDOT chains: non-faradaic charge transfer



$x_1 < x_2 < x_3$



Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Electropolymerisation

- Conductive polymer (PEDOT) with wide potential stability window of 4 V
- Control of anion insertion/removal by cyclic voltammetry

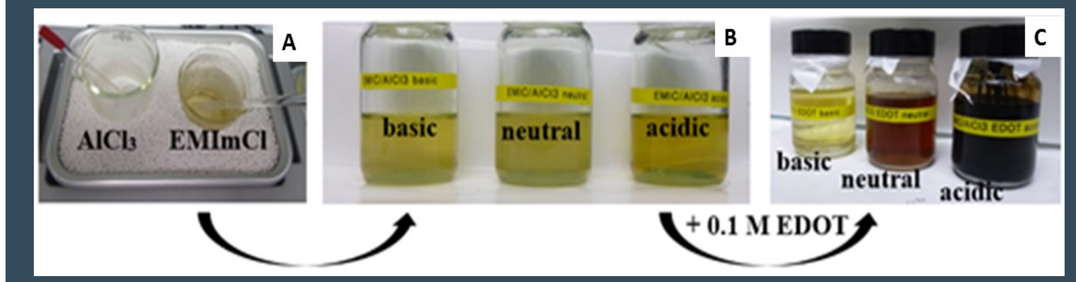
→ Definition of charge/discharge potentials

(A) Ionic liquid synthesis (EMImCl-$AlCl_3$)

(B) Lewis basic, neutral and acidic ionic liquid

(C) Ionic liquids with EDOT monomer

χ(EMImCl) / mol-%	χ($AlCl_3$) / mol-%	Lewis Acidity	Anions in Liquid
33.3	66.7	acidic	$Al_2Cl_7^-$, $AlCl_4^-$
50	50	neutral	$AlCl_4^-$
66.7	33.3	basic	$AlCl_4^-$, Cl^-



T. Schoetz et al. Electrochimica Acta 263, 176-183, 2018.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer Cathode

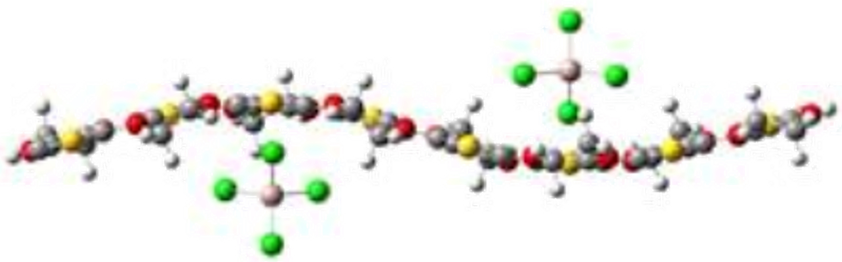
Electropolymerisation

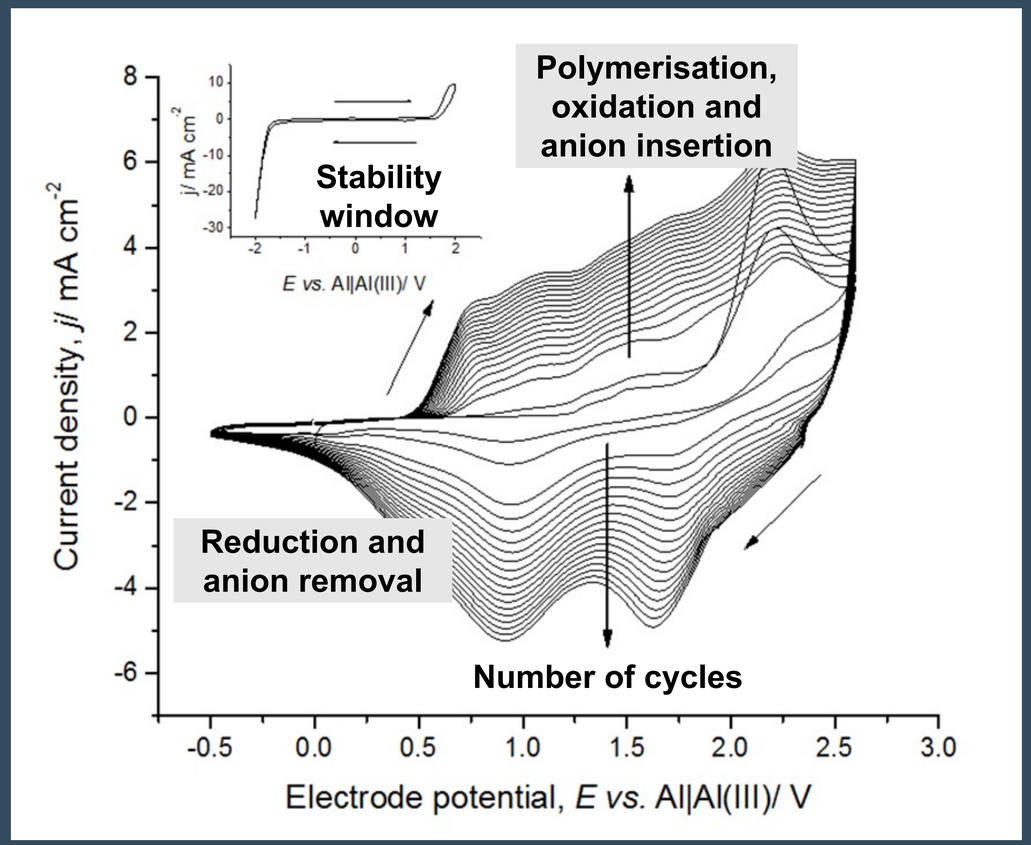
- Conductive polymer (PEDOT) with wide potential stability window of 4 V
- Control of anion insertion/removal by cyclic voltammetry

→ Definition of charge/discharge potentials

(Oxidation) Polymerisation and anion insertion into polymer structure at the same time

(Reduction) Anion removal without dissolving the polymer layers



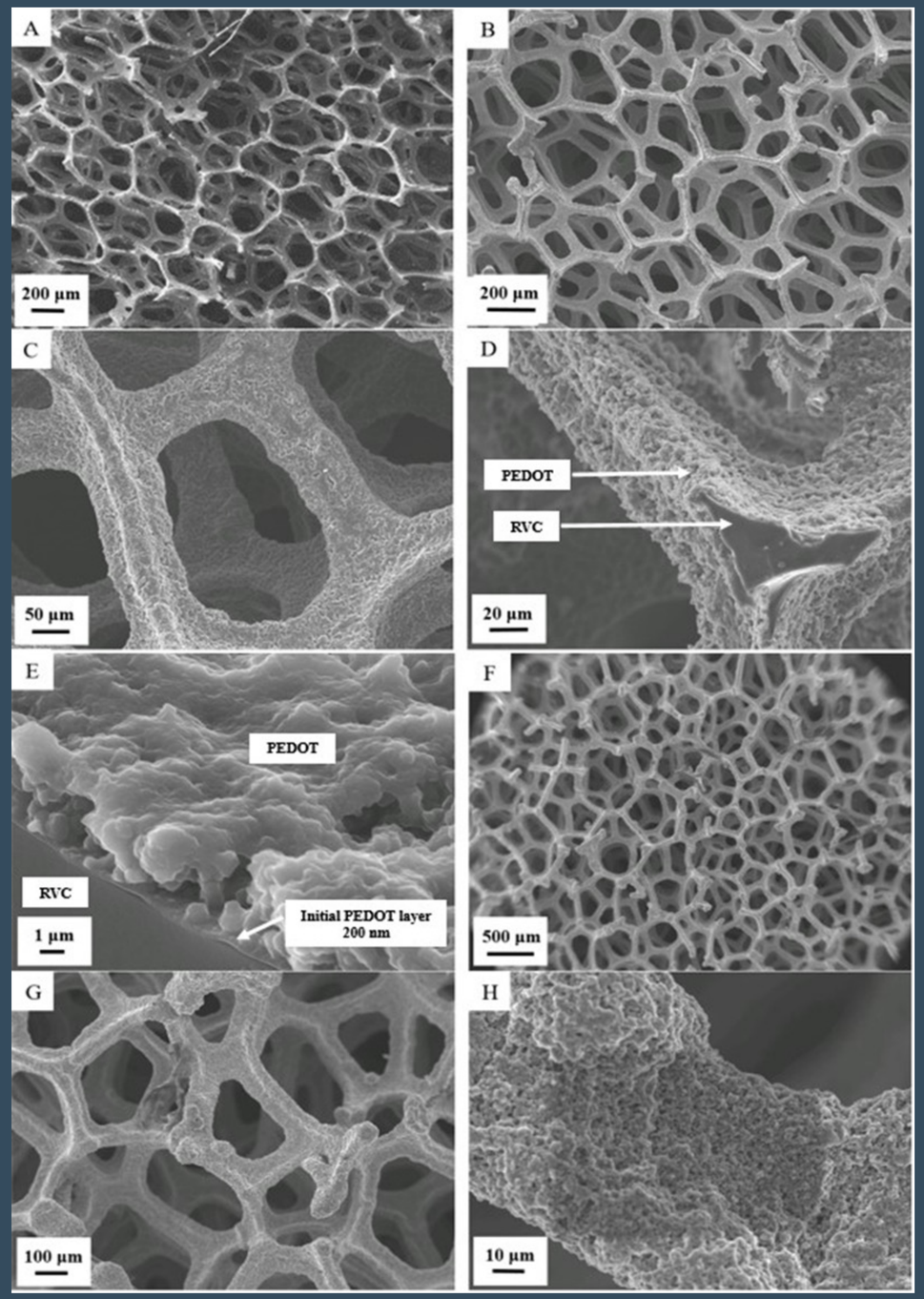


WE: PEDOT/vitreous carbon, CE: vitreous carbon, RE: Al, 100 mV s^{-1}, Lewis neutral EMImCl-$AlCl_3$, 25 ºC.

T. Schoetz et al. Electrochimica Acta 263, 176-183, 2018.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer Cathode

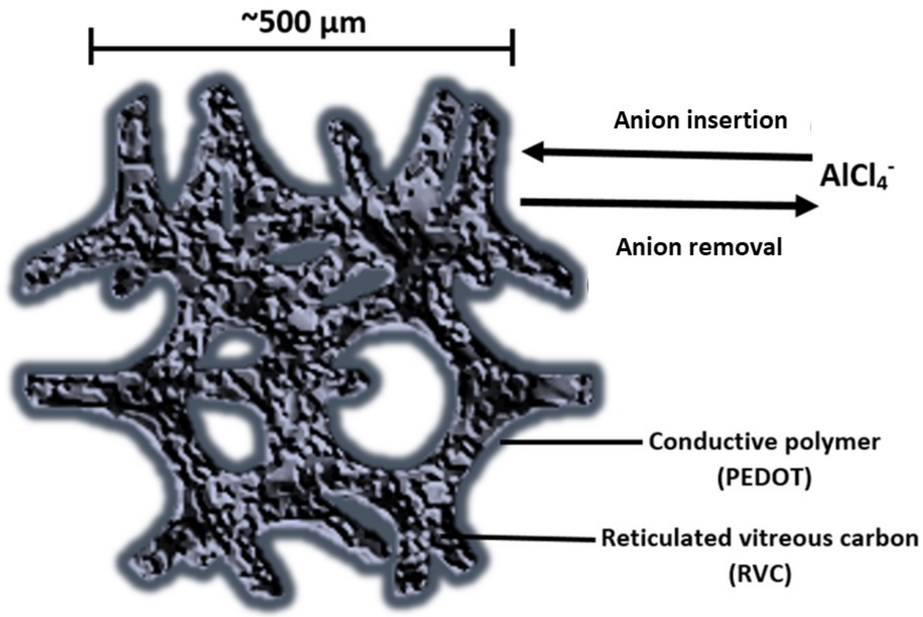


T. Schoetz et al. Electrochemistry Communications 89, 52-56, 2018.

Electropolymerisation on 3D Substrates

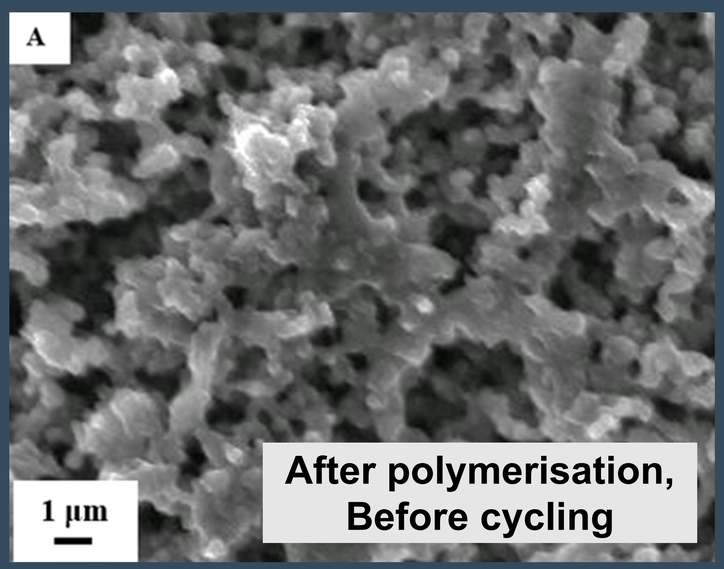
- Higher active electrode surface
- Maintenance structural integrity

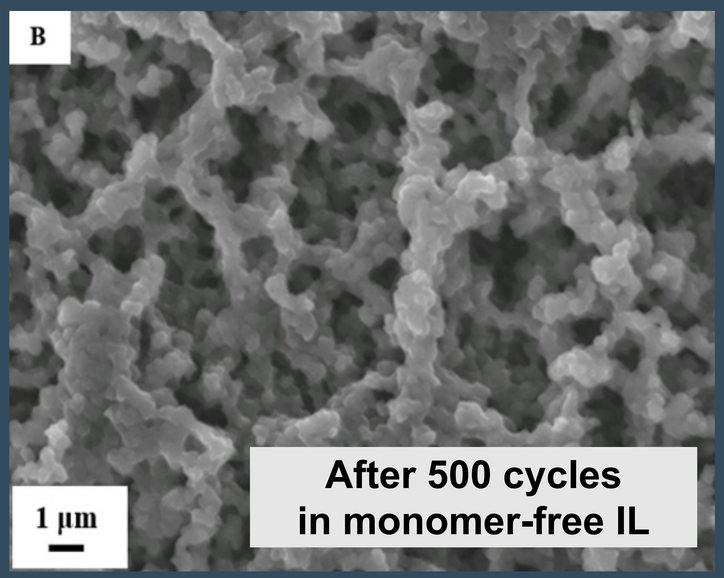
→ Allows internal polymer expansion/contraction without electrode degradation and volume change of the battery



Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer Cathode

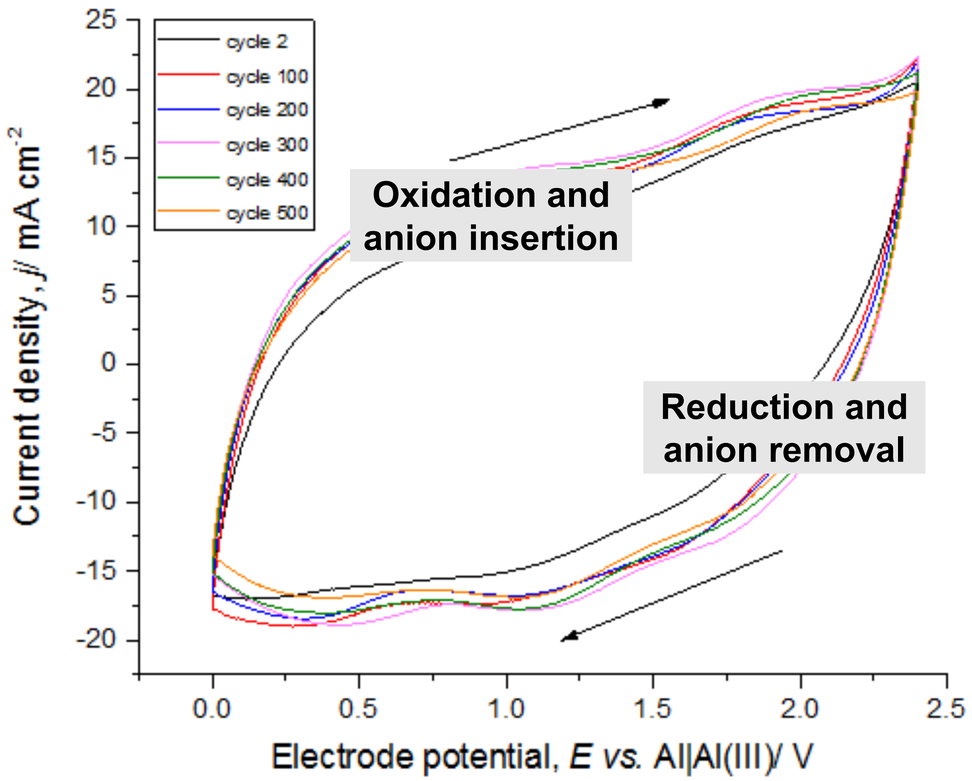




T. Schoetz et al. Electrochemistry Communications 89, 52-56, 2018.

Polymer Behaviour in Ionic Liquid

- High electrochemical stability
- Coulombic efficiency ≥97 %
- Anion insertion/removal potentials are predefined by electropolymerisation



WE: PEDOT/vitreous carbon,
CE: vitreous carbon,
RE: Al, 100 mV s^{-1}, Lewis neutral EMImCl-$AlCl_3$, 25 ºC.

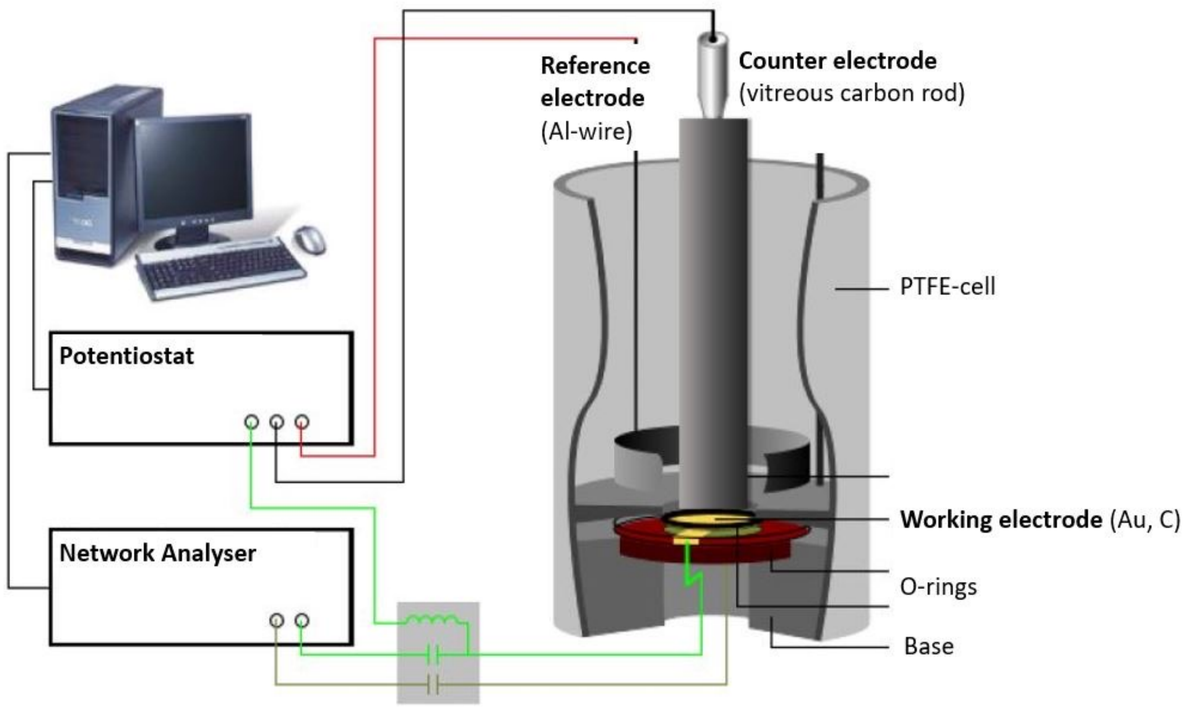
Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer Cathode

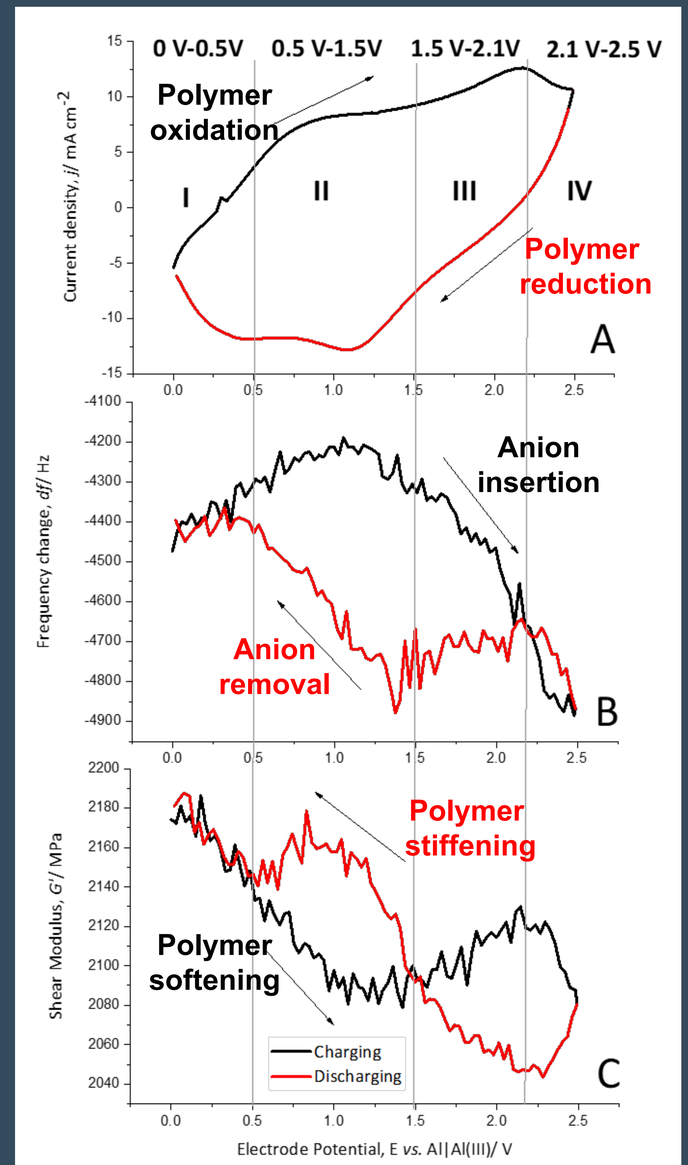
Hybrid Battery-Capacitor Behaviour

Electrochemical Quartz Crystal Microbalance

- **Determination change shear modulus during charging (oxidation, anion insertion) and discharging (reduction, anion removal)**



T. Schoetz et al. Journal of Materials Chemistry A 6, 17787-17799, 2018.



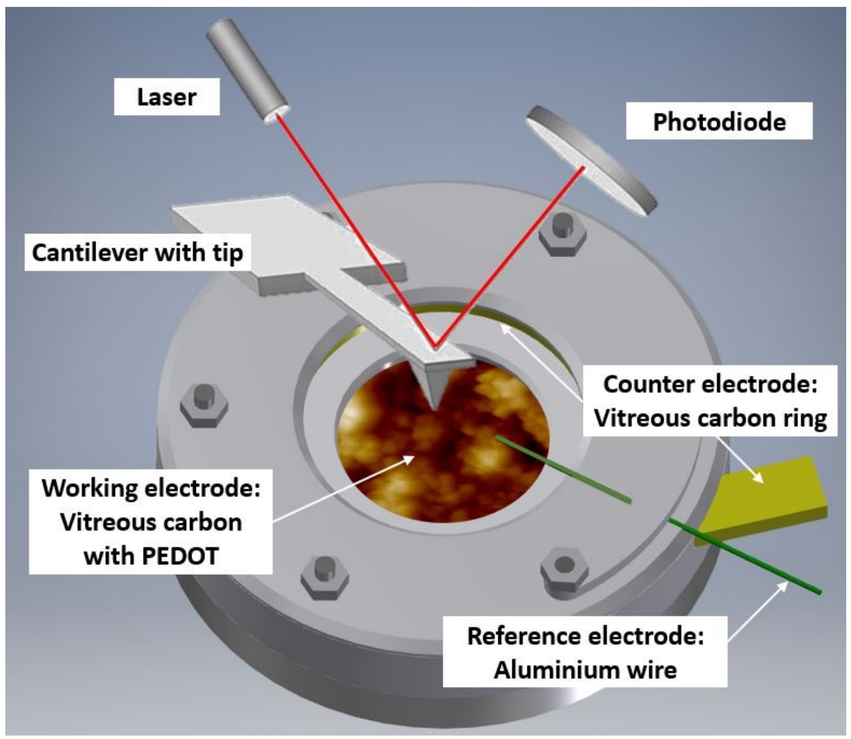
WE: PEDOT/gold,
CE: vitreous carbon,
RE: Al, 100 mV s^{-1}, Lewis neutral EMImCl-$AlCl_3$, 25 ºC.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

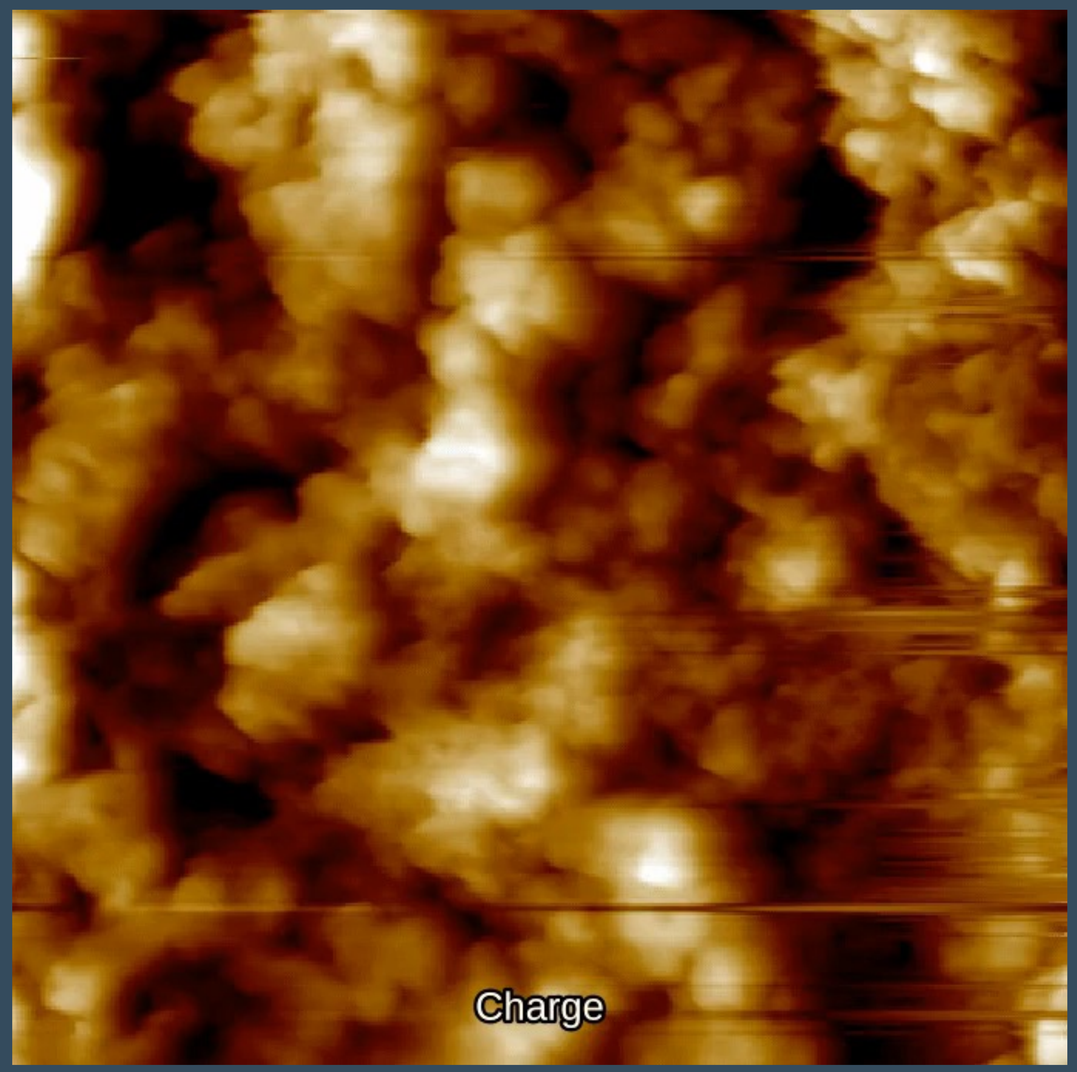
Hybrid Battery-Capacitor Behaviour

In-Operando Atomic Force Microscopy

- Visualisation morphological changes of the polymer surface during charging/discharging



T. Schoetz et al. Journal of Materials Chemistry A 6, 17787-17799, 2018.



WE: PEDOT/vitreous carbon, CE: vitreous carbon,
RE: Al, 100 mV s^{-1}, Lewis neutral EMImCl-$AlCl_3$, 25 ºC.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conductive Polymer Cathode

Hybrid Battery-Capacitor Behaviour

Polymer charging:

- Oxidation to $PEDOT^+$
- Generation positive charges in polymer backbone

  → Battery-like behaviour
- Repulsive forces open transport paths for anions
- Polymer swelling and softening
- Anion insertion and double layer formation

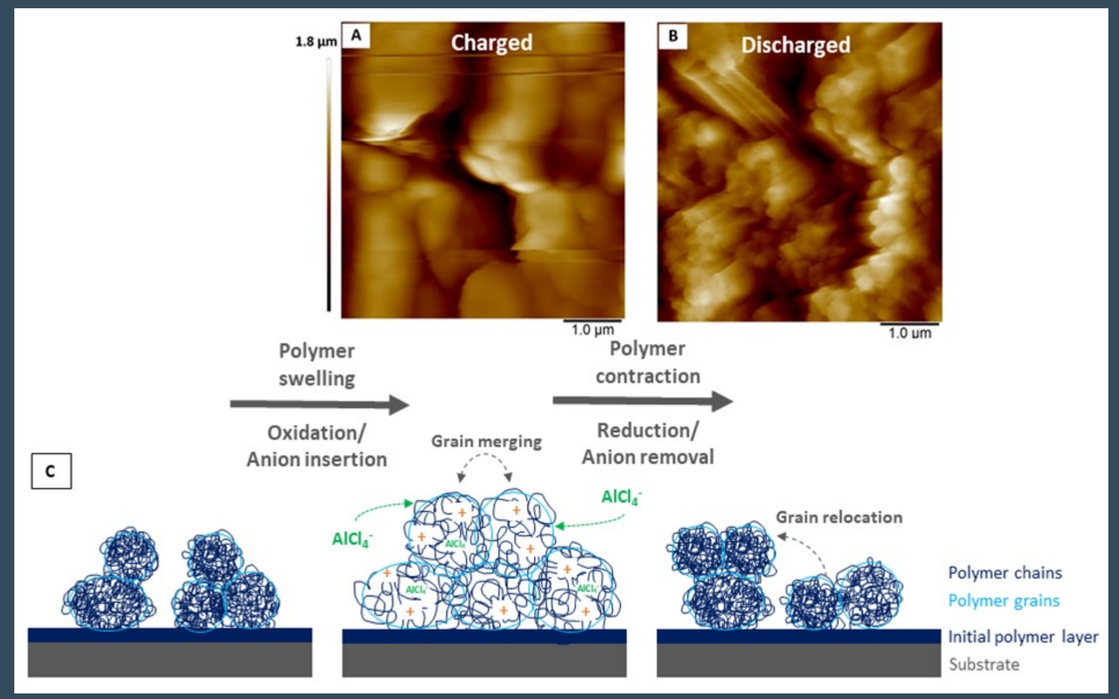
  → (Pseudo)-Capacitor-like behaviour
- Polymer stretching to its boundaries and stiffening

Polymer discharging:

- Reduction to $PEDOT^0$
- Anion removal due to open transport paths

  → (Pseudo)-Capacitor-like behaviour
- Removal positive charges

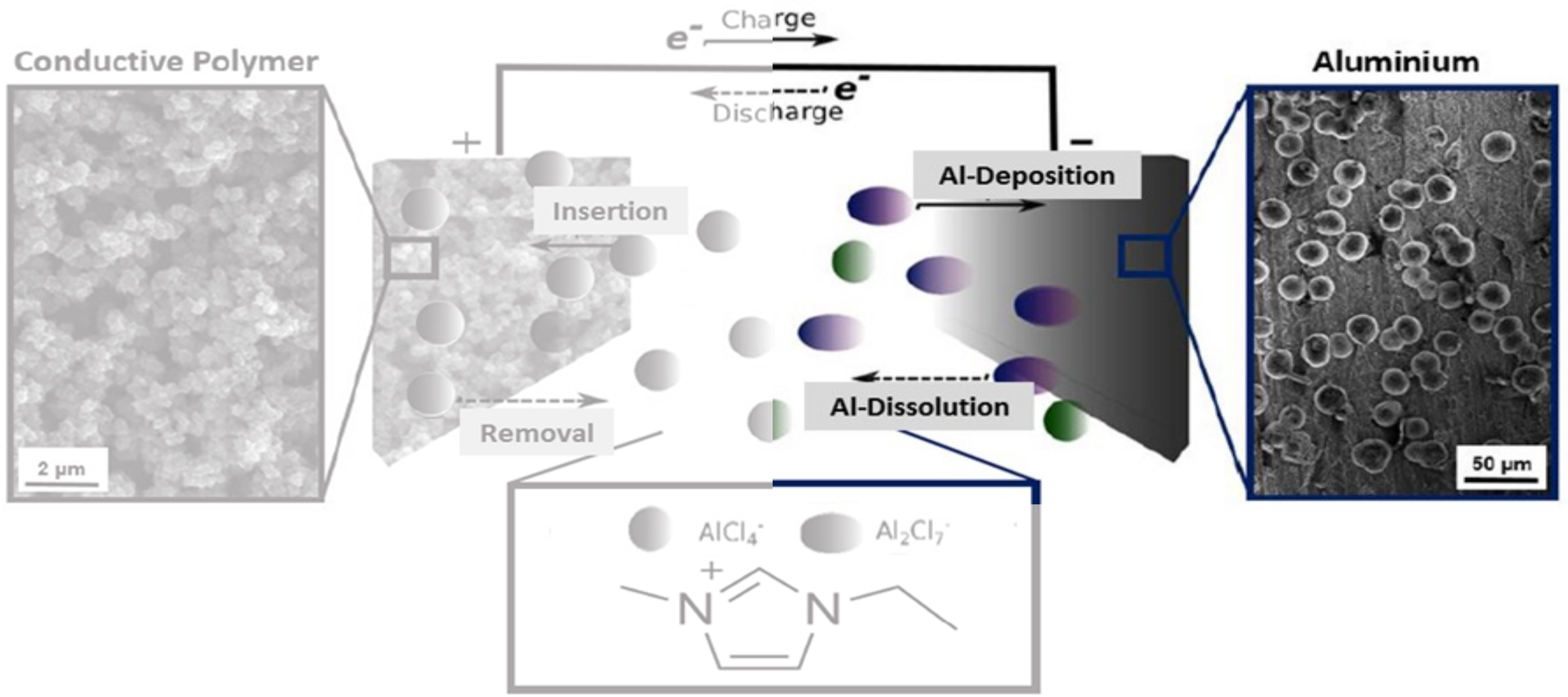
  → Battery-like behaviour
- Polymer contraction and grain relocation
- Closing transport paths
- Polymer stiffening



T. Schoetz et al. Journal of Materials Chemistry A 6, 17787-17799, 2018.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Aluminium Anode

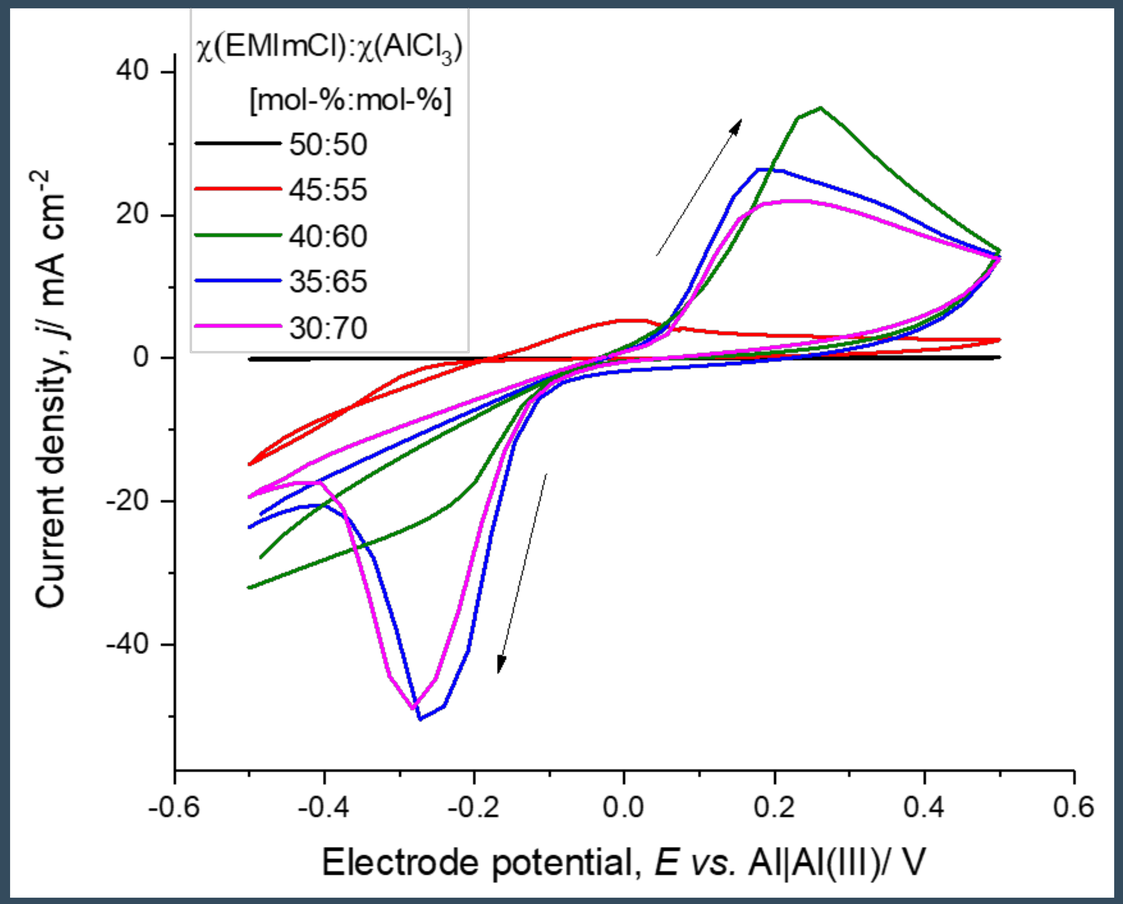


1-Ethyl-3-methylimidazolium chloride – Aluminium chloride

$$4Al_2Cl_7^- + 3e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Al + 7AlCl_4^-$$

T. Schoetz et al. Journal of Solid State Electrochemistry 21, 3237–3246, 2017.

Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

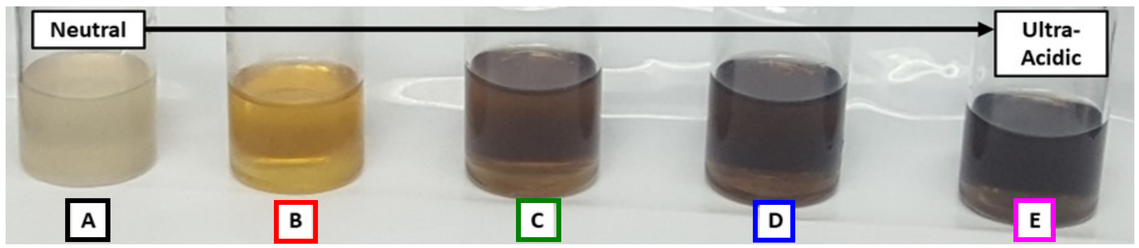


WE/CE: vitreous carbon, RE: Al, 100 mV s^{-1},
Lewis neutral to acidic EMImCl-$AlCl_3$, 25 ºC.

Electrodeposition of Aluminium in Ionic Liquids

Coulombic efficiency

- (50:50) neutral, no Al-deposition
- (45:55) very light-acidic, 63%
- (40:60) light-acidic, 66%
- (35:65) acidic, 80%
- (30:70) ultra-acidic, 65%



Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

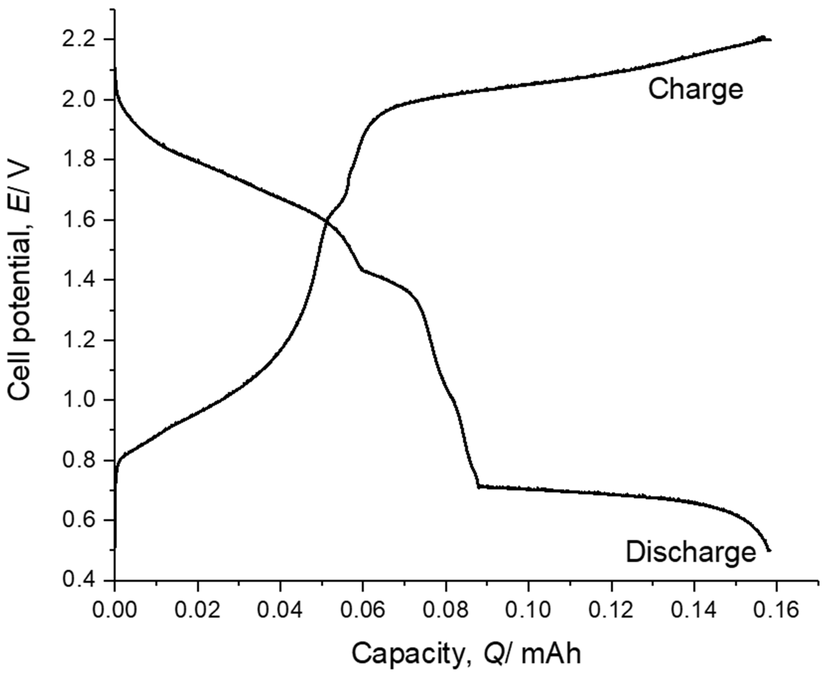
University of Southampton

PEDOT-Aluminium Battery

Zepler Institute

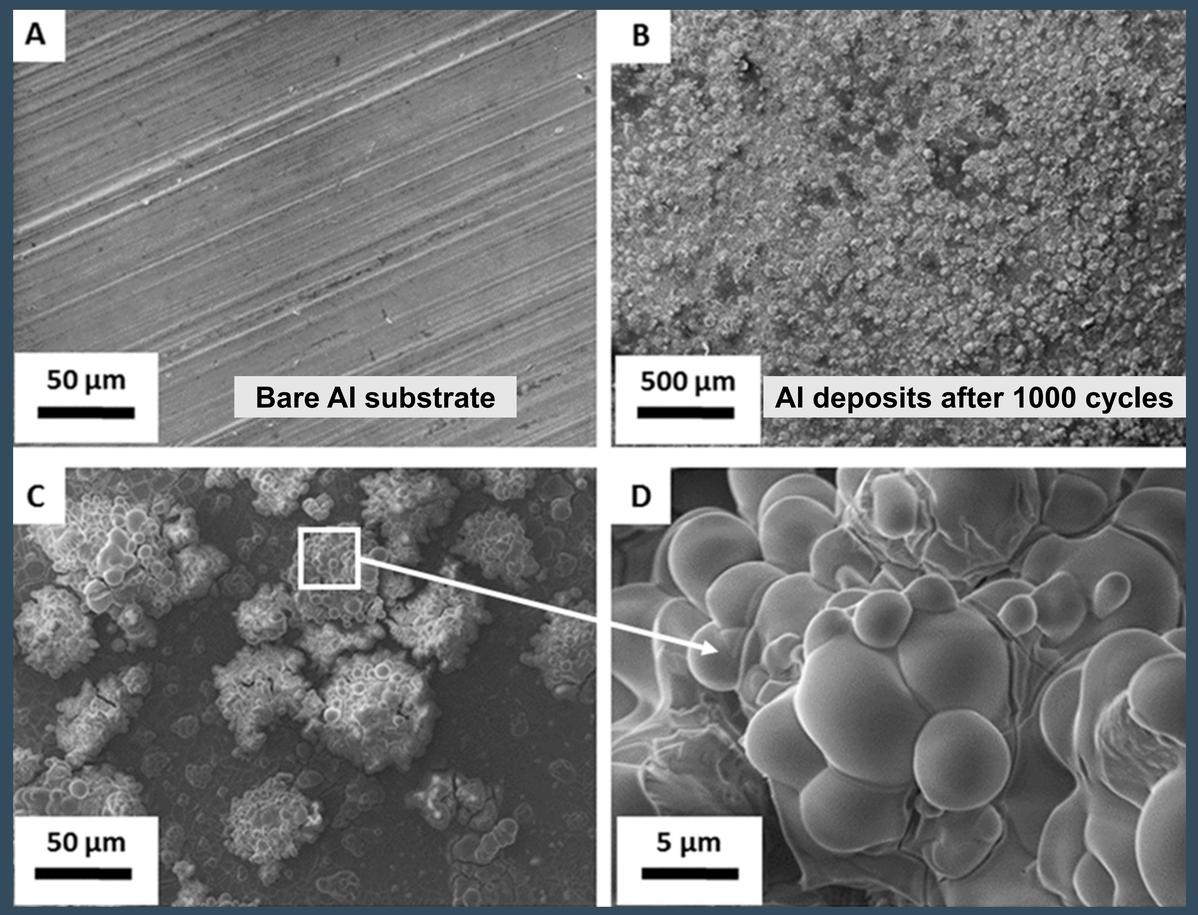
Battery Performance

- 40-180 Ah kg^{-1}
- 50-230 Wh kg^{-1}
- 30-140 W kg^{-1}
- Charge rate up to 80C
- ≥1000 cycles
- ≥95 % coulombic efficiency

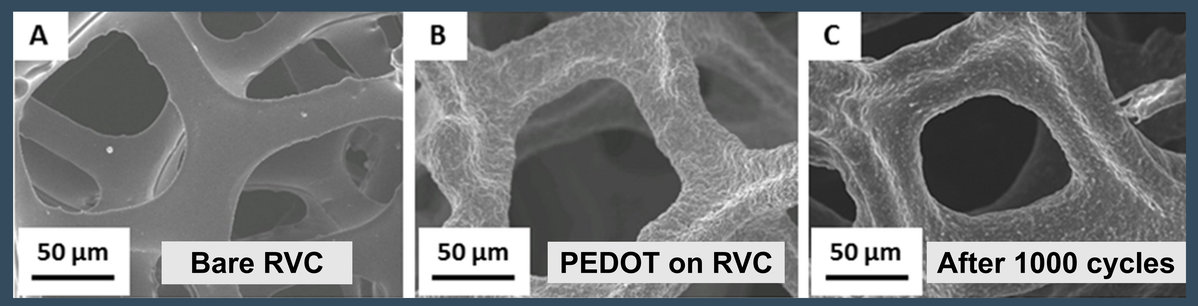


Anode: Al, Cathode PEDOT, ± 0.1 mA, Lewis neutral to acidic EMImCl-$AlCl_3$, 25 ºC.

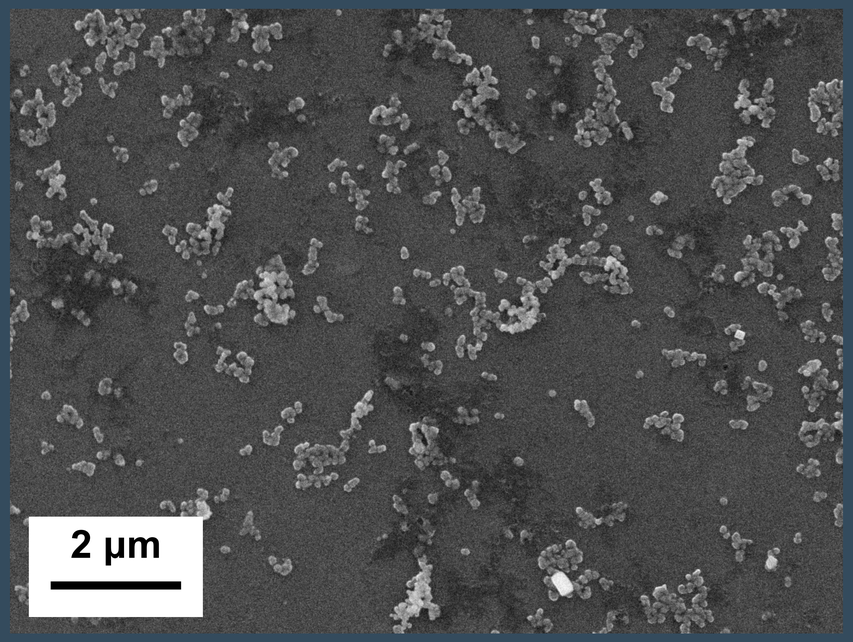
Aluminium Anode

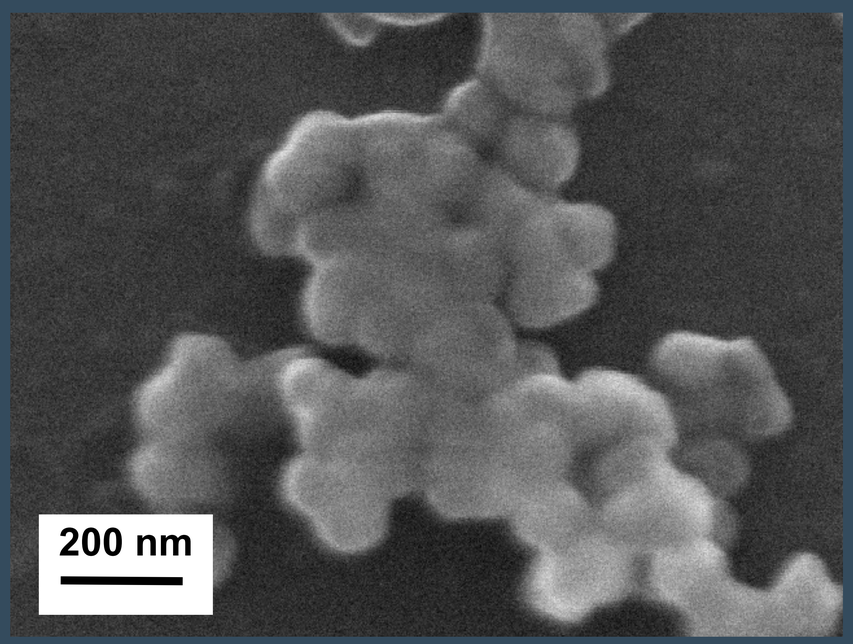


PEDOT Cathode



Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk



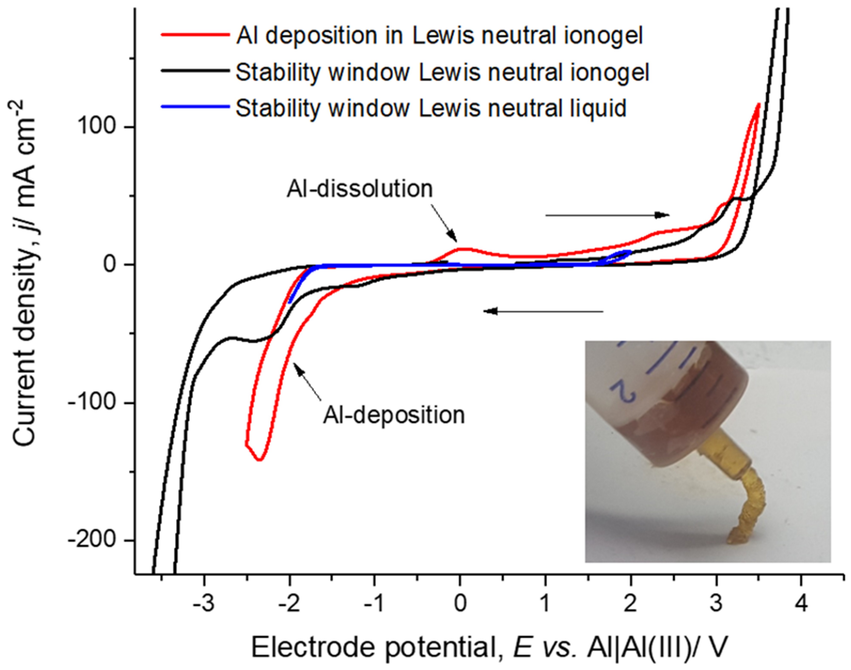


Electrodeposition of Aluminium in Ionogels

- Increase potential window by 2 V
- Removal separator battery cell
- Decrease active mass by factor 3

→ Increase cell potential (3 V discharge potential)

→ Increase specific capacity, specific energy and power (max. theo. 260 Ah kg^{-1}, 338 Wh kg^{-1} and 211 W kg^{-1})

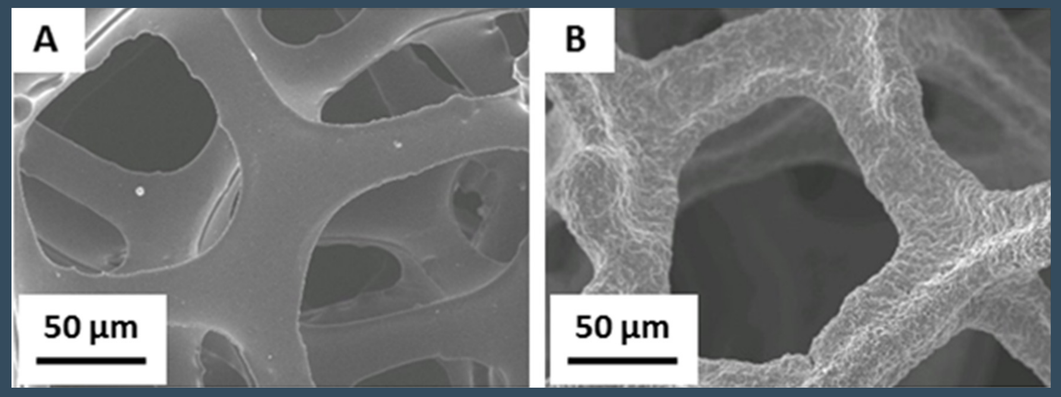


WE/CE: vitreous carbon, RE: Al, 100 mV s^{-1}, Lewis neutral EMImCl-$AlCl_3$ ionic liquid and ionogel, 25 ºC.

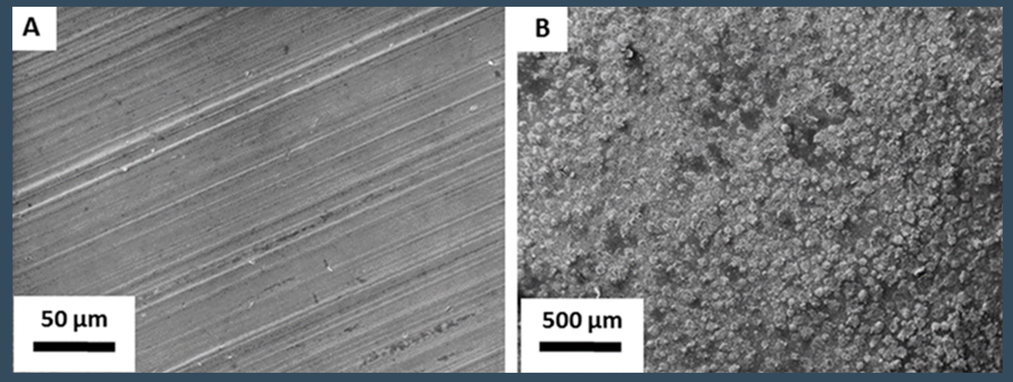
Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk

Conclusions

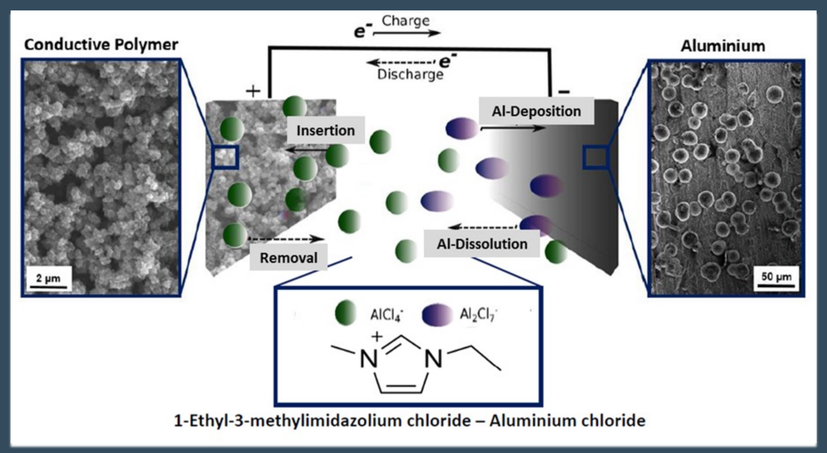
Electropolymerisation of conductive polymers suitable for energy storage



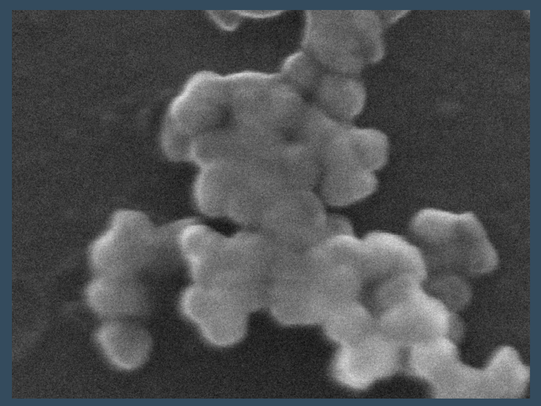
Electrodeposition of aluminium from ionic liquids

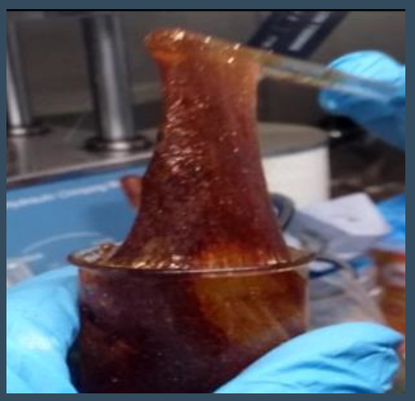


Development of alternative battery systems beyond lithium-ion



Improvement of aluminium batteries with ionogel electrolytes





Theresa Schoetz | University of Southampton | Zepler Institute | SO17 1BJ | UK
Telephone: +44 (0) 23 8059 8931 | Email: T.Schoetz@soton.ac.uk