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Towards printed lignin-based batteries

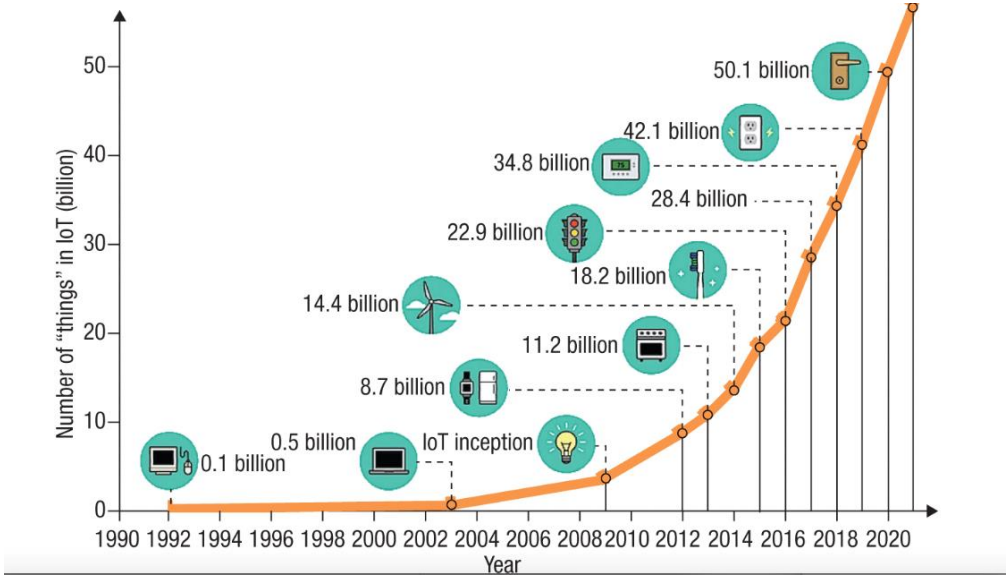
Xavier Crispin

WWSC is a joint research center at KTH, Chalmers and Linköping University

From IoT to Internet of Everything (IoE)

- IoT = **Machine-to-Machine** (M2M) communications
- IoE extends IoT to include **Machine-to-People** (M2P) and technology-assisted **People-to-People** (P2P) interactions.

In the years to come, the number of devices requiring connectivity will move **from billions to trillions**.



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Zero-energy devices

ericsson.com

Replace batteries

Energy Harvester

Energy storage

Electronic Antenna

Function

Solar cells
Thermoelectrics
Piezoelectrics

Small battery
supercapacitor

Sensor
Actuators
Trackers

High power energy storage becomes more important than high energy

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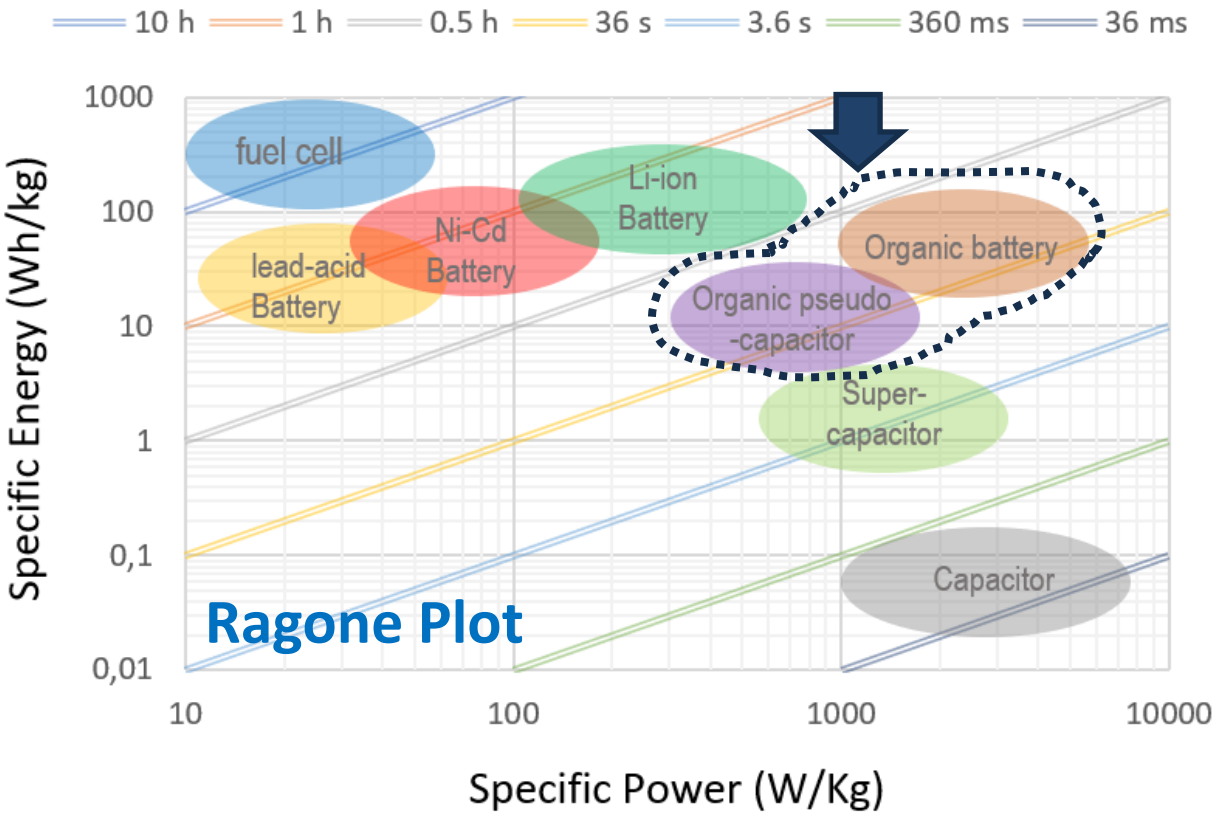
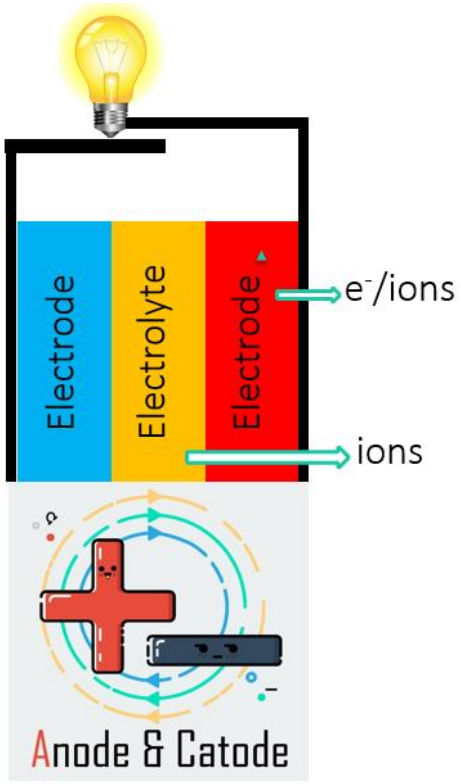
Organic batteries for IoE

$$E_g = \frac{1}{M}\int_0^{t_d} iV\,dt$$





$$P_g = \frac{E_g}{t_d}$$

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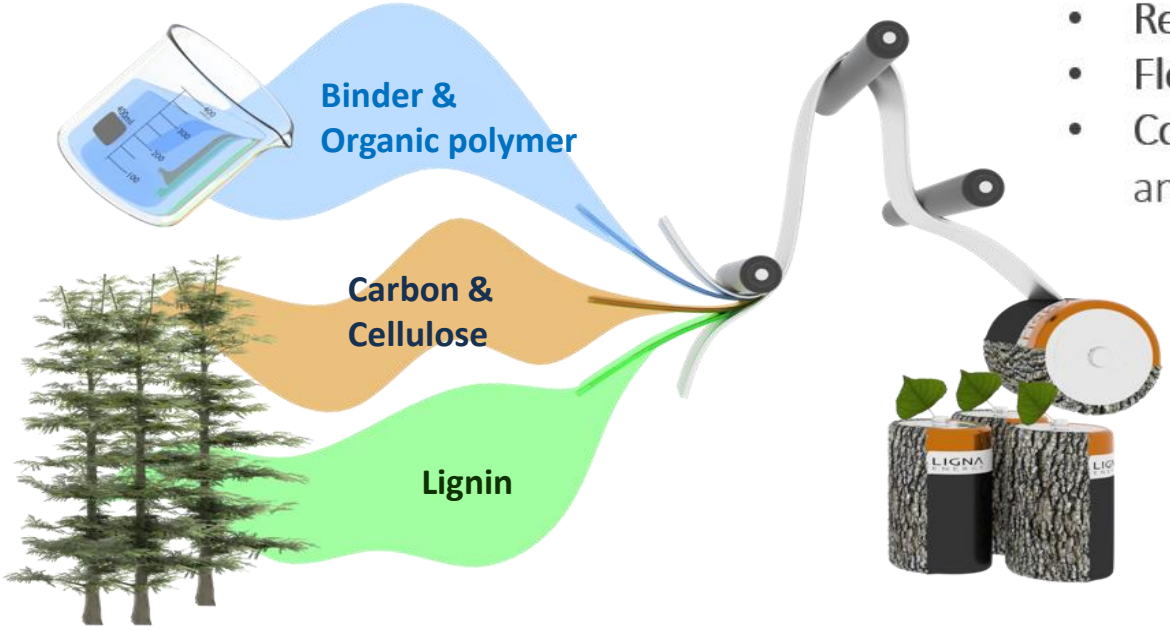
Organic sustainable batteries

Bio-material cell technology & energy storage solutions

- **Green** – a sustainable world
- **Safe** – for people and environment
- **Scalable** – production, abundant supply
- **Recyclable** – dispose or re-use
- **Flexible** – shape and design
- **Cost competitive** – materials and design



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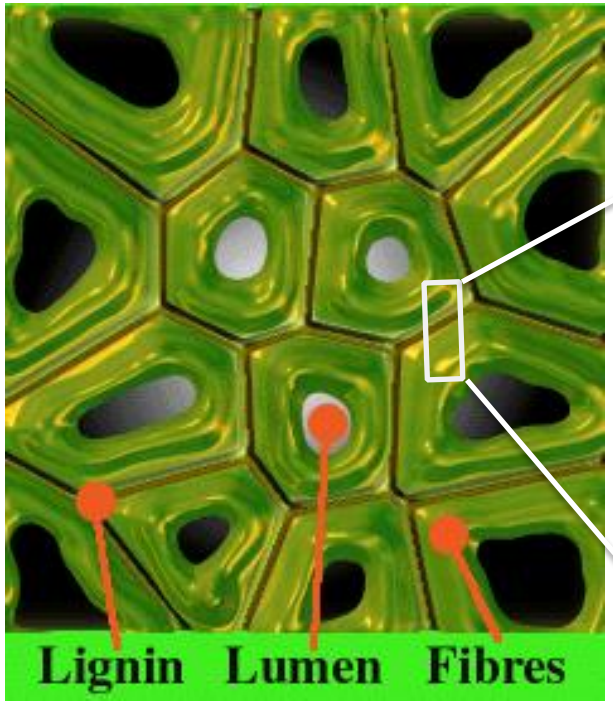
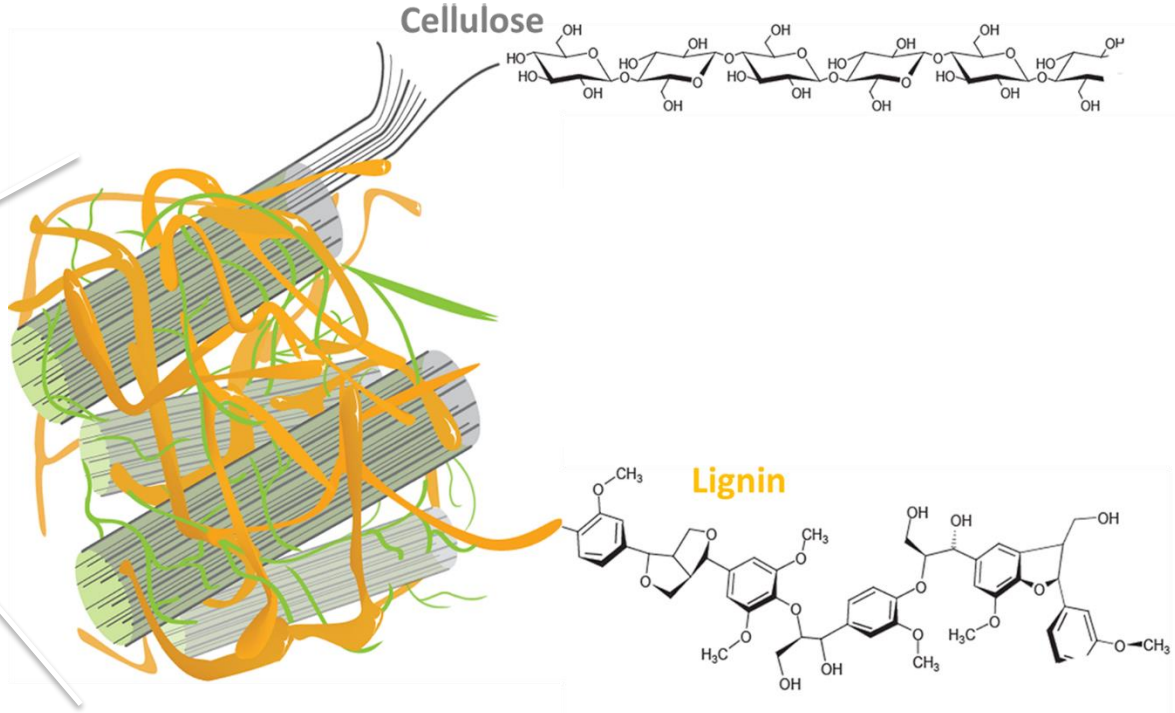
The biopolymer lignin

- Plants contain ~20% of lignin
- Lignin is the glue in plants bringing together cellulose as mechanical agent
- Extracted lignin : 50 million tons/y
- Potential production: 300 billion tons/y





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ACS Sustainable Chem. Eng. 2016, 4, 1, 35

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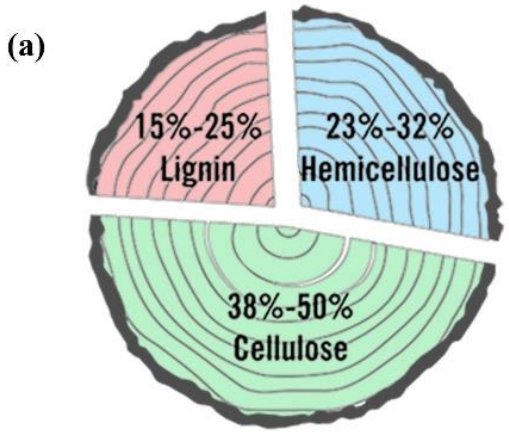
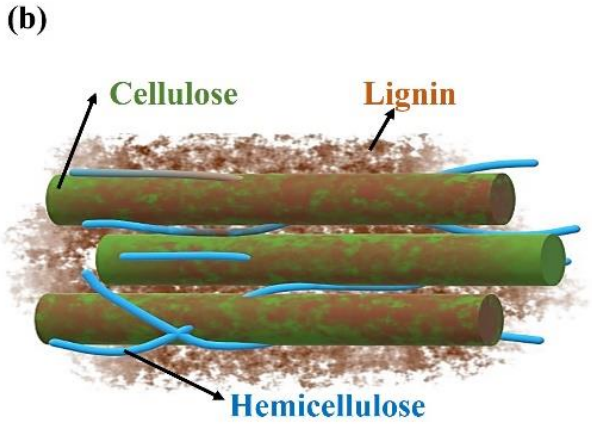
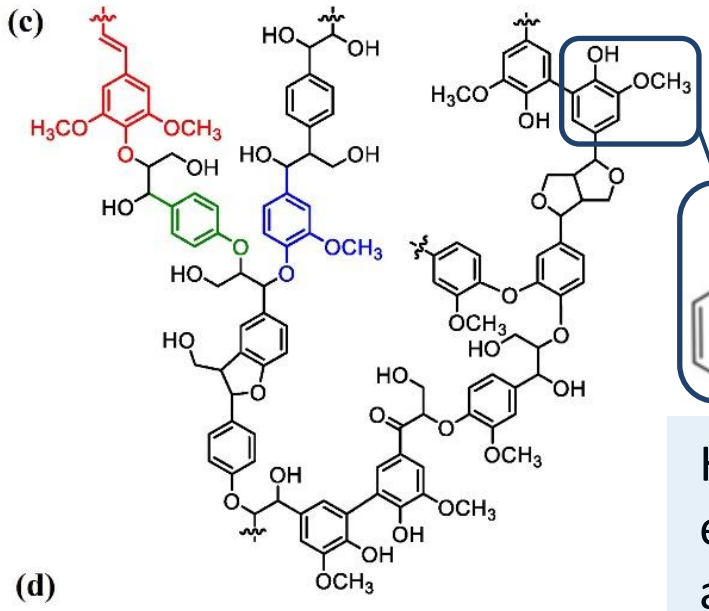
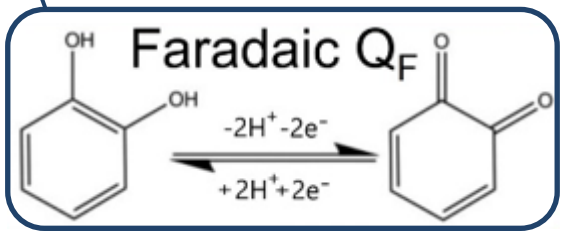
Lignin is redox active

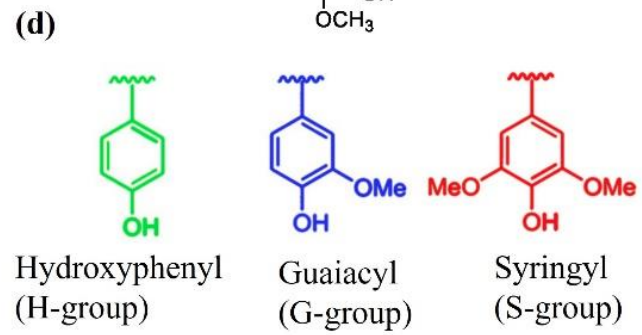








How could the electrons reach the aromatic ring if lignin is an insulator ?



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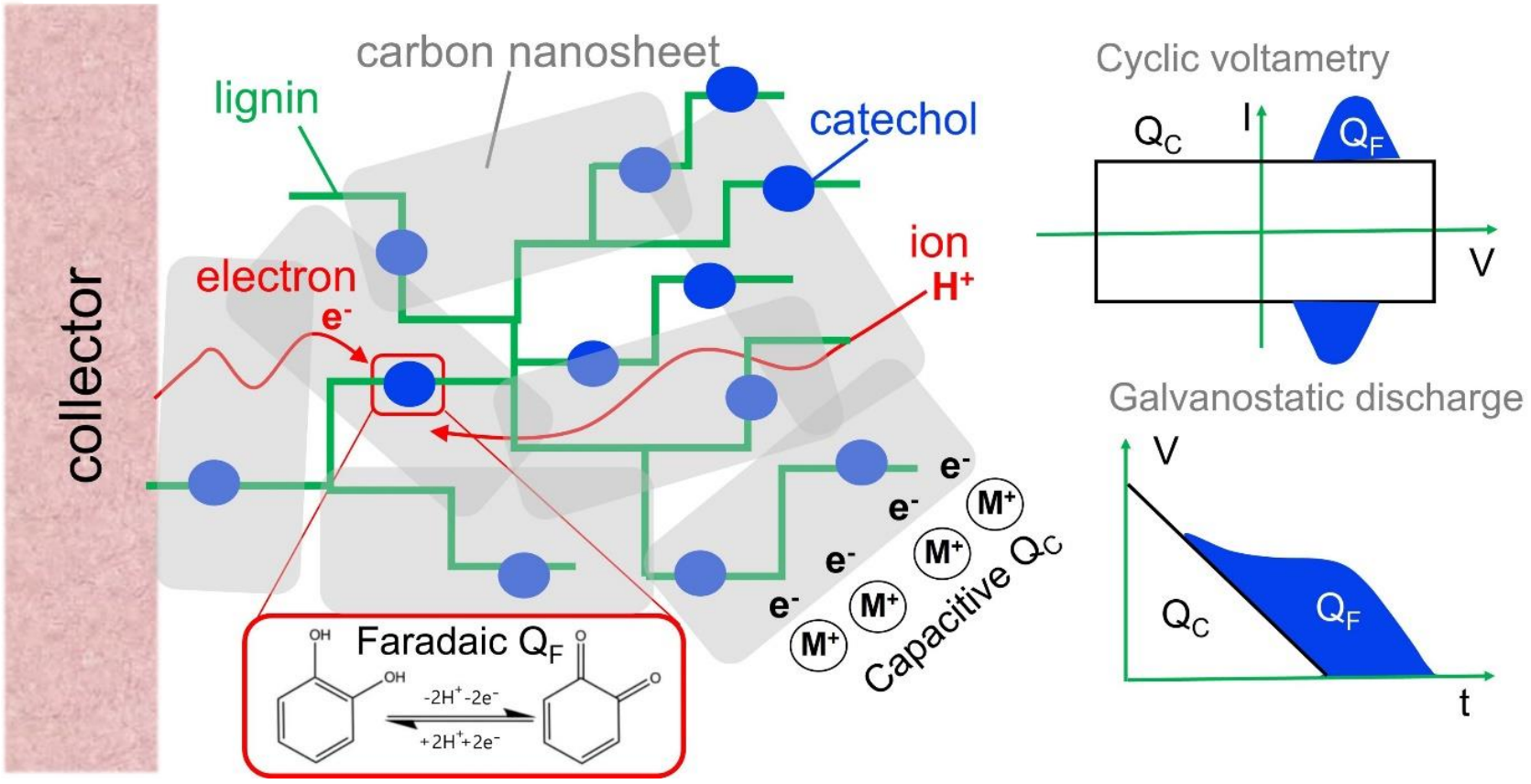
Lignin - Nanoconductor Composite



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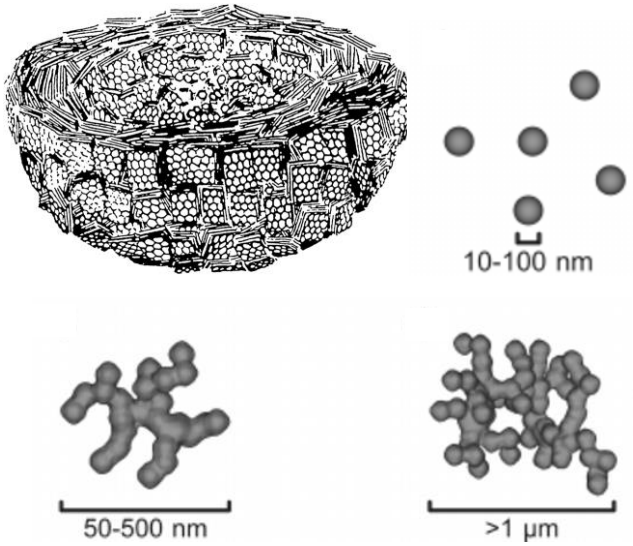
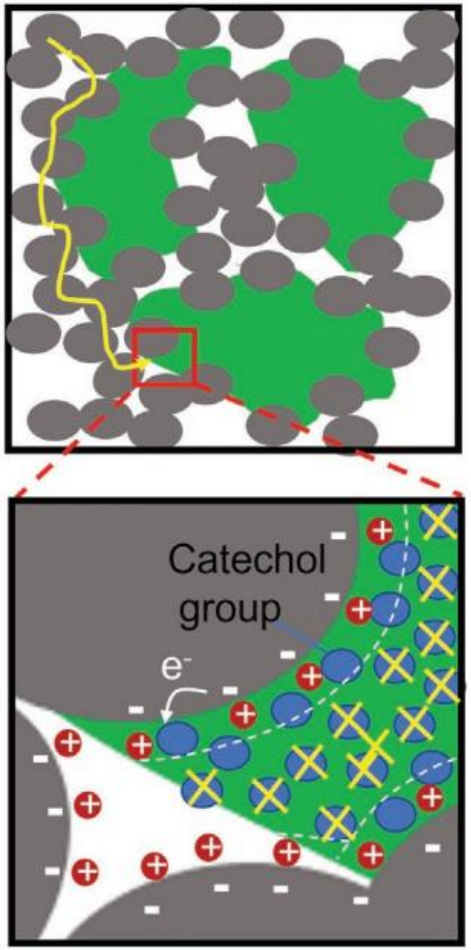
Lignin – Carbon Black Composite

Carbon black

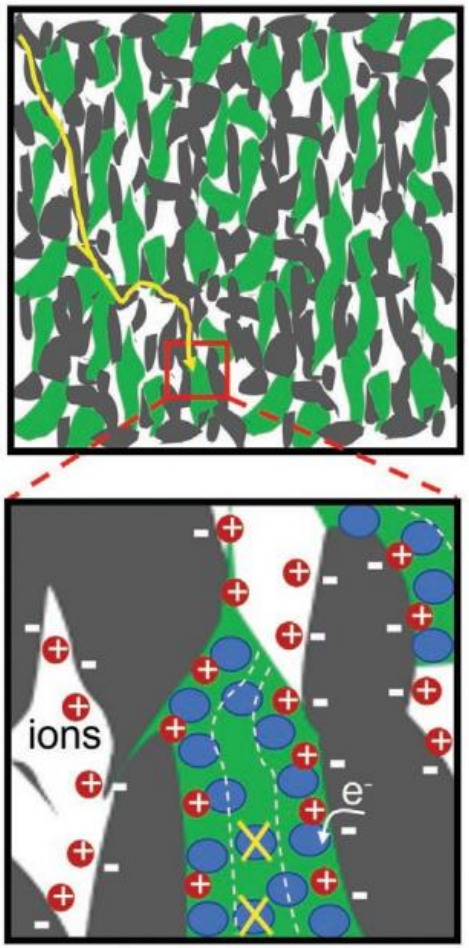


The smaller the carbon particles, the more redox groups of lignin are electrically connected, the higher the charge storage capacity

Manual mixing



Ball milling



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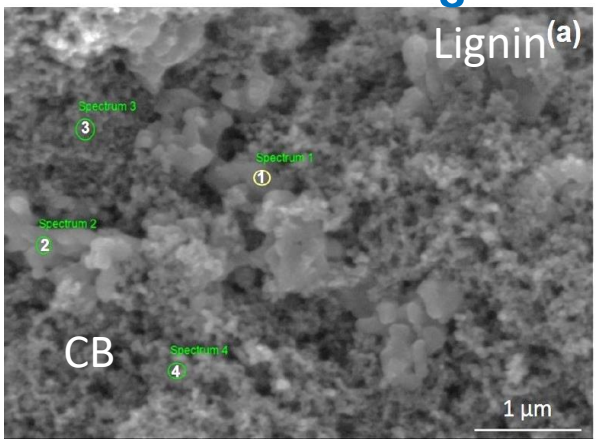
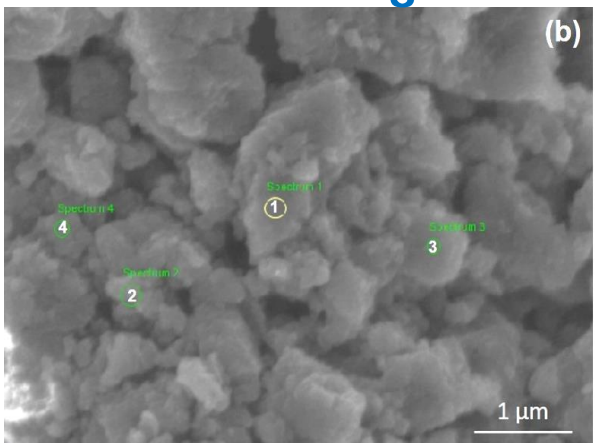
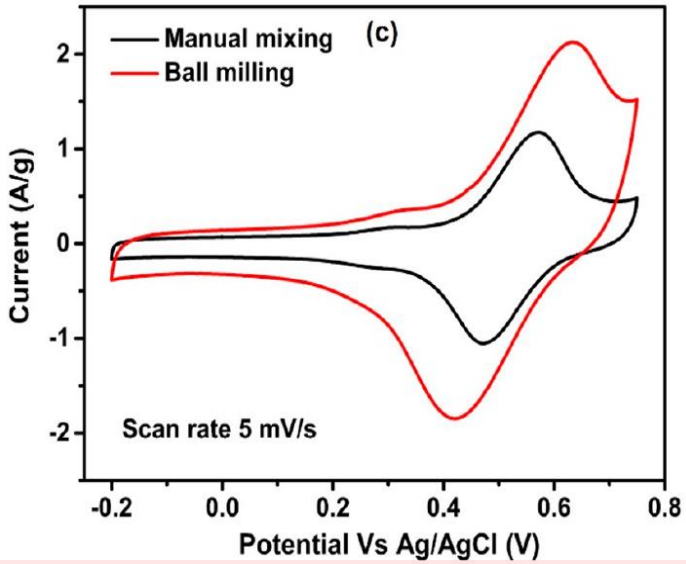
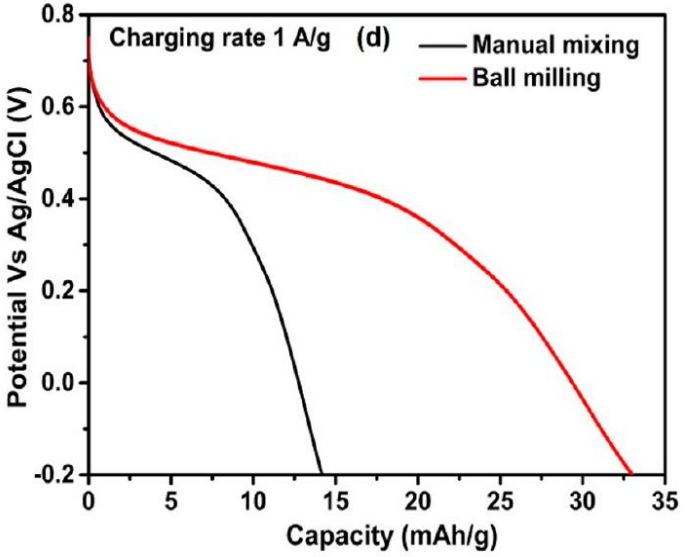
Manual mixing

Ball milling









Ball milling is an efficient and simple way to make a composite homogenous at the nanoscale: bring conductivity into the lignin.

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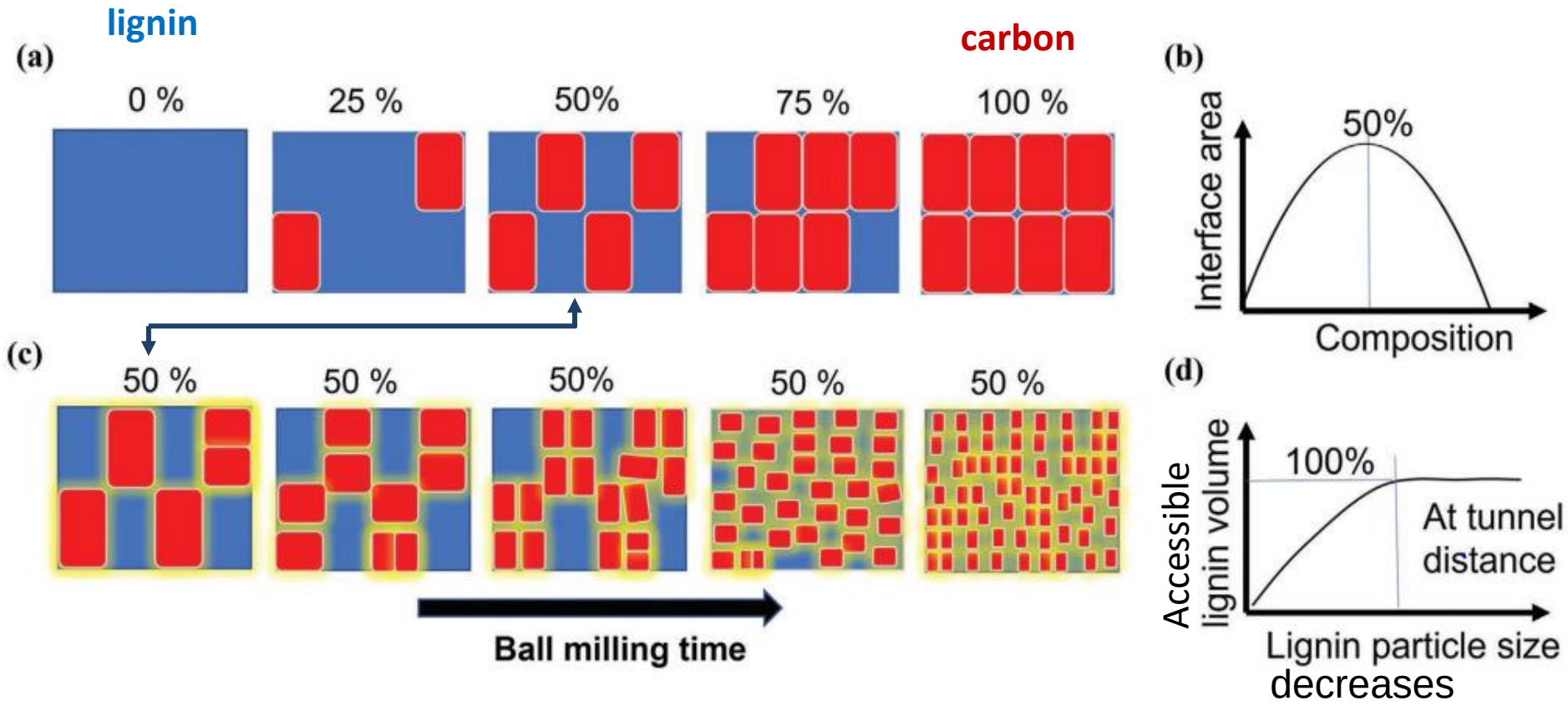
Composition and Morphology



Simple argument suggests an optimum composition at 50/50 ratio of lignin/carbon
The ballmiling time is expected to increase and saturate the capacity (lignin accessible)

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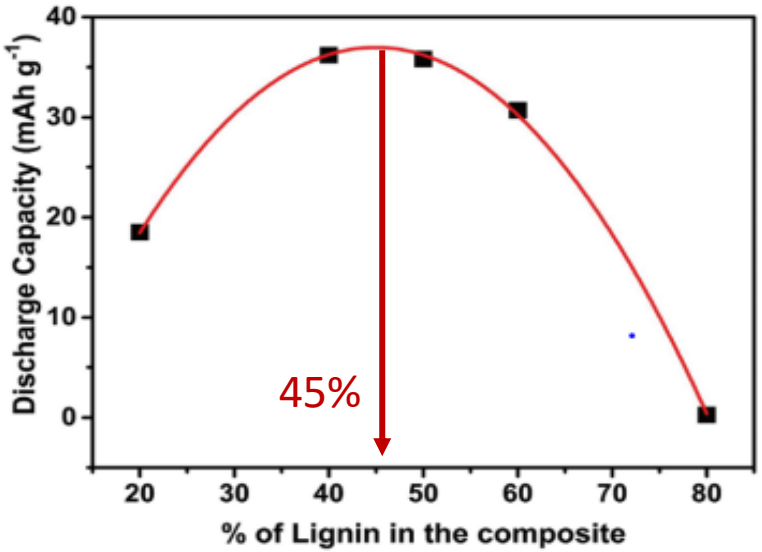
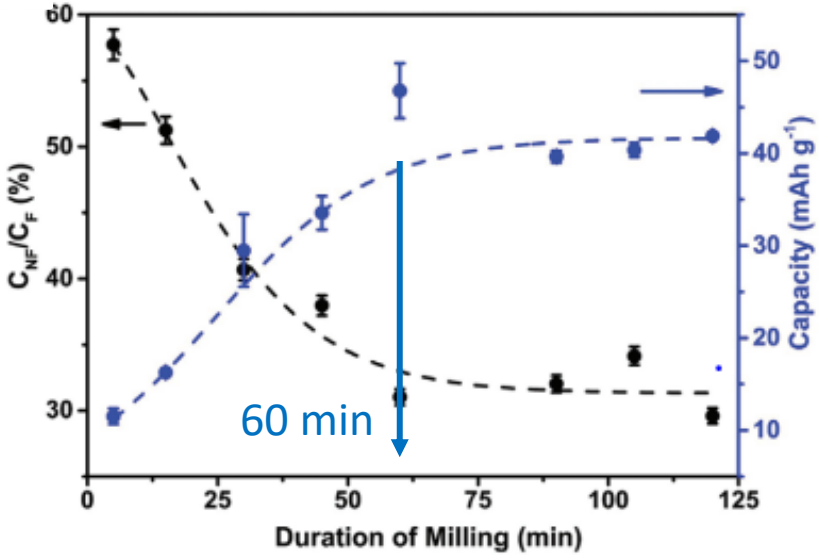
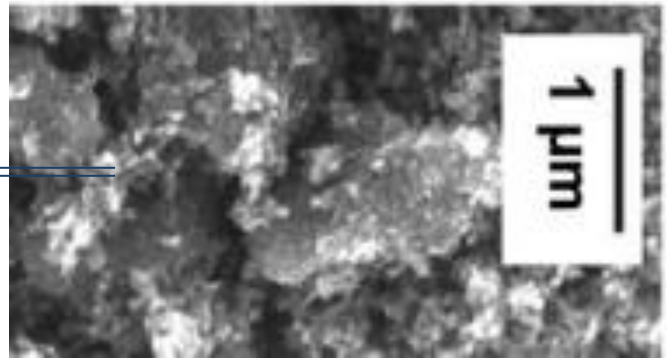
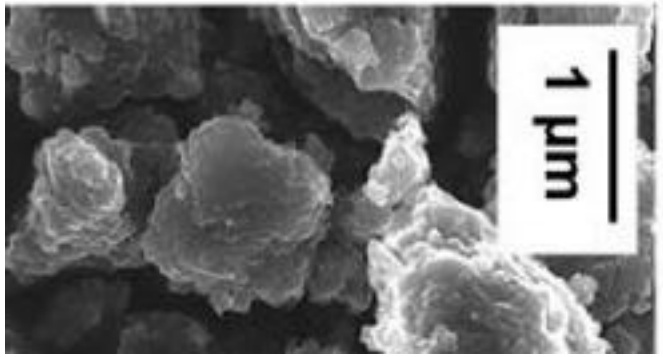
Composition and Morphology





10 nm
CB





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Adv. Sustainable Syst.
2022, 2200396

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Lignin-carbon coated electrodes

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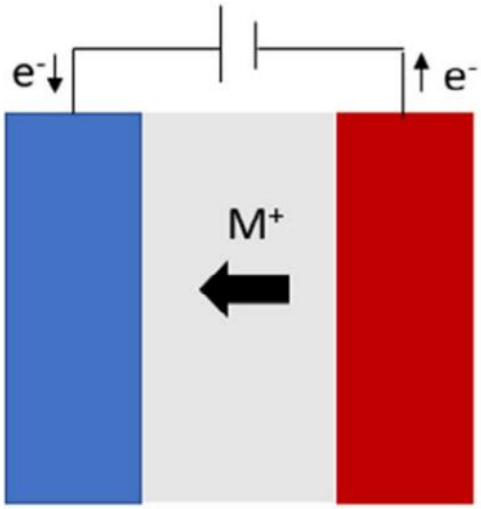
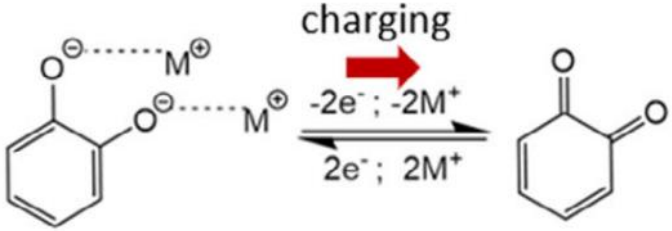
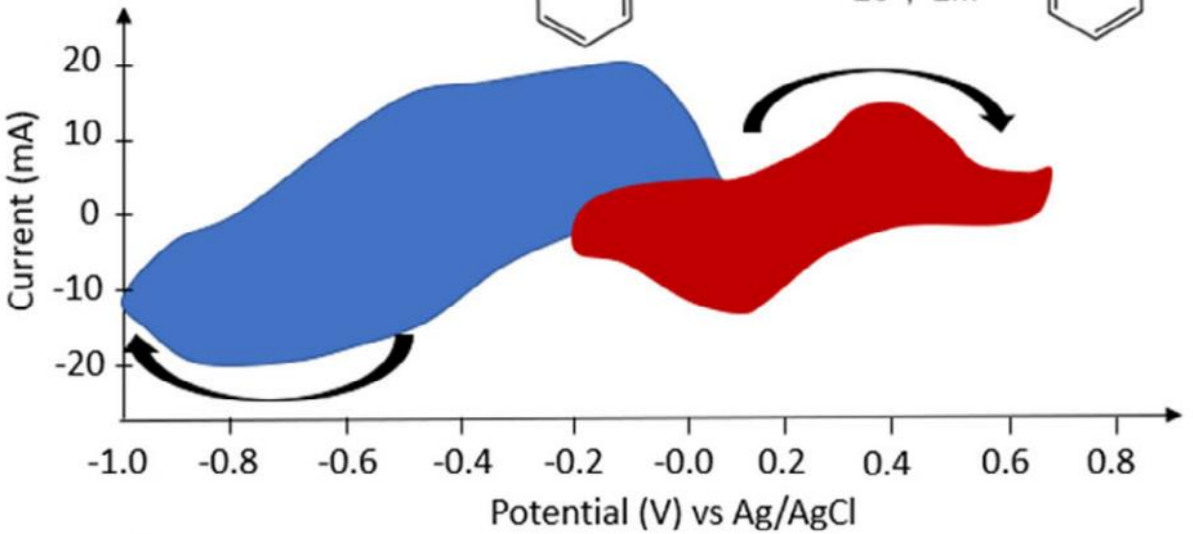
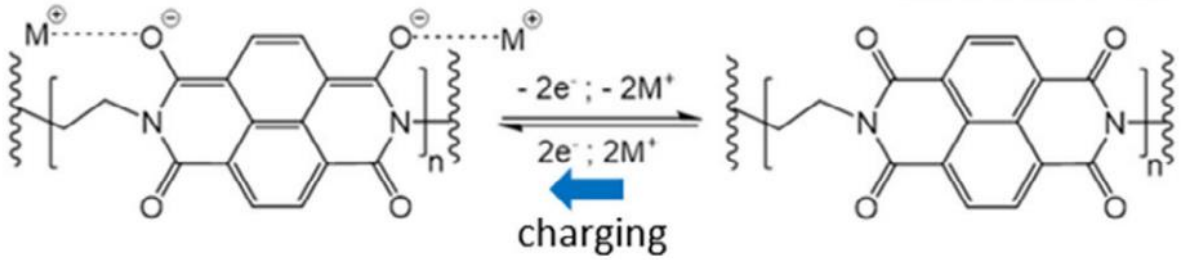
Lignin-polyimide battery

Oxidation releases M^+









Reduction captures M^+

Rocking chair-type of battery where only cations are transported.

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Adv. Energy Sustainability Res. 2022, 3, 2100165

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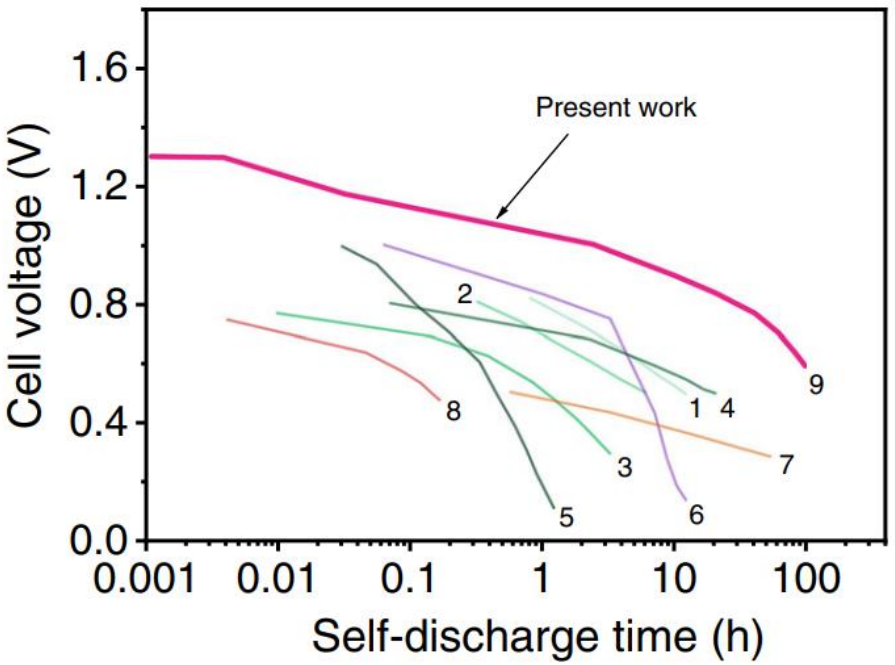
Aqueous-based organic batteries



- Non-flammable, green and scalable batteries would require water-based electrolytes
- With organic electrodes, there is a major issue with the self-discharge
- Aqueous electrolytes lead to high ionic conductivity (not limiting the power of the device)

Water-in-polyelectrolyte salt (WIPE) approach offers a solution

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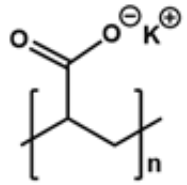
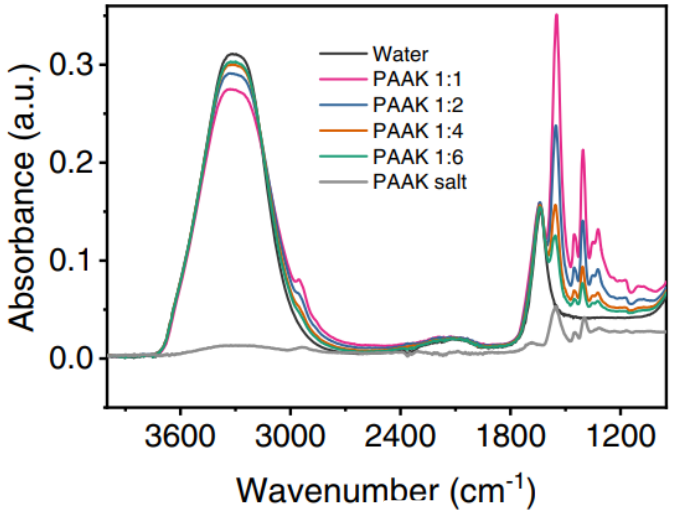
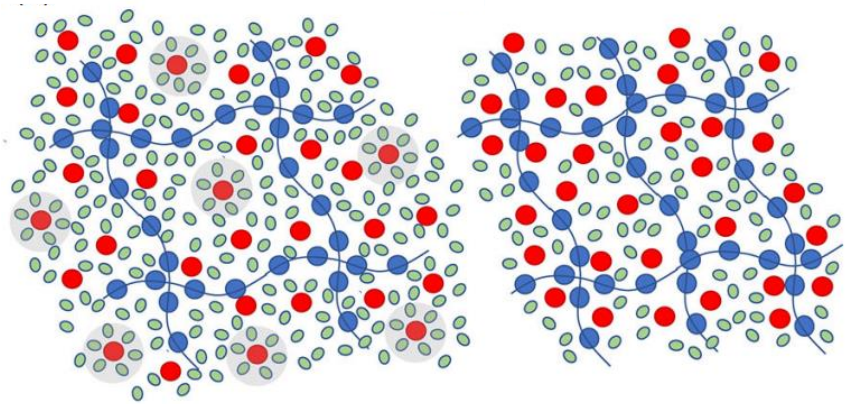
Water-in-K-polyacrylate



PAAK



- Low-cost, printable
- Extremely high solubility (weight ratio PAAK/water to 1:1)
- Non-flammable
- Bonded water and some water clusters (free water)



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Patented WO2021144050A1

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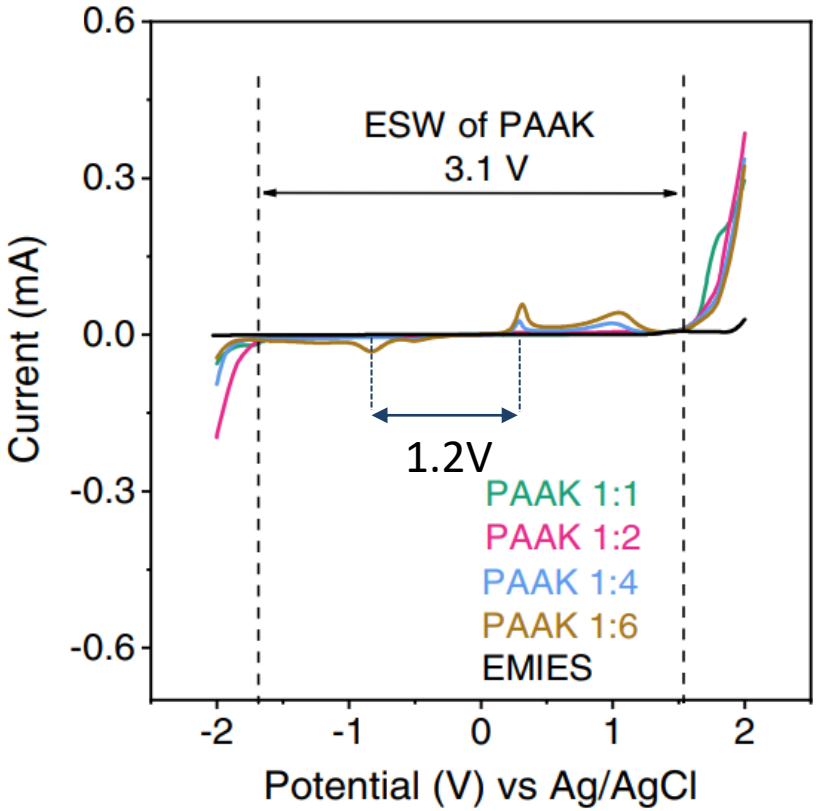
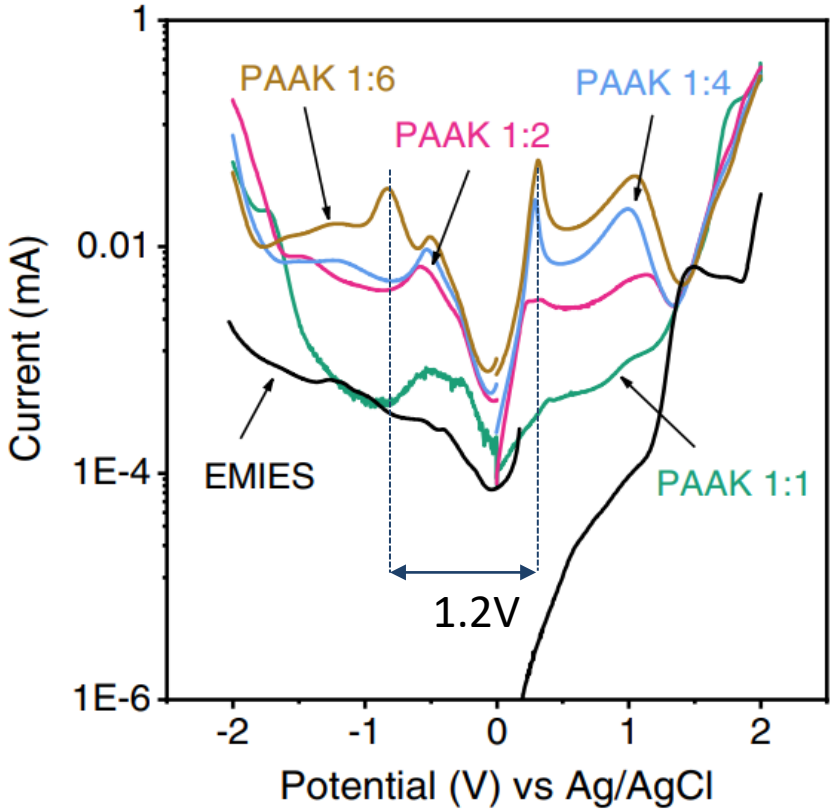
Electrochemical Stability Window (ESW)





Low content of water leads to low leakage current at low voltage and high ESW

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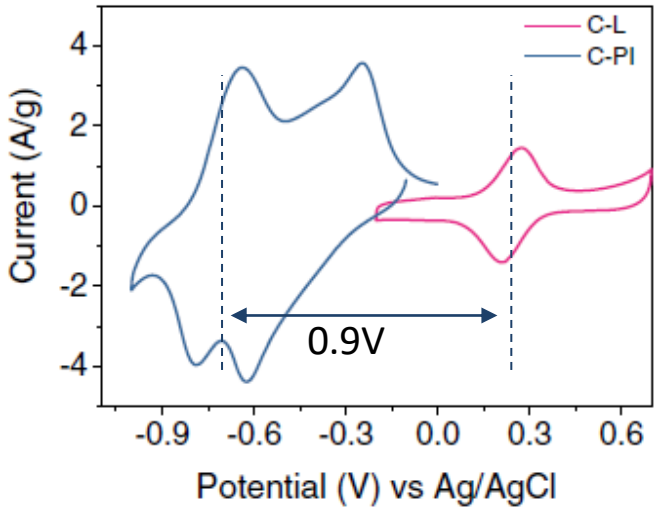
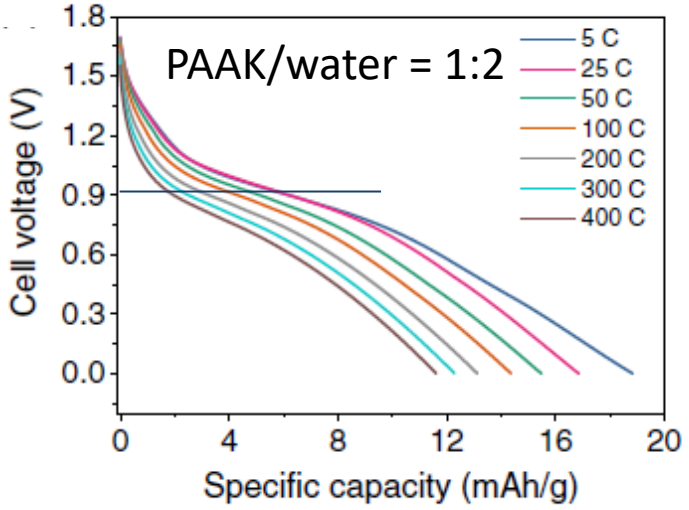
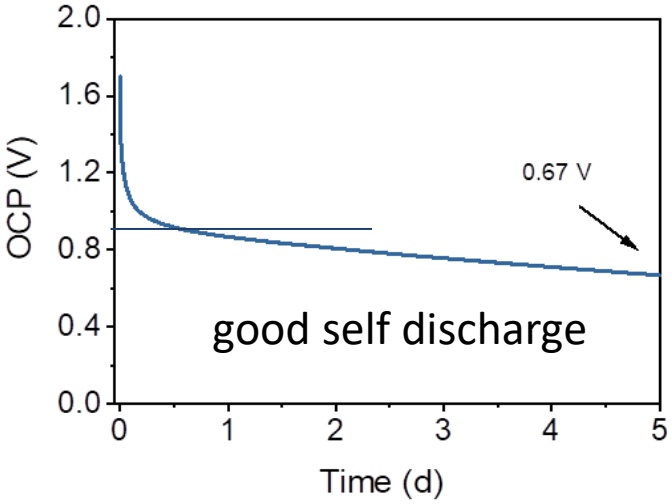
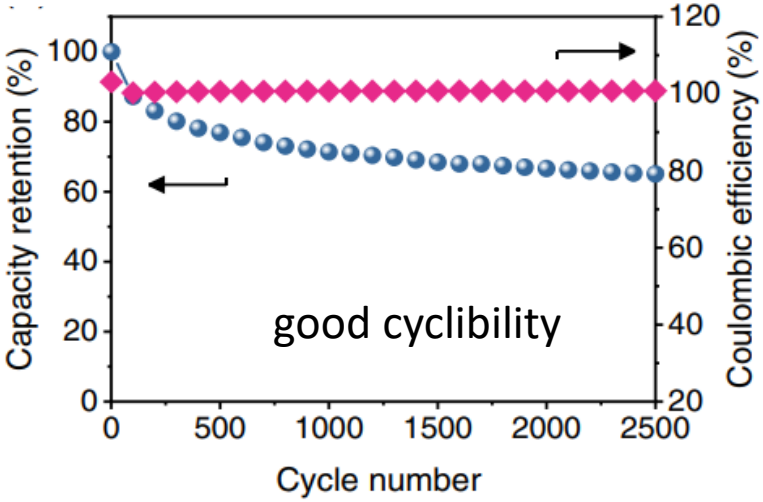
Lignin-polyimide battery









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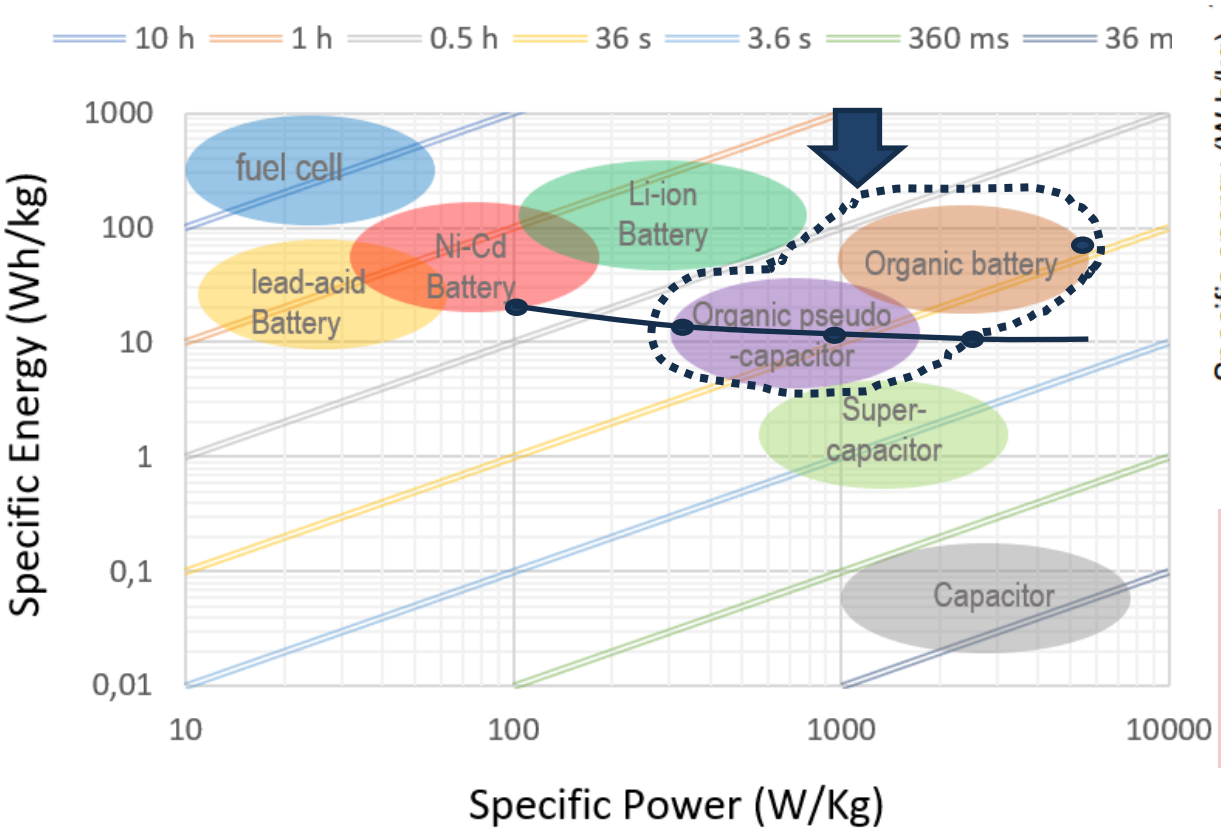
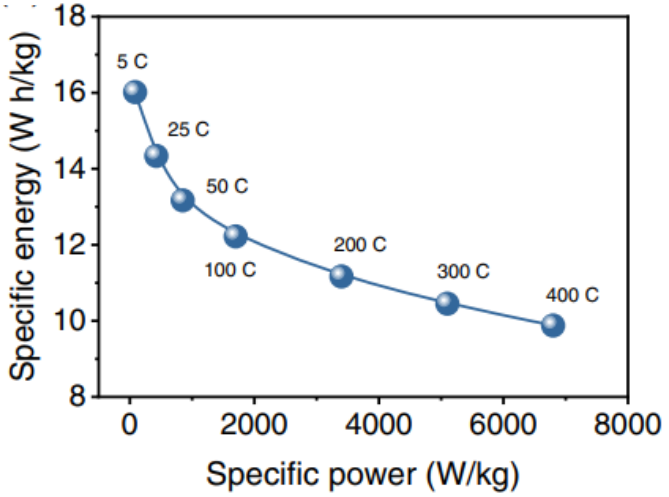
Lignin-polyimide cell in Ragone plot





The high ionic conductivity and the fast electron transfer at electrode lead to a high power device

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Conclusion

- ✓ Ball milling enables to bring the electrical conduction to the most intimate part of lignin forming a homogeneous nanocomposite at low cost.
- ✓ Lignin and aromatic polyimide are low-cost redox polymers that are the basis for cathode and anode of a cation rocking chair battery providing 0.9V.
- ✓ The main issue of self-discharge encountered in non-flammable aqueous based organic batteries is solved by the concept of water-in-K polyacrylate.
- ✓ Water-in-PAAK provides an electrolyte with high ionic conductivity (~100 mS/cm) that is independent on the viscosity (from liquid to gel type)
- ✓ Polyimide-lignin rocking chair battery of high power and decent energy is a possible alternative for IoE

Acknowledgements


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LIGNA ENERGY

Knut och Alice Wallenbergs Stiftelse

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Thank you

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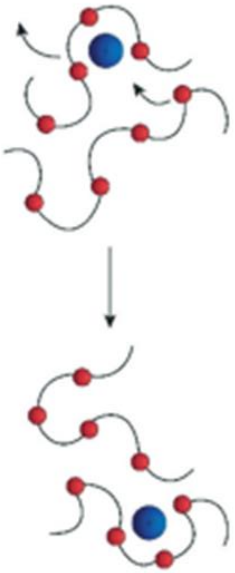
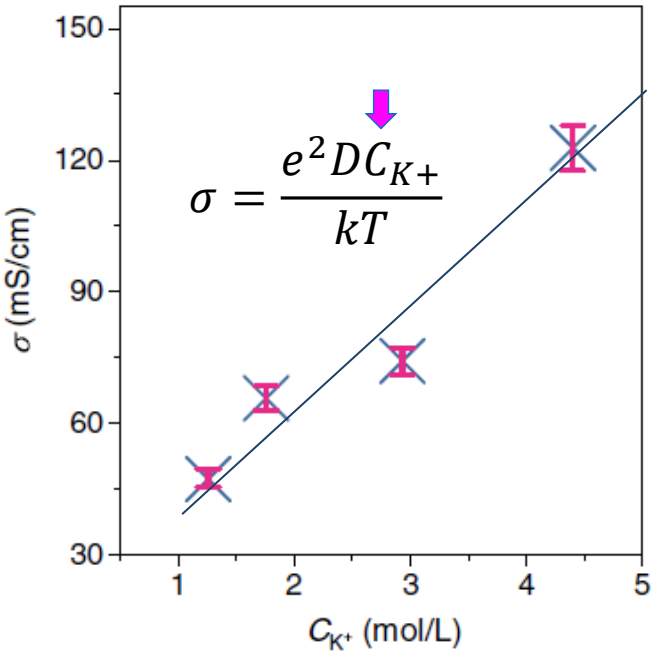
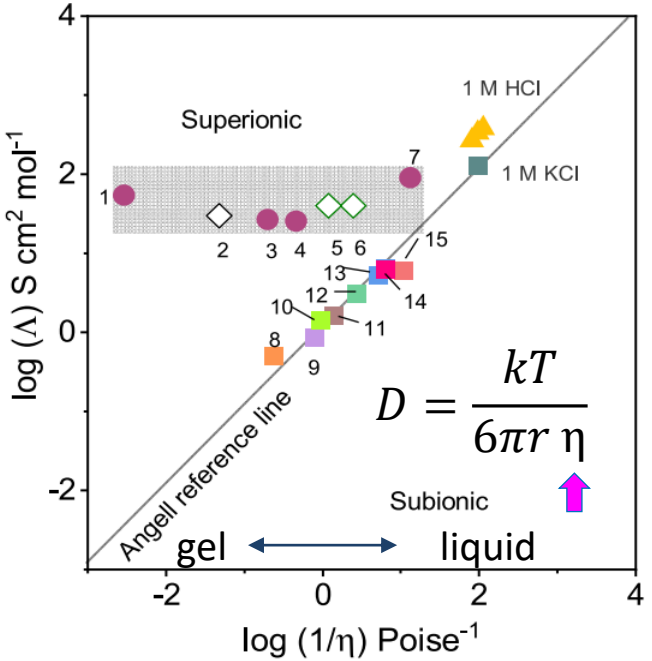
Conductivity independent on viscosity

Advantageous for printing high power batteries







- High ionic conductivity (σ=100 mS/cm) ÷ concentration ions C_{K+}

-> good dissociation (few ”neutral” ion pairs)

- M_w tunes the viscosity η over 4 orders of magnitude
- Molar conductivity Λ ÷ diffusion coefficient D are independent on η

-> ”superionic” driven by microscopic chain relaxation dynamics

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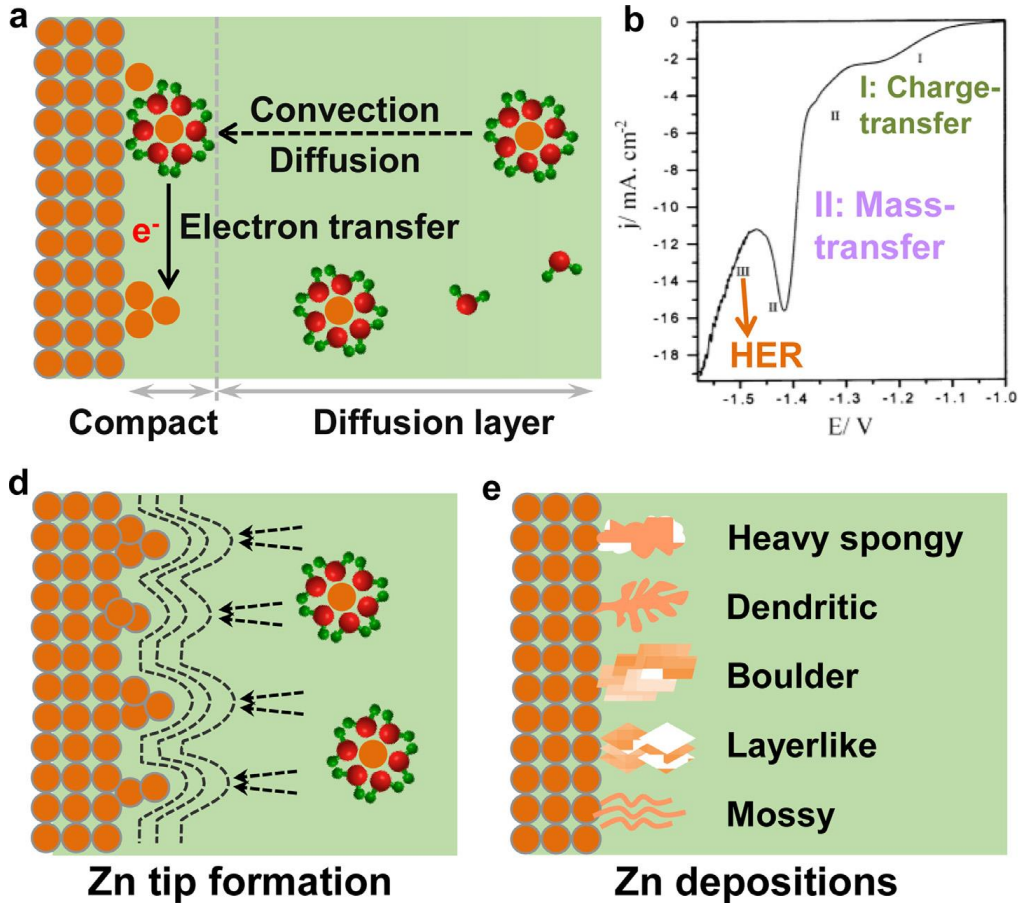
Towards Zinc batteries



Dendritic growth leads to high electric field promoting the H_2 evolution reaction:

- Gas bubbles destroy the battery
- Dendrites create short circuits

The aim is to find an electrolyte that prevents the dendritic growth and limits the HER.
Could ”Water-in-PAAK” be a good starting point?

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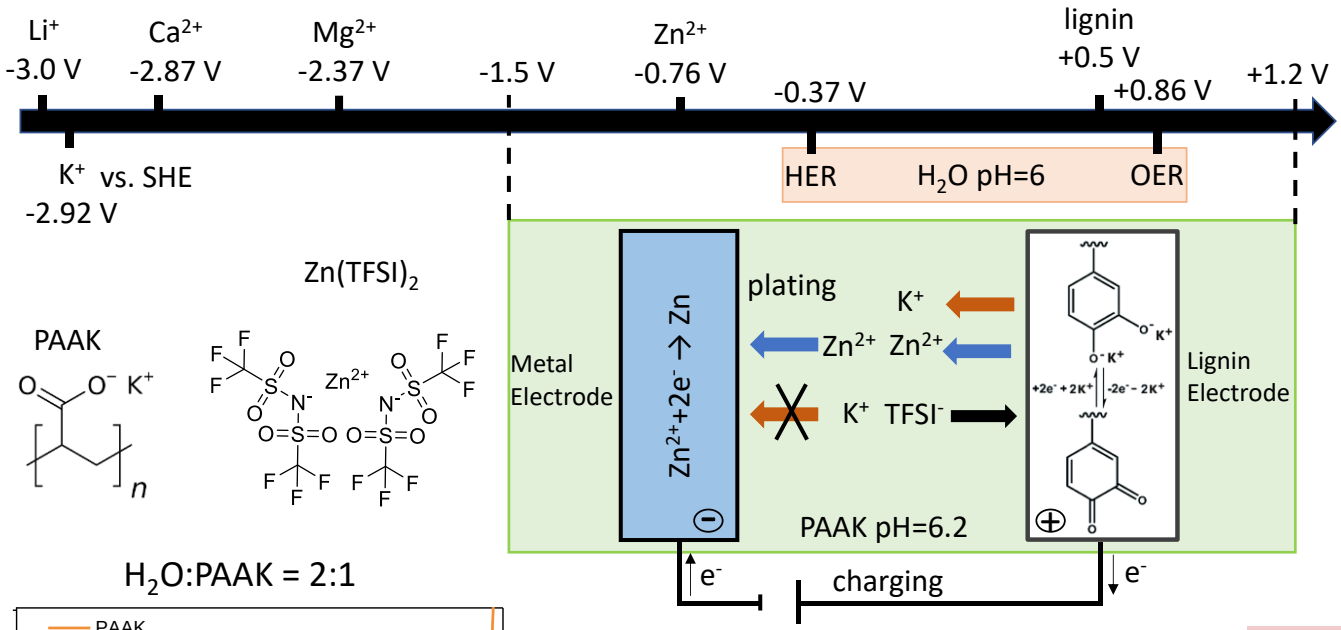
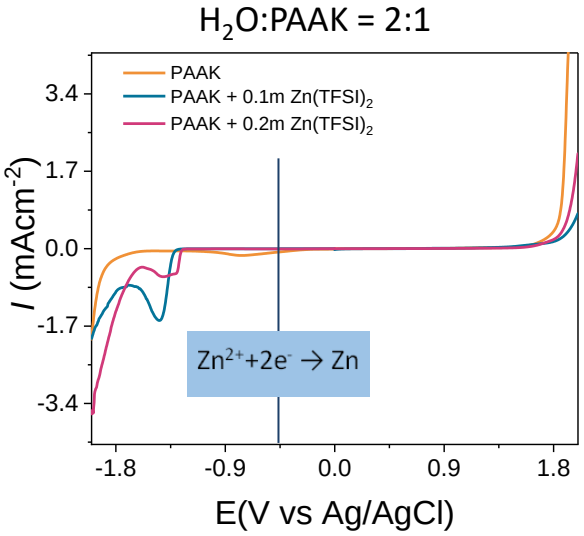
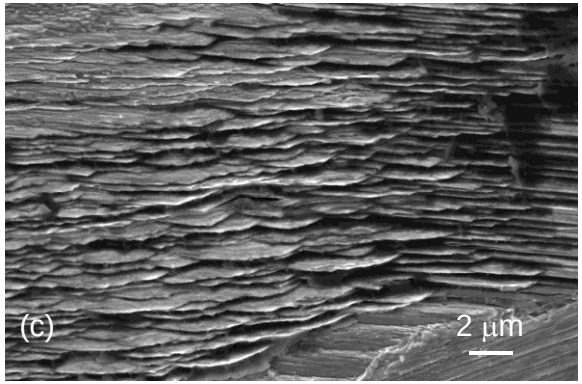
PAAK + ZnTFSI for Zn-battery



No H_2 evolution at the Zn deposition potential





Zn deposition without dendrites

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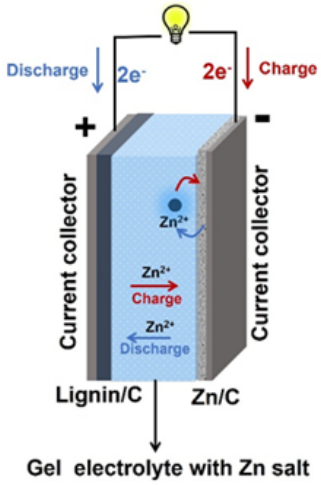
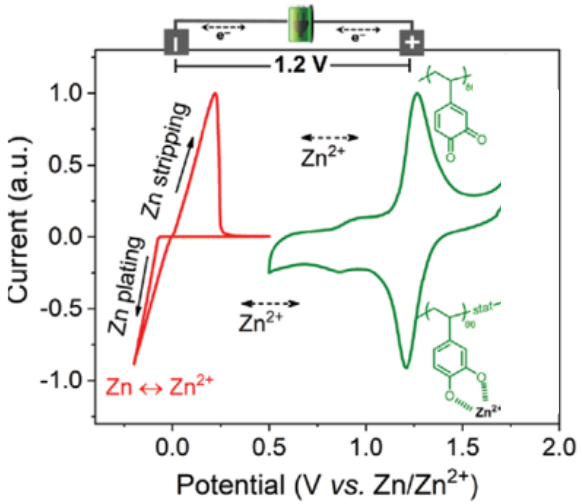
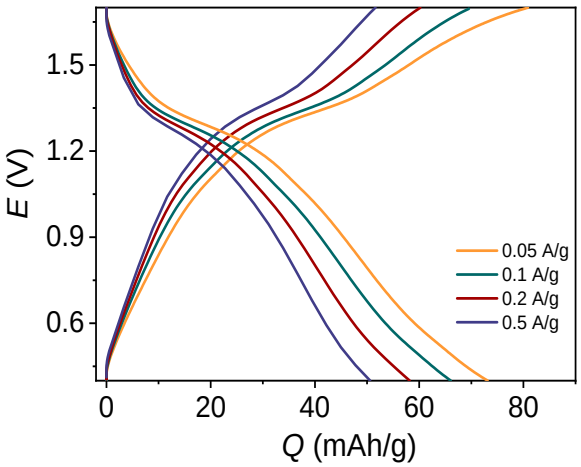
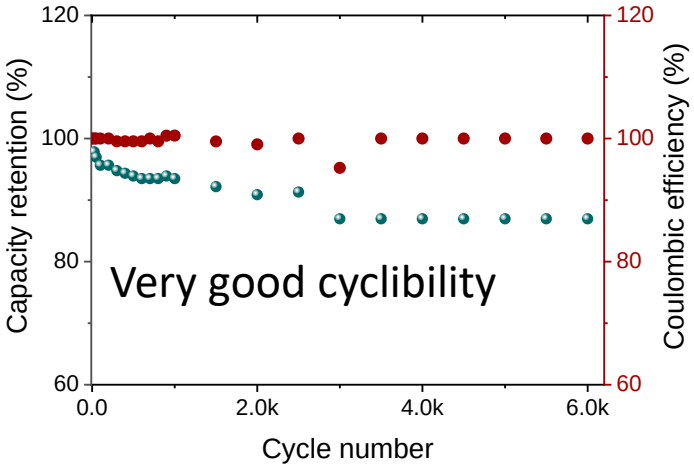
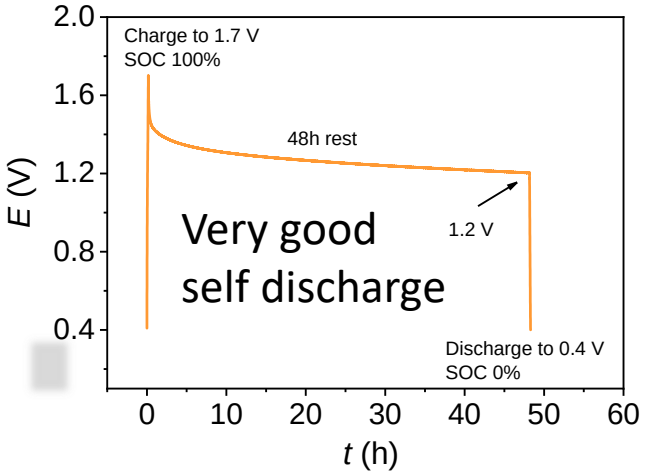
Lignin-Zinc battery











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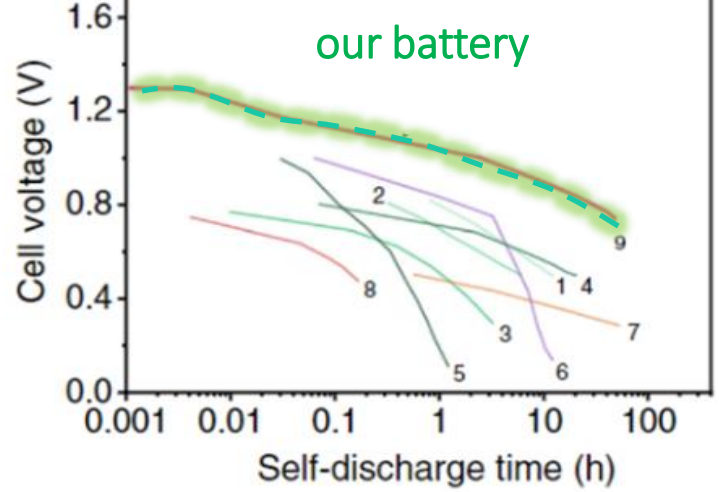

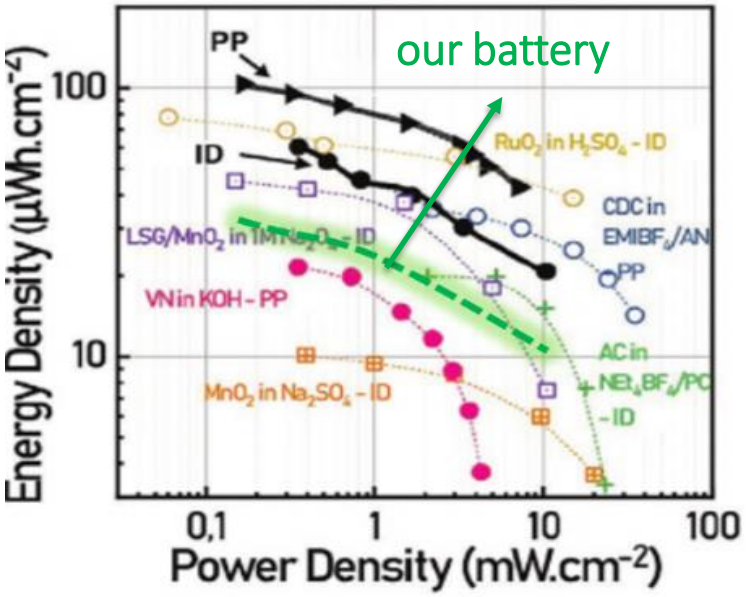

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