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CONDUCTING POLYMER MICROSTRUCTURES AND COMPOSITES FOR SUPERCAPACITORS

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Conducting Polymer Microstructures and Composites for Supercapacitors

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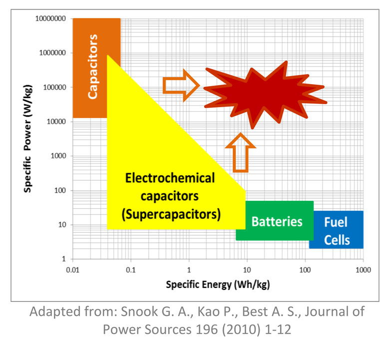
Objective

To increase the performance of conducting polymer electrodes for supercapacitors by controlling polymer assembly, ion transport, electron transfer, and redox processes. The electrode morphology and electrochemical performance are studied.

Motivation

Energy Storage



Adapted from: Snook G. A., Kao P., Best A. S., Journal of Power Sources 196 (2011) 1-12

New energy storage technologies face many challenges, such as material availability, efficiency, charge storage capacity, long term cycle-ability, and cost effectiveness.

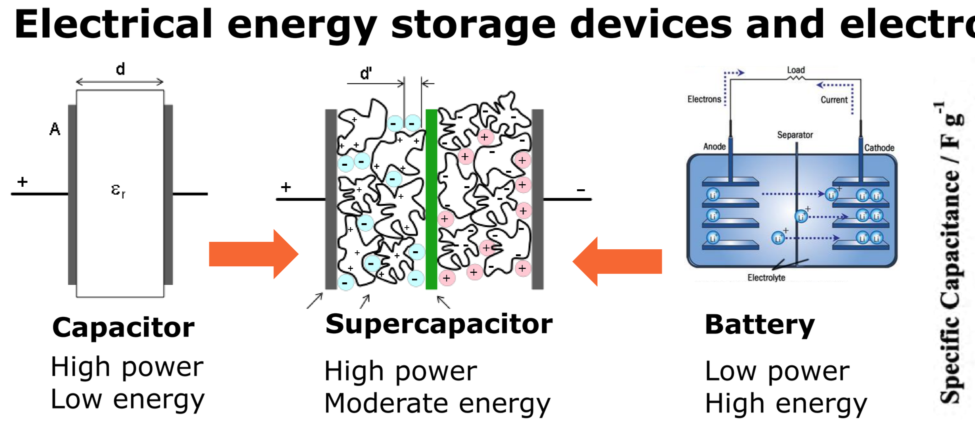
Emerging devices, such as supercapacitors, have the potential to provide high energy capacity and fast discharge rates to bridge the gap between traditional batteries and high-power capacitors.

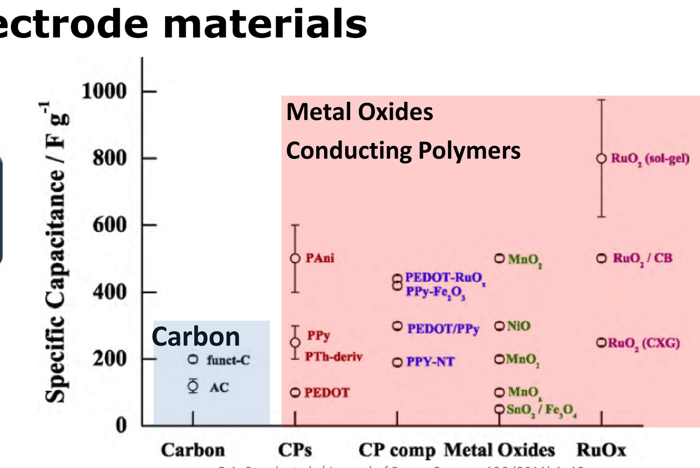
Need for high-power & large-format energy storage

Intermittent energy sources — Portable Electronics — Transportation

Introduction

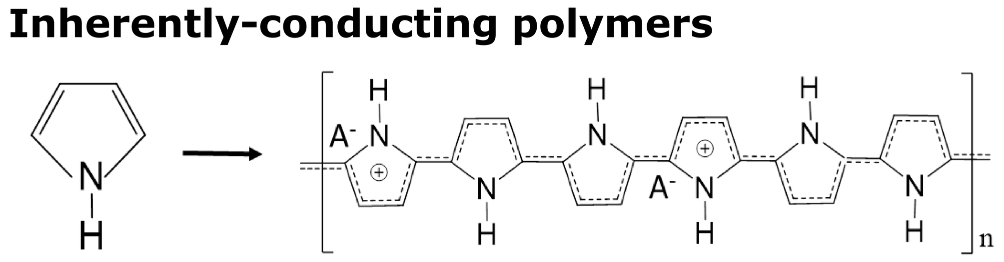
Electrical energy storage devices and electrode materials

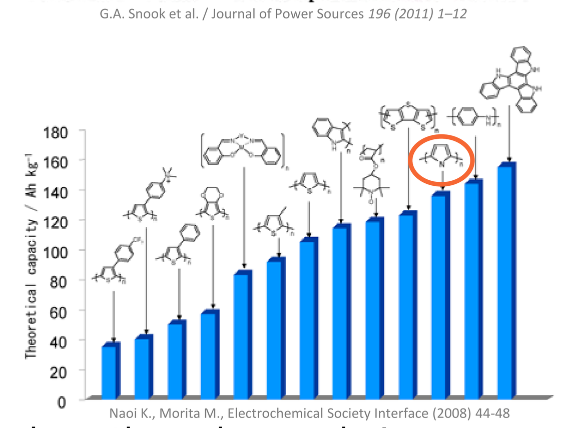




G.A. Snook et al. / Journal of Power Sources 196 (2011) 1–12

Inherently-conducting polymers


Polypyrrole (PPy) conjugated structure

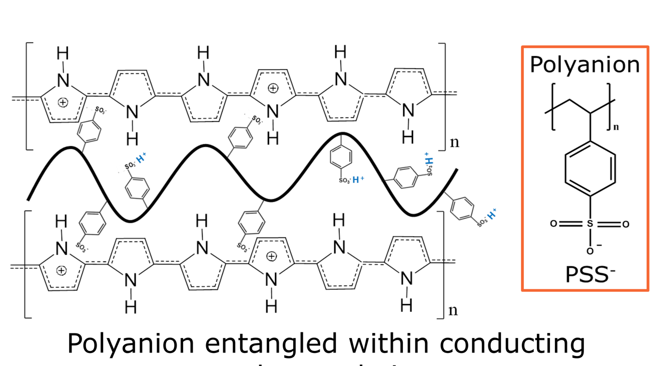

Naoi K., Morita M., Electrochemical Society Interface (2008) 44-48

- ✓ Conjugated systems, alternating single and double bonds along the polymer chain
- ✓ Mobility of electrons throughout the polymer backbone
- ✓ Electrically conductive in the doped state

Polymer dopants

To drive Structure:

Entrapped polymer dopants within the conducting polymer film aid in control of polymer assembly and ion transport.

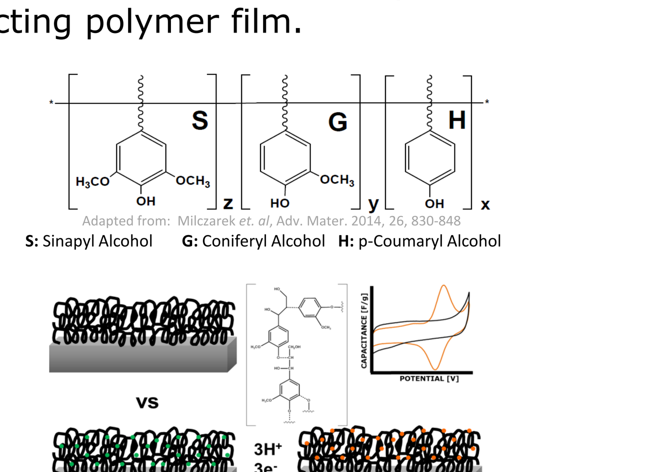


Polyanion entangled within conducting polymer chains

- ✓ Macromolecules are entrapped within the polymer film during polymerization
- ✓ Protons compensate the doped polymer during discharge

To increase Energy Capacity:

Entrapped renewable redox biopolymer helps to increase the redox capacitance in the conducting polymer film.

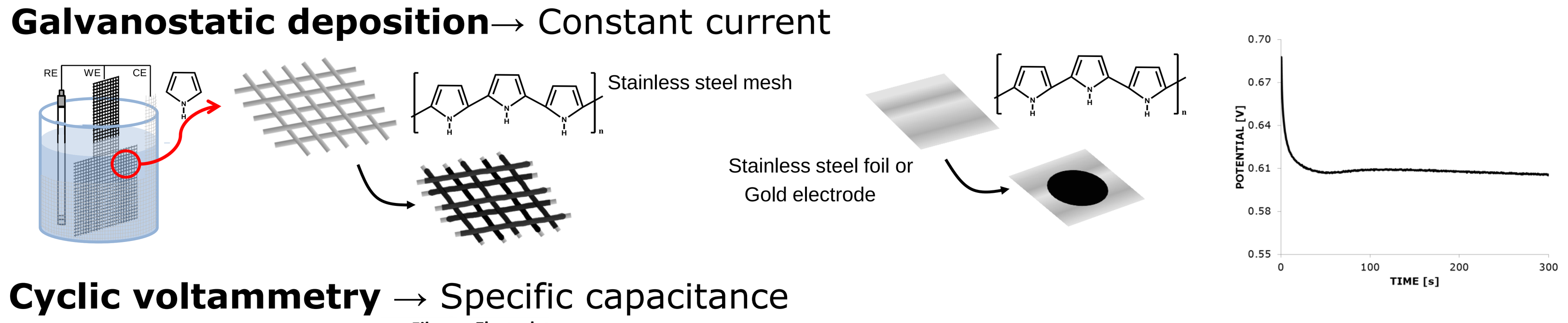


Adapted from: Milczarek et al. Science 2012

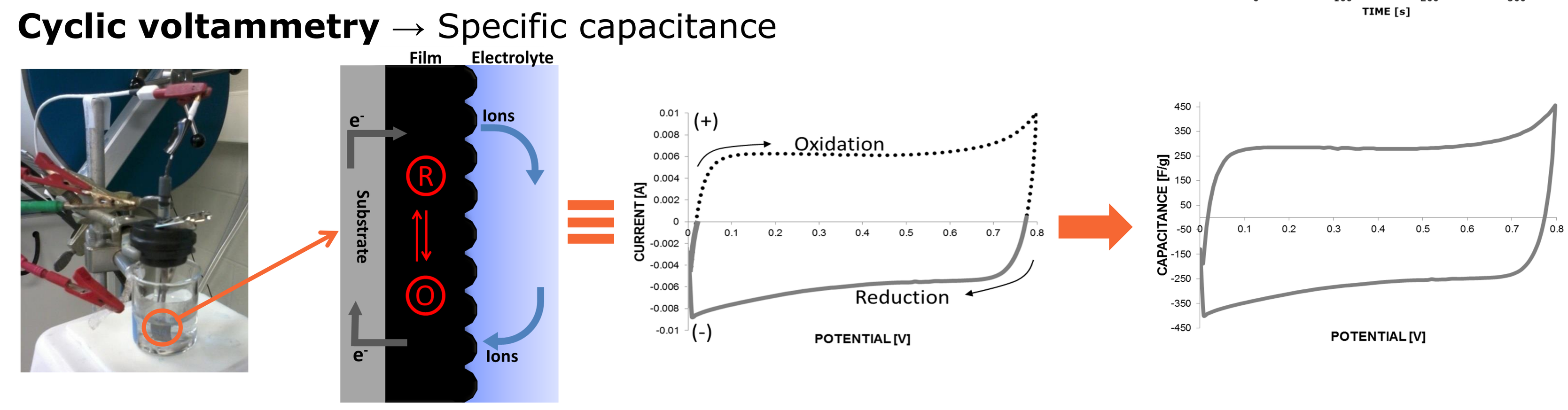
- ✓ Redox Polymer: non-conjugated polymer with redox groups that can be reversibly reduced and oxidized
- ✓ Lignin: comprises 20-30% of the mass of plants and is the second most abundant natural polymer in the world after cellulose

Film Preparation & Characterization

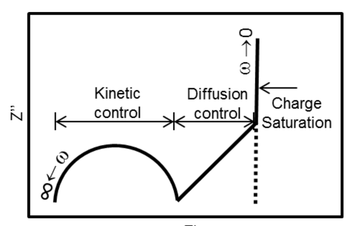
- ✓ **Galvanostatic deposition** → Constant current



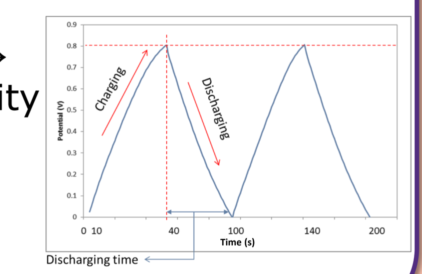
- ✓ **Cyclic voltammetry** → Specific capacitance



- ✓ **Impedance** → mass/charge transfer limitations



- ✓ **Charge-discharge** → Specific charge/capacity

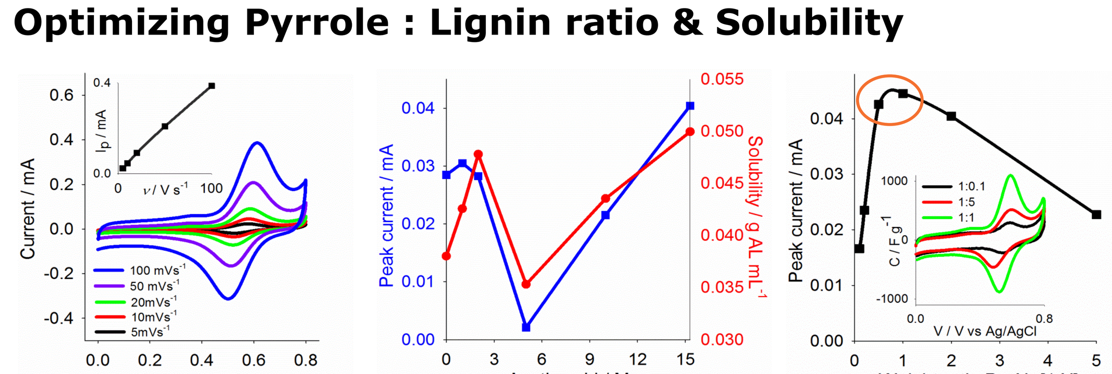


- ✓ **Scanning electron microscopy** → Morphology & thickness

Results & Discussion

To increase Energy Capacity

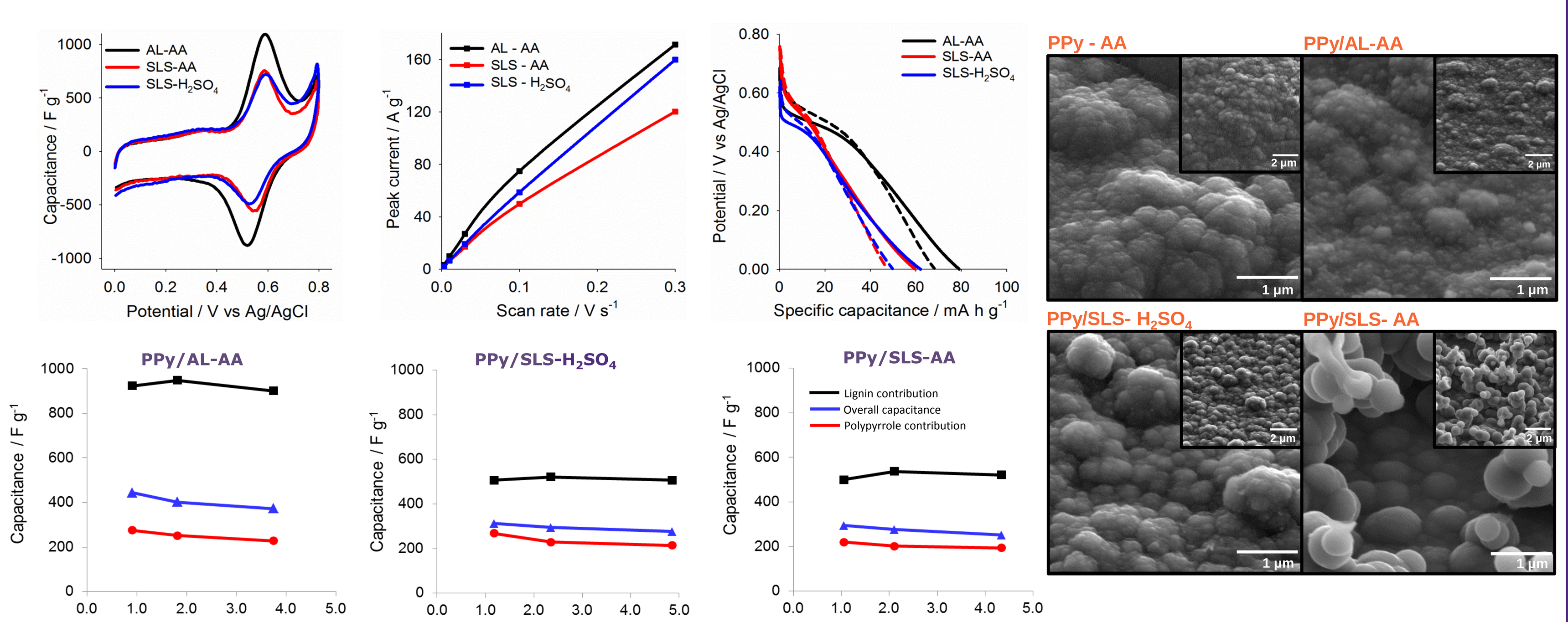
Optimizing Pyrrole : Lignin ratio & Solubility



S. Leguizamon*, K. P. Díaz-Orellana*, J. Velez, M. C. Thies, M. E. Roberts, (2015) submitted to Journal of Material Chemistry A

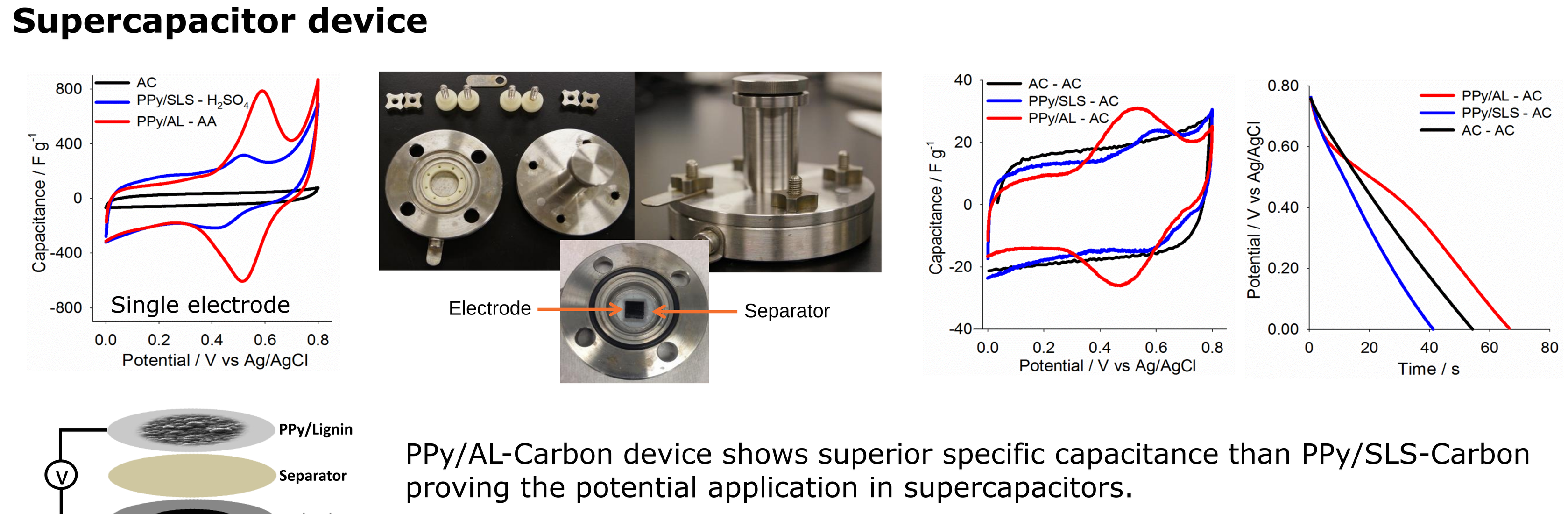
Alkali lignin is the most abundant type of Lignin. The maximum solubility of Alkali lignin was found at 15.3 M acetic acid. Optimum Pyrrole:Lignin ratios are 1:1 or 1:2

Polypyrrole composite films: Sodium Lignosulfonate vs Alkali Lignin



PPy/AL-AA films show ~20% higher capacitance than PPy/SLS-H_2SO_4 and ~30% higher than PPy/SLS-AA. PPy/SLS-AA and PPy/SLS-H_2SO_4 present similar capacitance, however, rapid ion exchange is observed in PPy/SLS-AA which exhibit a granular, openly porous structure that allows for increased electrode/electrolyte contact.

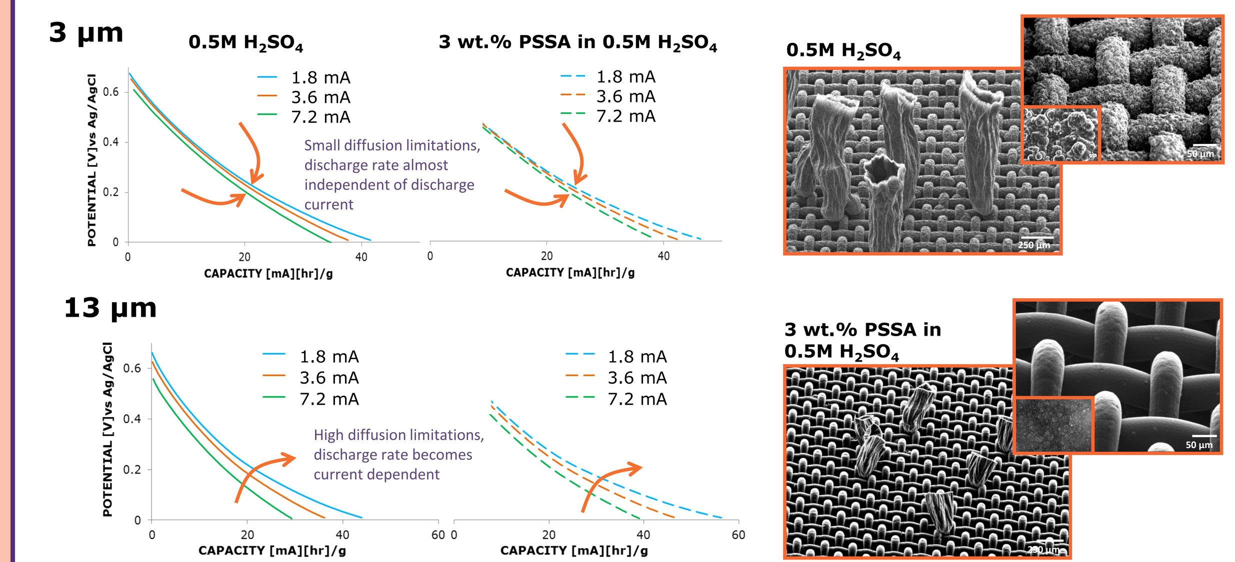
Supercapacitor device



PPy/AL-Carbon device shows superior specific capacitance than PPy/SLS-Carbon proving the potential application in supercapacitors.

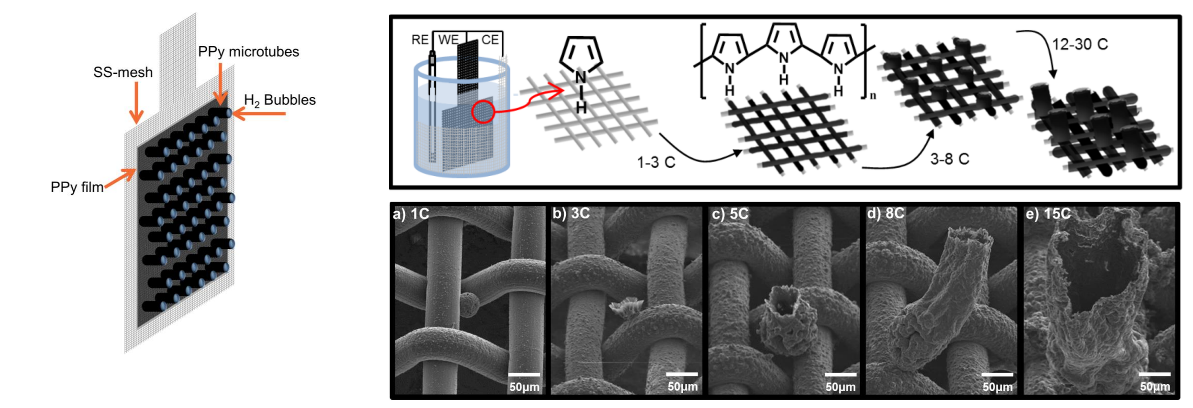
To drive Structure

Polypyrrole/PSSA films with different thickness



For films with thicknesses greater than 5μm, addition of PSSA does not improve the ion transport within the conducting polymer chain.

Polymer microtube growth on stainless steel mesh substrates



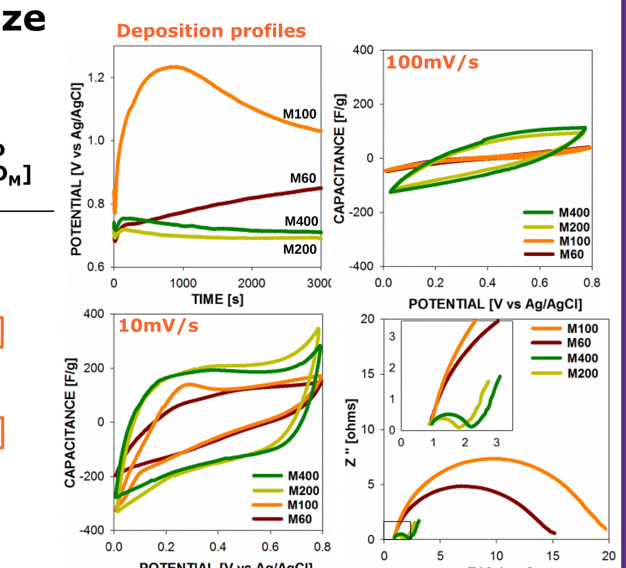
K. P. Díaz-Orellana, M. E. Roberts, (2014) submitted to RSC Advances

Hydrogen gas nucleates on mesh surface, specifically at the joints of two distinct wires. Small polymer clusters form around these bubbles guiding the growth of the polymer.

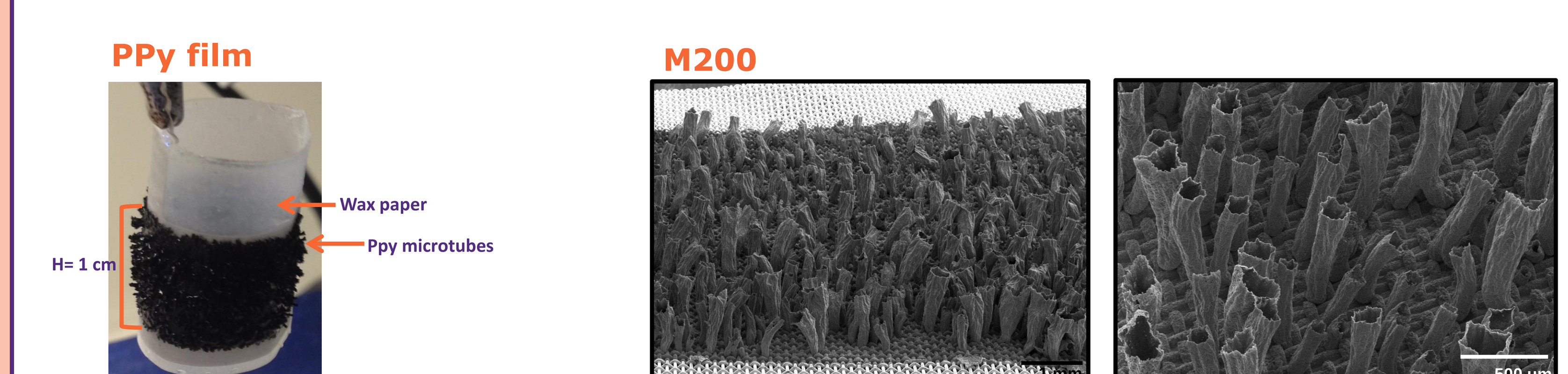
Microtubes properties depend on substrate mesh size

Mesh size is shown to influence in the structure and electrochemical performance of the microtubes by confining the gas bubble to a specific size. Cylindrical tubes are found on finer mesh (M200-M400) while conical structures on coarser meshes.

Substrate [mesh]	Film [μm]	Height [μm]	Ratio [D_T to D_M]
M40	12	700	2.2
M60	12	720	2.7
M100	9.1	720	5.6
M200	16	940	1.2
M250	13	340	3.0
M325	15	620	2.2
M400	17	1300	1.9



Toward large-scale microtubes production



Our polymer microtube synthesis process is scalable to large area substrates, and has been used to reproducible generate polypyrrole forests on 4 cm by 1 cm substrates.

Conclusions

- Alkali lignin/PPy composite films has shown up to 30% increase in capacitance compared with sulfonated lignin/PPy films. Lignin comprises between the 40 to 60 wt.% of the entire composite film having a higher contribution to the capacitance than PPy
- The PSSA improves the electrochemical performance of films up to ~5 μm by facilitating the ion diffusion. Although, for thicker films no improvements have been observed
- The change in the substrate morphology with changes in the polymerization conditions has shown to be an ease and effective way to control the polypyrrole self-assembly

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