



Building College-University
Partnerships for Nanotechnology
Workforce Development

Nanotechnology, Energy, and Energy Storage

Friday, April 10th, 2015

The webinar will begin at 1pm Eastern Time

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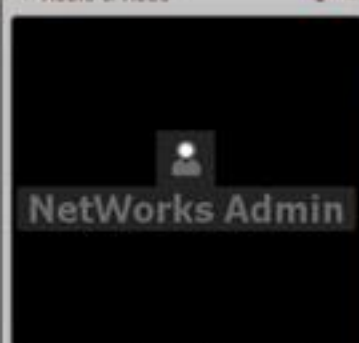
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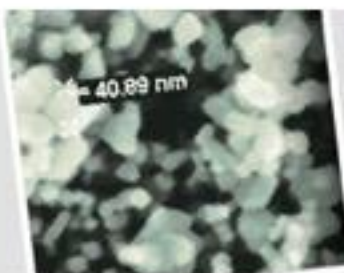


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The NACK Network, established at the Pennsylvania State College of Engineering, and funded in part by a grant from the National Science Foundation (DUE 1205105).



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Today's Presenter



Dr. Hongli Zhu

Dr. Zhu is currently a postdoctoral research associate at the Energy Research Center of University of Maryland. Her work focuses on the research of environmentally friendly green biomaterials, electronics, energy storage and energy harvesting, including: 1) sodium- / lithium- ion battery and super capacitor; 2) design and application of novel transparent nano-structured paper for flexible electronics including solar cells, transistor, touch screen, antenna, actuator, and organic LED et al; 3) Nanomanufacturing, device manufacturing, multifunctional paper and fiber manufacturing.



**Moderator: Mike Lesiecki,
MATEC**



**Host: Roxanna Montoya
MATEC**

Grid Scale *Energy* Storage for Sustainable Future



Production

- Wind
- Heat
- Solar ...



Transmission

- Electrical grid



Usage

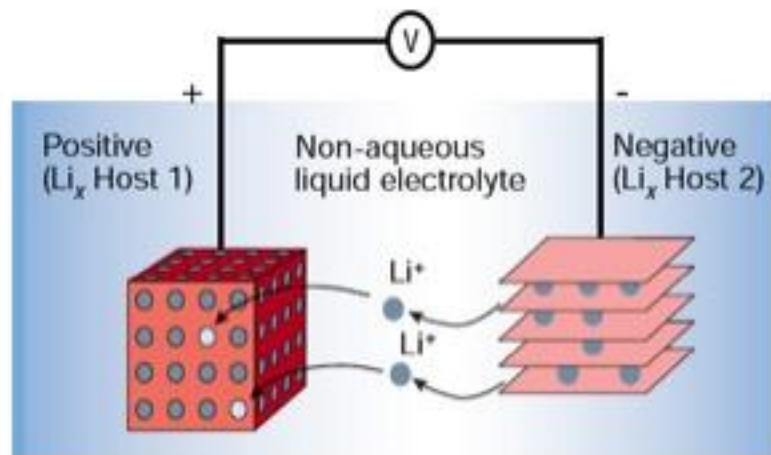
- Lighting
- Building
- Electric Vehicle ...



**Large scale energy storage:
Low Cost!
Longer Cycling!**

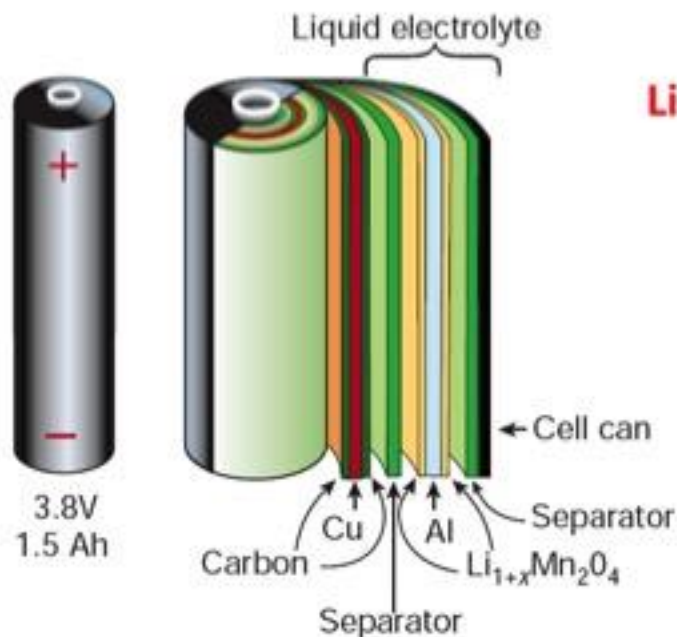


Common Structures



Supercapacitors
Ultracapacitor

Electrons \rightleftharpoons Ions

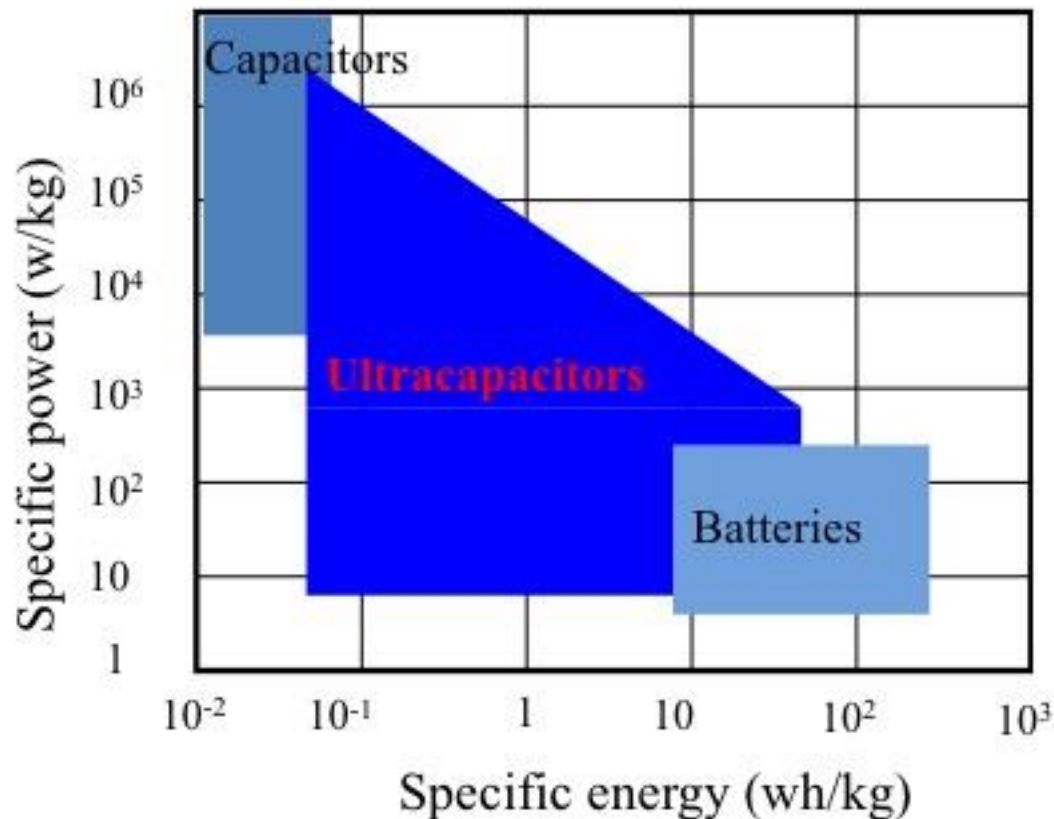


Li-ion Batteries

Terminology

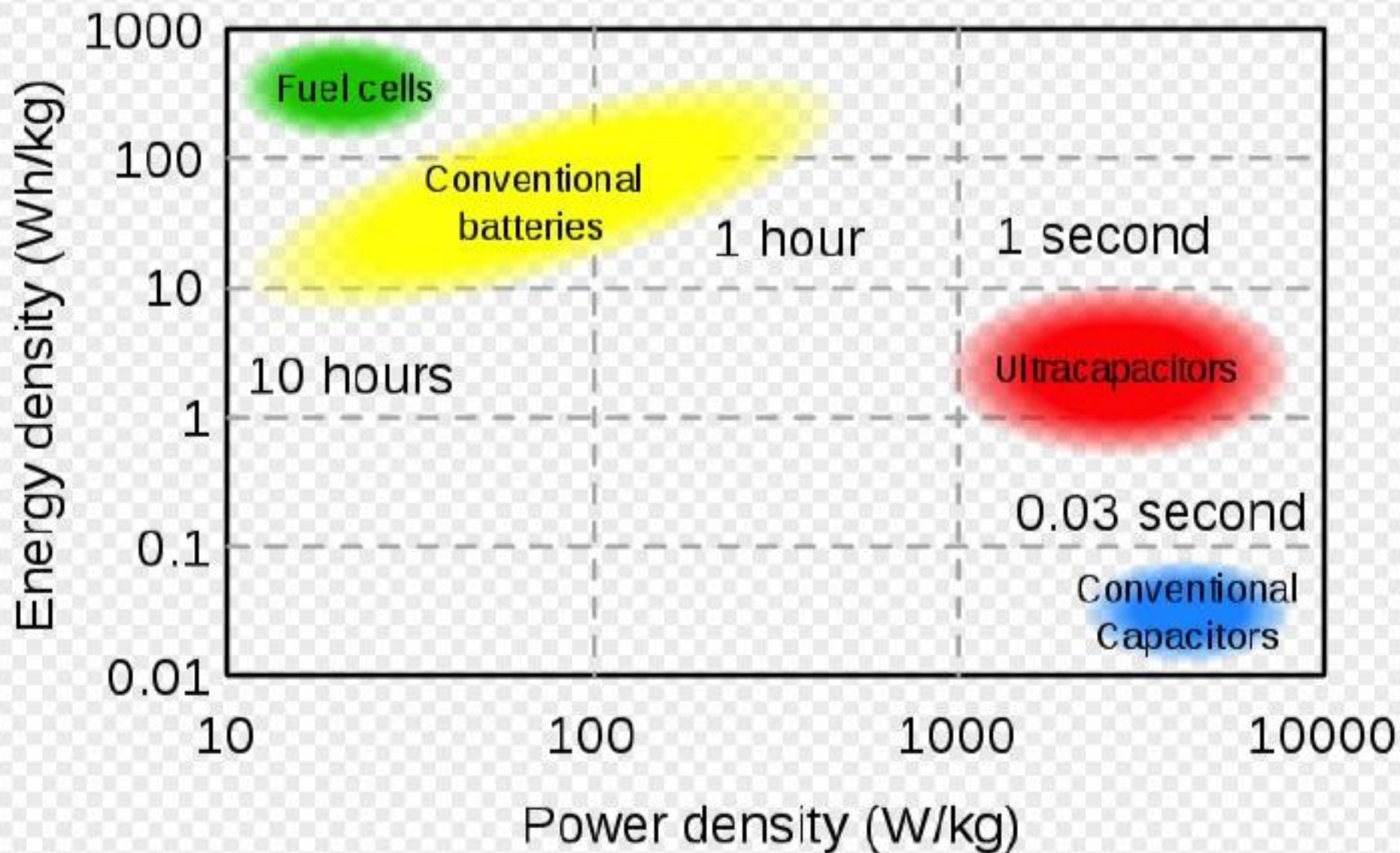
Current collector
Electrode materials
Separator
Electrolyte
Conductive additive
Polymer binder

Comparison in Energy and Power Density

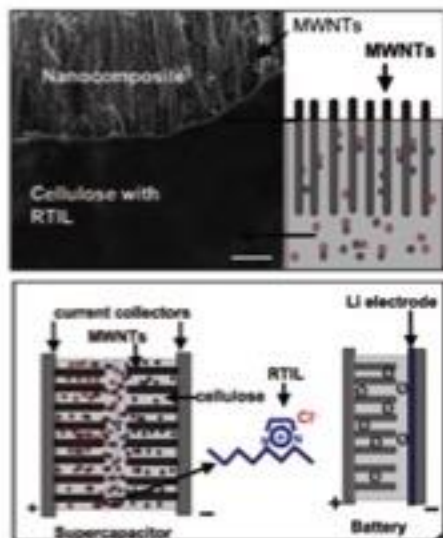


Battery: bulk storage

Ultracapacitor: surface storage
(high power, long cycling)

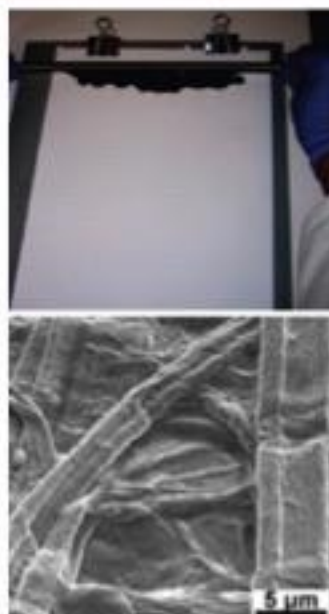


Previous Paper Energy Devices

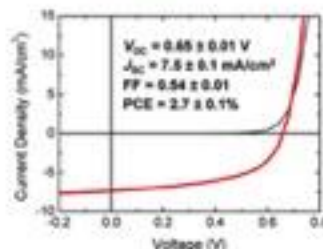
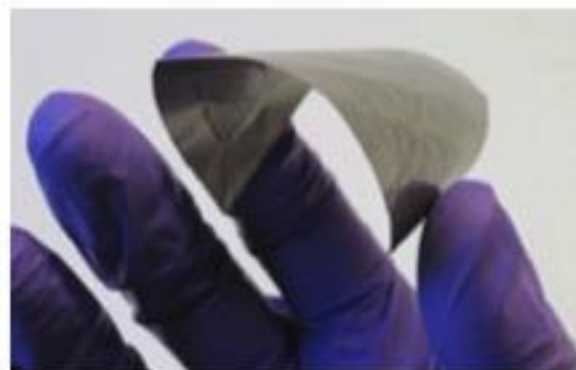


Paper Supercapacitor

Ajayan et al. *PNAS*, 2007

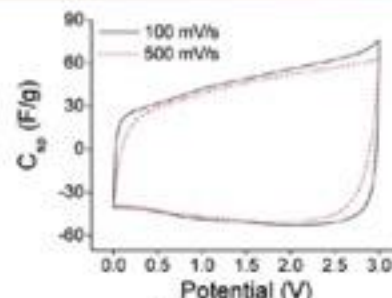


Hu et al. *PNAS*, 2009



Paper Battery

<http://www.paperbatteryco.com/>



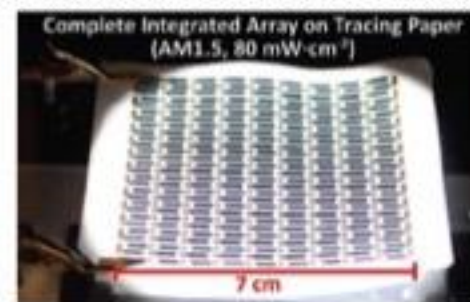
Paper Supercapacitor

Kim et al. *ACS Nano* 2012



Battery Separator

Kim et al. *J. Mater Chem.* 2012



Paper Solar Cells

Bulovic, Gleason et al. *Adv Mater.* 2011

Kippelen et al., *Scientific Report*, 2013

Batteries: Opportunities and Challenges



Na Ion and Na Ion Batteries (Why & What)

Table 1 The comparison between Na and Li elements⁹⁻¹²

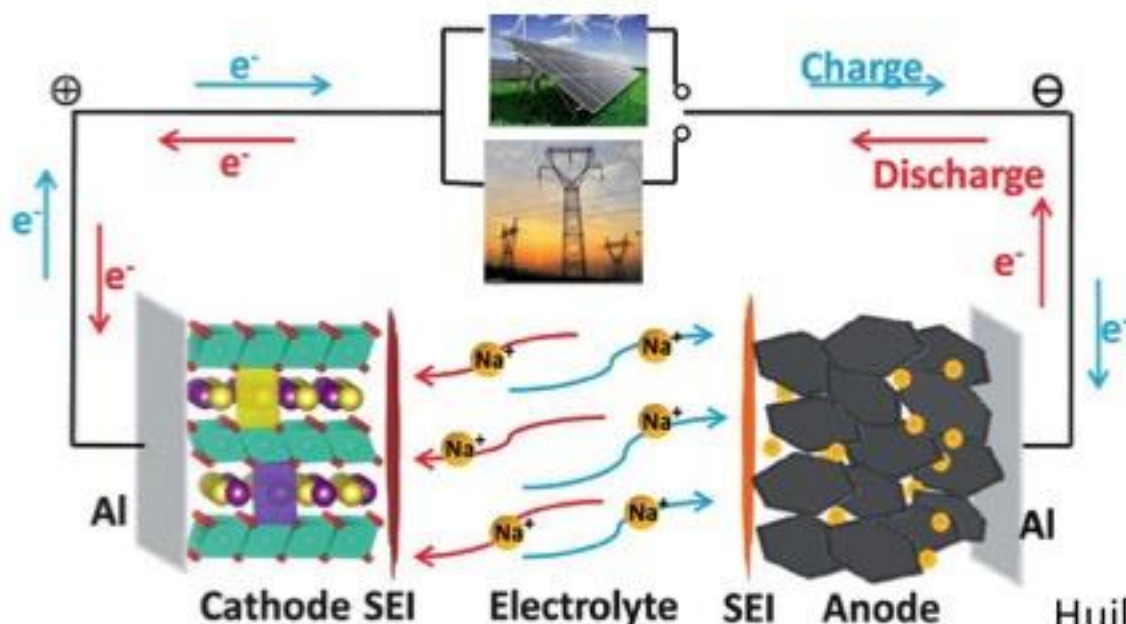
	Na	Li
Cation radius	97 pm	68 pm
Atomic weight	23 g mol ⁻¹	6.9 g mol ⁻¹
E_0 vs. SHE	-2.7 V	-3.04 V
A-O coordination	Octahedral or prismatic	Octahedral or tetrahedral
Melting point	97.7 °C	180.5 °C
Abundance	23.6 × 10 ³ mg kg ⁻¹	20 mg kg ⁻¹
Distribution	Everywhere	70% in South America
Price, carbonates	~2 RMB per kg	~40 RMB per kg



R: 97pm
W: 23 g/mol



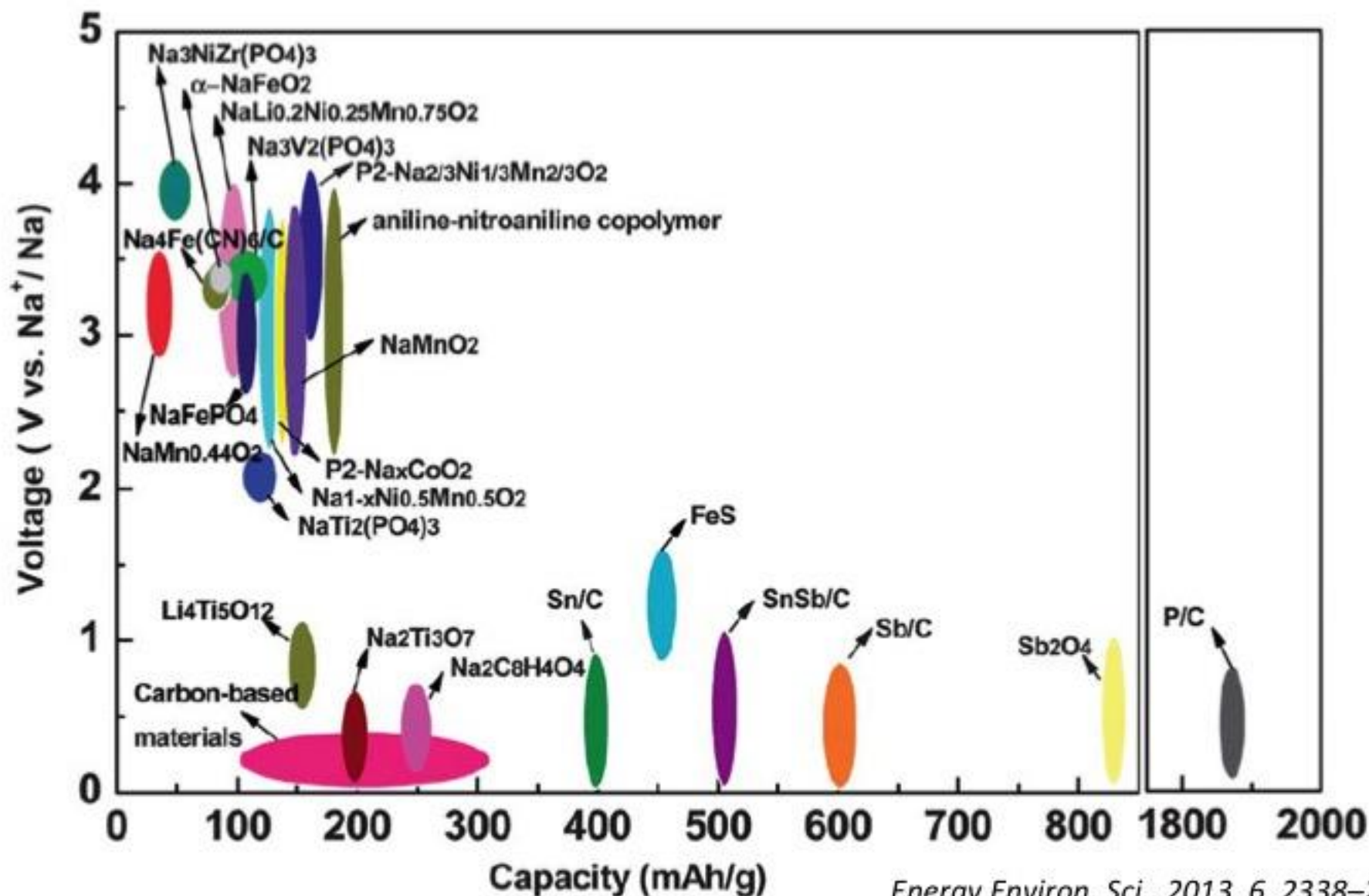
R: 68pm
W: 6.9 g/mol



• **Volume Expansion**
→ **Stress release**

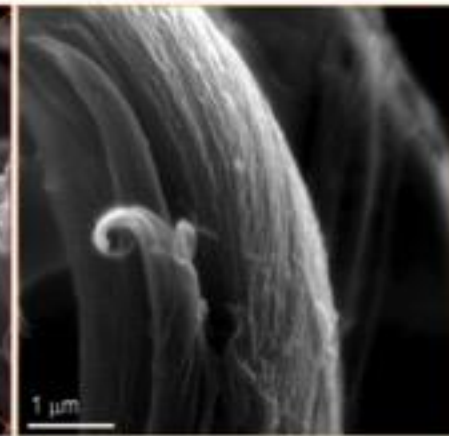
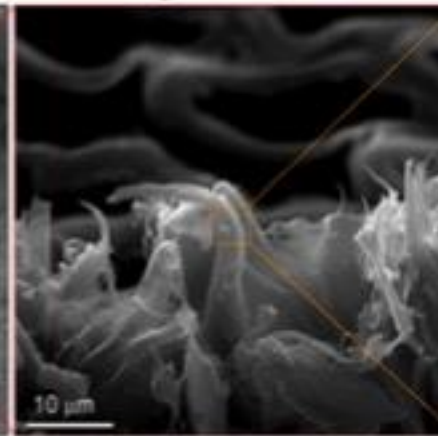
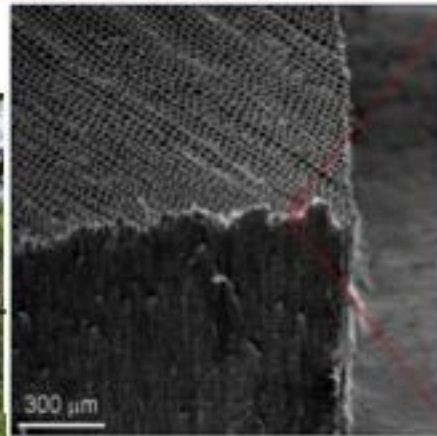
• **Slow Ion Diffusion**
→ **Diffusion channel**

Current Development for Cathode and Anode



Nature-Made Hierarchical Structure

Trees



Cellulose Fiber

$L = 1 - 5 \text{ nm}$
 $D = 20 - 50 \mu\text{m}$

Microfibril Bundle

$L > 2 \mu\text{m}$
 $D > 15 \text{ nm}$

Microfibril

$L > 2 \mu\text{m}$
 $D = 5 - 10 \text{ nm}$

Elementary Fibril

$L < 1 \mu\text{m}$
 $D = 1.5 - 3.5 \text{ nm}$

**Soft
Mesoporous**

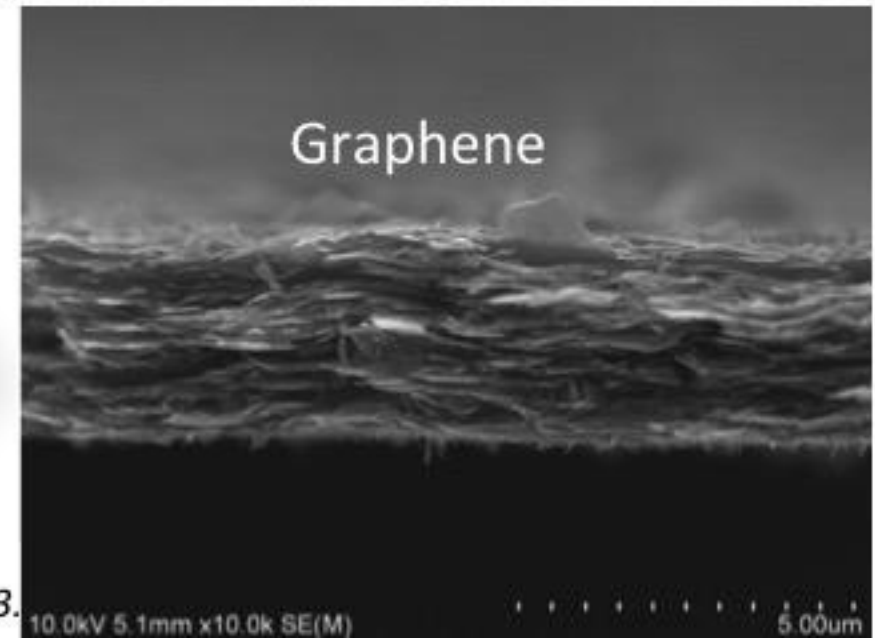
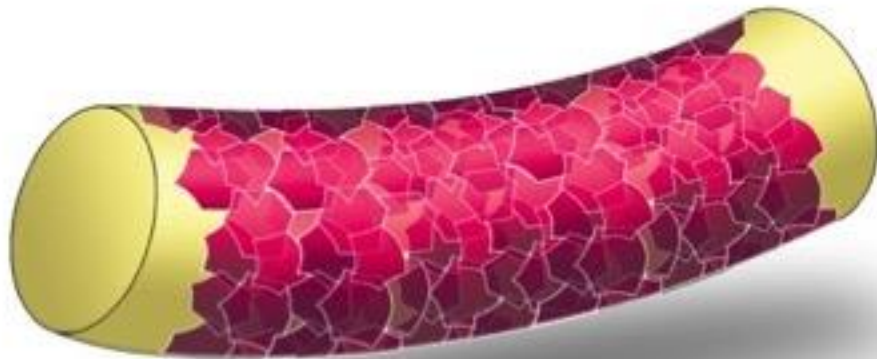
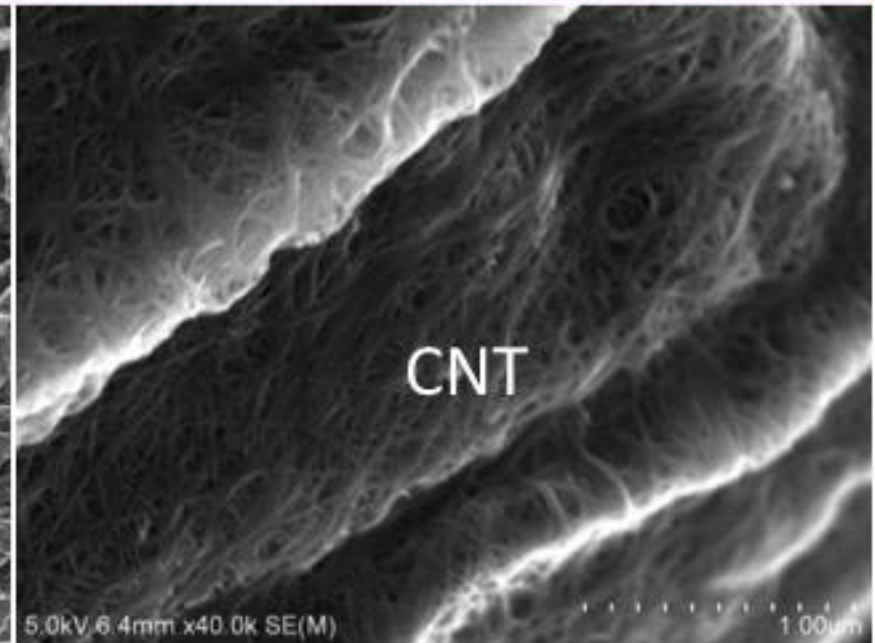
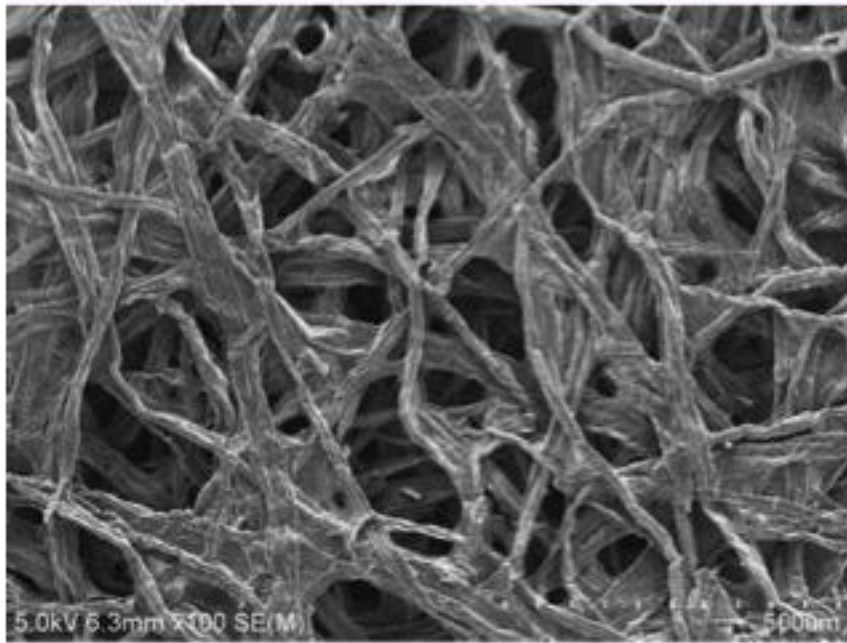
Macroscopic scale

Microscale

Nanoscale

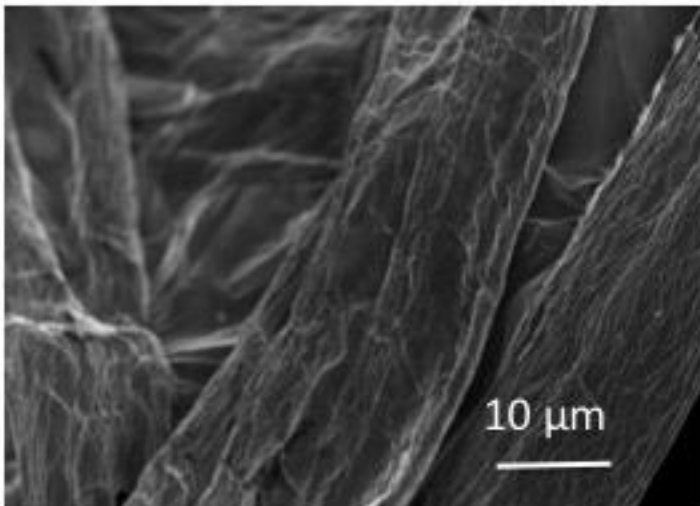
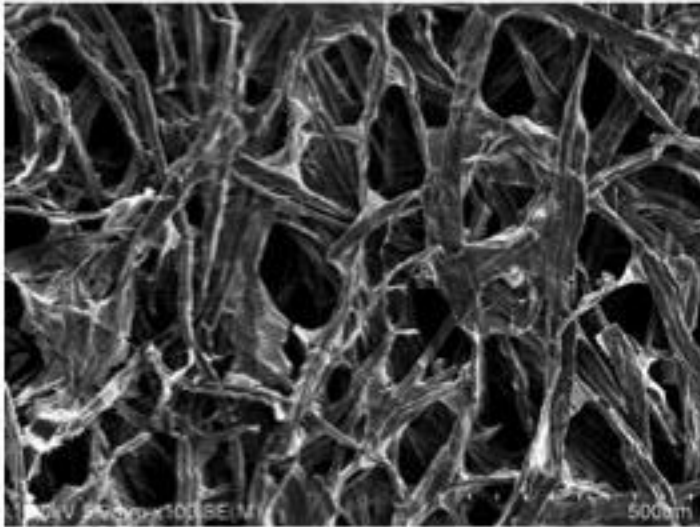
Molecular scale

Conductive Wood Fibers as Current Collectors

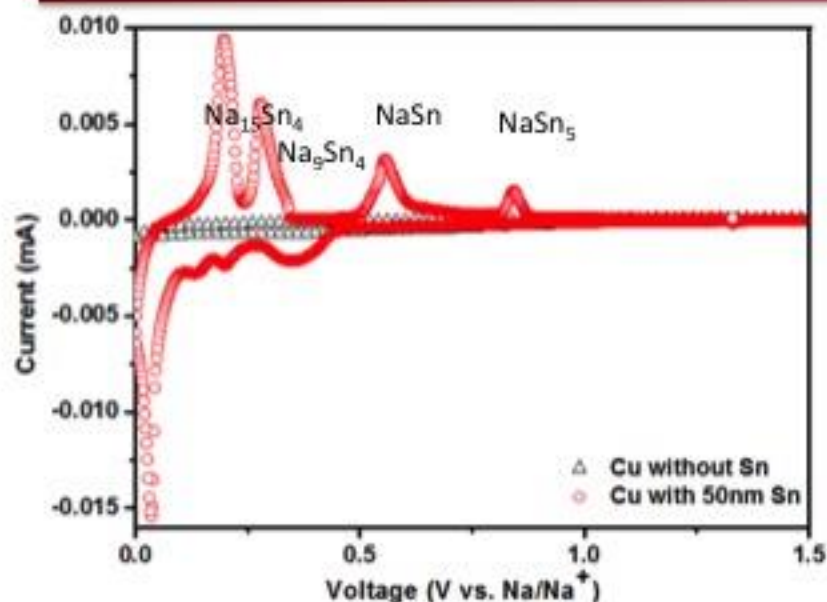


Sn Anode Preparation

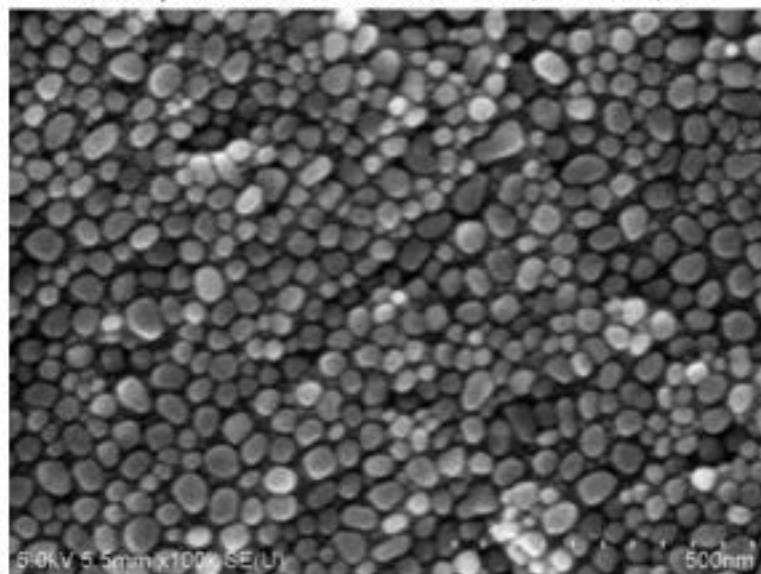
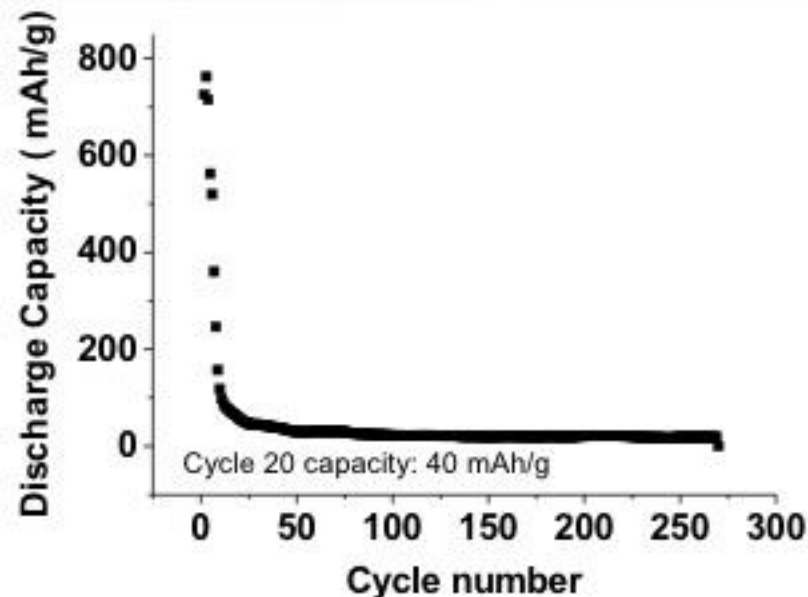
- Electrodeposition (Scalable)



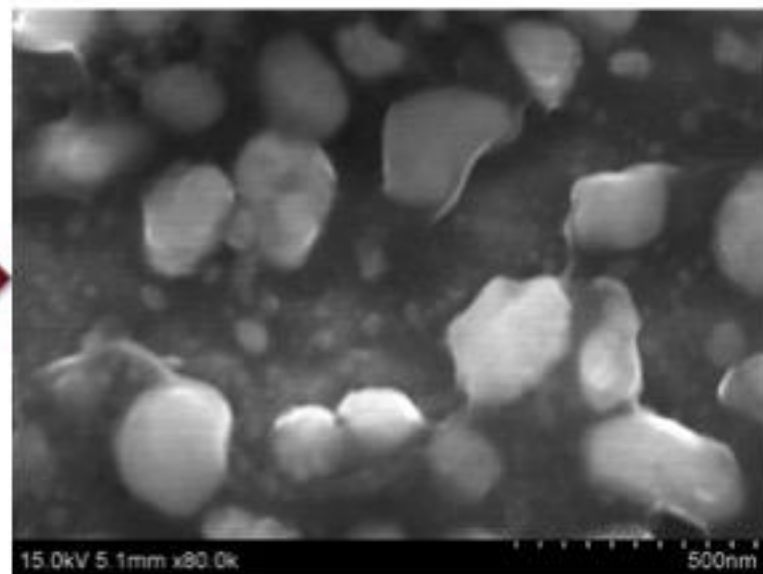
Control Experiment: Stiff Copper Foil as Substrate



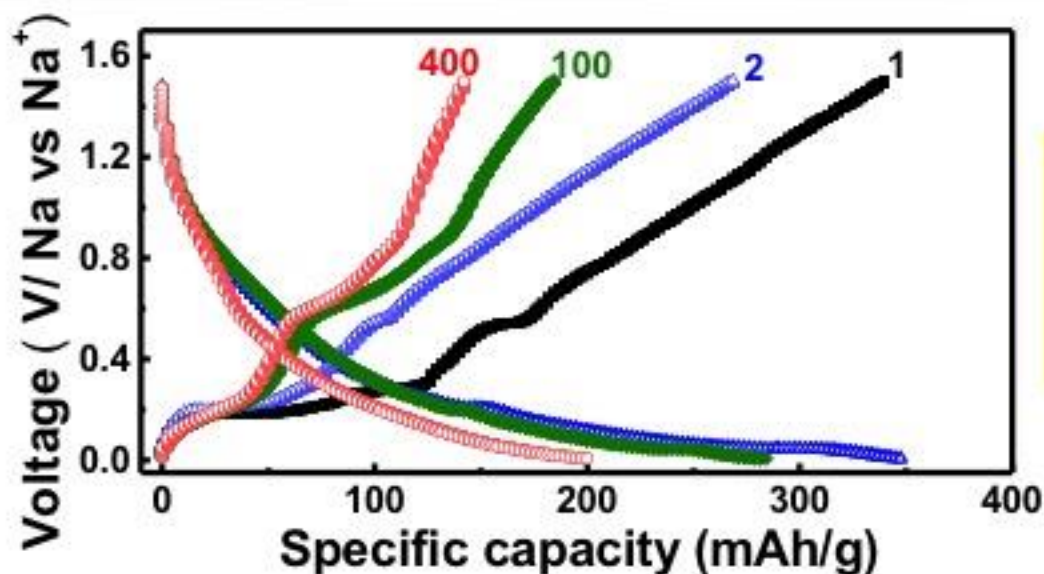
Electrolyte 1 M NaPF₆ in EC:DEC, Rate C/10



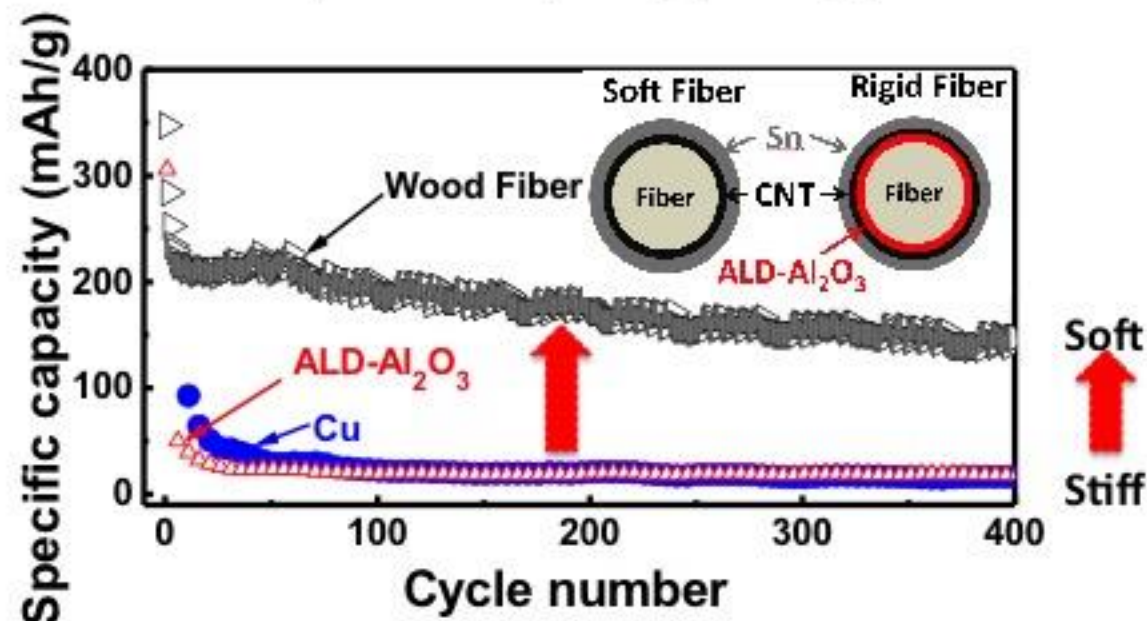
After
cycling



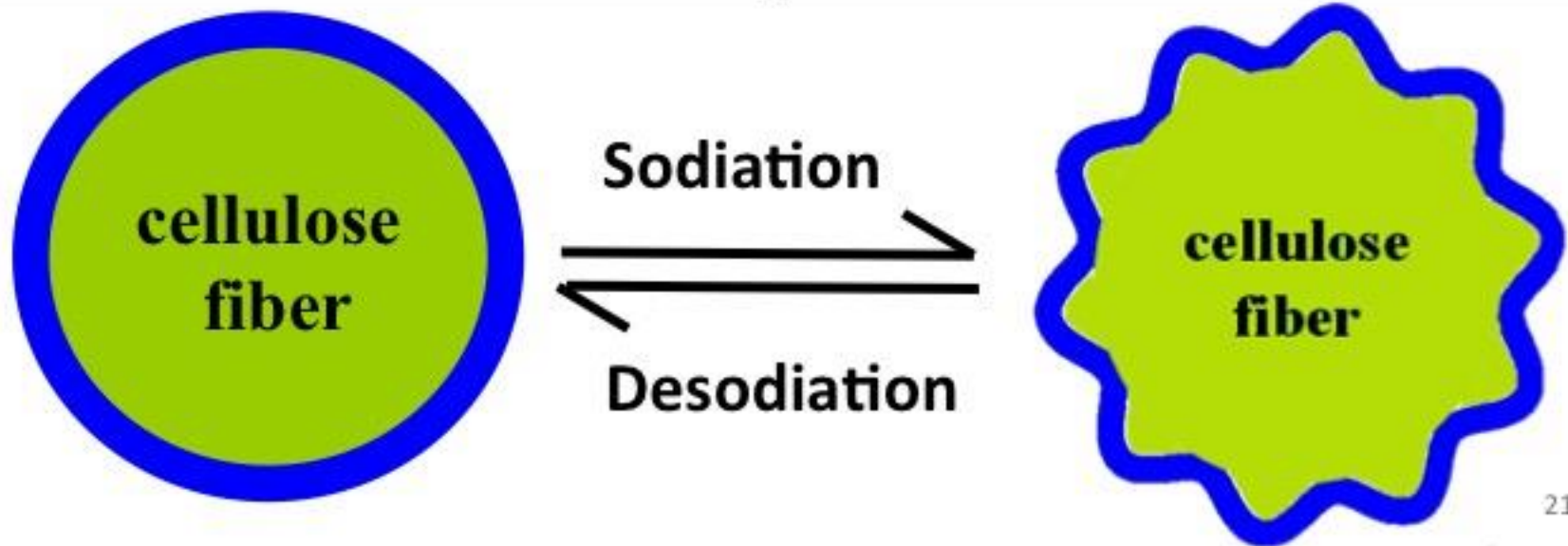
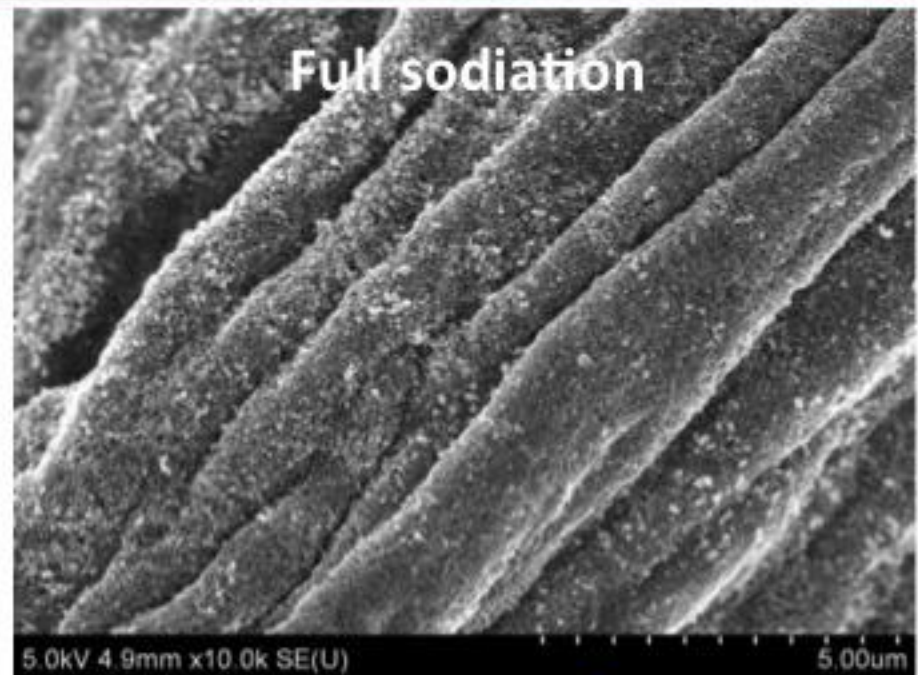
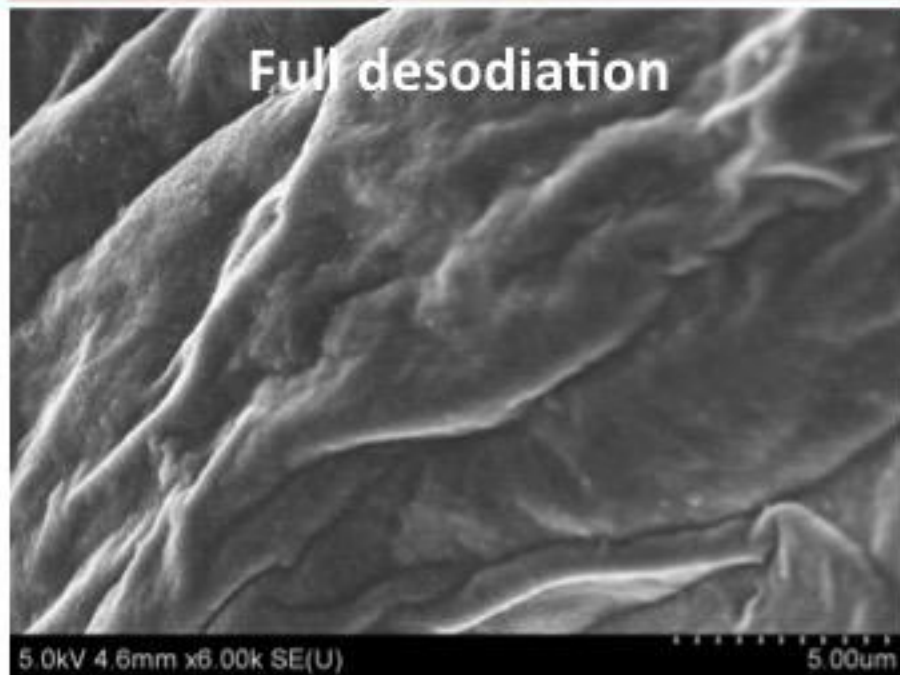
Compared with Stiff Cu Thin Film and Rigid Fiber



Stable electrode,
Stable cycling,
Longer cycling life.



Wrinkling to Release Mechanical Stress



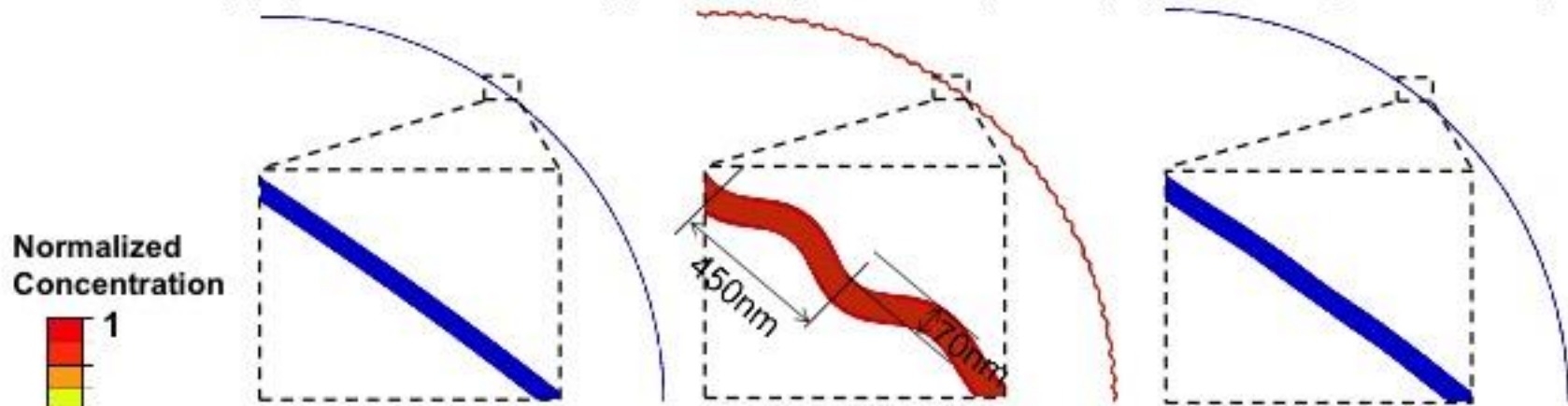
Wrinkling to Release Mechanical Stress

Sn film supported by a cellulose fiber

(a) pristine state

(b) after fully sodiated (NSS=1)

(c) after fully desodiated (NSS=0)



Sn film supported by a stiff substrate (e.g., Al_2O_3 or Cu)

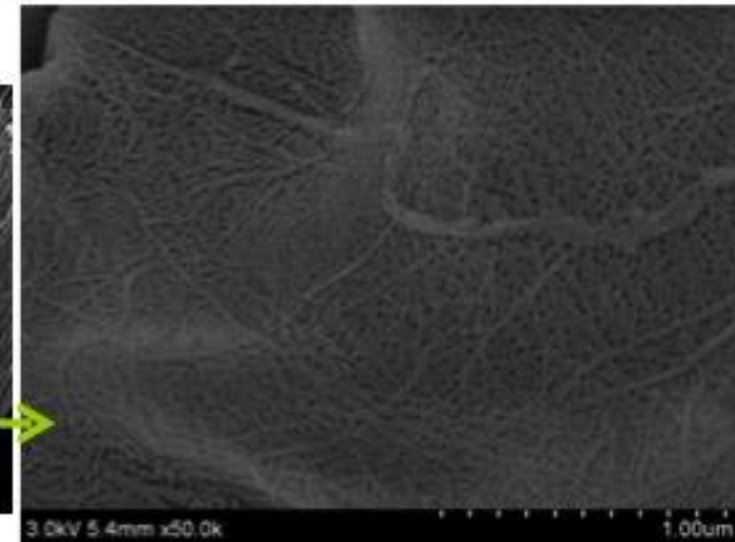
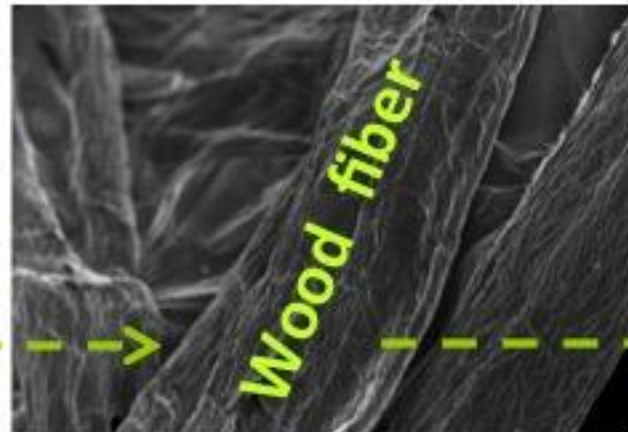
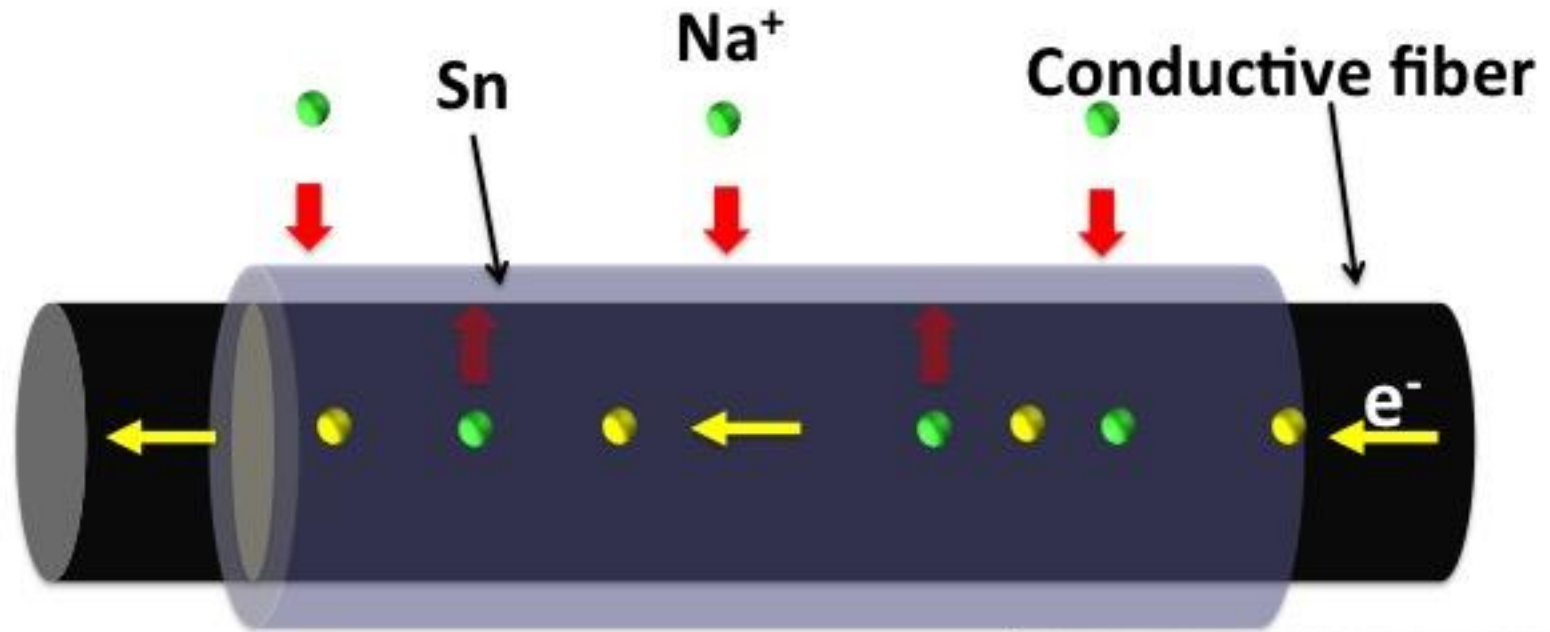
(d) pristine state

(e) after fully sodiated (NSS=1)

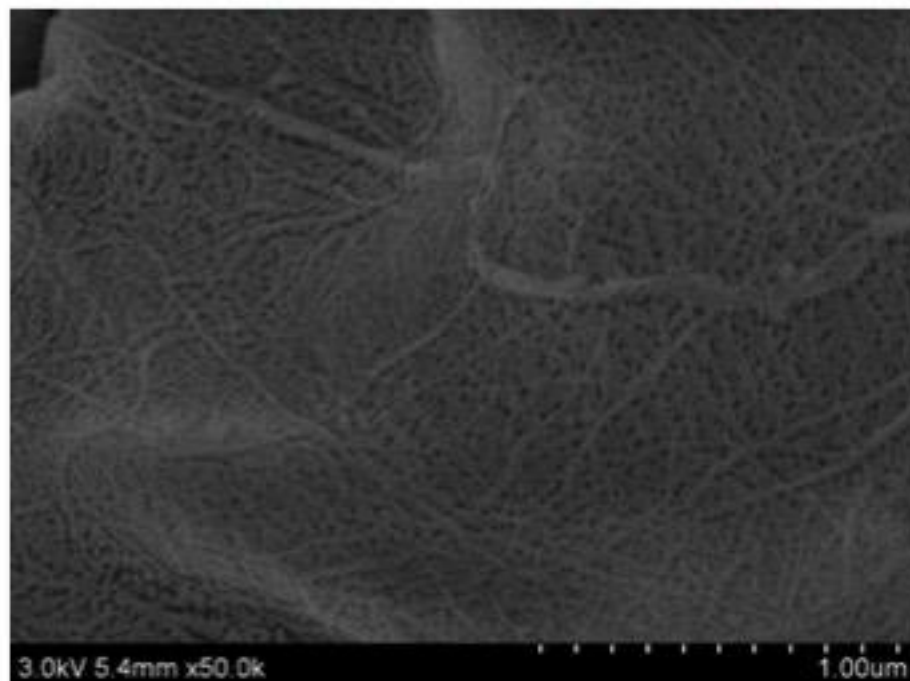
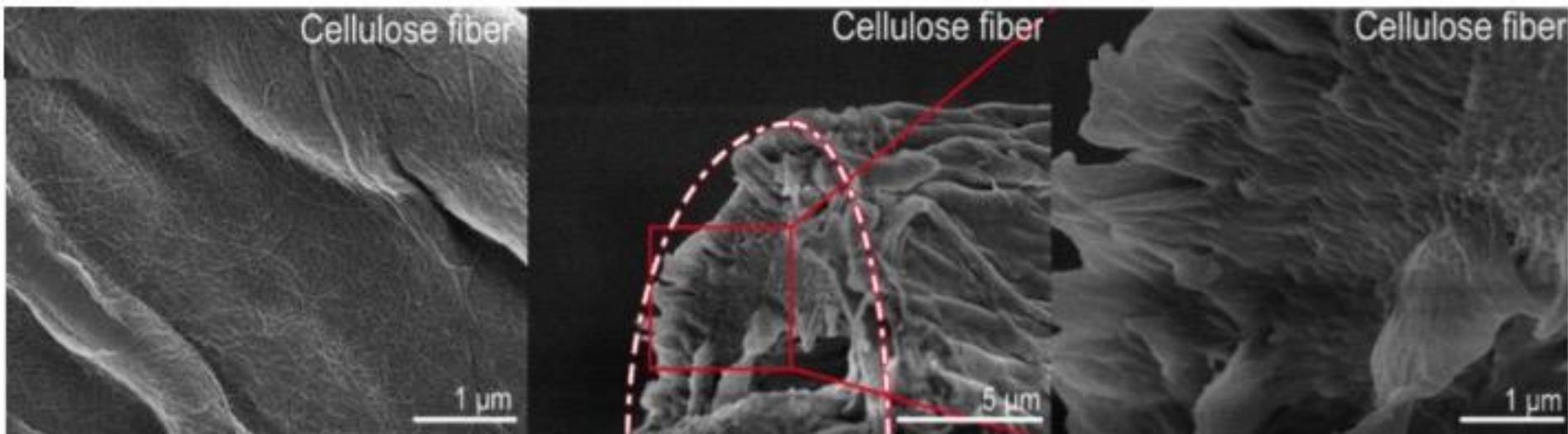
(f) after fully desodiated (NSS=0)



Mesoporous Structure for Improved Rate Performance



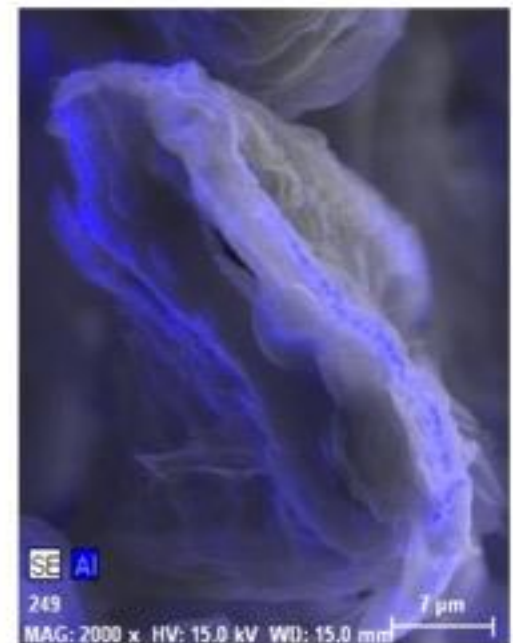
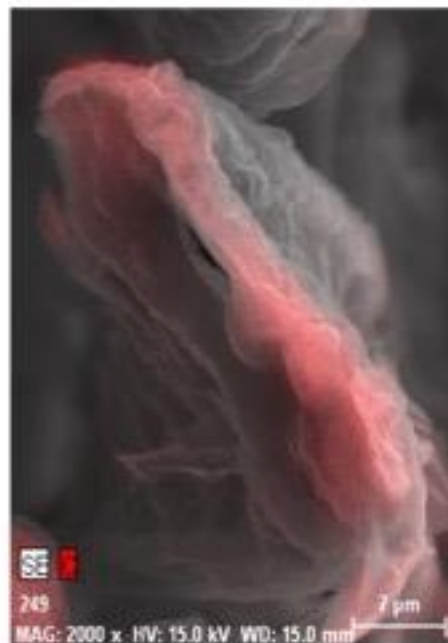
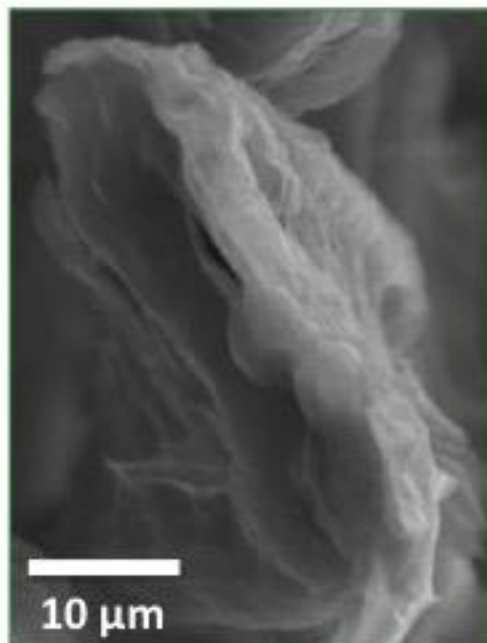
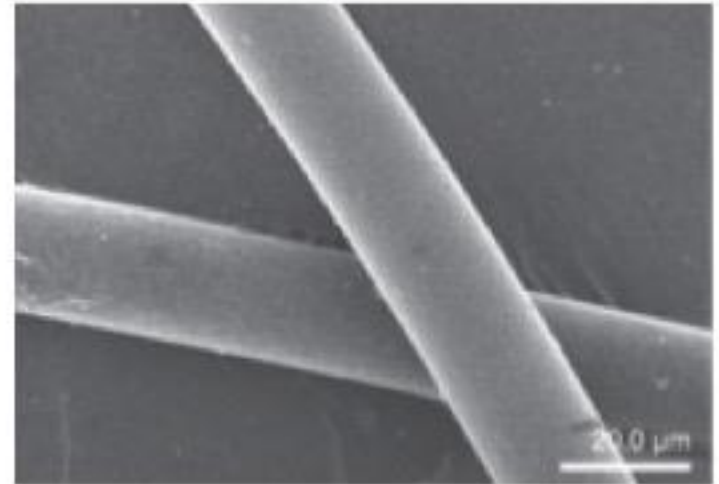
Nanoporous Cellulose Fibers



Two Control Experiments (no internal channels)

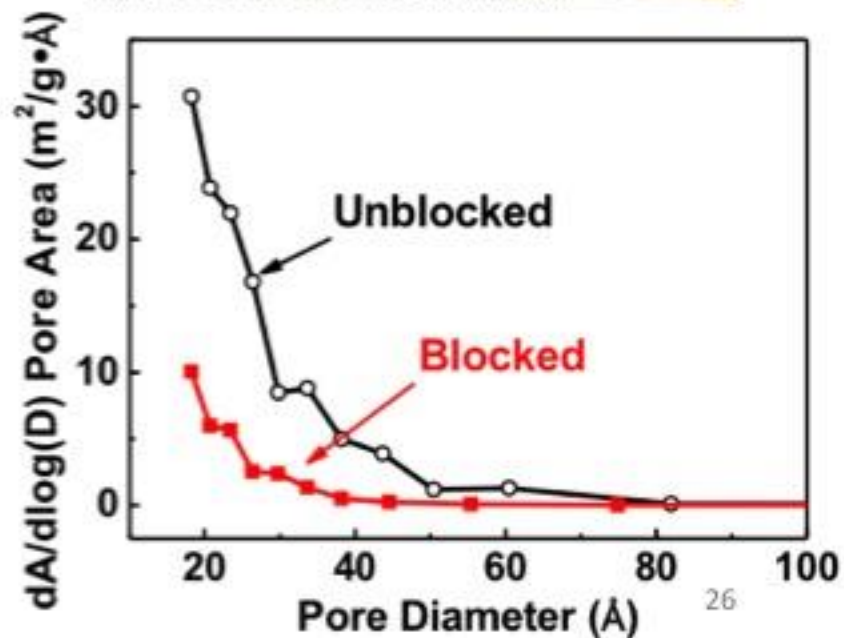
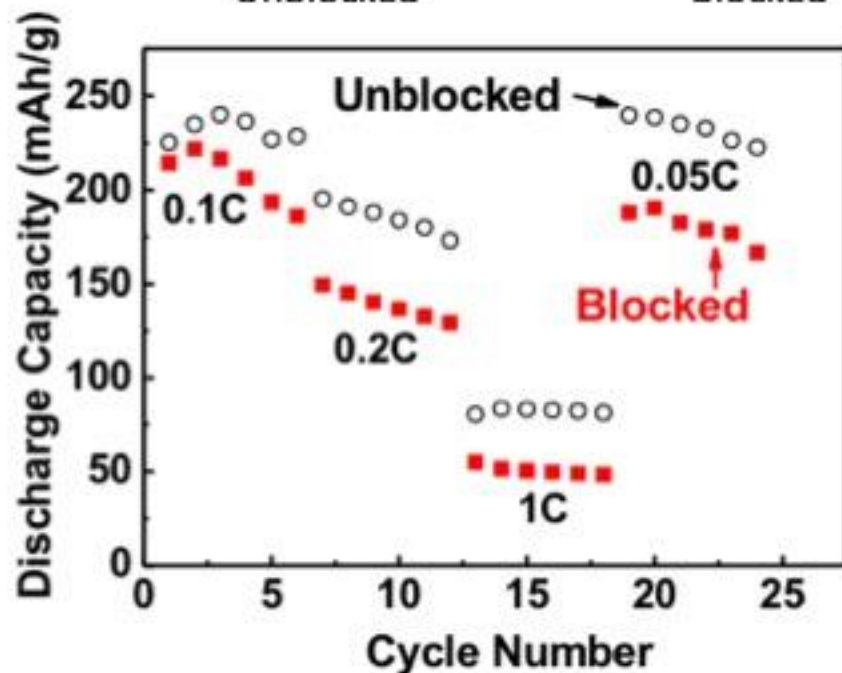
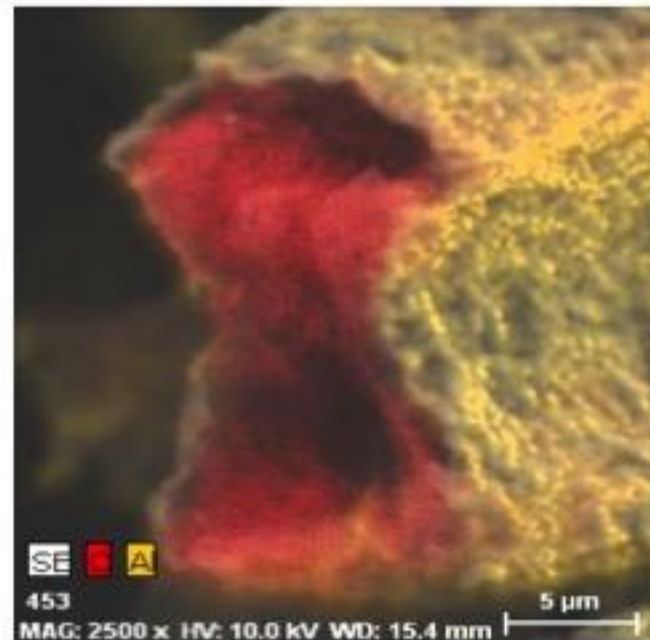
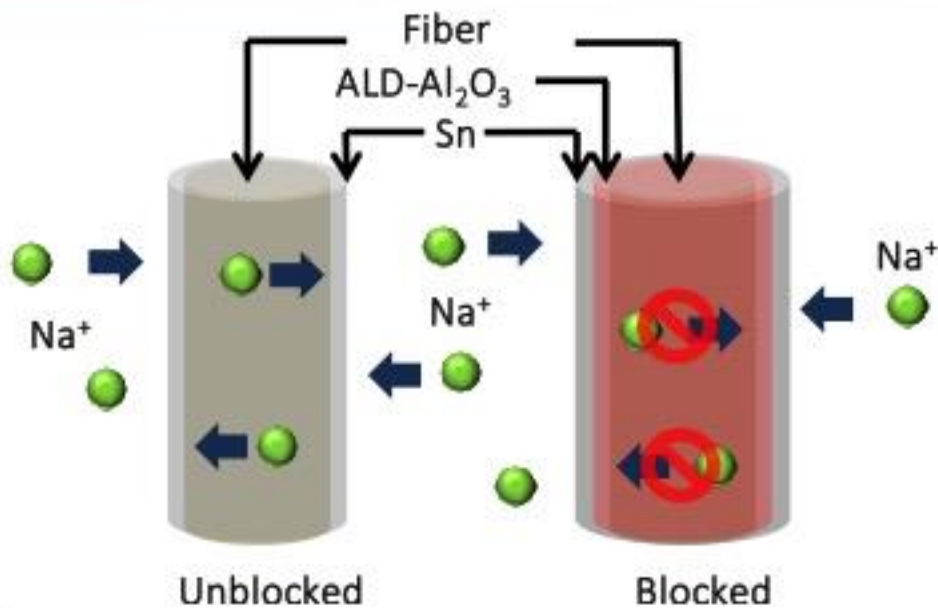
Control 1: Synthetic fibers

Control 2: ALD blocked cellulose fibers

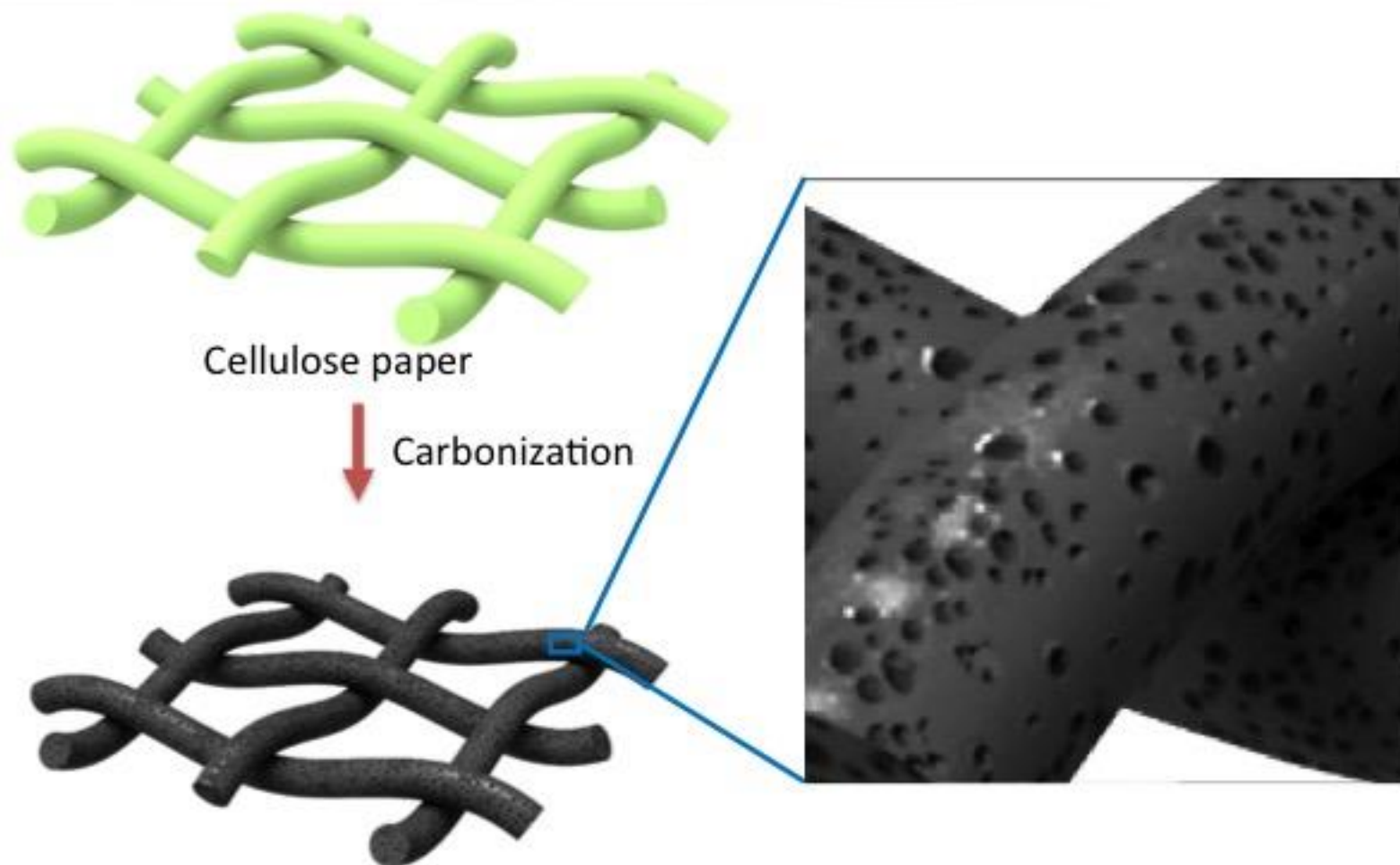


160°C with trimethyl aluminum [TMA, $\text{Al}(\text{CH}_3)_3$] and DI water precursors

Mesoporous Structure for Improved Rate Performance

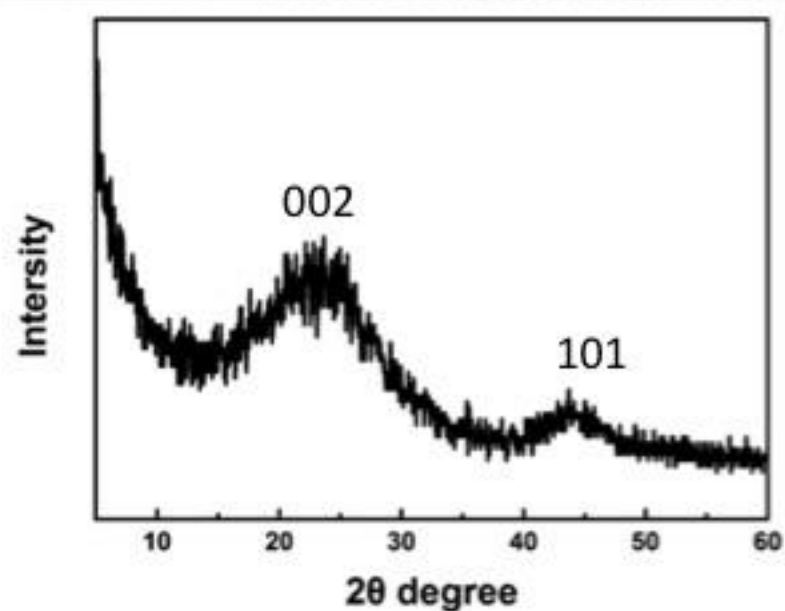
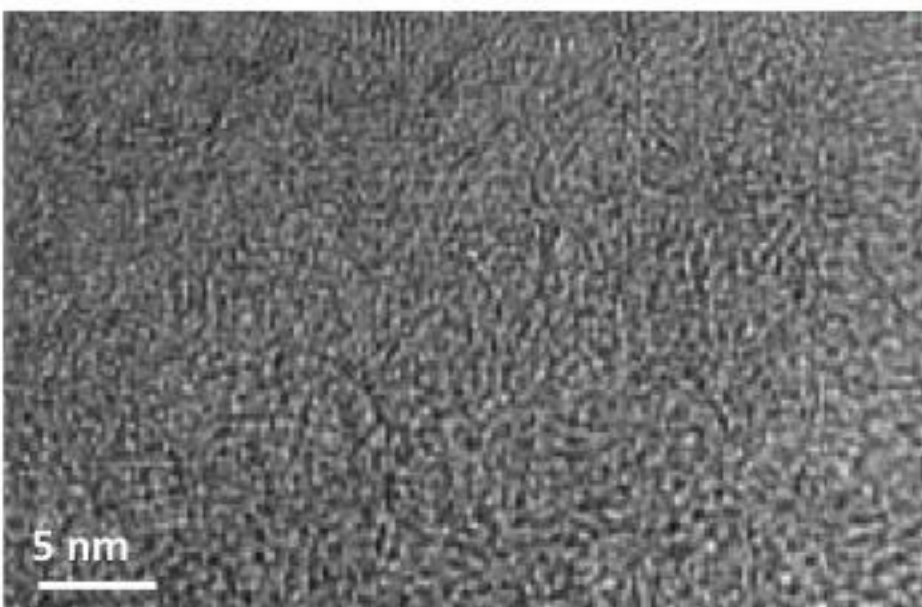
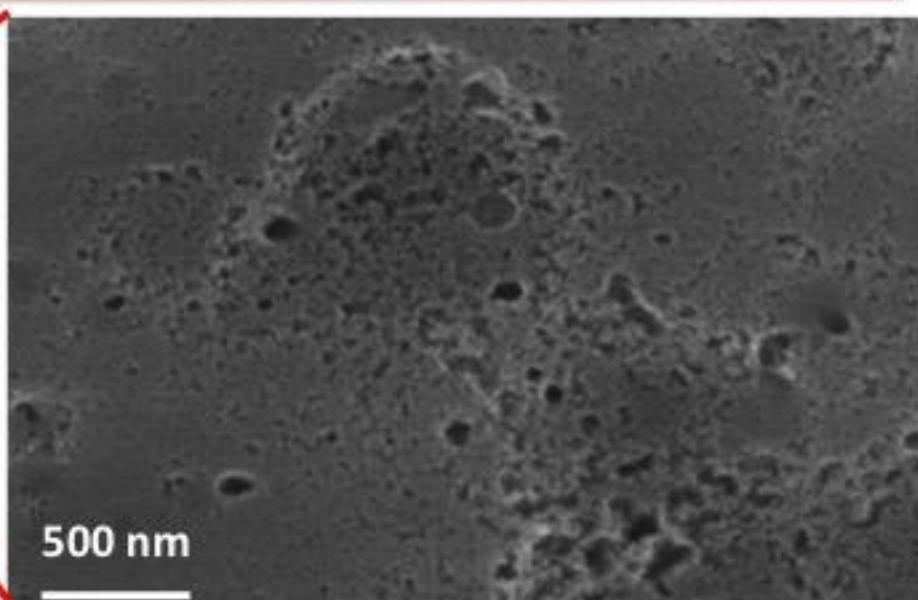
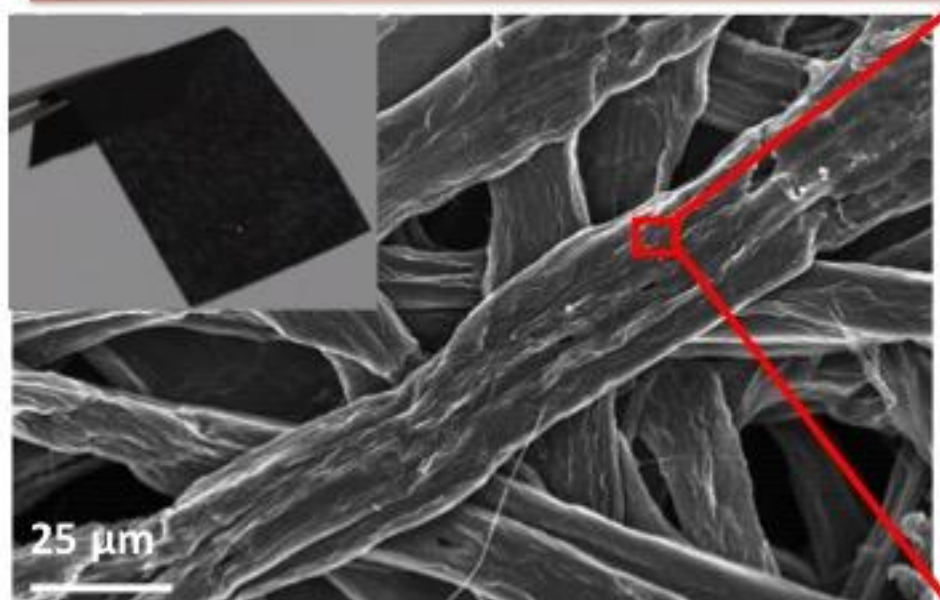


Carbonized Cellulose Paper for Na-ion Batteries

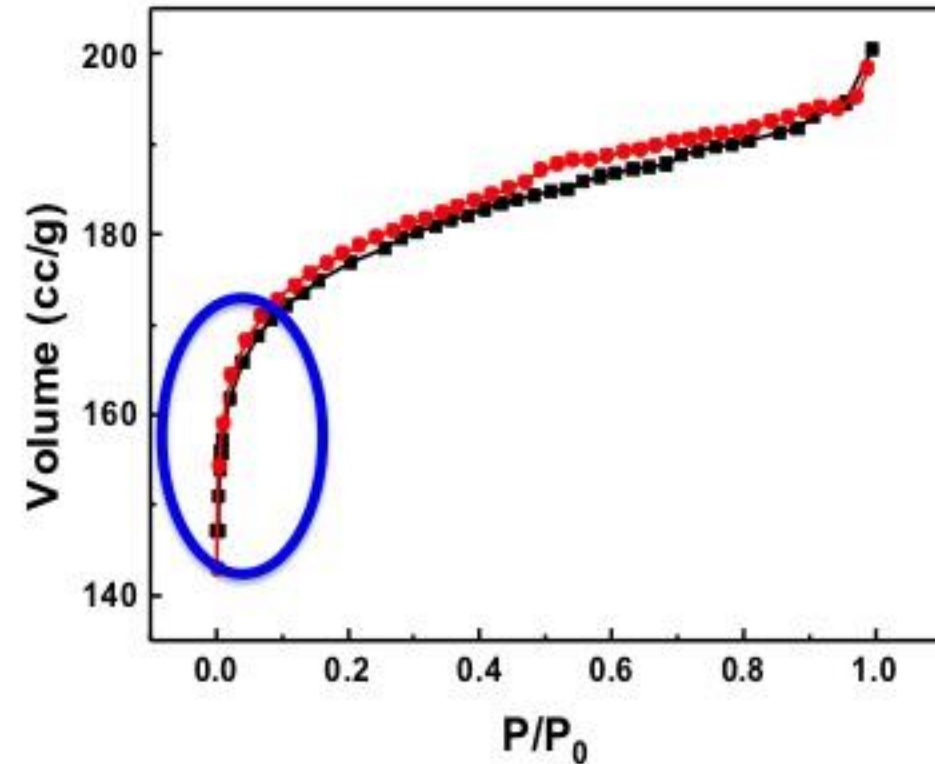


Conductive paper with nano-sized pores

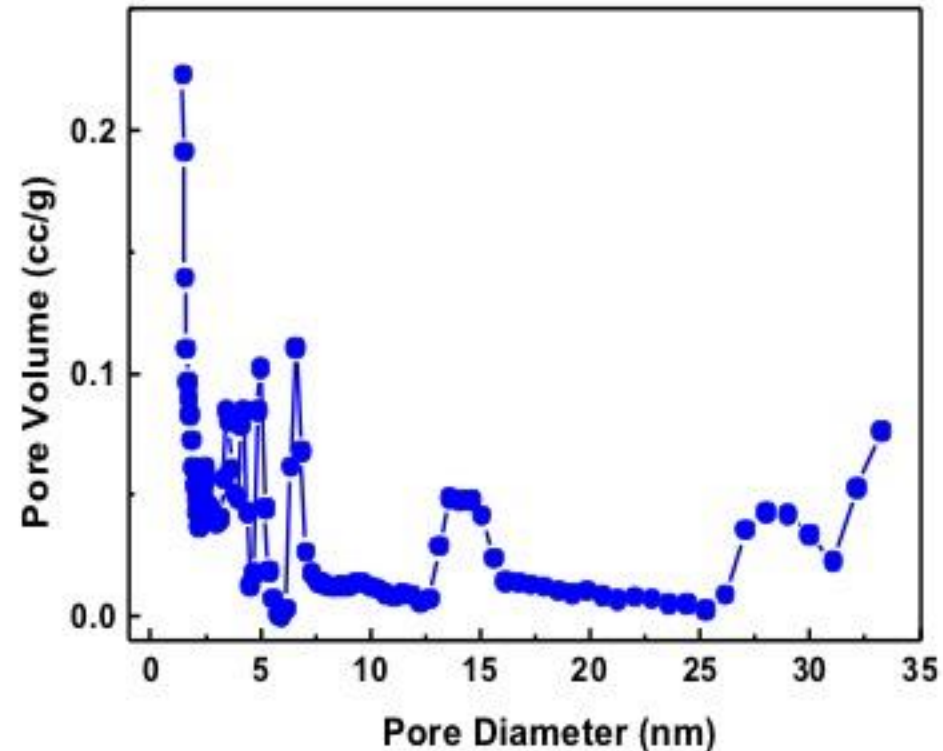
Morphology of Carbonized Paper



Nitrogen Adsorption-desorption



Isotherms



Pore size distribution(the DFT model)

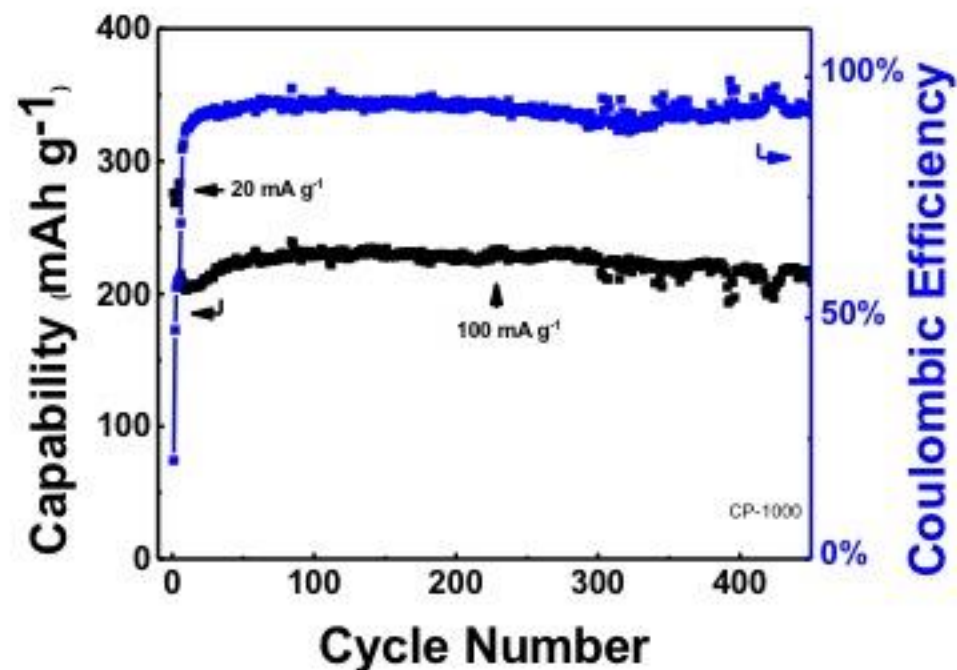
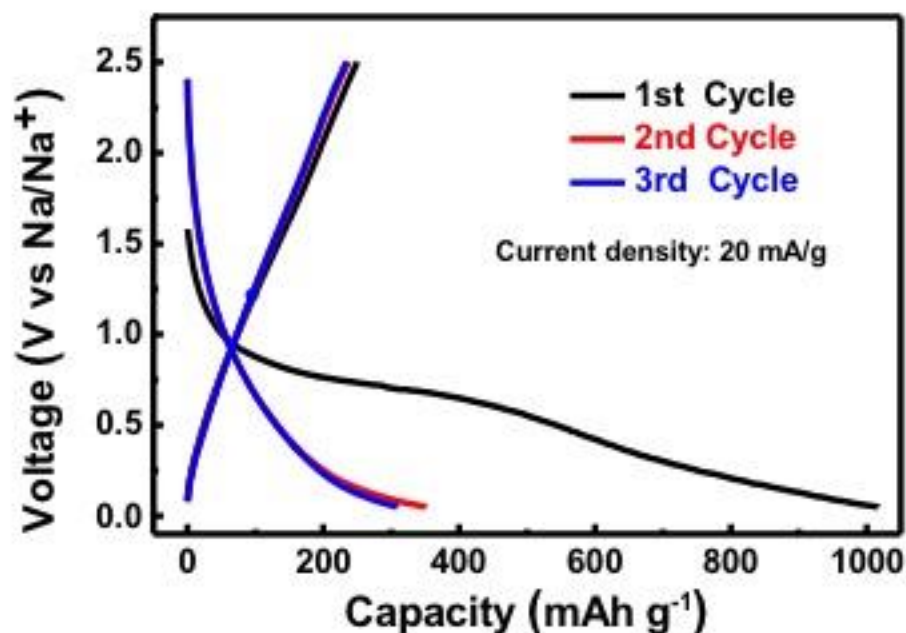
The specific Brunauer-Emmett-Teller (BET) surface area is $701\text{m}^2\text{g}^{-1}$.

High porosity and surface area can provide much more active reaction sites during sodiation and de-sodiation

Electrochemical Performances

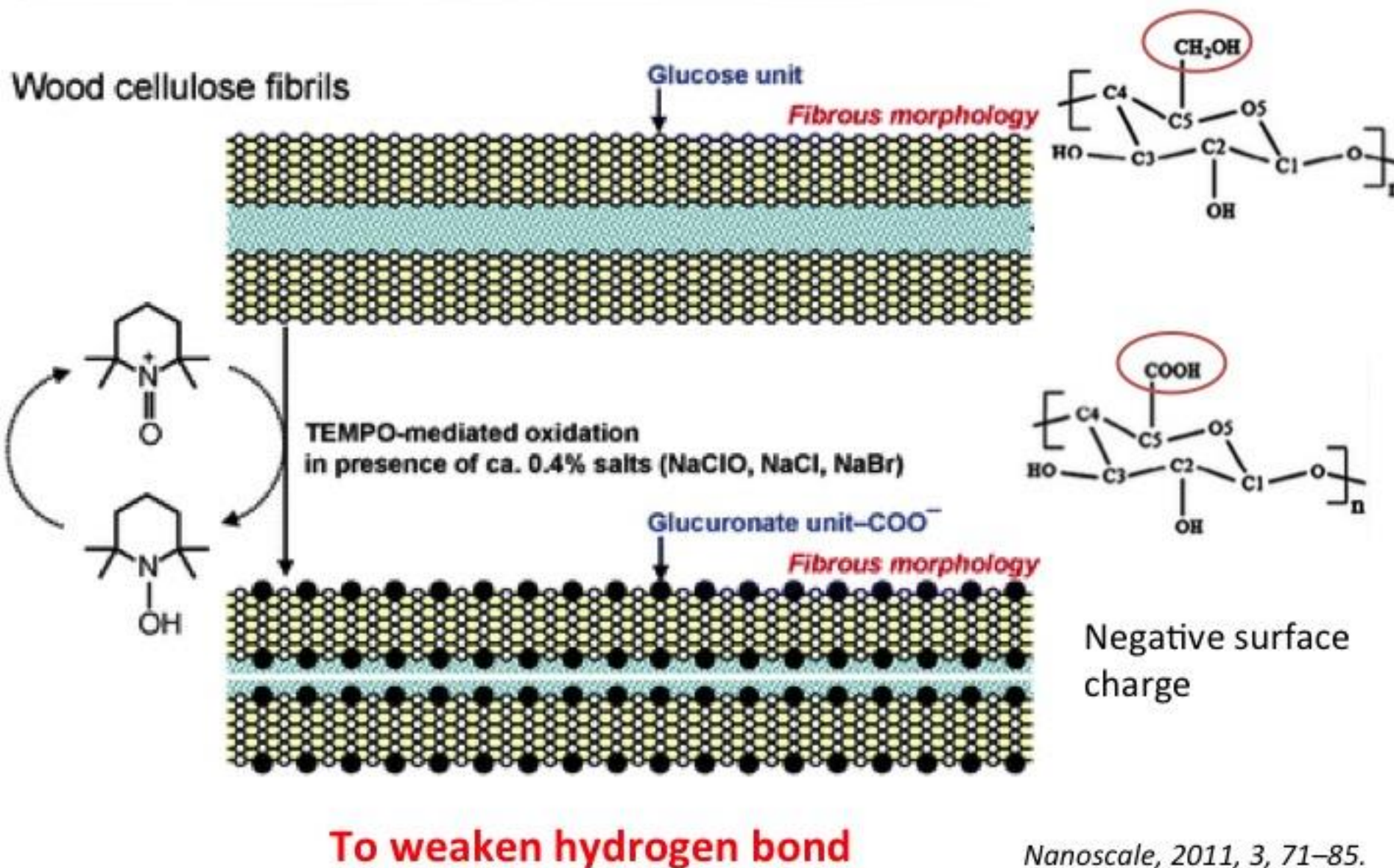


3/8" round discs were directly punched out of carbonized paper for use as binder free anode. Electrolyte 1M NaClO₄ in EC:PC (1:1).

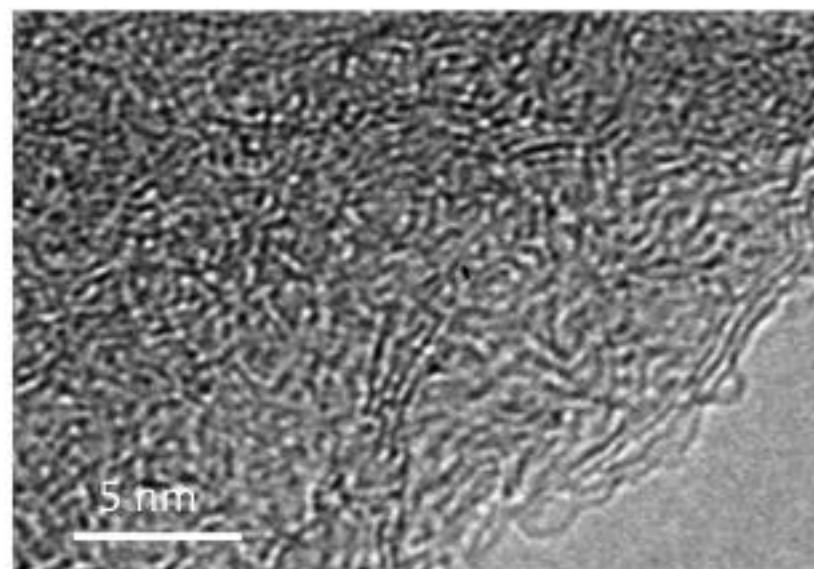
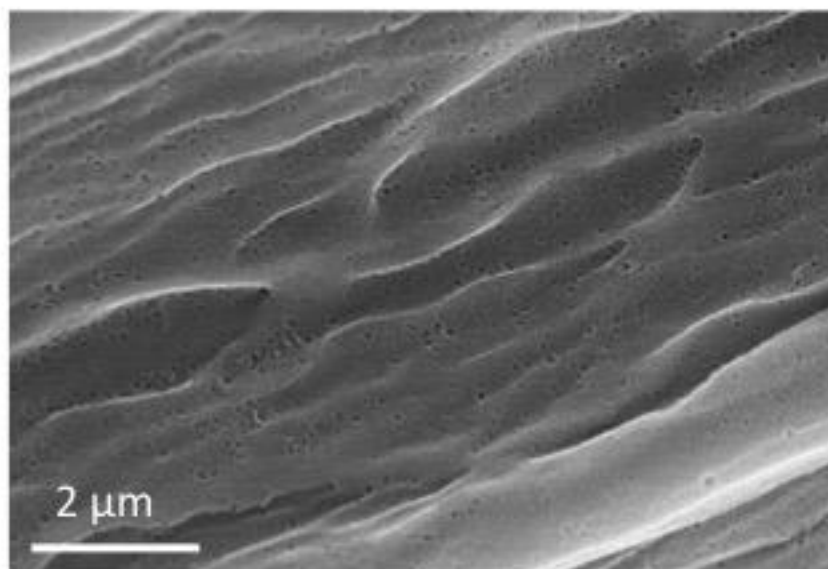
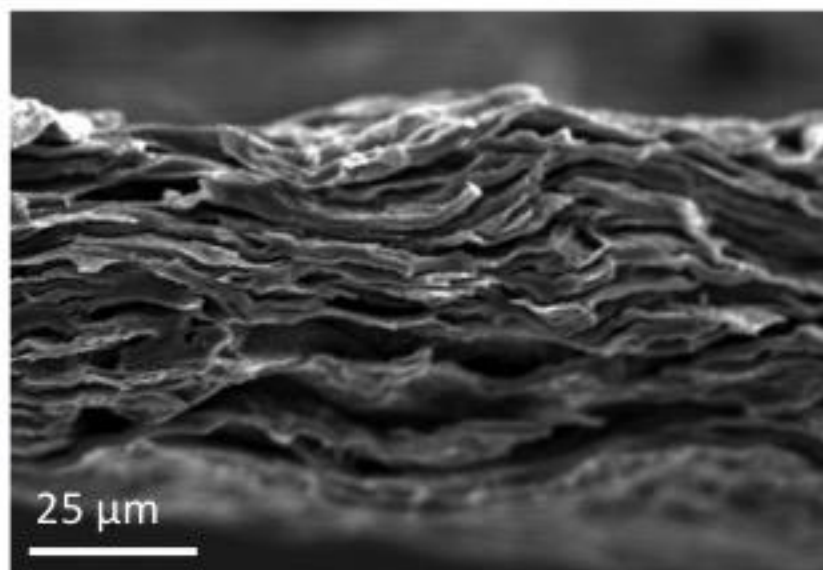


25% for the initial coulombic efficiency

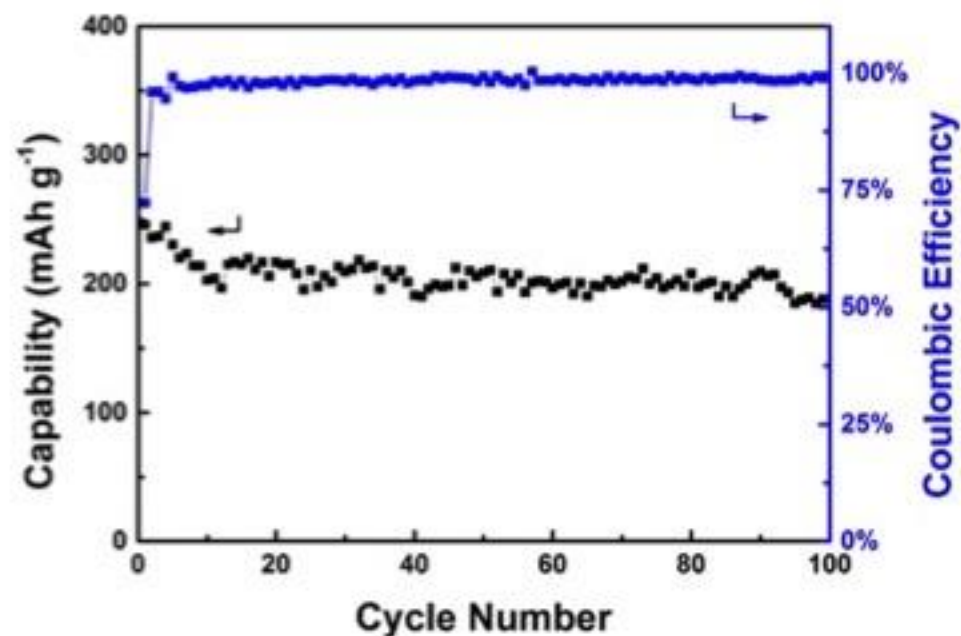
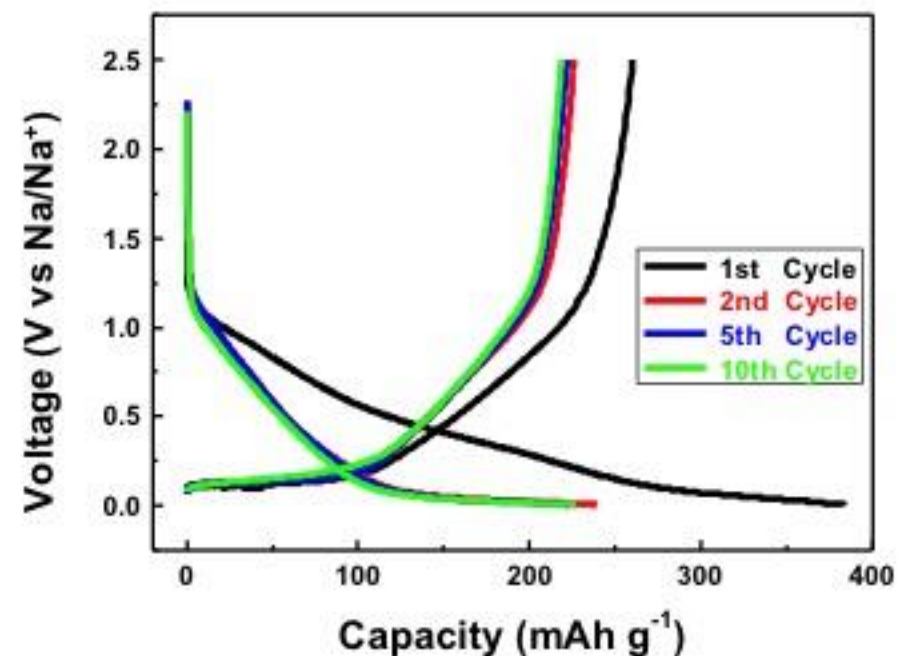
TEMPO-mediated Oxidation Process



Carbonized TEMPO Treated Paper--Much Denser!



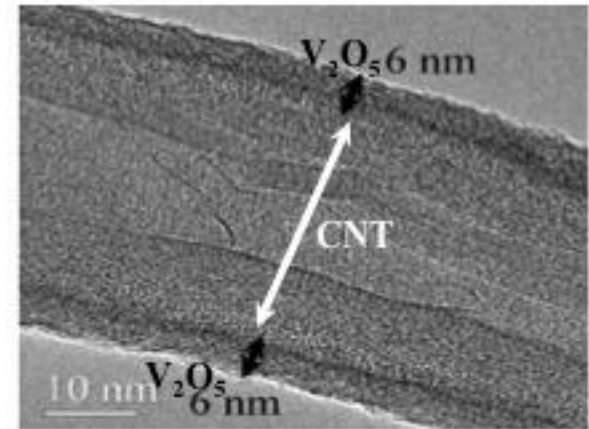
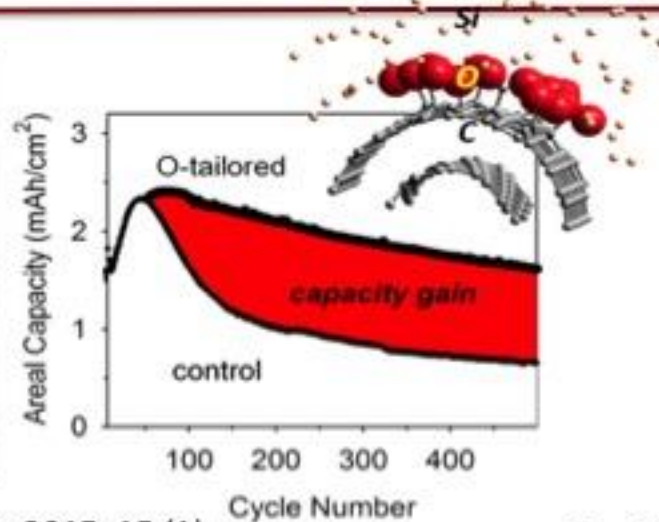
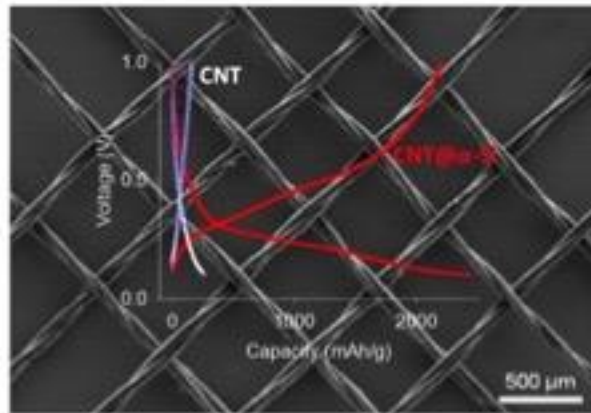
Electrochemical Performances



Initial coulombic efficiency 72%

In the subsequent, the CE raised to 95% for the 2nd cycle.

Energy Storage and Energy Harvesting



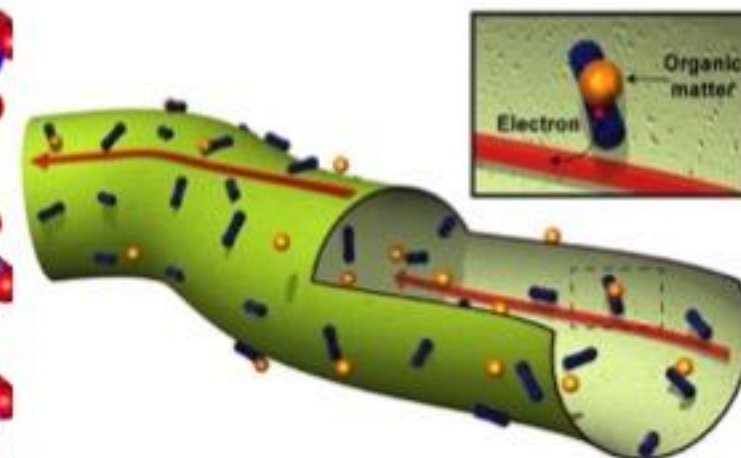
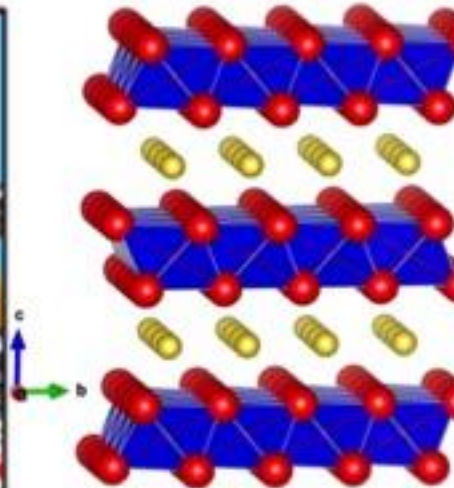
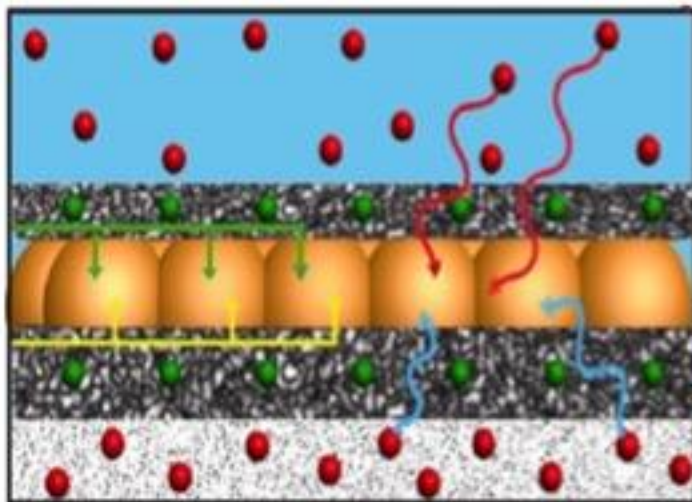
q Sun, C., Zhu, H., et al. **Nano Letters**, 2015, 15 (1).

q Gui, Z., * Zhu, H.,* et al. **ACS Nano**, 2013, 7(7).

q Sun, C., * Zhu, H.,* et al. **Nano Energy**, 2013 (2).

q Chen, X., Zhu, H., et al. **ACS Nano**, 2012, 6(9).

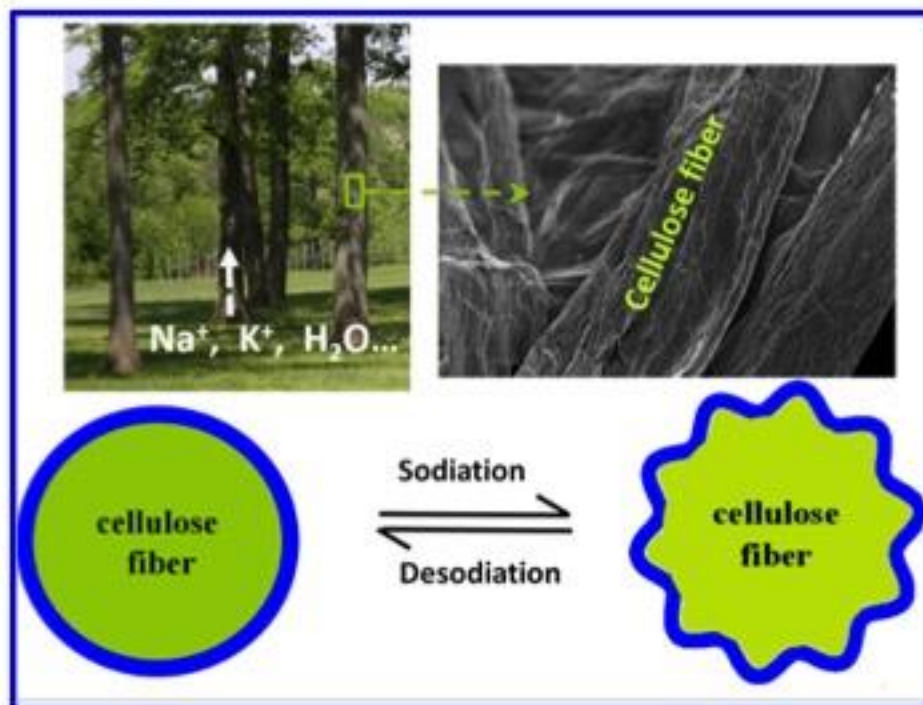
q Zhu, H. et al. **Nano Energy**. 2014, 10.



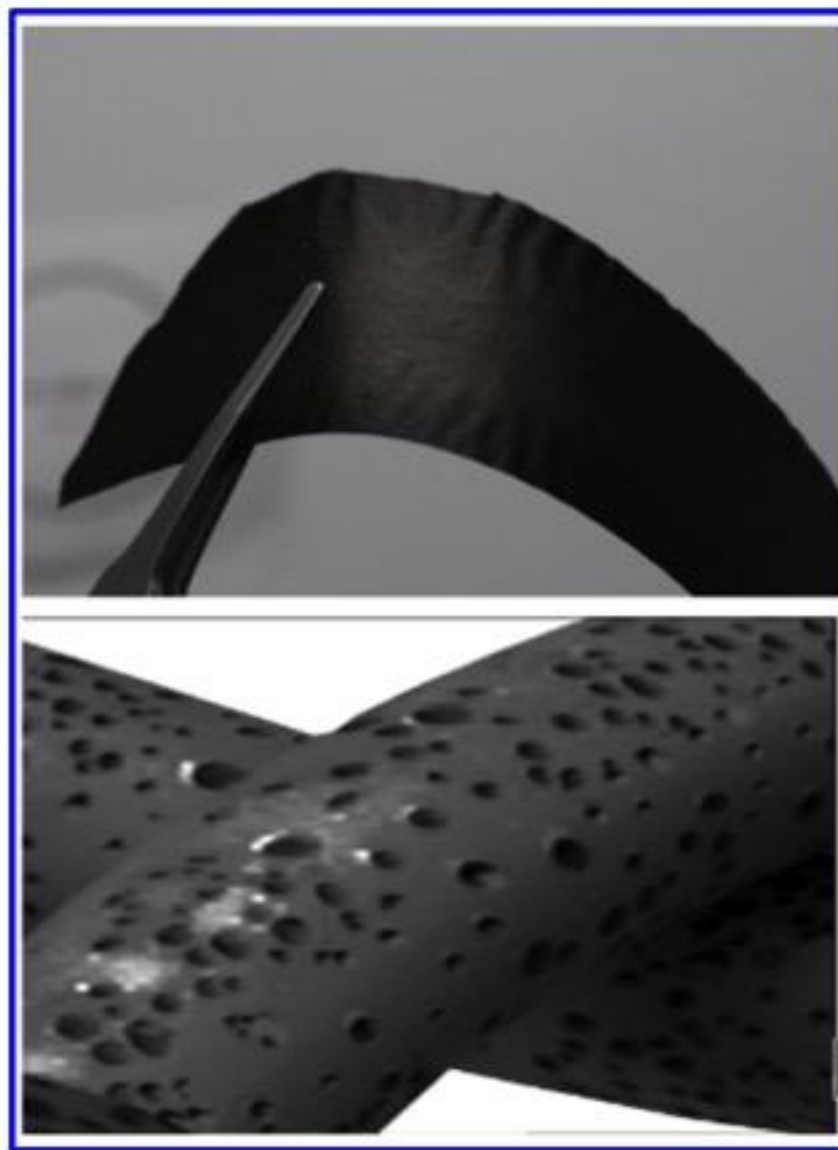
q Zhu, H. et al. **ACS Applied Materials and Interfaces**. 2014, 6(6).

Conclusions

Ø Natural wood fiber as mechanical buffer and electrolyte reservoir for Tin anode in sodium ion battery



Ø Carbonized Cellulose Paper as a free standing anode for Sodium ion battery



Acknowledgement

- Co-workers in Hu's group, University of Maryland, College Park



Hongli Zhu

hongli@umd.edu

Energy Research Center
University of Maryland
College Park



Questions?

How Can We Better Serve You?

Whether you are joining us live or watching the recorded version of this webinar, please take 1 minute to provide your feedback and suggestions.

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1.5 hour webinar and would like a
certificate of participation, please email:

sbarger@engr.psu.edu



2015 Events Calendar

May 21, 2015

Graphene & Other 2D Electronic Systems

Webinar

June 11, 2015

Self-Assembled Monolayers

Webinar

April 13 – 16, 2015

Nanotechnology Course Resources I: Safety,
Processing, and Applications

Workshop

May 12 – 14, 2015

Hands-On Introduction to Nanotechnology for
Educators

Workshop

Want more events? Visit www.nano4me.org/webinars for more details about these and other upcoming workshops and webinars in 2015.