Progress of Biochar Supercapacitors

Junhua Jiang

1st Midwest Biochar Conference
June 14, 2013

ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

Acknowledgement

- Management team and staff at the ISTC (Nancy Holm, Ed Delso, Xinying Wang, John Scott, et al.)
- Illinois Hazardous Waste Research Fund
- Dr. Lei Zhang and Prof. Frank Chen at the University of South Carolina
- Staff at the Beckman Institute, the Frederick Seitz Materials Research Laboratory, and the Illinois State Geological Survey of the UIUC

ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

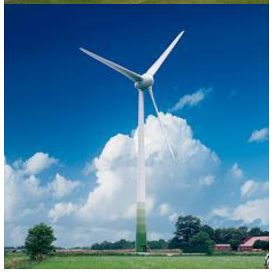
Supercapacitor Applications

- Traditional market
  - Electronics: camera, flashlights, PC cards, portable media players, and automated meter reading equipment
  - Telecom and others: Complementing batteries (uninterruptible power supplies, handle short interruptions)
- Emerging market
  - Transportation (electric vehicles, buses, aerospace)
  - Energy storage

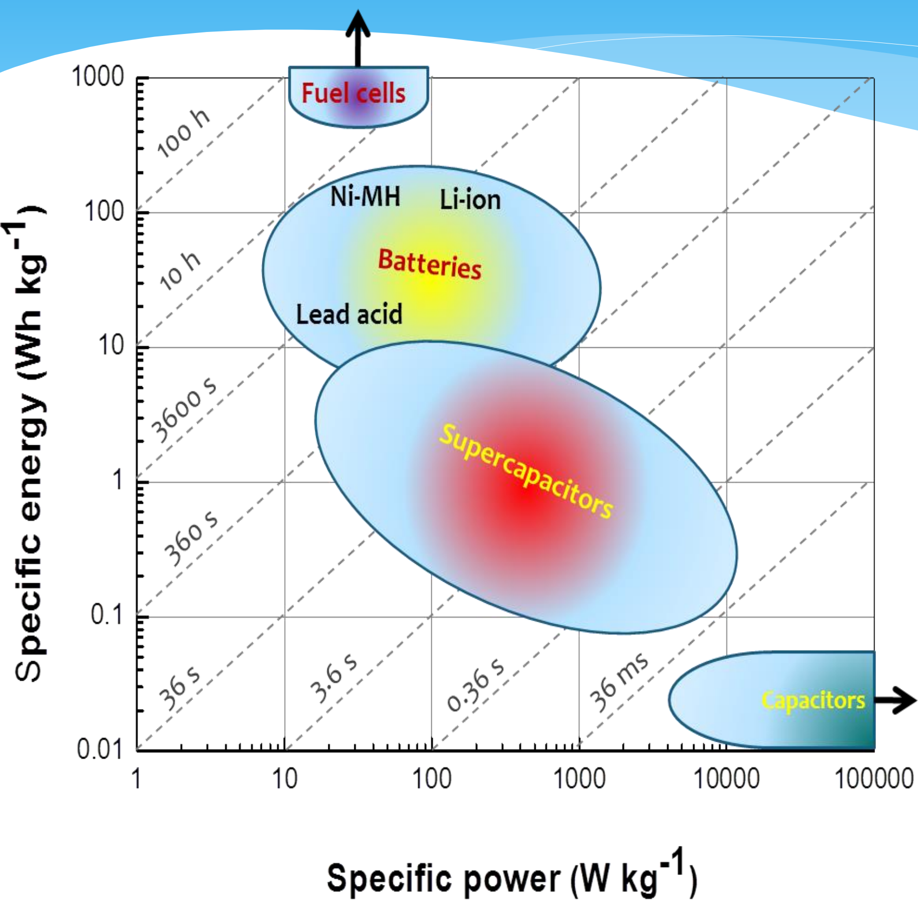




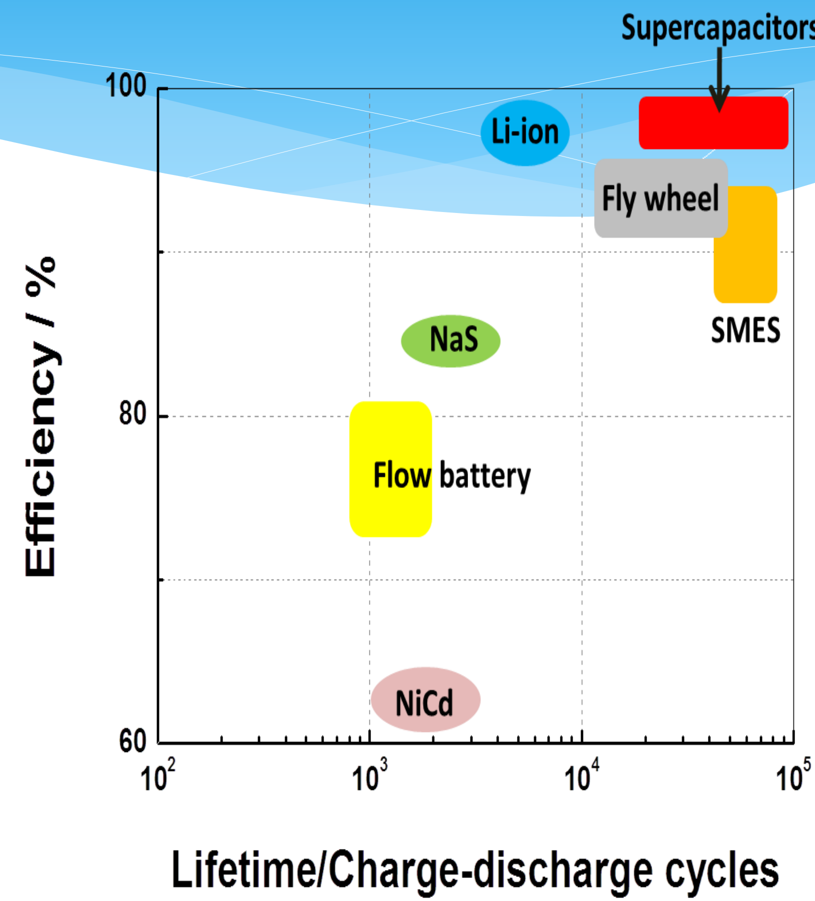




Supercapacitor Energy Storage

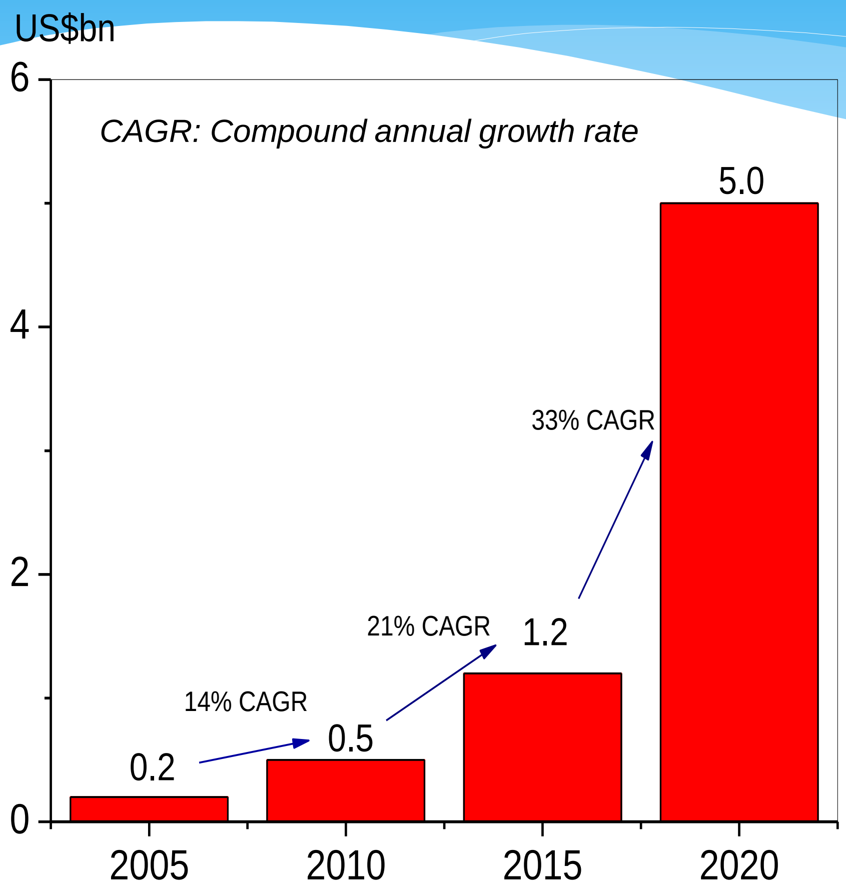


Energy storage-conversion Ragone plot



Efficiency-lifetime properties

Industry Outlook



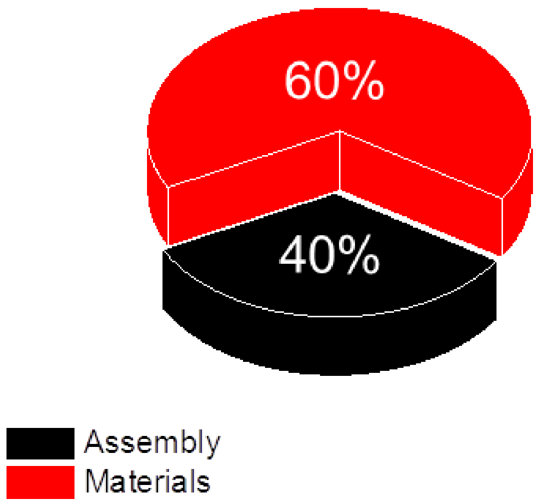
Source: Daiwa forecast

- Due to its fast charge-discharge capability (power density), we expect ultracapacitor use to rise along with batteries for future EV and ESS applications.
- New materials are being developed that should lead to the energy density of ultracapacitors increasing.
- We forecast the ultracapacitor market to expand tenfold, from US$0.5bn in 2010 to US$5.0bn by 2020.

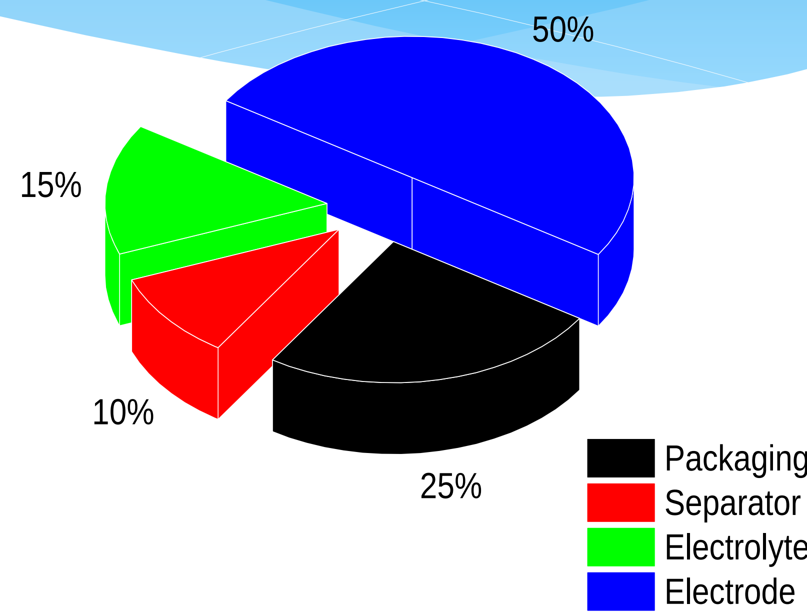
ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

Cost Breakdown

Production cost

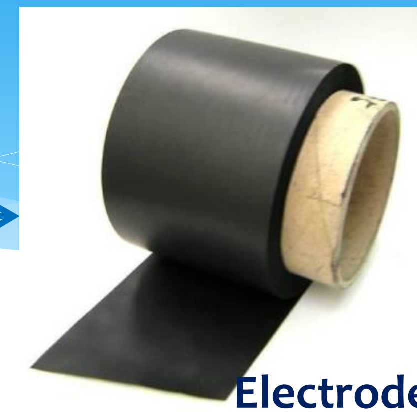


Material cost



- ❑ Cost is the key market consideration and barrier for mass adoption.
- ❑ Materials account for a large portion of overall costs compared to other storage technologies.
- ❑ Electrodes account for a significant portion of the materials.

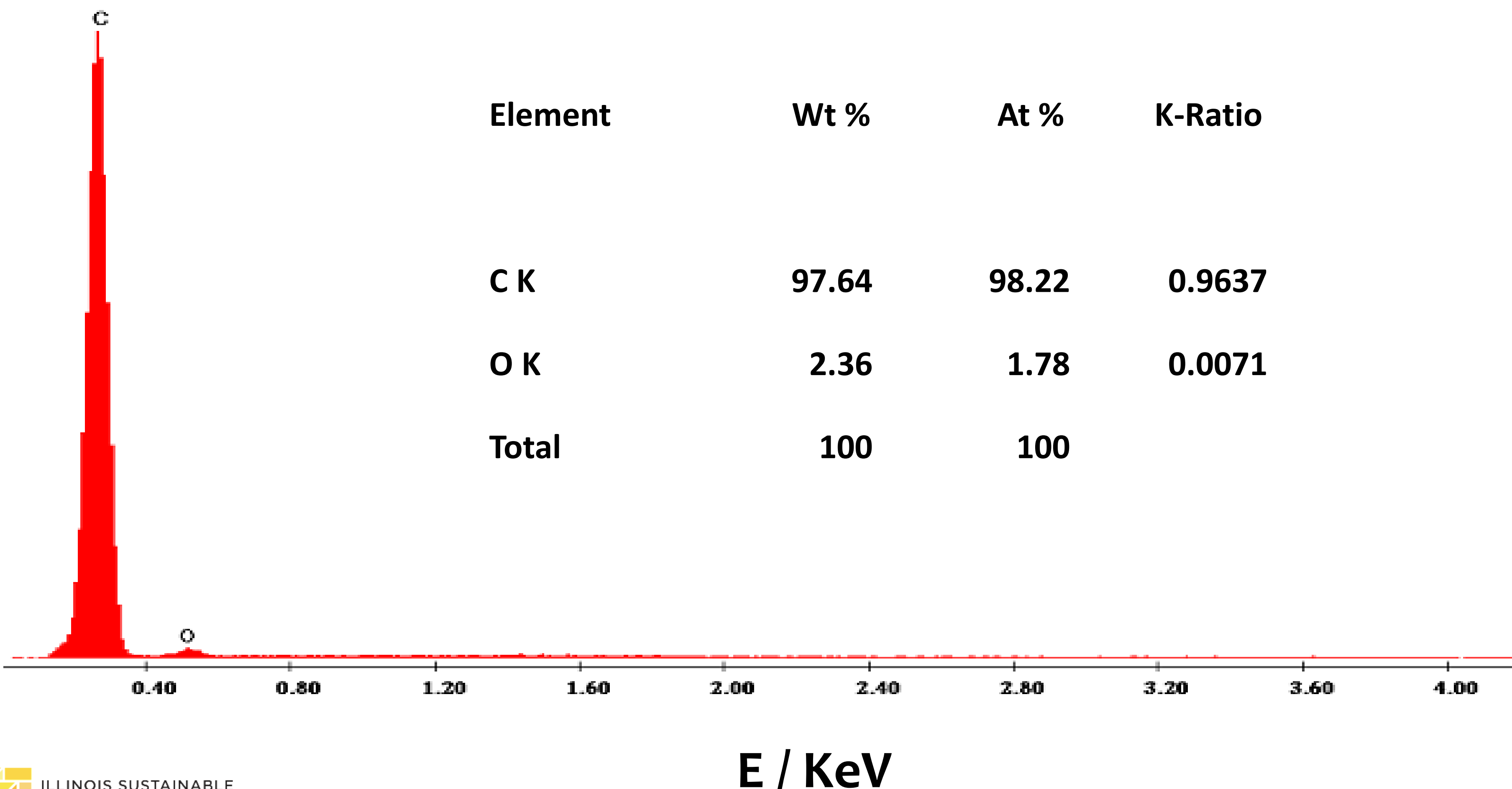
Biochar electrode



- *Potential low cost $0.1/kg vs $5/kg for activated carbon*
- *Low carbon footprint*
- *Highly developed surface area (~400 $m^2\ g^{-1}$)*

- *Excellent chemical and electrochemical stability*
- *High conductivity*
- *High utilization of surface area*

High-Carbon Zero-Ash Biochar

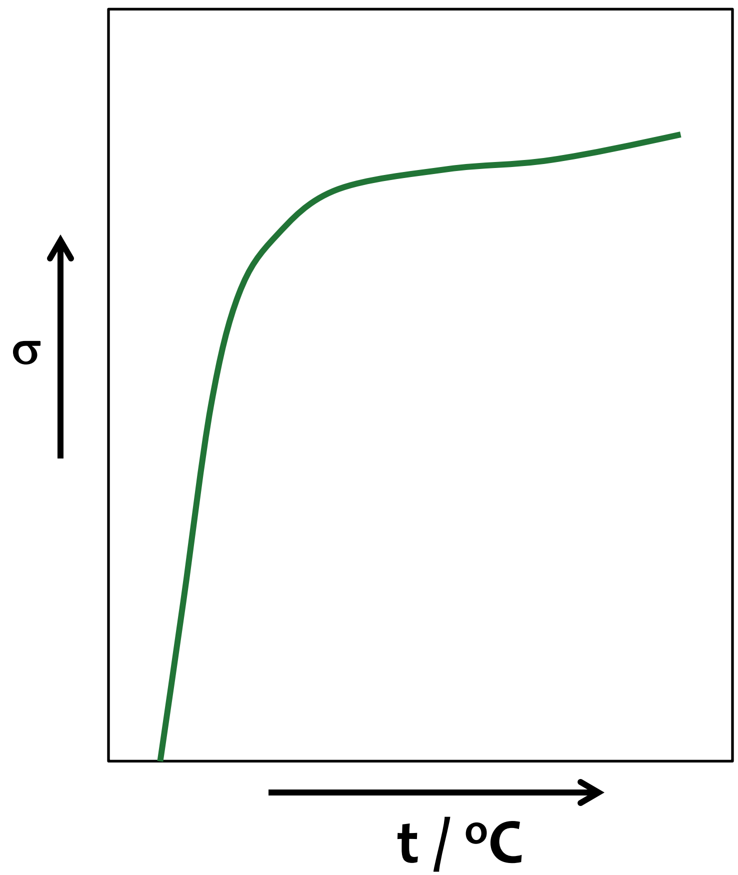


Element	Wt %	At %	K-Ratio
C K	97.64	98.22	0.9637
O K	2.36	1.78	0.0071
Total	100	100	

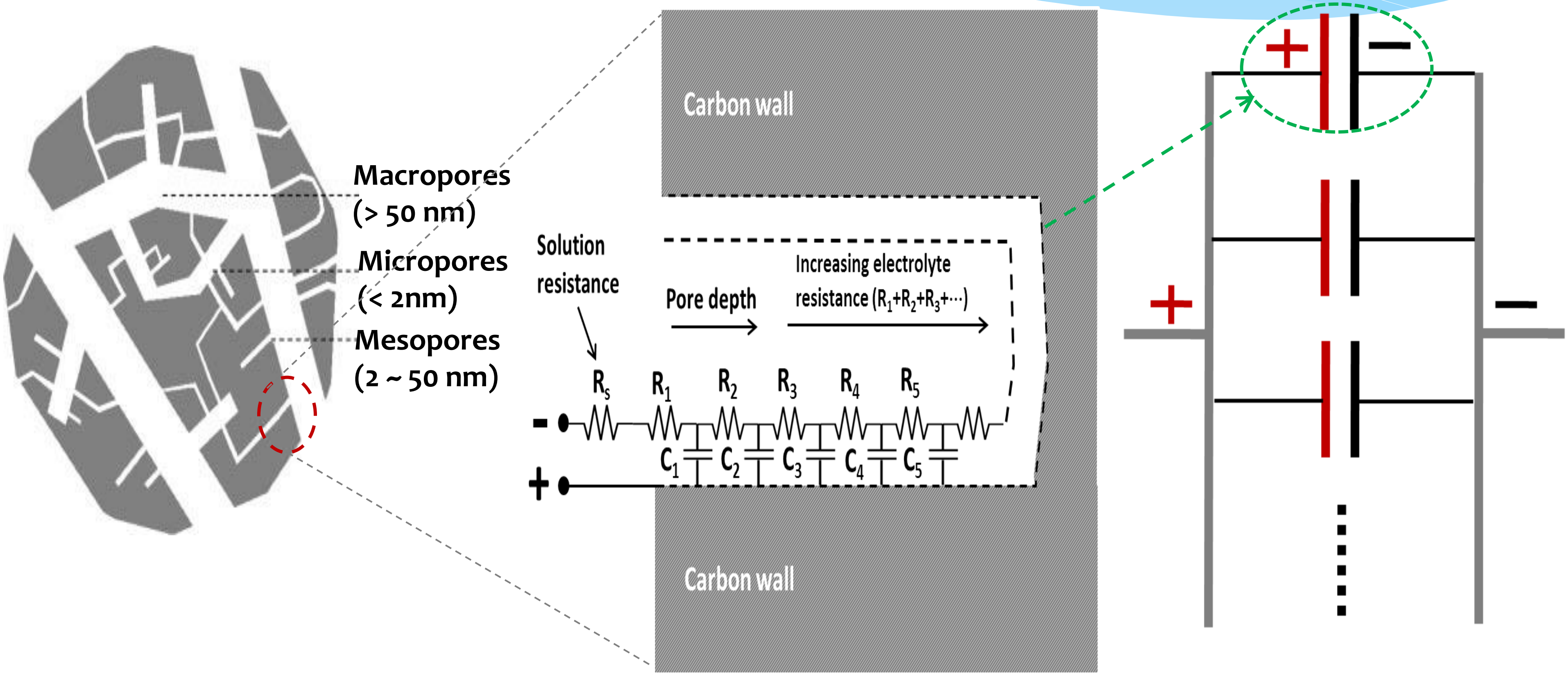
Electrical Conductivity

$$\sigma = \frac{1}{R}\frac{l}{A}\frac{1}{(1-\theta)} \quad (\theta\text{: porosity})$$

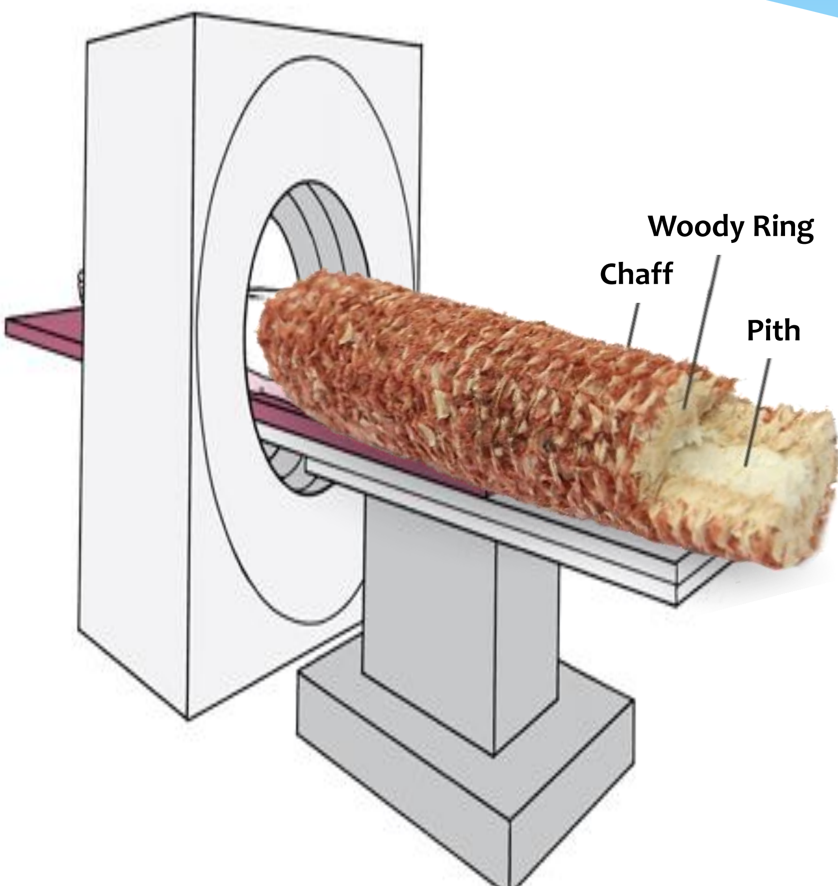
Sample	Conductivity / S cm^{-1}
Biochar	1.0 ~ 50
Vulcan 3	38.0
Vulcan 6	26.2
Black pearls 880	32.0
Black pearls 1300	34.1
Black pearls 2000	7.0
Sterling V	21.2
Graphite	300

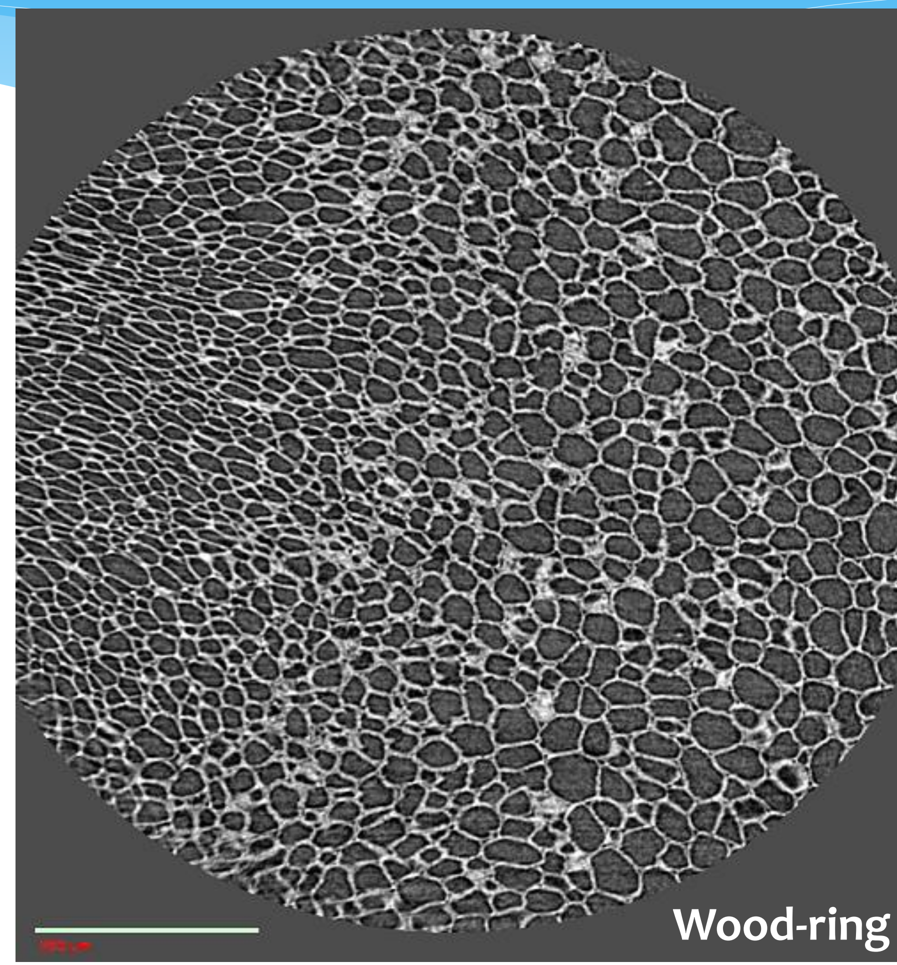


Porous model



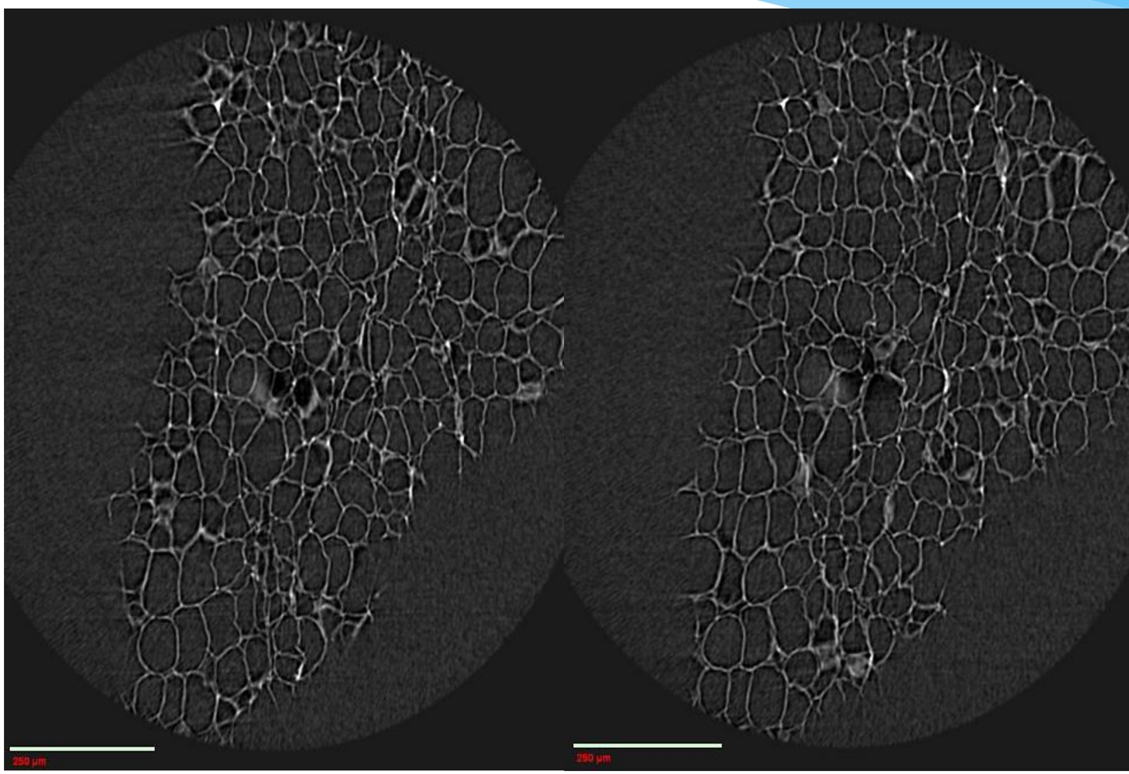
X-ray Computed Tomography of Corn Cob Biochar

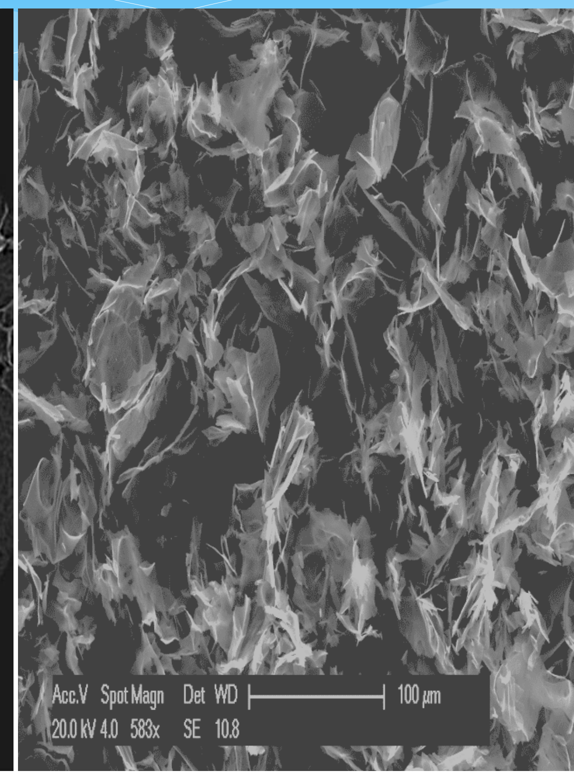




middle.mpg

CT of Corn Cob Pith

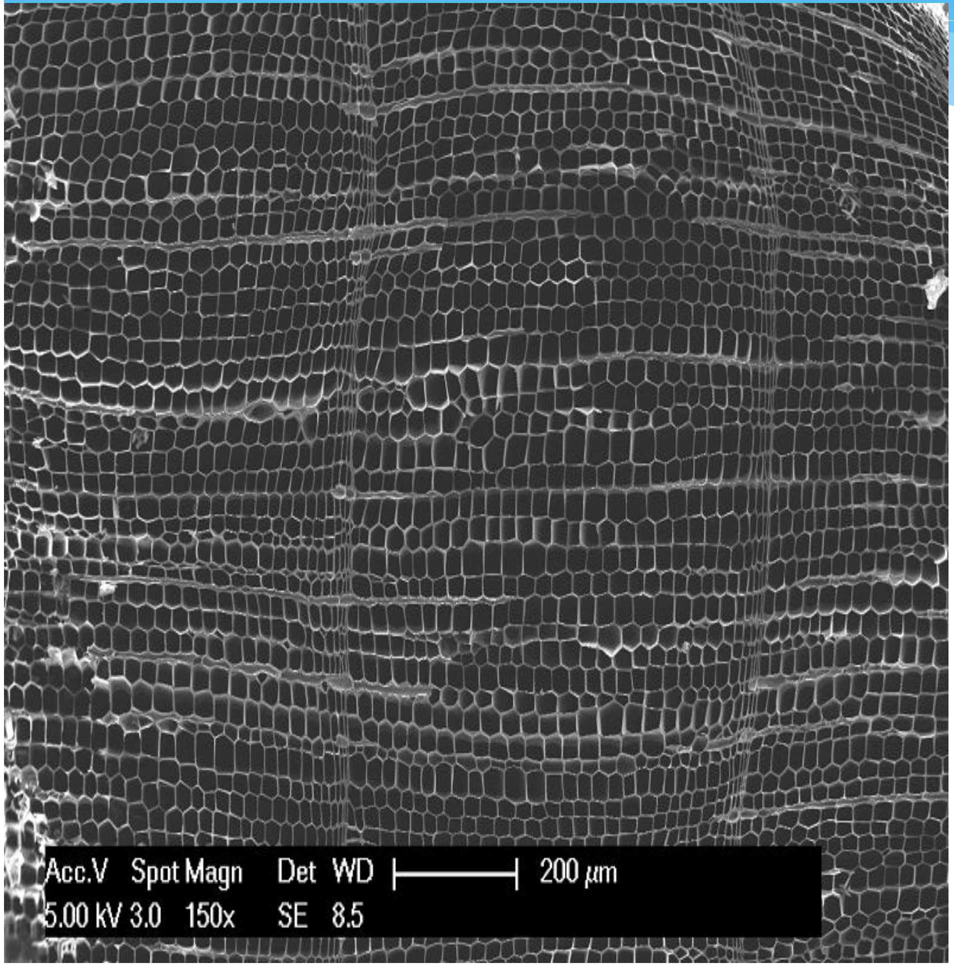


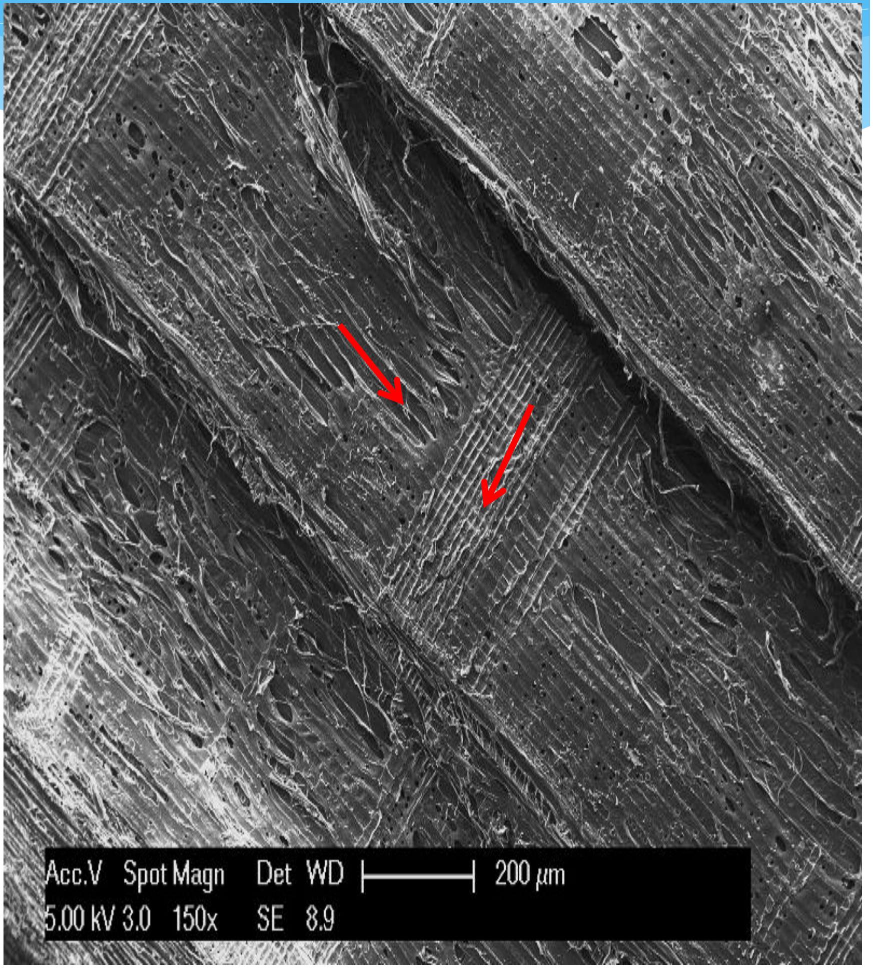


core.mpg

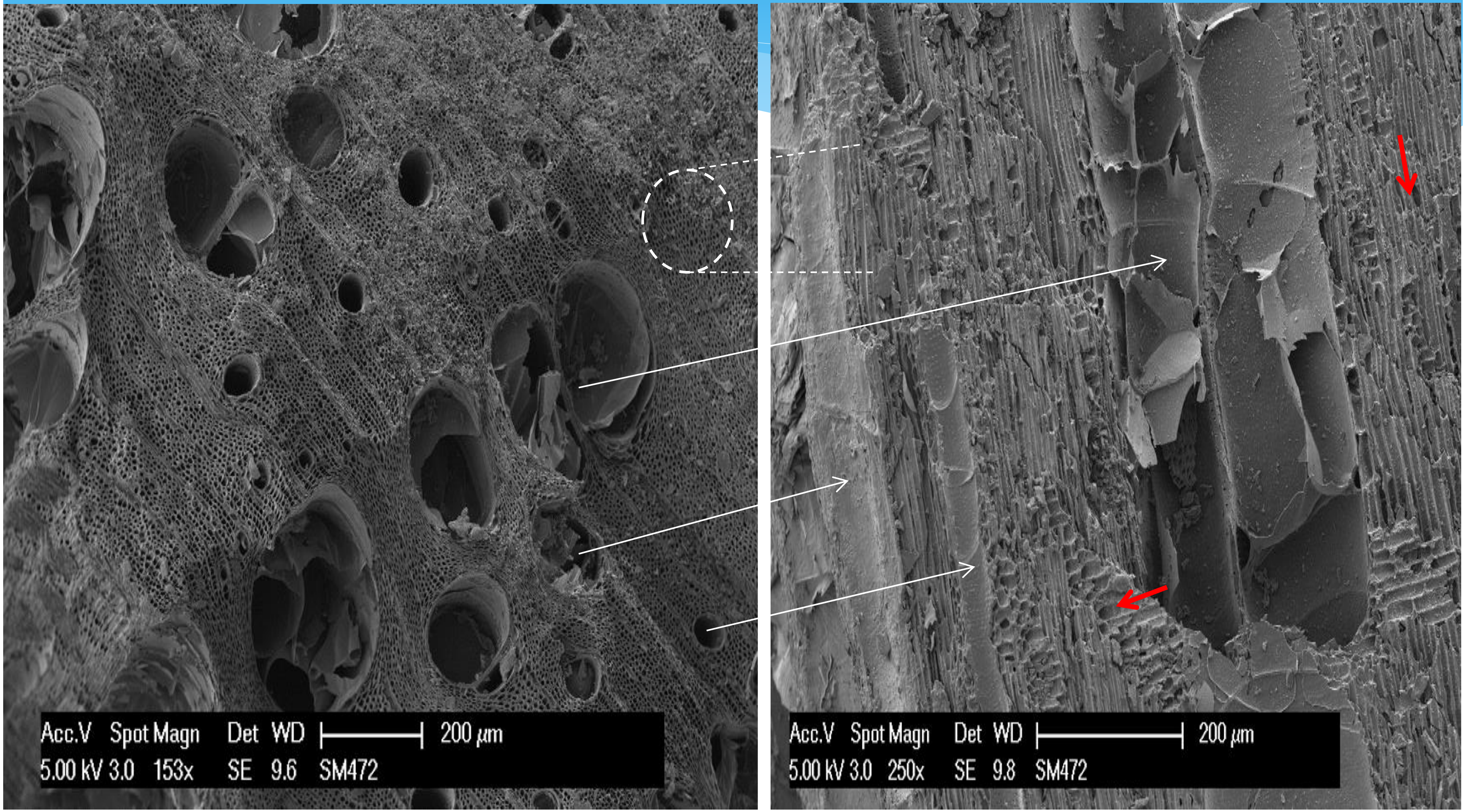
ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

Softwood Biochar



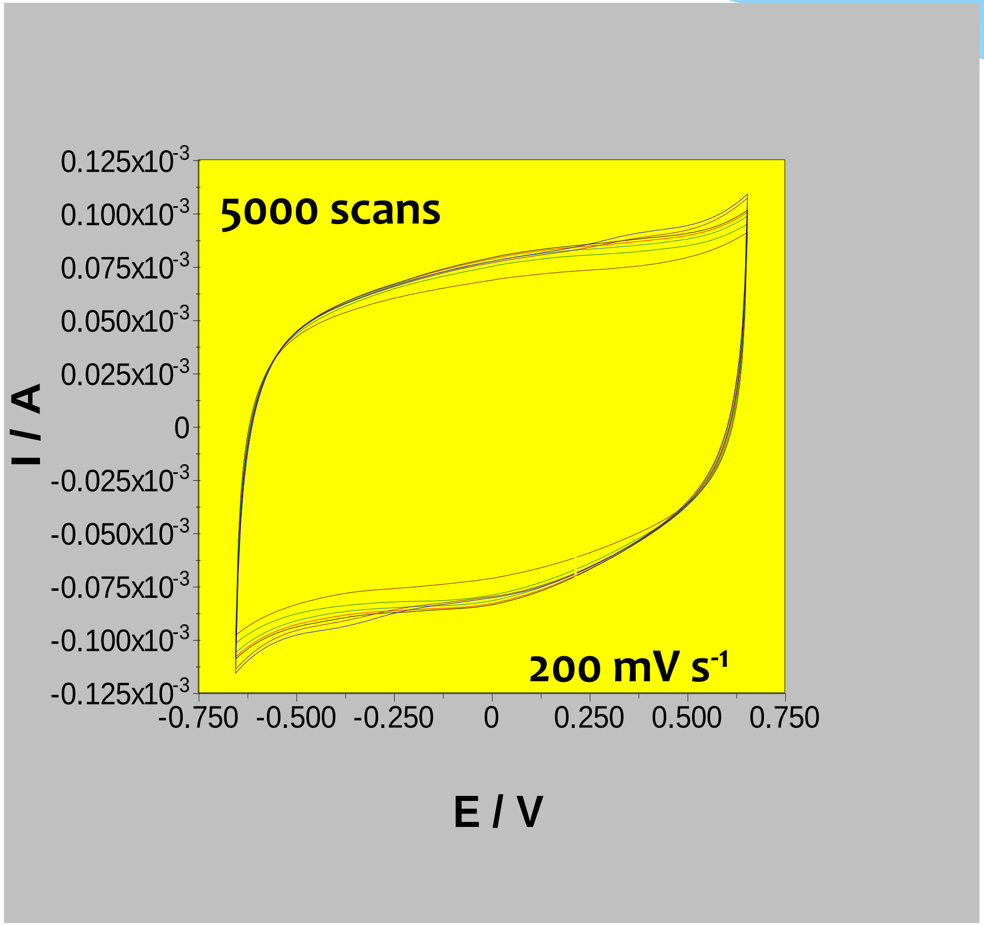


Hardwood Biochar



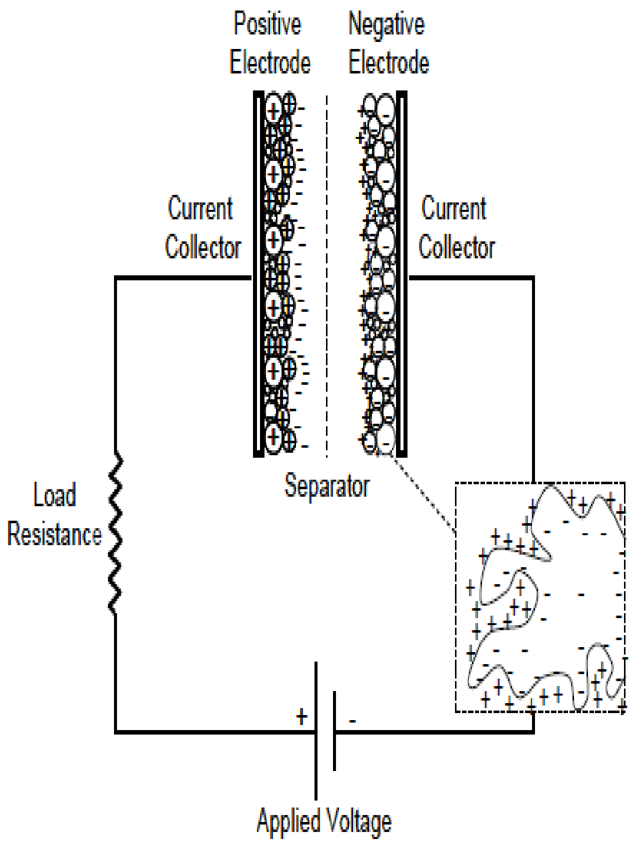
ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

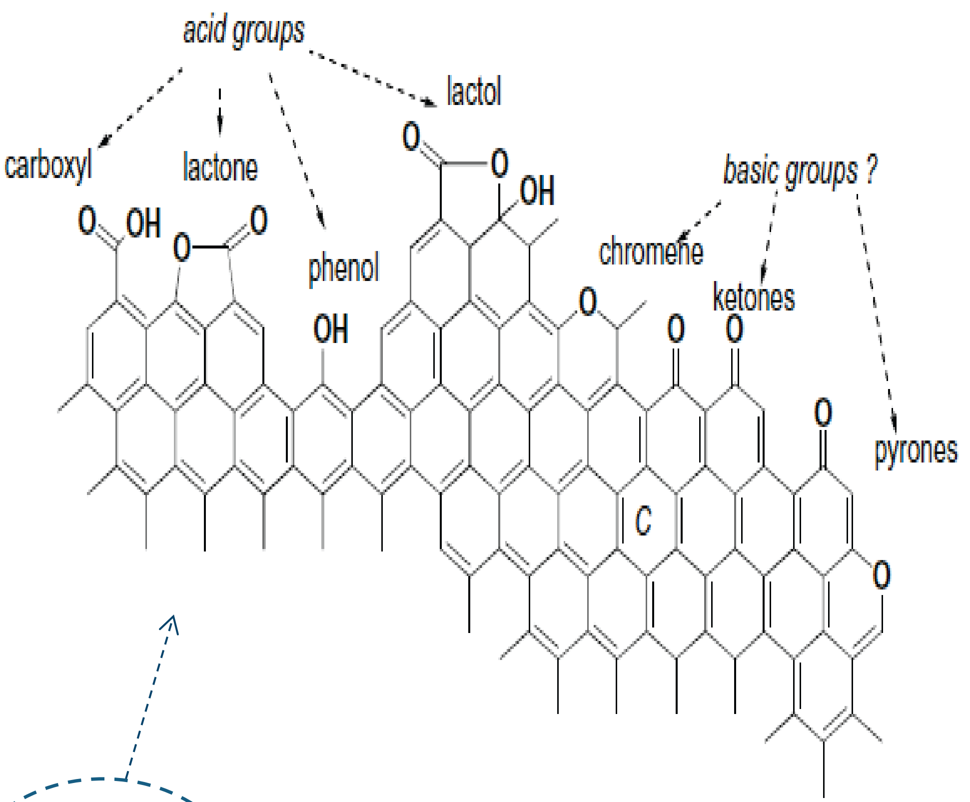
Original Biochar Supercapacitor



- ❑ Typical supercapacitor responses
- ❑ Fast charge-discharge bahavior
- ❑ Good lifetime
- ❑ Low environmental impact
- ❑ Low cost
- ❑ However, specific capacitance is low (10~20 F g^{-1})

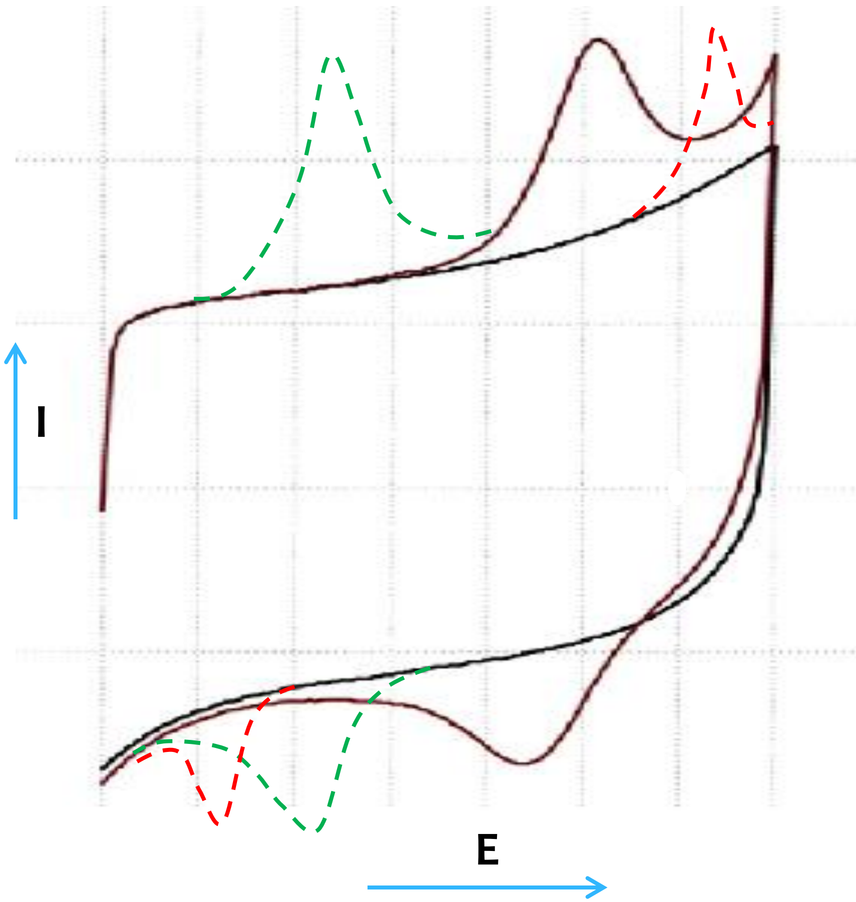
Pseudocapacitance

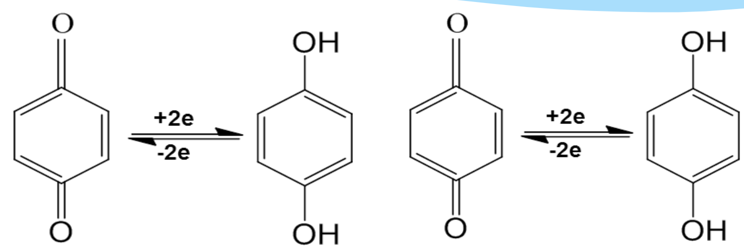




$$C = \sum \frac{nFm_j}{V} + \frac{\theta \varepsilon_0 \varepsilon_r A}{l}$$

Activity of O-groups





$$>C{=}O + e^- \longleftrightarrow >C{-}O^-$$

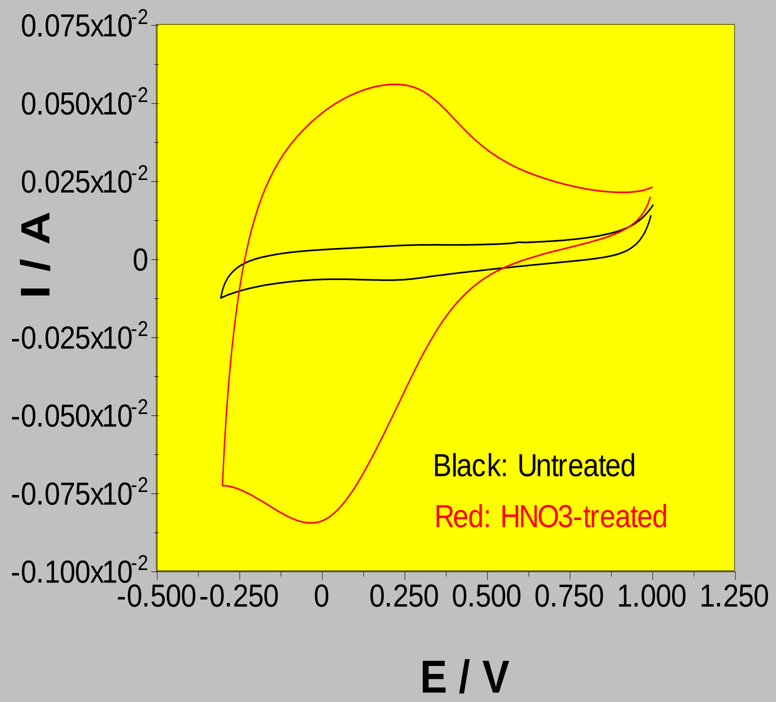
$$>C{-}OH \longleftrightarrow >C{=}O + H^+ + e^-$$

$$-COOH \longleftrightarrow -COO + H^+ + e^-$$

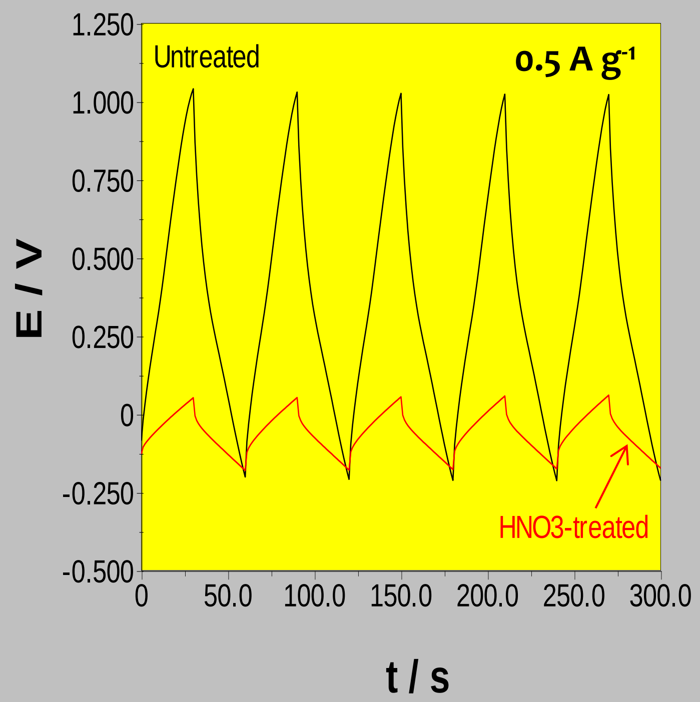
Decrease in activity

Activation of Biochar

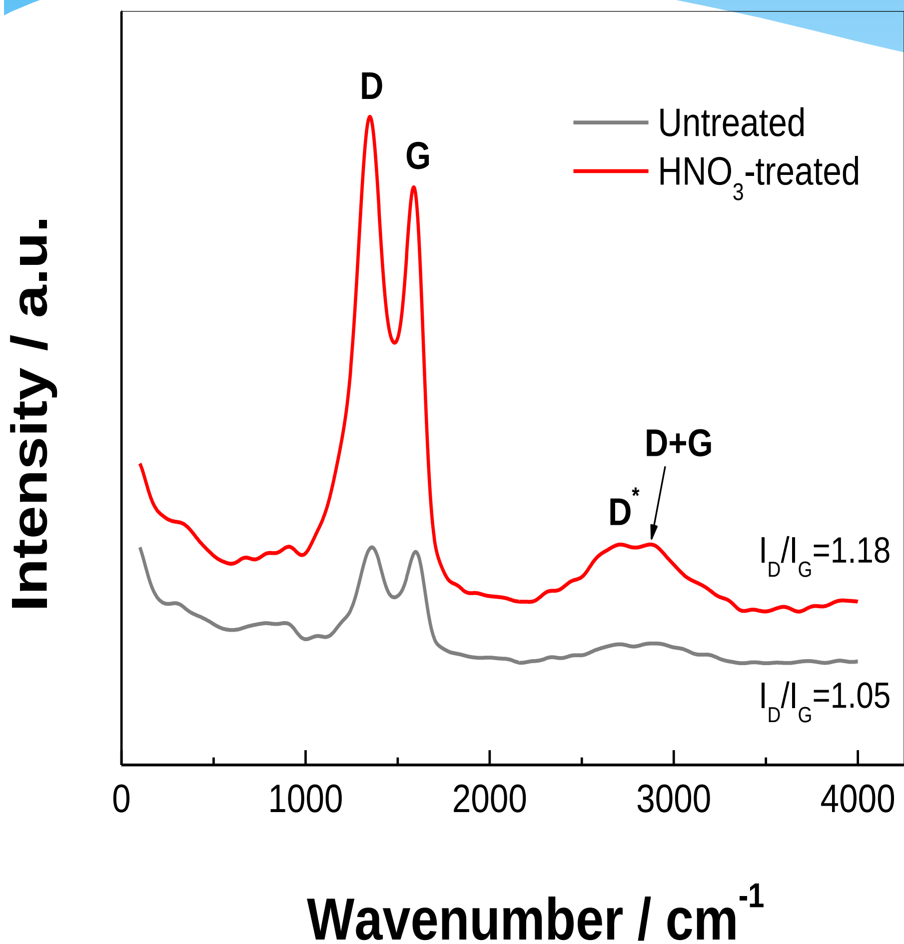
Current-potential curve

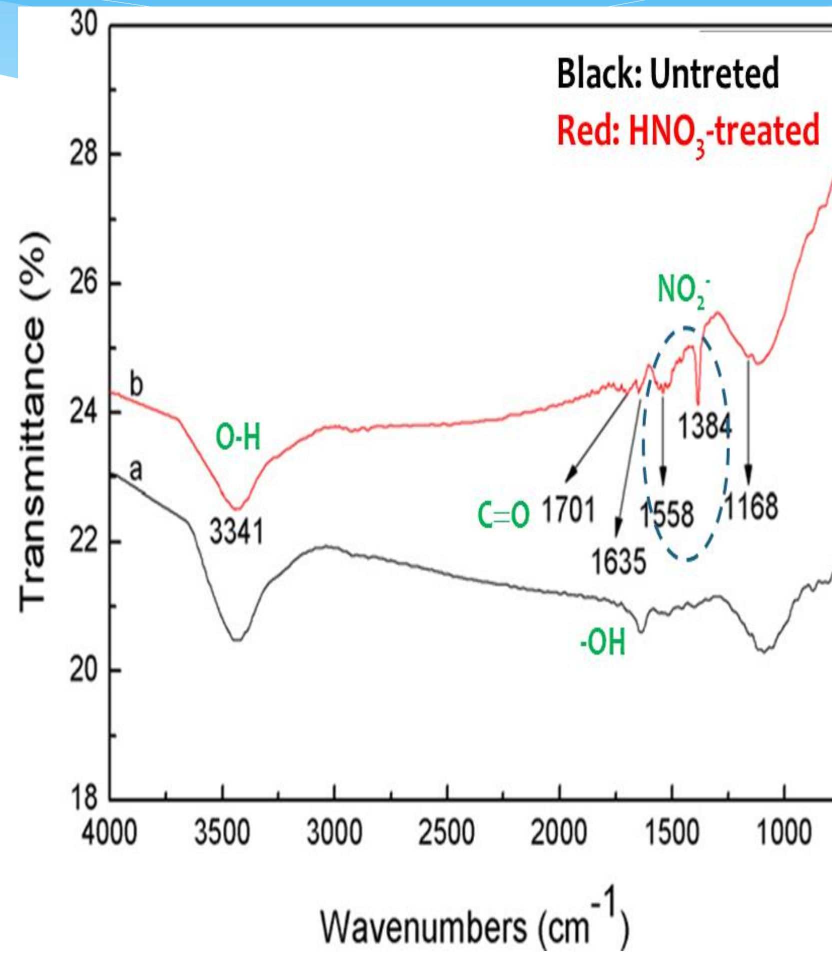


Constant current charge-discharge



Raman and FTIR Patterns





Capacity of Biochar in Aqueous Electrolyte

Electrode material	Specific capacitance ($F\ g^{-1}$)	BET Surface area ($m^2\ g^{-1}$)
Activated Biochar	100 to 300	300~400
Carbon black	100 to 300	1000~2000
Activated carbon	100 to 400	1000~3000
Mesoporous carbon	100 to 200	1500~2500
Reduced graphene oxide	150 to 250	2000~3000
Multiwall carbon nanotube	100 to 150	500~1000
Single-wall carbon nanotube	100 to 200	1500~2000

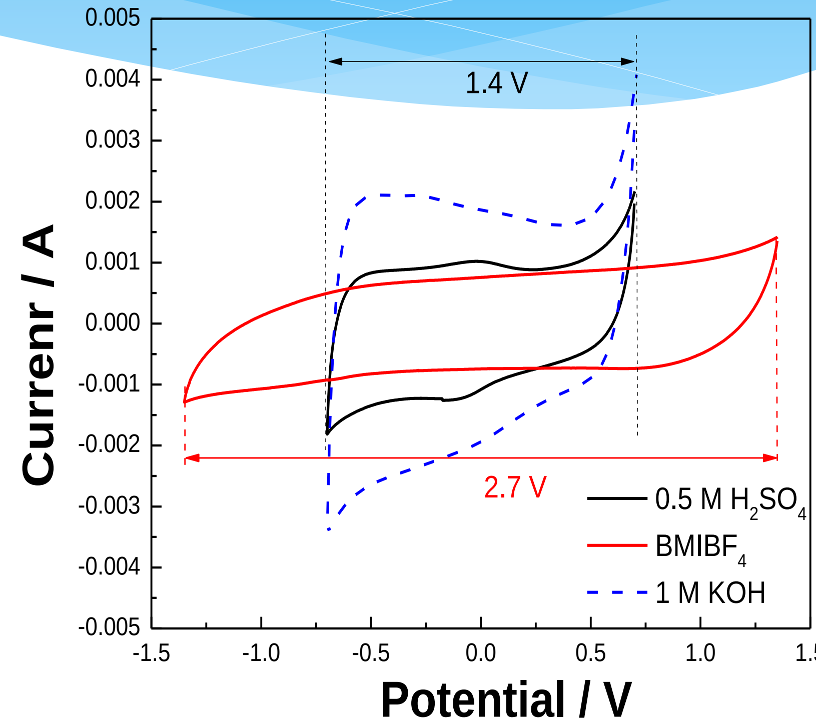
Source: Zhang & Zhao, ChemSusChem, 5 (2012) 818-841.

Electrolyte Dependence

Solvent Or salt	Anode potential limit / V	Cathode potential limit / V	Potential window / V
Water	-0.20	1.2	1.4
Acetonitrile	-2.8	3.3	6.1
Propylene carbonate	-3.0	3.6	6.6
$TEABF_4$	-3.0	3.65	6.65

*Potential vs SCE.

Source: Aurbach et al, Nonaqueous electrochemistry, Marcel, 1999



Maximum energy stored

E_{max} = CV²/2 (V: cell operating voltage)

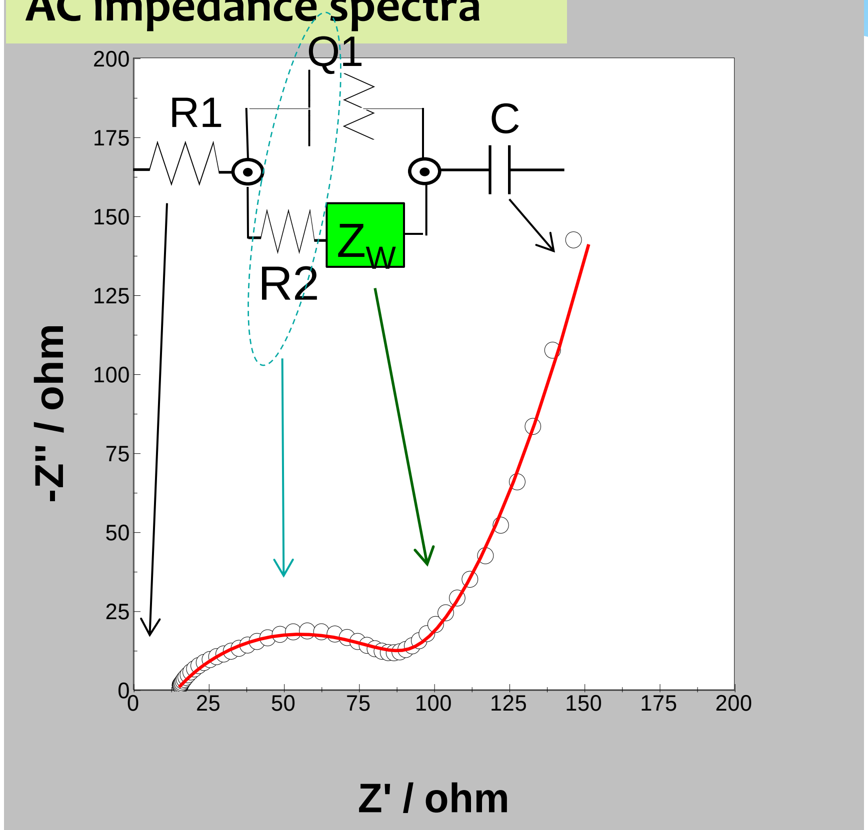
Specific Capacity of Biochar in non-Aqueous Electrolyte

Electrode material	Specific capacitance ($F\ g^{-1}$)	Surface area ($m^2\ g^{-1}$)
Biochar in $TEABF_4$	75	400
Biochar in $TEAPF_6$	35	400
Biochar in $TBAPF_6$	30	400
Activated carbon $TEABF_4$	90 to 140	1000 to 1400
Mesoporous carbon in $TEABF_4$	70 to 160	1500 to 2000
Graphene in $TEABF_4$	100	~3000
Carbon nanotube in $TEABF_4$	80 to 110	~2000

Source: J. Zhang & X. Zhao, ChemSusChem 5 (2012) 818-841.

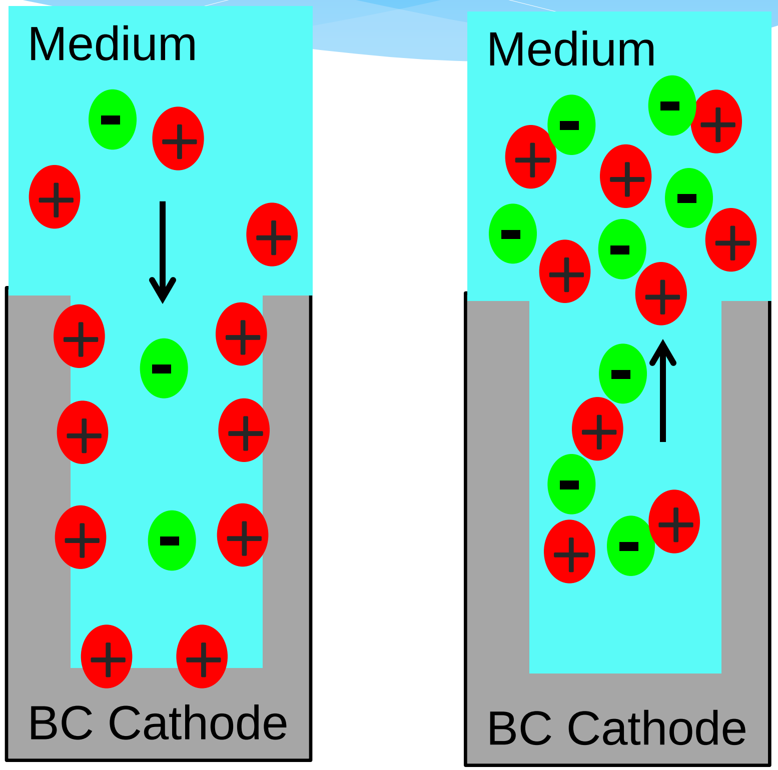
Charge Transport Model

AC impedance spectra



Z_W: Warburg transport resistance

Charge transport within a single pore



Charged *Discharged*

Conclusions

- Biochars have finger-print microstructures inherited their corresponding biomass precursors;
- Low ash even zero-ash high carbon bichars can be prepared from wood feedstocks;
- Biochar supercapacitors have demonstrated promising capacity and durability which are comparable to those of using advanced carbon materials, especially in aqueous media;
- Surface activation of biochars substantially increases their capacitance and degree of surface utilization;
- Woody biochars with developed surface area, good conductivity, electrochemical stability, and interesting pore network will be promising energy and environmental materials.

THANK YOU!