Development of Activated Carbons from Biomass for Energy Storage Applications

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Biomass for energy storage application

Sugarcane Bagasse (SB)

Waste : 390,000 tons/year

Lignin (LN)

Carbon Electrode for Supercapacitor

Palm Shell (PS)

Waste : 720,000 tons/year

Palm Empty Fruits Bunches (EFB)

Waste : 2,600,000 tons/year

Ref : biomass.dede.go.th

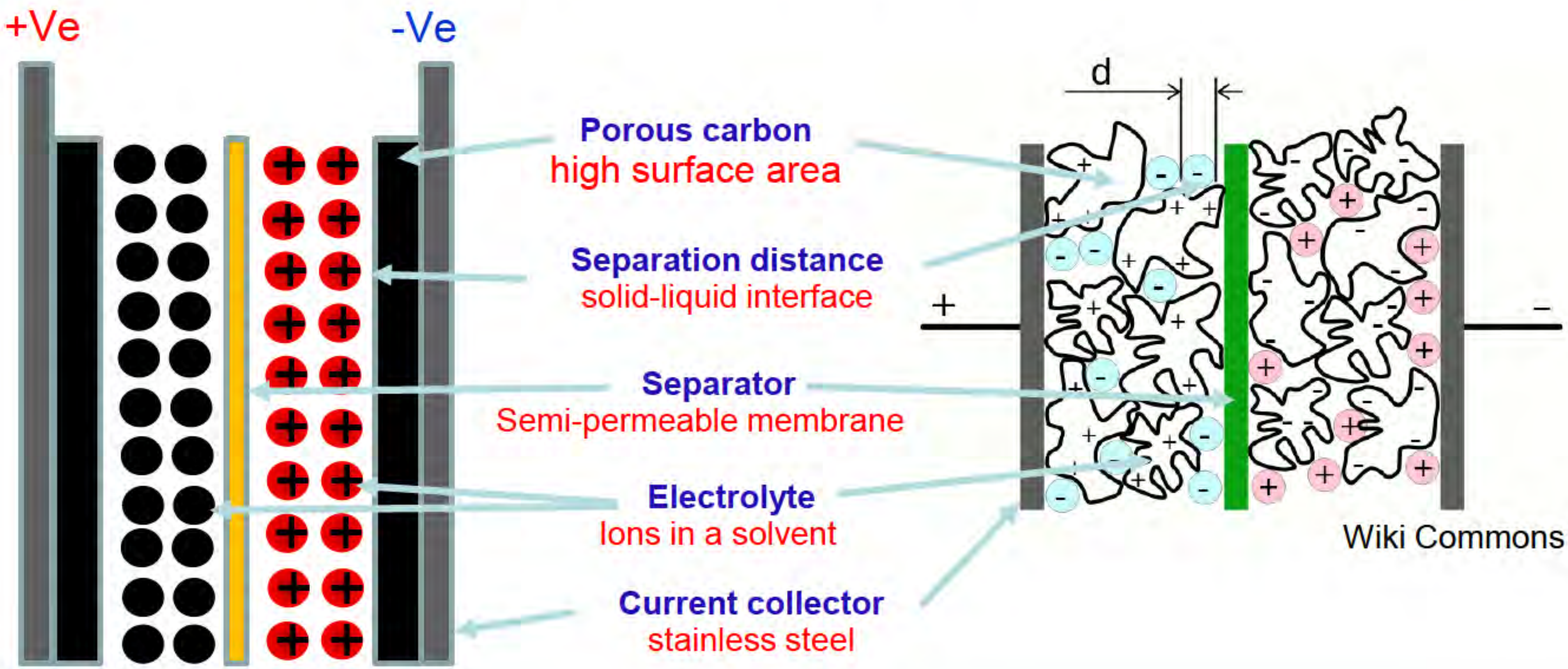
Characteristics of Biomass

Biomass	Proximate analysis (wt % DB)			Ultimate analysis (wt% DB)				Biomass constituent (wt% DB)		
	Volatiles	Fixed carbon	Ash	C	H	N	O	Lignin	Cellulose	Hemicellulose
Coconut shell	78.1	21.3	0.6	55.2	5.5	0.1	38.7	33.4	43.3	12.8
PEFB	**77.3**	**17.0**	**5.7**	**46.2**	**5.7**	**1.4**	**40.9**	**15.6**	**54.4**	**20.0**
Sugarcane bagasse	**75.0**	**16.2**	**8.8**	**47.6**	**5.8**	**0.6**	**37.4**	**10.3**	**39.3**	**23.4**
Palm shell	**77.0**	**21.2**	**1.8**	**54.0**	**5.2**	**0.6**	**38.4**	**47.3**	**42.2**	**5.6**
Corn husk	80.7	16.8	2.5	43.4	6.7	0.7	46.6	5.9	37.5	37.9
Cassava stalk	83.8	14.3	1.9	-	-	-	-	25.2	50.6	1.4
Eucalyptus wood	81.9	17.7	0.4	47.7	6.8	0.1	45.0	20.2	60.9	4.9

Note: Results from Renewable Energy Laboratory, MTEC, Thailand

- High ash content
- Low carbon content

What is a Supercapacitor?



- ❑ **Principle:**

Capacitance is proportional to the surface area of the carbon (A), divided by the charge separation distance (d)

$$C \propto A / d$$

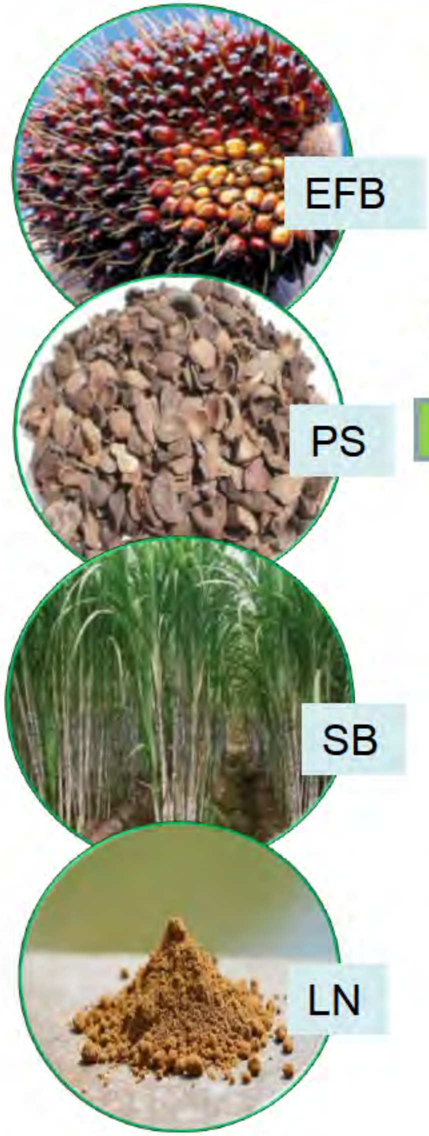
- ❑ **So as the surface area ↑, and charge separation distance ↓ : Capacitance ↑↑↑↑**

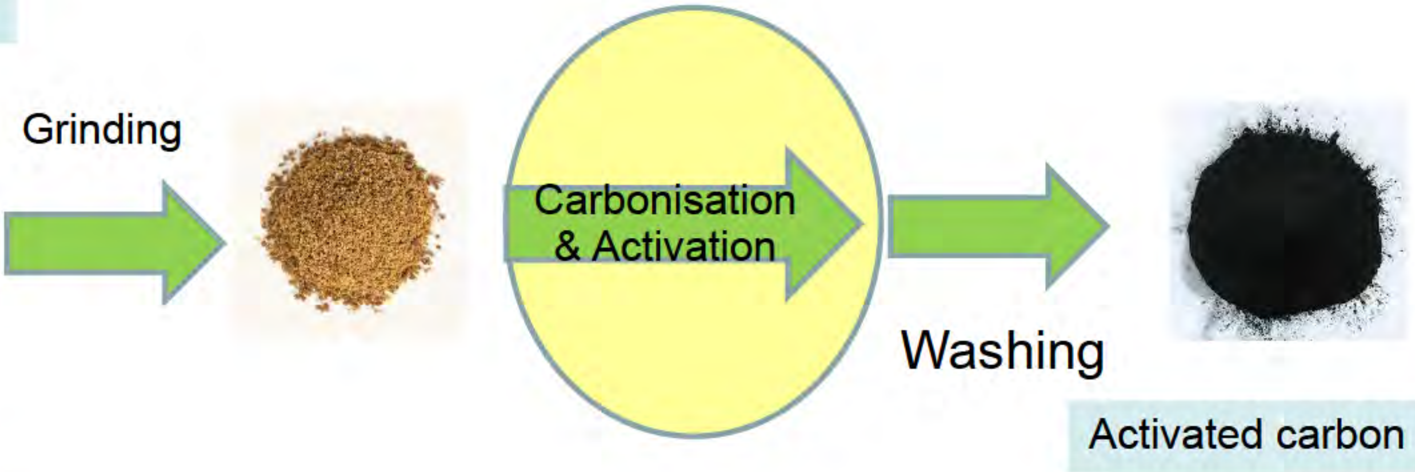
Active Electrode Material

Active Material Requirements:

- High specific surface area (> 1,000 m^2/g)
- Optimized pore-size distribution
- Good electrical conductivity
- Good electrolyte accessibility and wettability
- Resistant to undesirable chemical reactions
- Long-term stability
- Easy to process, high mechanical integrity
- Minimum self-discharge at open circuit
- Sufficient thermal conductivity to reduce heat build-up within the cell

Production of activated carbon from Biomass





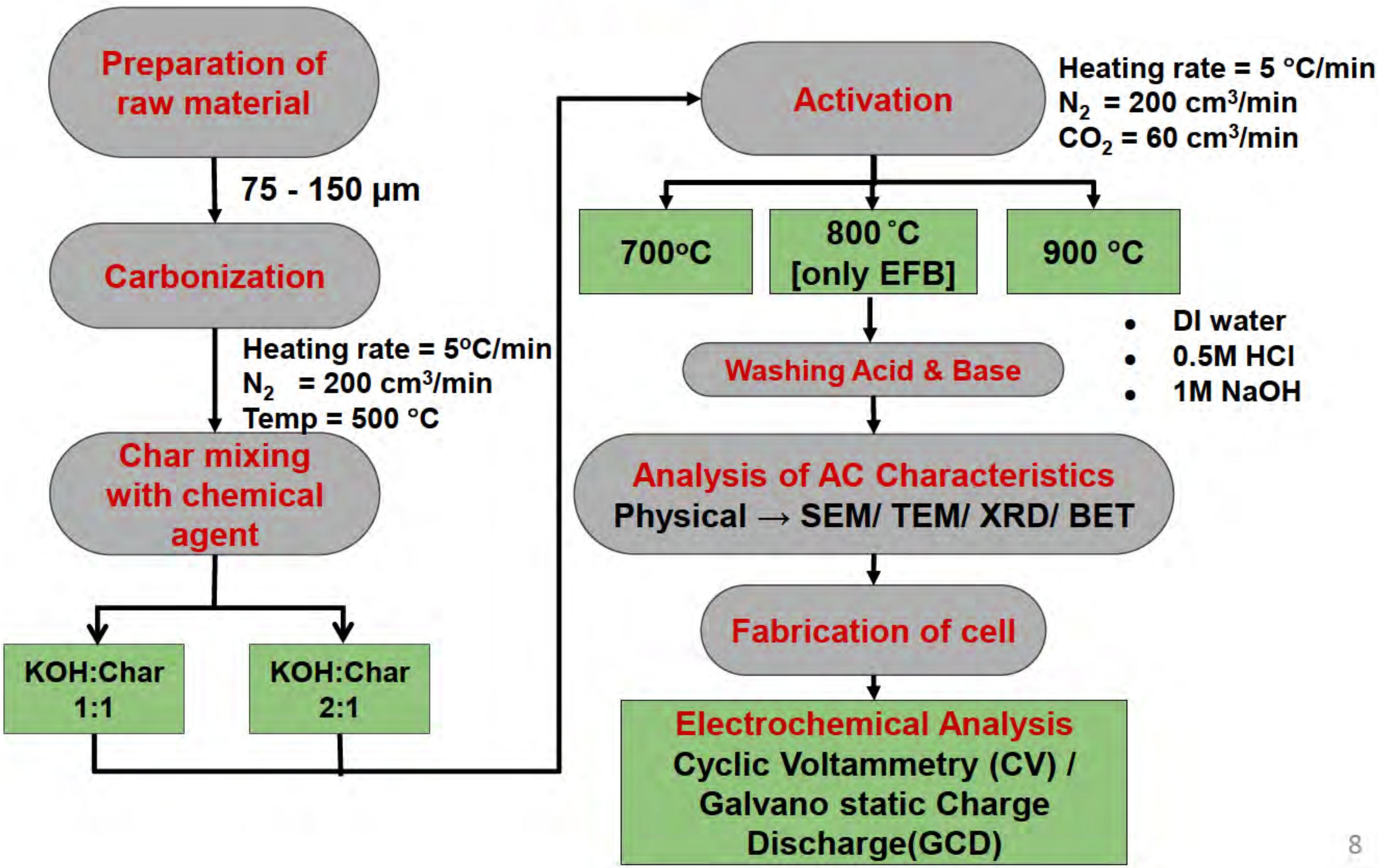
Activation method

- Physical activation
  - CO_2
  - Steam
  - Air/Oxygen
- Chemical activation
  - $ZnCl_2$
  - H_3PO_4
  - Alkali (i.e. KOH, NaOH)

Objective

Effect of activation temperature and KOH/C ratio on physical properties

Production of activated carbon from Biomass

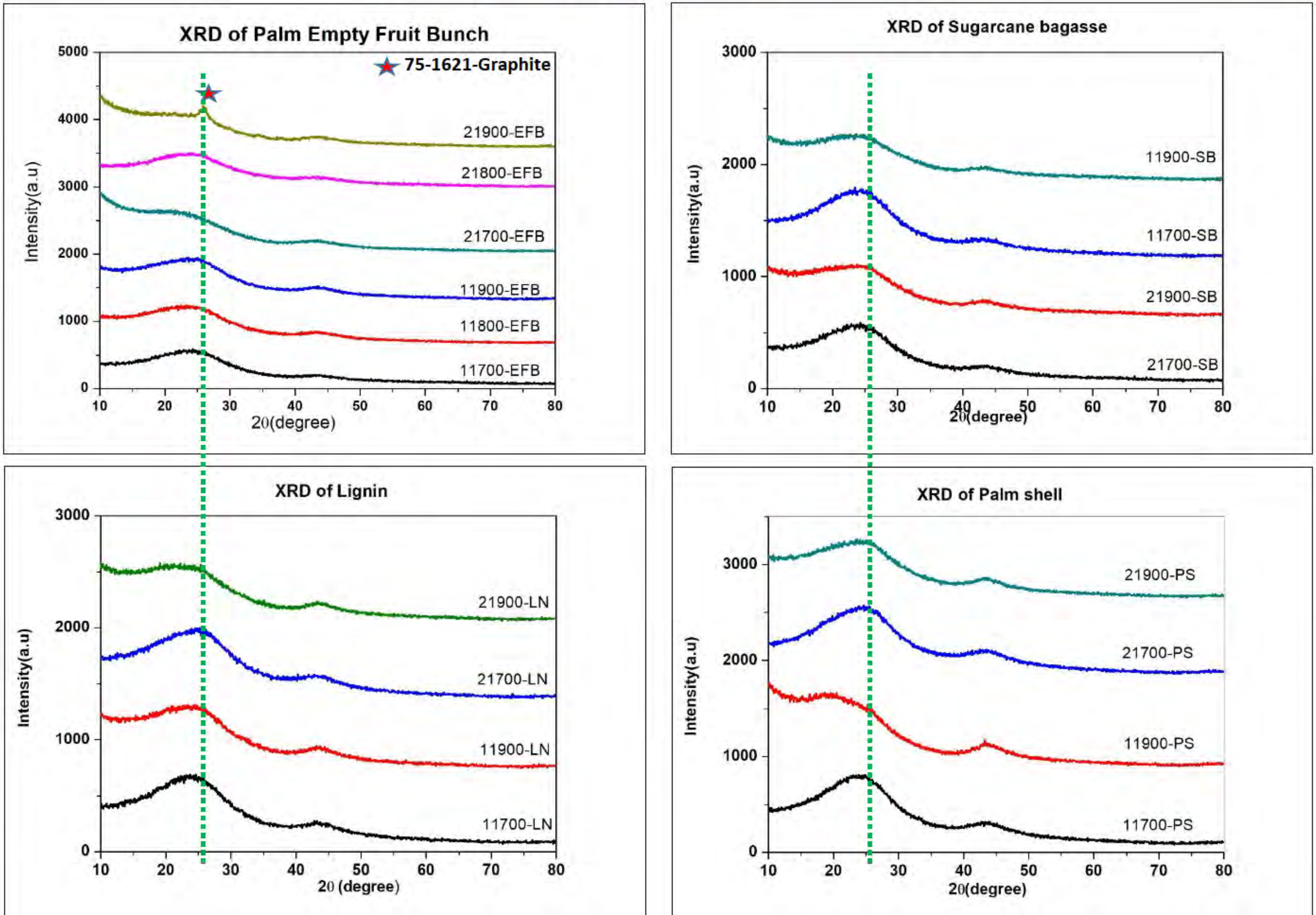


Production of activated carbon from Biomass

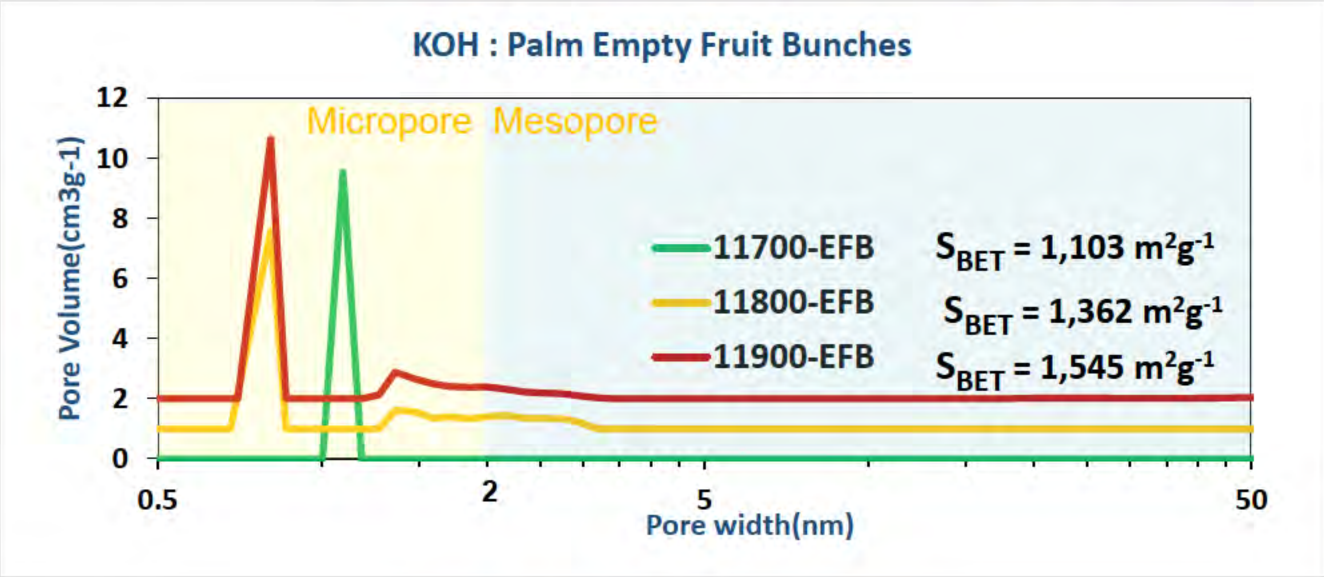
Preparation Conditions

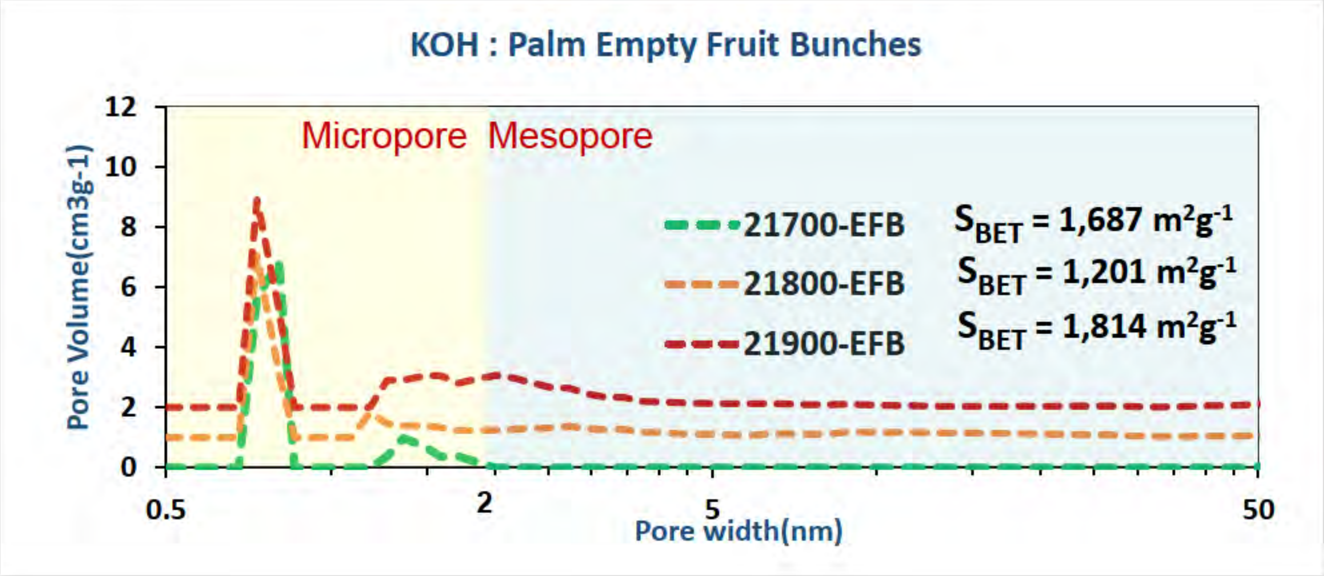
- **EFB**
  - 1:1 700 °C
  - 1:1 800 °C
  - 1:1 900 °C
  - 2:1 700 °C
  - 2:1 800 °C
  - 2:1 900 °C
- **Palm Shell**
  - 1:1 700 °C
  - 1:1 900 °C
  - 2:1 700 °C
  - 2:1 900 °C
- **Sugarcane**
  - 1:1 700 °C
  - 1:1 900 °C
  - 2:1 700 °C
  - 2:1 900 °C
- **Lignin**
  - 1:1 700 °C
  - 1:1 900 °C
  - 2:1 700°C
  - 2:1 900 °C

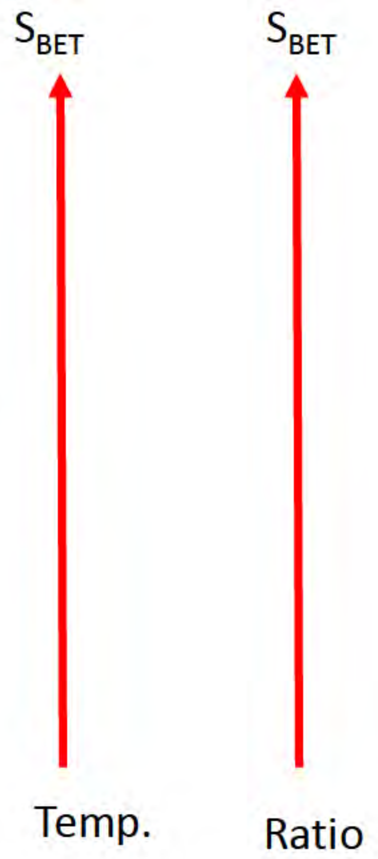
XRD of Activated Carbon



Palm Empty Fruit Bunch







Palm Empty Fruit Bunch

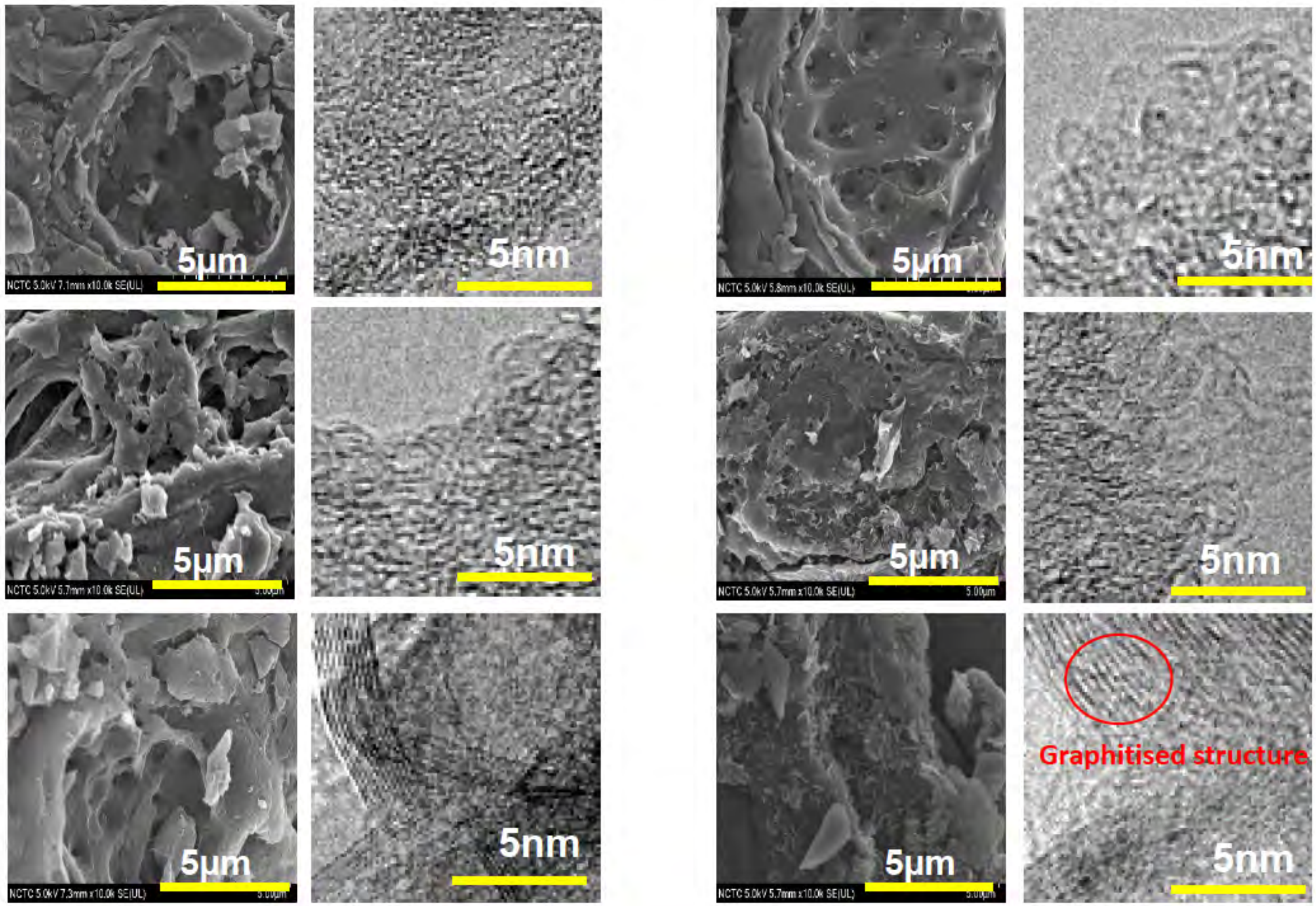
KOH : Char = 1:1

KOH : Char = 2:1

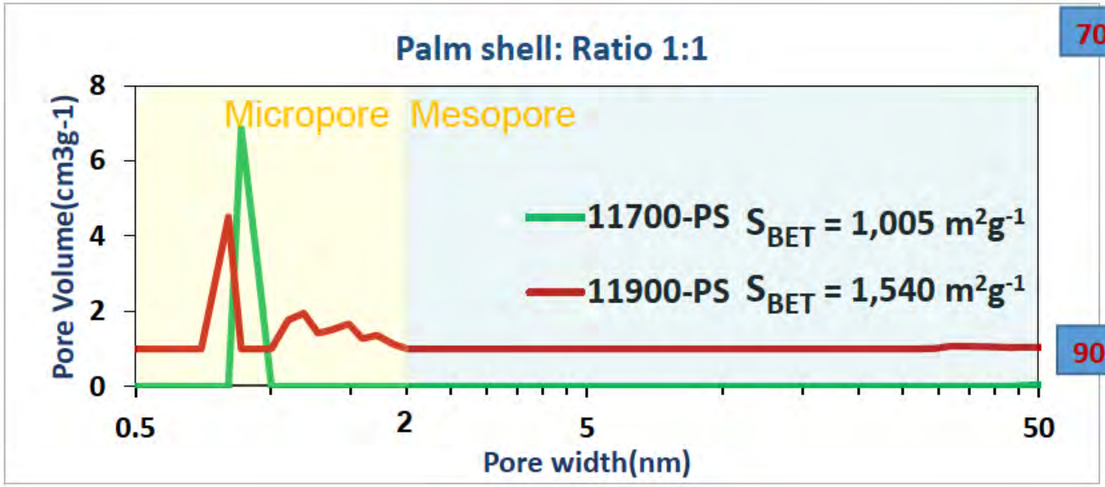
700 °C

800 °C

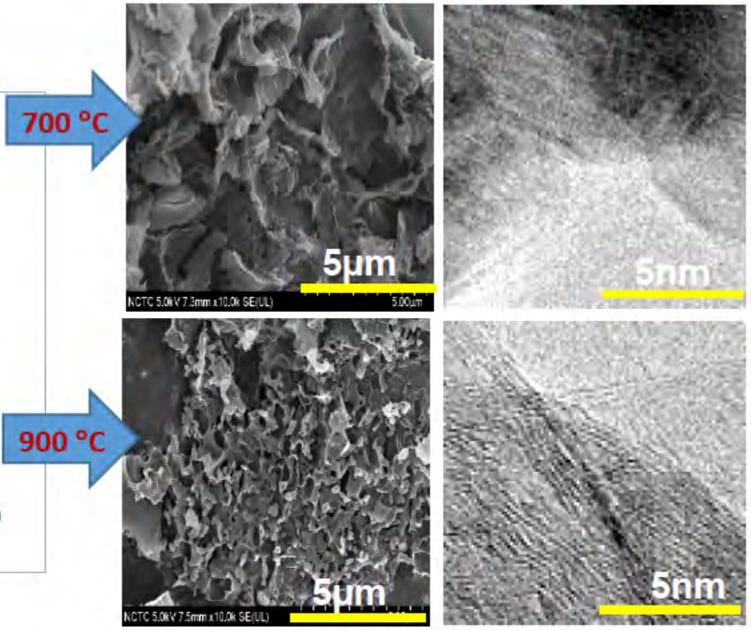
900 °C

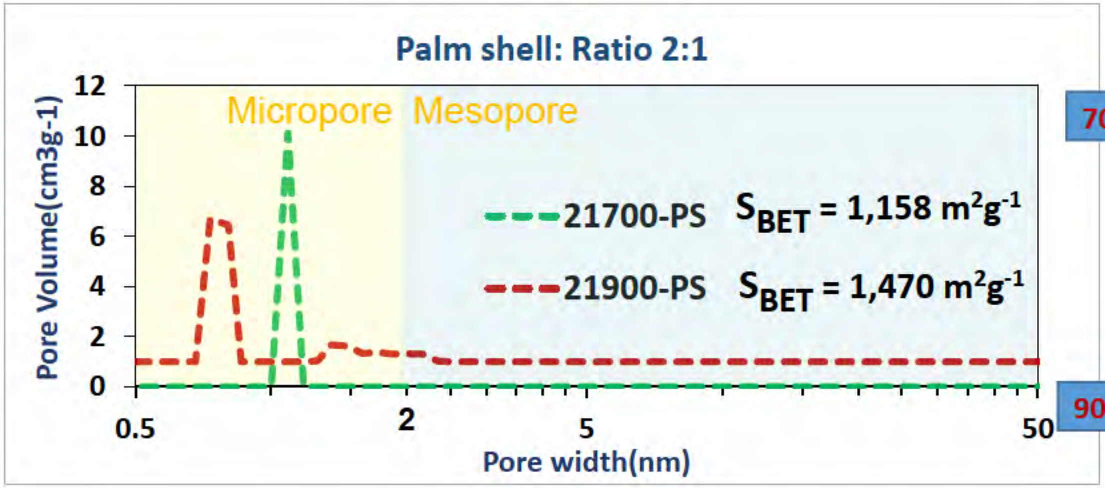


Palm shell

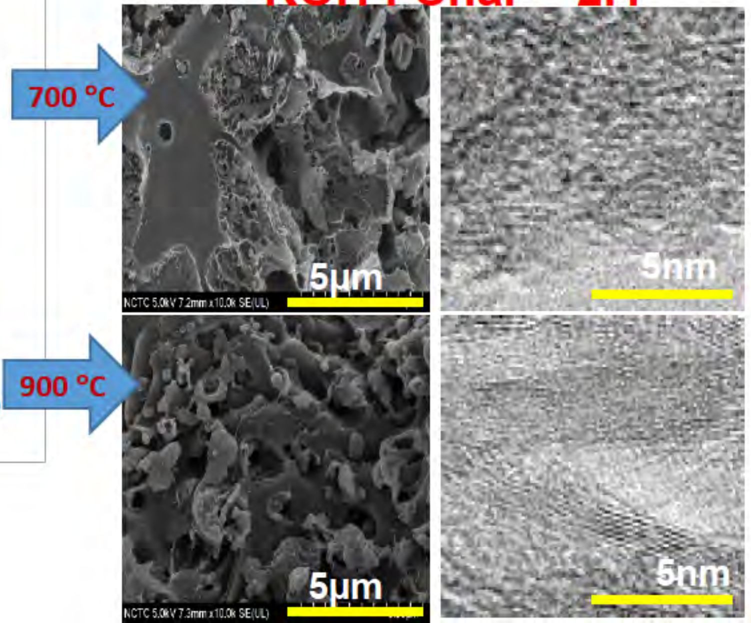


KOH : Char = 1:1

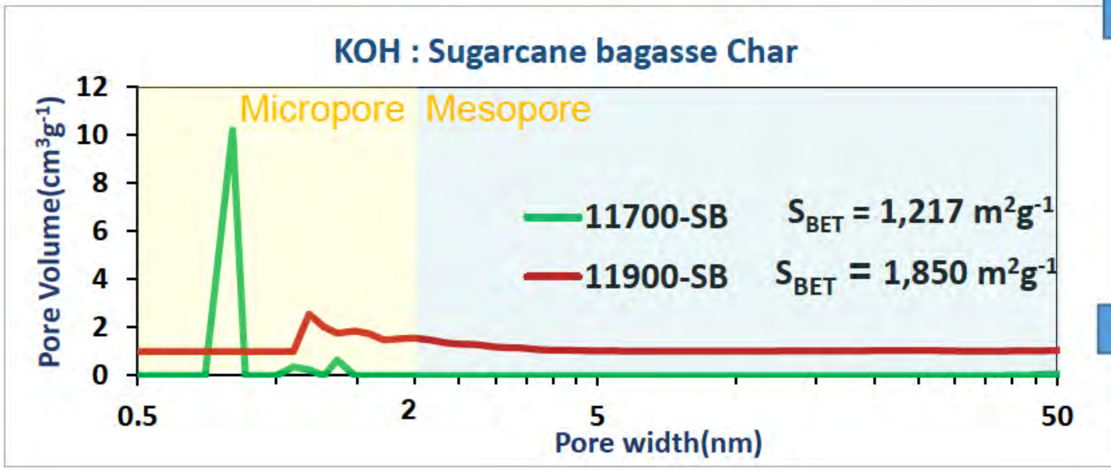




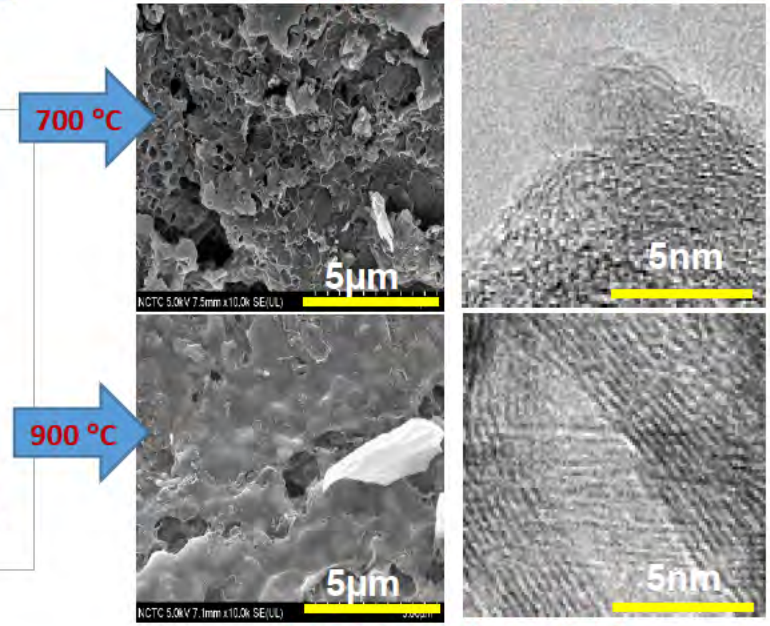
KOH : Char = 2:1

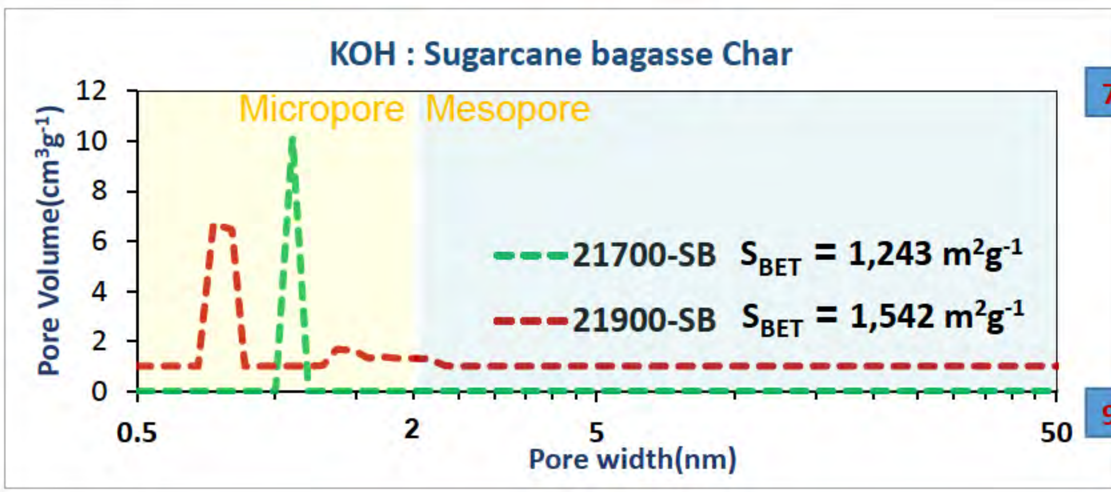


Sugarcane bagasse

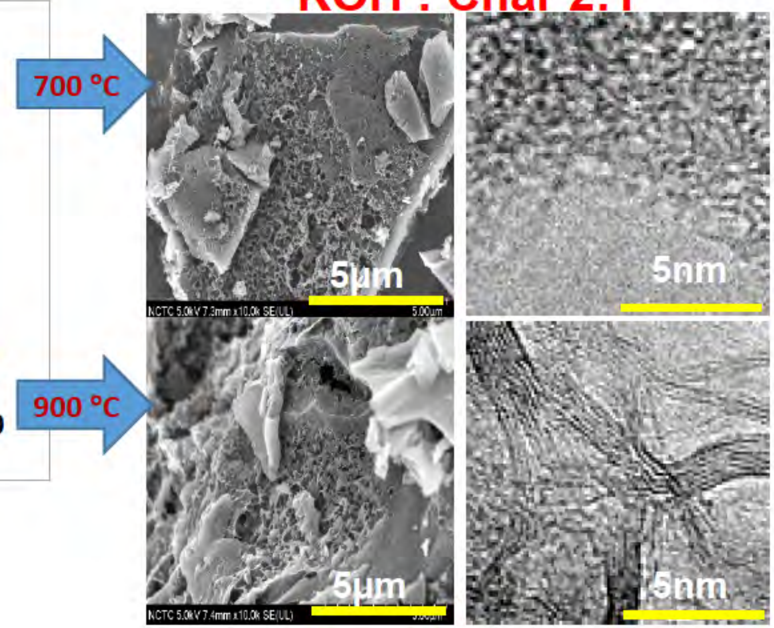


KOH : Char 1:1

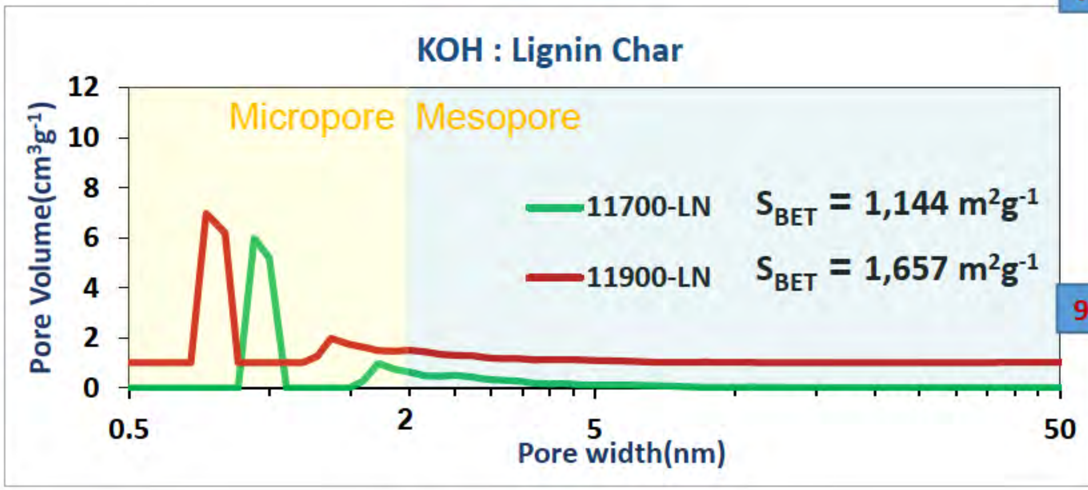




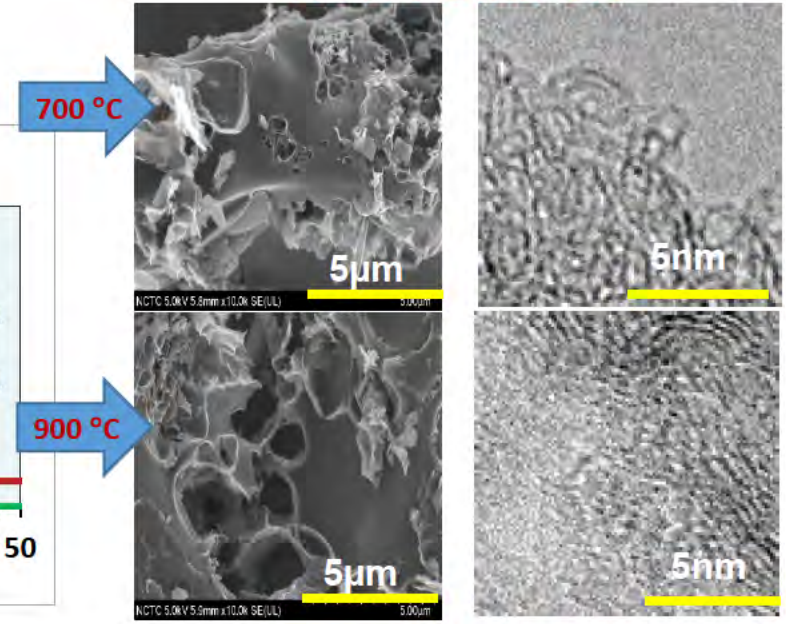
KOH : Char 2:1

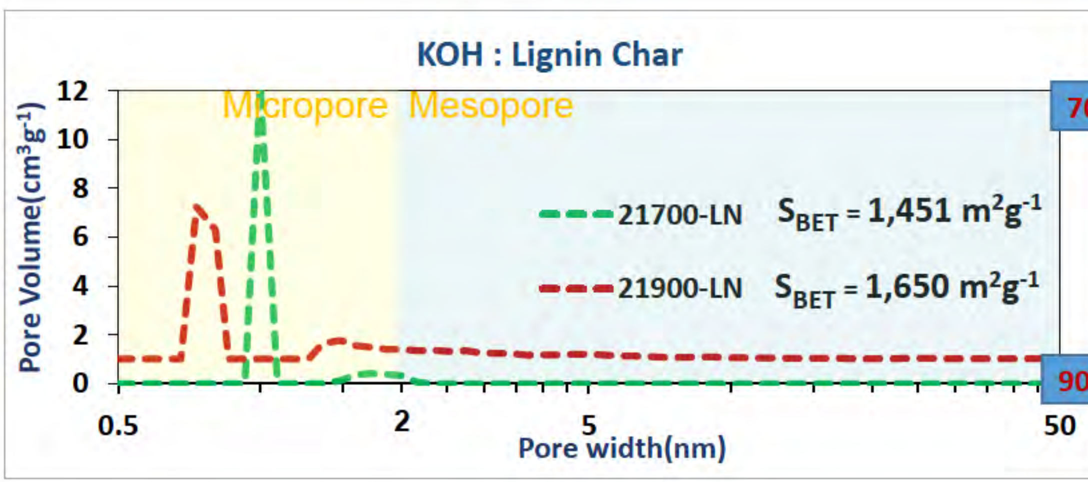


Lignin

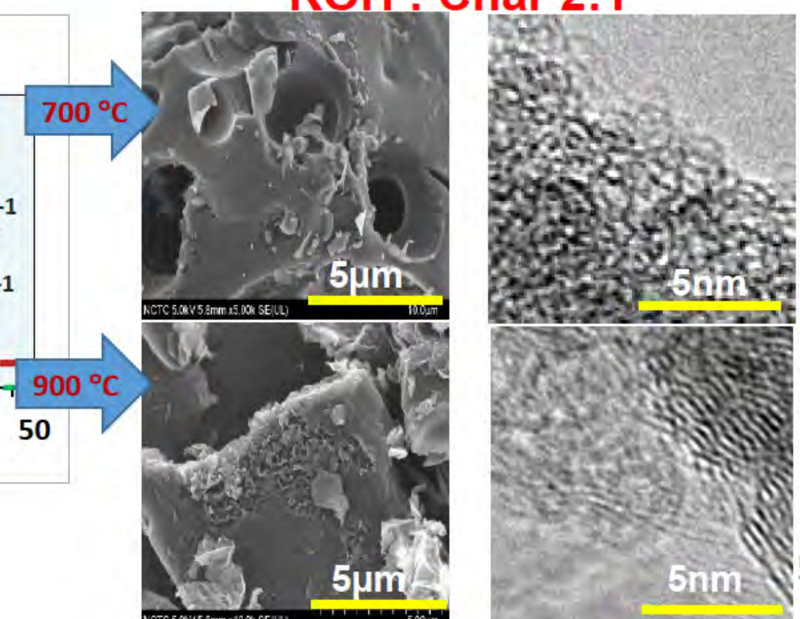


KOH : Char 1:1





KOH : Char 2:1



Fabrication of Carbon Electrode

Mixing = AC + Acetylene black
0.4 g   0.05 g

Added few drops of Ethanol

For well mixing + PTFE

Approximate similar thickness

0.05 g

Make a square (5 x 5 mm^2)

Carbon Electrode

Placed in vacuum oven overnight (110 °C)

Submerged in 1M H_2SO_4 and vacuum

Argon Purge → Electrochemical testing

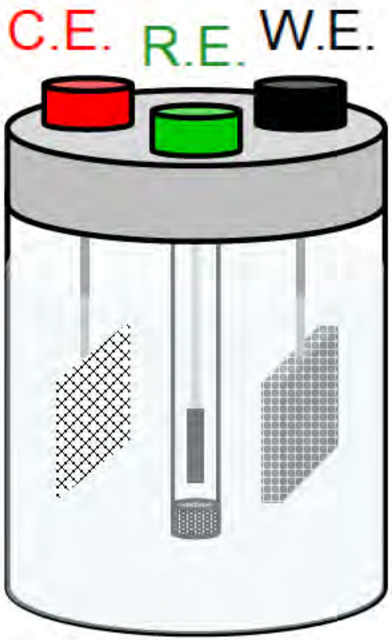
AC : Acetylene black : PTFE
8 : 1 : 1

By weight

Electrochemical Analysis

Electrochemical Testing

Working electrode (W.E.): Carbon electrode
Counter electrode (C.E.): Pt mesh
Reference electrode (R.E.): Ag/AgCl electrode
Electrolyte: Ar-saturated 1 mol dm^{-3} H_2SO_4



Cyclic voltammetry (CV): qualitative

Sweep range: -0.2 – +1.0 V vs. Ag/AgCl
Sweep rate: 1 – 20 mV s^{-1}

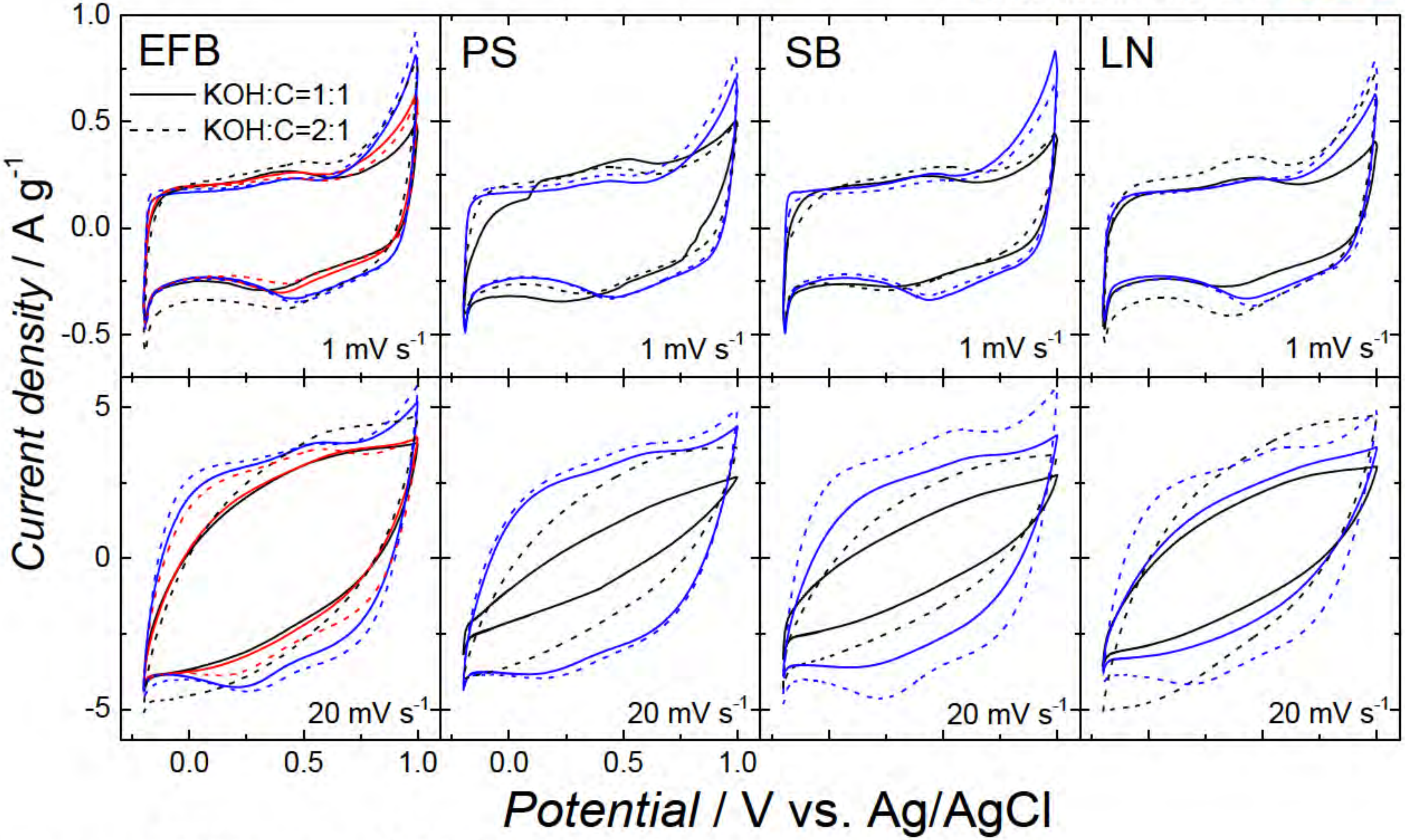
Charge and discharge (CD): quantitative

Cut off potential: 0 – +0.6 V vs. Ag/AgCl
Current: 0.1, 0.2, 0.5, 1, 2 A g^{-1}

by KU

Summary of CVs

*Activation @700°C 800°C 900°C

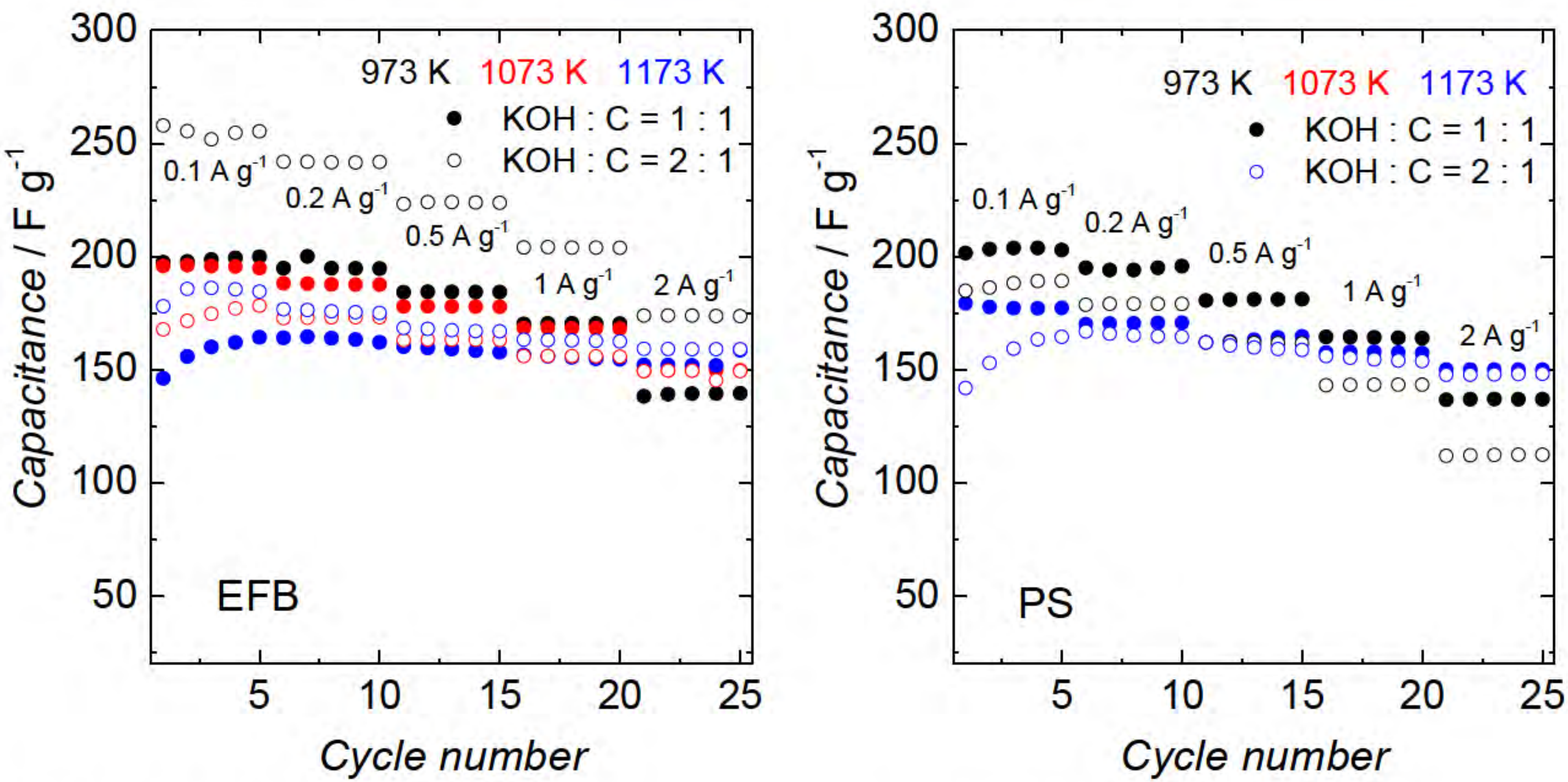


Increase of KOH ratio → higher capacity

Increase of activation temperature → square shape and larger CV area at 20 mV s^{-1}

EFB samples: most promising?

Charge-discharge Analysis (1)

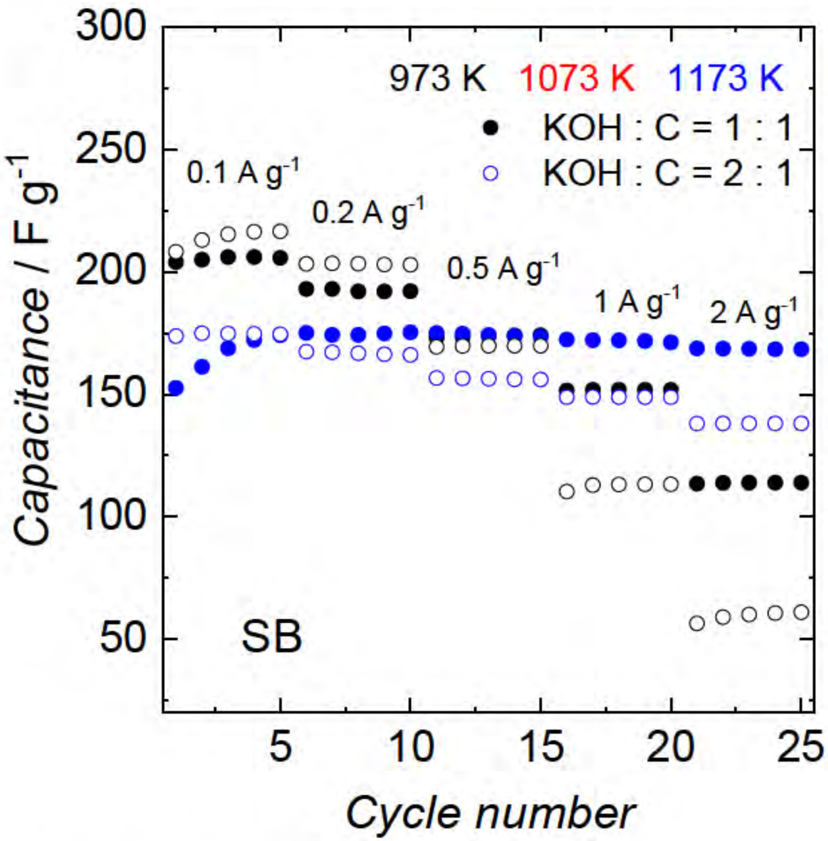


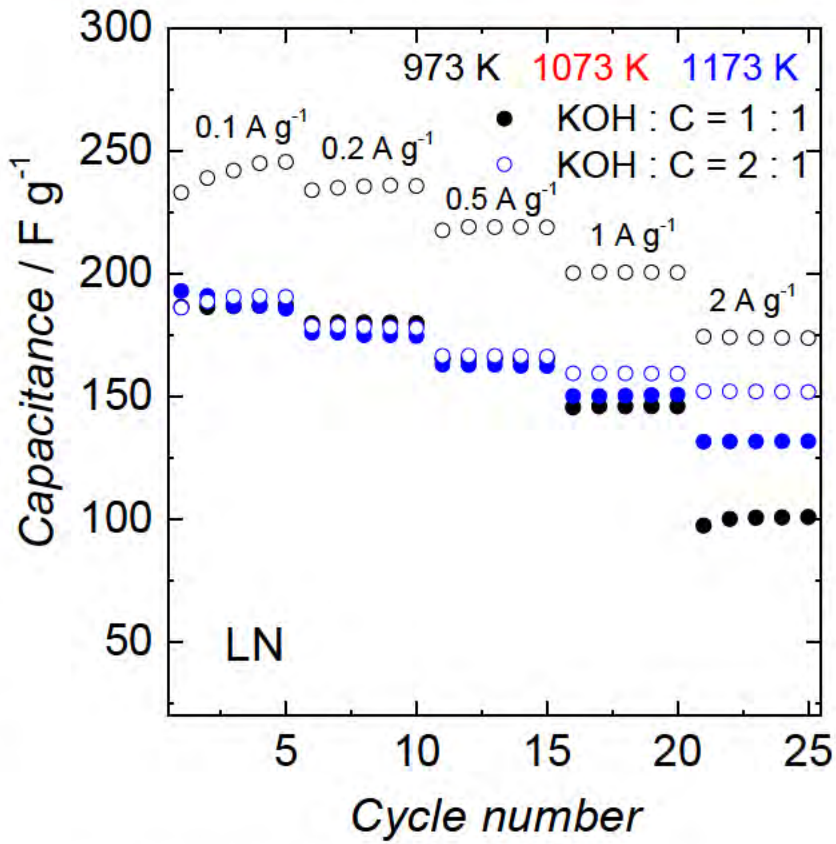
EFB activated with KOH/C=2 at 700°C
→ highest capacity at slow charge/discharge

PS activated at 700°C
→ better capacity at slow charge/discharge

Higher activation temperature
→ nearly independent capacitances on their current densities

Charge-discharge Analysis (2)





SB activated at 700°C
→ highest capacity at slow charge/discharge

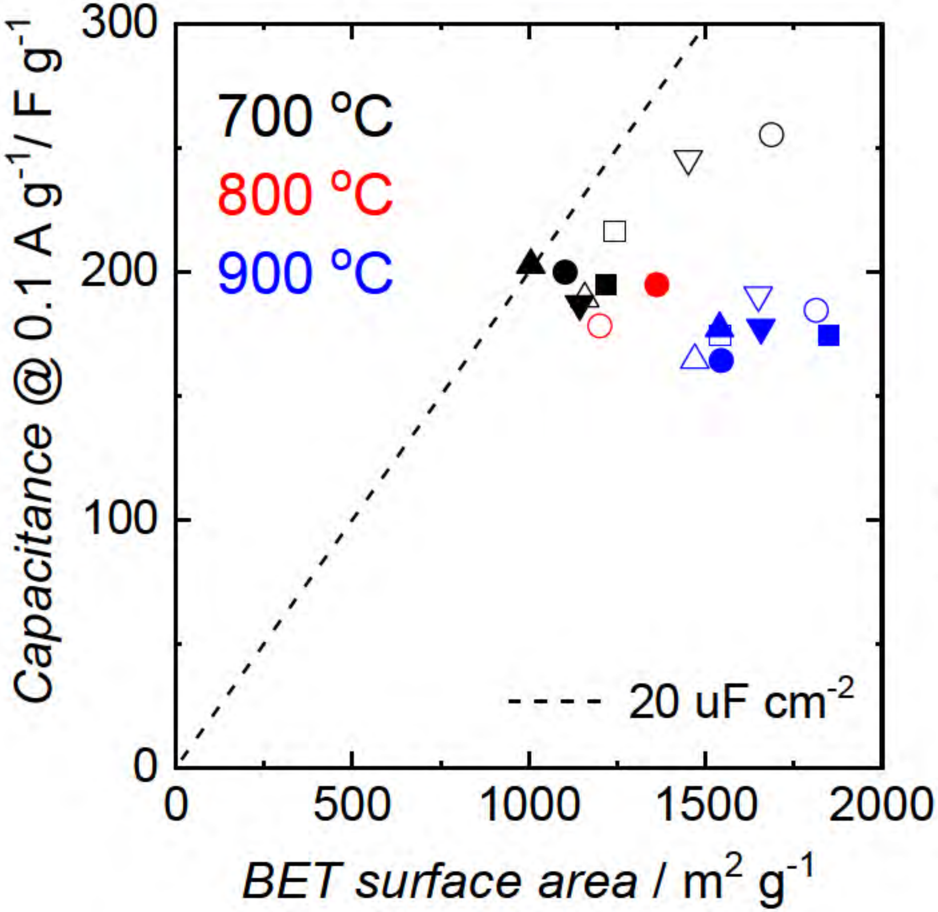
LN activated with KOH/C=2 at 700°C
→ better capacity at slow charge/discharge

Higher activation temperature
→ nearly independent capacitances on their current densities

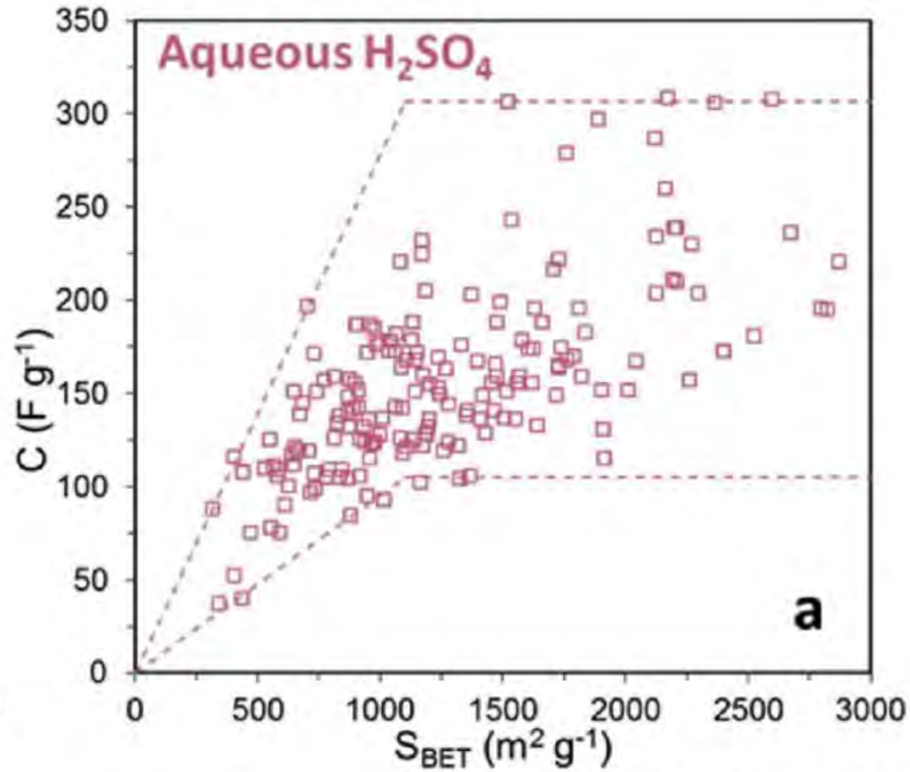
Summary of Capacitance

Materials	KOH:C by weight	Activation Temp. °C	Capacitance at each current density, F g^{-1} 0.1 A g^{-1}	0.2 A g^{-1}	0.5 A g^{-1}	1 A g^{-1}	2 A g^{-1}
Lignin (LN)	1:1	700	186.73	180.04	165.35	145.94	99.99
		900	176.55	170.39	160.41	149.38	123.28
	2:1	700	254.46	252.64	242.29	231.54	214.78
		900	189.35	178.36	166.47	159.40	151.99
Palm Empty Fruits Bunches (EFB)	1:1	700	198.58	195.80	184.25	170.30	139.07
		800	195.58	187.74	177.84	168.27	149.56
		900	157.61	163.53	158.94	155.39	153.20
	2:1	700	277.02	251.03	228.26	212.36	188.97
		800	175.28	172.93	163.08	155.87	148.55
		900	183.89	175.79	167.51	162.83	159.00
Sugarcane Bagasse (SB)	1:1	700	192.40	194.17	184.49	169.15	131.84
		900	165.78	174.73	174.21	171.87	168.51
	2:1	700	213.85	203.17	169.68	112.55	59.39
		900	178.14	166.72	156.29	148.84	138.06
Palm Shell (PS)	1:1	700	289.47	223.75	193.48	157.23	n/a
		900	182.06	170.43	163.30	157.59	149.97
	2:1	700	223.52	212.30	171.56	187.70	154.30
		900	156.31	165.37	159.99	154.61	147.82

Trend of capacitance vs. BET surface area



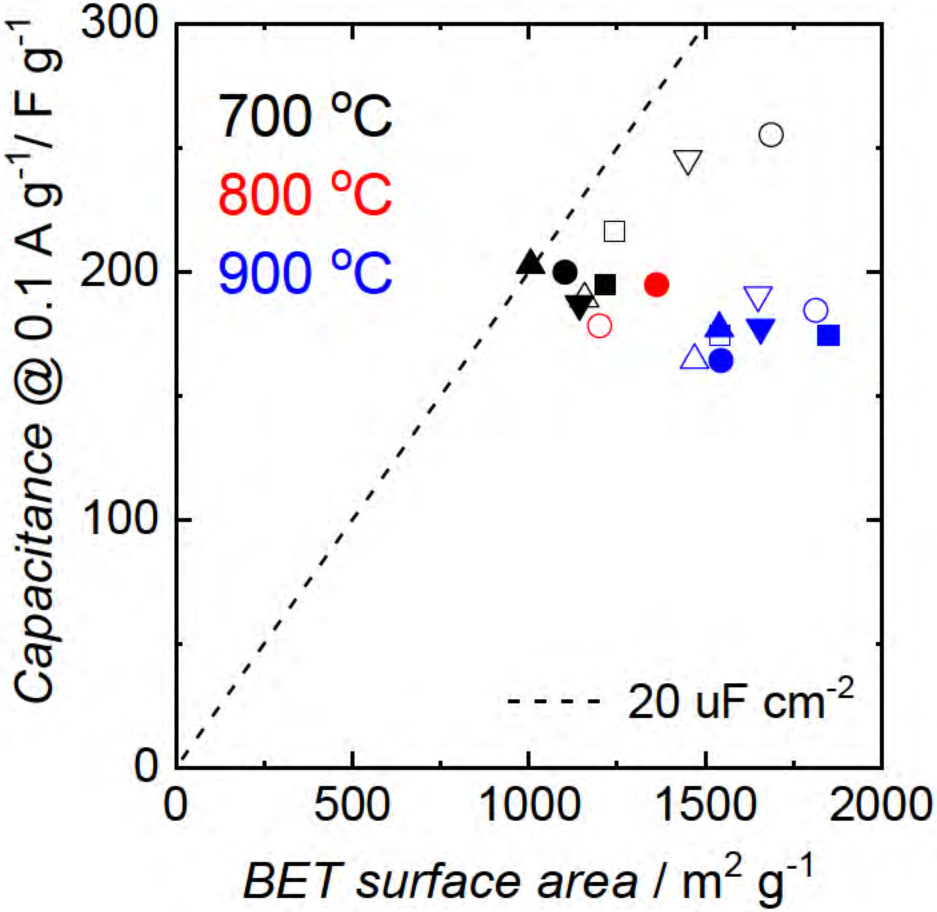
Database of the trend



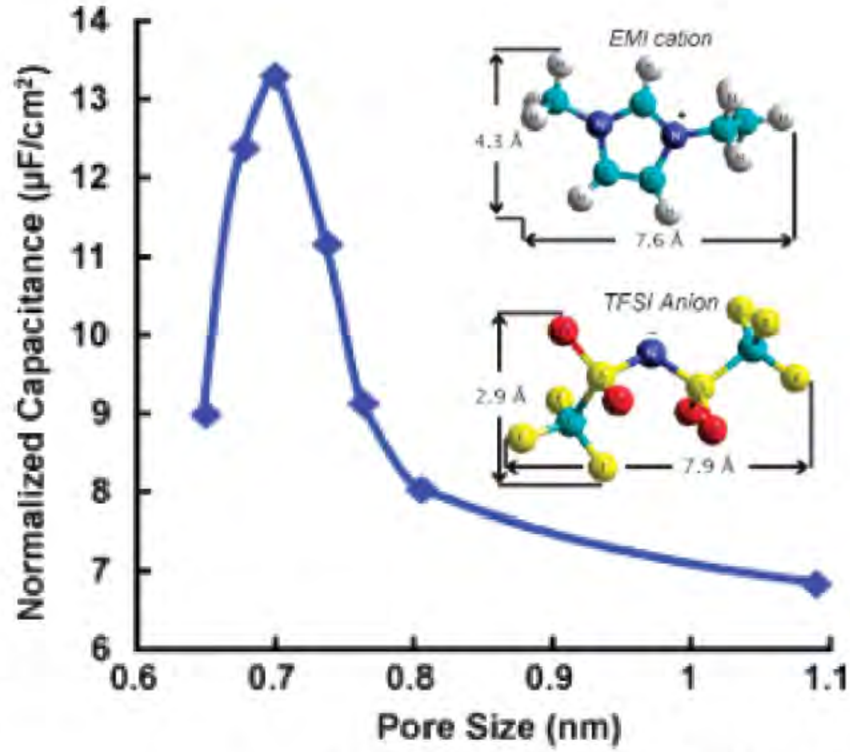
Carbon, **122** (2017) 434.

- At fixed activation temperature, capacitances were somewhat proportional to their BETs.

Trend of capacitance vs. BET surface area



Advantage of micropore



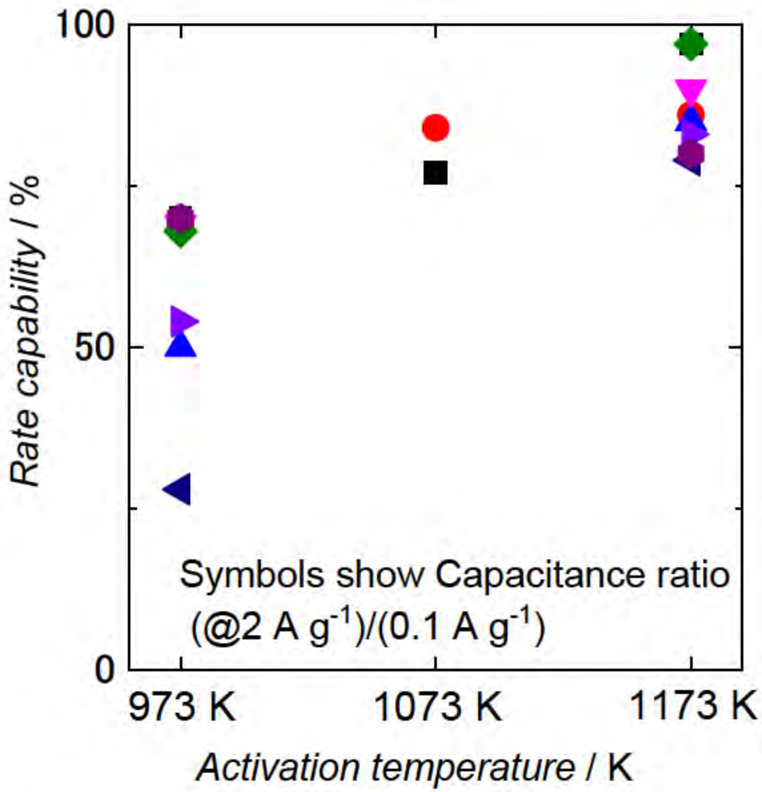
J. Am. Chem. Soc., **130** (2008) 2730.

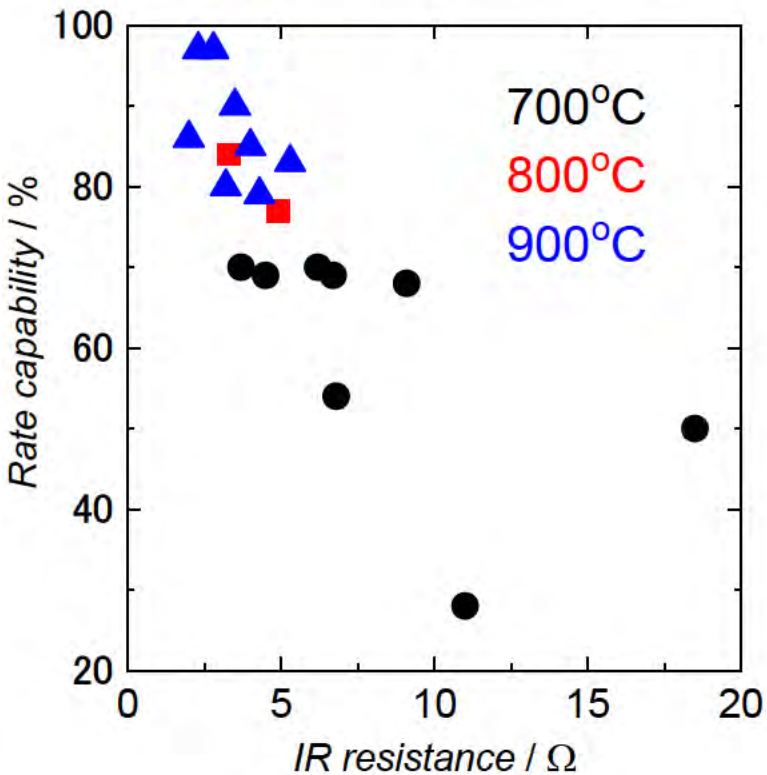
- At fixed activation temperature, capacitances were somewhat proportional to their BETs.
- Higher activation temperature led to lower areal capacity due to increase of mesopore.

Development of micropore is important for efficient charge accumulation.

Comparison of rate capability*

*Stability of capacitance at quick charge/discharge





Activation at higher temperature

- leads to increase mesopore, which is important for smooth ionic diffusion.
- leads to lower electrical resistance (graphite > amorphous carbon).

Activation at higher temperature: better rate capability

Correlation between N_2 adsorption/desorption results and capacitor properties for EFB

N_2 adsorption/desorption results of EFB

KOH:C	Temp.	BET	Micropore (t-plot)	External pore (t-plot)	Pores (1.7 – 300 nm)	Capacitance @ 0.1 A g^{-1}	Rate capability
1:1	700°C	1103 m^2 g^{-1}	1133 m^2 g^{-1}	-29 m^2 g^{-1}	1 m^2 g^{-1}	199.8 F g^{-1}	70%
1:1	800°C	1362 m^2 g^{-1}	1208 m^2 g^{-1}	153 m^2 g^{-1}	192 m^2 g^{-1}	194.8 F g^{-1}	77%
1:1	900°C	1841 m^2 g^{-1}	1449 m^2 g^{-1}	96 m^2 g^{-1}	134 m^2 g^{-1}	164.2 F g^{-1}	82%
2:1	700°C	1687 m^2 g^{-1}	1704 m^2 g^{-1}	-17 m^2 g^{-1}	1 m^2 g^{-1}	255.3 F g^{-1}	69%
2:1	800°C	1201 m^2 g^{-1}	967 m^2 g^{-1}	234 m^2 g^{-1}	247 m^2 g^{-1}	178.2 F g^{-1}	84%
2:1	900°C	1814 m^2 g^{-1}	1539 m^2 g^{-1}	275 m^2 g^{-1}	370 m^2 g^{-1}	184.4 F g^{-1}	86%

KOH:C=2:1 at 700°C sample: largest micropore volume → highest capacitance
(Increase of KOH ratio and low activation temperature might be the key?)

Trade-off correlation between capacitance and rate capability

Non-aqueous electrolyte-based capacitor

Compared with aqueous capacitor…

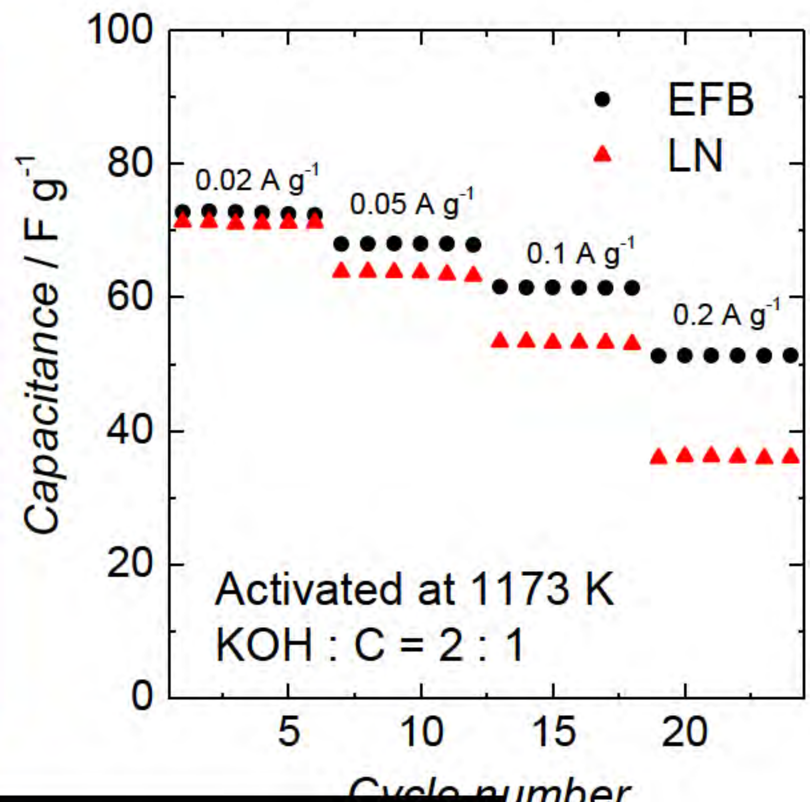
- ☺ Larger capacity
- ☺ Higher operating voltage up to 4 V (due to better electrochemical stability)
- ☹ Lower areal capacitance (roughly half, due to larger ionic size)
- ☹ Lower rate capability (due to lower ionic conductivity of electrolyte)

Electrochemical Testing

Working electrode (W.E.): Carbon electrode
Counter electrode (C.E.): Pt mesh
Reference electrode (R.E.): Ag/Ag^{+} electrode
Electrolyte: 1 M $(C_4H_9)_4NBF_4$/propylene carbonate

Charge and discharge (CD): quantitative

Cut off potential: -1 – 0 V vs. Ag/Ag^{+}
Current: 0.02, 0.05, 0.1, 0.2 A g^{-1}



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Summary

- Increase in activation temperature results in:
  - Higher surface area
  - More of larger and smaller pores in micropore/mesopore structure
  - Occurrence of graphitized structure 900°C on 21900 EFB
- Electrochemical Testing
  - Most biomass show decreased capacitance at higher current density
  - Optimum Temperature of Activation
    - 700°C gave the highest capacitance
  - Optimum Ratio of Activating Agent
    - 2:1 Ratio mostly gave higher capacitance (excepts Palm Shell)
  - Most Optimum Condition among EFB,PS and SB
    - 2:1 700 EFB
      - Best capacitance at both low and high current densities
      - Average of 5 cycles

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- 4th-year undergraduate students from Thammasat University:
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  - Mr. Tan Vongvarotai
- Kyoto University
- JASTIP
- NSTDA

Thank you