

# Development of Activated Carbons from Biomass for Energy Storage Applications

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Japan

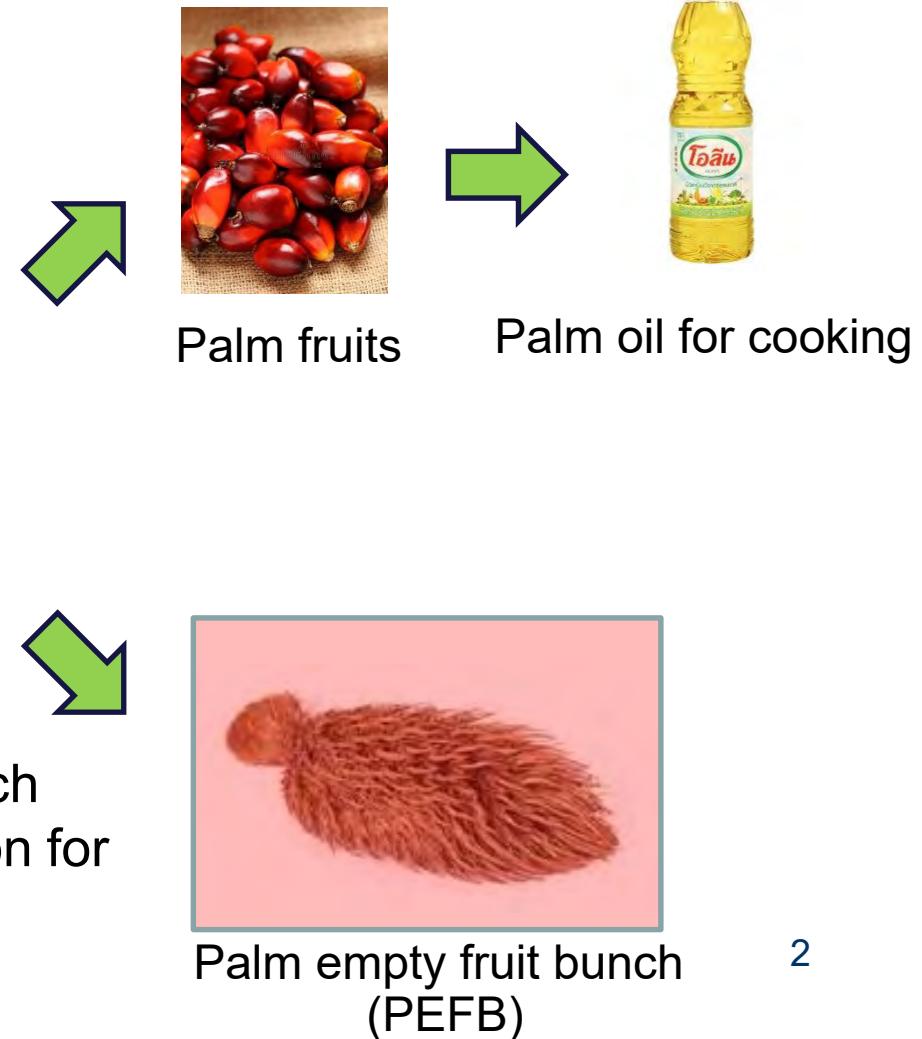
# Palm empty fruit bunch (PEFB) for energy storage application



Palm plantation



Palm fruit bunch



- PEFB is a carbon-based material which can be processed into activated carbon for energy storage application

# Characteristics of PEFB

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	78.10	21.30	0.60	55.18	5.46	0.11	38.71	33.36	43.26	12.82
PEFB	<b>77.30</b>	<b>17.00</b>	<b>5.70</b>	<b>46.24</b>	<b>5.67</b>	<b>1.44</b>	<b>40.94</b>	<b>13.28</b>	<b>36.42</b>	<b>18.81</b>
Sugarcane bagasse	75.00	16.20	8.80	47.55	5.79	0.55	37.38	6.67	29.02	24
Palm shell	77.00	21.20	1.80	54.02	5.19	0.57	38.36	46.69	32.97	12.94
Corn husk	80.70	16.80	2.50	43.41	6.76	0.72	46.62	5.99	37.46	37.93
Eucalyptus wood	81.90	17.70	0.40	47.67	6.79	0.13	45.01	20.18	60.99	4.99

Note: Results from Renewable Energy Laboratory, MTEC, Thailand

- High ash content
- Low carbon content

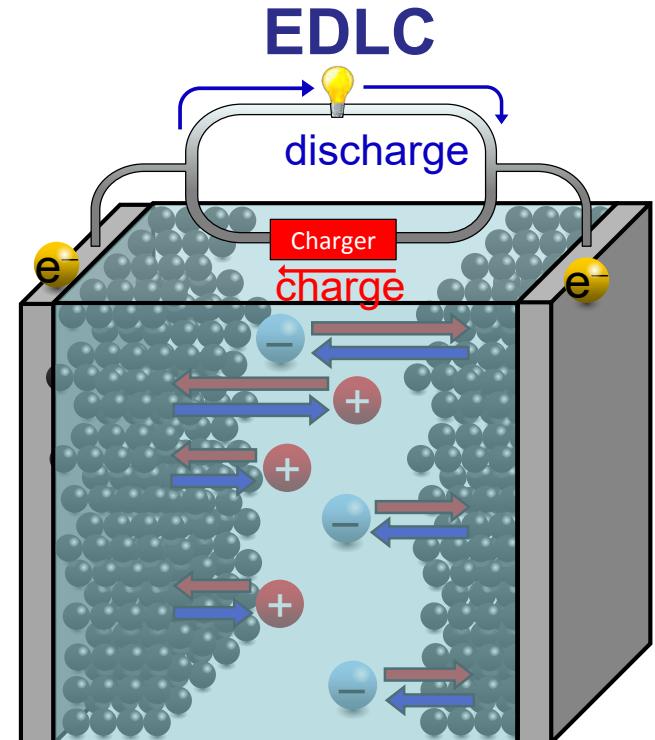
# Collaboration between MTEC/NSTDA & KU



Synthesis of  
activated carbon  
(MTEC/NSTDA)



Electrochemical  
testing  
(KU)



Positive  
electrode      Negative  
electrode

# Roadmap towards Sustainable Development Goals

7.a By 2030, enhance international cooperation to facilitate access to clean energy research and technology, including renewable energy, energy efficiency and advanced and cleaner fossil-fuel technology, and promote investment in energy infrastructure and clean energy technology

Preparation of activate carbon produced from carbonisation and activation process for energy storage application

2016



2017

Investigation of carbonisation parameters on carbon properties

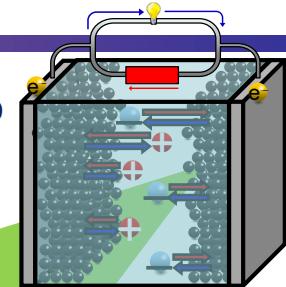


2019

Optimal condition/method to produced activated carbon for energy storage application

2020

Preparation of activate carbon produced from hydrothermal carbonisation and activation process for energy storage application



9.5 Enhance scientific research, upgrade the technological capabilities of industrial sectors in all countries, in particular developing countries, including, by 2030, encouraging innovation and substantially increasing the number of research and development workers per 1 million people and public and private expenditure on research and development as a GNI percentage

# Production of activated carbon from PEFB



## Activation method

- ❖ Physical activation
  - $\text{CO}_2$
  - Steam
  - Air/Oxygen

## ❖ Chemical activation

- $\text{ZnCl}_2$
- $\text{H}_3\text{PO}_4$
- Alkali (i.e.  $\text{KOH}$ ,  $\text{NaOH}$ )

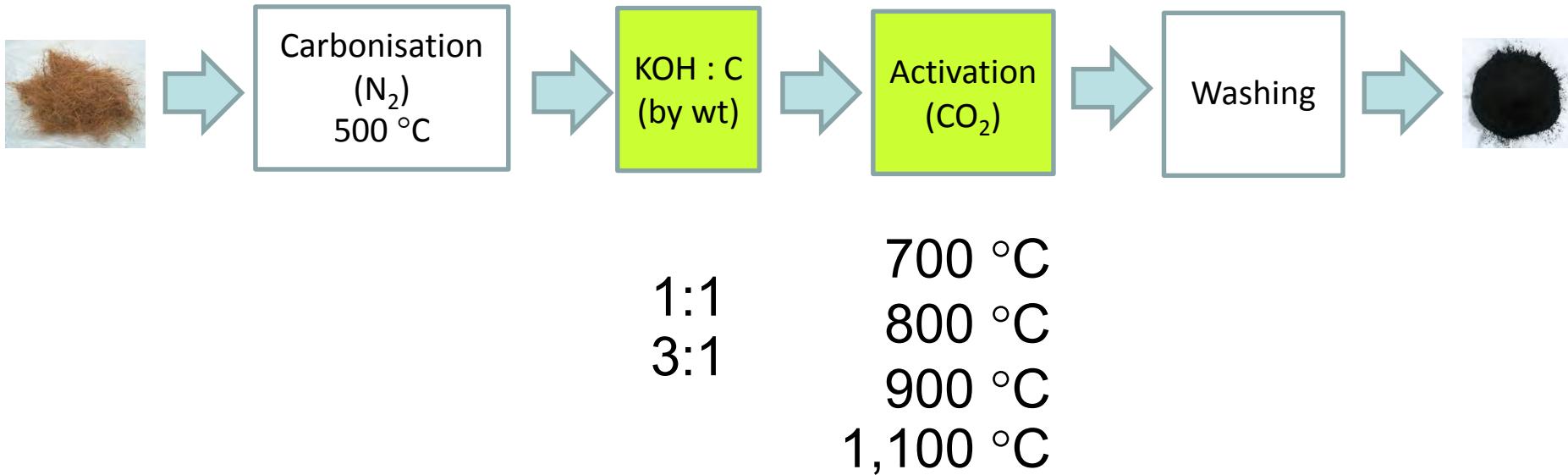
- 
1. Effect of activation temperature and KOH/C ratio on physical properties
  2. Effect of KOH-mixing sequence on physical properties

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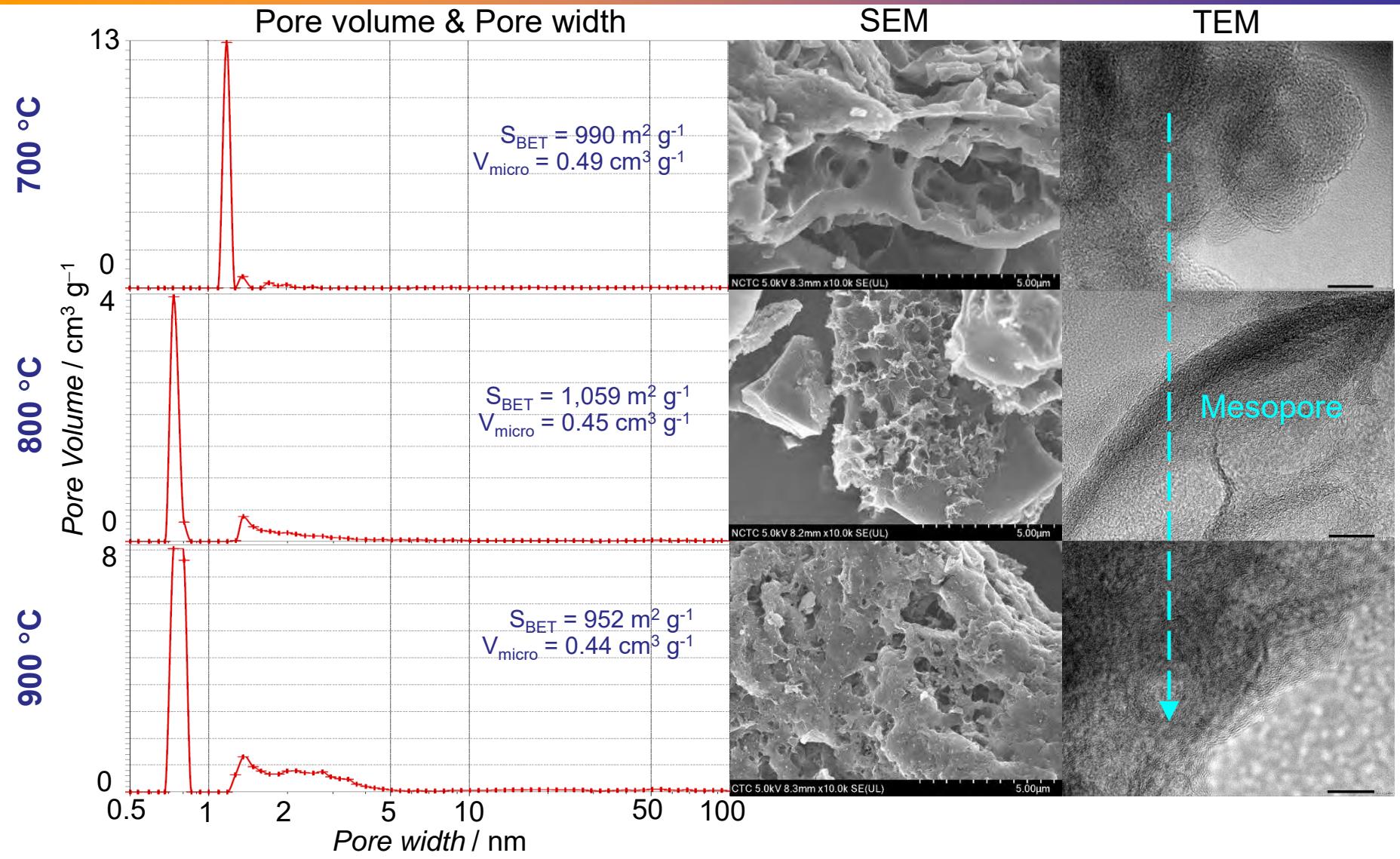
1. Effect of activation temperature and KOH/C ratio on physical properties

2. Effect of KOH-mixing sequence on physical properties

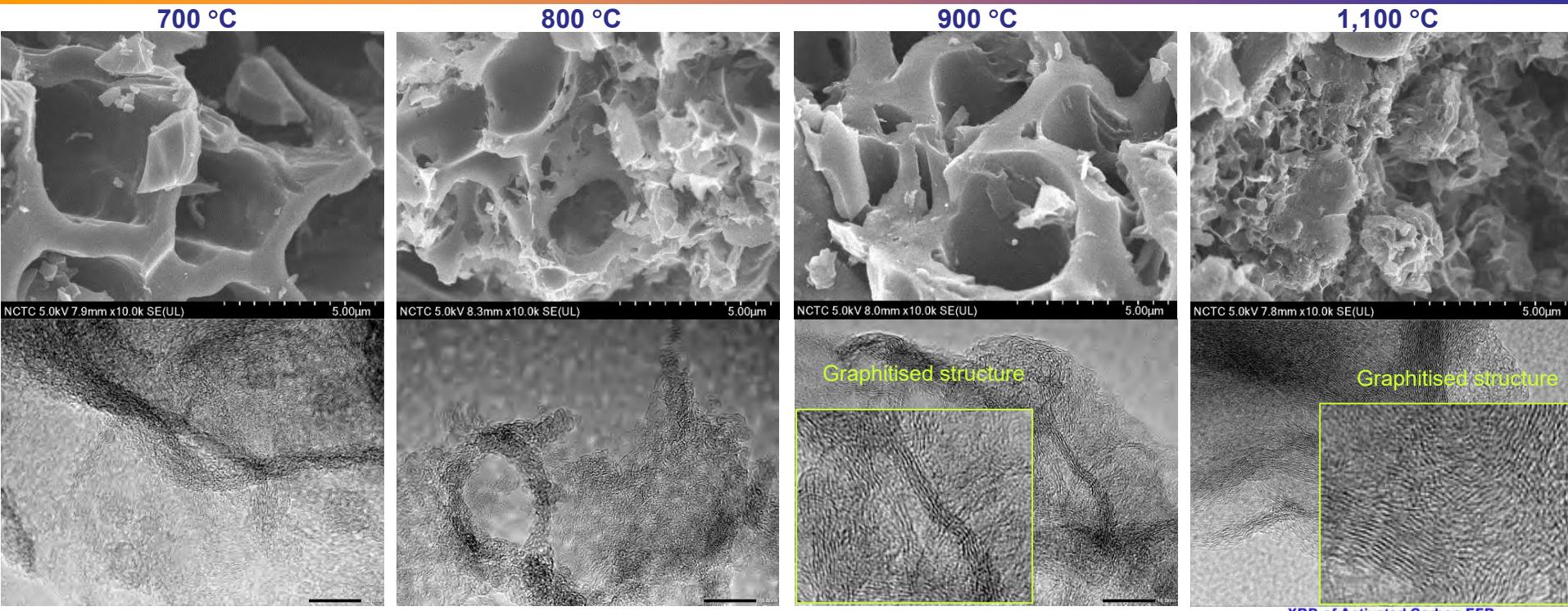
# 1. Effect of activation temperature and KOH/C ratio on physical properties



# KOH/C = 1

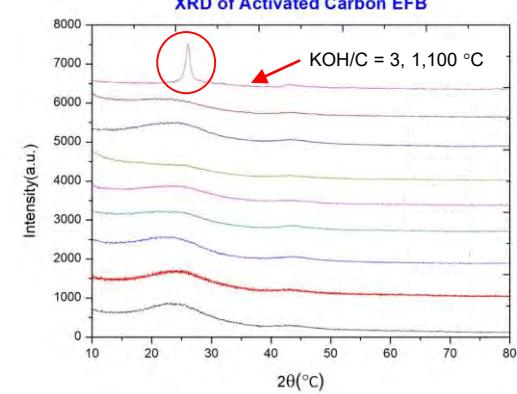


# KOH/C = 3 (1/2)

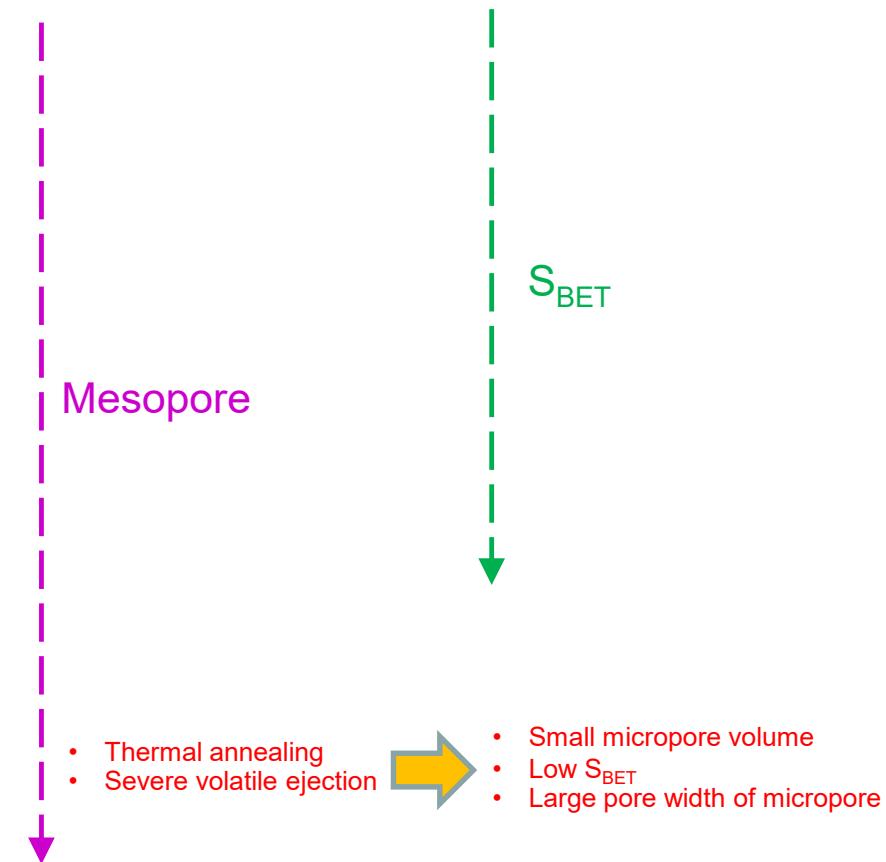
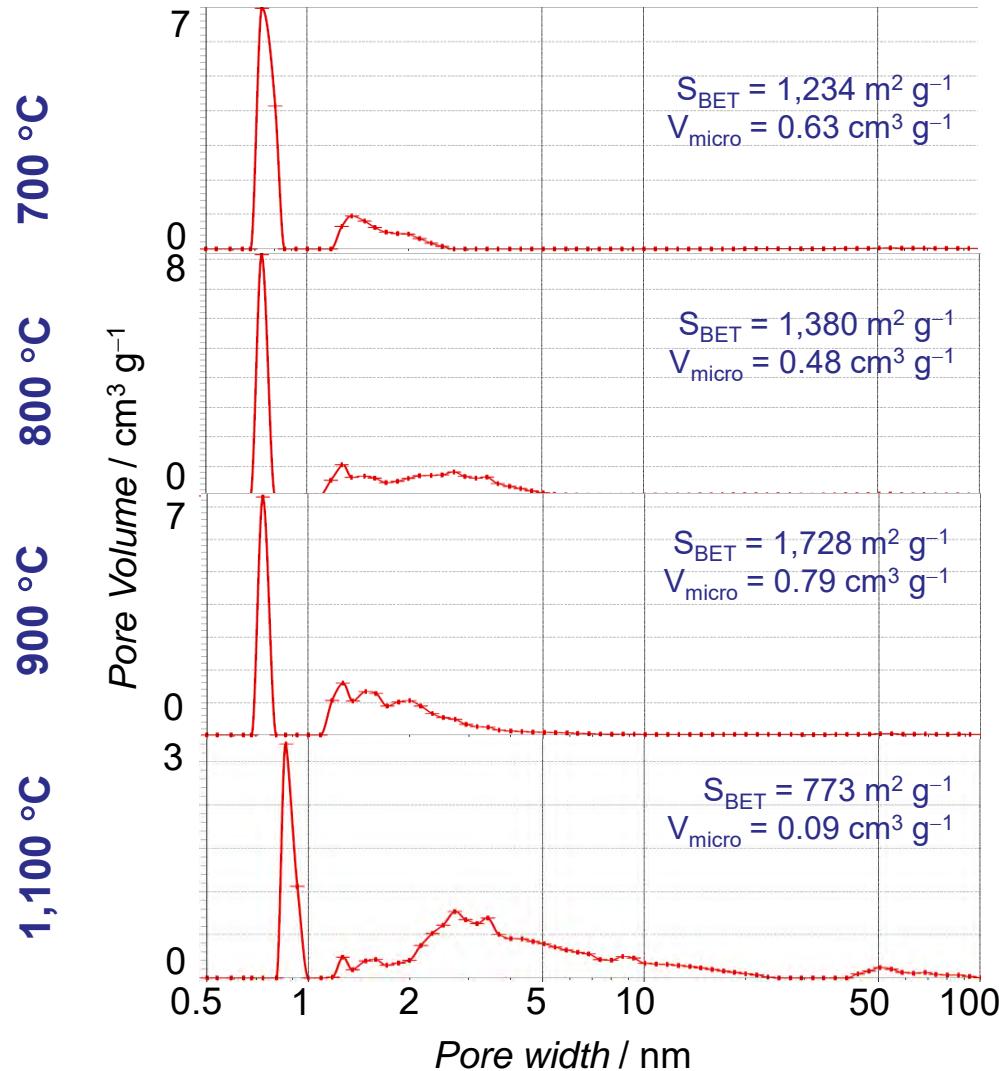


Graphitised carbon structure: 900 °C and 1,100 °C (TEM images)

Crystalline carbon: 1,100 °C (XRD spectrum)

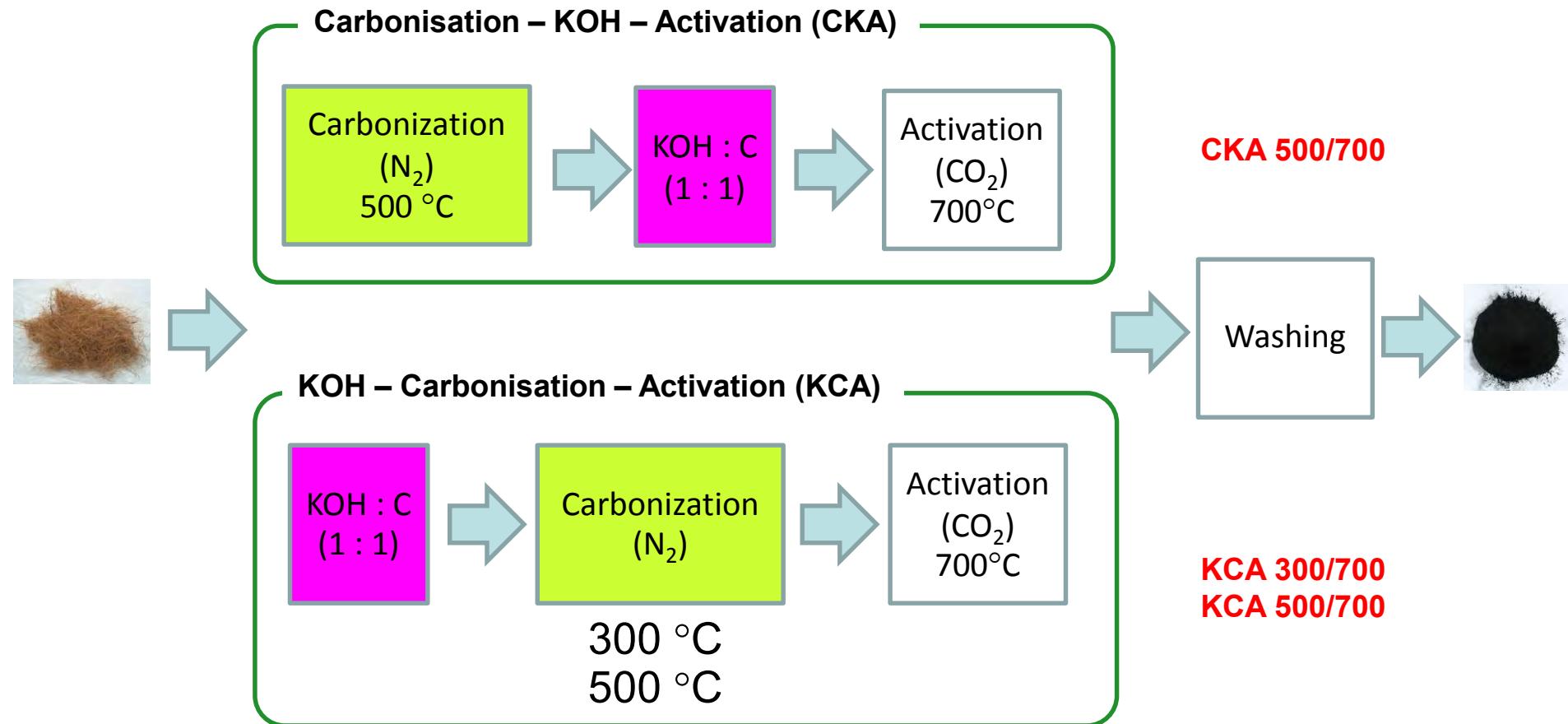


# KOH/C = 3 (2/2)

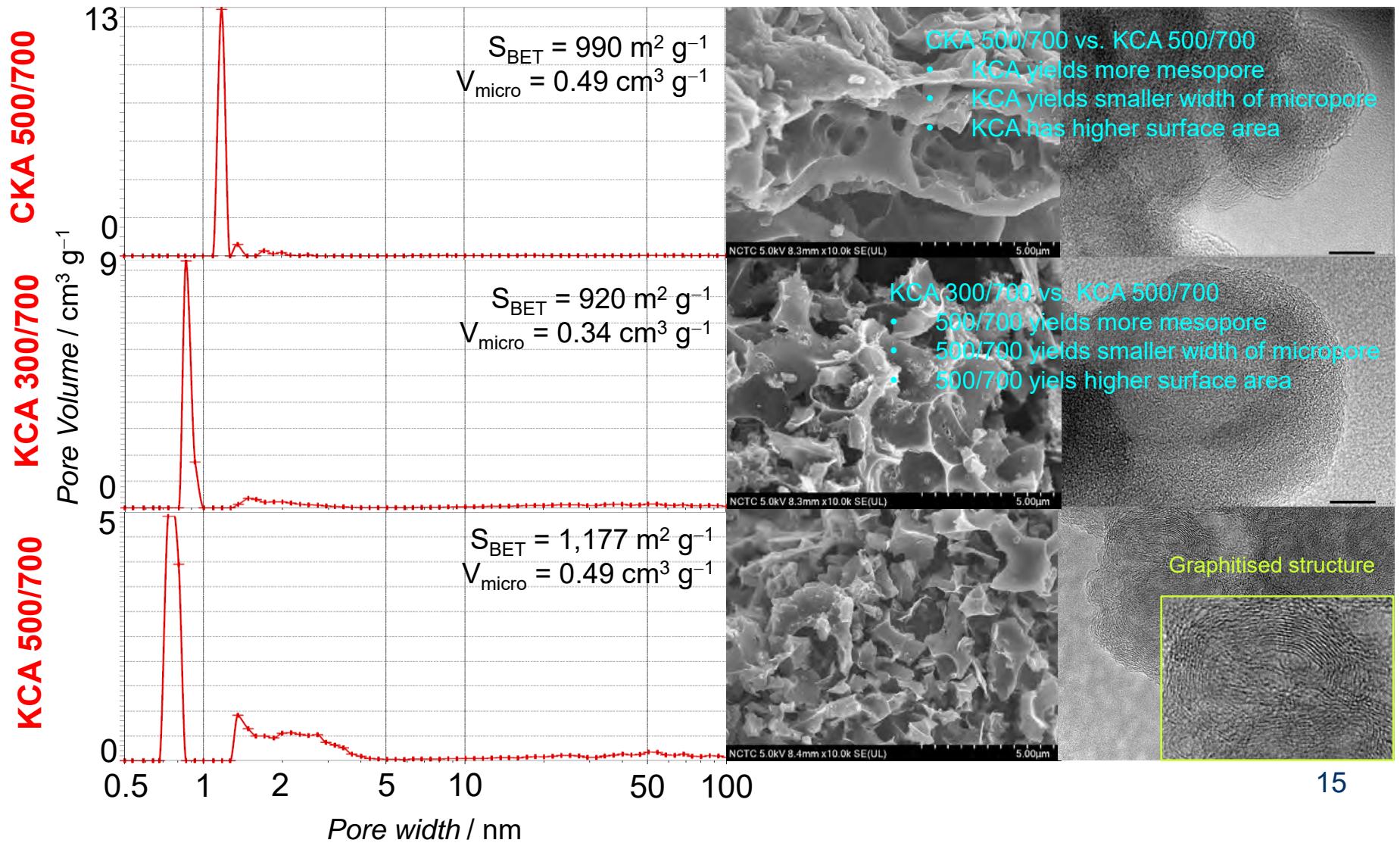


- 
1. Effect of activation temperature and KOH/C ratio on physical properties
  2. Effect of KOH-mixing sequence on physical properties

## 2. Effect of KOH-mixing sequence on physical properties



# CKA vs. KCA



# Summary

- Increase in KOH/C ratio results in higher degree of activation
- Increase in activation temperature results in:
  - Higher surface area
  - More mesoporous structure
  - Occurrence of graphitised structure
- Severe temperature treatment ( $1,100^{\circ}\text{C}$ , KOH/C = 3) causes small micropore volume, low surface area and large pore width of micropore.
- The sequence of KOH mixing affects the quality of pore characteristics.
  - KCA process >> CKA process
  - KCA process – activation temperature:  $500^{\circ}\text{C} >> 300^{\circ}\text{C}$

# Kyoto visit

## 04.01.18 – 26.01.18



# Acknowledgements

- MTEC: Dr. Sumittra Charojrochkul, Mr. Thanathon Sesuk
- 4<sup>th</sup>-year undergraduate students from Thammasart University: Ms. Nattida Konginyai, Ms. Pakawan Prasatsoong
- Kyoto University: Prof. Takeshi Abe, Asst. Prof. Yuto Miyahara
- JASTIP
- NSTDA

# Development of Activated Carbons from Biomass for Energy Storage Applications

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MTEC\*



# Use of biomass for energy storage applications

Kyoto University

Palm tree

Palm fruit



Empty fruit bunches, kernel shells, mill effluents



Functionalization

Bioenergies: Bioethanol, biogas, biohydrogen

Functionalized materials: Bioplastic, activated carbon



Adsorption of pollutants, energy storage applications

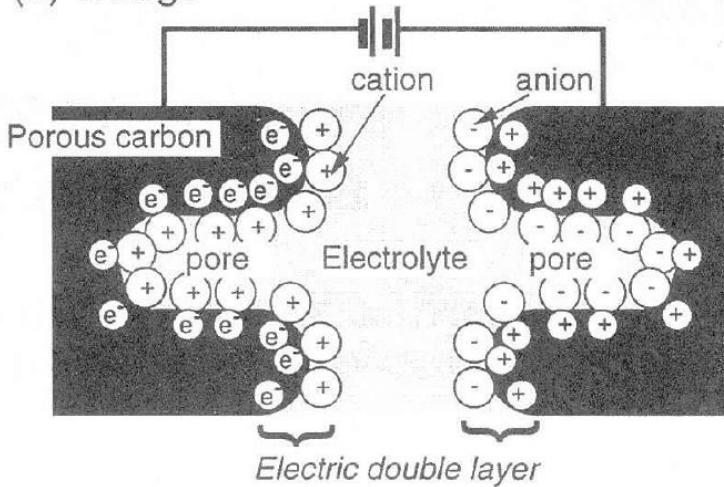
# Energy storage application

## Electric double-layer capacitor (EDLC)

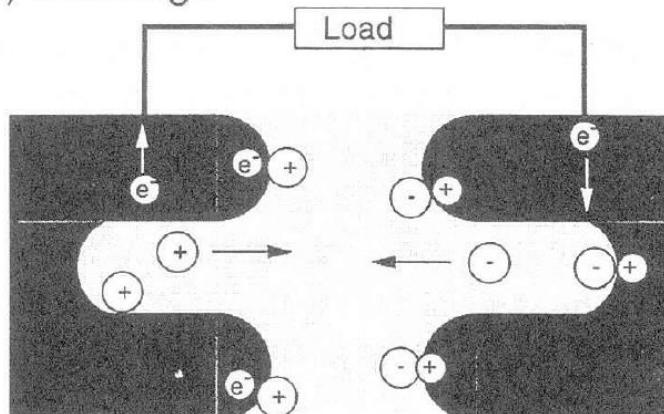
Kyoto University

### Schematic illustration of EDLC

(a) charge



(b) discharge



### Advantages of EDLC

- Long life (> 1,000,000 charge discharge)
- Fast charge and discharge
- High safety

*Reaction of EDLC; Adsorption and desorption of ion at the surface of electrode*

### Key factors for electrode

- Large surface area
- Electrochemical stability etc.

**Activated carbon: Suitable electrode material for EDLC**

# Objective: use of activated carbon from oil palm empty fruit bunch for EDLC electrode

Kyoto University

Oil palm empty fruit bunch



## Activation method

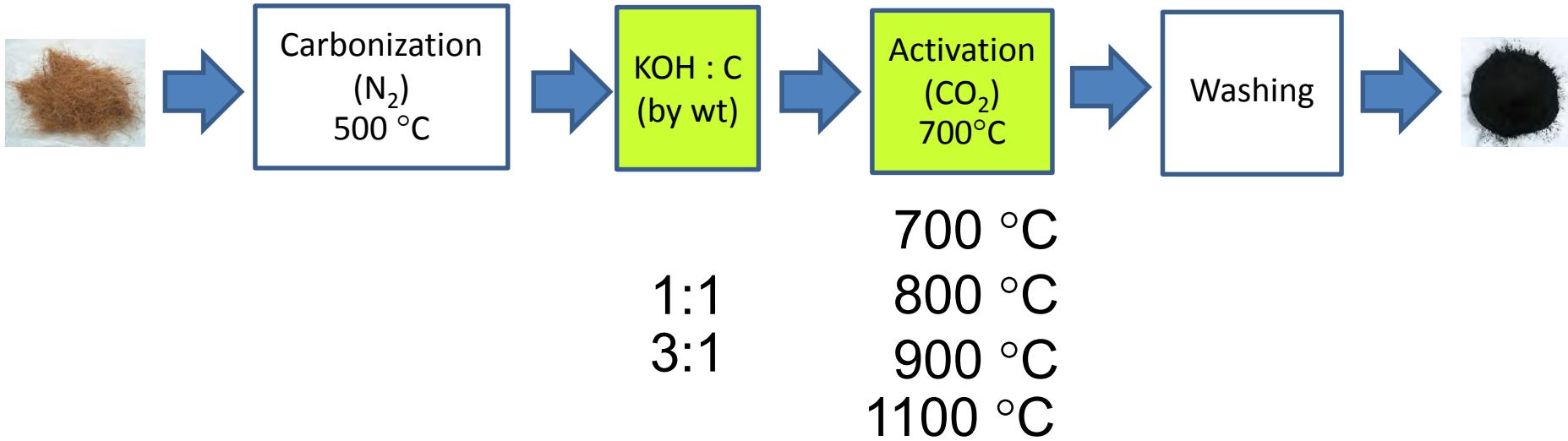
- Physical activation
  - CO<sub>2</sub> method
  - H<sub>2</sub>O method
  - Air (oxygen) method
- Chemical activation
  - Zinc chloride method
  - Phosphorus acid method
  - Alkali method

Measurement of EDLC performance of KOH-activated carbon synthesized from oil palm empty fruit bunches

Prepared by MTEC

# Effect of activation temperature and KOH/C ratio on EDLC performance

Kyoto University



by MTEC

# Electrochemical measurement of EDLC performance

Kyoto University

## Working electrode (W.E.)

Composite electrode enveloped by platinum foil

(biomass carbon : acetylene black : PTFE = 8 : 1 : 1 (by weight))

\*PTFE: Poly(tetrafluoroethylene), Teflon®

Counter electrode (C.E.): Pt mesh

Reference electrode (R.E.): Ag/AgCl electrode

Electrolyte: Ar-saturated 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

## Cyclic voltammetry (CV)

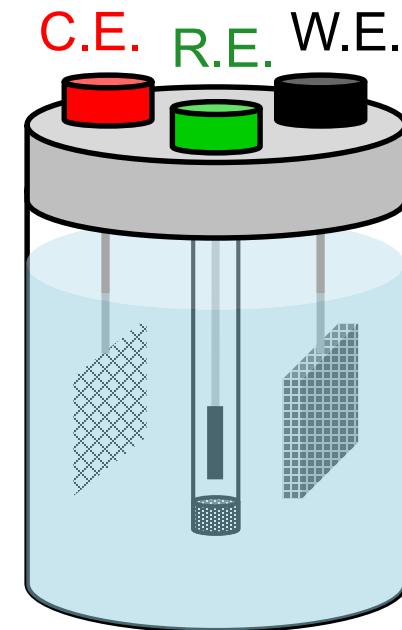
Sweep range: -0.2 ~ +1.0 V vs. Ag/AgCl

Sweep rate: 1 ~ 20 mV s<sup>-1</sup>

## Charge and discharge

Cut off potential: 0 ~ +0.6 V vs. Ag/AgCl

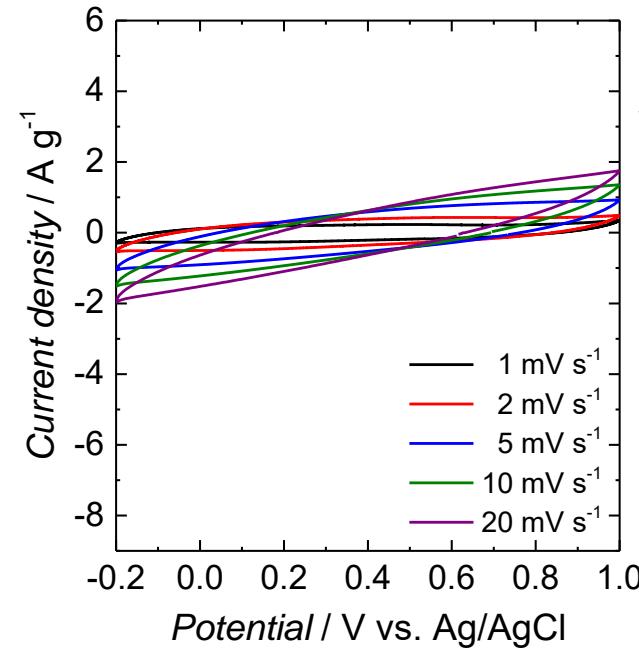
Current: 0.1, 0.2, 0.5, 1, 2 A g<sup>-1</sup>



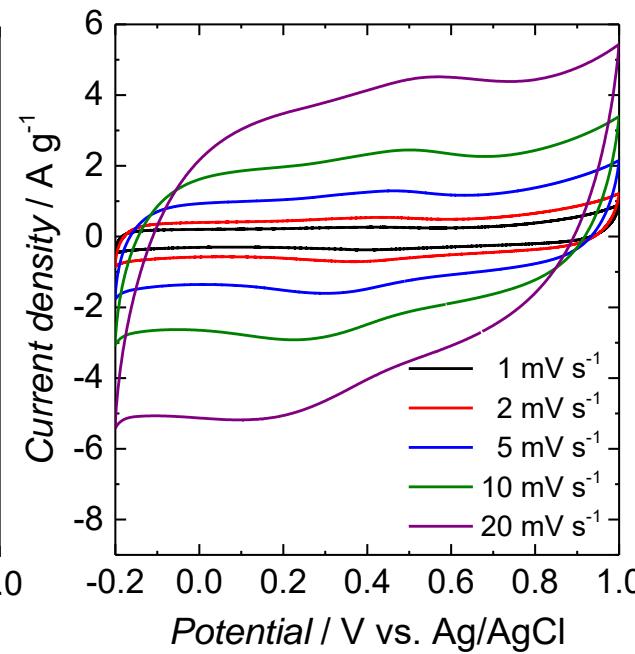
# CVs at various activation temperature (KOH/C = 1)

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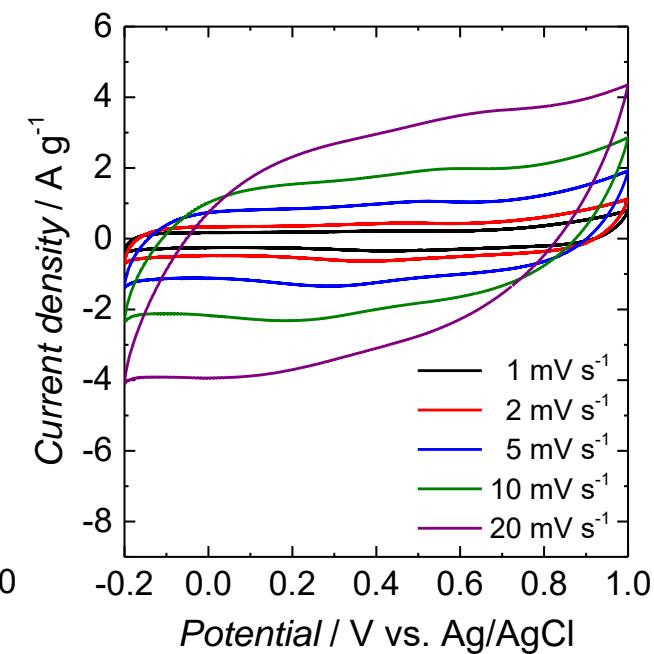
700 °C,  $S_{\text{BET}} = 990 \text{ m}^2 \text{ g}^{-1}$



800 °C,  $S_{\text{BET}} = 1059 \text{ m}^2 \text{ g}^{-1}$



900 °C,  $S_{\text{BET}} = 952 \text{ m}^2 \text{ g}^{-1}$

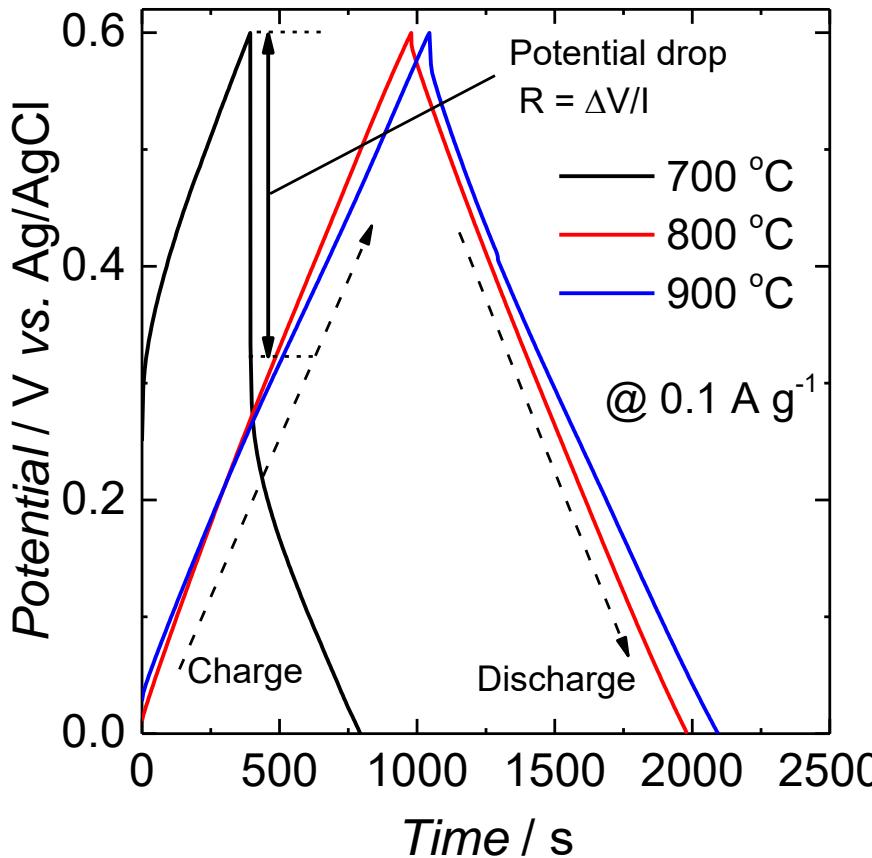


Carbons treated at 800 or 900 °C had large CV area.

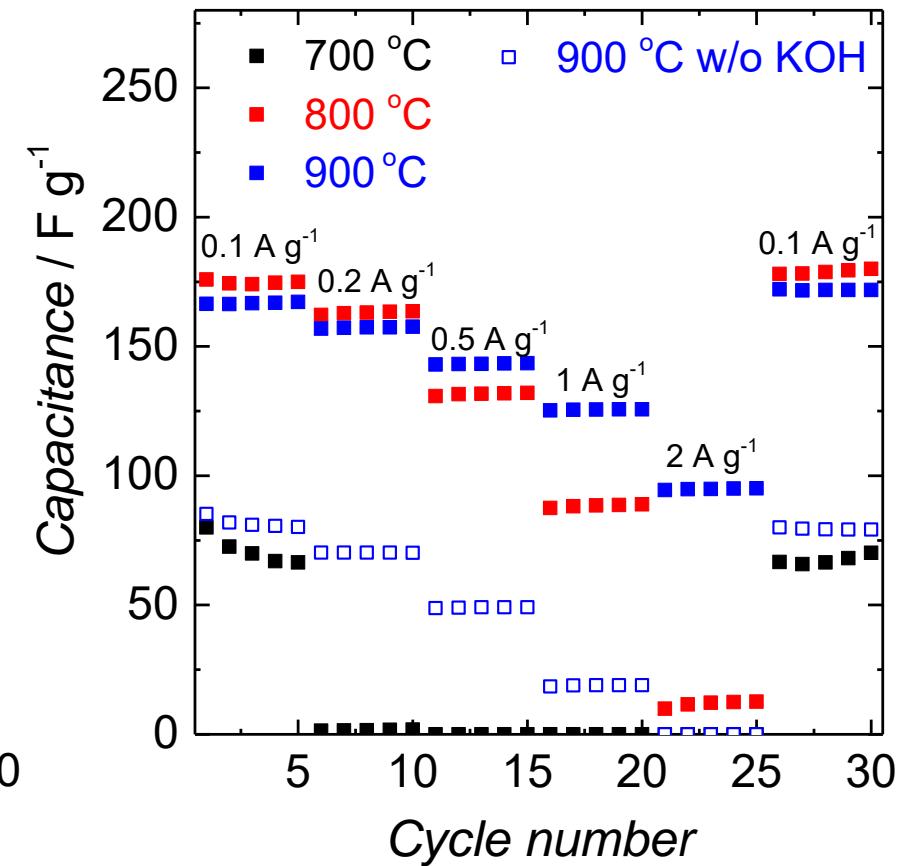
# Charge-discharge results at KOH/C = 1

Kyoto University

Profile of potential vs. time



Capacitance at each current density



700 °C: 370 [Ω]

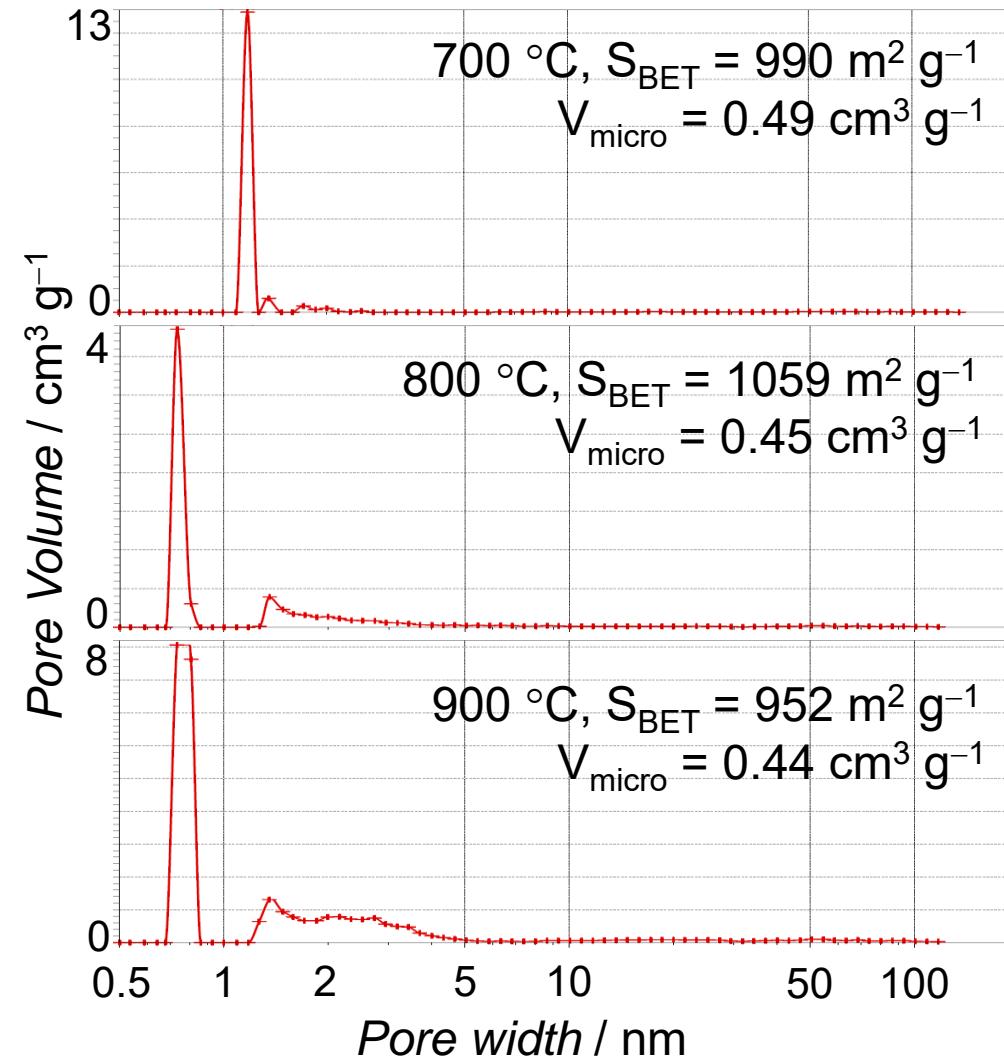
800 °C: 43 [Ω]

900 °C: 16 [Ω]

Higher temperature → better rate capability

# Discussion of the observed trend (KOH/C = 1) (1)

## Pore volume vs. Pore width

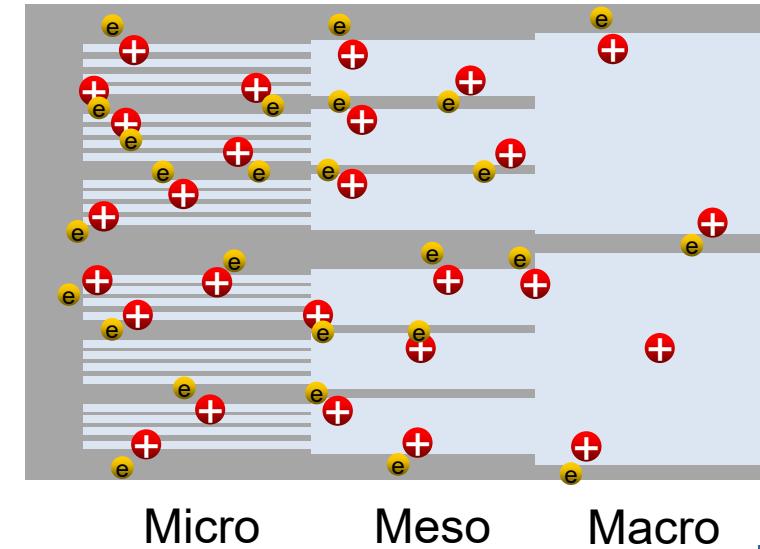


## Function of...

Micropore (< 2 nm)  
 Essential for high capacitance

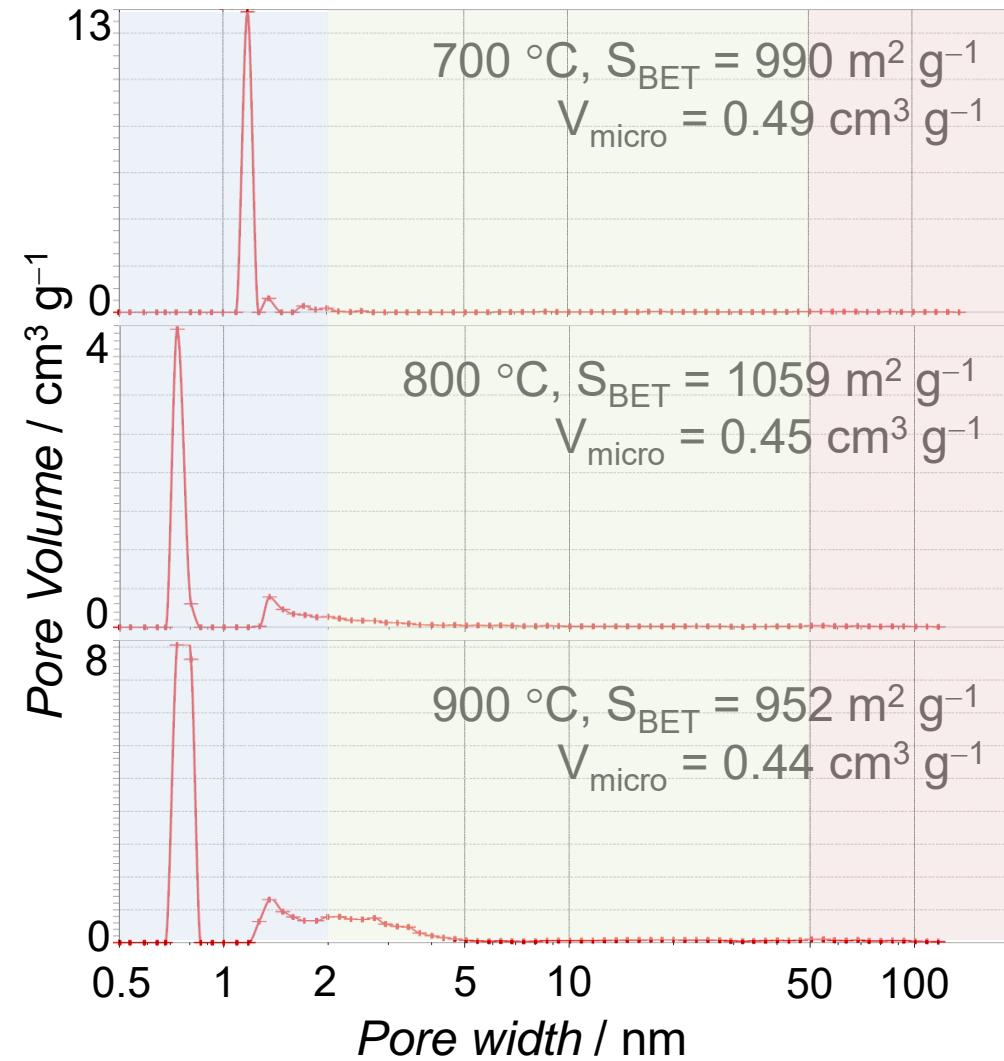
Mesopore (2 ~ 50 nm)  
 Essential for high rate capability

Macropore (> 50 nm)  
 Not essential



# Discussion of the observed trend (KOH/C = 1) (1)

## Pore volume vs. Pore width

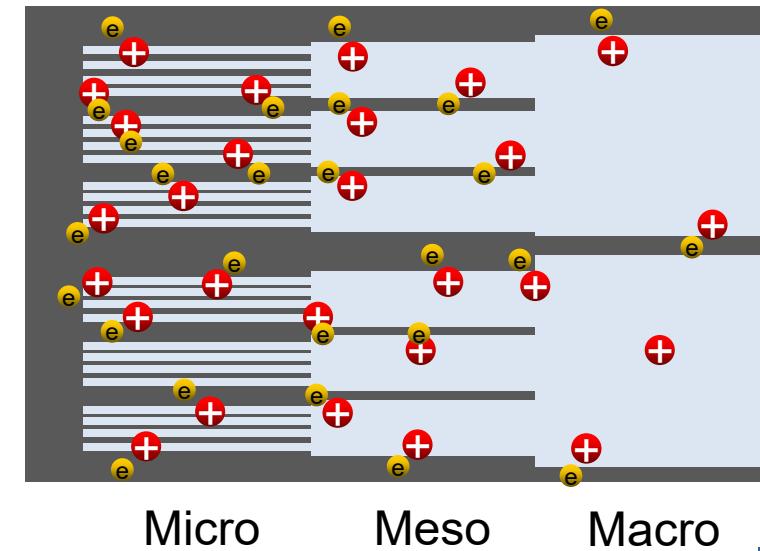


## Function of...

micropore (< 2 nm)  
 Essential for high capacitance

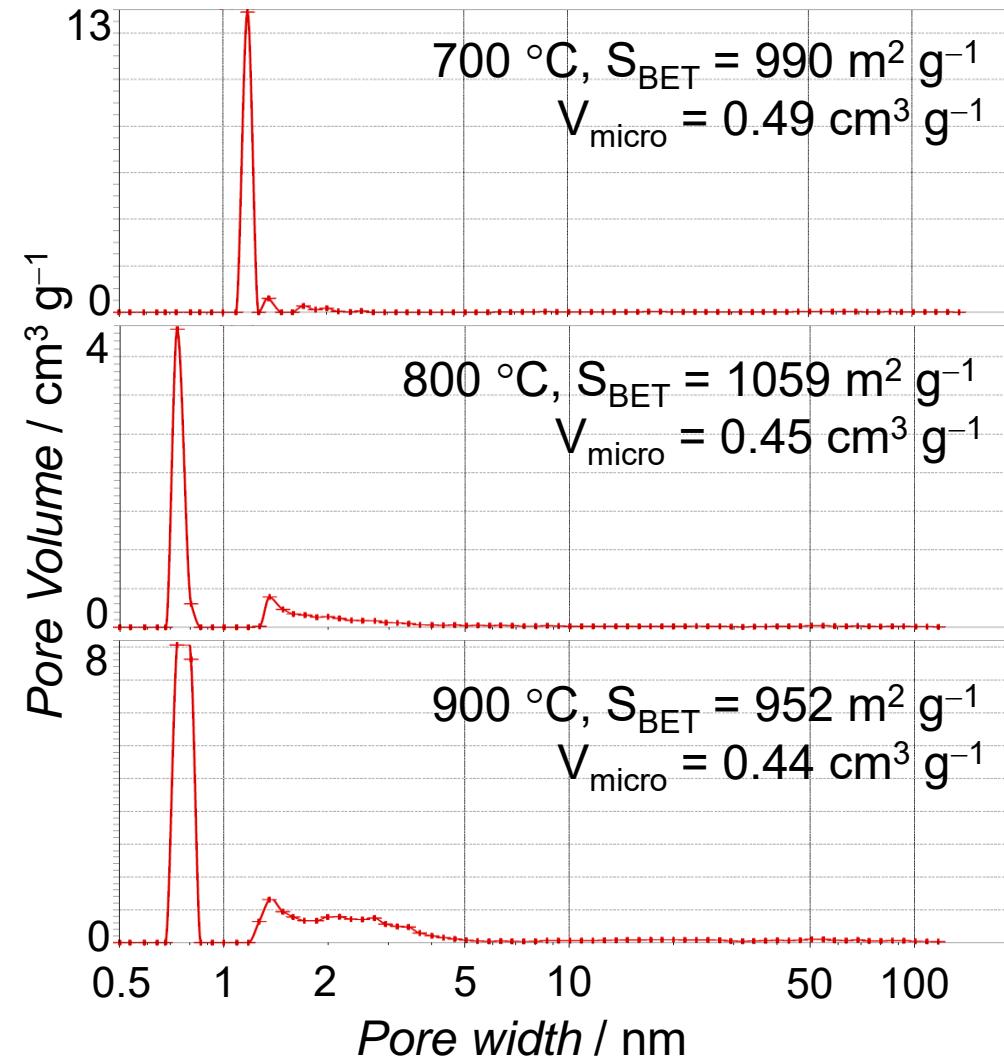
mesopore (2 ~ 50 nm)  
 Essential for high rate capability

macropore (> 50 nm)  
 Not essential



# Discussion of the observed trend (KOH/C = 1) (2)

## Pore volume vs. Pore width



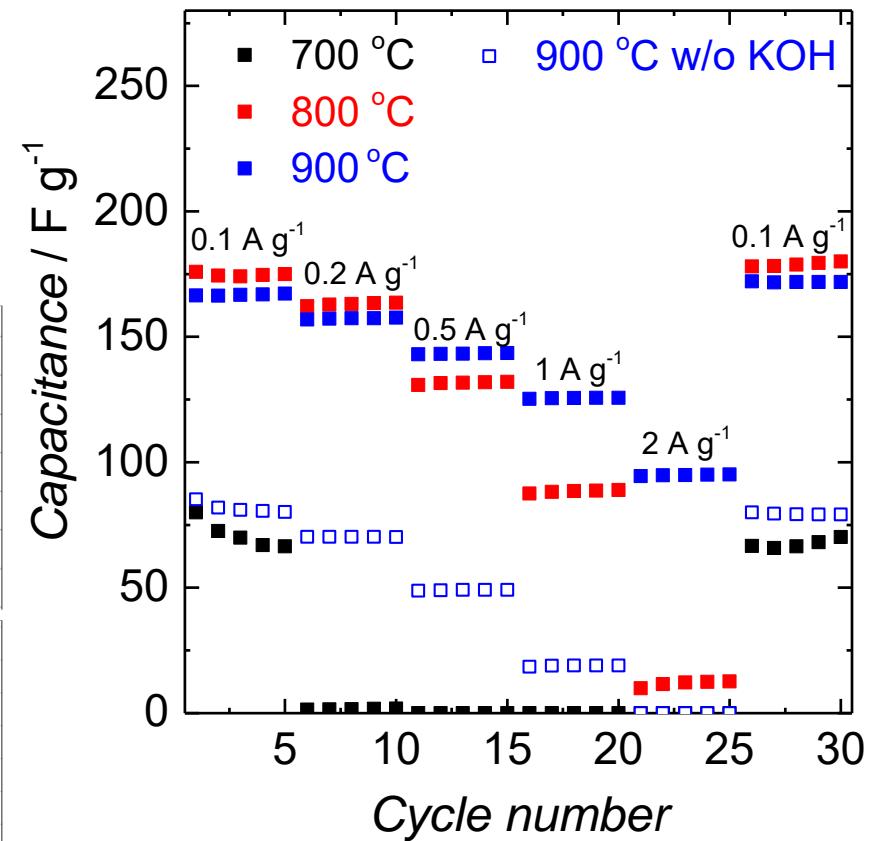
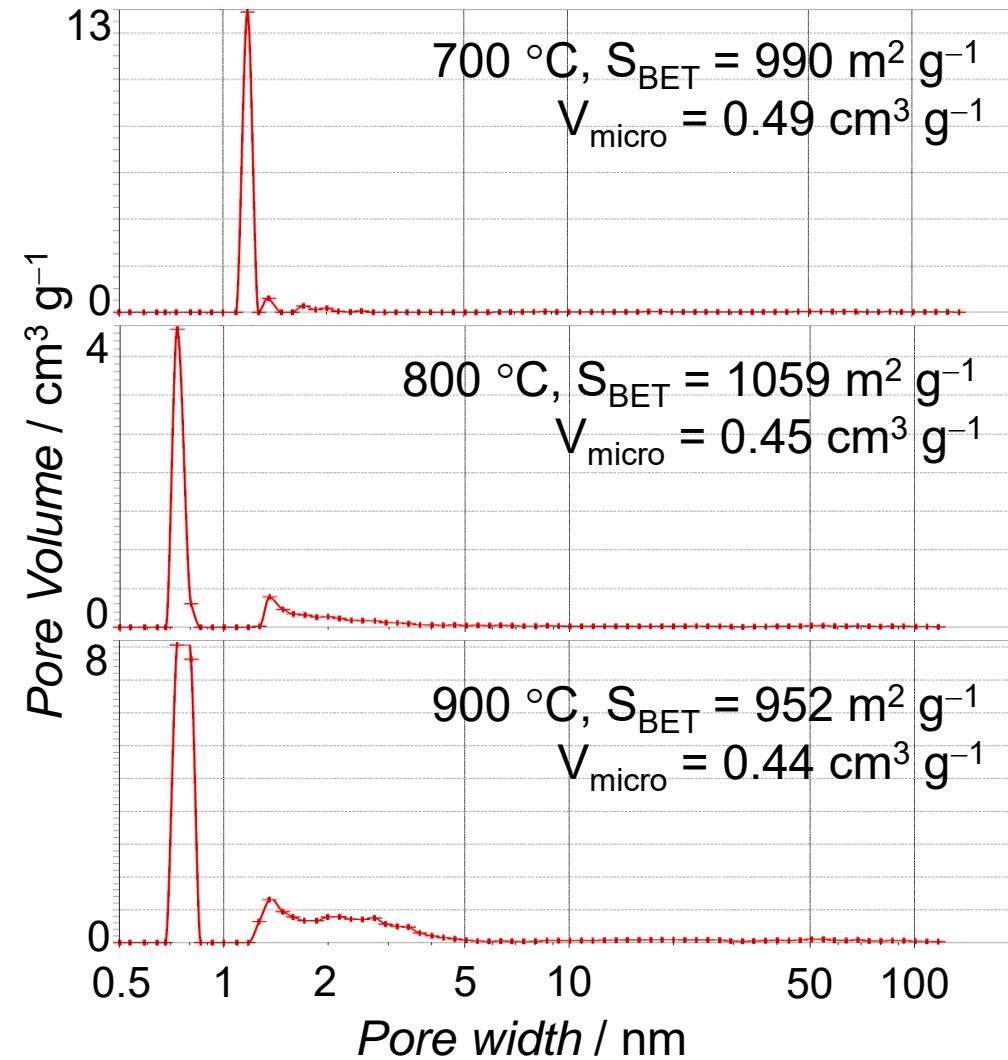
Mostly micropore

Compared with 700 °C...  
Slight development of mesopore  
Decrease of micropore volume

Compared with 800 °C...  
Development of mesopore  
Slight decrease of micropore volume

# Discussion of the observed trend (KOH/C = 1) (3)

## Pore volume vs. Pore width

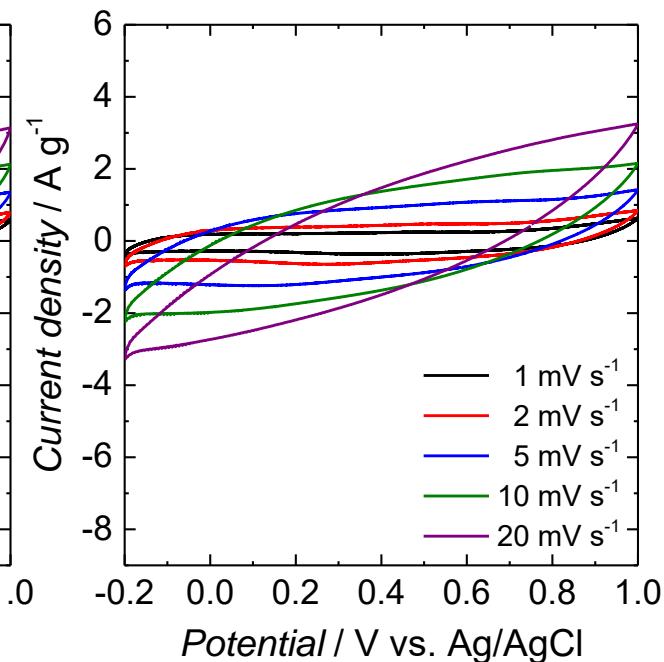
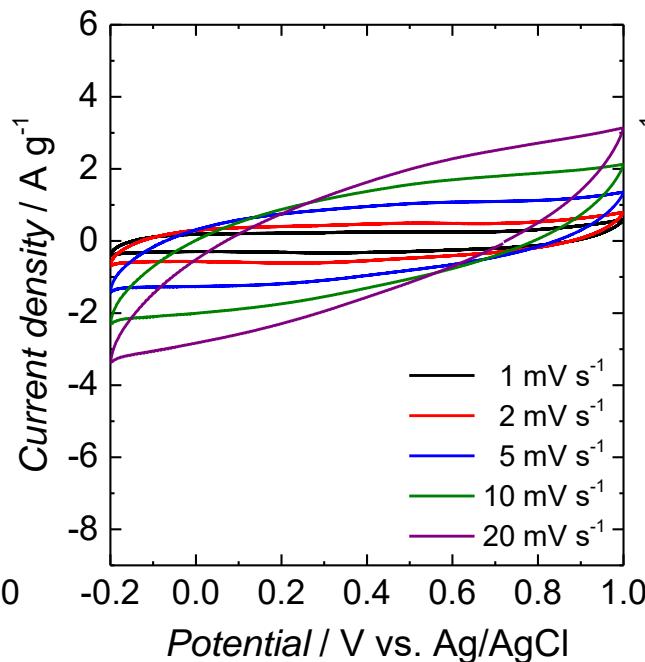
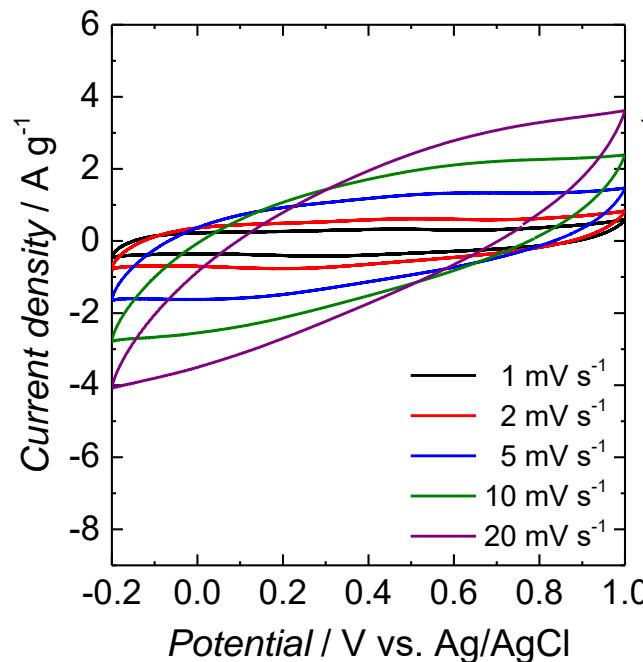


Capacitance – pore distribution  
→ Good correlation

# CV at various activation temperature (KOH/C = 3) (1)

Kyoto University

700 °C,  $S_{\text{BET}} = 1234 \text{ m}^2 \text{ g}^{-1}$    800 °C,  $S_{\text{BET}} = 1380 \text{ m}^2 \text{ g}^{-1}$    900 °C,  $S_{\text{BET}} = 1728 \text{ m}^2 \text{ g}^{-1}$

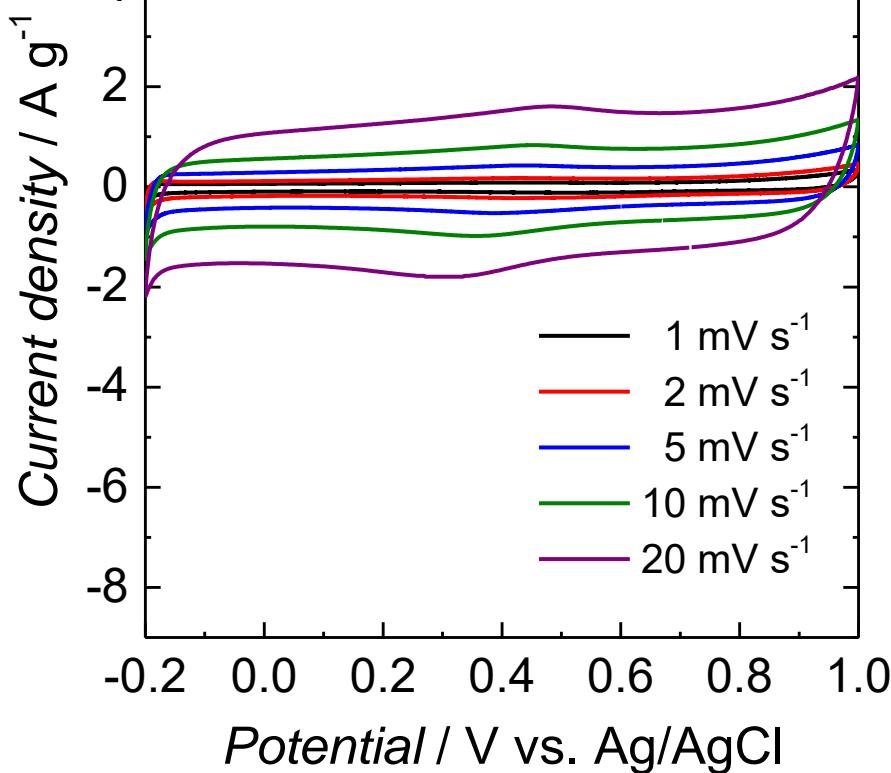


No obvious difference from CV results

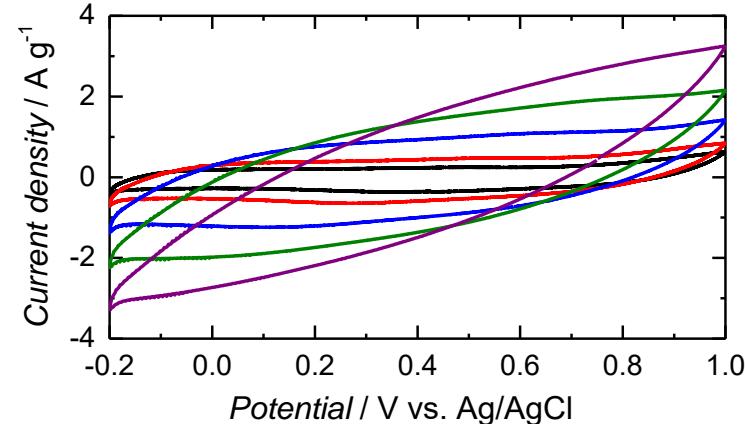
# CV at various activation temperature (KOH/C = 3) (2)

Kyoto University

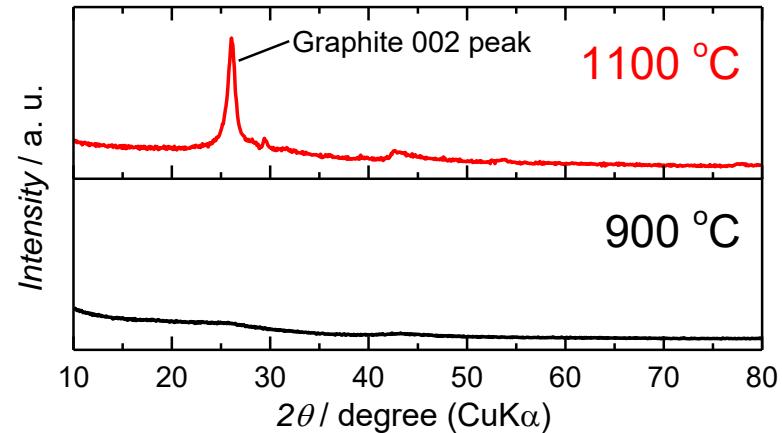
$1100\text{ }^{\circ}\text{C}$ ,  $S_{\text{BET}} = 773\text{ m}^2\text{ g}^{-1}$



ca.  $900\text{ }^{\circ}\text{C}$ ,  $S_{\text{BET}} = 1728\text{ m}^2\text{ g}^{-1}$



## X-ray diffraction patterns

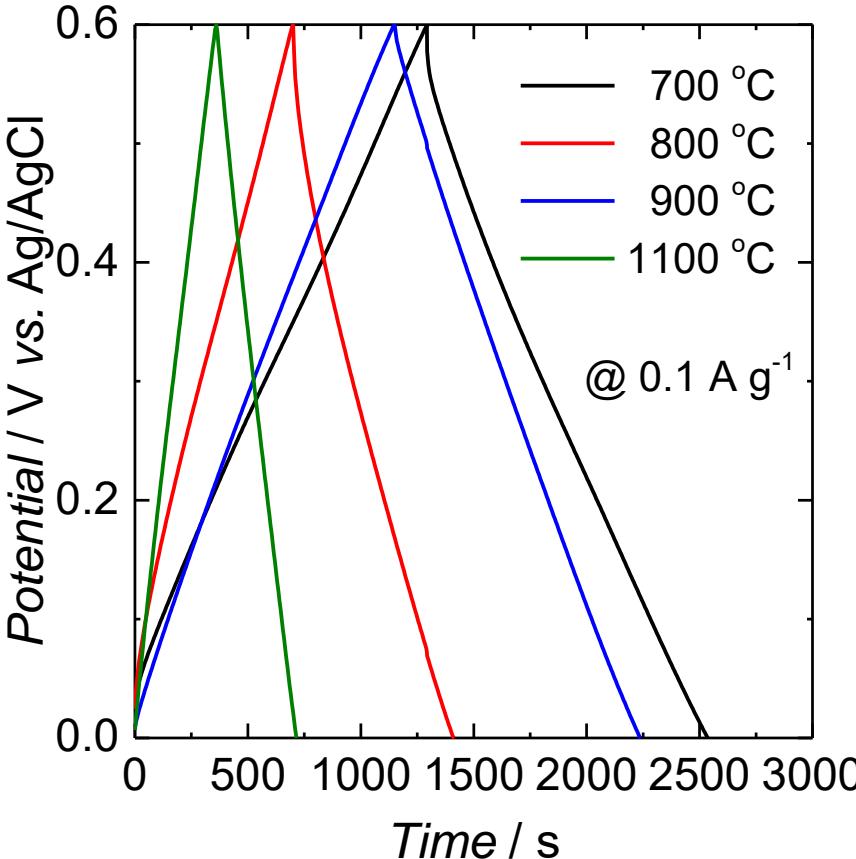


1100 °C sample: graphitized structure to its bulk  
 → better performance at higher sweep rate

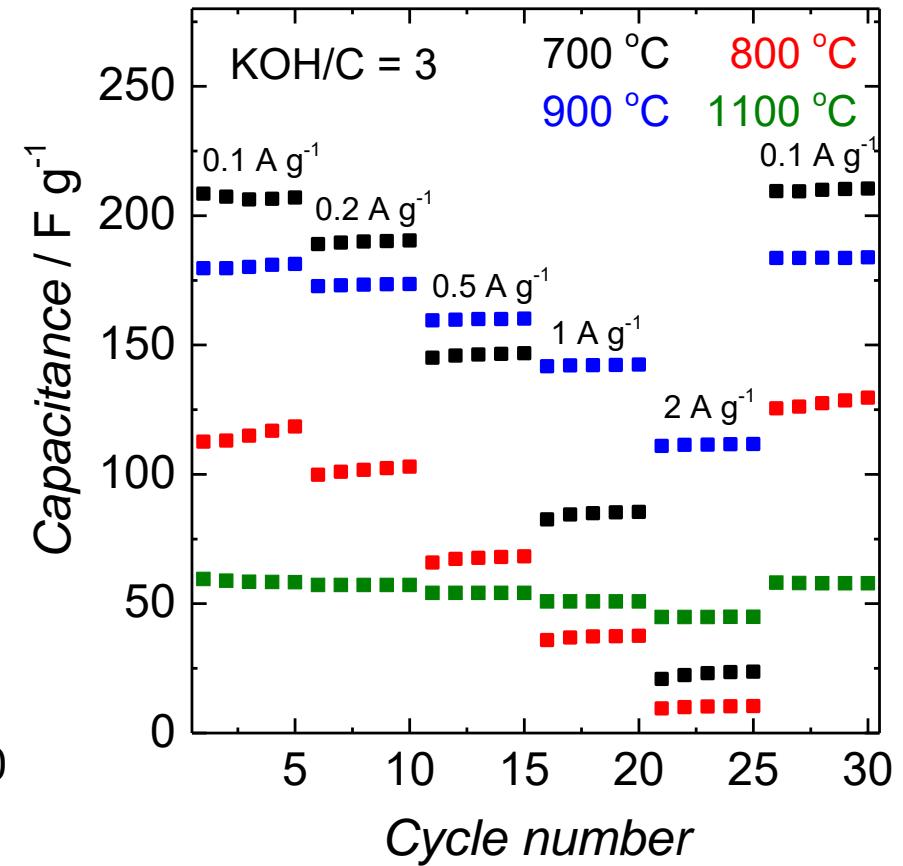
# Charge-discharge results at KOH/C = 3

Kyoto University

Profile of potential vs. time



Capacitance at each current density



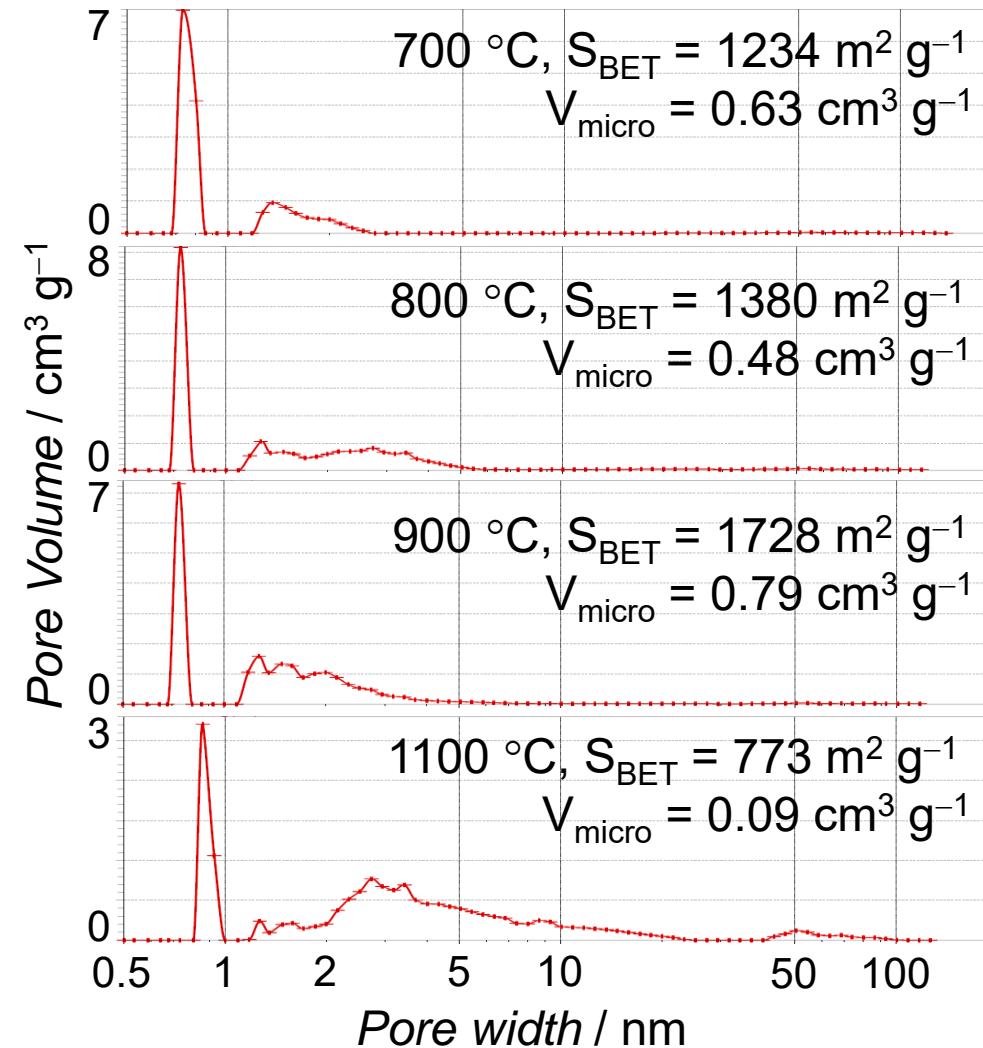
700 °C: 39 [Ω]  
900 °C: 13 [Ω]

800 °C: 33 [Ω]  
1100 °C: 9 [Ω]

Higher temperature → better rate capability

# Discussion of the observed trend (KOH/C = 3) (1)

## Pore volume vs. Pore width



Mostly micropore

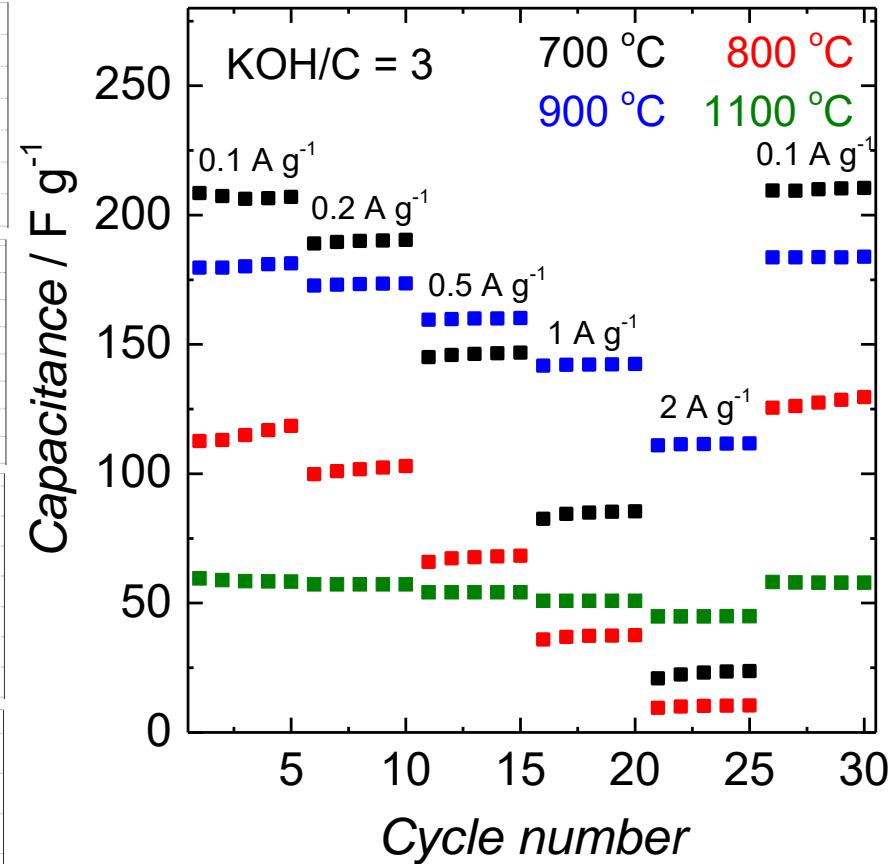
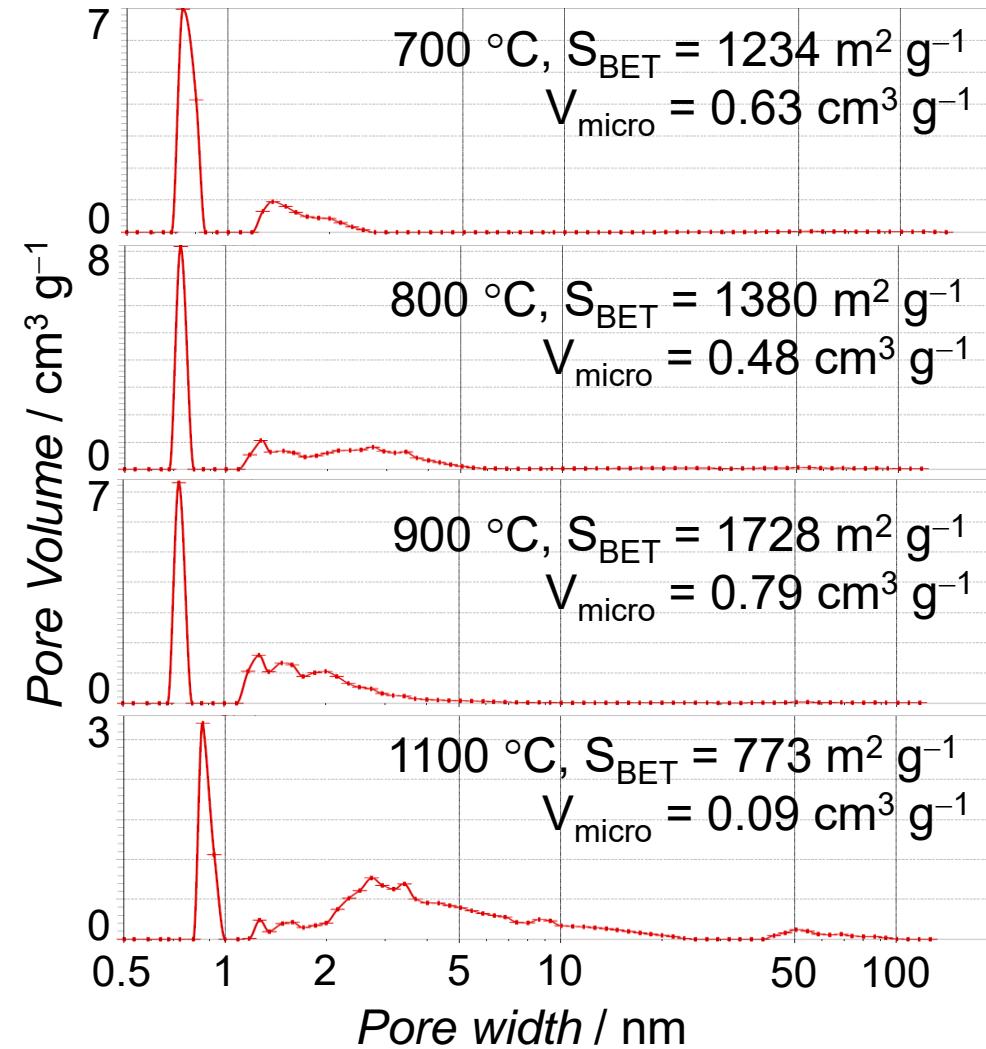
Compared with 700 °C...  
Development of mesopore  
Decrease of micropore volume

Compared with 800 °C...  
Comparable mesopore  
Increase of micropore volume

Compared with 900 °C...  
Drastic increase of mesopore  
Drastic decrease of micropore volume

# Discussion of the observed trend (KOH/C = 3) (2)

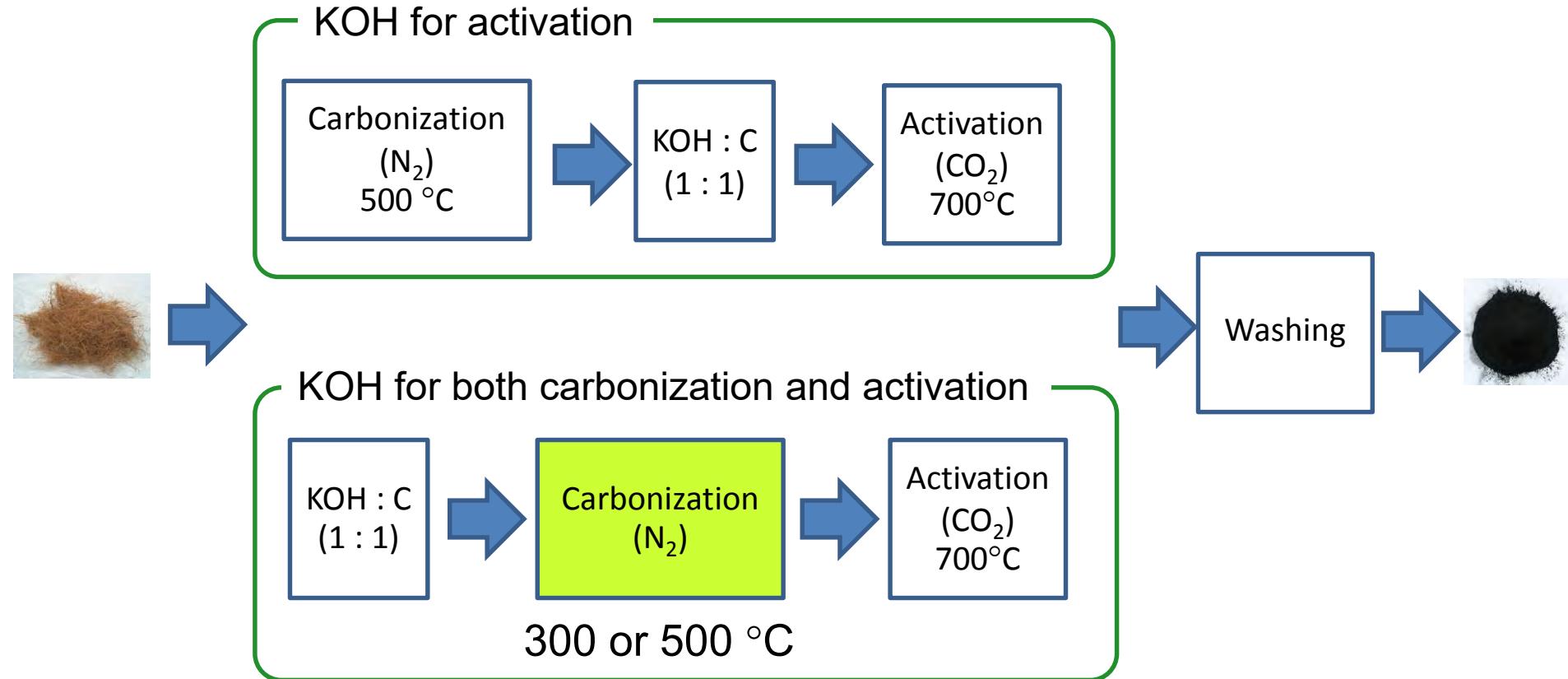
## Pore volume vs. Pore width



Capacitance – pore distribution  
 → Good correlation

# Effect of KOH-mixing sequence on EDLC performance

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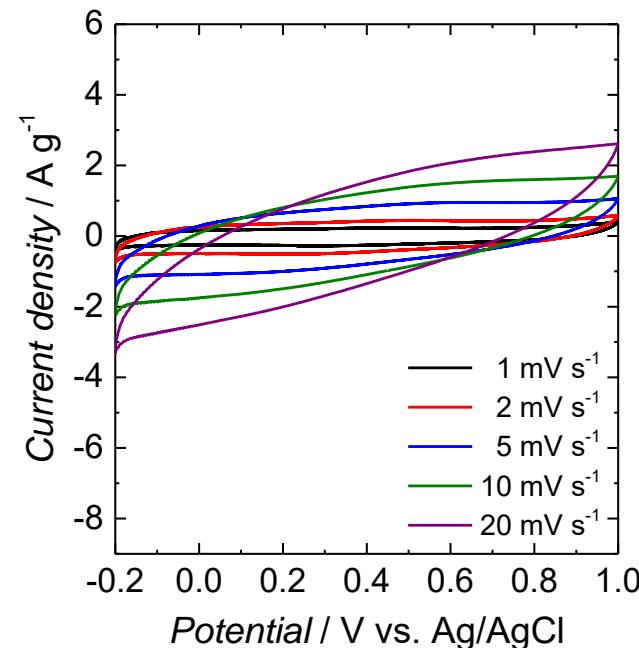
Sample name: KOH for both

$300/700\text{ }^\circ C$   
 $500/700\text{ }^\circ C$

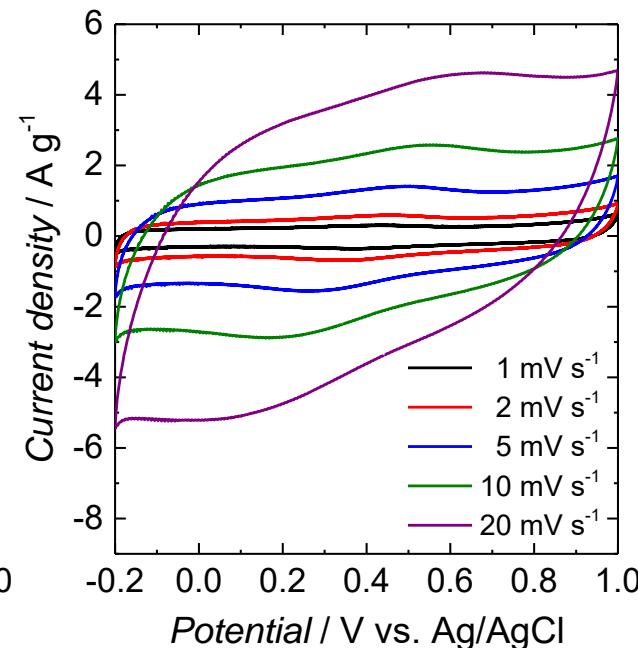
by MTEC

# CVs of resultant activated carbons

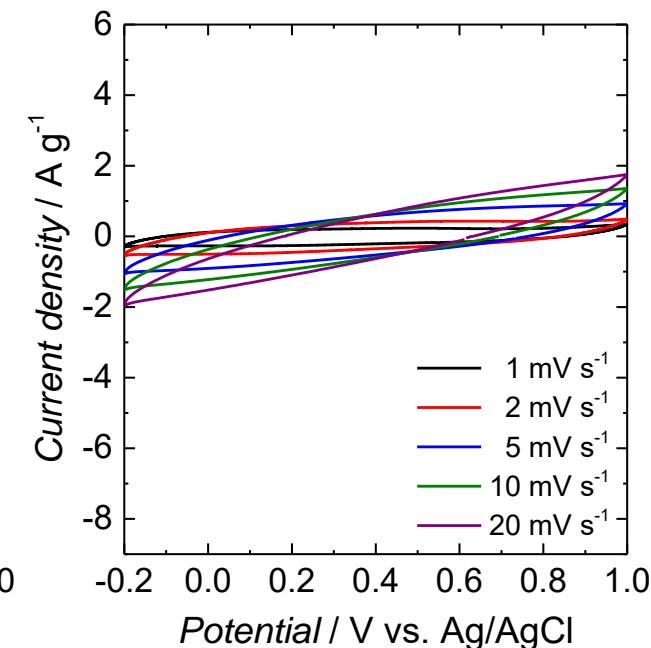
300/700 °C  
 $S_{\text{BET}} = 920 \text{ m}^2 \text{ g}^{-1}$



500/700 °C  
 $S_{\text{BET}} = 1177 \text{ m}^2 \text{ g}^{-1}$



700 °C  
 $S_{\text{BET}} = 990 \text{ m}^2 \text{ g}^{-1}$

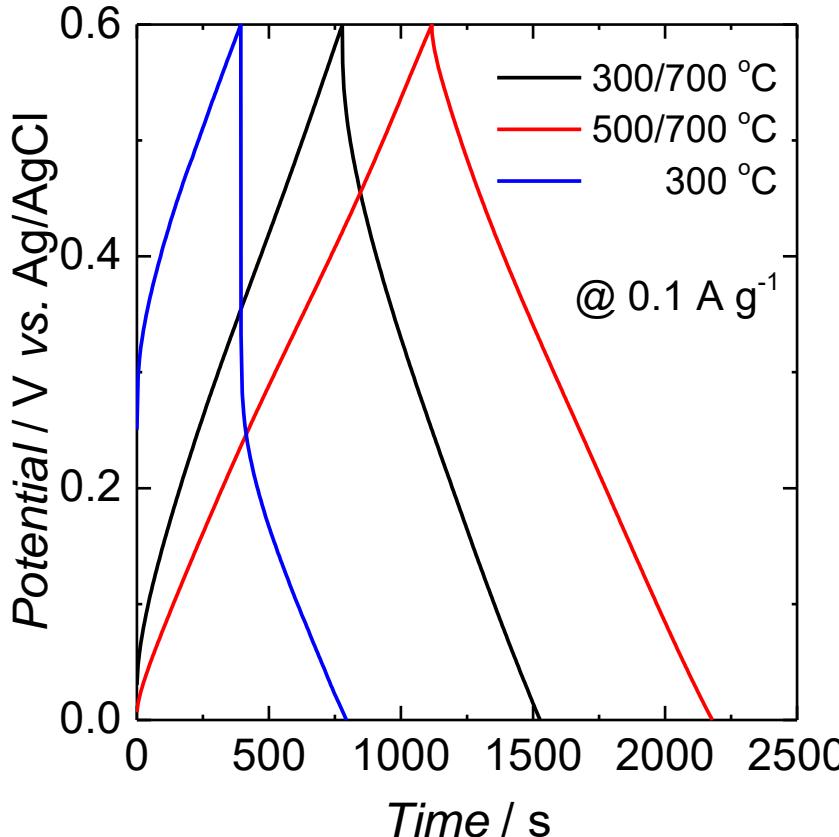


“KOH for both” samples had much better CVs.

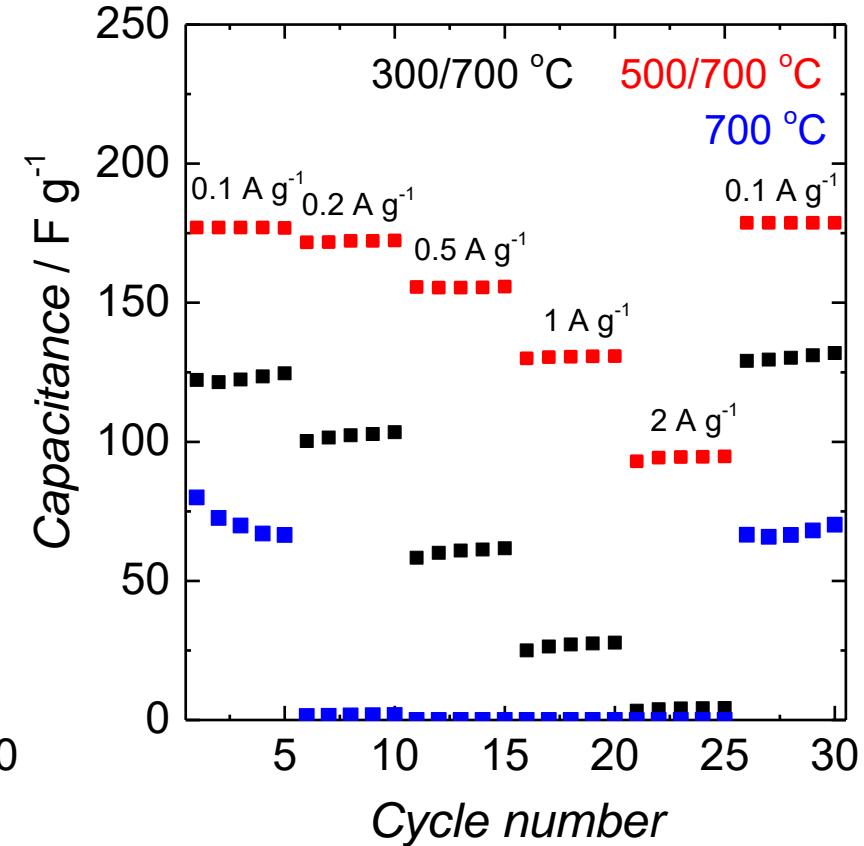
# Charge-discharge results for “KOH for both”

Kyoto University

Profile of potential vs. time



Capacitance at each current density



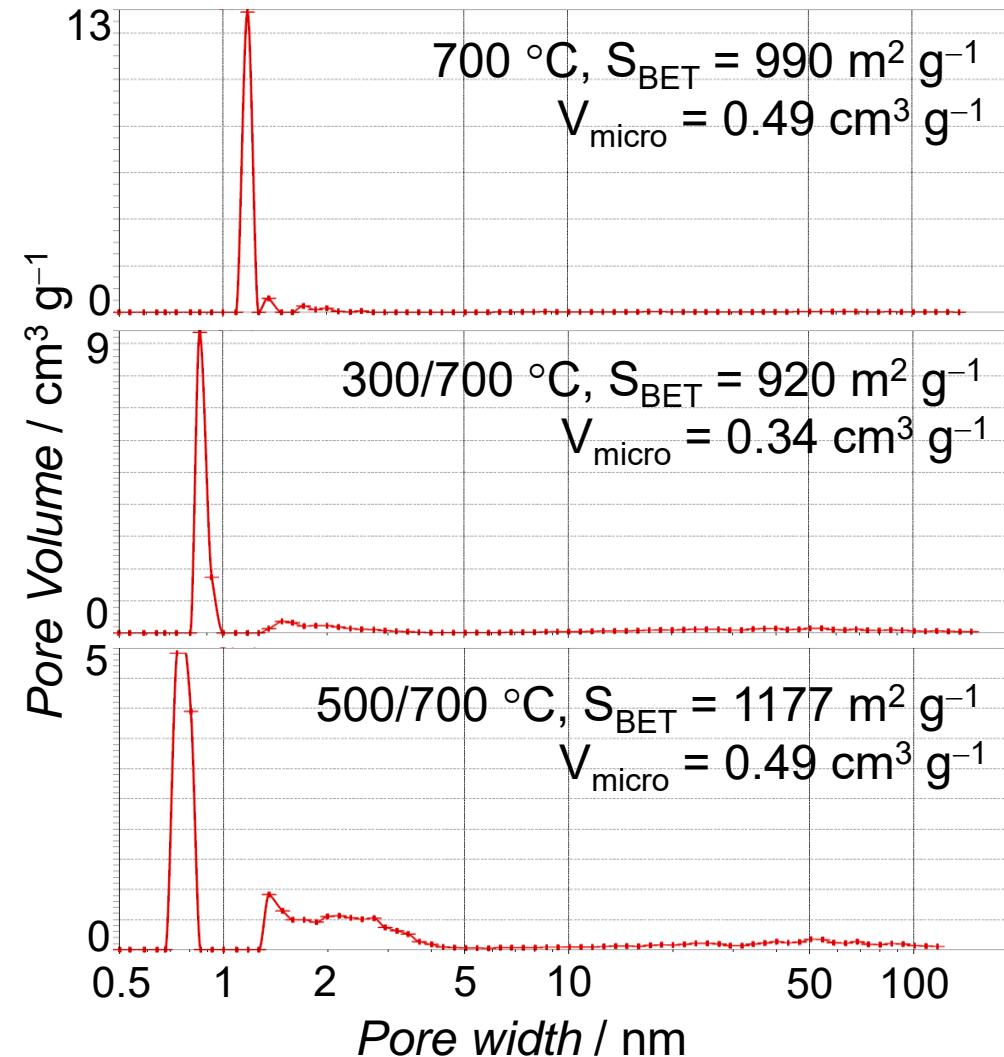
700 °C: 370 [Ω]  
 300/700 °C: 55 [Ω]  
 500/700 °C: 12 [Ω]

Higher temperature → better rate capability

# Discussion of the observed trend (step dequence) (1)

Kyoto University

## Pore volume vs. Pore width



Mostly micropore

Compared with 700  $^\circ\text{C}$ ...  
Slight development of mesopore  
Decrease of micropore volume

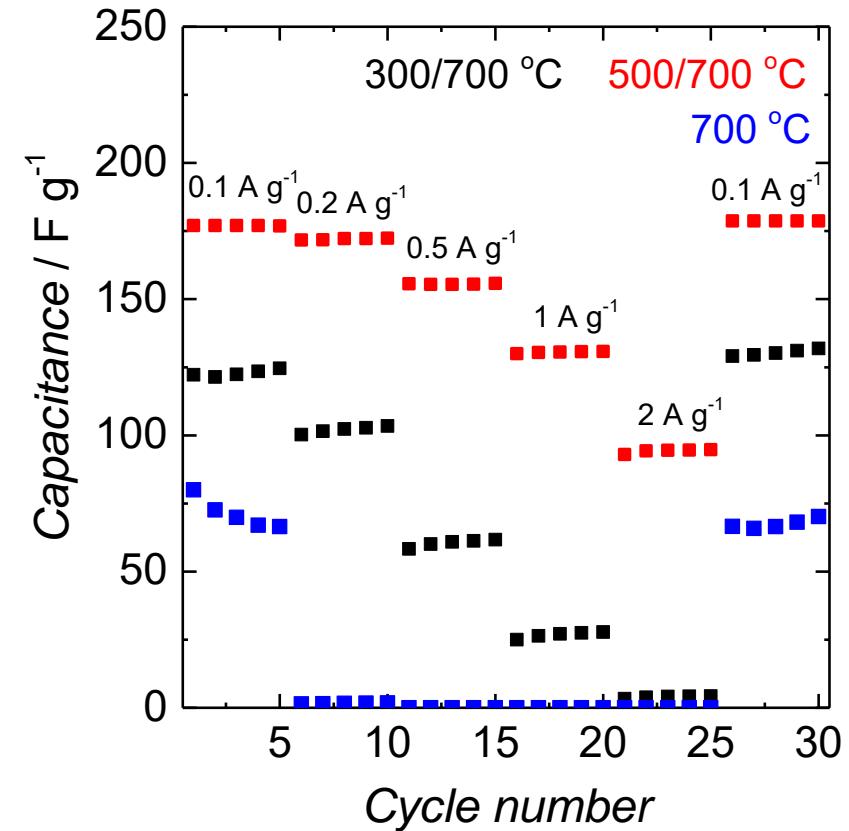
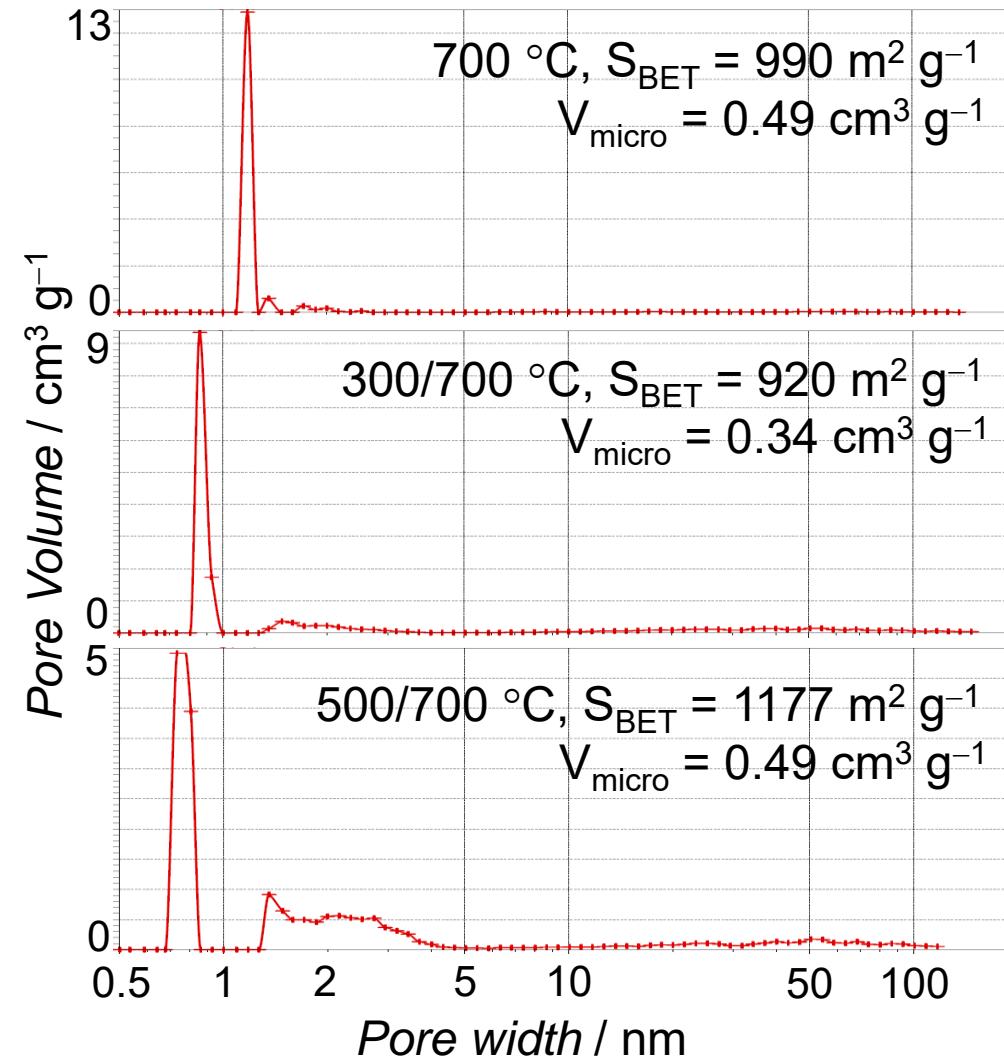
Compared with 300/700  $^\circ\text{C}$ ...  
Drastic development of mesopore  
Increase of micropore volume

by MTEC

# Discussion of the observed trend (step dequence) (2)

Kyoto University

## Pore volume vs. Pore width

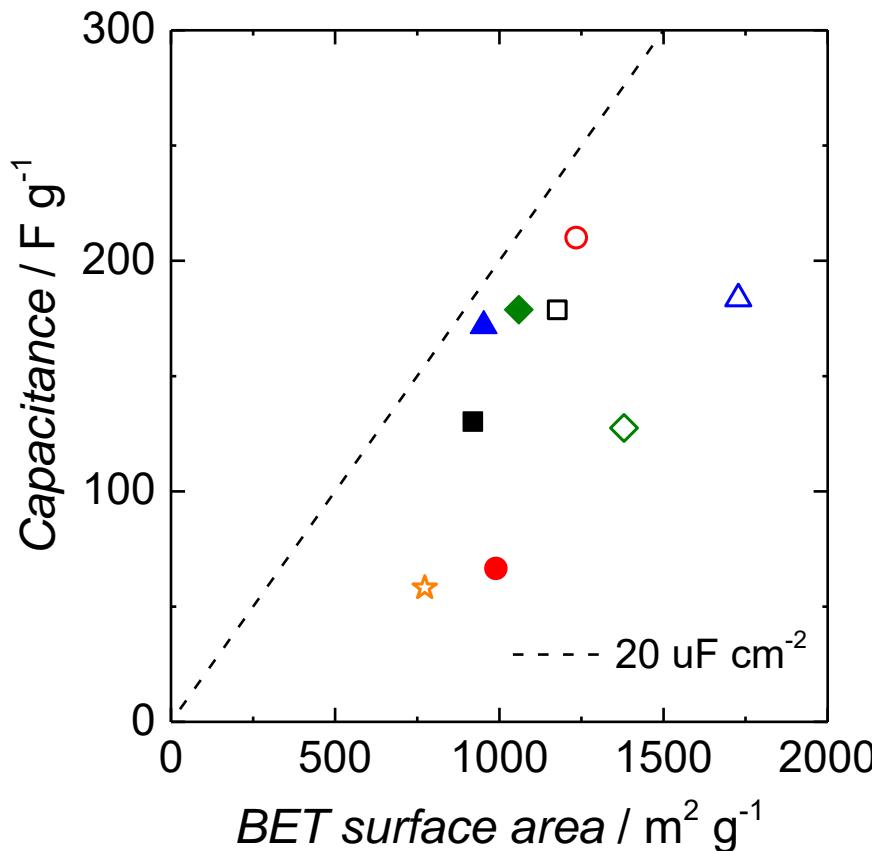


Capacitance – pore distribution  
 → Good correlation

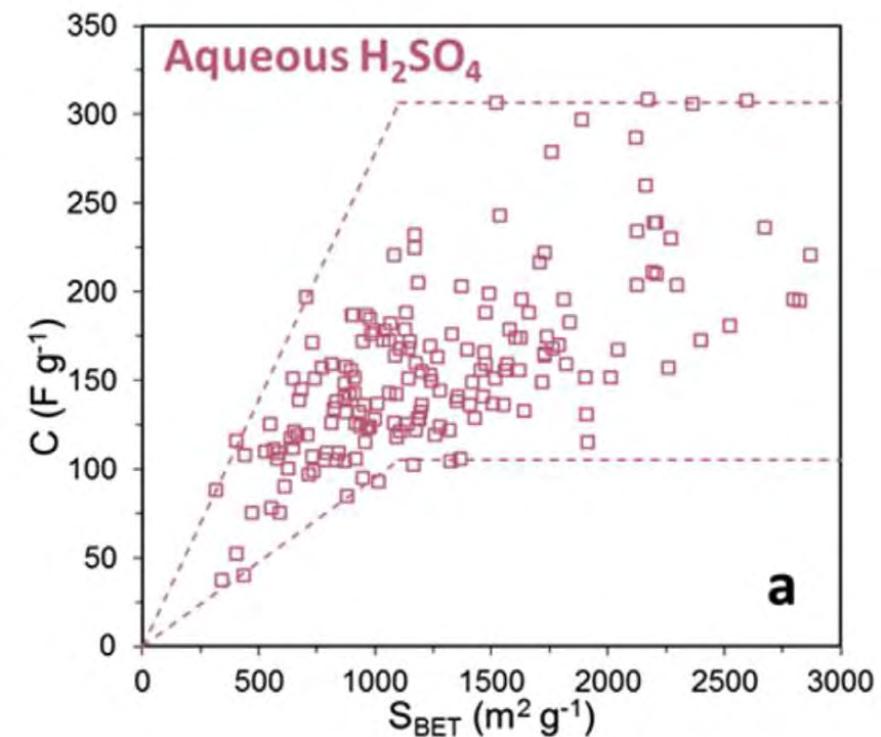
# Correlation between capacitance and BET surface area

Kyoto University

Capacitance vs. BET surface area



Database of the trend



Carbon, 122 (2017) 434.

Pore distribution as well as  $S_{BET}$  is important for further enhancement of EDLC performance.

# Summary

Kyoto University

- Influence of KOH/C ratio, temperature, and treatment sequence on EDLC performance were investigated.
- As for KOH/C = 1, activation at higher temperature resulted in better EDLC performance .
- As for KOH/C = 3, synthesis conditions should be optimized to obtain the best EDLC performances from the viewpoint of capacitance and rate capability.
- Sequence of KOH mixing is also important to optimize physicochemical property of PEFB-derived activated carbon.
- Pore distribution should be considered for the further enhancement of EDLC performance of PEFB-derived activated carbon.