2nd JASTIP-WP2 Annual Workshop
3 February 2017

Development of Activated Carbons from Biomass for Energy Storage Applications

Yuto Miyahara, Kohei Miyazaki, Tomokazu Fukutsuka, Takeshi Abe, Sumittra Charojrochkul*, Yatika Somrang*, Worawarit Kobsiriphat*, Thanathon Sesuk*

Kyoto Univ. and MTEC*

Use of biomass for energy storage applications

Palm tree

- Palm fruit

- *Empty fruit bunches*, kernel shells, mill effluents

Functionalization

- Bioenergies: Bioethanol, biogas, biohydrogen

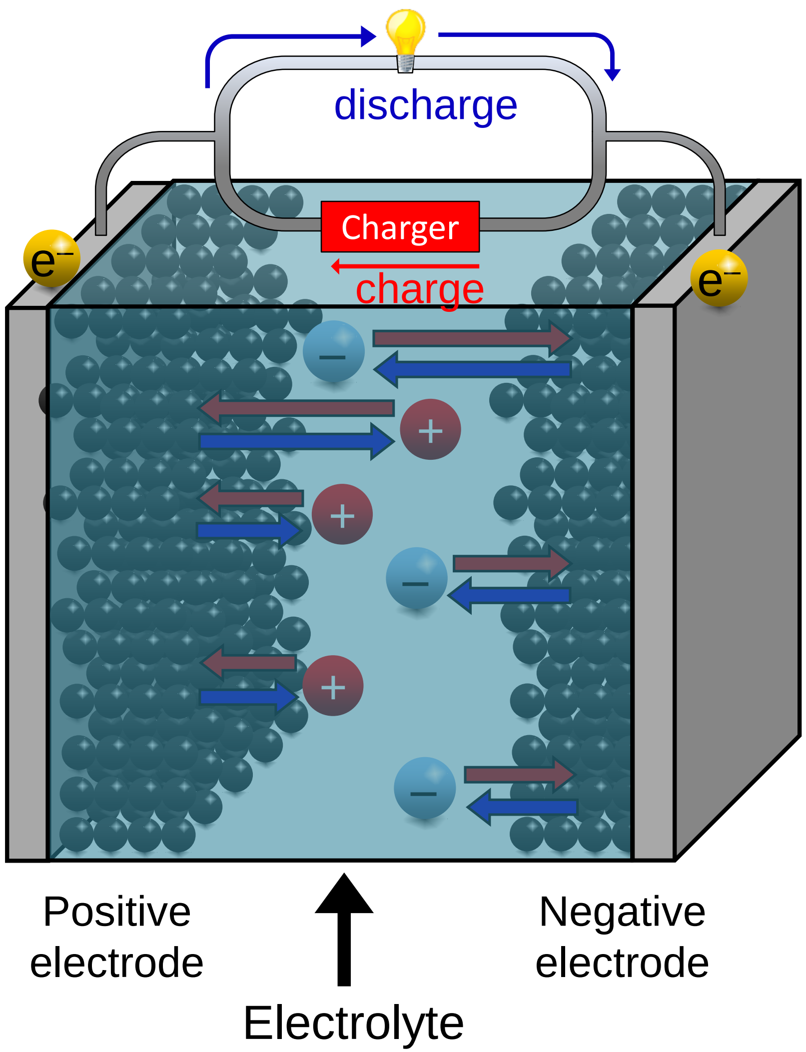
- Functionalized materials: Bioplastic, *activated carbon*

Adsorption of pollutants, *energy storage applications*

Photo from Wikipedia, Alibaba, KPSR Construction, Operation Boost, The Future Build

Energy storage application (1)
Electric double-layer capacitor (EDLC)

Schematic illustration of EDLC



Advantages of EDLC

- Long life (Theoretically > 100,000)
- 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

Oil palm empty fruit bunch → Carbonization → *Activation* → Activated carbon

Activation method

- Physical activation
  - CO_2 method
  - H_2O method
  - Air (oxygen) method
- Chemical activation
  - Zinc chloride method
  - Phosphorus acid method
  - Alkali method

Measurement of EDLC performance of CO_2-activated carbon synthesized from oil palm empty fruit bunches

Prepared by MTEC

Outline

- ➢ Synthesis and characterization of carbon samples from oil palm empty fruit bunch

by MTEC

- ➢ EDLC performance of the biomass carbons
  - Cyclic voltammetry
  - Charge and discharge measurement

by KU

- ➢ Performance of the biomass carbons for metal-air rechargeable battery
  - Oxygen reduction reaction activity evaluation

by KU

Outline

- Synthesis and characterization of carbon samples from oil palm empty fruit bunch

by MTEC

- EDLC performance of the biomass carbons
  - Cyclic voltammetry
  - Charge and discharge measurement

by KU

- Performance of the biomass carbons for metal-air rechargeable battery
  - Oxygen reduction reaction activity evaluation

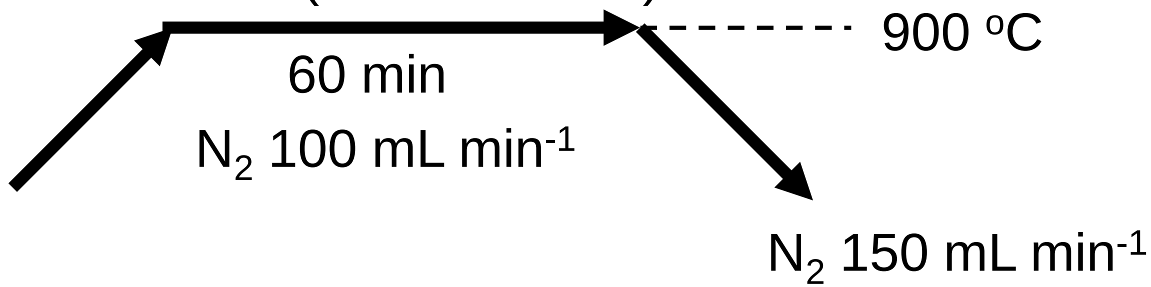
by KU

Synthetic route of carbon powders

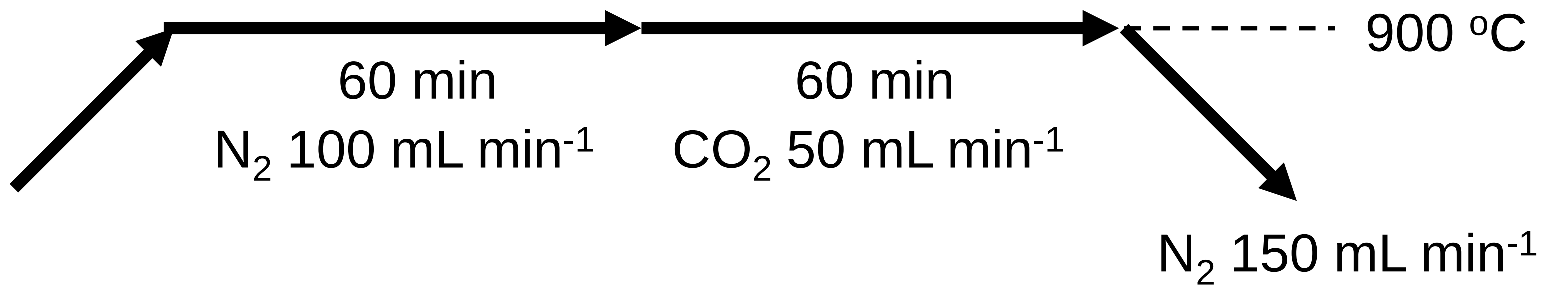
Synthetic route

by MTEC

Without activation (w/o activation)



Activation treatment with CO_2 (CO_2 activation)

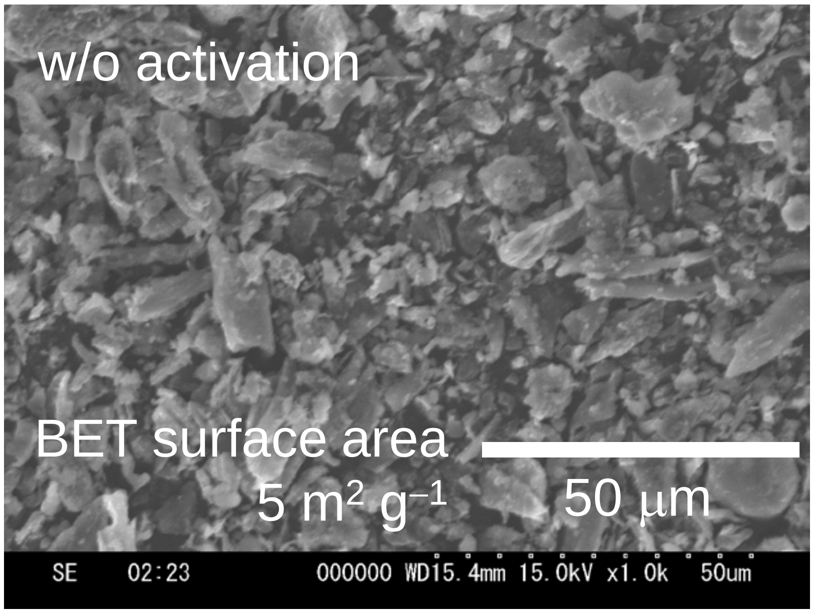


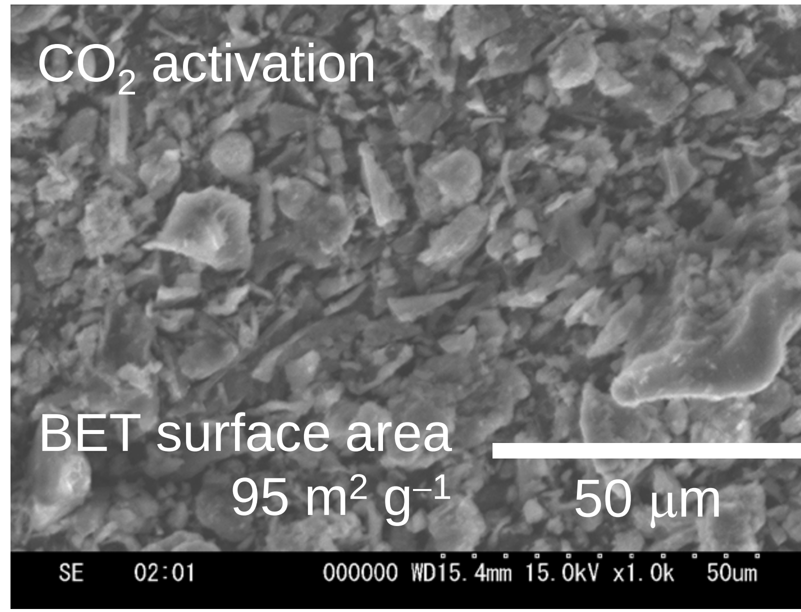
Characterization

by KU

- Scanning electron microscopy (SEM)
- N_2 adsorption (for BET surface area)

SEM images and surface areas





Particle size: unchanged
BET surface area: drastic increase

Pore development after CO_2 activation

Outline

- Synthesis and characterization of carbon samples from oil palm empty fruit bunch

by MTEC

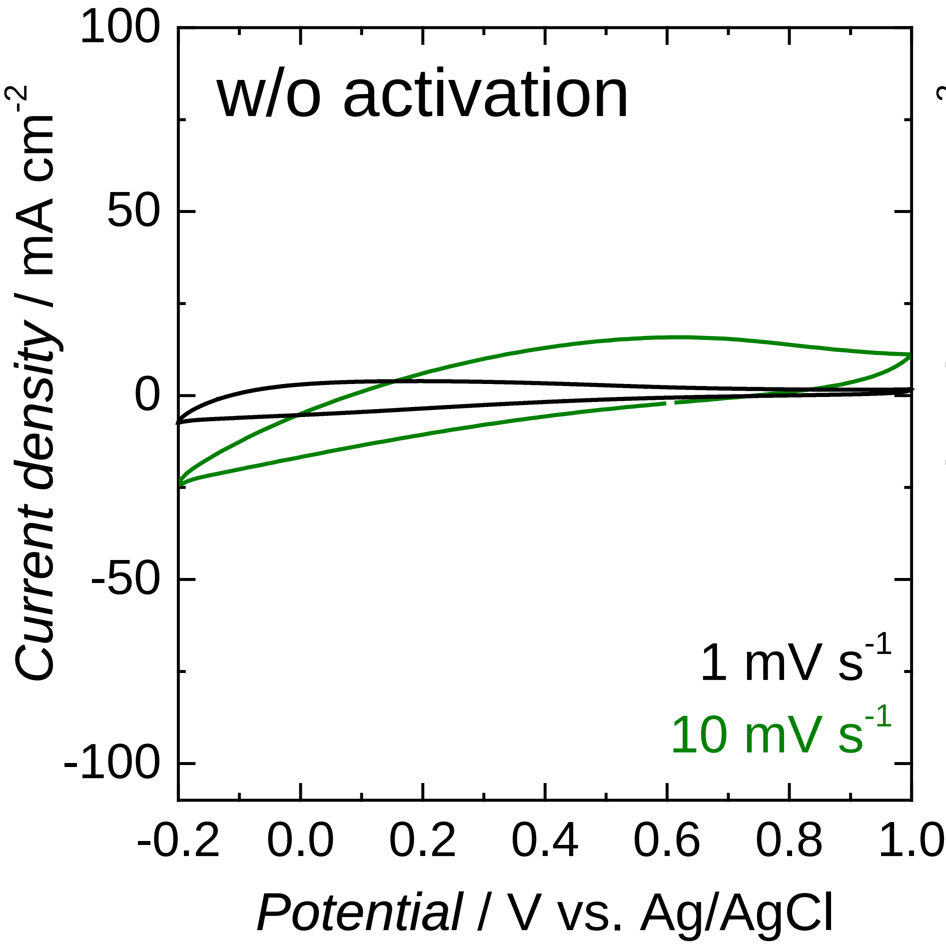
- EDLC performance of the biomass carbons
  - Cyclic voltammetry
  - Charge and discharge measurement

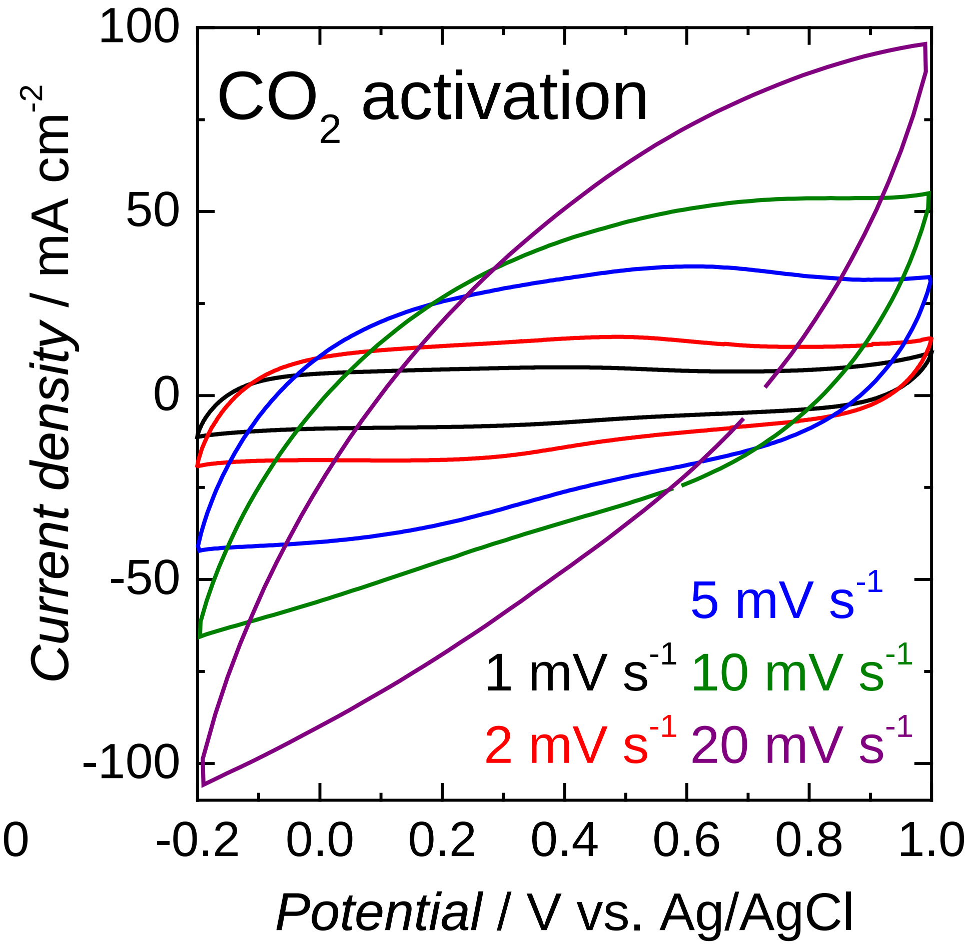
by KU

- Performance of the biomass carbons for metal-air rechargeable battery
  - Oxygen reduction reaction activity evaluation

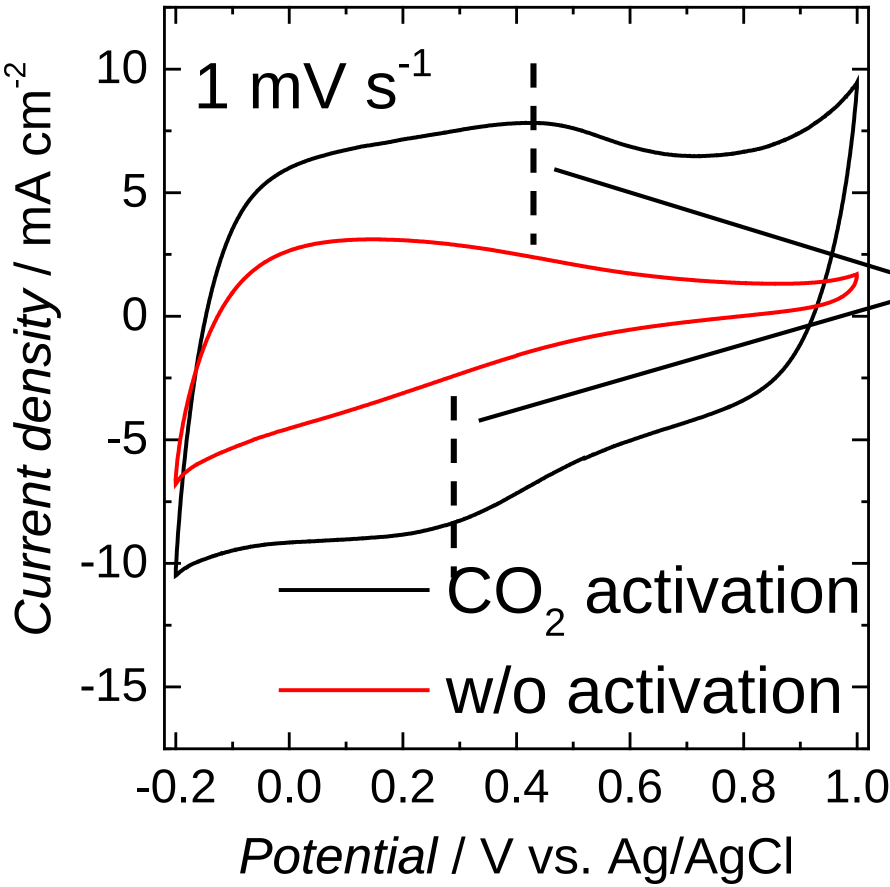
by KU

Cyclic voltammograms

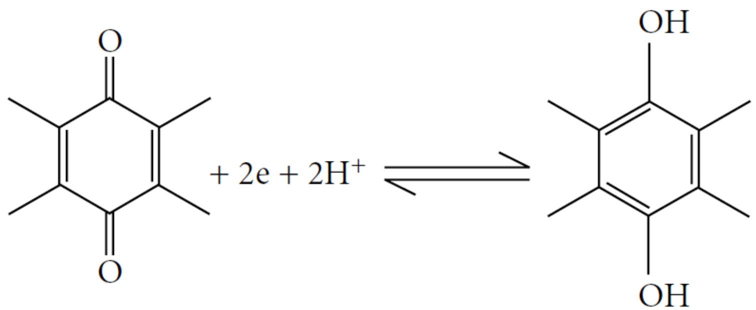




Comparison of cyclic voltammograms



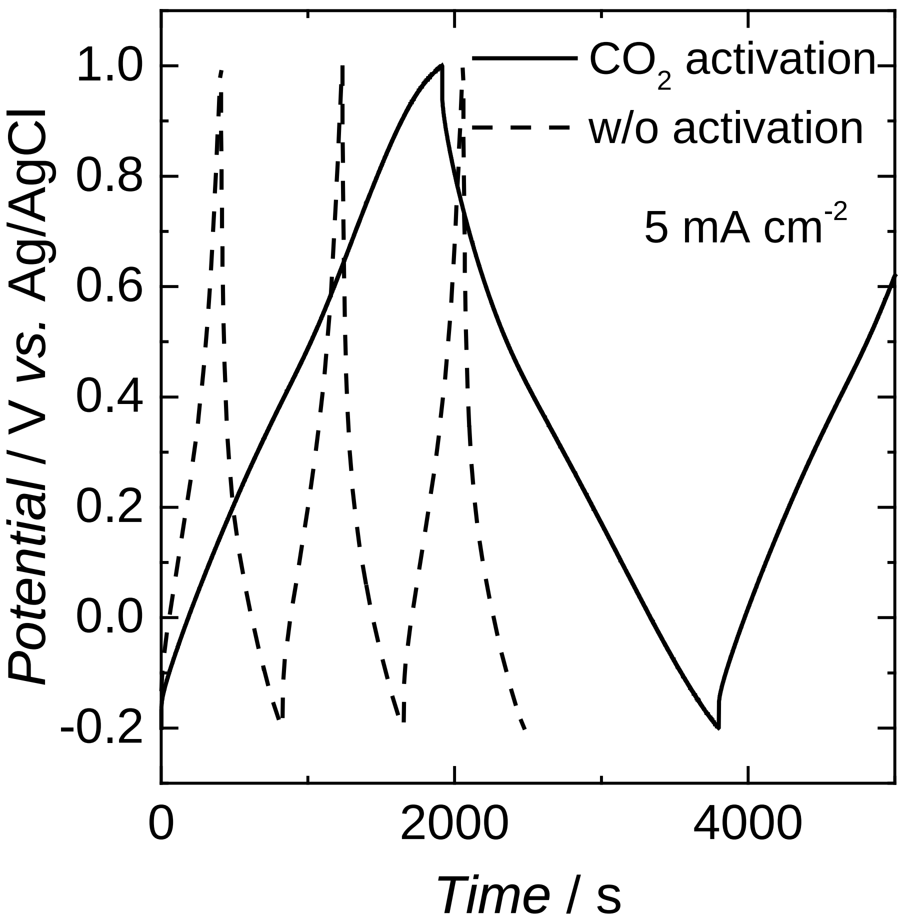
Quinone/hydroquinone redox

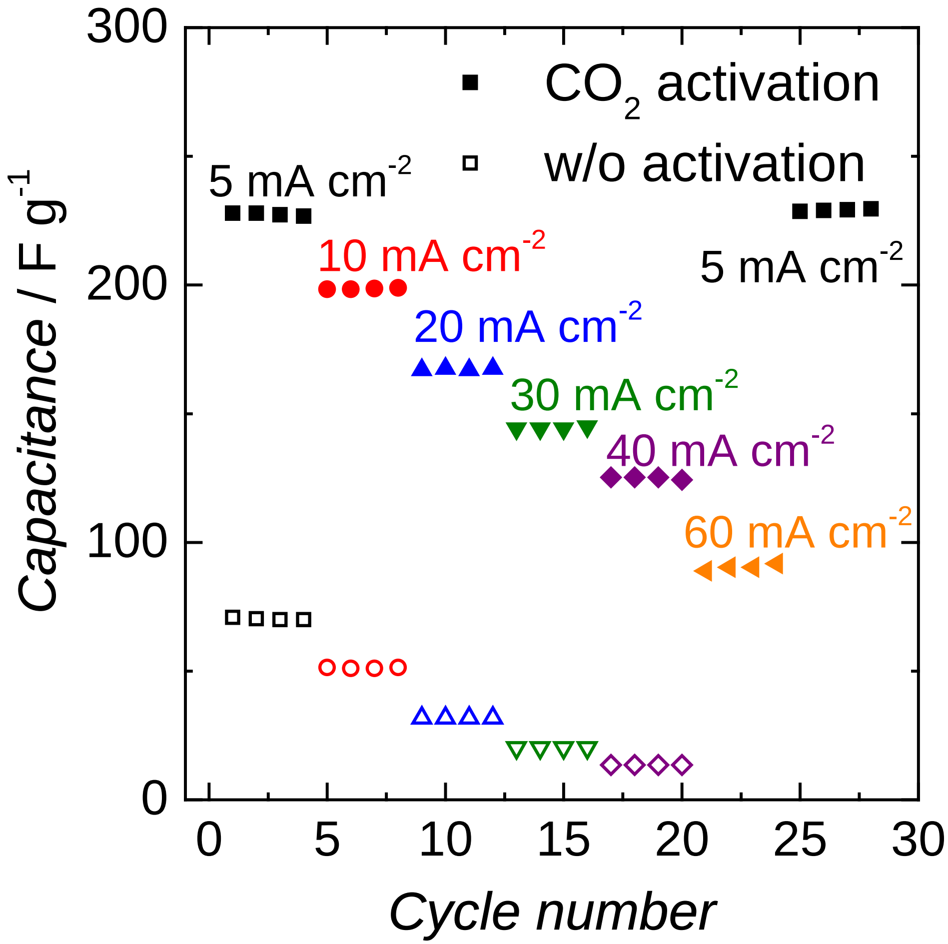


CO_2-activated carbon: larger current

→better performance

Capacitance by charge and discharge measurement





CO_2-activated carbon gave larger capacitance

Outline

- Synthesis and characterization of carbon samples from oil palm empty fruit bunch

by MTEC

- EDLC performance of the biomass carbons
  - Cyclic voltammetry
  - Charge and discharge measurement

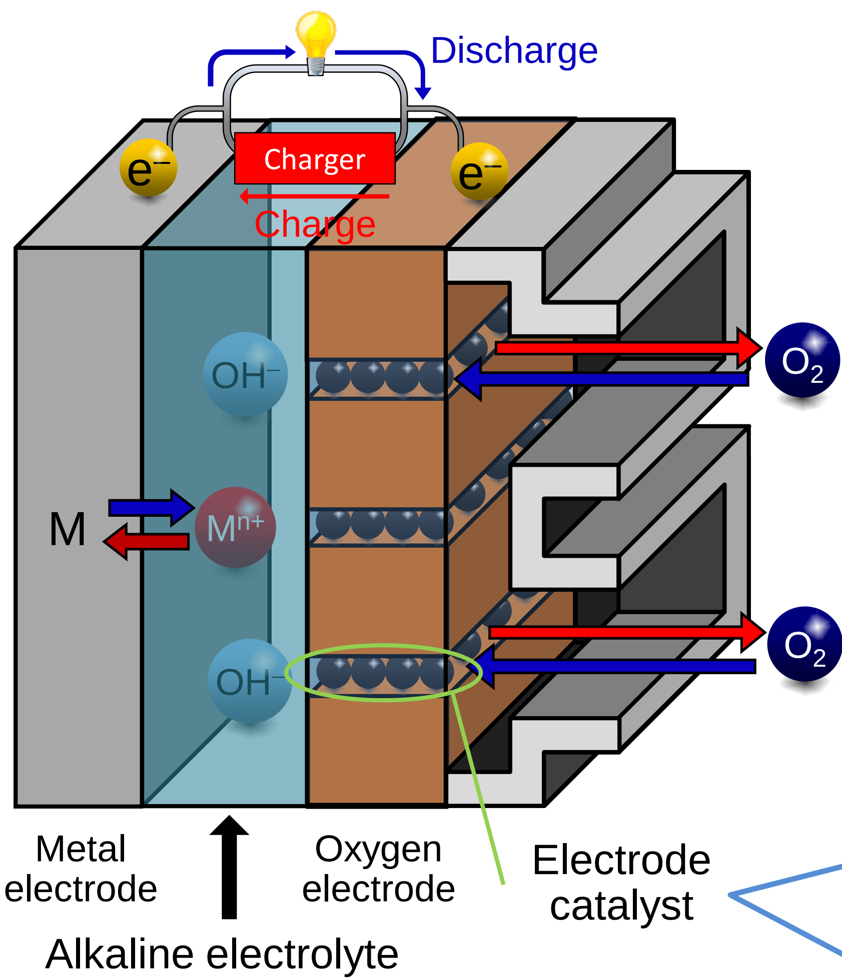
by KU

- Performance of the biomass carbons for metal-air rechargeable battery
  - Oxygen reduction reaction activity evaluation

by KU

Energy storage application (2)
Metal–air rechargeable battery (MARB)

Schematic illustration of MARB



Electrode reactions

Oxygen electrode : $nO_2 + 2nH_2O + 4ne^- \rightleftarrows 4nOH^-$

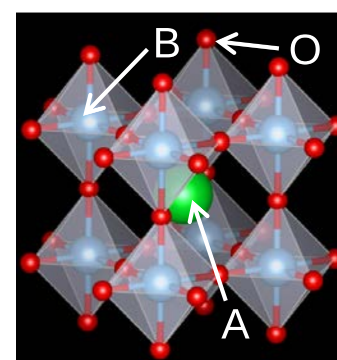
Metal electrode : $4M \rightleftarrows 4M^{n+} + 4ne^-$

Properties

- ○ High energy density
  (Zn:1350 Wh kg^{-1} >> 400 Wh kg^{-1} Li-ion battery)
- ○ High safety
- ○ Availability of cost-effective materials

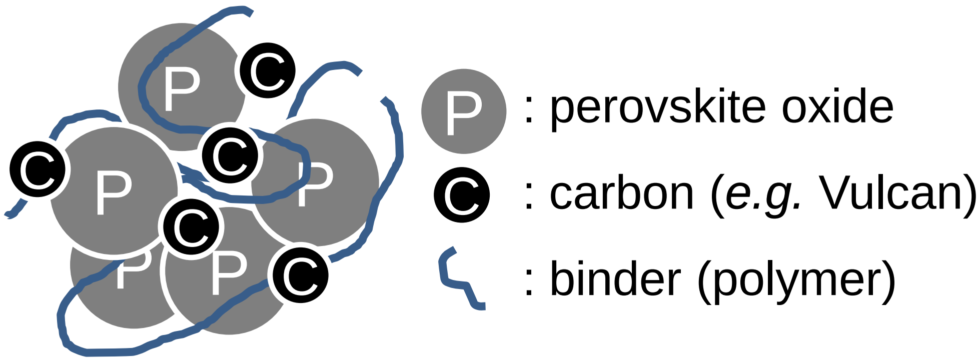
Cost-effective oxygen electrocatalyst

Perovskite oxide (ABO_3)
+
Carbon
+
Binder (polymer)

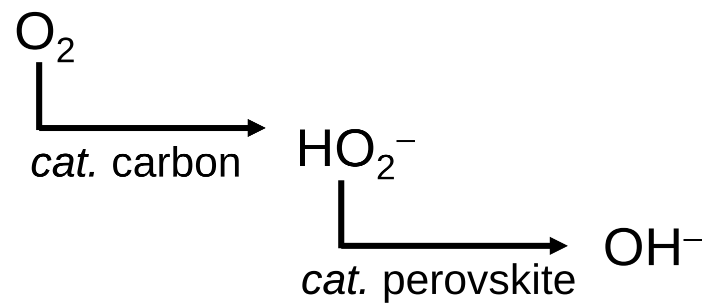


Catalytic role of carbon in oxygen reduction reaction (ORR)

Schematic illustration of oxygen electrode catalysts



Discharge (ORR) route



Functions of each component during ORR

Perovskite oxide: catalyst ($HO_2^- \rightarrow OH^-$)
Carbon: electrically conductive additive + *catalyst ($O_2 \rightarrow HO_2^-$)*
Binder: preservation of catalyst-layer structure

Candidate of active site for carbon: quinone-like structure

Measurement of ORR performance of CO_2-activated carbon

Electrochemical measurement of MARB performance

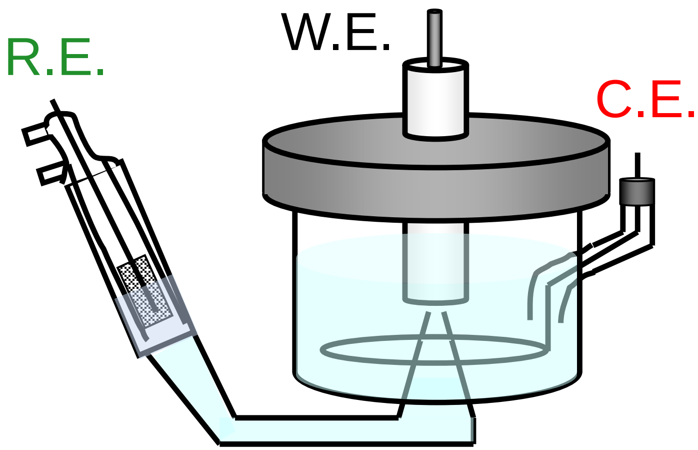
W.E.: Carbons (Vulcan or CO_2 activation) + binder

Perovskite powder + carbons + binder

C.E.: Platinum wire

R.E.: Reversible hydrogen electrode (RHE)

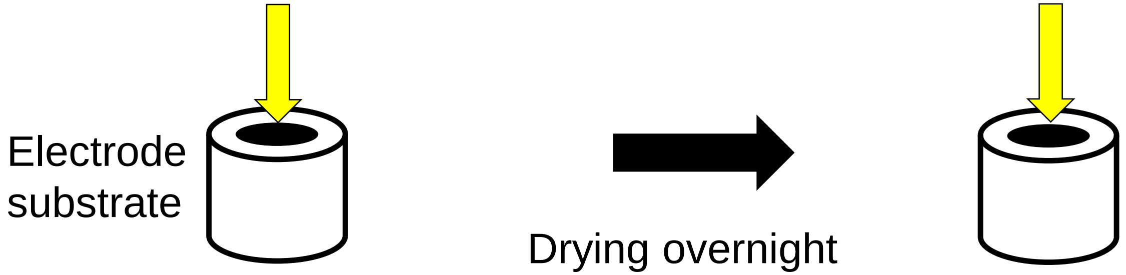
Electrolyte: O_2-saturated 1.0 mol dm^{-3} KOH solution



Fabrication of catalyst layer on electrode substrate

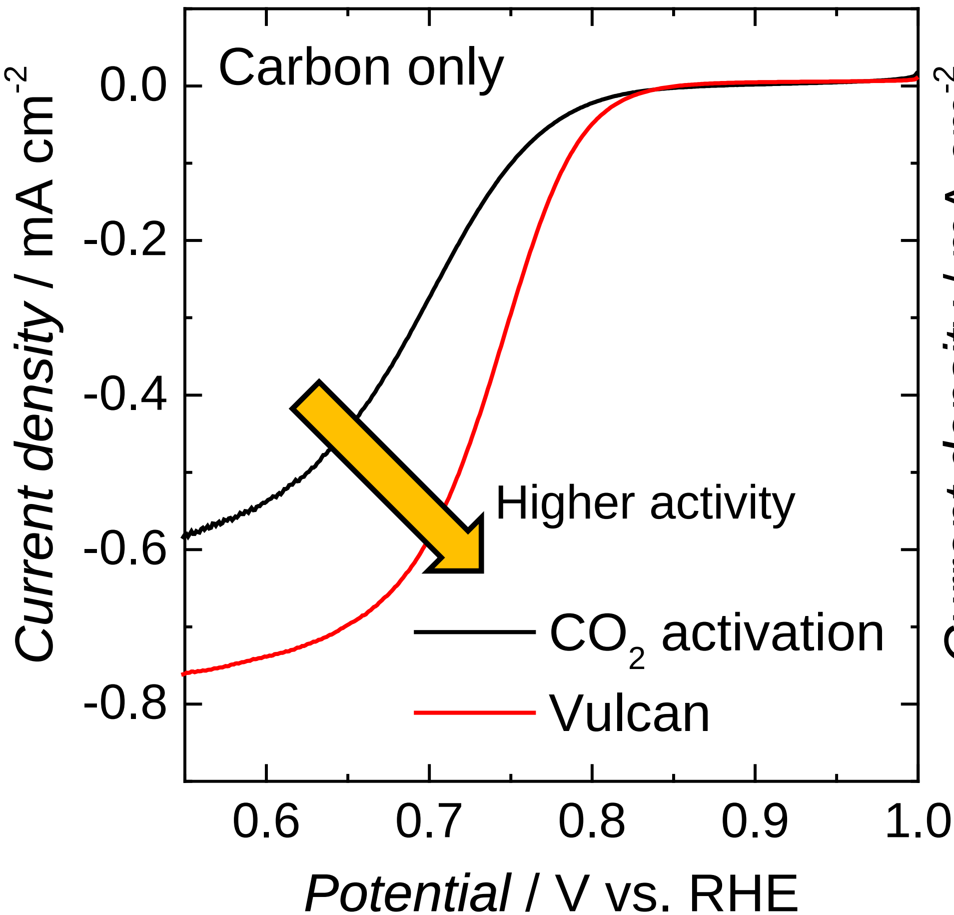
(10 mg mL^{-1} perovskite (250 μg cm^{-2}))
2 mg mL^{-1} carbon (50 μg cm^{-2})
(dispersed in 1-hexanol)

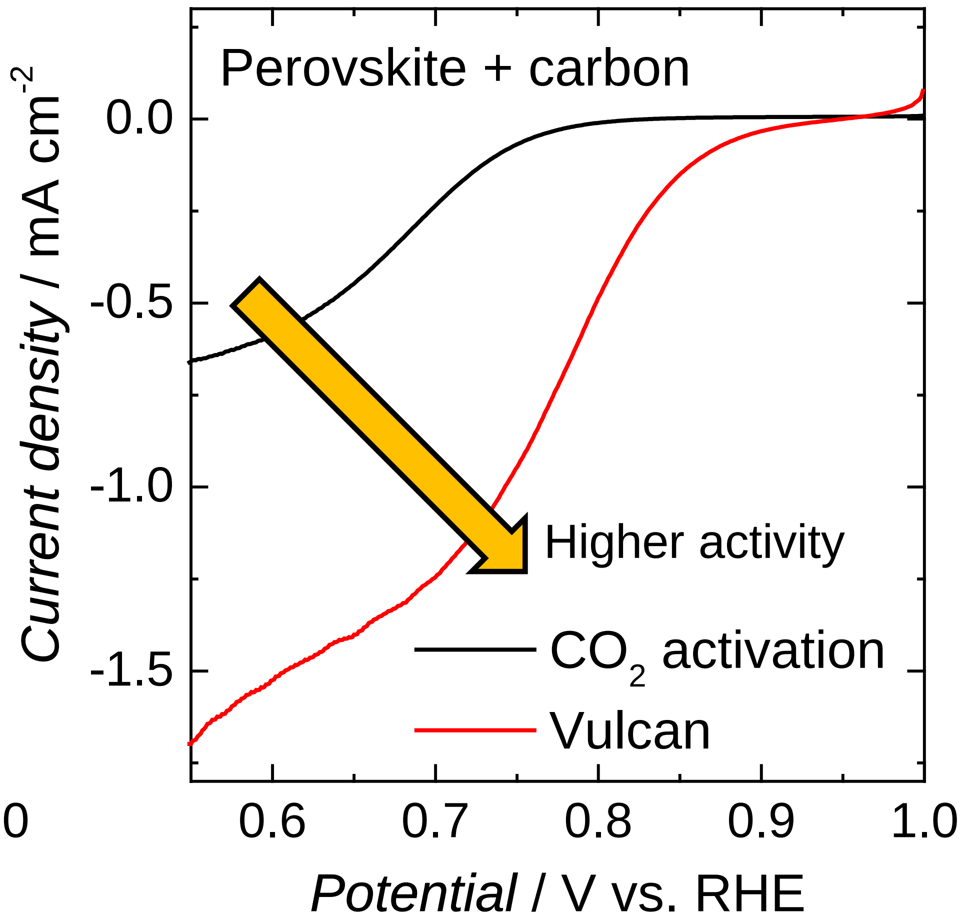
2 mg mL^{-1} binder (50 μg cm^{-2})
(dispersed in 1-propanol)



Kyoto University

ORR performance

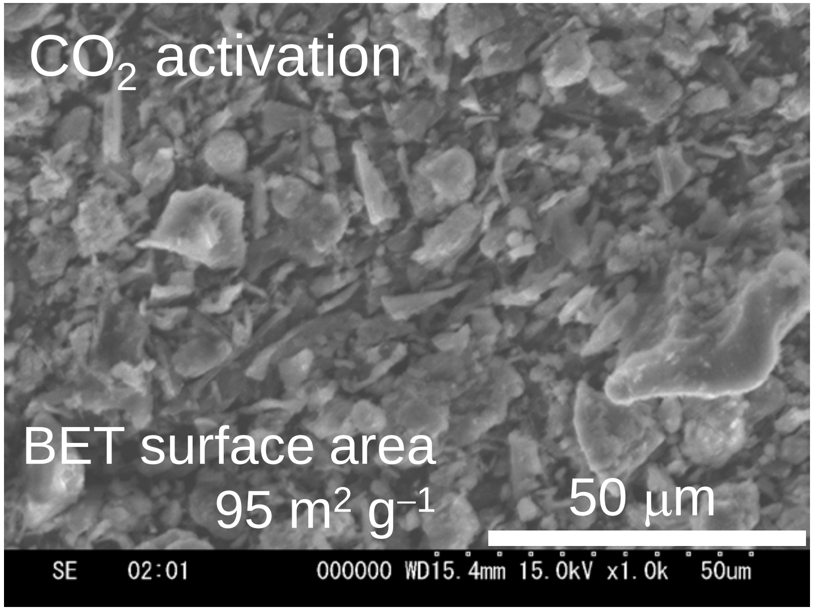




CO_2-activated carbon: lower activity than Vulcan

Possible properties correlating with ORR performance

SEM image



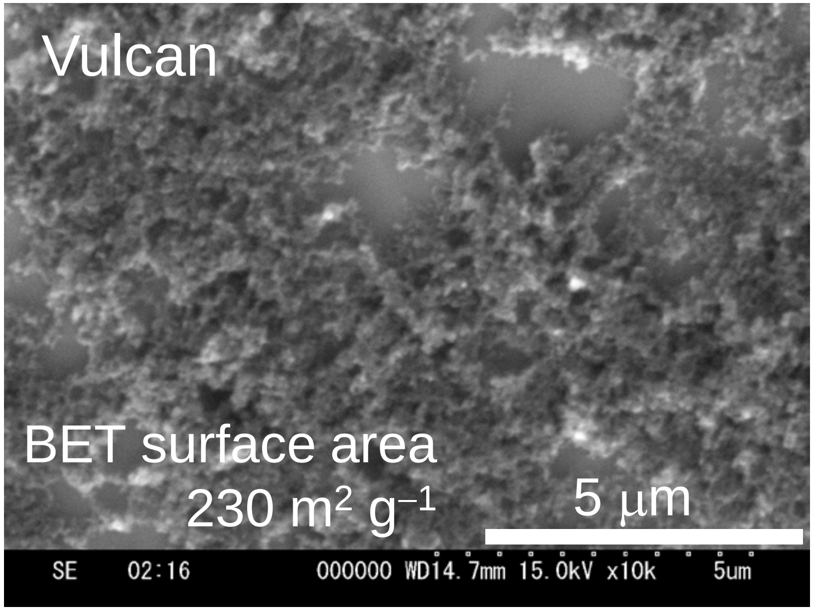
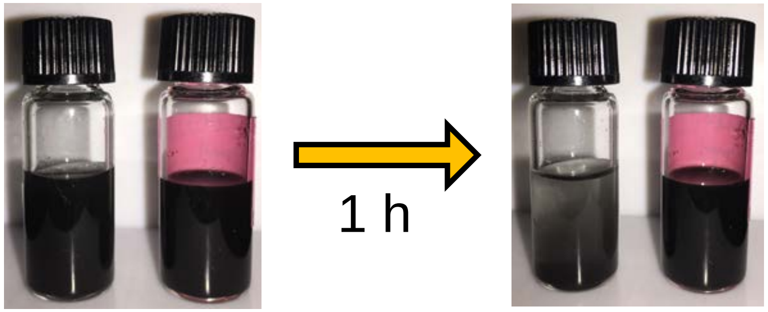


Photo of catalyst ink



CO_2-activated carbon

- Large particle size
- Low dispersibility

Reason for the low activity of CO_2-activated carbon

Summary

- Biomass carbon from oil palm empty fruit bunches were applied to EDLC electrodes and an air electrode in MARB.

- Pore development and increase in defects were observed after CO_2 activation.

- The performance of EDLC was drastically enhanced after the CO_2 activation.

- Reduction of particle size and enhancement of dispersibility are required to apply present carbon to the air electrode in MARB.