Application of carbon-coated anodic aluminum oxide film for biofuel cell

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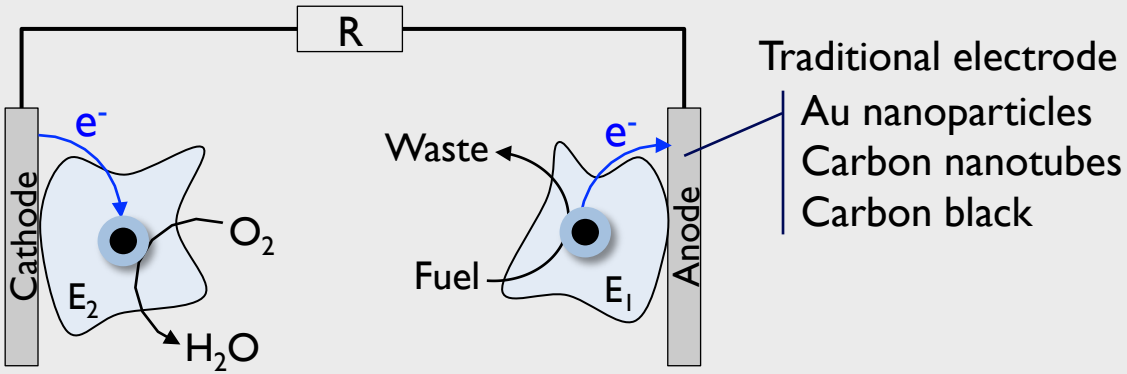
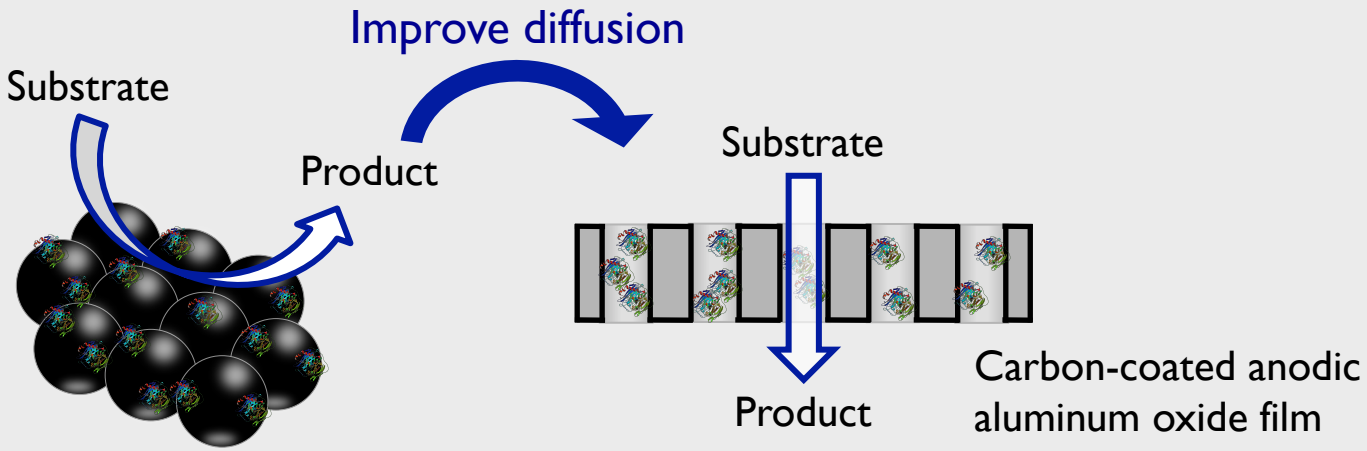
Enzymatic biofuel cell

Energy conversion device that transforms chemical energy to electrical energy by using enzyme as electrocatalysts and can operate under mild conditions

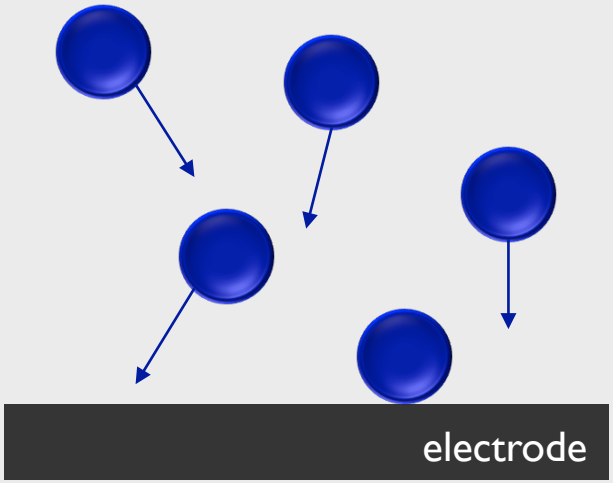
→ Safe electrical generator



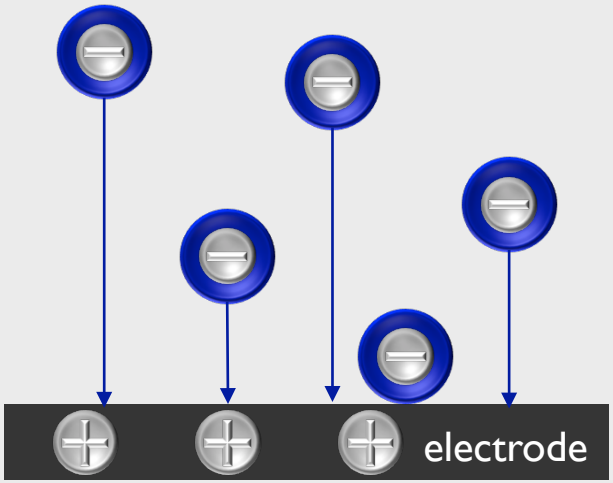


Immobilization of enzyme

Physical adsorption method



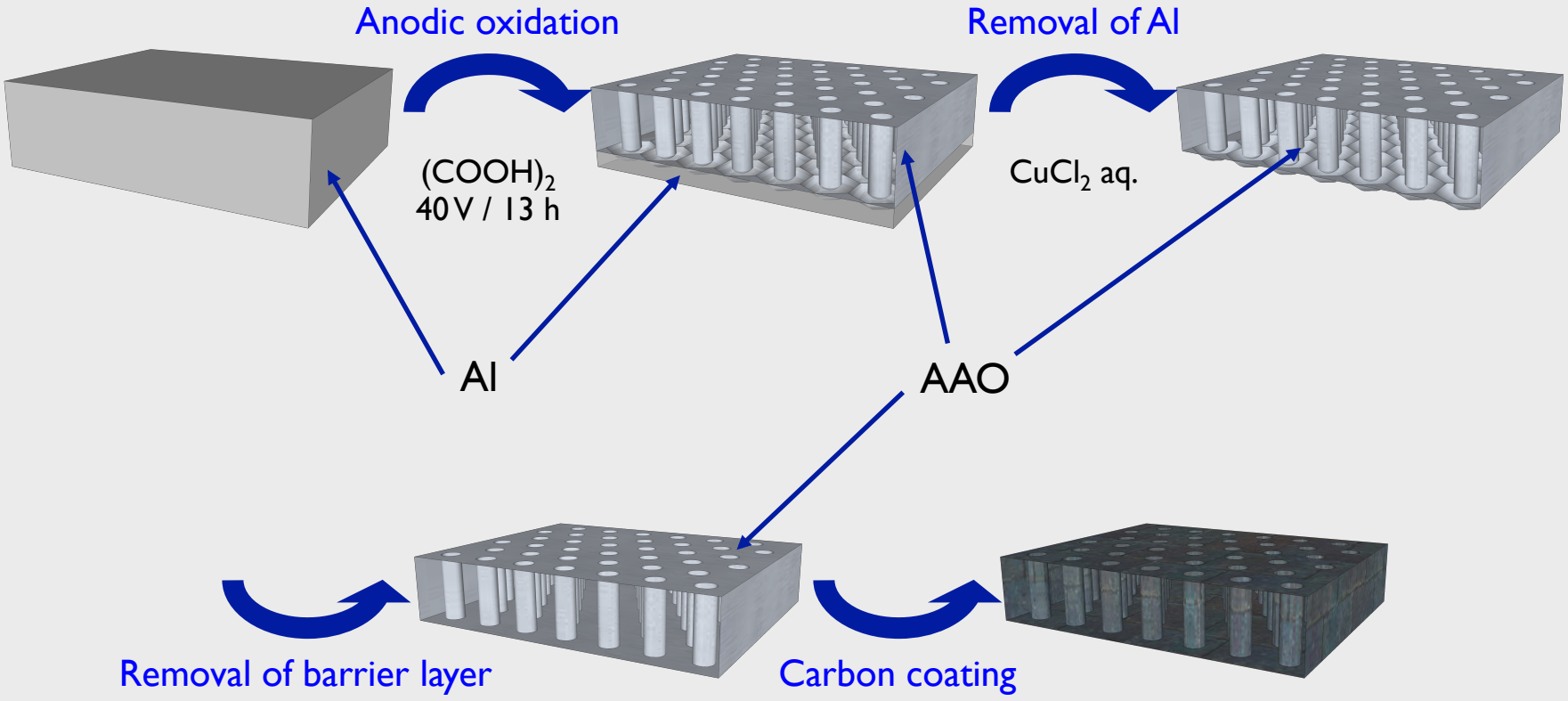
Electrophoresis method

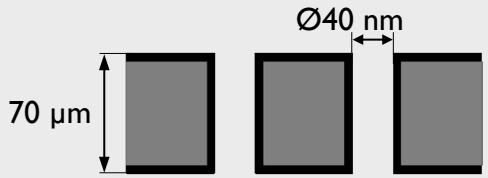


Objective of this study

To prepare enzymatic electrodes for biofuel cells by immobilizing enzyme onto the CAAO film in two ways and consider about enzyme immobilization method

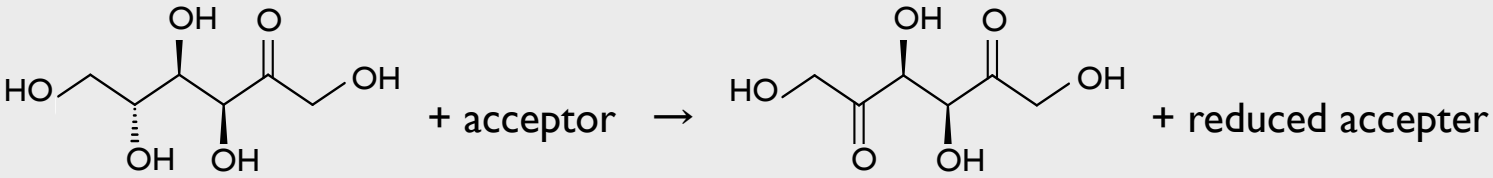
Preparation of carbon-coated anodic aluminum oxide (CAAO) film





Immobilization of enzyme into the CAAO nanochannels

Anode Fructose dehydrogenase (FDH)



Cathode Laccase

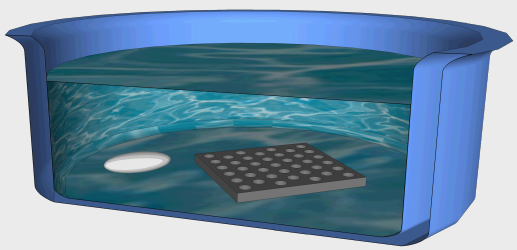
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

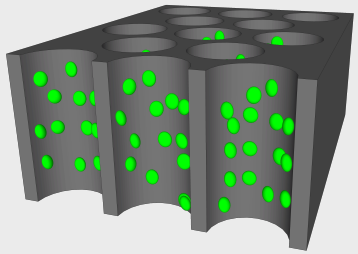
Physical adsorption method

McIlvaine buffer solution (pH 5)

Anode ⇒ 0.5 mg/ml FDH, 15 h

Cathode ⇒ 11 μg/ml laccase, 48 h

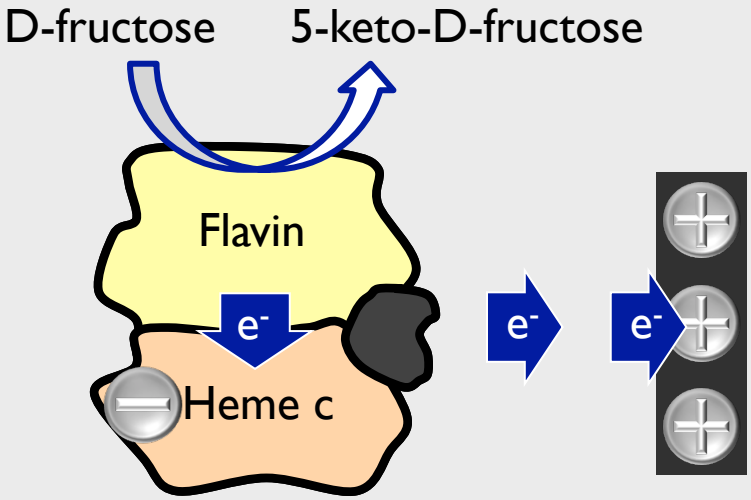




Immobilization of enzyme into the CAAO nanochannels

Electrophoresis method

Anode

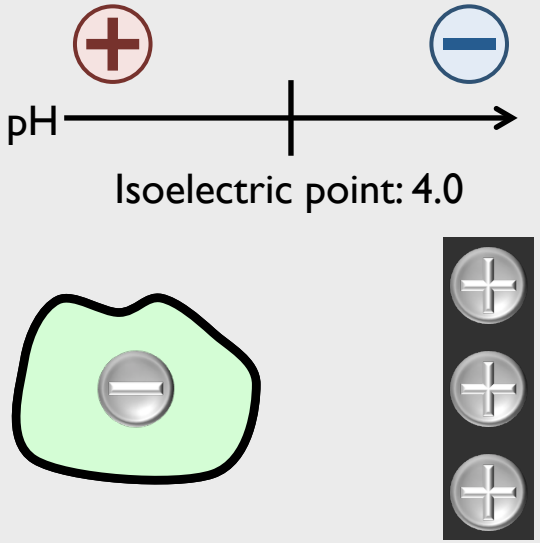


+ 0.6 V vs. Ag / AgCl, 1 h

McIlcaine buffer solution (pH 5)

3 mg/ml FDH – 200 mM D-fructose

Cathode

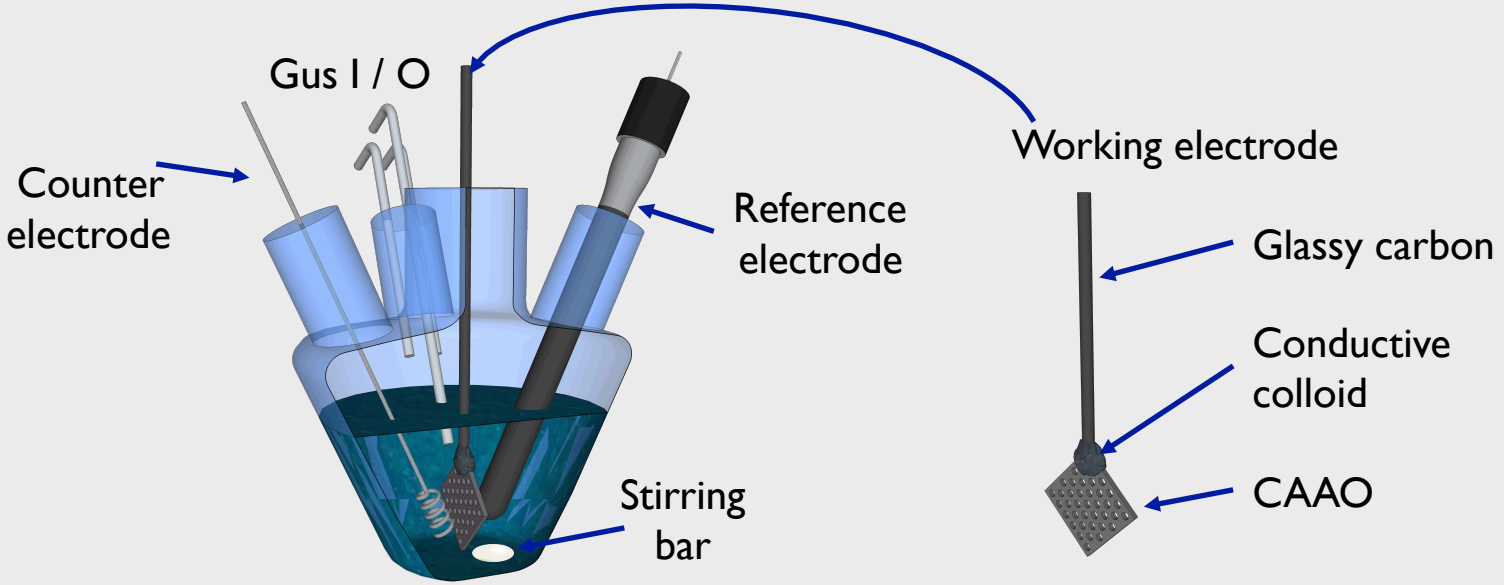


+ 0.65 V vs. Ag / AgCl, 3 h

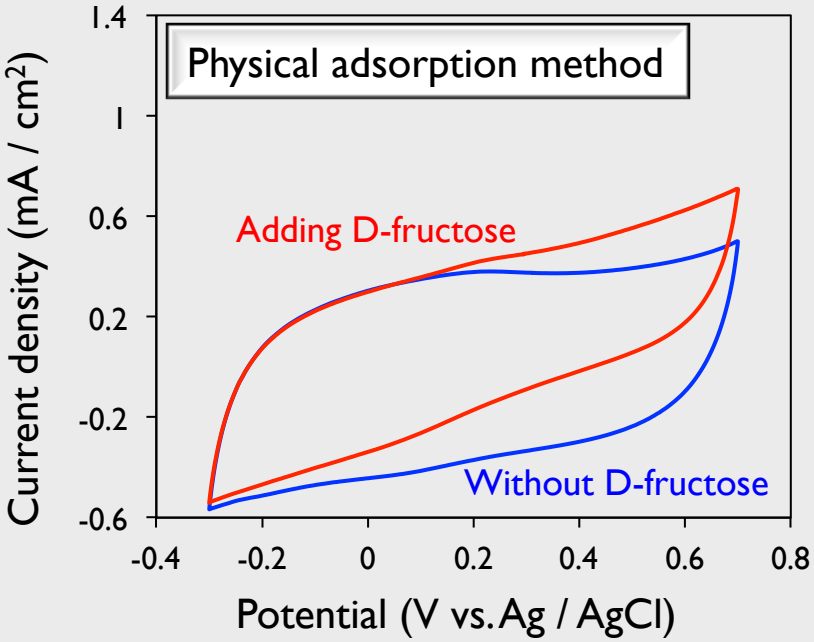
McIlvaine buffer solution (pH 5)

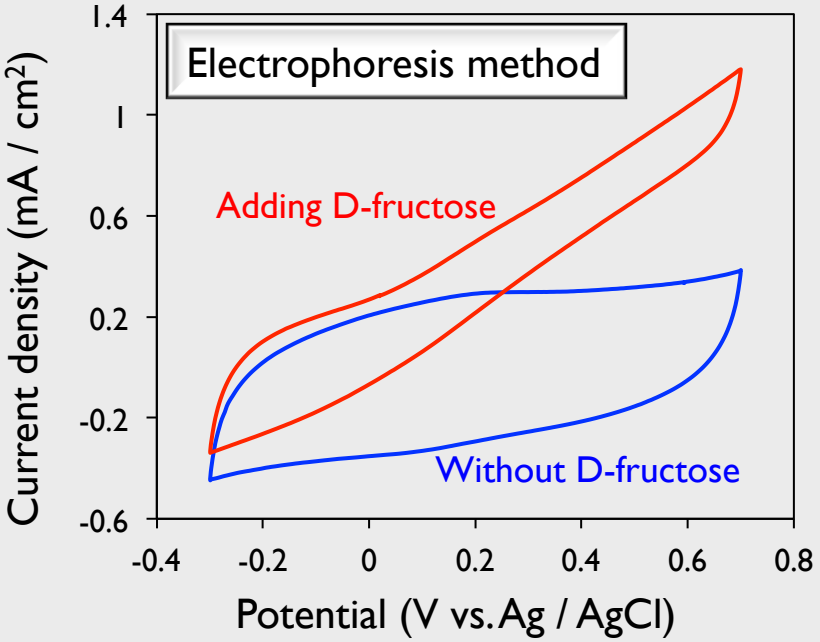
4.5 μg/ml laccase

Measurement of electrical performance (Cyclic voltammetry)



Working electrode	⇒ CAAO with glassy carbon
Counter electrode	⇒ Pt wire
Reference electrode	⇒ Ag / AgCl / KCl (sat.)
Electrolyte	⇒ (Anode) McIlvaine buffer solution (pH 5) + 200 mM D-fructose (Cathode) McIlvaine buffer solution (pH 5) / O_2 sat.
Temperature	⇒ 25°C
Potential (vs. Ag / AgCl)	⇒ (Anode) -0.3 ~ 0.7 V / (Cathode) 0.0 ~ 0.8 V
Cycle number	⇒ 4 cycles





Maximum current density

Physical adsorption method
⇒ 0.7 mA / cm^2 at 0.7 V

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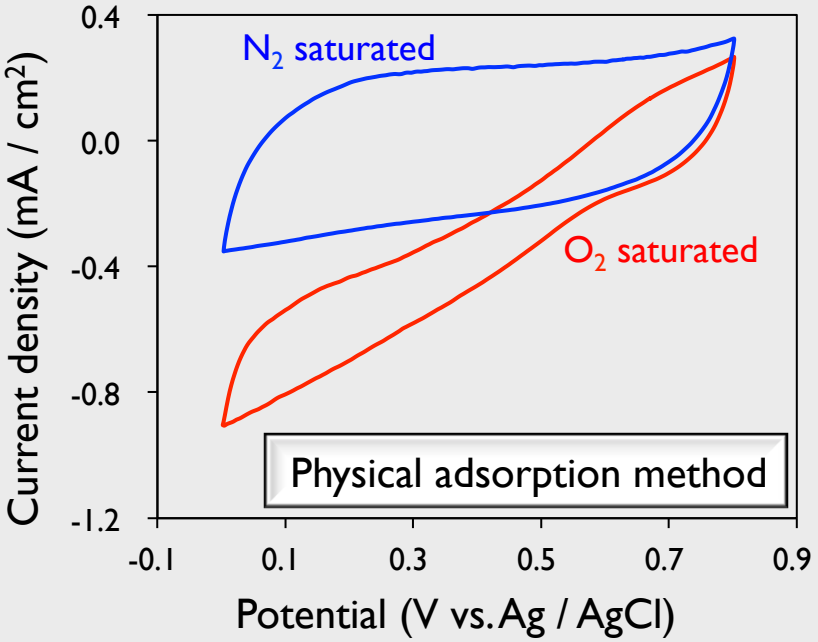
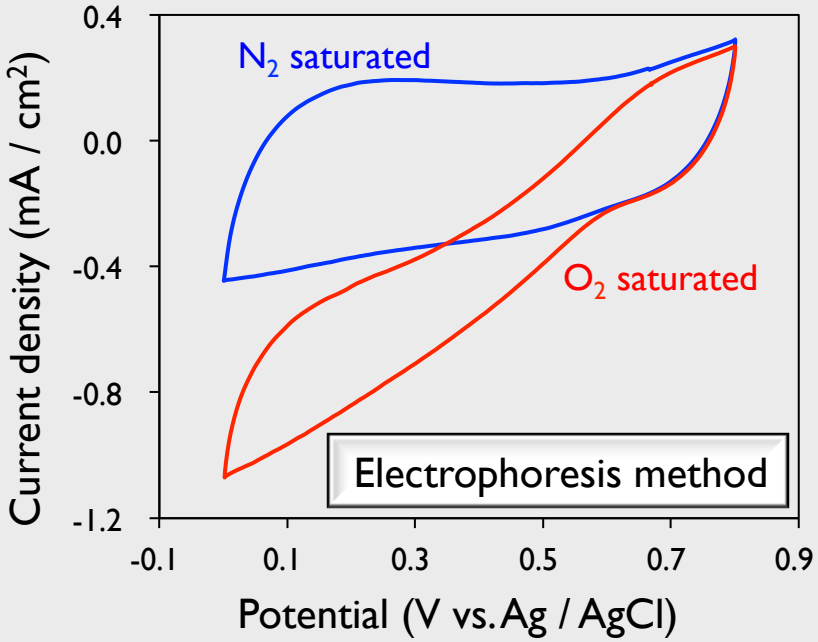
Electrophoresis by enzymatic reaction
⇒ 1.2 mA / cm^2 at 0.7 V





Maximum current density

Physical adsorption method
⇒ -0.9 mA / cm^2 at 0 V

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Electrophoresis by pH control
⇒ -1.1 mA / cm^2 at 0 V

- Carbon-coated anodic aluminum oxide films can used as enzymatic electrode

- Electrophoresis method is a more efficient way of enzyme immobilization than physical adsorption method

  ⇒ Development of Enzymatic biofuel cells with high electrical performance is expected by using electrophoresis method

Future works

- Quantitative determination of immobilized enzyme

  BCA method ⇒ Common protein quantification method

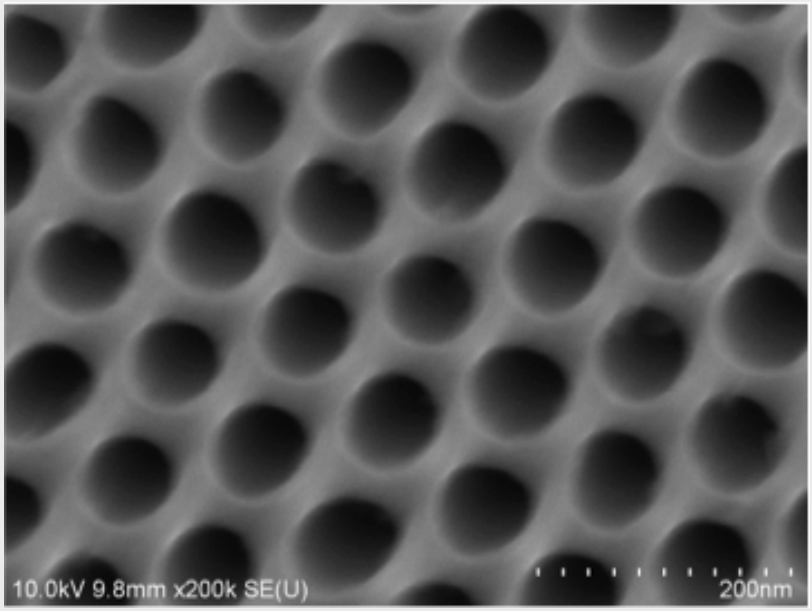
  TPD method ⇒ Analyze gas desorbed from sample by heating under high vacuum

- Investigation of diffusion effect

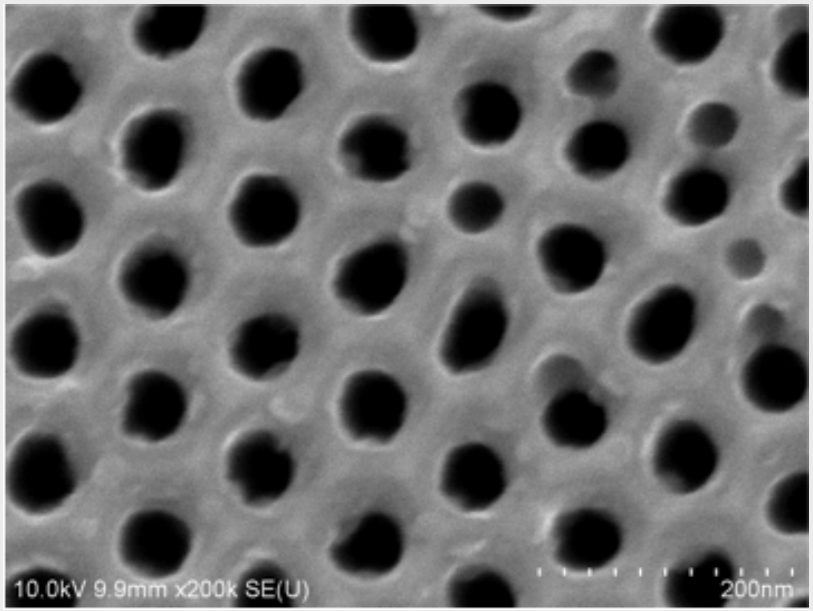
- Investigation of stability of enzymatic electrode

SEM images of CAAO

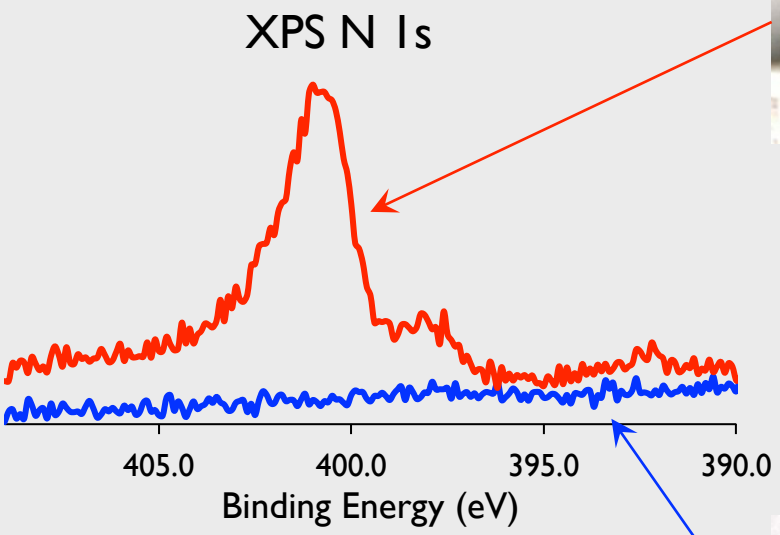
Pore layer

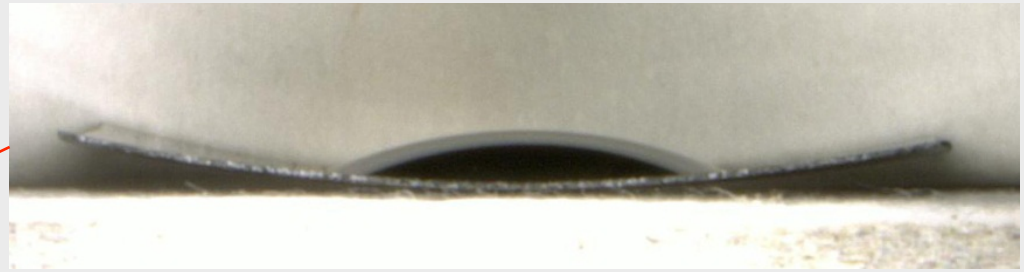


Barrier layer

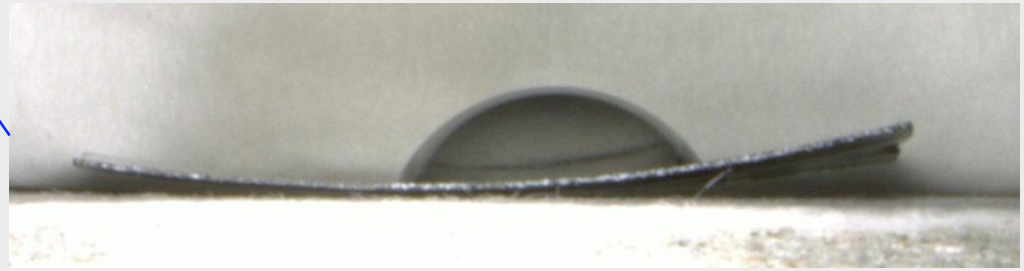


Hydrophilicity of CAAO

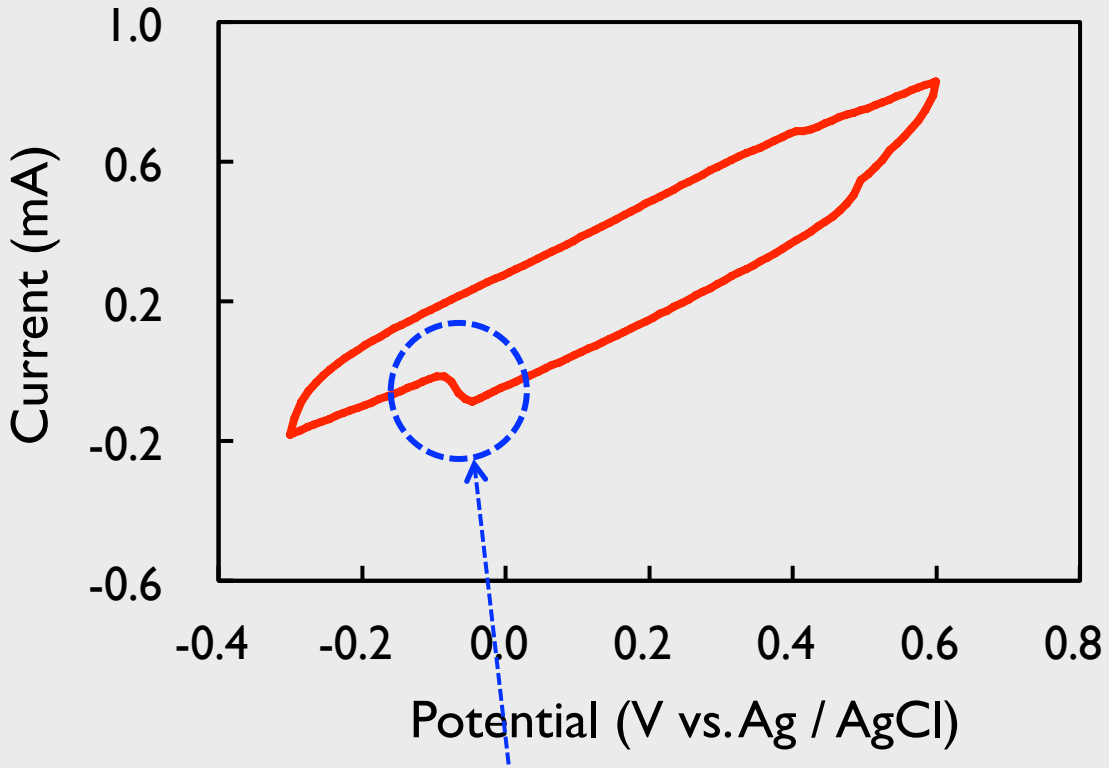


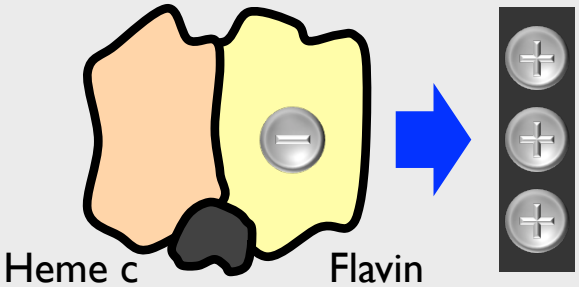


(CVD) CH_3CN / 800°C / 4 h
(Heat treatment) 900°C / 1 h



(CVD) C_2H_2 / 600°C / 4 h
(Heat treatment) 900°C / 1 h



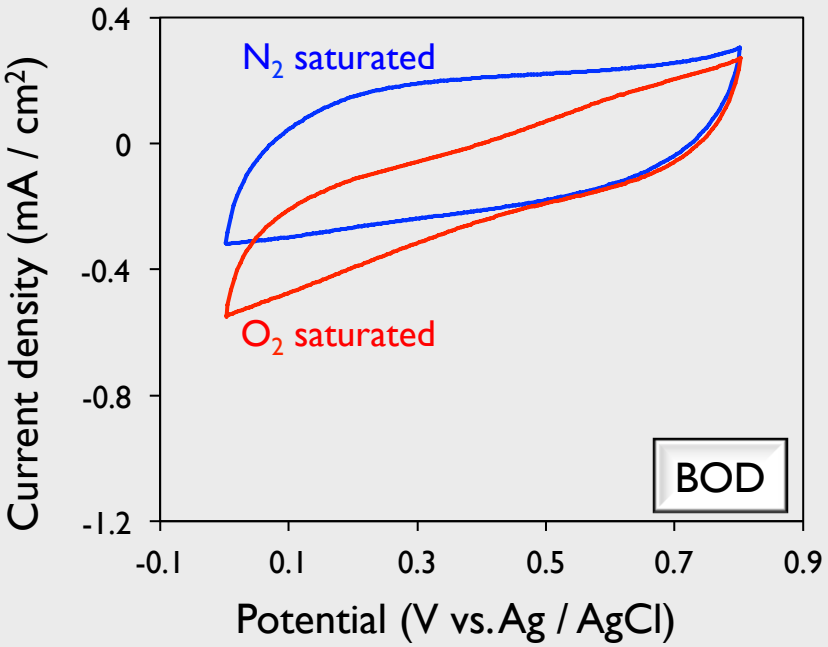


This peak derives from pyrroloquinoline quinone in flavin site

⇓

Electron doesn't transfer from heme site to electrode successfully

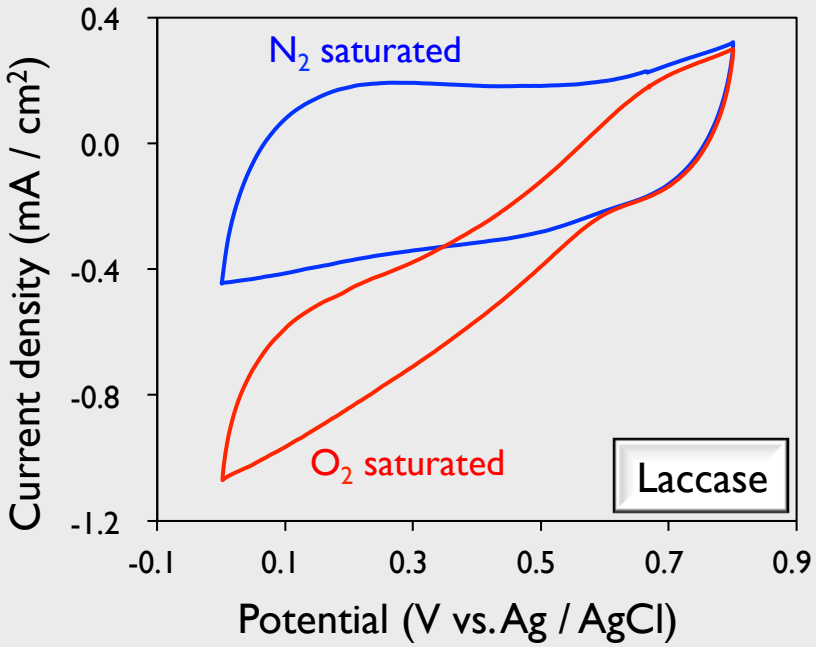
Comparison of laccase with bilirubin oxidase (BOD)



+ 0.60 V vs. Ag / AgCl, 3 h

McIlvaine buffer solution (pH 5)

250 µg/ml BOD



+ 0.65 V vs. Ag / AgCl, 3 h

McIlvaine buffer solution (pH 5)

4.5 µg/ml laccase

Redox potential ⇒ BOD < Laccase

Maximum current density ⇒ BOD < Laccase

Laccase id more suitable than BOD to develop enzymatic electrode with high electrical performance