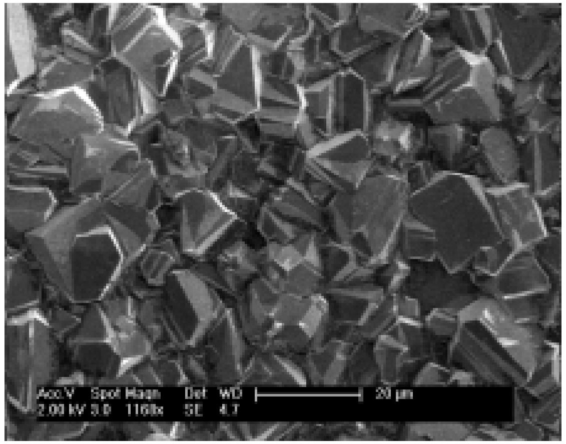
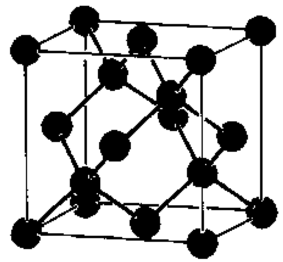
Electrochemical application on boron-doped diamond electrodes



Yasuaki Einaga

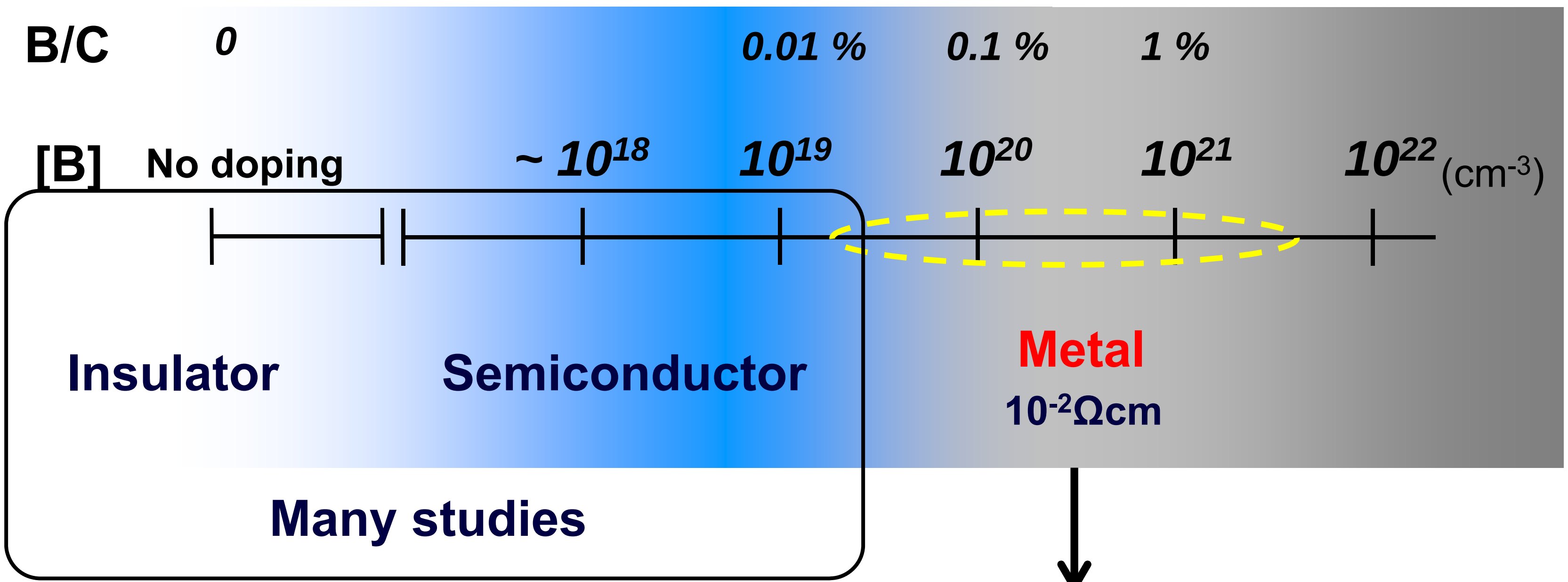
Department of Chemistry
Keio University
Japan

Boron-doped Diamond (BDD)



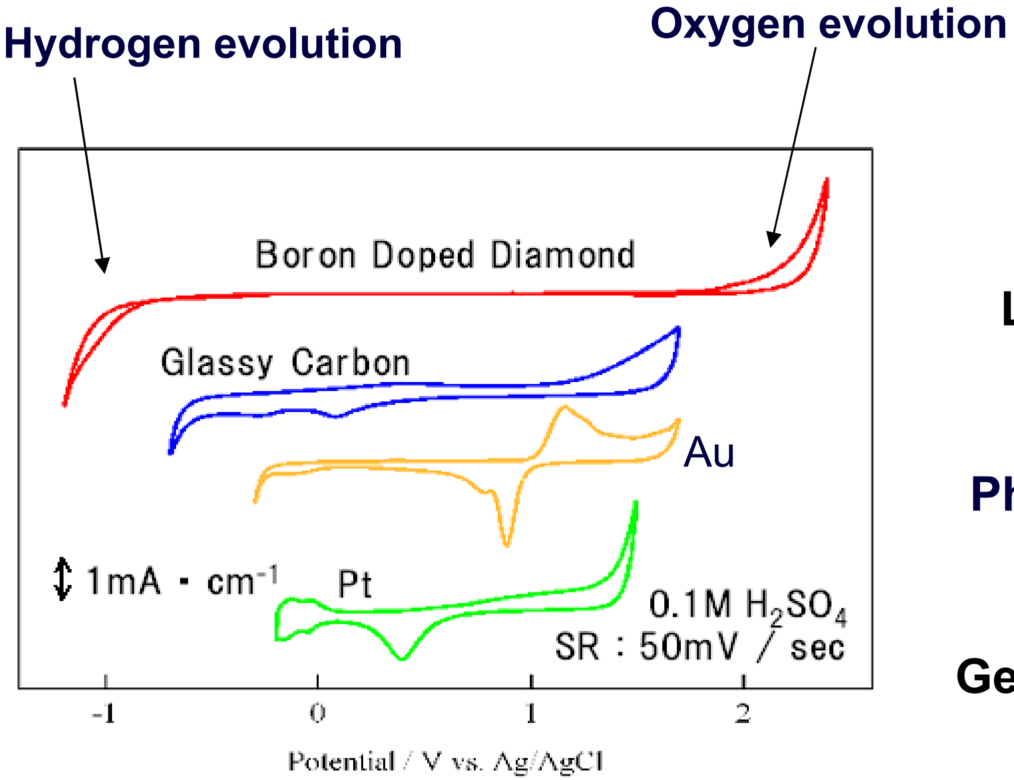
Boron concentration

carbon density in diamond = 1.76×10^{23}
boron solubility into diamond ≥ 1.4×10^{22}



Diamond Electrodes

Electrochemical Properties of Boron-doped Diamond (BDD) Electrodes



Wide potential window
（-1.2～2.0V）

Low background current
（100 nAcm^{-2})

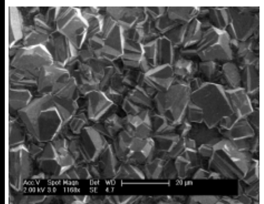
Physically and chemically stable

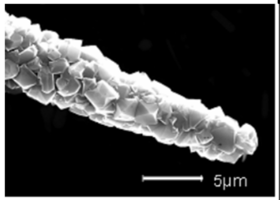
Generation of active species
(･OH etc)

Development of diamond electrodes (2000～)

Heavy metals, Chlorine, etc

Environmental sensors



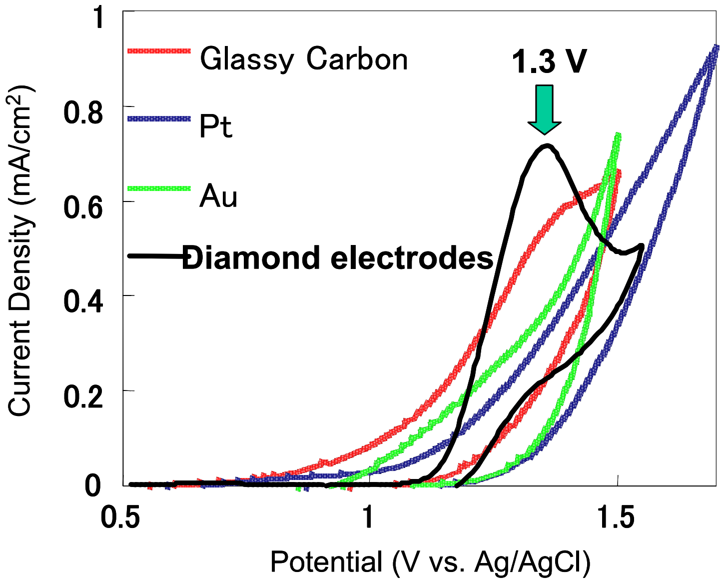


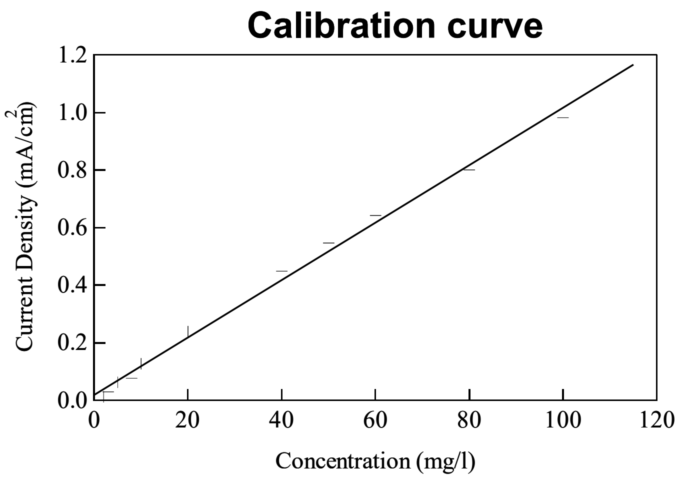
Diamond Electrodes

Bio, Medical sensors

Glucose, Uric acid, Oxalic acid,
Cancer marker, Neurotransmitter

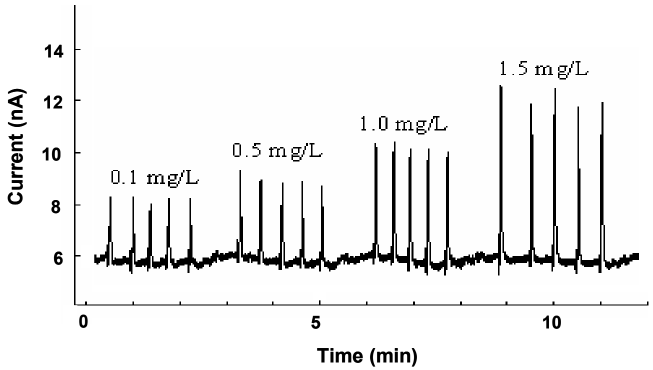
Detection of free chlorine

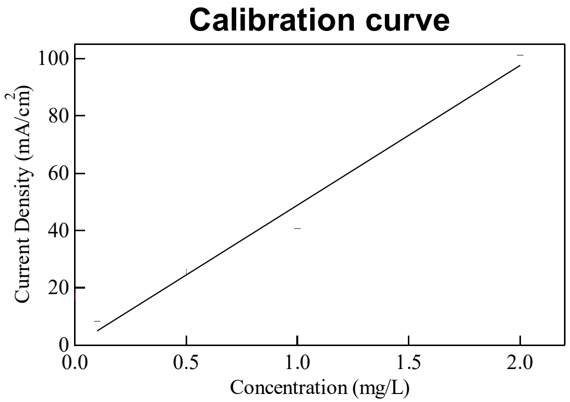




$$6ClO^- + 3H_2O \rightleftarrows 3ClO_3^- + Cl^- + 6H^+ + 3/2O_2 + 6e^-$$

Hypochlorite ion

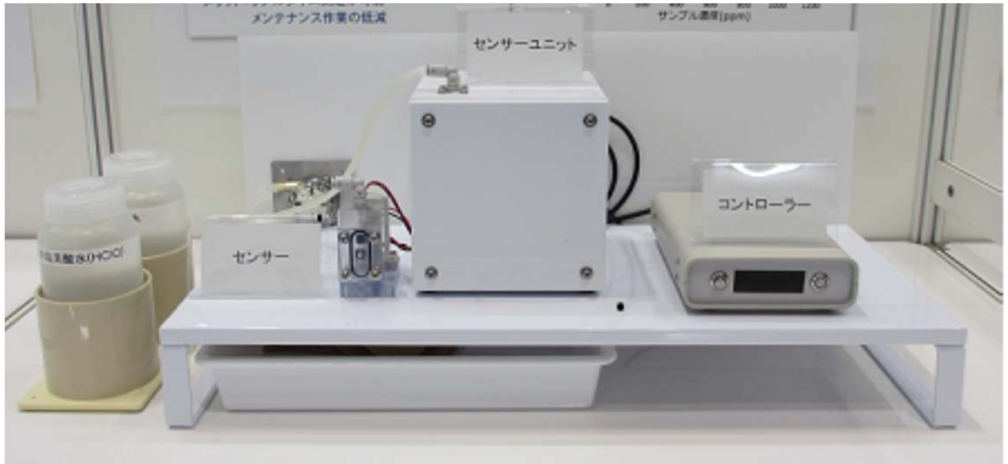




Even in low concentration region（0－2ppm）, the detection was possible.

***J. Electroanal. Chem.*, 612, 29 (2008).**

Prototype of Residual Chlorine Monitor (2018)



HORIBA Advanced Techno

Functional Water Foundation

Press release: Aug. 30th, 2018

In China (2019)

Institute for Electronics and Information Technology in Tianjin, Tsinghua University

清华大学天津电子信息研究院 ・ HORIBA（堀場製作所）

Cd detection in rice

2019/7/26 清华大学天津电子信息研究院 - Institute for Electronics and Information Technology in Tianjin, Tsinghua University

大米镉浓度的测定

应用背景

目前我国大米加工企业、大米贸易公司以及众多的食品企业都需要在购买稻谷和大米原料对镉浓度进行检测，以确保食品安全。所以，大米镉浓度检测仪将随着人们对食品安全的重视而得到关注和推广。

仪器名称	便携式大米测镉仪
应用	大米镉浓度国家标准 0.2ppm筛查
测试范围	0~1.00mg/kg（PPM）

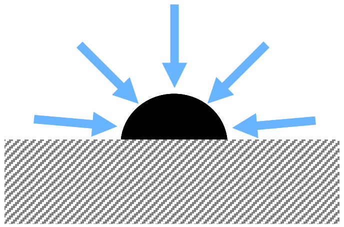
技术简介

当前食品卫生与安全是社会关注的问题。环境污染有可能带来的粮食重金属污染，其中以镉污染最为严重。为提高大米中镉含量测定的速度及简便性，确保大米质量安全，我院偕同 HORIBA 公司研制了便携式大米测镉仪，采用公司特制高灵敏度金刚石电极，可快速、高效、准确地检测大米中的镉含量

Next generation electrodes for sensor

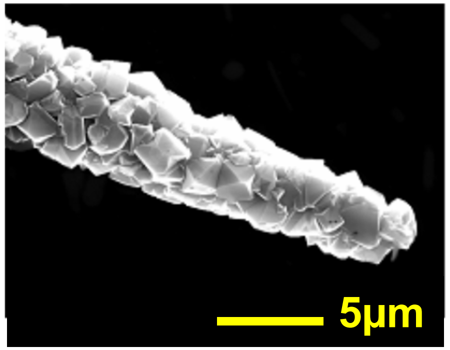
Electrochemical analysis by BDD microelectrodes

< Remarkable properties of microelectrodes >



three dimensional diffusion

- High current density
- High sensitivity
- Steady-state current response
- Negligible effect of IR drop

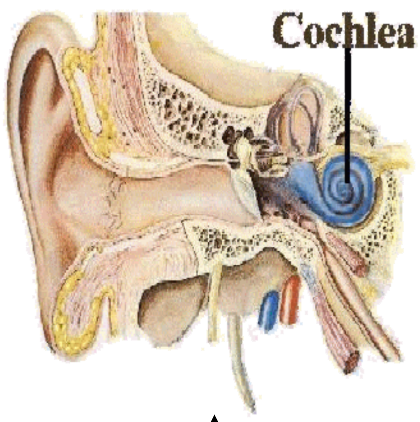


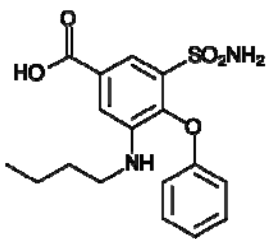
In vivo detection

Recent Topics

Simultaneous detection of phermacokinetics

Drug concentration (Diamond microelectrode) ⟷ **Hearing ability** (Glass microelectrode)



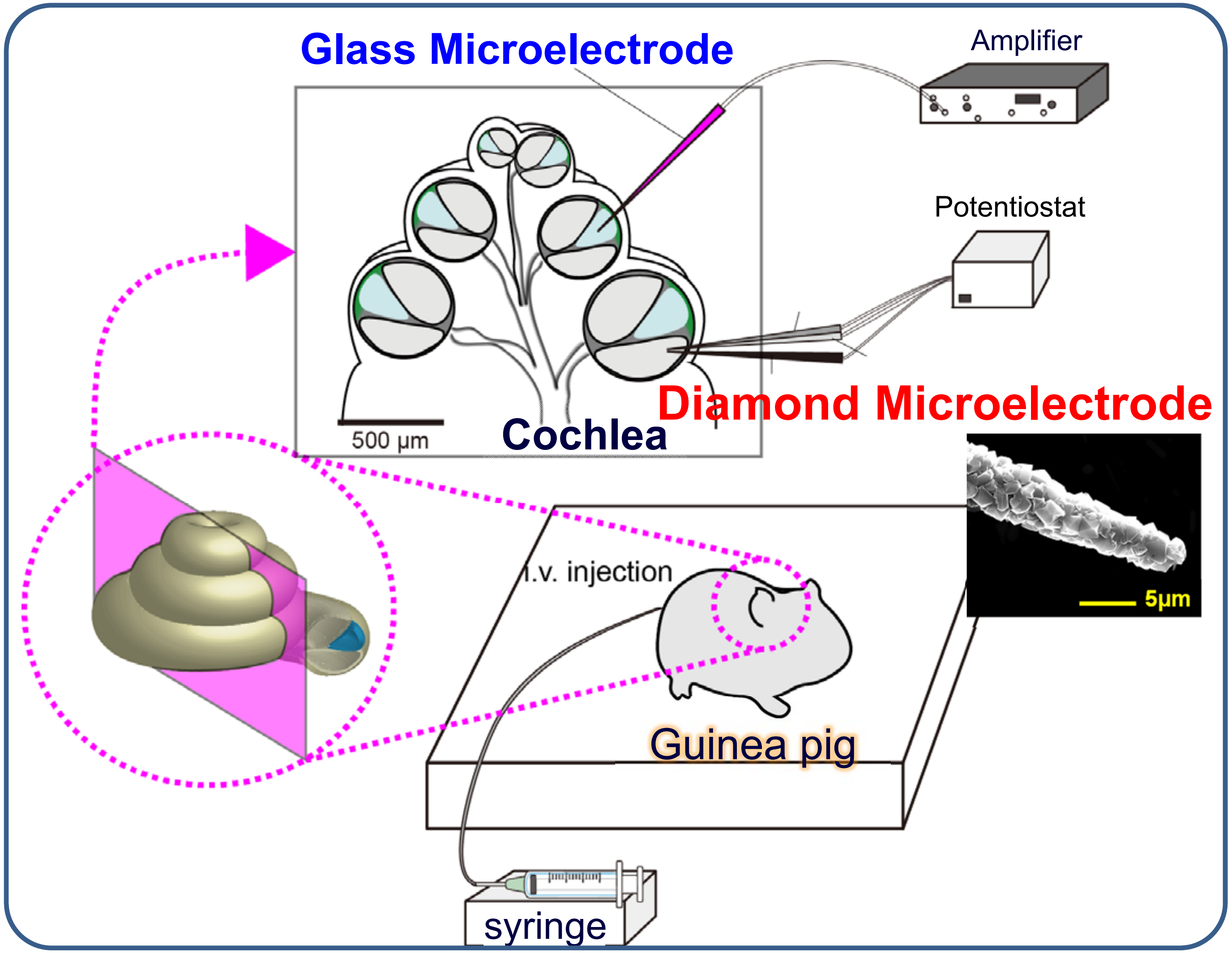


Bumetanide

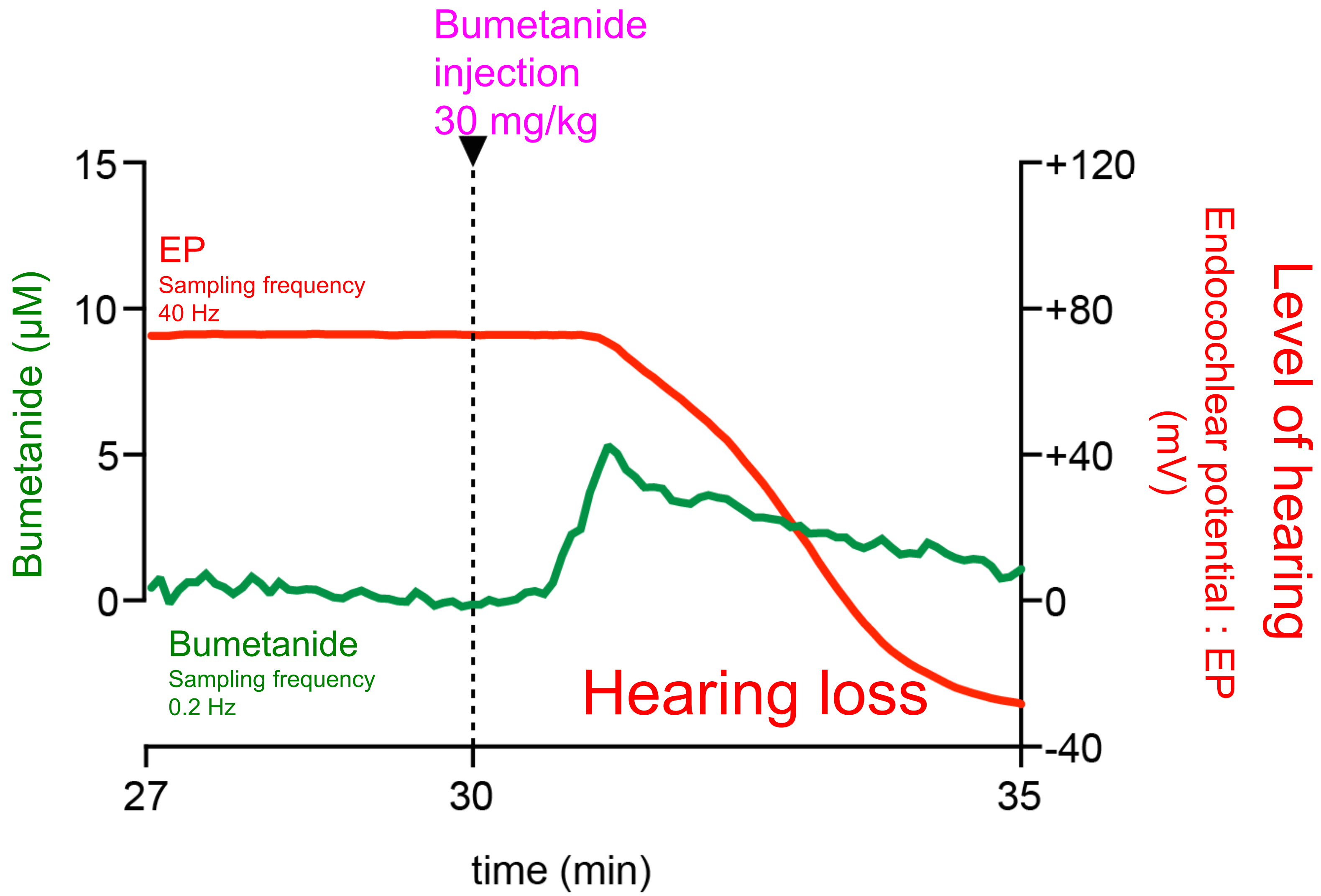
loop diuretic drug

[Uses] edema, neonatal seizures

[Side Effects] **hearing loss**

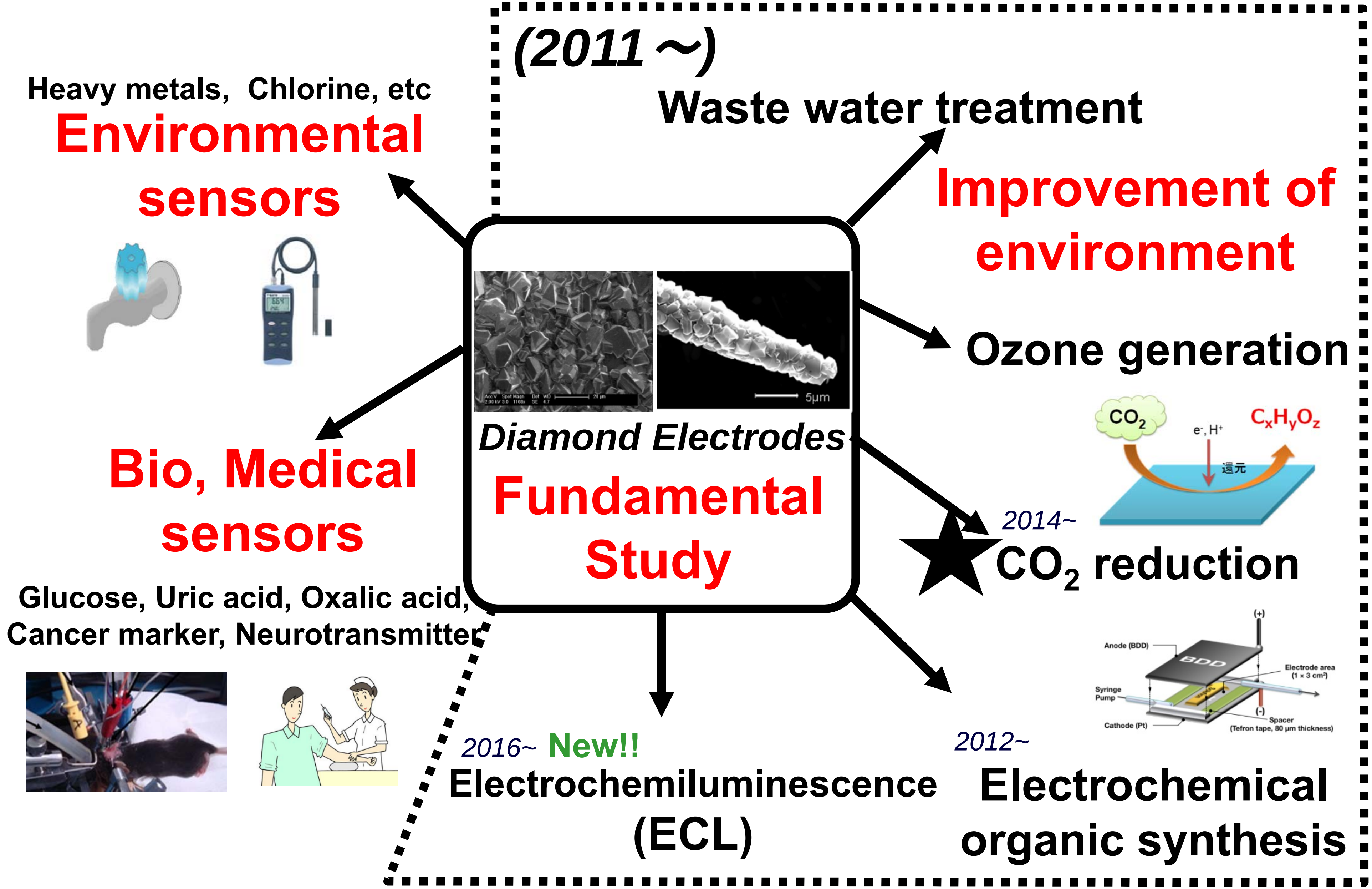


Real time measurement

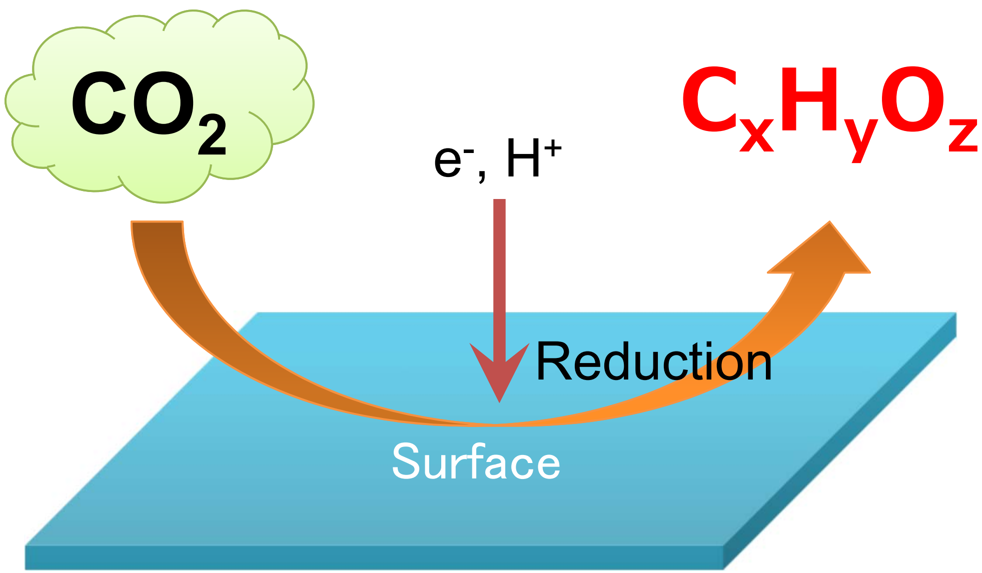


Nature Biomed. Eng. 1, 654 (2017).
Science 359, 1287 (2018).[Highlight]

Development of diamond electrodes



CO_2 Reduction

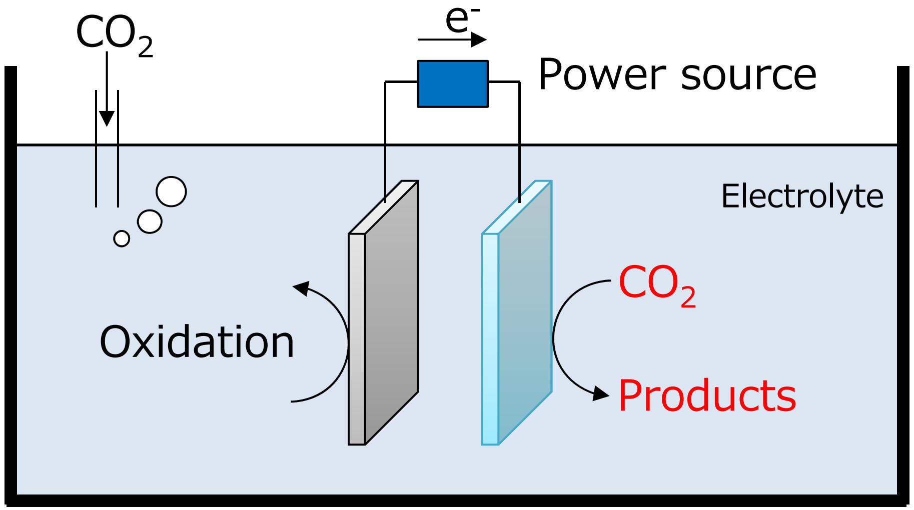


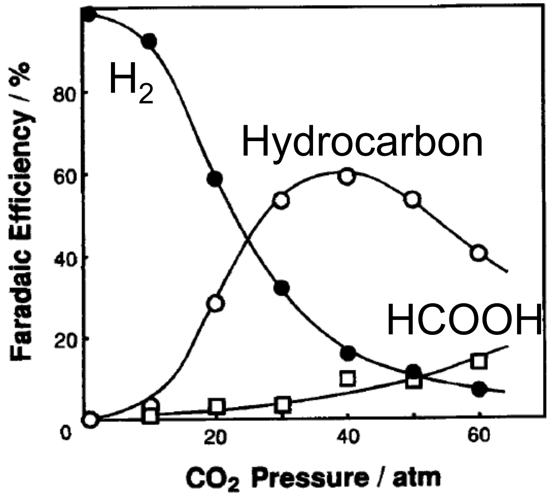
- **Fuel**

- **Plastics**

CO_2 reduction using BDD electrodes

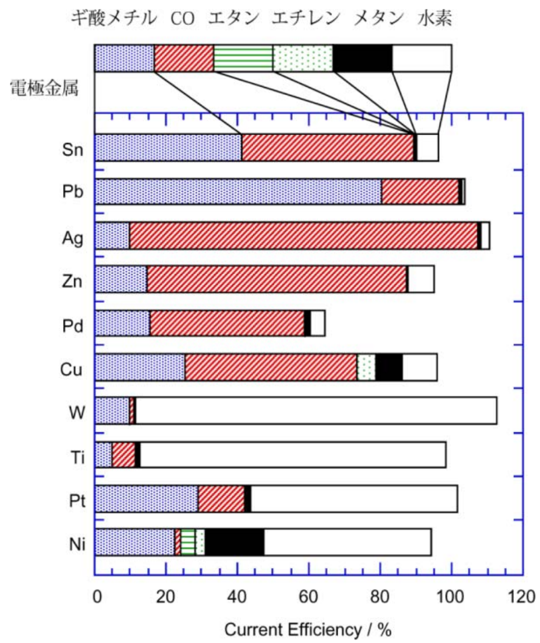
Electrochemical reduction of CO_2 by conventional electrodes (1980~)





Cu electrodes
in H_2O
1-60 atm
25 ^oC

1) $CO_2 + 2H^+ + 2e^- \rightarrow$ **CO** $+ H_2O$
2) $CO_2 + 2H^+ + e^- \rightarrow$ **HCOOH**
3) $CO_2 + 6H^+ + 6e^- \rightarrow$ **CH_3OH** $+ H_2O$
4) $CO_2 + 8H^+ + 8e^- \rightarrow$ **CH_4** $+ 2H_2O$
5) $2H^+ + 2e^- \rightarrow$ **H_2**

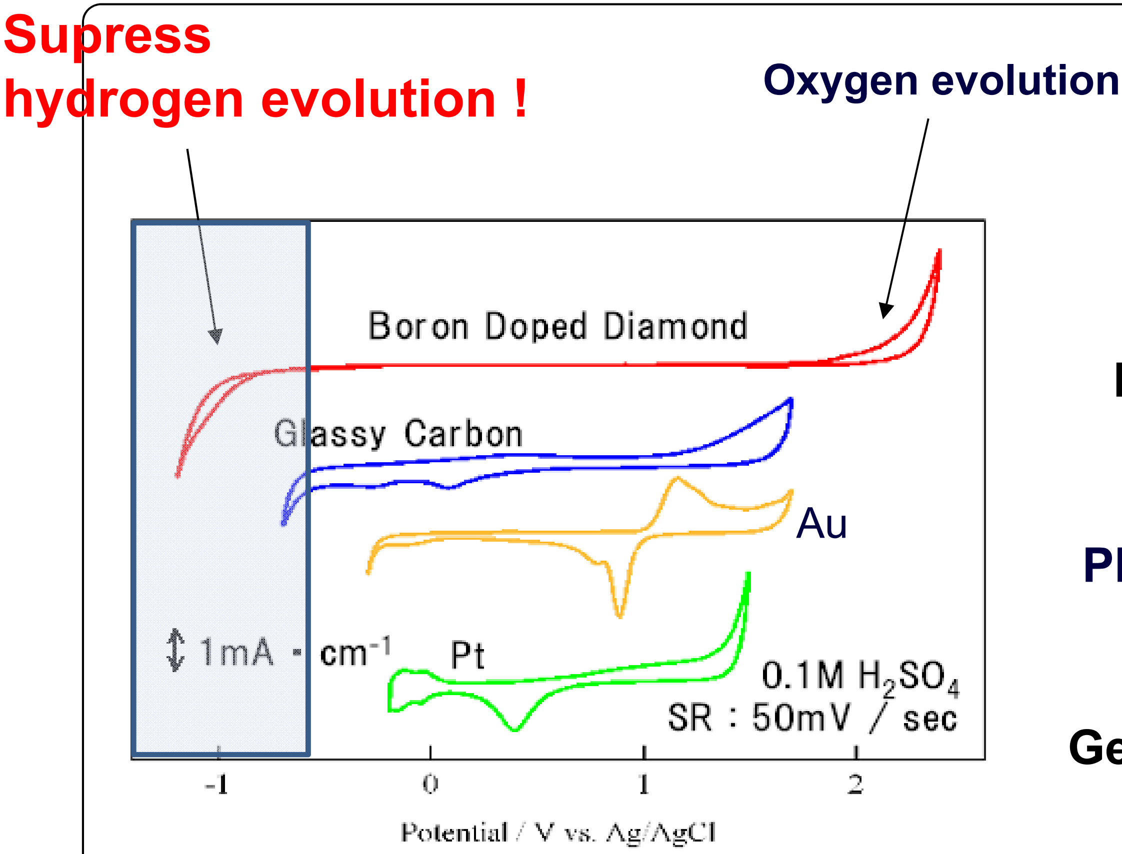


in MeOH
41 atm
25 ^oC

Low efficiency
High pressure
Low stability

J. Electrochem. Soc., 141, 2097 (1994); *J. Electroanal. Chem.*, *404*, 299 (1996).

Electrochemical Properties of Boron-doped Diamond (BDD) Electrodes



Wide potential window
(-1.2～2.0V)

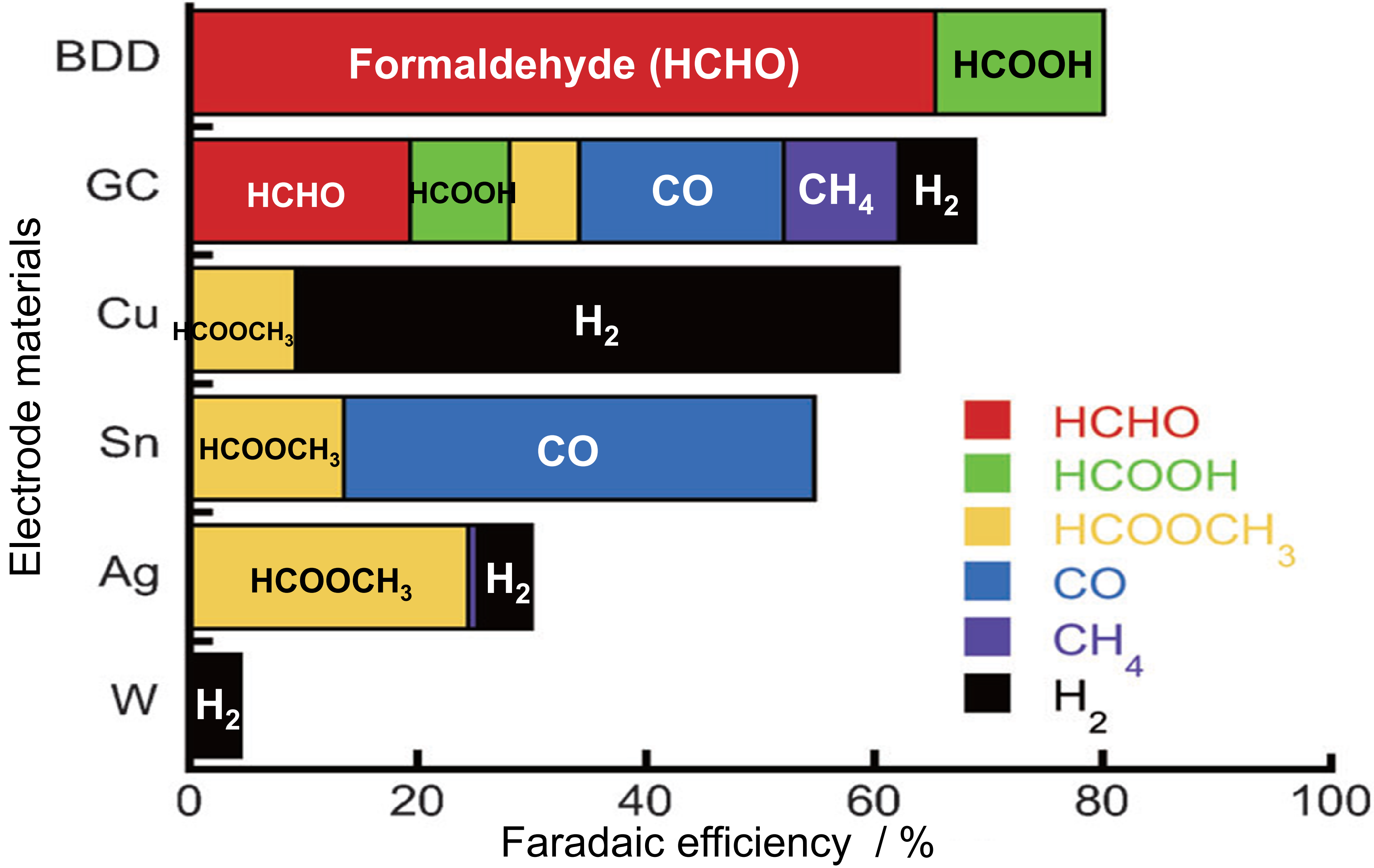
Low background current
(100 nAcm^{-2})

Physically and chemically stable

Generation of active species
(·OH etc)

Reduction of CO_2

Room Temperature
Ambient pressure



***Angew. Chem. Int. Ed.*, 53, 871 (2014).**

Recent trial for CO_2 reduction

→ 1. 100% Faradaic efficiency

2. Produce more valuable compounds

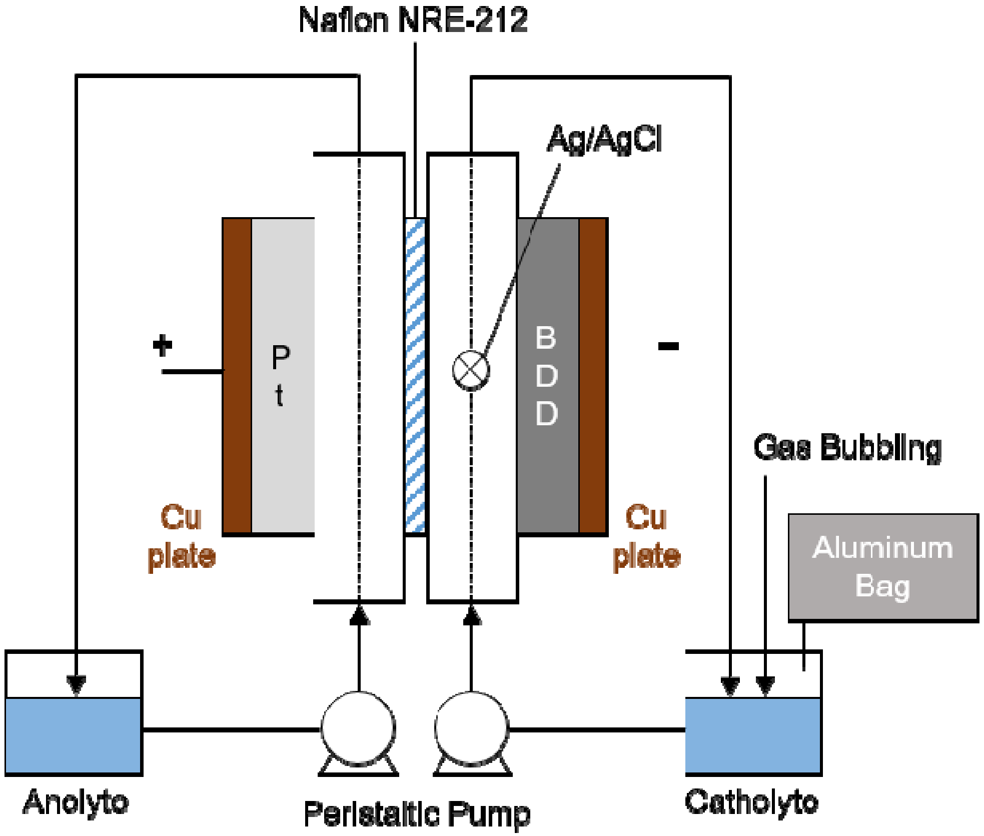
Formic acid production

$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$

Catholyte: 0.5 M KCl aq.
Anolyte: 1.0 M KOH aq.

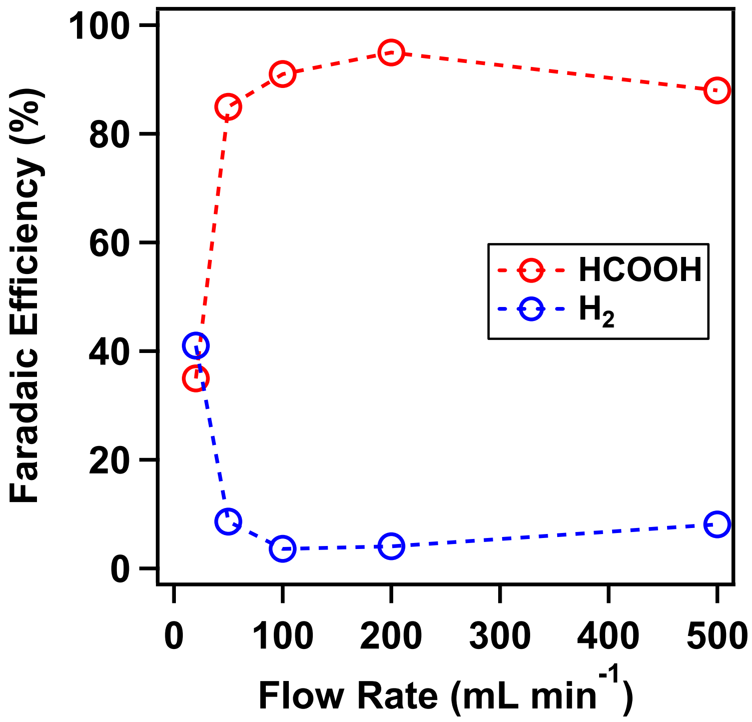
(Current density: 2, 5, 10, 20 mA cm^{-2})

Flow cell



Dependence of electrolyte flow rate

Faradaic efficiency @ 2 mA cm^{-2}



Flow rate (mL min^{-1})	FE of HCOOH (%)	FE of H_2 (%)	Total FE (%)
20	35	41	76
50	85	8.6	95
100	91	3.6	95
200	95	4.1	100
500	88	8.1	99

Faradaic efficiency of HCOOH increased up to 95% with increasing flow rate.

⇒ Progress of CO_2 mass-transport

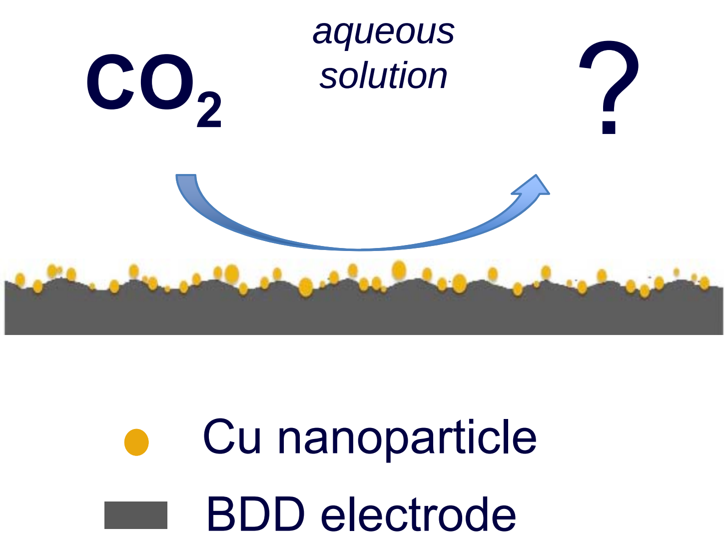
***Angew. Chem. Int. Ed.*, 57, 2639 (2018).**

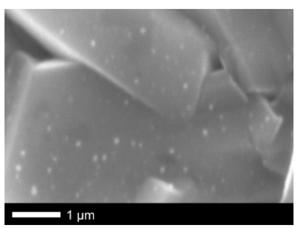
Recent trial for CO_2 reduction

1. 100% Faradaic efficiency

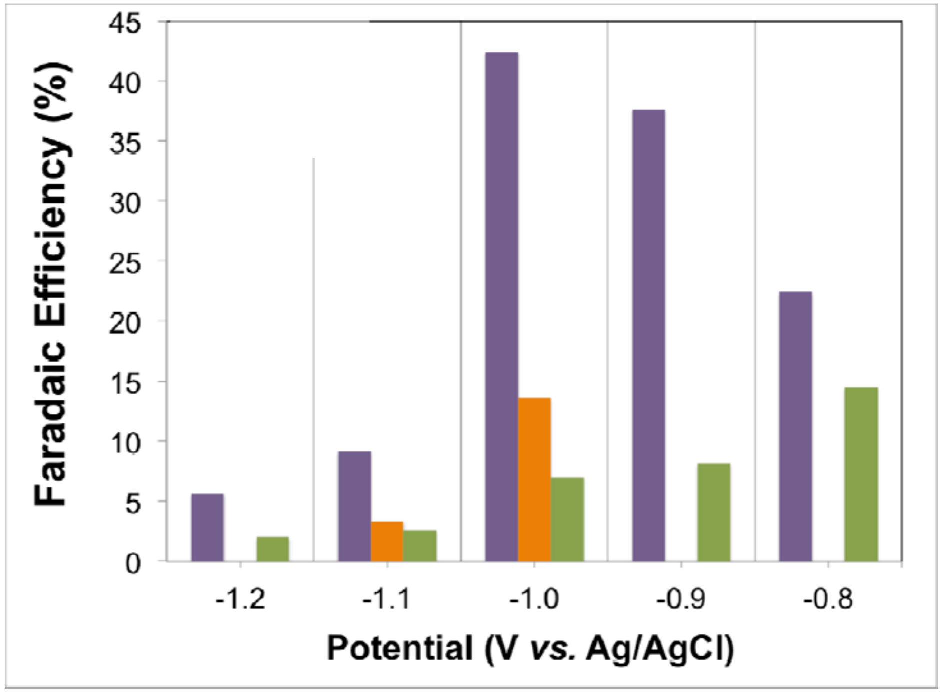
→ 2. Produce more valuable compounds
   (To control of the production)

(1) Cu-modified BDD electrodes





Anolyte: KOH 0.5 M
Catholyte: KCl 0.5 M



C_2H_5OH (Ethanol)

CH_3CHO (Acetaldehyde)

$(CH_3)_2CO$ (Acetone)

C2/C3 compounds were produced!

***Electrochim. Acta*., 266, 414 (2018).**

(2) In Amine Solution

Amine solutions are used for CO_2 absorber….

Examples :

1. MEA (Monoethanolamine)
2. EAE (N-Ethylamino ethanol)
3. DEA (Diethanolamine),
4. **Ammonia solution**

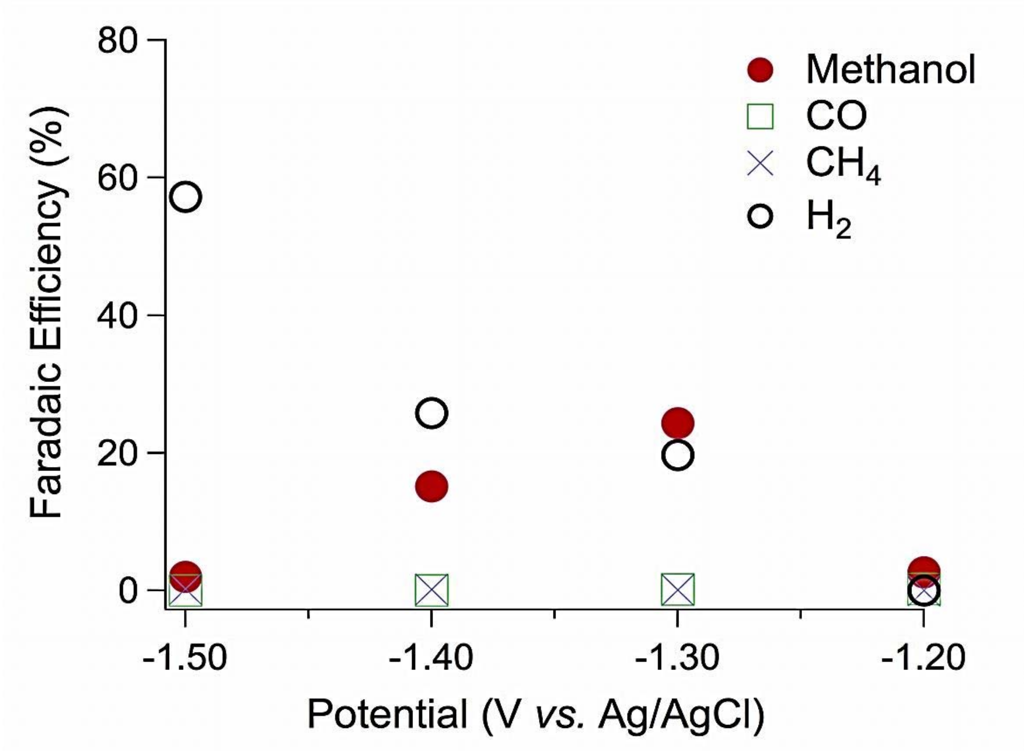
[high loading capacity : 1.76 kg CO_2/kg NH_3

MEA = 0.55-0.58 kg CO_2/kg MEA]

Mani, F. *et al*. *Green. Chem.* **2006**, *8*, 995-1000

Purpose :

$$NH_{3(aq)} + CO_2 \xrightarrow{\text{Reduction on BDD}} ?$$

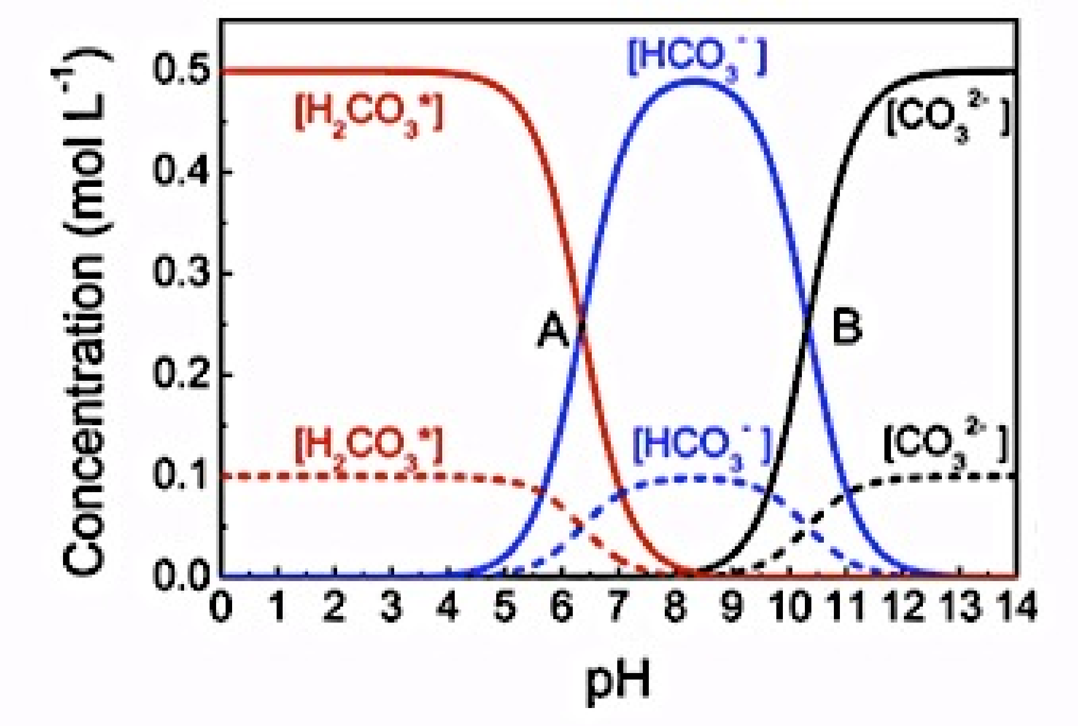


Methanol is the main product

$$NH_3 + CO_2 + H_2O \rightleftarrows NH_4^+ + HCO_3^-$$

$$HCO_3^- + 5H_2O + 6e^- \rightleftarrows \mathbf{CH_3OH} + 7OH^-$$

CO_2 HCO_3^- CO_3^{2-}



$$CO_{2\,(aq)} + H_2O_{\,(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)} \quad pK_1 = 6.35$$

$$H^+_{(aq)} + HCO_3^-{}_{(aq)} \rightleftharpoons 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \quad pK_2 = 10.33$$

Zhong, H. *et al. J. Phys. Chem. C.*, **2015**, *119*, 55-61.

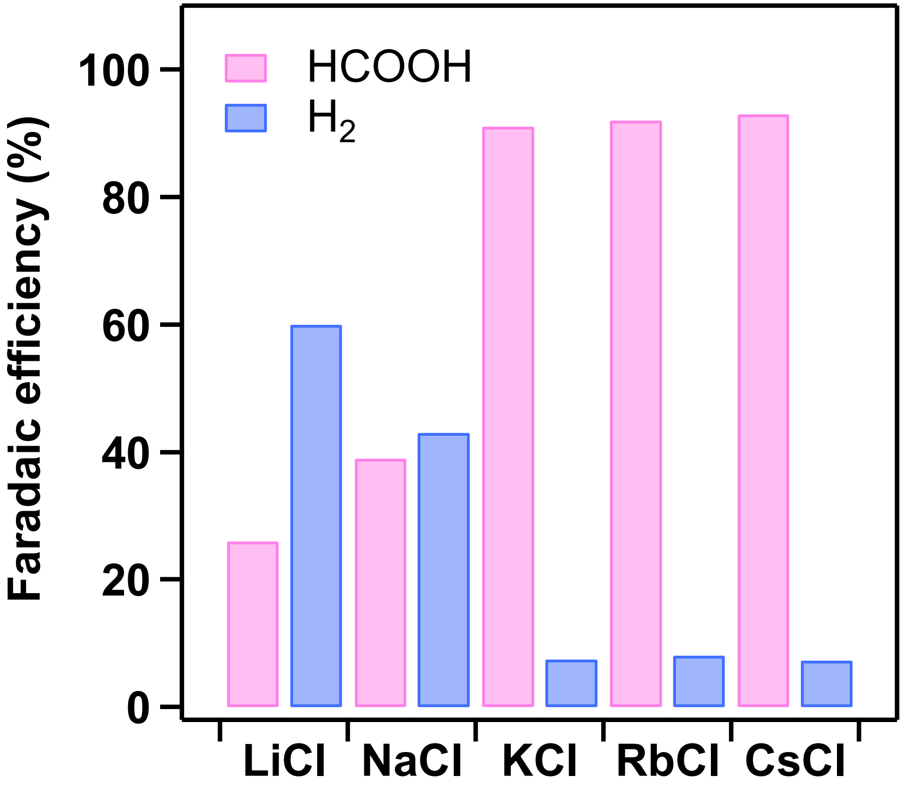
pH 7.5 - 9.0 : HCO_3^- is dominant

pH is also an important factor for the production!!

***RSC Adv.*, 6, 102214 (2016).**

(3) Electrolyte

Cation dependence



Faradaic efficiency for HCOOH production

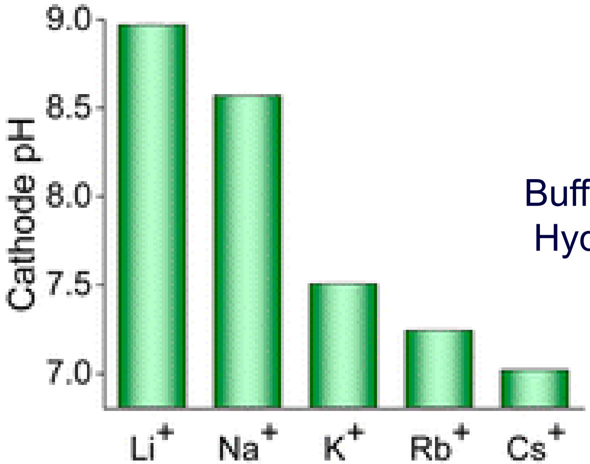
Li, Na << K, Rb, Cs

Buffer effects of alkali cation

CO_2 reduction by Ag electrodes

Singh, M. R. et al. *J. Am. Chem. Soc.* **2016**, *138*, 13006-13012.

pH near cathode



pH increase (near cathode)

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

$2H^+ + 2e^- \rightarrow H_2$

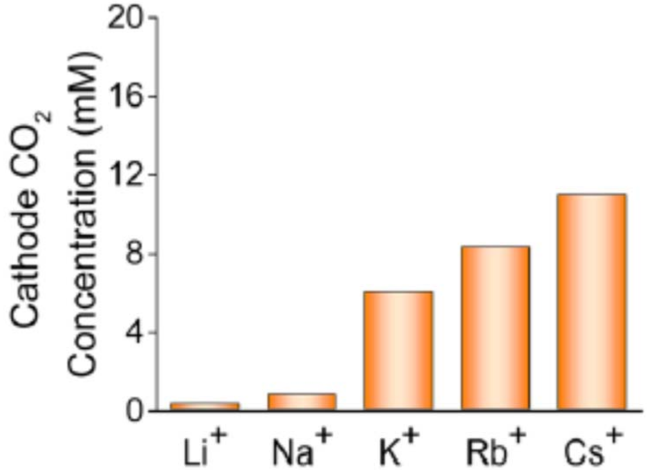
Buffering effect by Hydrated cations

$[M^+(H_2O)_n] \rightleftarrows [MOH(H_2O)_{n-1}] + H^+$

Large cation ⇒ High buffering effect

K^+, Rb^+, Cs^+ : pH (near cathode) is stable

CO_2 concentration near cathode



K^+, Rb^+, Cs^+: pH is stable

⬇

CO_2 concentration is high

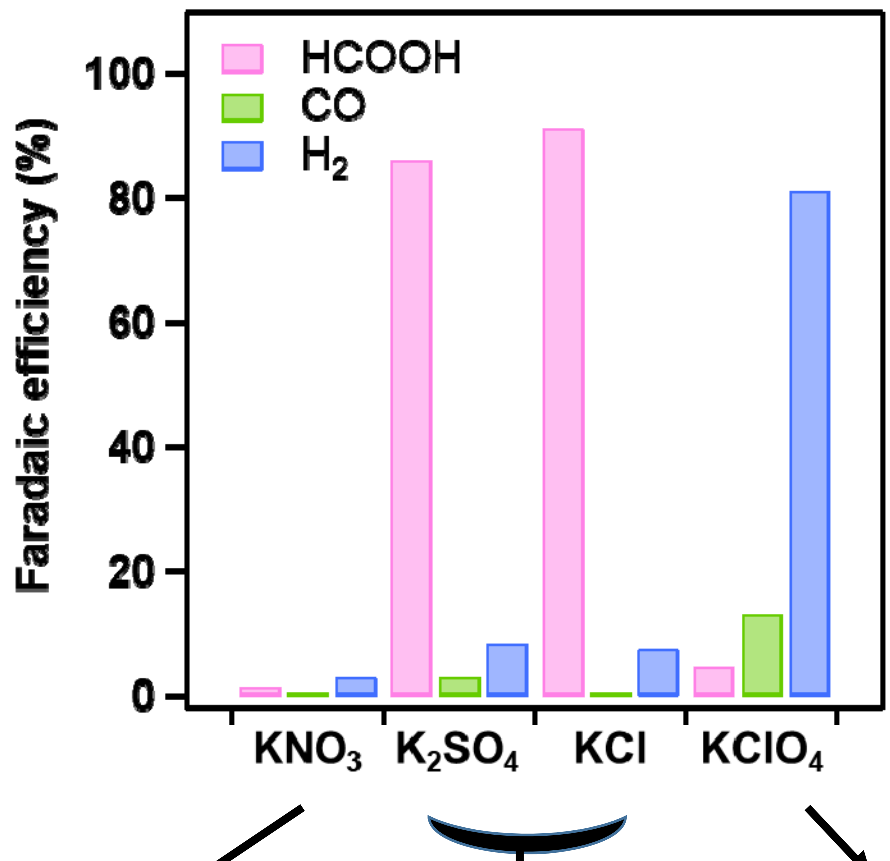
($CO_2 + H_2O \leftarrow H^+ + HCO_3^-$)

⬇

K, Rb, Cs

High efficiency for HCOOH production

Anion dependence



NO_3^- + H_2O + $2e^-$
→ NO_2^- + $2OH^-$

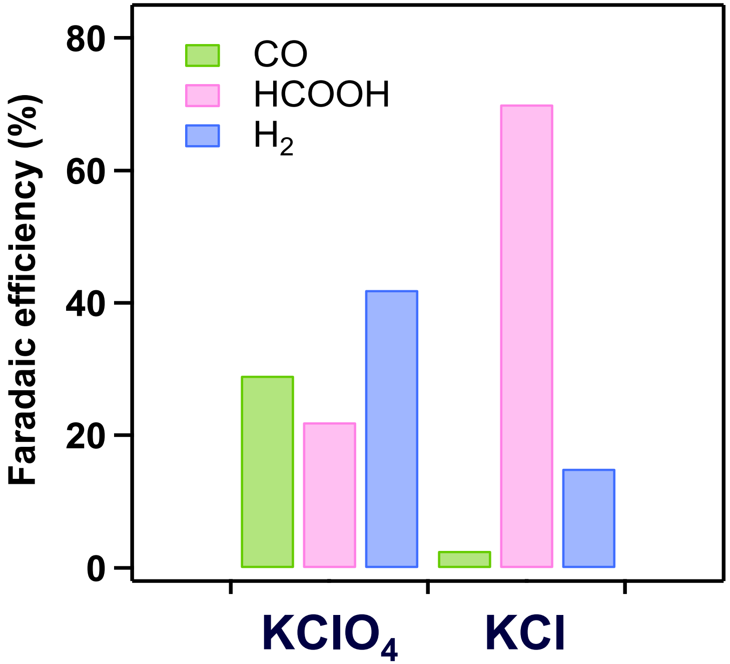
HCOOH
production

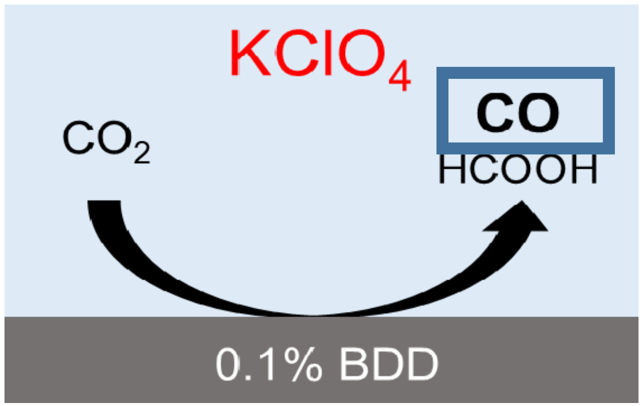
CO
production

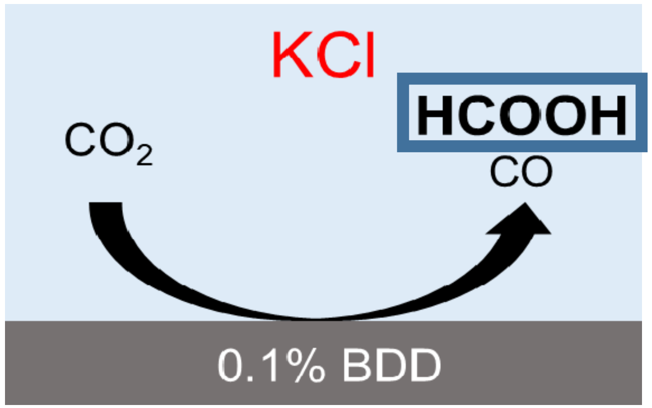
ChemistrySelect, *3*, 10209 (2018).

CO production in $KClO_4$

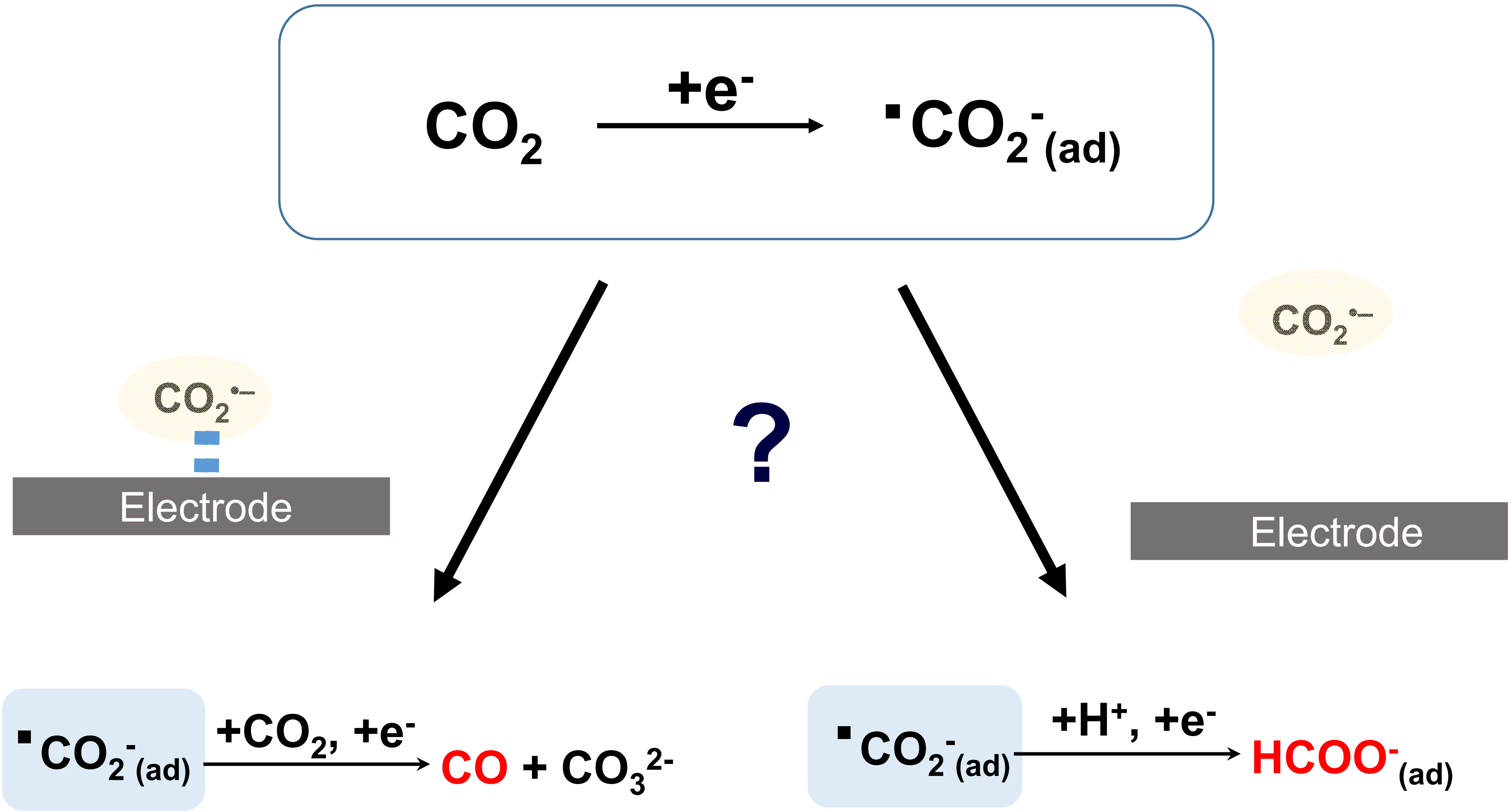
(−2.1 V *vs.* Ag/AgCl)

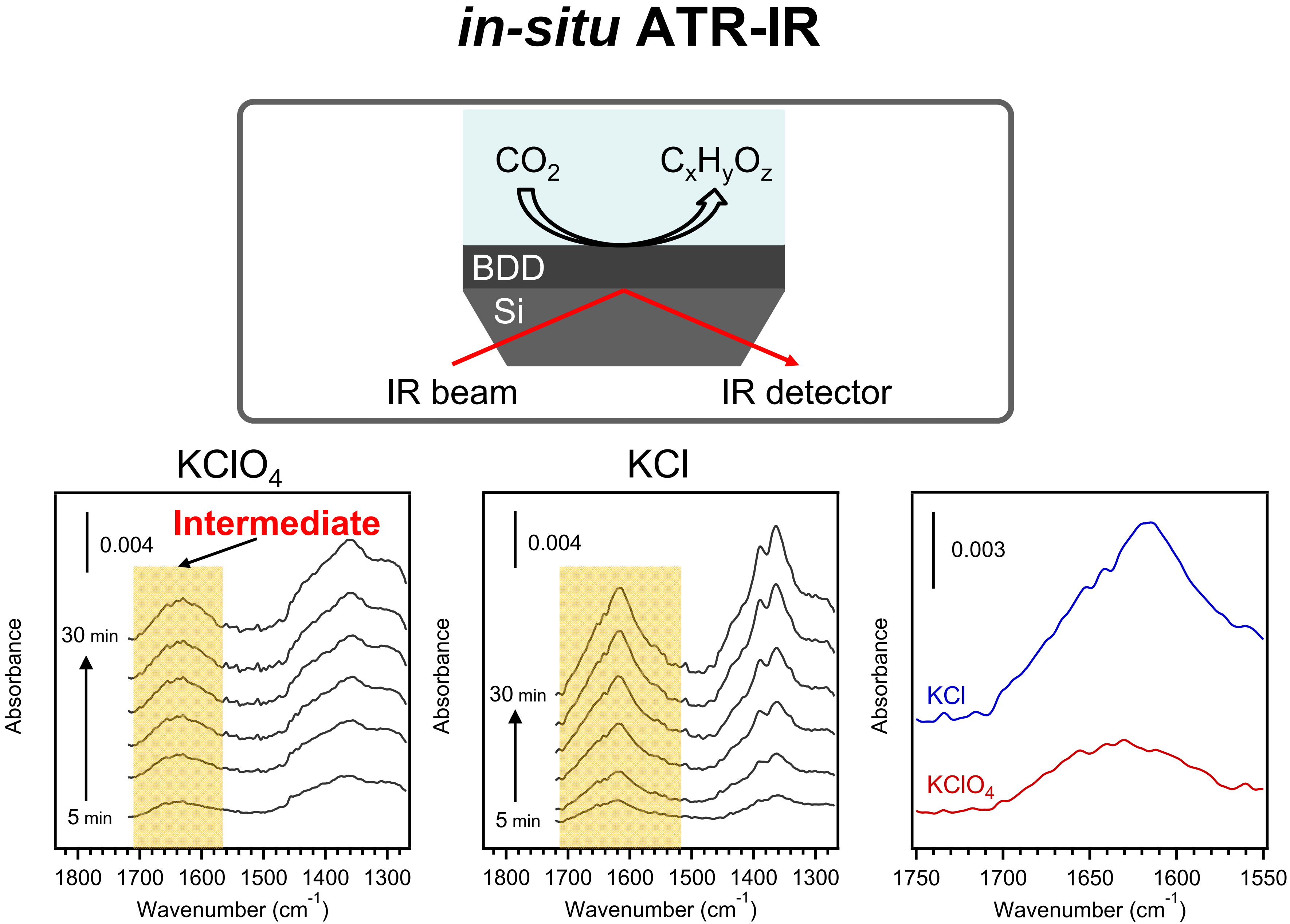






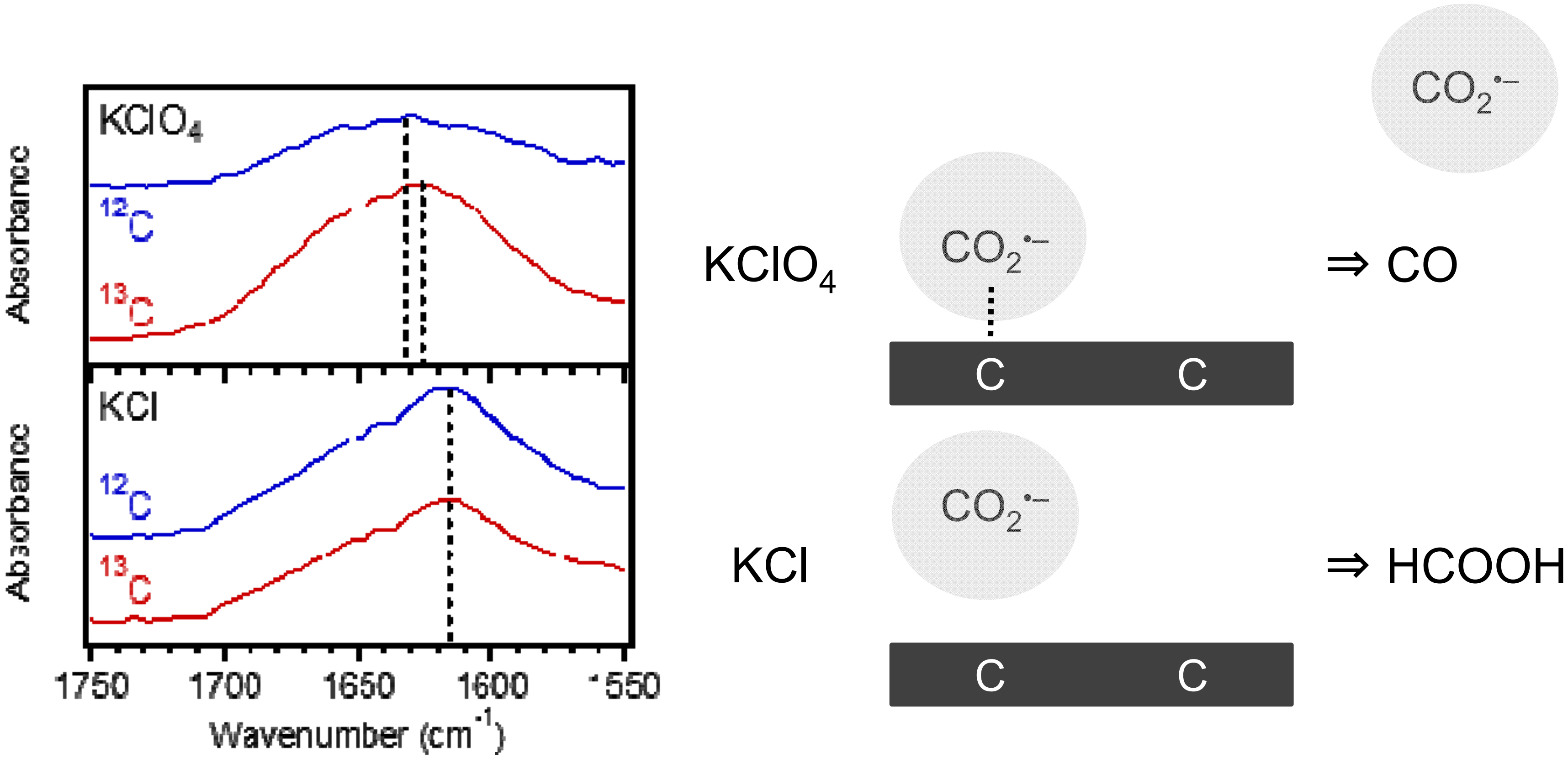
***J. Am. Chem. Soc.*, 141, 7414 (2019).**


CO2
+e-
•CO2-(ad)
CO2•−
Electrode
?
CO2•−
Electrode
•CO2-(ad)
+CO2, +e-
CO + CO32-
•CO2-(ad)
+H+, +e-
HCOO-(ad)



in-situ ATR-IR
CO2
CxHyOz
BDD
Si
IR beam
IR detector
KClO4
KCl
Intermediate
0.004
30 min
5 min
Absorbance
Wavenumber (cm-1)
0.003

Measurement by ^{13}C BDD



Interaction between intermedeates ($CO_2^{\bullet -}$) and BDD electrodes are different.

***J. Am. Chem. Soc.*, 141, 7414 (2019).**