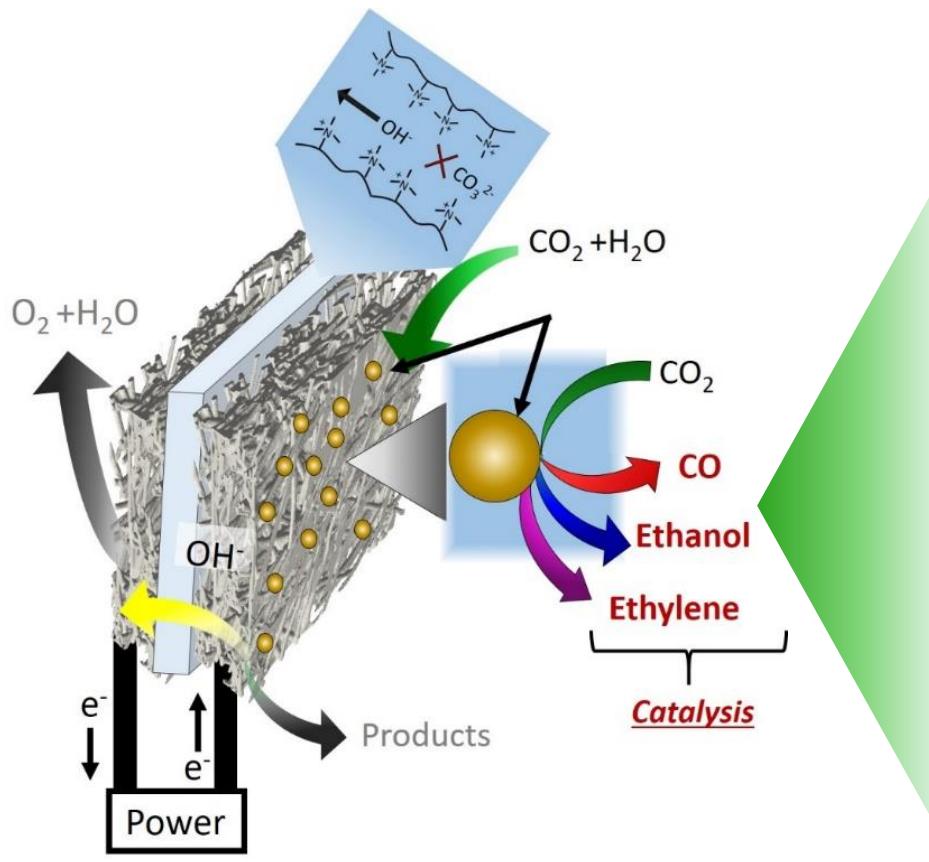
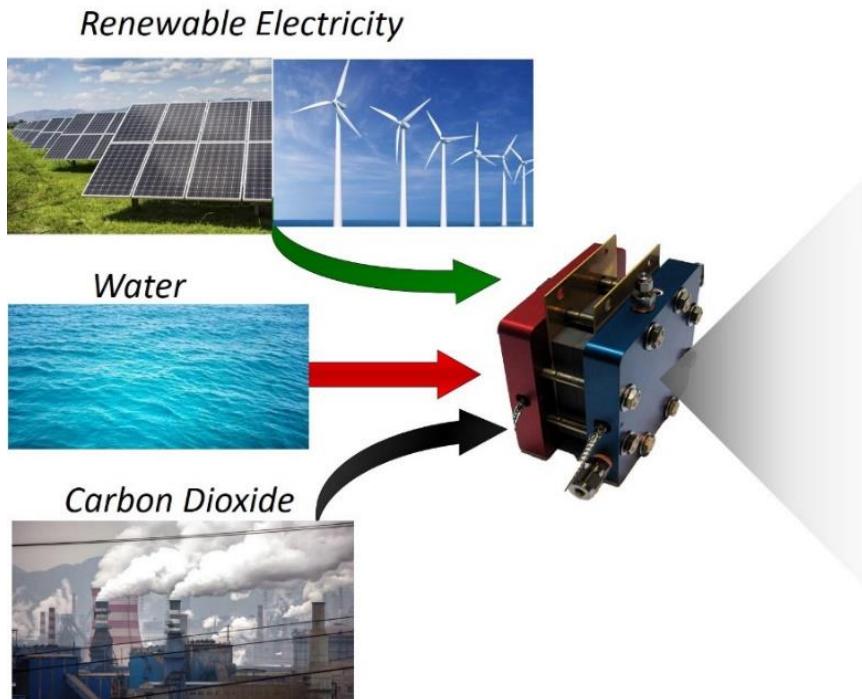


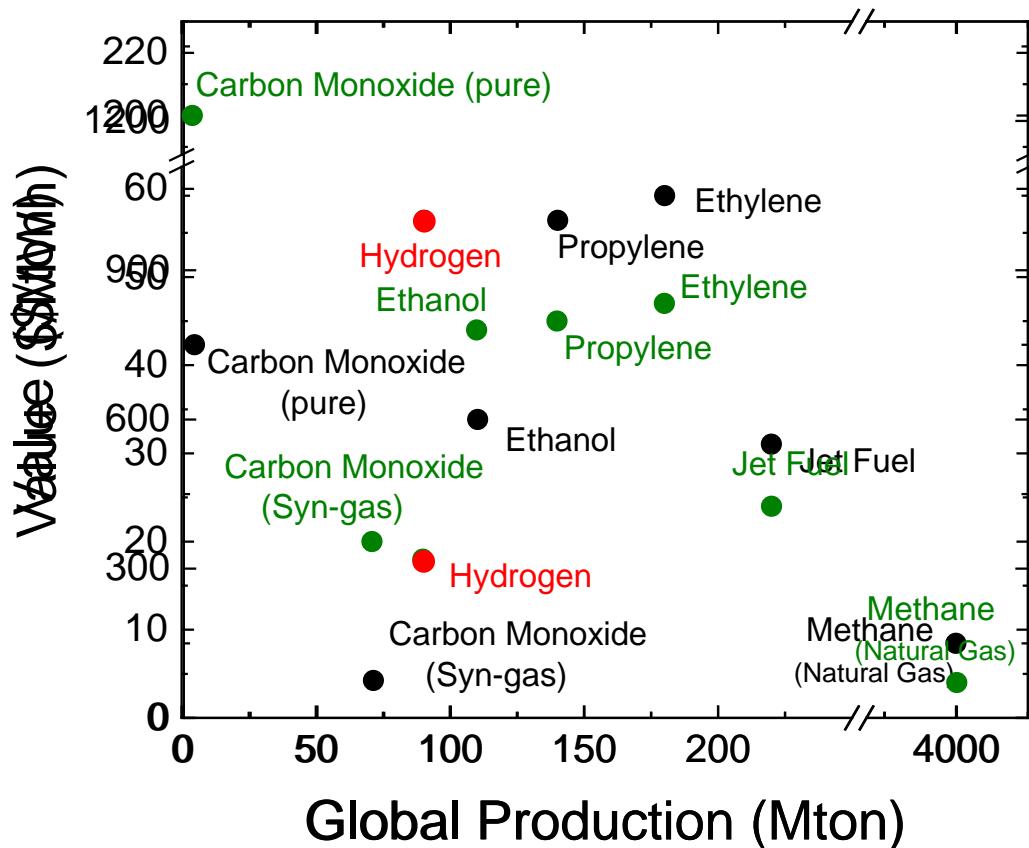
# Using Deuterated Water to Analyze Reaction Mechanisms in CO<sub>2</sub> Electrolysis

2022 Spring ECS Vancouver  
02-06-2022

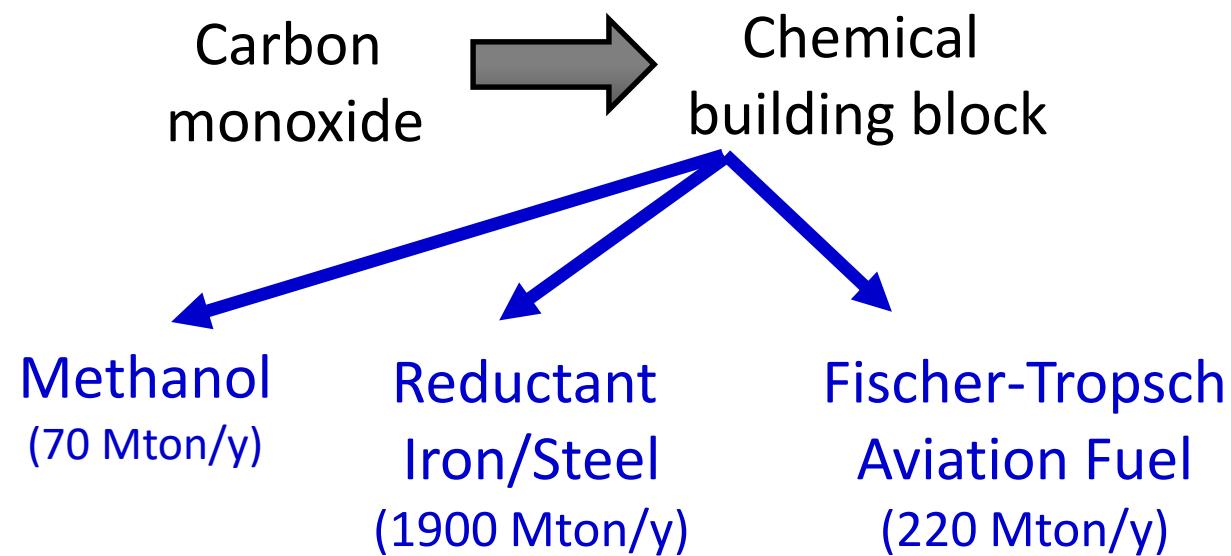


# What are we trying to do?

- Chemicals are 7% of EU's greenhouse gasses emissions

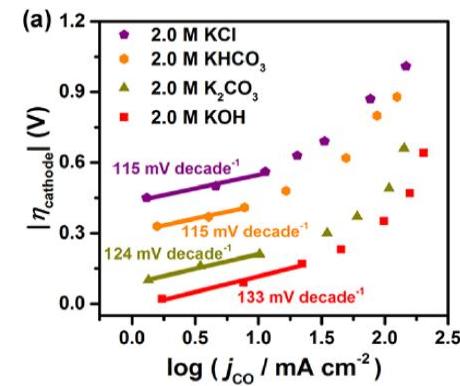


## Applications of chemicals

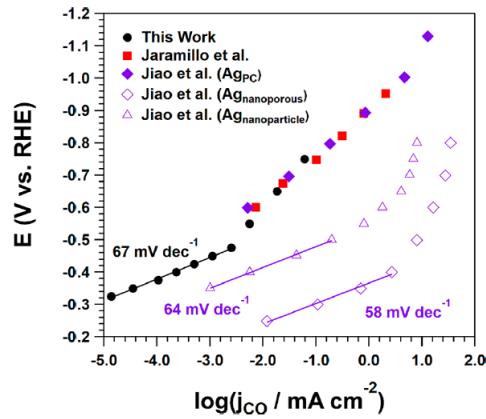
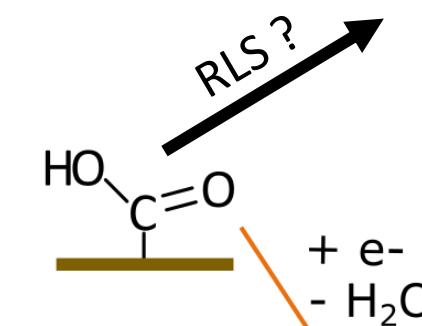
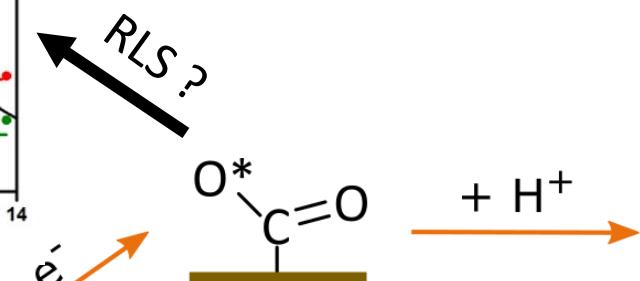
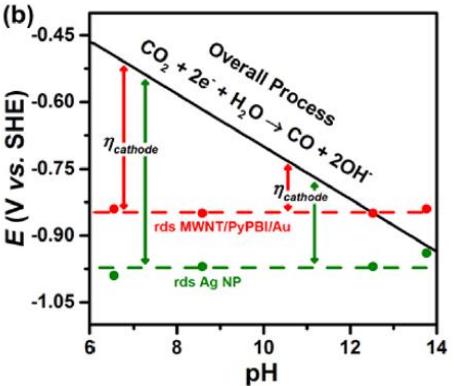


- If all of USA's electricity went to CO production, we would only produce 4.3 times are need of world's carbon monoxide.

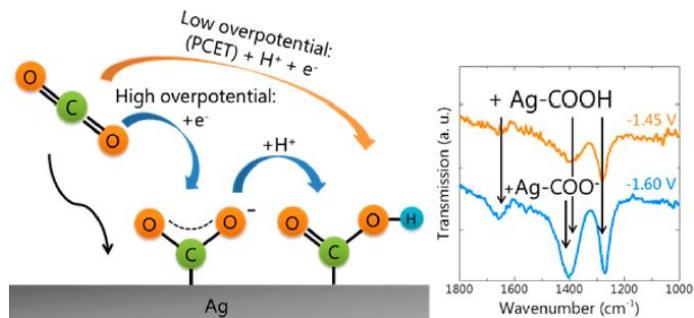
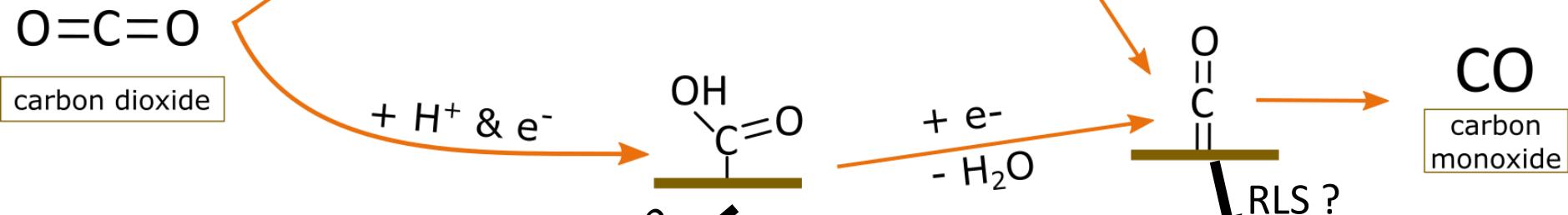
# What is the rate limiting step for CO (RLS)?



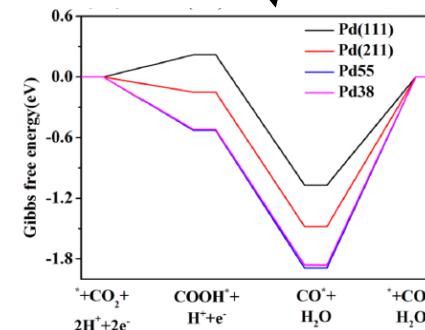
Verma et al., ACS Energy Let, 2018



Dunwell et al., ACS Cat, 2018



Nienke et al., ACS Cat., 2016



Gao et al., JACS, 2015

# CO<sub>2</sub> to CO Rate limiting step

**Different Pathways**

Step <sup>b</sup>	Possible RLS	Proposed Rate Expression	Type	Tafel slope (mV/dec)
A1	$\text{CO}_2 + * + e^- \rightarrow * \text{CO}_2^-$	$j_{\text{CO}} = 2Fk_{A1}^0 a[\text{CO}_2] \theta^* \exp(-\alpha f h)$	ET	118
A2	$* \text{CO}_2^- + H^+ \rightarrow * \text{COOH}$	$j_{\text{CO}} = 2Fk_{A2}^0 K_{A1}^0 a[\text{CO}_2] \theta^* a[H^+] \exp(-f h)$	PT	59
A3	$* \text{COOH} + e^- \rightarrow * \text{COOH}^-$	$j_{\text{CO}} = 2Fk_{A3}^0 K_{A2}^0 K_{A1}^0 a[\text{CO}_2] \theta^* a[H^+] \exp[-(1+\alpha) f h]$	ET	39
A4	$* \text{COOH}^- + H^+ \rightarrow * \text{CO} + H_2O$	$j_{\text{CO}} = 2Fk_{A4}^0 K_{A3}^0 K_{A2}^0 K_{A1}^0 a[\text{CO}_2] \theta^* a^2[H^+] \exp(-2 f h)$	PT	30
A5	$* \text{CO} \rightarrow \text{CO} + *$	$j_{\text{CO}} = 2Fk_{A4}^0 K_{A3}^0 K_{A2}^0 K_{A1}^0 a[\text{CO}_2] \theta^* a^2[H^+] \exp(-2 f h) / a(H_2O)$	D	30
a1	$\text{CO}_2 + * + e^- \rightarrow * \text{CO}_2^-$	$j_{\text{CO}} = 2Fk_{a1}^0 a[\text{CO}_2] \theta^* \exp(-\alpha f h)$	ET	118
a2	$* \text{CO}_2^- + H_2O \rightarrow * \text{COOH} + OH^-$	$j_{\text{CO}} = 2Fk_{a2}^0 K_{a1}^0 a[\text{CO}_2] \theta^* a[H_2O] \exp(-f h)$	PT	59
a3	$* \text{COOH} + e^- \rightarrow * \text{COOH}^-$	$j_{\text{CO}} = 2Fk_{a3}^0 K_{a2}^0 K_{a1}^0 a[\text{CO}_2] \theta^* a[H^+]$	ET	39
a4	$* \text{COOH}^- \rightarrow * \text{CO} + OH^-$	$j_{\text{CO}} = 2Fk_{a4}^0 K_{a3}^0 K_{a2}^0 K_{a1}^0 a[\text{CO}_2] \theta^* a$	PT	30
a5	$* \text{CO} \rightarrow \text{CO} + *$	$j_{\text{CO}} = 2Fk_{a5}^0 K_{a4}^0 K_{a3}^0 K_{a2}^0 K_{a1}^0 a[\text{CO}_2] \theta^* a^2[H^+] a[H_2] \exp(-2 f h) / K_W^2$	D	30
B1	$\text{CO}_2 + * + e^- + H^+ \rightarrow * \text{COOH}$	$j_{\text{CO}} = 2Fk_{B1}^0 a[\text{CO}_2] \theta^* a[H^+] \exp(-\alpha f E)$	PCET	118
B2	$* \text{COOH} + e^- \rightarrow * \text{COOH}^-$	$j_{\text{CO}} = 2Fk_{B2}^0 K_{B1}^0 a[\text{CO}_2] \theta^* a[H^+] \exp[-(1+\alpha) f h]$	ET	39
B3	$* \text{COOH}^- + H^+ \rightarrow * \text{CO} + H_2O$	$j_{\text{CO}} = 2Fk_{B3}^0 K_{B2}^0 K_{B1}^0 a[\text{CO}_2] \theta^* a^2[H^+] \exp(-2 f E)$	PT	30
B4	$* \text{CO} \rightarrow \text{CO} + *$	$j_{\text{CO}} = 2Fk_{B4}^0 K_{B3}^0 K_{B2}^0 K_{B1}^0 a[\text{CO}_2] \theta^* a^2[H^+] \exp(-2 f h) / a(H_2O)$	D	30
b1	$\text{CO}_2 + * + e^- + H_2O \rightarrow * \text{COOH} + OH^-$	$j_{\text{CO}} = 2Fk_{b1}^0 a[\text{CO}_2] \theta^* a[H_2O] \exp(-\alpha f h)$	PCET	118
b2	$* \text{COOH} + e^- \rightarrow * \text{COOH}^-$	$j_{\text{CO}} = 2Fk_{b2}^0 K_{b1}^0 a[\text{CO}_2] \theta^* a[H_2O] a[H^+] \exp[-(1+\alpha) f h] / K_W$	ET	39
b3	$* \text{COOH}^- \rightarrow * \text{CO} + OH^-$	$j_{\text{CO}} = 2Fk_{b3}^0 K_{b2}^0 K_{b1}^0 a[\text{CO}_2] \theta^* a[H_2O] a[H^+] \exp(-2 f h) / K_W$	PT	30
b4	$* \text{CO} \rightarrow \text{CO} + *$	$j_{\text{CO}} = 2Fk_{b4}^0 K_{b3}^0 K_{b2}^0 K_{b1}^0 a[\text{CO}_2] \theta^* a[H_2O] a^2[H^+] \exp(-2 f h) / K_W^2$	D	30
C1	$\text{CO}_2 + * + e^- + H^+ \rightarrow * \text{COOH}$	$j_{\text{CO}} = 2Fk_{c1}^0 a[\text{CO}_2] \theta^* a[H^+] \exp(-\alpha f h)$	PCET	119
C2	$* \text{COOH} + e^- + H^+ \rightarrow * \text{CO} + H_2O$	$j_{\text{CO}} = 2Fk_{c2}^0 K_{c1}^0 a[\text{CO}_2] \theta^* a^2[H^+] \exp[-(1+\alpha) f h]$	PCET	39
C3	$* \text{CO} \rightarrow \text{CO} + *$	$j_{\text{CO}} = 2Fk_{c3}^0 K_{c2}^0 K_{c1}^0 a[\text{CO}_2] \theta^* a^2[H^+] \exp(-2 f h) / a(H_2O)$	D	30
c1	$\text{CO}_2 + * + e^- + H_2O \rightarrow * \text{COOH} + OH^-$	$j_{\text{CO}} = 2Fk_{c1}^0 a[\text{CO}_2] \theta^* a[H_2O] \exp(-\alpha f h)$	PCET	119
c2	$* \text{COOH} + e^- \rightarrow * \text{CO} + OH^-$	$j_{\text{CO}} = 2Fk_{c2}^0 K_{c1}^0 a[\text{CO}_2] \theta^* a[H_2O] a[H^+] \exp[-(1+\alpha) f h] / K_W$	PCET	39
c3	$* \text{CO} \rightarrow \text{CO} + *$	$j_{\text{CO}} = 2Fk_{c3}^0 K_{c2}^0 K_{c1}^0 a[\text{CO}_2] \theta^* a[H_2O] a^2[H^+] \exp(-2 f h) / K_W^2$	D	30

Others focus on this

We focus on this

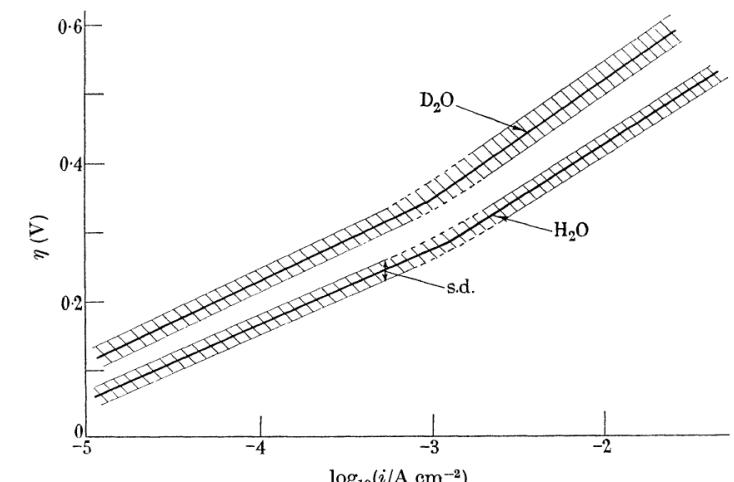
# How do we test for rate order?

To investigate whether H<sup>+</sup> is part of reaction order

- Vary the electrolyte pH
- if H<sup>+</sup> is involved in the RLS, current will vary versus potential on an absolute scale (i.e. vs. SHE)

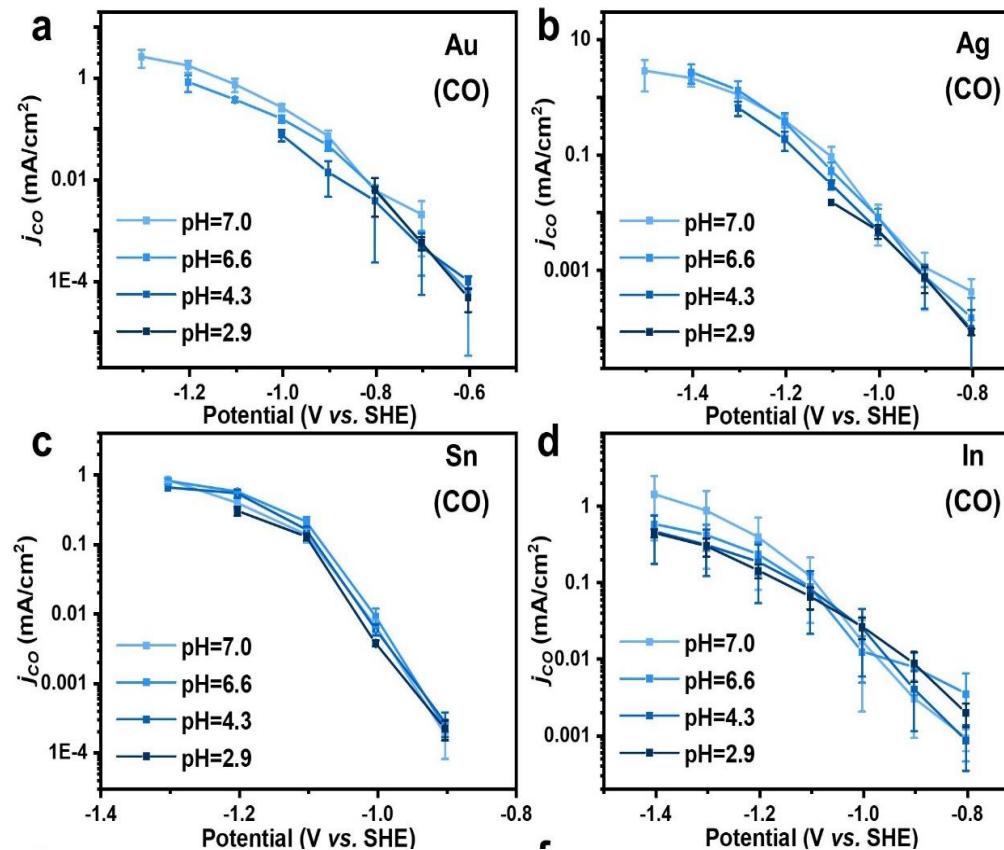
To investigate whether H<sub>2</sub>O is part of reaction order

- Use deuterated water (i.e D<sub>2</sub>O versus H<sub>2</sub>O)
- If water is involved in the RLS, current will vary versus potential on an absolute scale (i.e. vs. SHE)

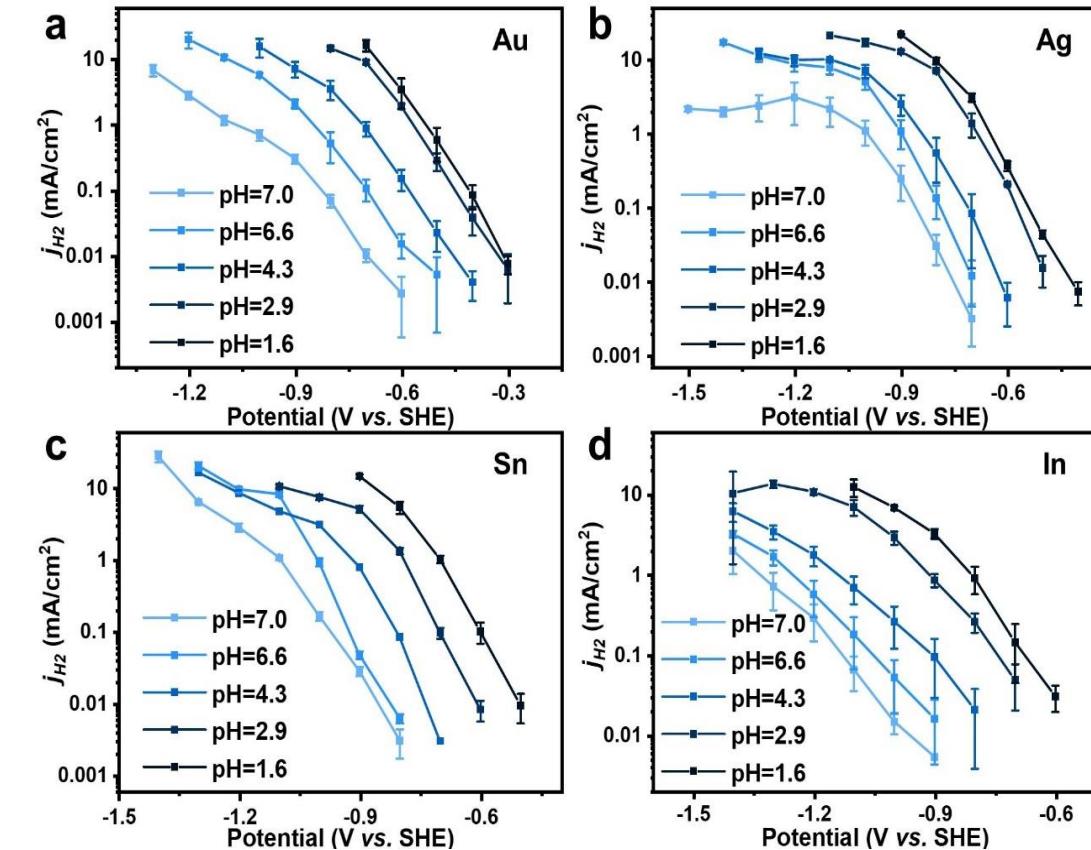


# Testing with pH variations

pH has no effect on CO production  
for 4 catalysts.

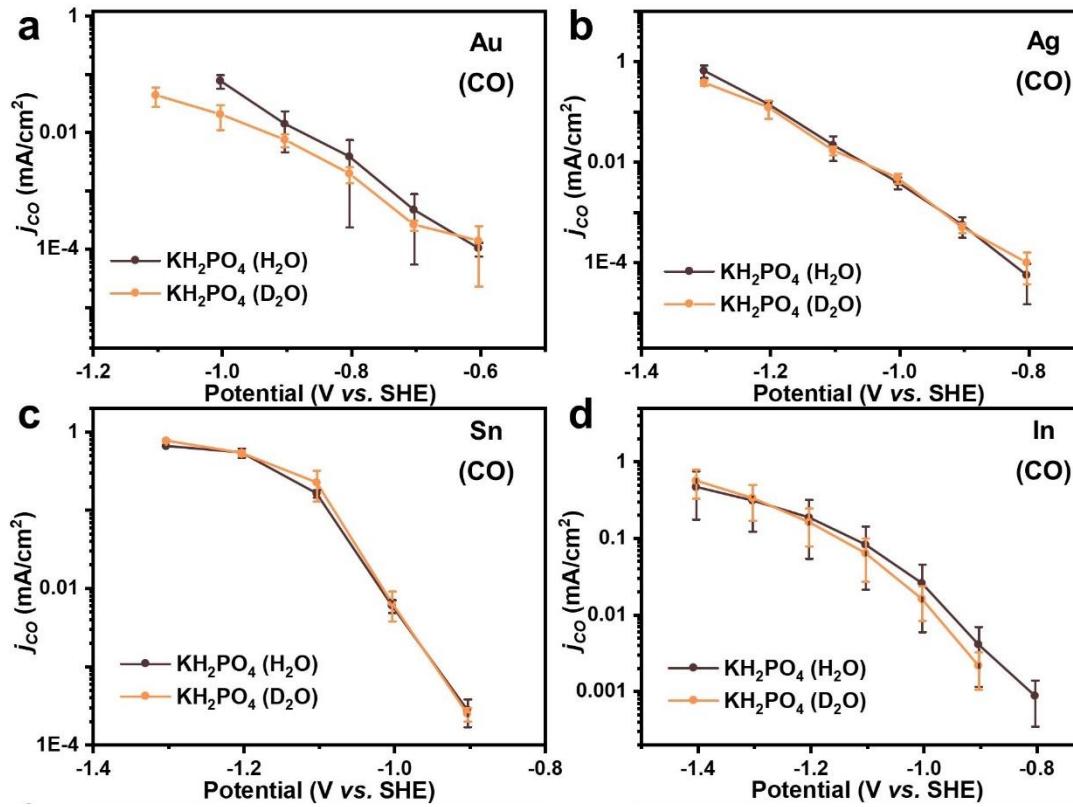


pH has substantial effect on H<sub>2</sub> production for 4 catalysts.

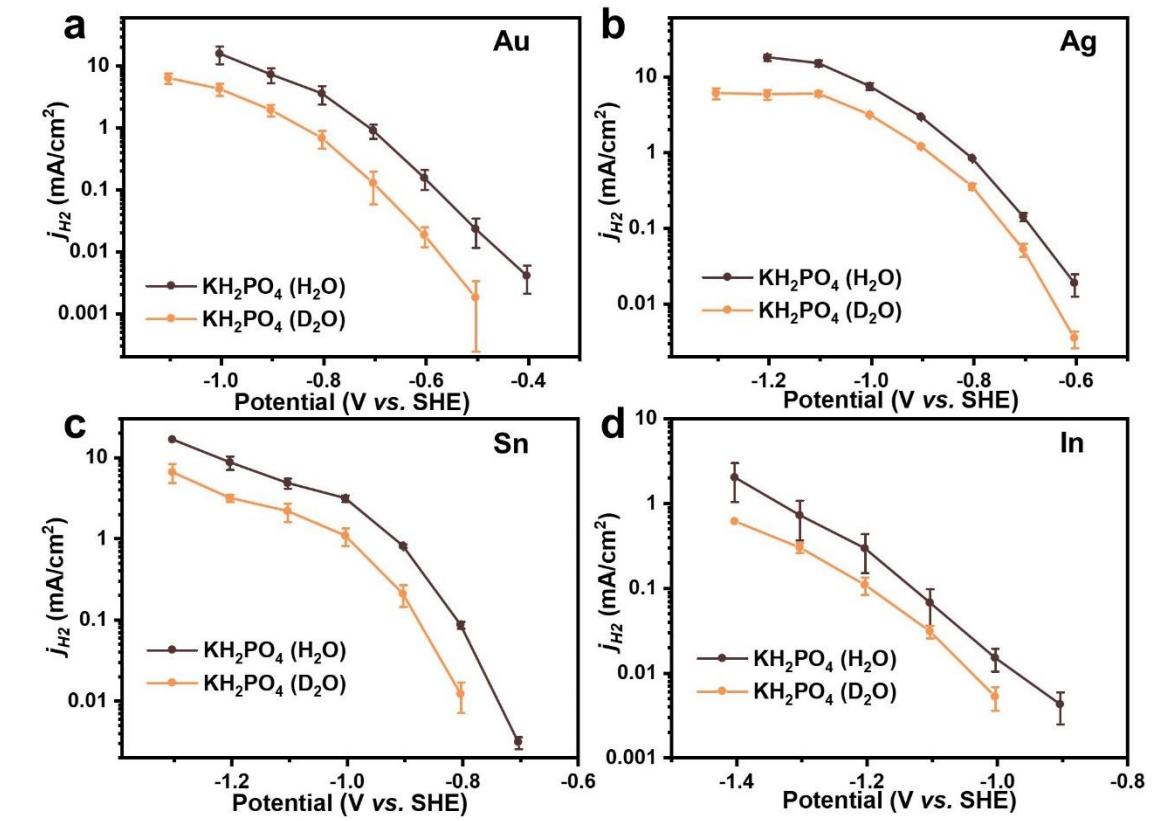


# Effects of Deuterated Water

$\text{D}_2\text{O}$  shows no effect on CO production for 4 catalysts.



$\text{D}_2\text{O}$  shows substantial effect on  $\text{H}_2$  production for 4 catalysts.



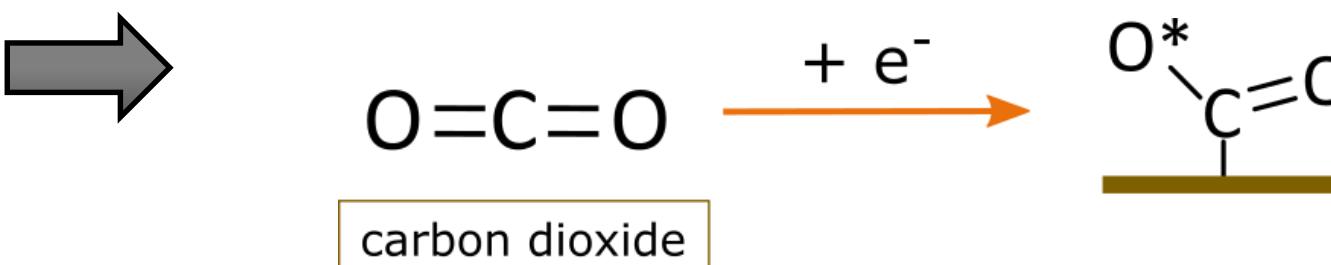
# Analysis on rate limiting step for CO production

Technique	Species of Focus	Rate Order
pH Variation	H <sup>+</sup>	0
Deuterated water	H <sub>2</sub> O	0

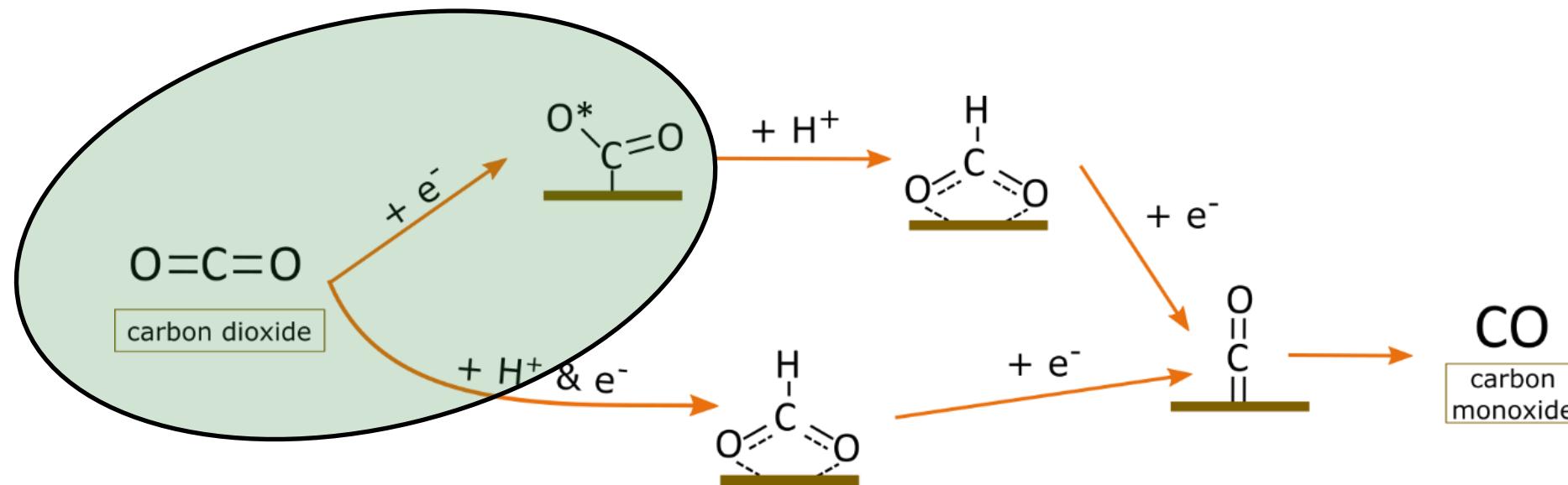
## Reaction Kinetics

Step <sup>a</sup>	Possible RLS	Proposed Rate Expression	Type	Tafel slope (mV/dec)	H <sup>+</sup> order	H <sub>2</sub> O order
A1	*CO + *e <sup>-</sup> + H <sup>+</sup> → *CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 \exp(-\alpha H)$	ET	138	0	0
A2	*CO + H <sup>+</sup> → *COOH	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-\alpha H)$	PT	59	1	0
A3	*COOH + e <sup>-</sup> → *COOH <sup>*</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-1-\alpha H)$	ET	39	1	0
A4	*COOH + H <sup>+</sup> → *CO + H <sub>2</sub> O	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-2H)$	PT	39	2	0
A5	*CO → CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	D	30	2	-1
a1	*CO + *e <sup>-</sup> → *CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 \exp(-\alpha H)$	ET	138	0	0
a2	*CO + H <sub>2</sub> O → *COOH + OH <sup>-</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-1+\alpha H)/[H_2O]$	PT	59	1	1
a3	*COOH → *COOH <sup>*</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	ET	39	1	1
a4	*COOH <sup>*</sup> → CO + OH <sup>-</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-2H)/[H_2O]$	PT	39	1	1
a5	*CO → CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	D	30	2	1
B1	CO <sub>2</sub> + *e <sup>-</sup> + H <sup>+</sup> → *COOH	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-\alpha H)$	PCET	138	1	0
B2	*COOH + e <sup>-</sup> → *COOH <sup>*</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-1+\alpha H)$	ET	39	1	0
B3	*COOH + H <sup>+</sup> → *CO + H <sub>2</sub> O	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)$	PT	39	2	0
B4	*CO → CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	D	30	2	-1
b1	CO <sub>2</sub> + *e <sup>-</sup> + H <sup>+</sup> → *COOH + OH <sup>-</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-\alpha H)$	PCET	138	0	1
b2	*COOH + e <sup>-</sup> → *COOH <sup>*</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-1+\alpha H)/[H_2O]$	ET	39	1	1
b3	*COOH <sup>*</sup> → CO + OH <sup>-</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	PT	39	1	1
b4	*CO → CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	D	30	2	1
C1	CO <sub>2</sub> + *e <sup>-</sup> + H <sup>+</sup> → *COOH	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-\alpha H)$	PCET	139	1	0
C2	*COOH + e <sup>-</sup> + H <sup>+</sup> → *CO + H <sub>2</sub> O	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-1+\alpha H)$	ET	39	2	0
C3	*CO → CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	D	30	2	-1
c1	CO <sub>2</sub> + *e <sup>-</sup> + H <sup>+</sup> → *COOH + OH <sup>-</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-\alpha H)$	PCET	139	0	1
c2	*COOH + e <sup>-</sup> → *CO + OH <sup>-</sup>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}) [0]^2 [H] \exp(-1+\alpha H)/[H_2O]$	ET	39	1	1
c3	*CO → CO <sub>2</sub>	$j_{in} = 2\pi k_b T_a^2 \ln(\text{CO}_2) [0]^2 [H] \exp(-2H)/[H_2O]$	D	30	2	1

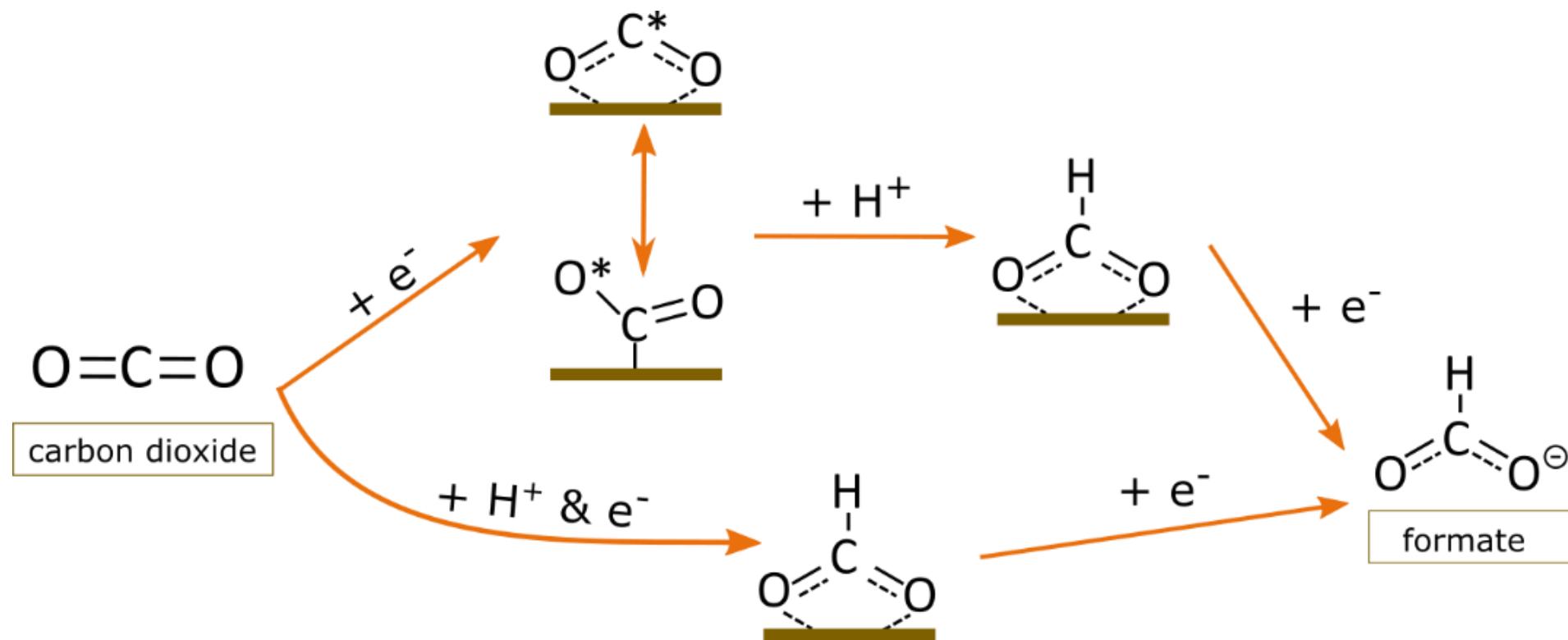
*Only elementary step  
with 0,0 rate order*



# What is the rate limiting step (RLS)?



# What is rate limiting step of CO<sub>2</sub> to formate?



# Formate: Not a wanted product



- We never produce formate, but rather potassium formate
- Where does the K come from?
- $\text{KHCO}_3$  is produced commercially via bubbling  $\text{CO}_2$  in  $\text{KOH}$



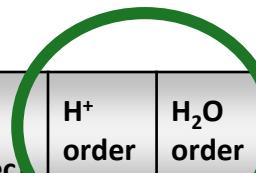
Name	Value (\$/ton)	Value (\$/Mmole)
Potassium hydroxide	1800	16
Potassium formate	1000	5

# What is the rate limiting step (RLS)?

- Apply same analysis as  $\text{CO}_2 \rightarrow \text{CO}$  for  $\text{CO}_2 \rightarrow \text{formate}$

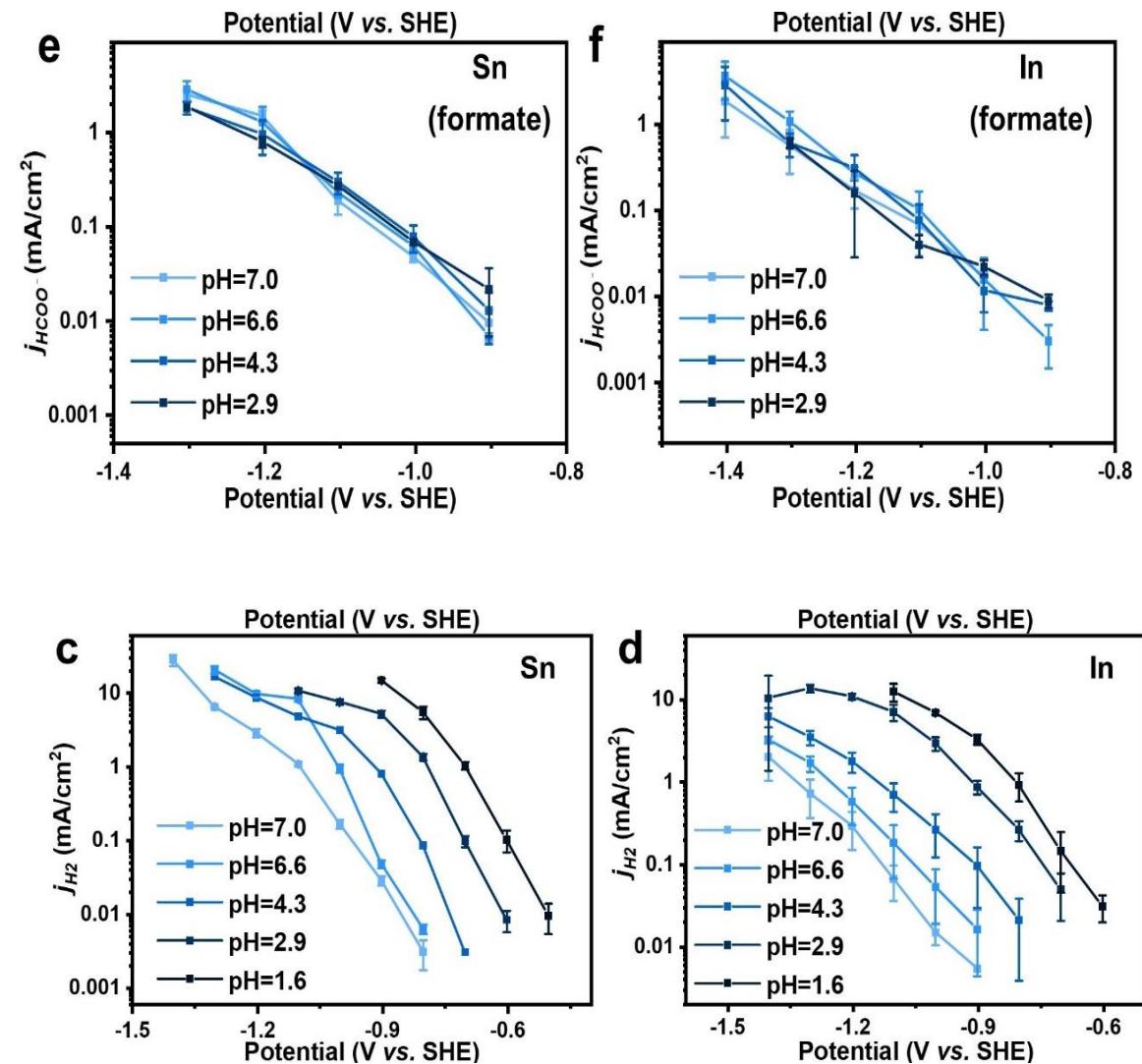
Step	Possible RLS	Proposed Rate Expression	Type	Tafel slope (mV/dec)	$\text{H}^+$ order	$\text{H}_2\text{O}$ order
D1	$\text{CO}_2 + * + e^- \rightarrow * \text{CO}_2^-$	$j_{\text{HCOO}^-} = 2Fk_{D1}^0 a[\text{CO}_2] \theta^* \exp(-\alpha fh)$	ET	118	0	0
D2	$* \text{CO}_2^- + \text{H}^+ \rightarrow * \text{OOCH}$	$j_{\text{HCOO}^-} = 2Fk_{D2}^0 K_{D1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] \exp(-fh)$	PT	59	1	0
D3	$* \text{OOCH} + e^- \rightarrow * \text{OOCH}^-$	$j_{\text{HCOO}^-} = 2Fk_{D3}^0 K_{D2}^0 K_{D1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] \exp[-(1+\alpha)fh]$	ET	39	1	0
D4	$* \text{OOCH}^- \rightarrow \text{HCOO}^- + *$	$j_{\text{HCOO}^-} = 2Fk_{D4}^0 K_{D3}^0 K_{D2}^0 K_{D1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] \exp(-2fh)$	PT	30	1	0
d1	$\text{CO}_2 + * + e^- \rightarrow * \text{CO}_2^-$	$j_{\text{HCOO}^-} = 2Fk_{d1}^0 a[\text{CO}_2] \theta^* \exp(-\alpha fh)$	ET	118	0	0
d2	$* \text{CO}_2^- + \text{H}_2\text{O} \rightarrow * \text{OOCH} + \text{OH}^-$	$j_{\text{HCOO}^-} = 2Fk_{d2}^0 K_{d1}^0 a[\text{CO}_2] \theta^* a[\text{H}_2\text{O}] \exp(-fh)$	PT	59	0	1
d3	$* \text{OOCH} + e^- \rightarrow * \text{OCOH}^-$	$j_{\text{HCOO}^-} = 2Fk_{d3}^0 K_{d2}^0 K_{d1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] a[\text{H}_2\text{O}] \exp[-(1+\alpha)fh] / K_w$	ET	39	1	1
d4	$* \text{OOCH}^- \rightarrow \text{HCOO}^- + *$	$j_{\text{HCOO}^-} = 2Fk_{d4}^0 K_{d3}^0 K_{d2}^0 K_{d1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] a[\text{H}_2\text{O}] \exp[-2fh] / K_w$	PT	30	1	1
E1	$\text{CO}_2 + * + e^- + \text{H}^+ \rightarrow * \text{OOCH}$	$j_{\text{HCOO}^-} = 2Fk_{E1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] \exp(-\alpha fh)$			1	0
E2	$* \text{OOCH} + e^- \rightarrow * \text{OOCH}^-$	$j_{\text{HCOO}^-} = 2Fk_{E2}^0 K_{E1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] \exp[-(1+\alpha)fh]$	ET	39	1	0
E3	$* \text{OOCH}^- \rightarrow \text{HCOO}^- + *$	$j_{\text{HCOO}^-} = 2Fk_{E3}^0 K_{E2}^0 K_{E1}^0 a[\text{CO}_2] \theta^* a[\text{H}^+] \exp[-2fh]$	PT	30	1	0
e1	$\text{CO}_2 + * + e^- + \text{H}_2\text{O} \rightarrow * \text{OOCH} + \text{OH}^-$	$j_{\text{HCOO}^-} = 2Fk_{e1}^0 a[\text{CO}_2] \theta^* a[\text{H}_2\text{O}] \exp(-\alpha fh)$	PCET	118	0	1
e2	$* \text{OOCH} + e^- \rightarrow * \text{OOCH}^-$	$j_{\text{HCOO}^-} = 2Fk_{e2}^0 K_{e1}^0 a[\text{CO}_2] \theta^* a[\text{H}_2\text{O}] a[\text{H}^+] \exp[-(1+\alpha)fh] / K_w$	ET	39	1	1
e3	$* \text{OOCH}^- \rightarrow \text{HCOO}^- + *$	$j_{\text{HCOO}^-} = 2Fk_{e3}^0 K_{e2}^0 K_{e1}^0 a[\text{CO}_2] \theta^* a[\text{H}_2\text{O}] a[\text{H}^+] \exp(-2fh) / K_w$	PT	30	1	1

We focus on this



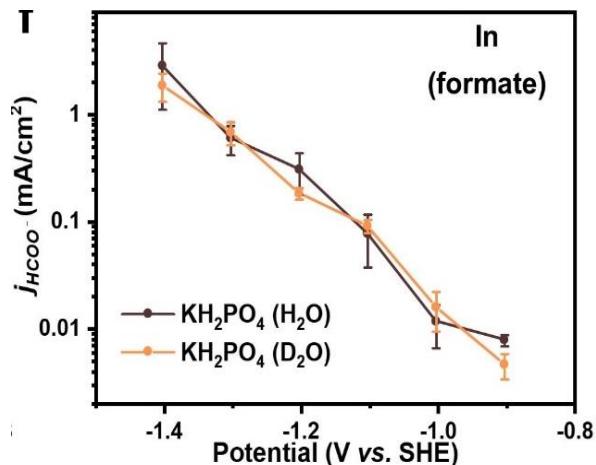
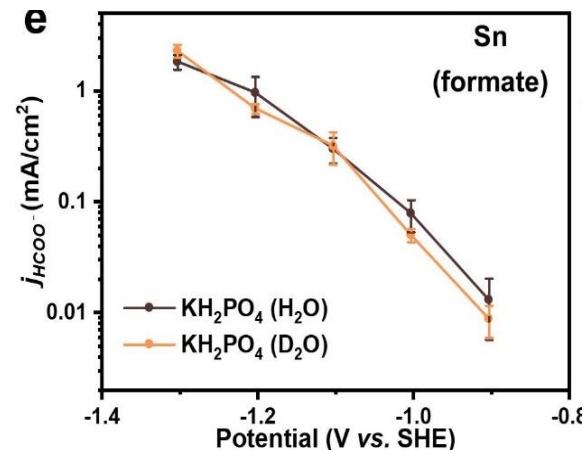
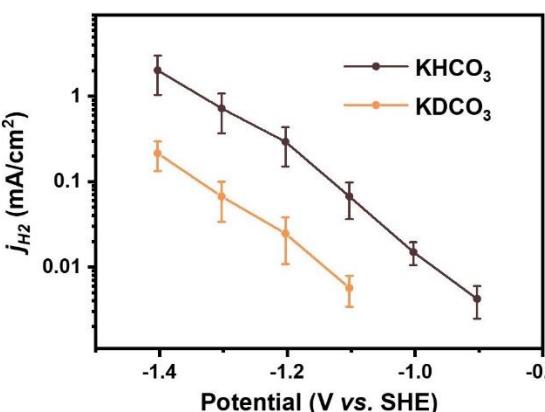
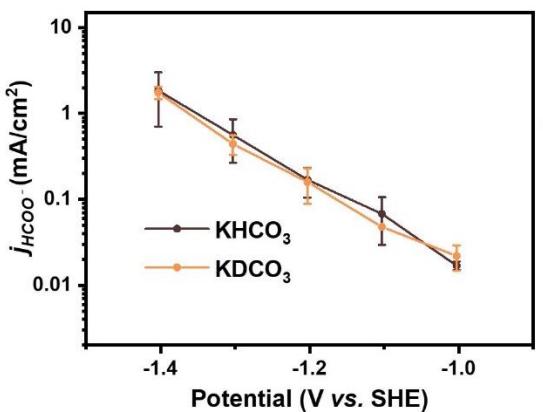
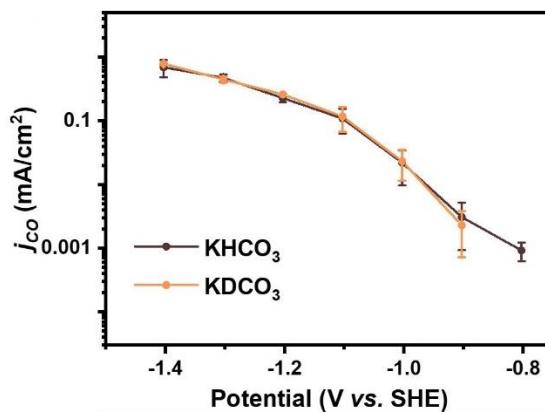
# Testing with pH variations

- Sn and In produce both CO and formate
- Formate does production is not a function of pH
- Testing for  $H_2$  evolution validates that this technique can show a pH effect.



# Effects of Deuterated Water

- Deuterated water experiments did not show any change for formate production.
- We were worried the hydrogen in our phosphate could contaminate D<sub>2</sub>O with a little H<sub>2</sub>O
- Deuterated carbonate was hydrogen free and showed same results.

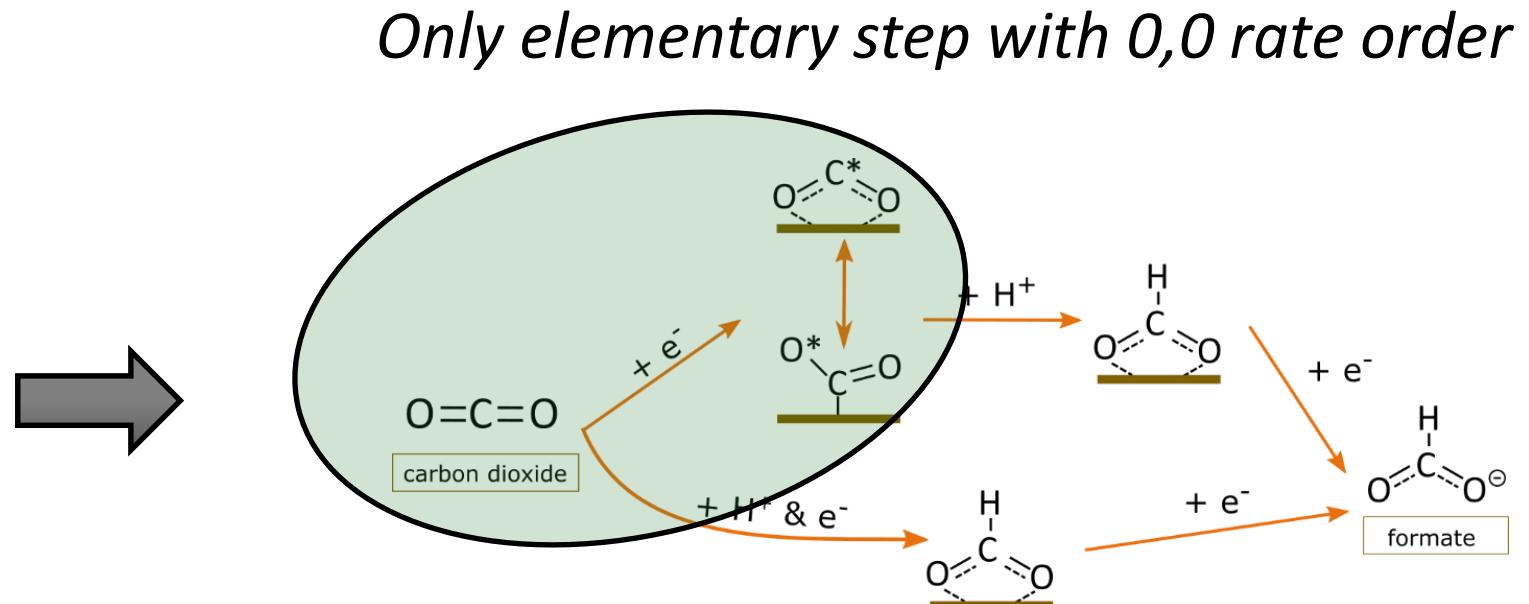


# Analysis on rate limiting step for formate production

Technique	Species of Focus	Rate Order
pH Variation	H <sup>+</sup>	0
Deuterated water	H <sub>2</sub> O	0

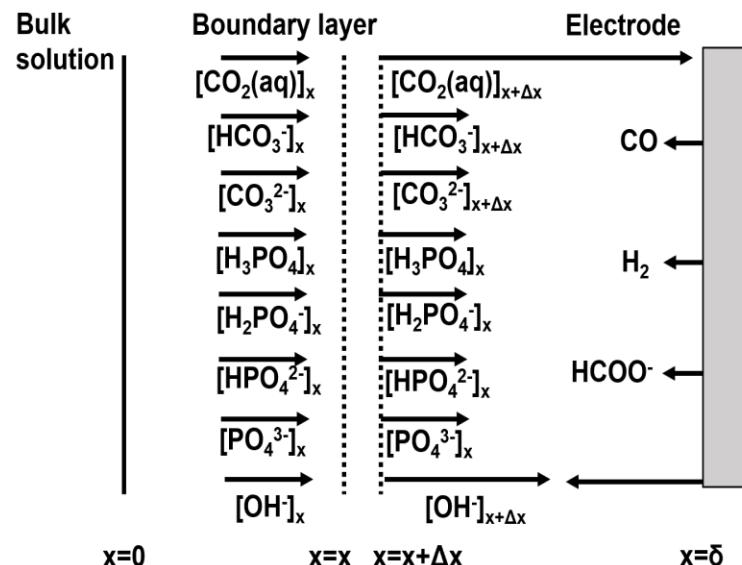
## Reaction Kinetics

Step	Possible RLS	Proposed Rate Expression	Type	Tafel slope (mV/dec)	H <sup>+</sup> order	H <sub>2</sub> O order
D1	CO <sub>2</sub> + * + e <sup>-</sup> → *CO <sub>2</sub> <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{D1}\theta^a[\text{CO}_2]\theta^b\exp(-\alpha f\eta)$	ET	118	0	0
D2	*CO <sub>2</sub> <sup>-</sup> + H <sup>+</sup> → *OOCH	$j_{\text{HCOO}^-} = 2Fk_{D2}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp(-f\eta)$	PT	59	1	0
D3	*OOCH + e <sup>-</sup> → *OOCH <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{D3}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-(1+\alpha)f\eta]$	ET	39	1	0
D4	*OOCH <sup>-</sup> + * → HCOO <sup>-</sup> + *	$j_{\text{HCOO}^-} = 2Fk_{D4}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-2f\eta]$	PT	30	1	0
d1	CO <sub>2</sub> + * + e <sup>-</sup> → *CO <sub>2</sub> <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{d1}\theta^a[\text{CO}_2]\theta^b\exp(-\alpha f\eta)$	ET	118	0	0
d2	*CO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O → *OOCH + OH <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{d2}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}_2\text{O}]\exp(-f\eta)$	PT	59	0	1
d3	*OOCH + e <sup>-</sup> → *OOCH <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{d3}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-(1+\alpha)f\eta]/K_w$	ET	39	1	1
d4	*OOCH <sup>-</sup> → HCOO <sup>-</sup> + *	$j_{\text{HCOO}^-} = 2Fk_{d4}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-2f\eta]/K_w$	PT	30	1	1
E1	CO <sub>2</sub> + * + e <sup>-</sup> + H <sup>+</sup> → *OOCH	$j_{\text{HCOO}^-} = 2Fk_{E1}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp(-\alpha f\eta)$	PCET	118	1	0
E2	*OOCH + e <sup>-</sup> → *OOCH <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{E2}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-(1+\alpha)f\eta]$	ET	39	1	0
E3	*OOCH <sup>-</sup> → HCOO <sup>-</sup> + *	$j_{\text{HCOO}^-} = 2Fk_{E3}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp(-2f\eta)$	PT	30	1	0
e1	CO <sub>2</sub> + * + e <sup>-</sup> + H <sub>2</sub> O → *OOCH + OH <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{e1}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}_2\text{O}]\exp(-\alpha f\eta)$	PCET	118	0	1
e2	*OOCH + e <sup>-</sup> → *OOCH <sup>-</sup>	$j_{\text{HCOO}^-} = 2Fk_{e2}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-(1+\alpha)f\eta]/K_w$	ET	39	1	1
e3	*OOCH <sup>-</sup> → HCOO <sup>-</sup> + *	$j_{\text{HCOO}^-} = 2Fk_{e3}\theta^a[\text{CO}_2]\theta^b\theta^a[\text{H}]\exp[-2f\eta]/K_w$	PT	30	1	1

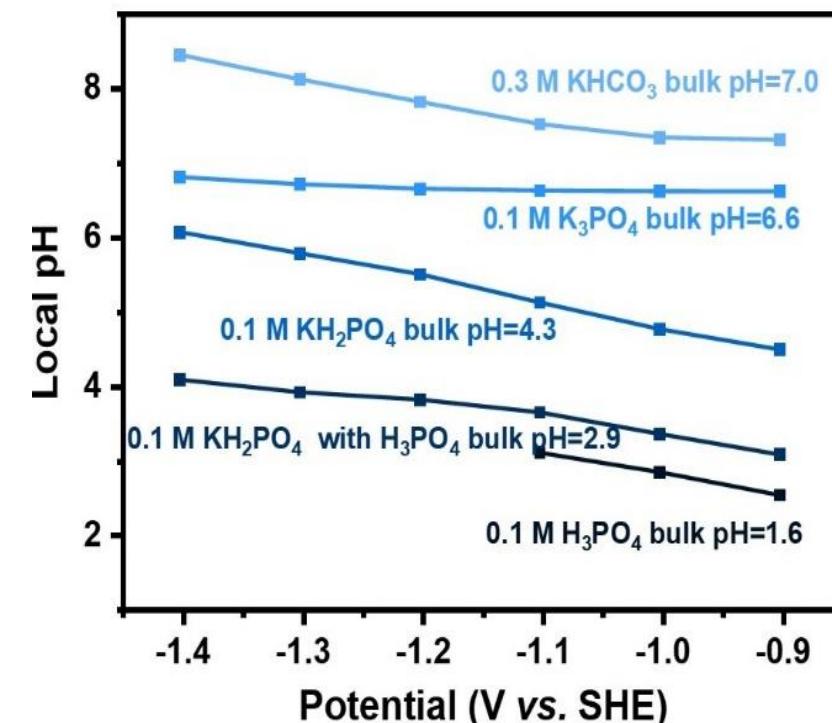


# Local pH

- Local pH could have an effect on our results
- We measured a boundary layer of 8  $\mu\text{m}$  using ferricyanide redox couple.
- We then modelled surface pH based off the Gatrell model.

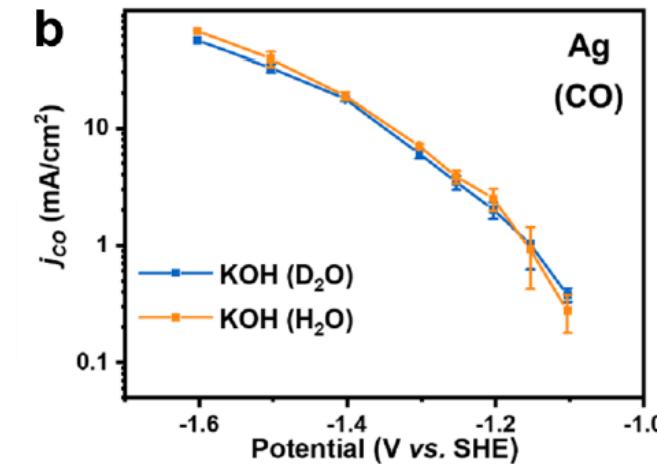
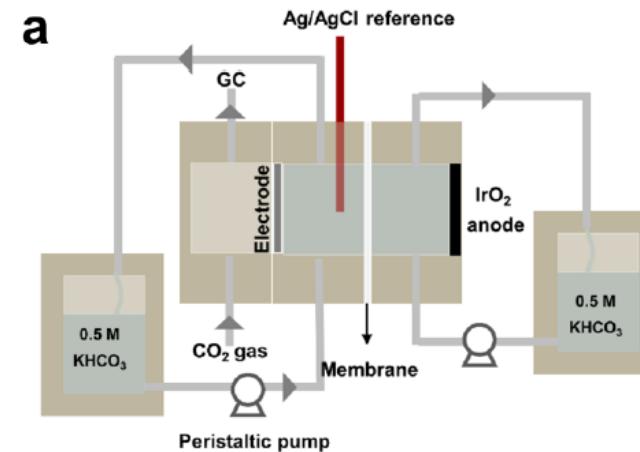


Model based off Gupta et al, J.  
Appl. Elec., 2006



# Ensuring sufficient mass transfer

- 8  $\mu\text{m}$  boundary layer thickness is quite small
- Our reactor, designed by Ezra Clark, bubbles  $\text{CO}_2$  in a separate chamber and the reactor itself only sees a very fast flow of saturated  $\text{CO}_2$ .



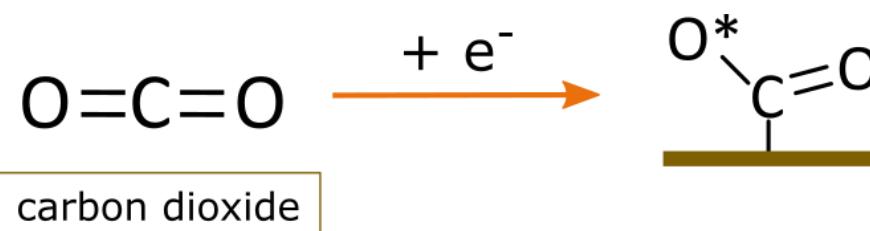
- This quick mass transfer may even allow us to measure  $\text{CO}_2$  reduction in KOH in an H-cell design

# Conclusions

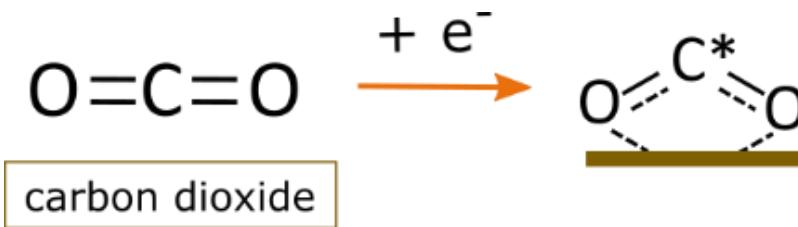
- Using pH & deuterated water gives us unique insight into reaction mechanisms
- pH variations and deuterated experiments are simple to do.
- We feel this provides clarity to determining rate limiting steps for CO<sub>2</sub> electrolysis.

## Rate Limiting Step

*For CO production*



*For formate production*



# Acknowledgements

The VILLUM Center for the Science of Sustainable Fuels and Chemicals

THE VELUX FOUNDATIONS

VILLUM FONDEN ✕ VELUX FONDEN



Wanyu Deng



*To learn more about our research go to  
SegerResearch.com*



Bjørt  
Joensen



Clara  
Jensen



Sahil  
Garg



Asger  
Moss



Carlos  
Rodriguez



Yu Qiao



Degenhart  
Hochfilzer



Ib  
Chorkendorff



Jinlong  
Gong

