



# Inline benchtop NMR studies of copper-catalyzed electrochemical CO<sub>2</sub> reduction at high current density

Zhiyu Zhu,<sup>1</sup> Kaan Çolakhasanoğlu,<sup>1</sup> Joris Meurs,<sup>1</sup> Simona M. Cristescu,<sup>1</sup> Thomas Burdyny,<sup>2</sup> Evan Wenbo Zhao<sup>1\*</sup>

<sup>1</sup>Magnetic Resonance Research Center, Institute for Molecules and Materials, 6525 AJ Nijmegen, Radboud University

<sup>2</sup>Department of Chemical Engineering, 2629 HZ Delft, Delft University of Technology

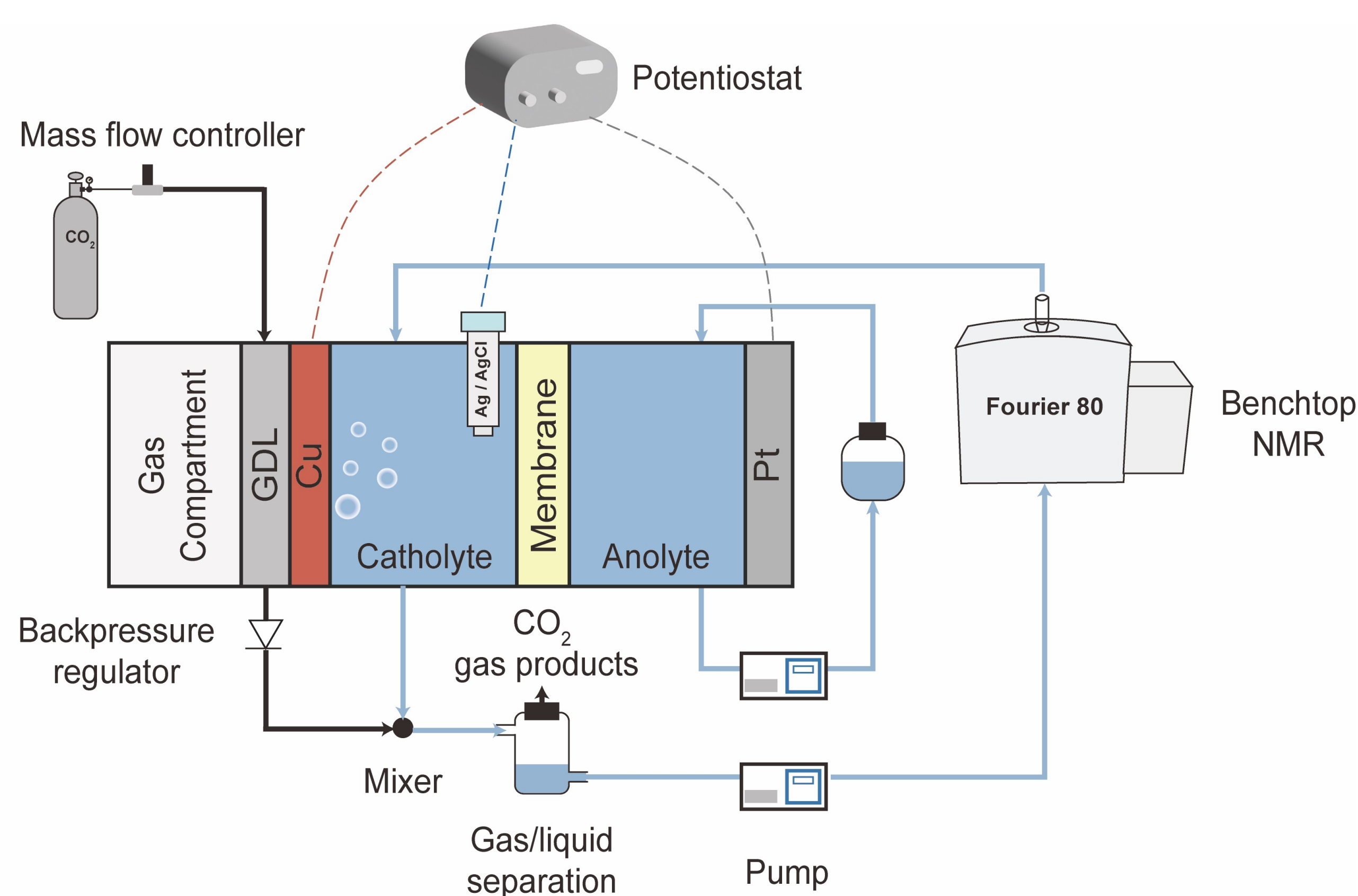
<https://www.ewzhaogroup.org/>; <https://www.ru.nl/science/magneticresonance/>

zhiyuzhu@science.ru.nl

## Introduction

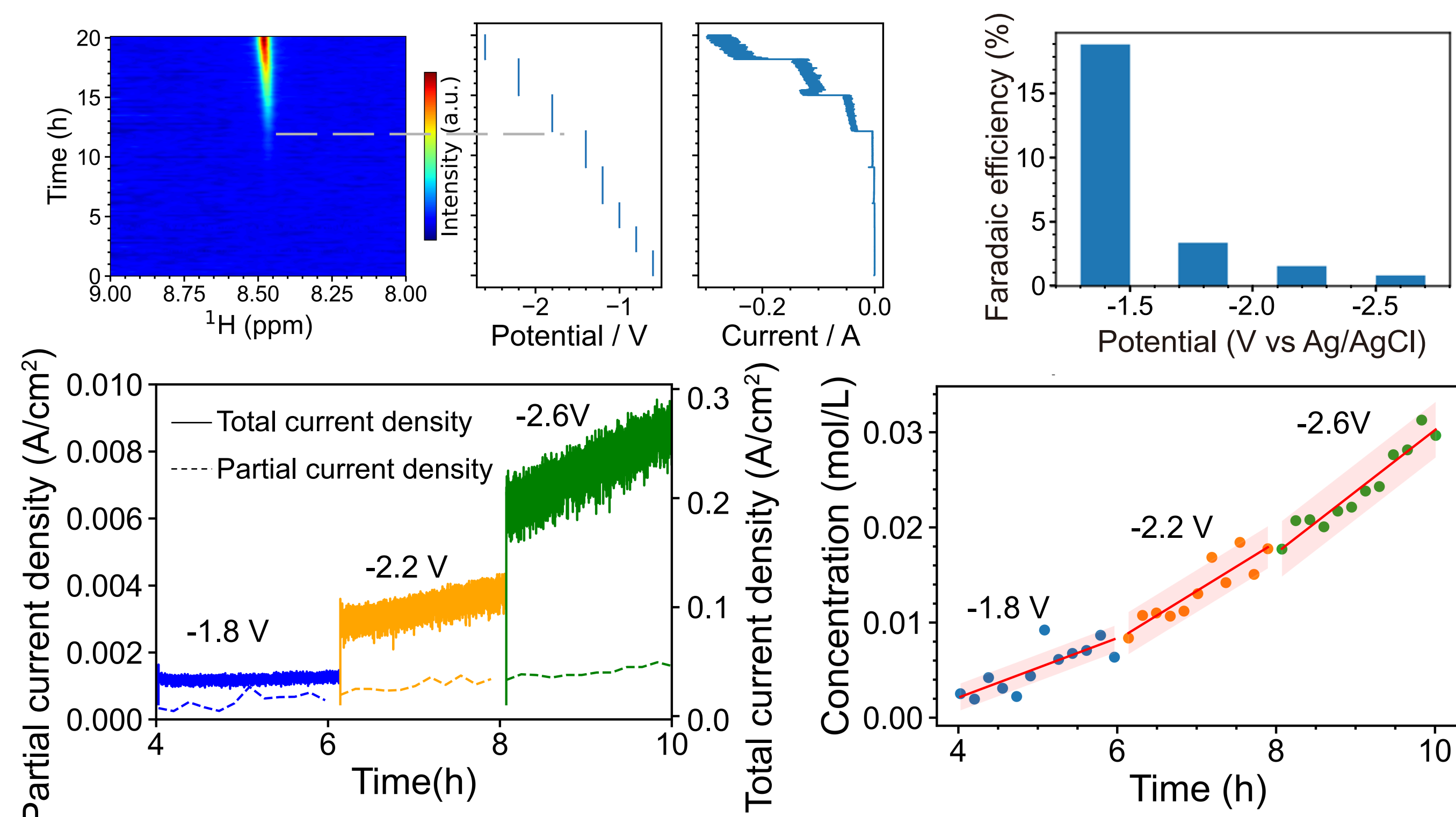
Product analysis and characterization for electrochemical CO<sub>2</sub>/CO reduction is critical due to a wide variety of products, and the propensity for product formation to change over time.<sup>1</sup> For these reasons operando characterization is gaining growing interests due to its ability to avoid possible contamination, track reaction kinetics and detect short-lived intermediates. Chromatography and mass spectrometry are the prevalent techniques.<sup>2</sup> However, they require a specialized cell and normally it was adapted from a single compartment cell. So, the current density is low. For practical applications, high current densities are required. The selectivity and reaction pathway might change as a function of current, which necessitates new development of operando techniques that allows high current. In this study, for the first time we demonstrate the inline (operando) benchtop NMR methods in quantifying the liquid products of eCO<sub>2</sub>RR on copper catalyst. It can integrate with common flow cells easily, allowing for effective monitoring of electrolyte solutions at high current densities.

## Inline benchtop NMR setup



## Results

### Quantifying formate at different potentials

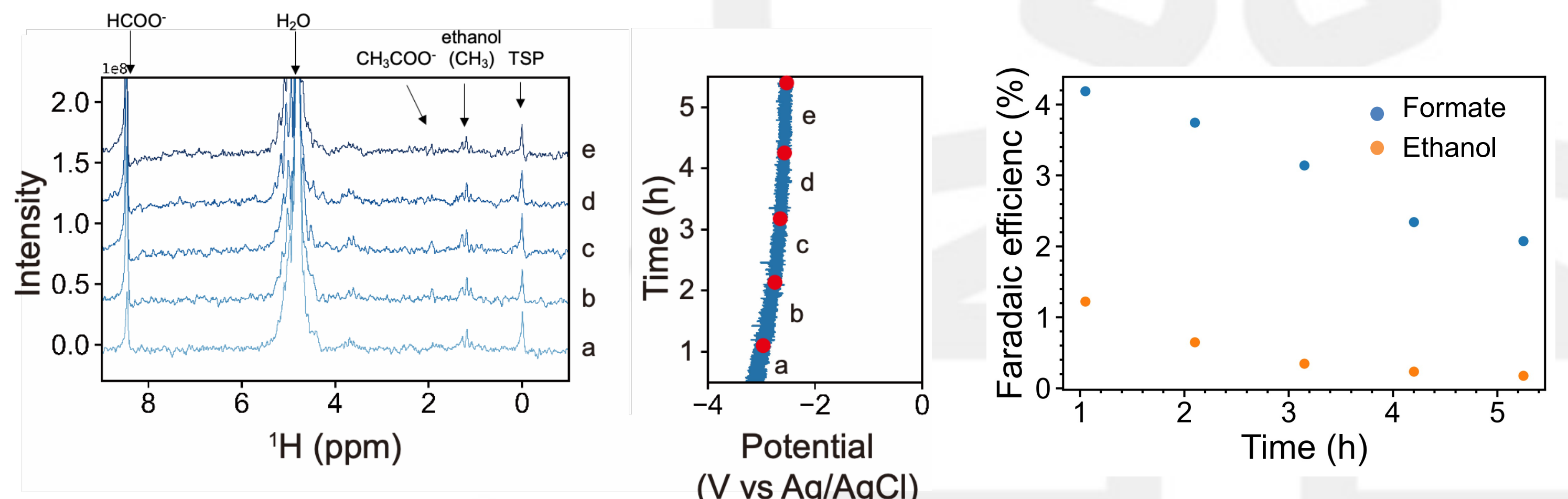


- The partial current density of formate and its reaction rate increased at higher potential while Faradaic efficiency showed the opposite trend
- The decreased selectivity towards formate at higher potential is likely due to the competing c-c coupling becoming more favorable

## Conclusion

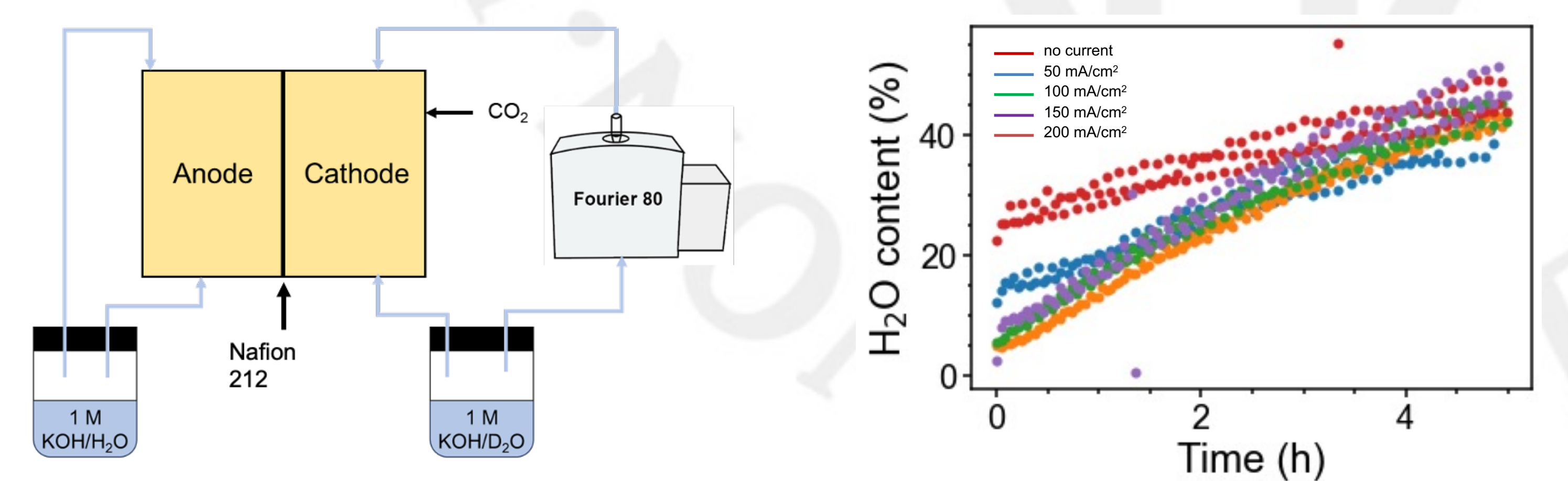
- Inline (operando) benchtop NMR method was developed and applied for studying eCO<sub>2</sub>RR
- Reaction selectivity of liquid products was tracked as a function of time and applied potentials
- Water crossover was observed during the reaction and has a current dependence
- Conversion of OH<sup>-</sup> and CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> concentration change and pH change were observed by monitoring the chemical shift of water

### Monitoring C<sub>2</sub><sup>+</sup> liquid products on sputtered Cu at 100 mA/cm<sup>2</sup>



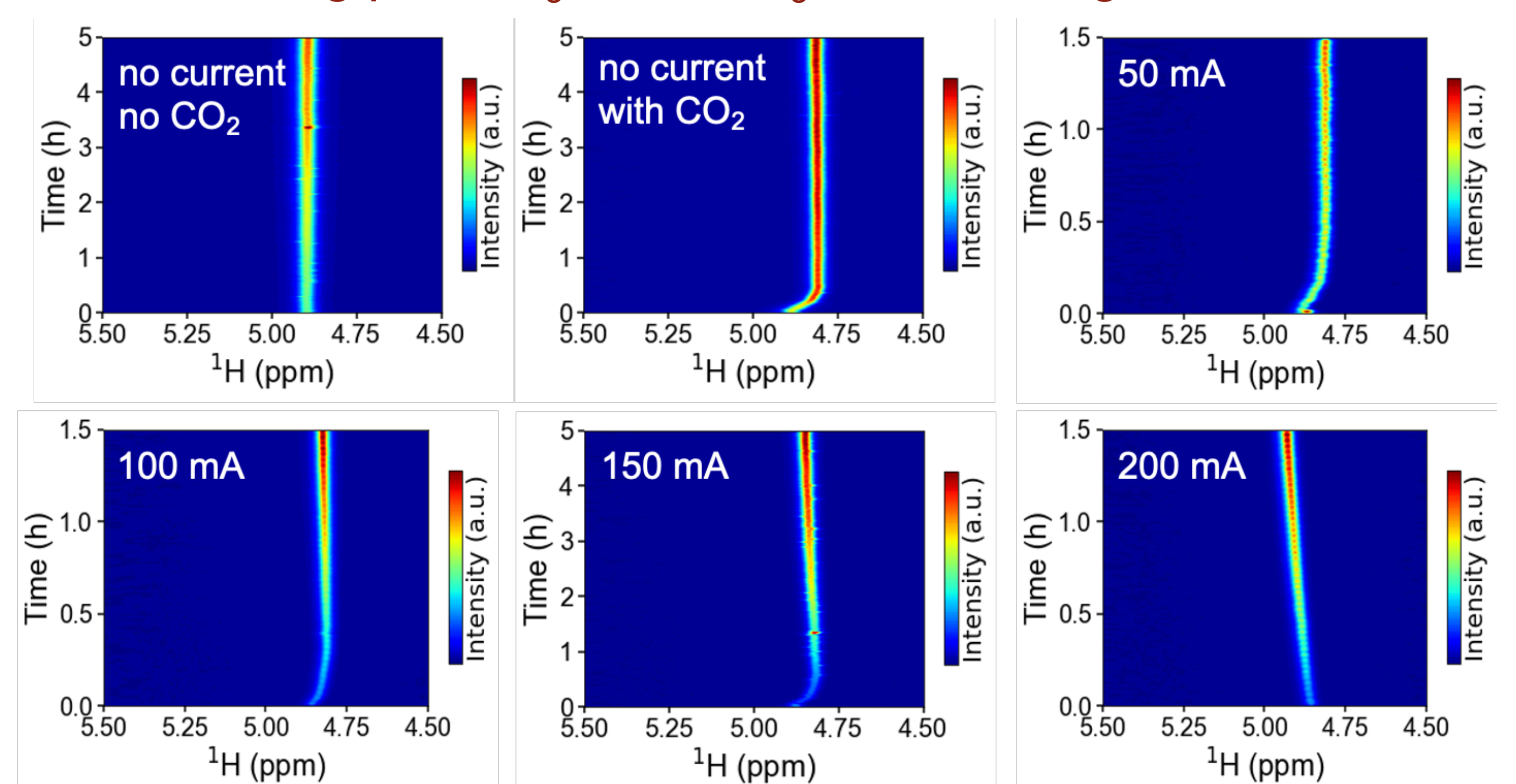
- The concentration of C<sub>2</sub><sup>+</sup> products increased initially and then decreased, ascribed to: (1) reaction rate decrease due to Cu surface reconstruction; (2) severe water and ethanol crossover
- Low Faradaic efficiency of ethanol was observed since KOH was converted into KHCO<sub>3</sub> within one hour (see section *Monitoring pH, CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> conc. changes*)

### Investigating water crossover



- The H<sub>2</sub>O concentration profile was linear within the first 2 hours and then the slope gradually decreased due to migration of K<sup>+</sup> and competing concentration gradient
- Small differences between high current densities (100, 150, 200 mA/cm<sup>2</sup>) can be attributed to water crossover gradually reaching saturation
- Product concentration would be underestimated by approximately 10% if water crossover is overlooked

### Monitoring pH, CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> conc. changes



- The shift of water resonance towards lower frequency in the first hour was caused by the decrease of pH via reaction  $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$
- The shift towards higher frequency afterwards is due to the concentration increase of OH<sup>-</sup> from water dissociation and CO<sub>2</sub> reduction, and its further react with CO<sub>2</sub> to form CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup>

## Reference

1. Nitopi et al. *Chem. Rev.*, **2019**, 119, 7610
2. Peyman et al. *Angew. Chem. Int. Ed.*, **2019**, 58, 7273
3. Mark et al., *ACS Appl. Energy Mater.* **2022**, 5, 5983