

# Addressing the stability challenges in Zero-Gap Membrane Electrode Assembly CO<sub>2</sub> Electrolyzer by modulating operating conditions

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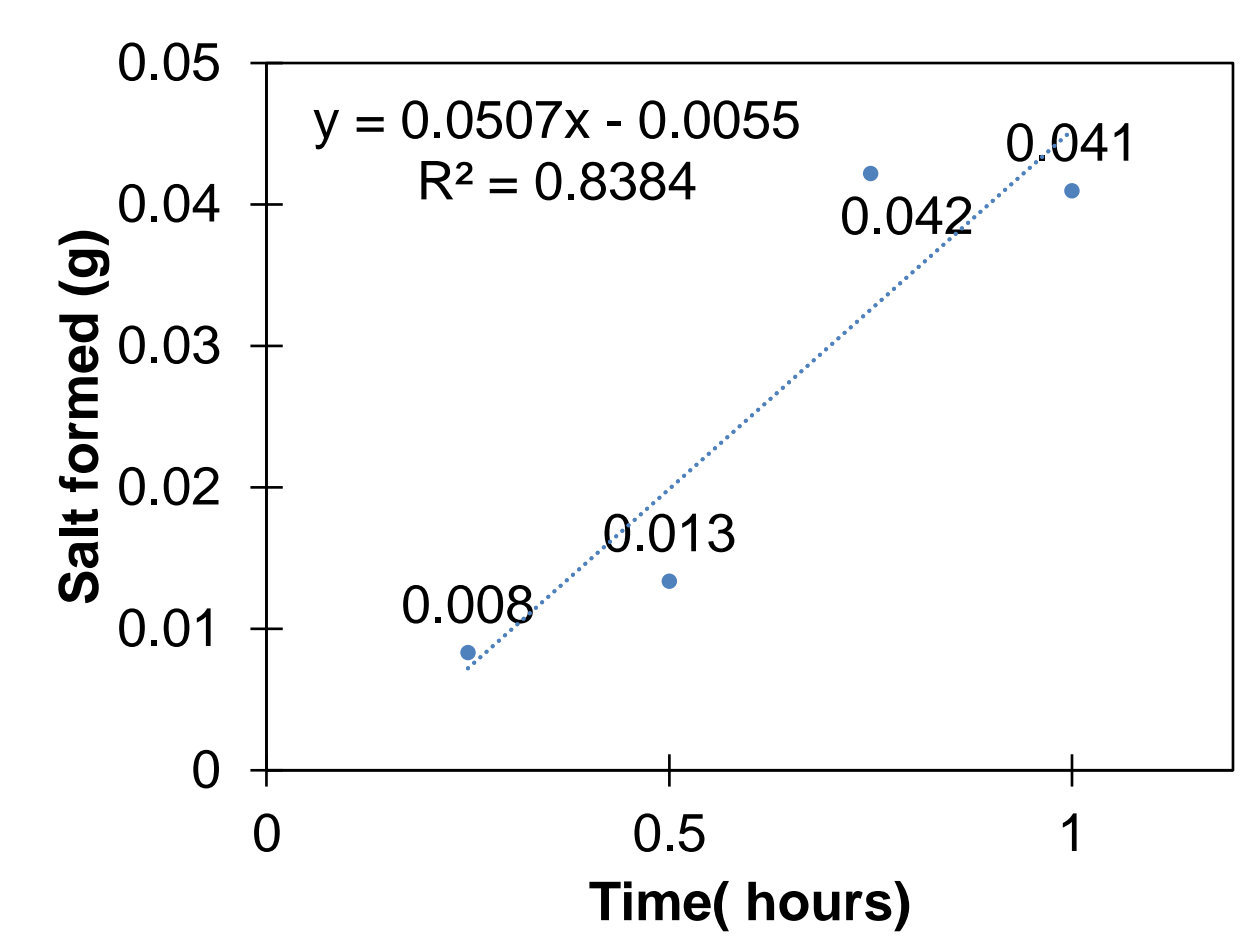
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## Background and Motivation

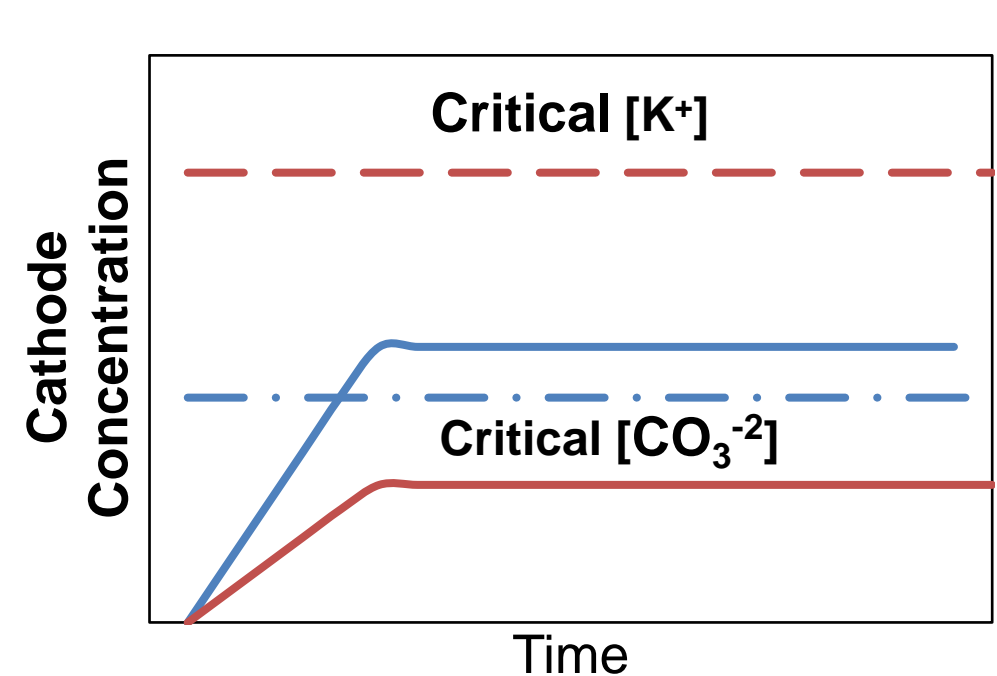
- **Membrane-Electrode Assembly (MEA)** CO<sub>2</sub> electrolyzers have gained attention for their strong performance and high faradaic efficiency in producing products with high selectivity at high current density, making them crucial for the industry. However, these electrolyzers often encounter stability issues due to salt formation, also known as 'salting out'.
- Salt formation occurs when CO<sub>2</sub> reacts with available OH<sup>-</sup> (product of CO<sub>2</sub> Reduction Reaction) to form carbonate ions. Over time, cations from the anolyte cross the membrane, reaching their solubility limit and forming salt, which precipitates out and reduces the availability of CO<sub>2</sub> for electrochemical conversion.
- While existing literature offers strategies to address salt formation, it does not fully explore the key parameters and their impact on salt formation, and there is no available literature on the **quantification** of salt precipitation.
- This research aims to identify key parameters influencing salt formation, such as anolyte concentration, cation type, and membrane thickness, and their impact on the stability of the electrolyzer and salt formation rate, with a focus on **salt collection** and **analysis** to measure the salt formation rate.

## Quantification of Salt Formation: Methodology

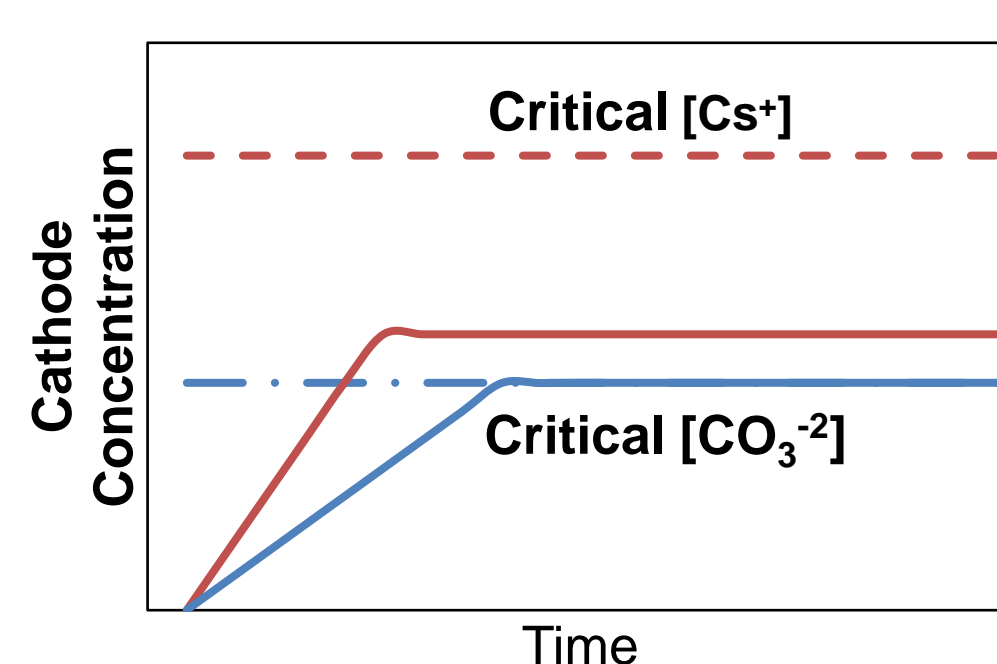
- **Chronopotentiometry (CP)** was conducted at a current density of 200 mA/cm<sup>2</sup> to determine the stable operating period for a set of parameters. Then, CP was also used to measure the rate of salt formation in the **stable regime**, which has a linear time dependency.
- To calculate the amount of salt produced in each trial, the cathode side of the MEA cell was rinsed with water to remove any precipitated salts. **Ion chromatography (IC)** analysis was then performed to quantify the concentration of potassium ions in the water collected from the cathode side. This allowed us to calculate the amount of salt that had formed during the experiment.



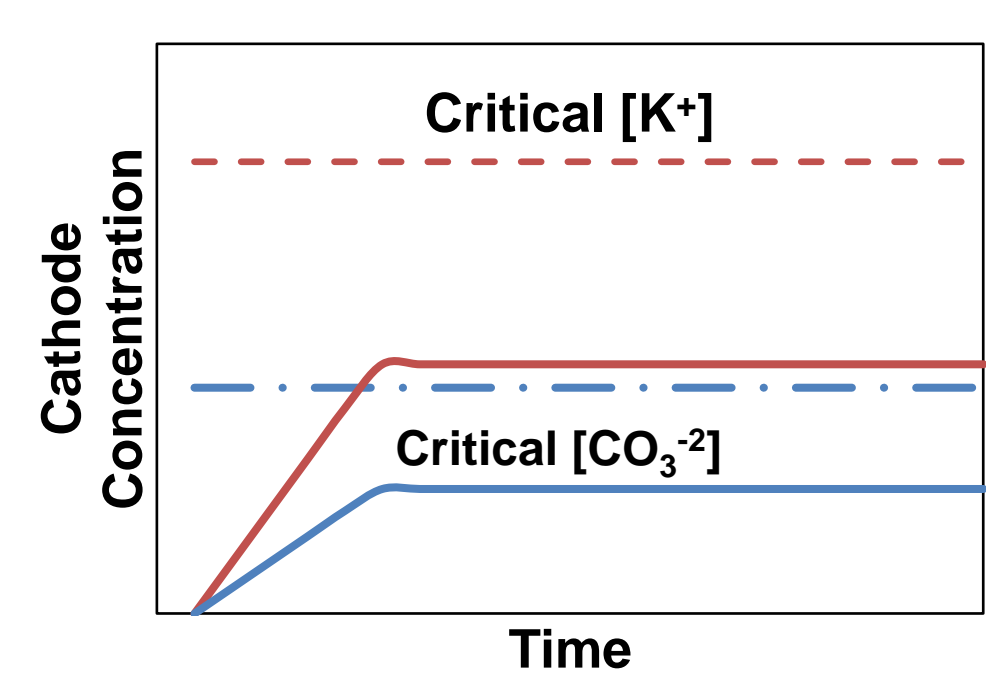
## Parameters Selected



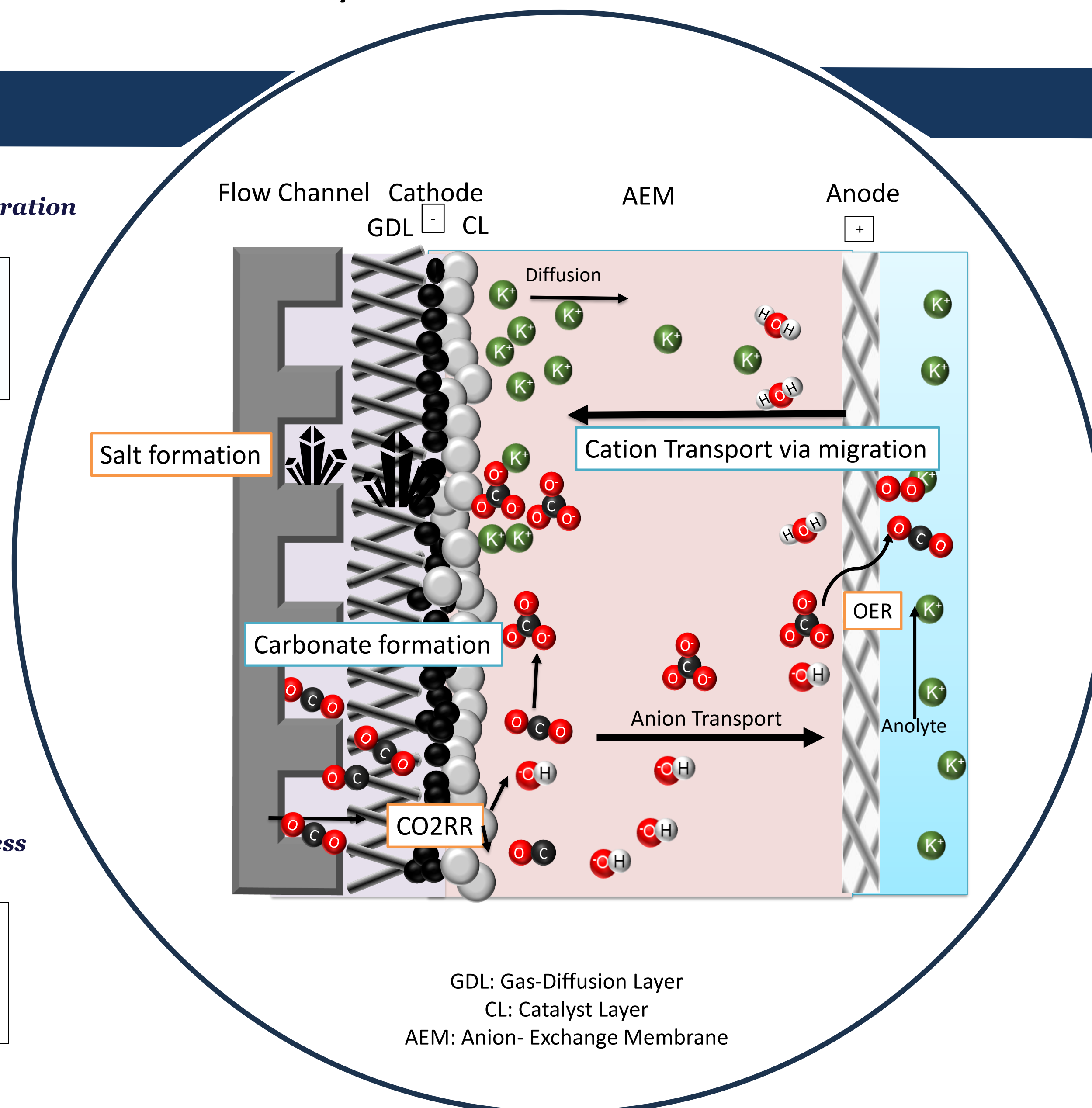
Anolyte concentration



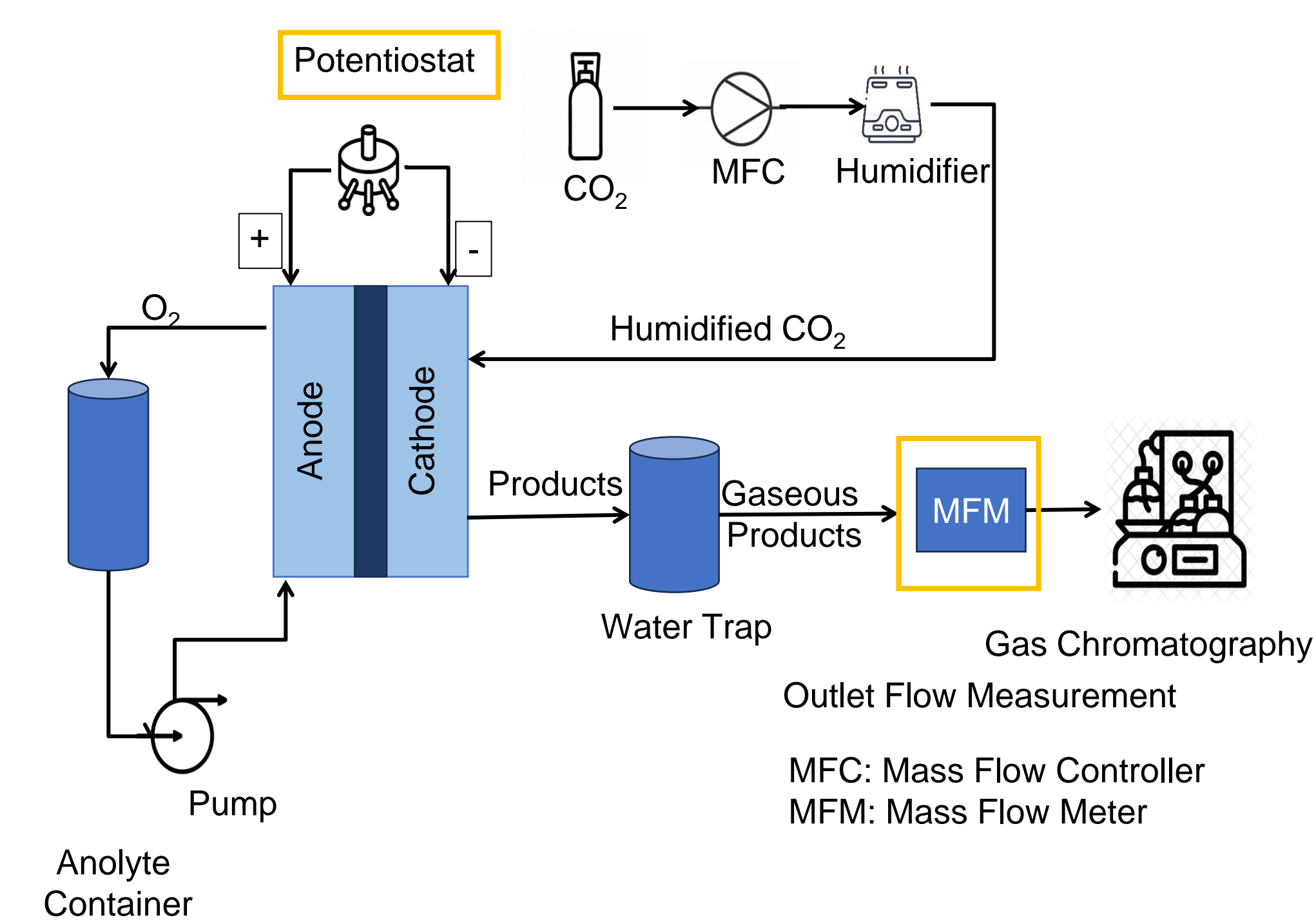
Cation's species



AEM thickness



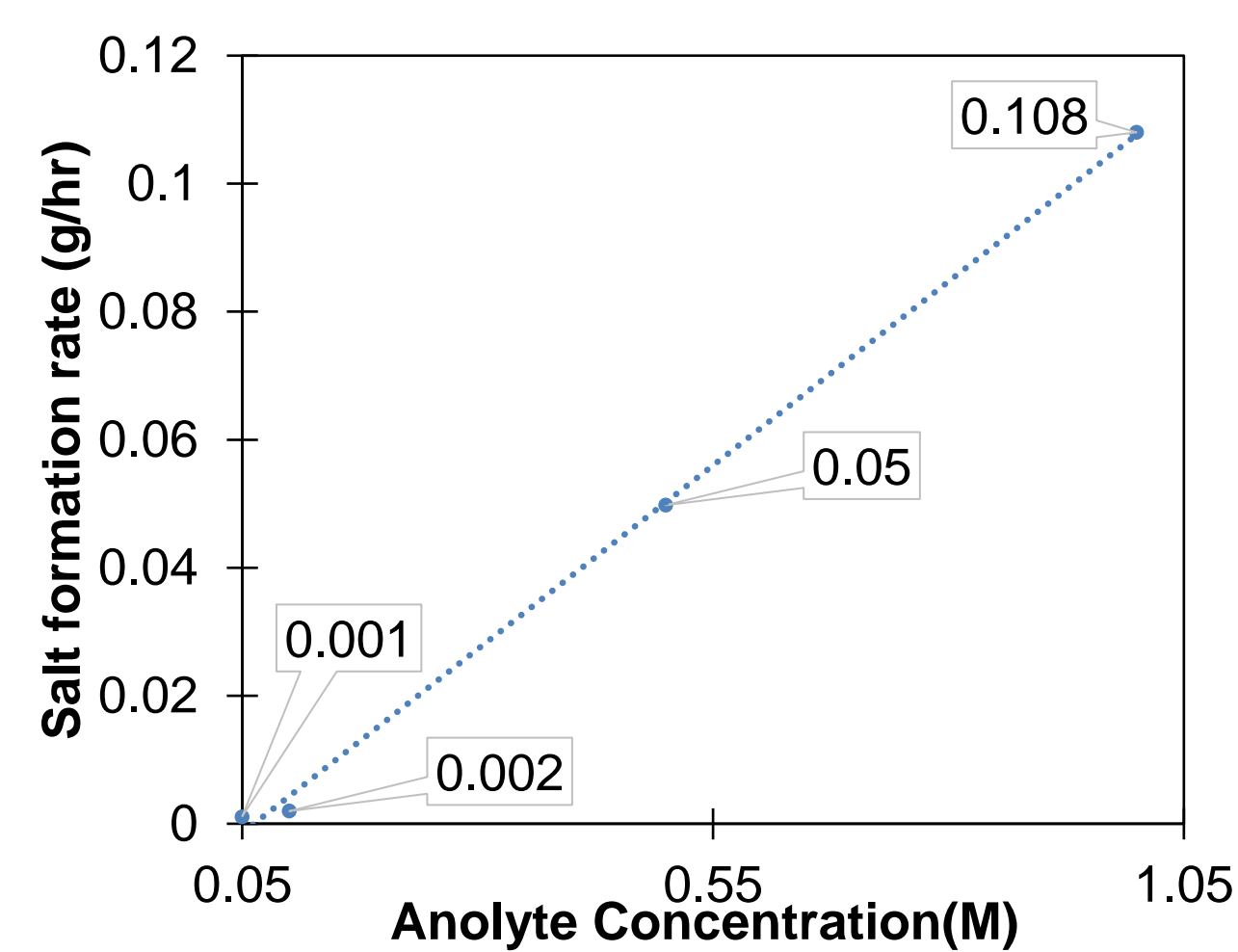
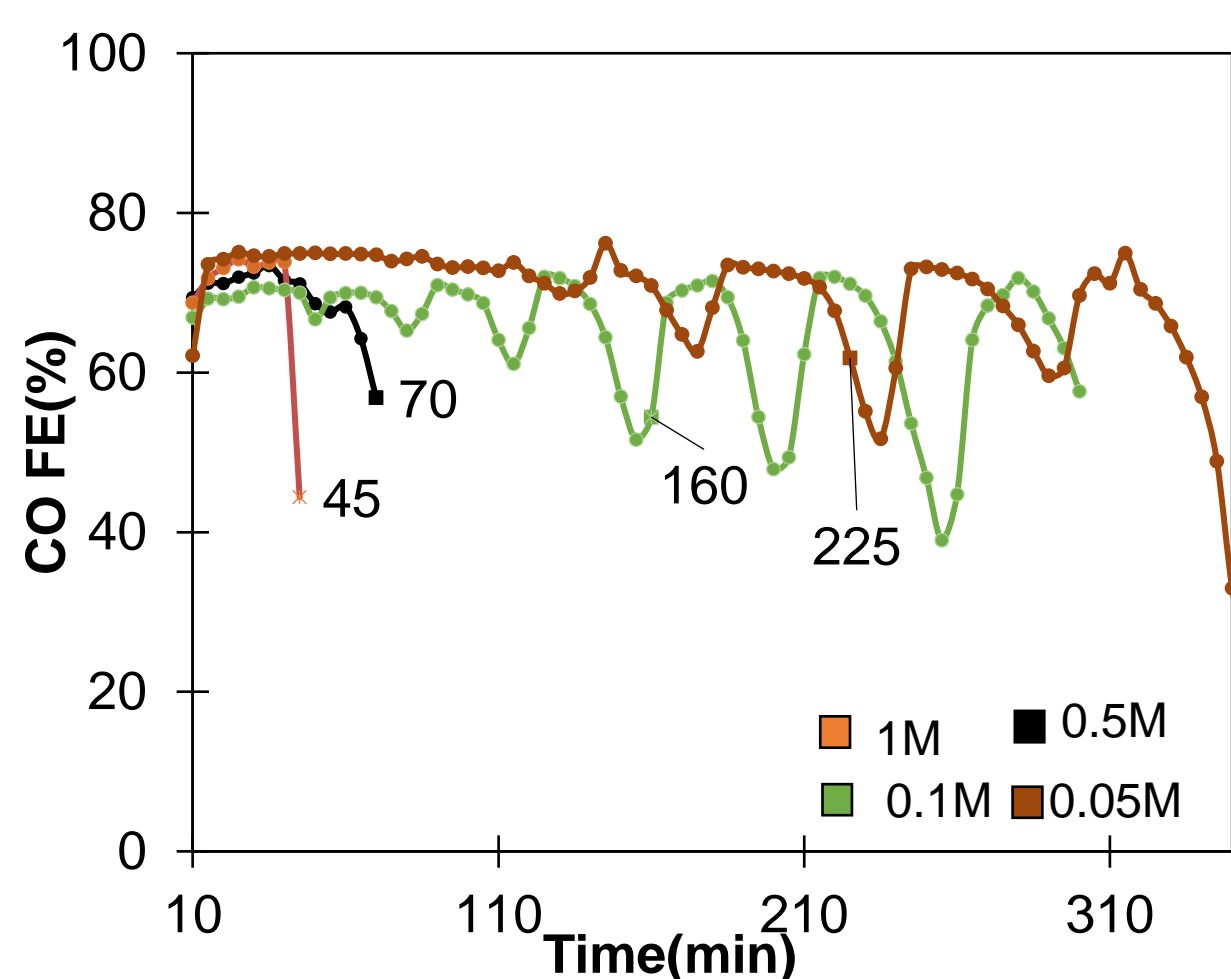
## Electrolysis System Design



**Fixed Parameters:**  
CO<sub>2</sub> Humidified flowrate: 50 ml/min  
**Anode Catalyst:** IrO<sub>2</sub>(HP Now)  
**Cathode Catalyst:** Ag Spurred on GDE sigracet 39-BB

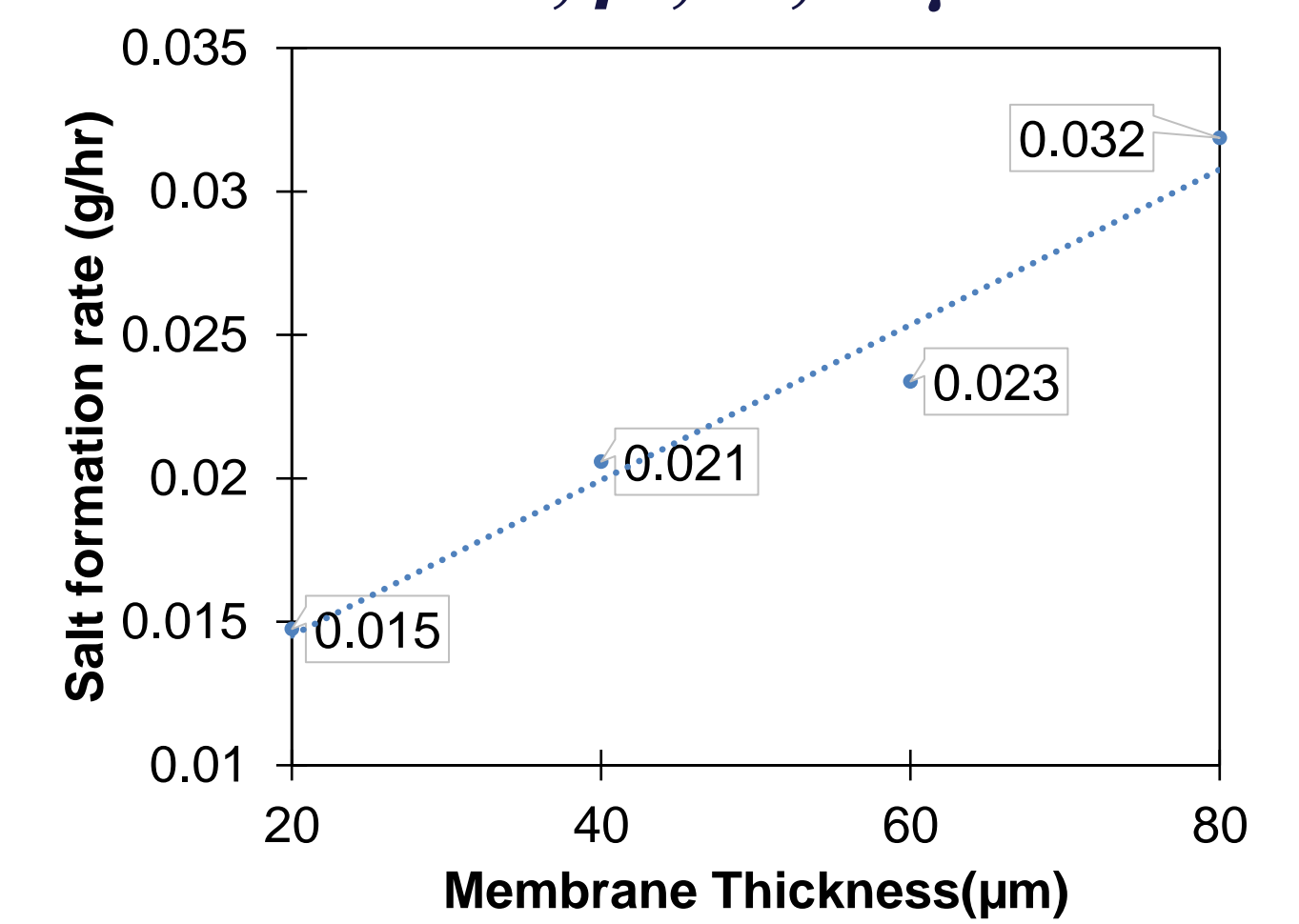
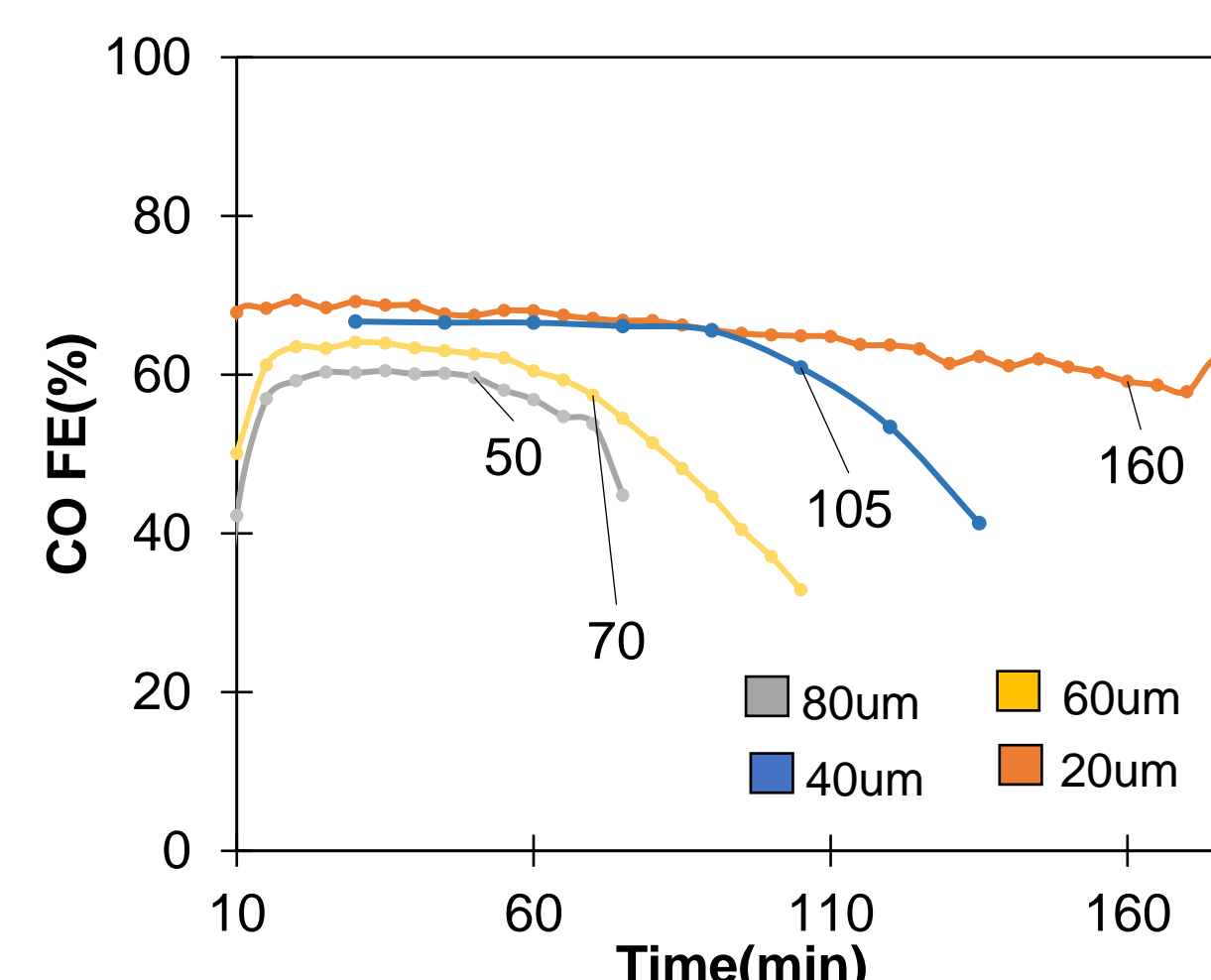
## Results and Discussions

### Variations in Anolyte Concentration: 1,0.5,0.1,0.05M



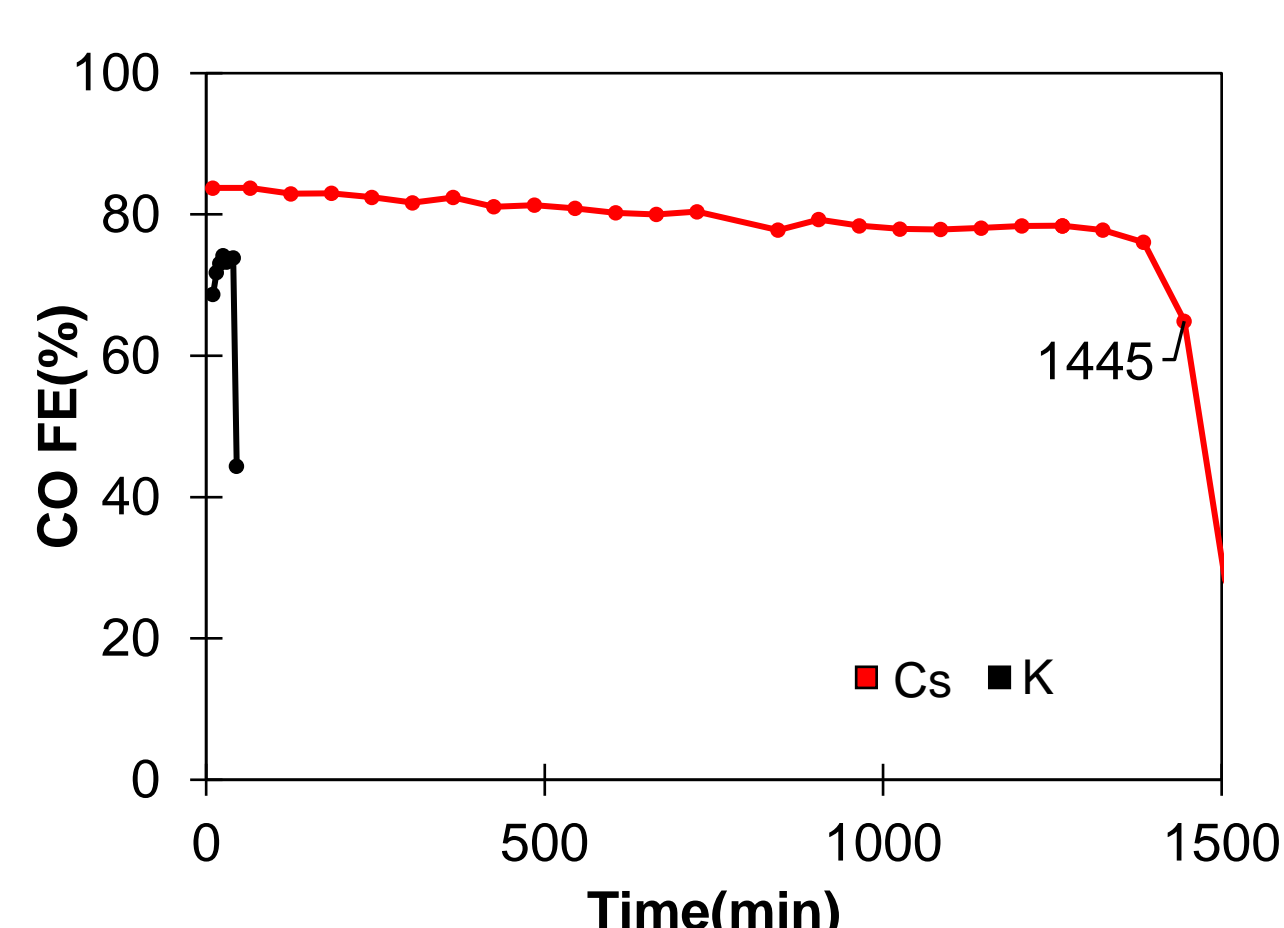
- FE for CO remained stable for longer at lower anolyte concentrations. Lowering the anolyte concentration limited the crossover of K<sup>+</sup>, delaying the 'salting out' effect.
- Oscillation indicated the presence of small flooding and dissolution at lower concentrations.

### Variations in AEM Thickness: 20,40,60,80 μm



- FE CO reached 73% with a 20 μm membrane, which remains stable over 3 hours.
- Thinning the membrane increased the transfer of CO<sub>3</sub><sup>2-</sup> across AEM. Thus, keeping the CO<sub>3</sub><sup>2-</sup> below it is precipitation limit at the cathode ensures longer stability.
- The PiperION® membrane demonstrated greater perm-selectivity for K<sup>+</sup> compared to Sustainion® which resulted in better performance.

### Change in Cation Species: Cs



- FE CO remained stable at 80% for 24 hours when 0.5 M CsHCO<sub>3</sub> was used as anolyte, which marked a 24-fold increase in performance in comparison to 0.5 M KHCO<sub>3</sub>.
- This improvement is attributed to the higher solubility and low hydration number of Cs.

## Conclusion

- **Quantification** of Salt formation is performed to gain a deeper understanding of the influence of **process parameters** on salt formation and precipitation, to address the associated system instability.
- Decreasing the concentration of the anolyte minimize salt precipitation, making long-term stable experiments possible.
- Cs-based anolyte demonstrate superior performance in terms of CO FE and sustained operational stability.
- By reducing the thickness of the membrane, CO<sub>3</sub><sup>2-</sup> ion conductivity is increased, and PiperION® AEMs are more selective in transferring K<sup>+</sup> ions to the cathode.

## Future Recommendations

- The next phase of our research will focus on determining how **temperature** affects ion transfer and the rate of salt formation.
- Based on the outcomes of these experiments, we will then develop a mitigation strategy aimed at ensuring the system can achieve over 10,000 hours of operational time.

## References

- Sassenburg, Mark, et al. "Zero-gap electrochemical CO<sub>2</sub> reduction cells: challenges and operational strategies for prevention of salt precipitation." *ACS Energy Letters* 8.1 (2022): 321-331.
- Garg, Sahil, et al. "How alkali cations affect salt precipitation and CO<sub>2</sub> electrolysis performance in membrane electrode assembly electrolyzers." *Energy & Environmental Science* 16.4 (2023): 1631-1643.
- Garg, Sahil, et al. "How membrane characteristics influence the performance of CO<sub>2</sub> and CO electrolysis." *Energy & Environmental Science* 15.11 (2022): 4440-4469.

## Acknowledgement

- Department of Chemical Engineering, TU Delft
- Dr Tom Burdyny, Department of Chemical Engineering, TU Delft