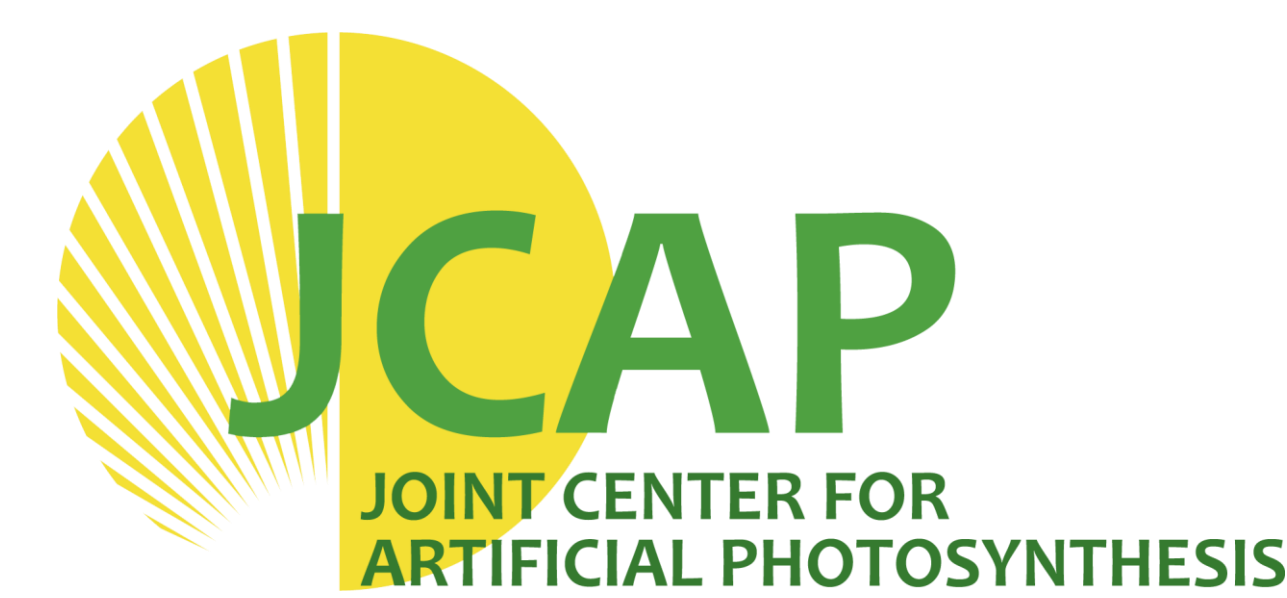


Tuning Distribution of Products Obtained by Pulsed Electrochemical CO₂ Reduction on Cu Catalyst

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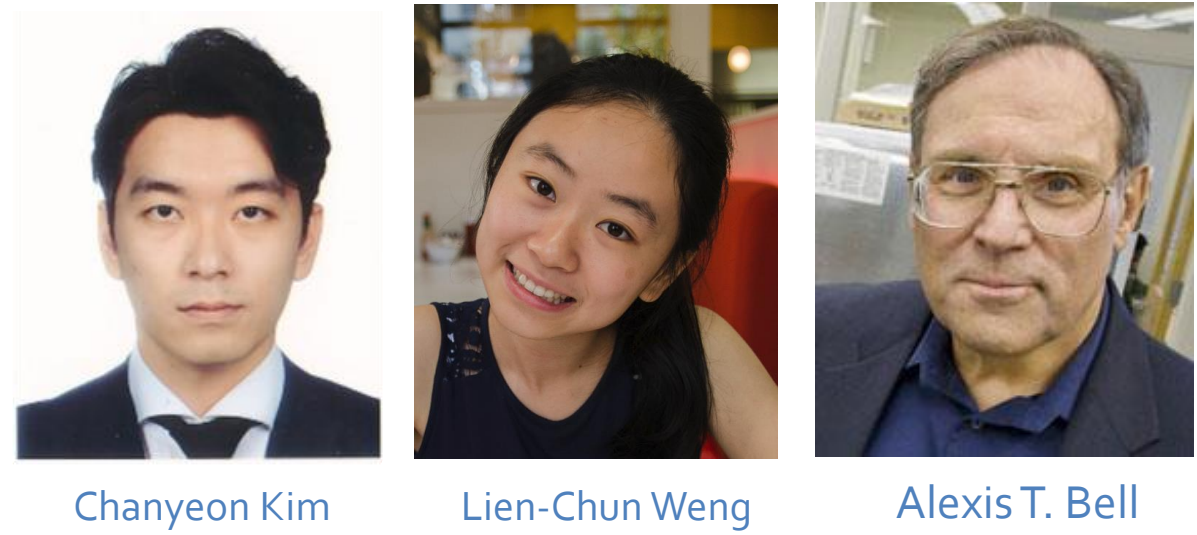
Abstract:

Pulsed electrolysis can minimize hydrogen evolution and maximize C₂₊ production even though it is consisting of potentials incapable of surface reconstruction of Cu catalyst. The temporal analysis using differential electrochemical mass spectroscopy (DEMS) reveals that product concentrations near the cathode stays in phase at the initial but out of phase with extended time, increasing the concentration of C₂H₄ at the expense of CO and H₂. We attribute these trends to an increased ratio of adsorbed CO to H on the Cu surface. Simulation of pulsed electrolysis also shows that the local concentration of CO₂ near the cathode builds up during anodic period that allows electrolysis with a higher CO₂ concentration during the cathodic period than could be achieved for static electrolysis.

Introduction

Pulsed electrolysis has been reported that it can enhance C₂₊ production. But most of previous reports have focused on oxidation of Cu surface during anodic period although enhanced C₂₊ production was also observed at anodic potentials incapable of surface oxidation. This study aims at developing a detailed understanding of how pulsed electrolysis impacts on evolution of products over Cu and in particular increases the formation of C₂₊ products.

Team



Outlook

Our study provides a detailed understanding of the CO₂RR under conditions of pulsed electrolysis using DEMS to reveal the temporal evolution of products at a Cu cathode.

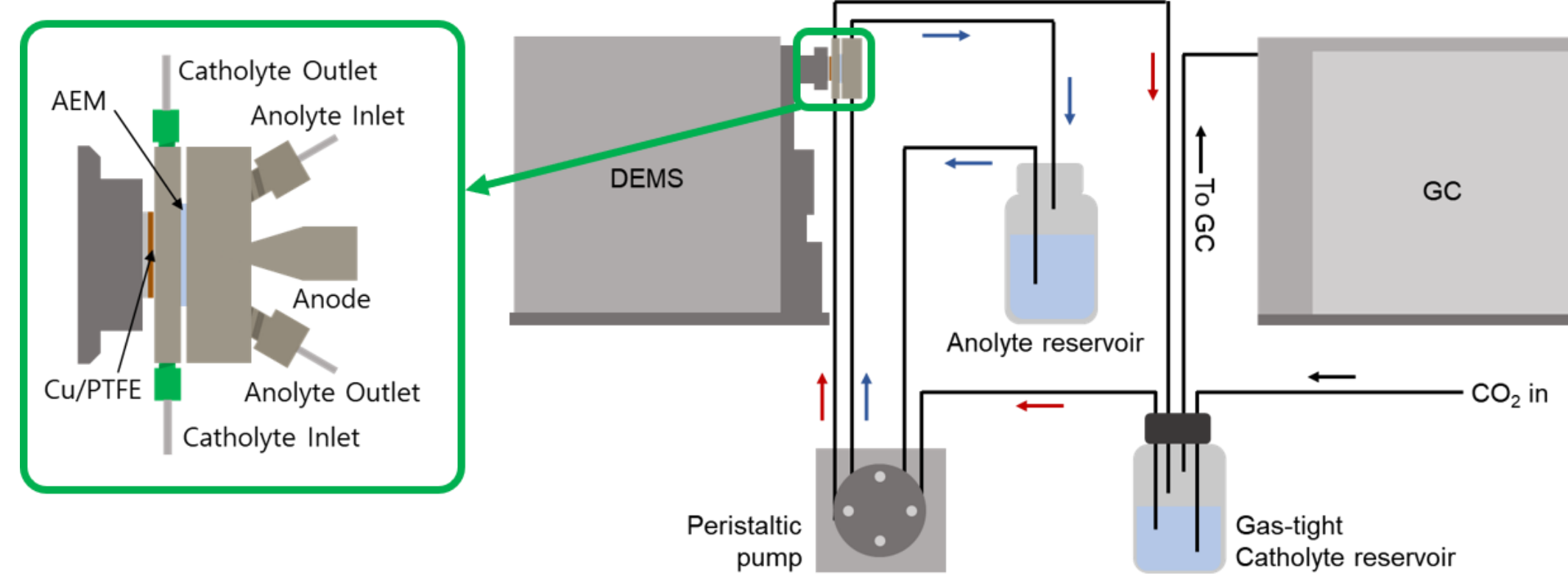
The pulsed CO₂RR can minimize hydrogen evolution and maximize C₂₊ production when duration at each potential was shorter than that requires to reach the steady state.

This study provides an insight for the unsteady state behavior during CO₂RR

Acknowledgments

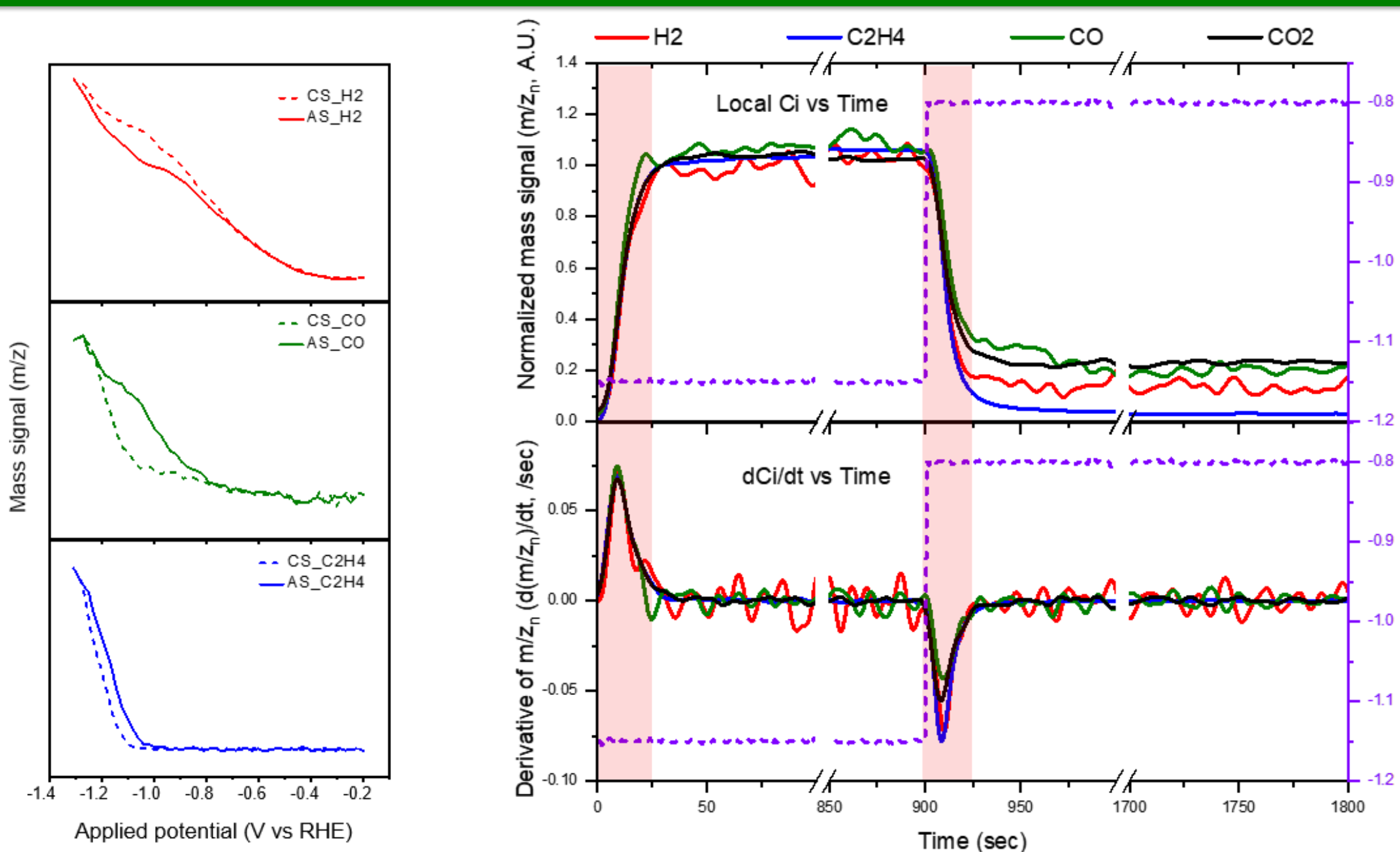
This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

Results, Highlights, and Accomplishments



Experimental setup for pulsed electrochemical CO₂ reduction equipped with online DEMS, GC and HPLC.

Variables for square-wave potential pulse



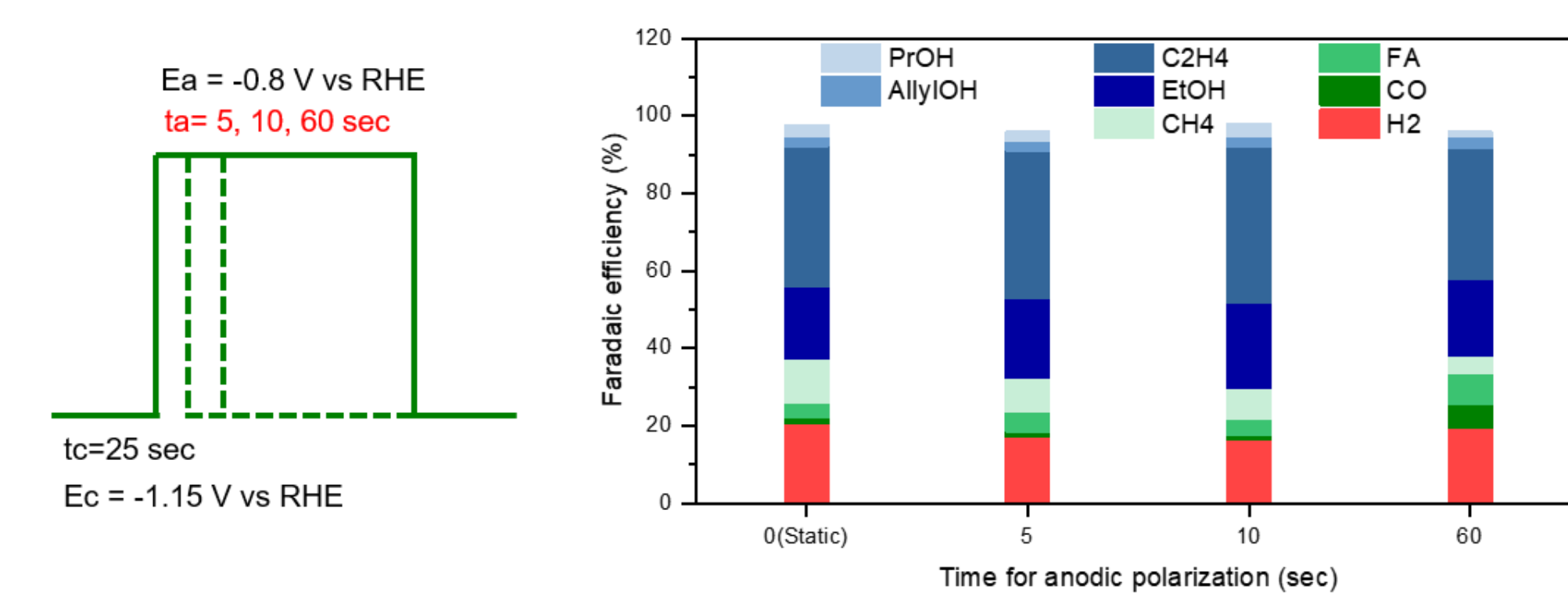
Potential for cathodic and anodic polarization: Hysteresis in DEMS analysis during CV. Local concentration of C₂H₄ & CO ↑ while H₂ ↓ during anodic sweep.

- E_a : on-set E for hysteresis of CO, E_c : E with maximum Δ(anodic-cathodic) of C₂H₄

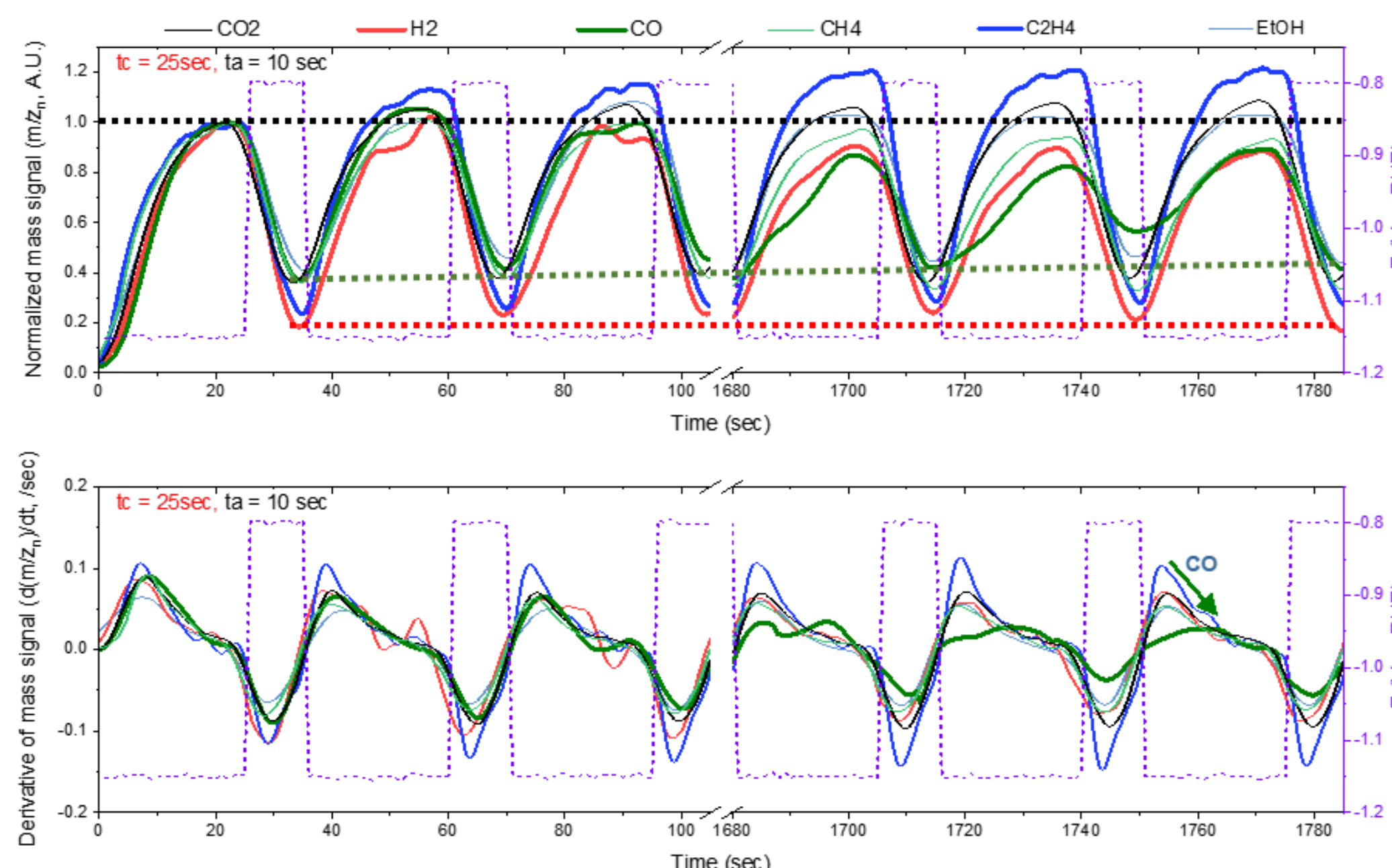
Duration for cathodic and anodic polarization: DEMS analysis during stepped CA

- Around 25sec, system approaches to the steady state

Effect of anodic duration



Product distribution at bulk electrolyte (GC and HPLC) after pulsed electrolysis with different t_a : For t_a ≤ 10 sec, HER ↓, CO₂RR ↑, C₂₊ ↑, C₁ ↓ (optimum at 10 sec) in comparison with static electrolysis



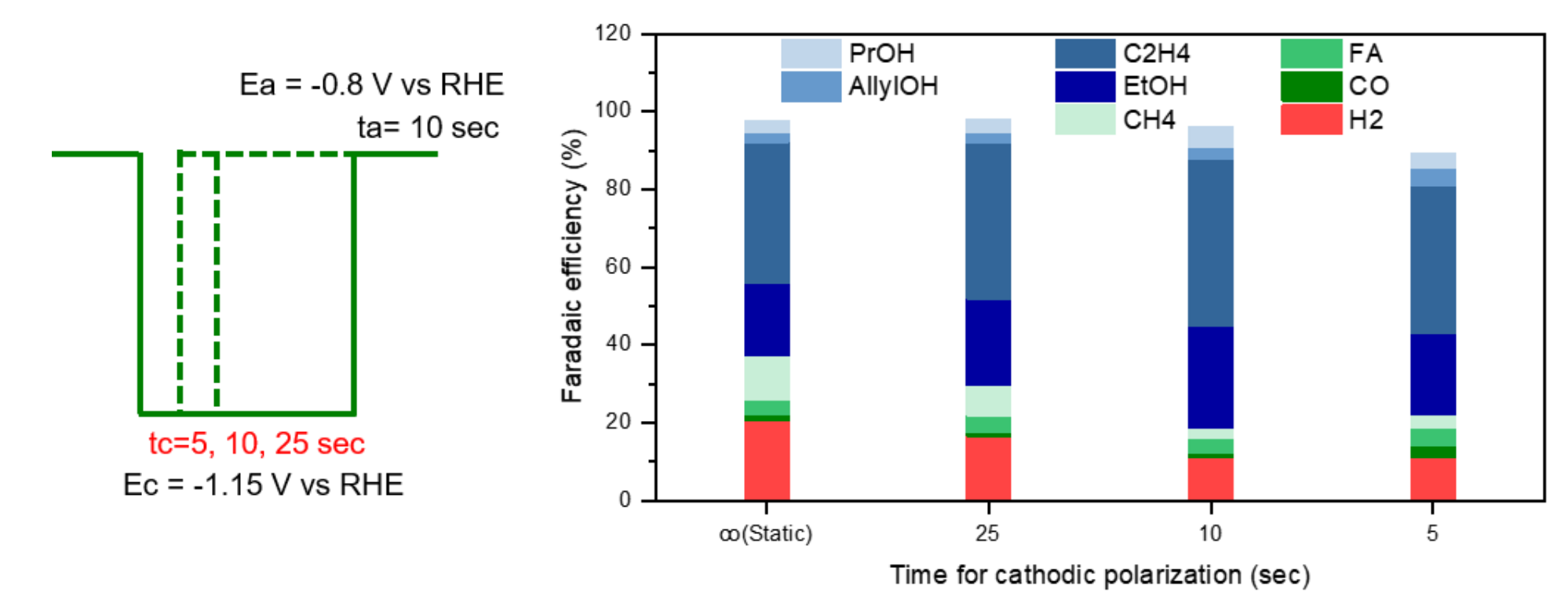
Local concentration during pulsed electrolysis with 25 sec of t_c and 10 sec of t_a

- Cathodic polarization: local C₂H₄ & C_{CO2} ↑, but C_{H2} & C_{CO} ↓
- Anodic polarization: local C_{CO} > local C_{H2}, Initiating subsequent reaction at E_c with higher & C_{CO} and lower C_{H2}.

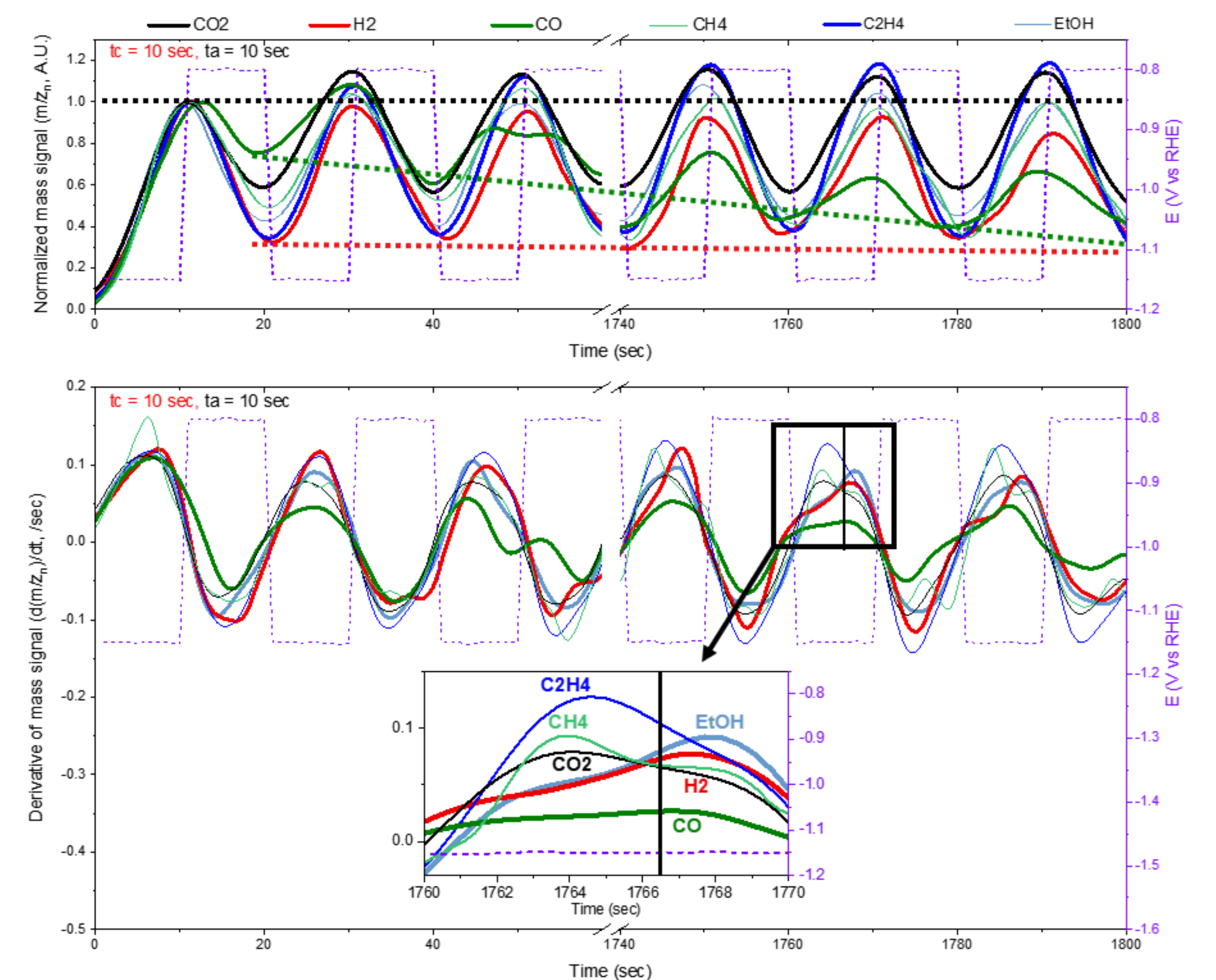
Temporal analysis of local concentration during cathodic polarization

- Peak shift and reduction of time derivative of local CO concentration
- Reduction of CO desorption : (CO_{ad} → CO) < (CO_{ad} → ½ C₂)

Effect of cathodic duration



Pulsed electrolysis with different t_c : For 10 sec of t_c, HER ↓ from 20 to 11%, C₂₊ ↑ from 60% to 77% in comparison with static electrolysis



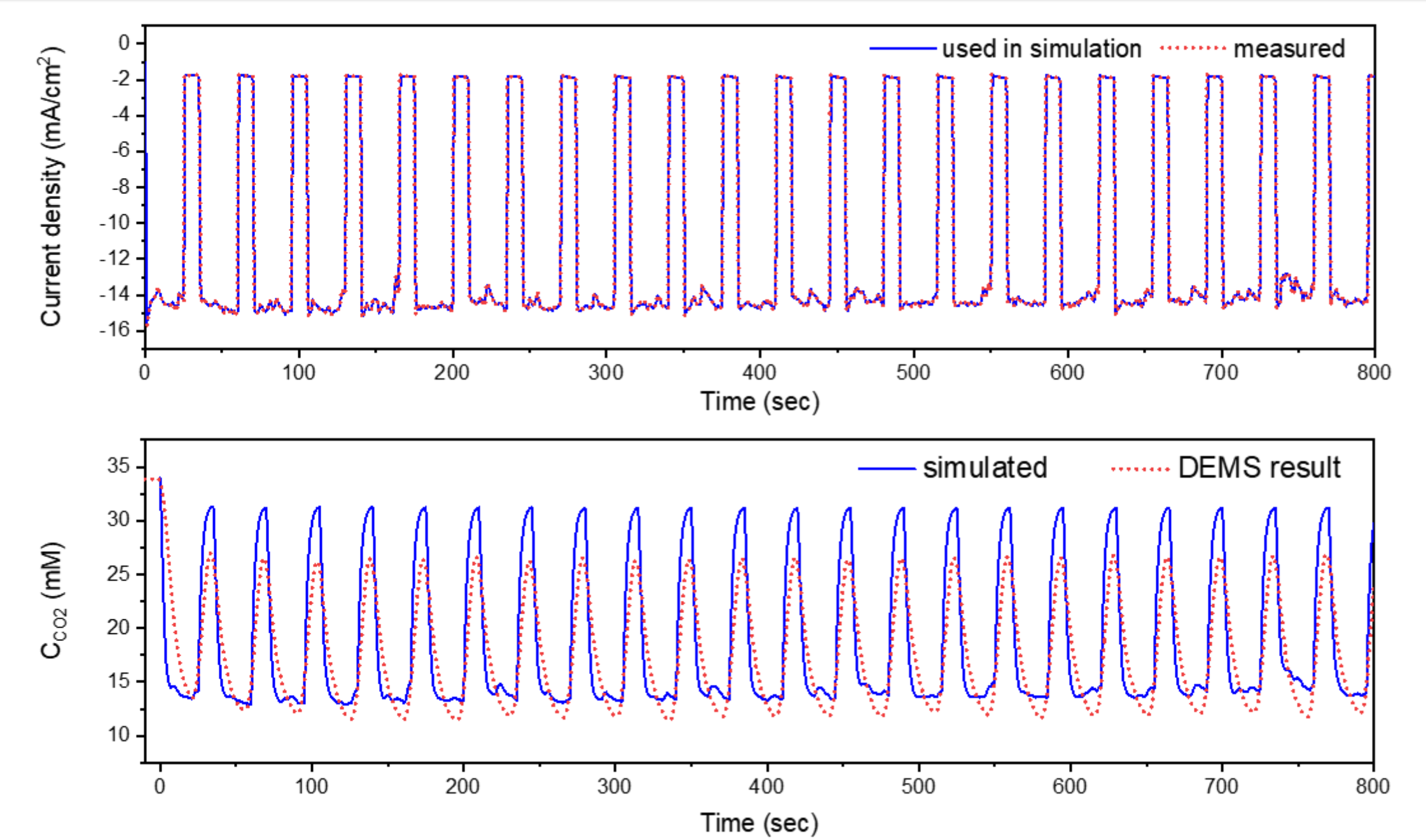
Local concentration during pulsed electrolysis with 10 sec of t_c

- Cathodic polarization: Maximum value of local C₂H₄ & C_{CO2} ↑, but C_{H2} & C_{CO} ↓
- Anodic polarization: Minimum value of C_{CO} >> C_{H2} after 1st pulse and then C_{CO} ↓

Temporal analysis of local concentration during cathodic polarization

- At 1st cathodic polarization, all the species stays in phase then out of phase with extended time.
- Further reduced hydrocarbons, CH₄ and C₂H₄ appears earlier than Oxygenates (CO & EtOH) and H₂ : retarded peak
- Initial: rise of hydrocarbons → H and CO consumption ↑
- H limited regime, retardation of oxygenate evolution

Simulation of pulsed electrolysis



- At the end of each anodic pulse, local C_{CO2} ↑ to 31mM (13mM for static electrolysis). Consequently, next cathodic polarization begins with an elevated local C_{CO2}.
- If the t_c < required time for steady state electrolysis, the average C_{CO2} near the cathode is higher than that present under steady-state condition.
- Since the rate of CO₂ reduction ∝ C_{CO2}, it will be higher under conditions of pulsed rather than static electrolysis.
- It then follows rate of CO formation ↑ and correspondingly, concentration of adsorbed CO ↑ at the surface