

# 76<sup>th</sup> Annual Meeting

of the International Society of Electrochemistry

7 - 12 September 2025

*Mainz, Germany*

Electrochemistry -  
From Basic Insights  
to Sustainable Technologies



## PROGRAM

<https://annual76.ise-online.org>

e-mail: [events@ise-online.org](mailto:events@ise-online.org)

# Surface Interactions between CO, Cl<sup>-</sup>, and OH<sup>-</sup> during Ethanol Electro-oxidation on Platinum in Alkaline Seawater-like Electrolytes Probed by *In Situ* Vibrational SFG

Thiago V. Barros Ferraz<sup>1,2</sup>, R. Kramer Campen<sup>2</sup>, Hamilton Varela<sup>1</sup>, Yujin Tong<sup>2</sup>

<sup>1</sup>São Carlos Institute of Chemistry, University of São Paulo, São Carlos, Brazil

<sup>2</sup>Faculty of Physics, University of Duisburg-Essen, Duisburg, Germany

thiago.vbferraz@usp.br

Replacing water oxidation with the electro-oxidation of small organic molecules such as ethanol is a promising strategy to reduce anodic overpotentials in hybrid seawater electrolyzers while co-producing value-added compounds. However, the high Cl<sup>-</sup> concentration typical of seawater hinders this approach, as chloride strongly adsorbs onto platinum surfaces, blocking access to reactants and intermediates. Alkaline conditions have been shown to mitigate these effects by reducing Cl<sup>-</sup> surface coverage through competitive OH<sup>-</sup> adsorption, thereby facilitating ethanol access to catalytic sites. Understanding how these changes influence the interfacial environment is key to designing chloride-tolerant, alcohol-assisted anodes for seawater electrolysis [1]. Adsorbed CO is a central intermediate in ethanol oxidation pathways involving C-C bond cleavage, but also acts as a strong catalytic poison. Its vibrational properties offer a useful probe of adsorption geometry, site occupancy, and lateral interactions. In this context, vibrational sum-frequency generation (vSFG) spectroscopy provides surface-specific vibrational insight under potential control, being intrinsically insensitive to bulk contributions. Its application to electrochemical systems has yielded valuable information on interfacial species and local field effects [2,3]. In this study, *in situ* vSFG spectroscopy was employed to investigate ethanol electro-oxidation on a polycrystalline platinum electrode in 0.5 M NaCl or NaClO<sub>4</sub> (used as a non-adsorbing reference electrolyte), both containing 1 M ethanol, with pH adjusted to 12, 13, or 14 using NaOH. All measurements were performed using the thin-layer configuration described in reference [4]. The resonant and non-resonant components were extracted by fitting a Lorentzian lineshape model [5]. From these fits, we obtained the non-resonant phase and amplitude, as well as the intensity, central frequency, and full width at half maximum (FWHM) of the resonant CO signal — where the resonance corresponds to surface-adsorbed CO, while the non-resonant signal reflects interfacial potential distribution (linked to both the electrode and adsorbates). Our analysis initially focused on the atop CO band, which consistently appeared as the dominant feature in the spectral region under investigation. We found that: (i) Between 0.05 V and 0.2 V, the Pt surface is primarily covered by adsorbed hydrogen across all pH values. Within this potential window, the adsorption of Cl<sup>-</sup>, OH<sup>-</sup>, and CO remains negligible. (ii) In the range of 0.2 V to 0.5 V, ethanol dissociation and fragmentation occur. The influence of adsorbed Cl<sup>-</sup> on this process is minimal at pH 12 and pH 14, but becomes significantly more pronounced at pH 13 as seen by the resonant amplitude of the signal. (iii) Between 0.5 V and 0.9 V, the oxidation of adsorbed CO takes place. In this potential region, Cl<sup>-</sup> adsorption can effectively block the continuously formed CO. (iv) At potentials above 0.9 V, the bulk oxidation pathway mediated by the growing platinum oxide layer is activated. In this high-potential region, competitive adsorption between Cl<sup>-</sup> and OH<sup>-</sup> is still observed at pH 12 and pH 13, whereas at pH 14, surface coverage is predominantly governed by adsorbed OH<sup>-</sup> species. This information is important for optimising the system parameters in hybrid seawater electrolyzers.

- [1] T. V. De B. Ferraz, G. Tremiliosi-Filho, H. Varela, *J Solid State Electrochem* (2025).
- [2] Y. Tong, R.K. Campen, in: *Encyclopedia of Interfacial Chemistry*, Elsevier, 2018, pp. 280–286.
- [3] Y. Tong, in: *Encyclopedia of Solid-Liquid Interfaces*, Elsevier, 2024, pp. 750–759.
- [4] I.Y. Zhang, G. Zwachka, Z. Wang, M. Wolf, R.K. Campen, Y. Tong, *Phys. Chem. Chem. Phys.* 21 (2019) 19147–19152.
- [5] Y.R. Shen, *Nature* 337 (1989) 519–525.