

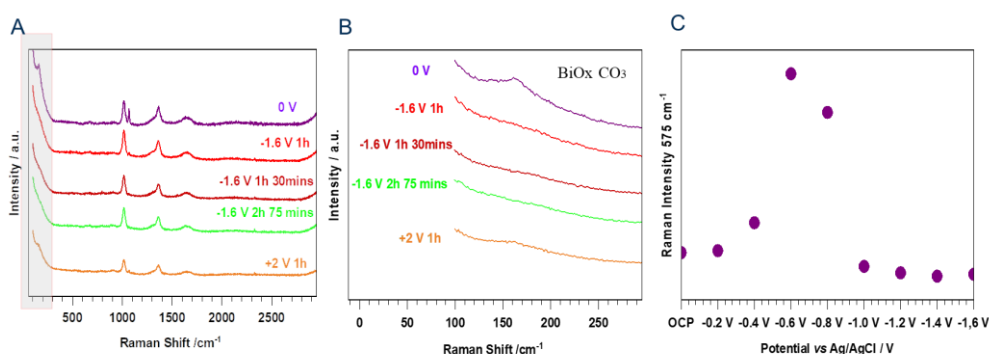
# Unraveling The Degradation Mechanism In Metal-Based Electrodes For CO<sub>2</sub> Electroreduction With In-Situ Raman Spectroscopy

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The electrochemical reduction of carbon dioxide (CO<sub>2</sub>RR) offers a viable strategy for capturing, storing, and utilizing carbon dioxide, with the potential to transform greenhouse gas emissions into valuable carbon feedstocks like carbon monoxide (CO) and formic acid (HCOOH), as well as high-value C<sub>2+</sub> products such as alcohols and hydrocarbons<sup>1,2</sup>. However, challenges persist in the empirical and ambiguous aspects of catalyst design, performance evaluation, and structure–property correlation, primarily due to limited identification and understanding of active sites and reaction pathways under operational conditions. When catalysts interact with surrounding reactants or products under reducing conditions, they often undergo structural self-reconstruction, leading to changes in morphology and structure. This phenomenon can result in unpredictable deviations from targeted activities and electrocatalytic performance.<sup>3</sup> This stability issue is the major bottleneck in bringing the CO<sub>2</sub>RR technology to the industry. The judicious monitoring and regulation of material reconstruction within operational parameters emerge as pivotal pursuits, crucial for the precise identification of active sites, comprehensive understanding of reaction- or degradation mechanisms, and deliberate design of advanced catalysts.<sup>4</sup> The current study is focused on elucidating the manifestation of intermediates skin formation on metal electrodes as well as time-dependent behavior under electrochemical conditions. For example, multiple investigations into electrocatalytic processes and mechanisms have proposed the possibility that the adsorption of carbonate (\*CO<sub>3</sub>H) on the catalyst's surface acts as a potential intermediate. By using in-situ Raman spectroscopy, we observed and confirmed such metastable oxo-carbonate species on the surface of our Bismuth (Bi) electrode. In our study, we systematically examined the behavior of this oxo-carbonate species to ascertain its dependence on solution conditions and electrode potential. Additionally, we studied and compared the presence of this intermediate with other metal electrodes, typically known for producing formate (tin) and CO (silver). A comparable trend was discerned in the case of metallic tin (Sn), which is presumably related to the reaction mechanism toward formate. In Fig. 1, it can be seen that the presence of the oxo-carbonate species on Bi and Sn is potential-dependent. We used this to extend the operational times of the CO<sub>2</sub>RR process, which is a first step in tweaking the system to achieve a stable process.



**Figure 1:** (A) The In-Situ Raman spectra obtained from the surface of a Bi foil during CO<sub>2</sub>RR. (B) The enlarged image from the highlighted portion in (A) shows the evolution of a subcarbonate species over time. (C) The intensity of the Raman signal at 575 cm<sup>-1</sup> obtained from a Sn foil under different operating potentials.

## References

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