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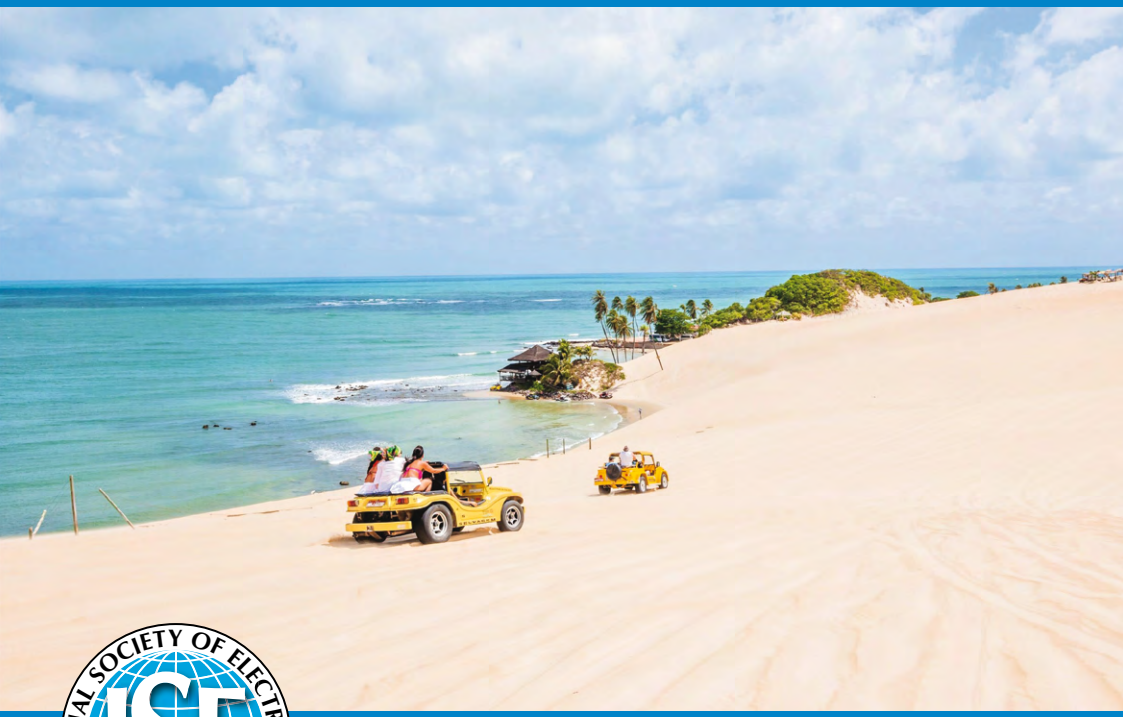

PROGRAM

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Combining N-coordinated Copper Single-Atoms and Copper Clusters for CO_2 Electrochemical Reduction

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The shift toward a clean and sustainable energy landscape is essential for advancing beyond fossil fuel dependency. Among various approaches, the electrocatalytic reduction of CO_2, when integrated with renewable energy sources, represents one of the most effective pathways for producing clean fuels and high-value chemicals, including hydrocarbons and alcohols. Copper remains the only metal-based electrocatalyst capable of converting CO_2 into C_1 and C_{2+} products, such as hydrocarbons, methane, ethylene, and ethanol at decent selectivity and productivity. However, this metal exhibits limited selectivity for a single product, and is prone to electrode deactivation, primarily due to carbonaceous deposits formed by reaction intermediates [1], and morphological alterations arising from its inherent dynamic behavior of dissolution and restructuration. Considering that Cu^{2+} species suffers partial *in-situ* reduction to metallic copper clusters at low potentials [2], one can intentionally explore the CO_2 reduction on N-coordinated copper Cu^{2+} and Cu^0 species in substrates that primarily retain Cu ions and metallic copper clusters within their structure [3]. The hypothesis raised in this work is based on the principle that a material labeled Cu-N-C such as single copper atoms embedded in a highly rich nitrogen doped carbon matrix, demonstrates the ability to anchor copper ions and clusters, simultaneously, thus performing a Tandem electrocatalysis process of the CO_2 electrochemical reduction Herein, by combining the techniques of Transmission Electron Microscopy (TEM), On-line Differential Electrochemical Mass Spectrometry (DEMS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) coupled to electrochemical flow cell, we show that the selectivity of CO_2 electrochemical reduction depends on the stability of the N-coordinated Cu ions (single-atoms) and Cu clusters formed during the cathodic regime. Furthermore, by using a Rotating Ring-Disk Electrode (RRDE) with IrO_x electrodeposited on the ring as a local pH probe, it was demonstrated that the cooper dissolution is function of the interfacial pH changing due to protons consumption from the electrolyte by both CO_2 reduction and the competitive Hydrogen Evolution Reaction (HER). This was ascribed to the formation of CuO_xH_y species, which are soluble in the electrolyte, as evidenced by the nature of the high alkaline metal species on the electrode surface post-electrolysis evidenced by means of the X-ray Photoelectron Spectroscopy (XPS). Quantitative Gas Chromatography (GC) analysis further demonstrated the stability of the Cu-N-C catalyst for CO formation at -1.0 V vs. RHE, achieving a high Faradaic efficiency of 80%.

References:

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