



Bicarbonate-to-CO electroreduction over NiCu catalysts with confined pore structures

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ARTICLE INFO

Keywords:

Bicarbonate electroreduction
NiCu
Porous catalysts
Pore confinement

ABSTRACT

Electrochemical bicarbonate reduction reaction offers a promising pathway of integrating carbon capture and conversion, which could bypass the energy-intensive upstream CO₂ regeneration and downstream CO₂ separation processes. Since the limited in-situ CO₂ (*i*-CO₂) generation at the electrochemical interface, designing catalysts with highly exposed active sites and optimized structures is the key to achieve efficient bicarbonate reduction. In this work, we prepared a series of NiCu-based porous catalysts, using SiO₂ hard templates of different sizes to tune the pore structure. There exist an optimal mesopore size that could balance the mass transport, local *i*-CO₂ enrichment, and active-site distribution in bicarbonate electroreduction to CO. The optimal catalyst NiCu-TE achieved a bicarbonate-to-CO electrolysis at 100 mA cm⁻² with 92.4% Faradaic efficiency (FE) and 41.3% energy efficiency (EE) in the membrane electrode assembly (MEA). It maintained a FE CO of 68.3% at a current density of -300 mA cm⁻². We found that pore architecture engineering, rather than pore size alone, is crucial in constructing efficient electrochemical microenvironments for bicarbonate electroreduction.

1. Introduction

The continuous rise in atmospheric carbon dioxide (CO₂) concentration is mainly attributed to the widespread use of fossil fuels and various industrial activities, which is the main cause of global warming (Jiménez-de-la-Cuesta and Mauritsen, 2019; Zhu et al., 2024). Carbon capture, utilization, and storage (CCUS) have been developed as a promising approach for directly capturing CO₂ from industrial sources and converting it into valuable products, thereby mitigating overall emissions. Electrochemical CO₂ reduction reaction (CO₂RR) has gained significant attention due to its high efficiency, flexibility and environmental compatibility. However, conventional gas-fed CO₂RR systems generally require an additional and energy-demanding CO₂ regeneration process and suffer from limited carbon utilization efficiency (Liu et al., 2024; Xu et al., 2021; Gu et al., 2022). These factors increase the operational expenses and reduce the overall energy efficiency (EE), ultimately restricting the large-scale practical application of gas-fed CO₂RR technologies (Ozden et al., 2022).

Reactive carbon capture (RCC) has gained considerable attention as

a promising approach that could enable direct conversion of captured carbon into value-added products without upstream CO₂ regeneration and downstream CO₂ separation processes (Khiaarak et al., 2025; Kumar De et al., 2023). Among various carbon-containing feedstocks, (bi)carbonates are the dominant products in many aqueous CO₂ capture systems (Tzirakis et al., 2025). In electrochemical (bi)carbonate reduction systems, (bi)carbonate acts as the carbon donor, first releasing in-situ CO₂ (*i*-CO₂) within the reaction layer (Gutiérrez-Sánchez et al., 2022; Li et al., 2019; Li et al., 2019). The *i*-CO₂ then serves as the actual reactant, undergoing reduction at the electrode-electrolyte interface. Recent studies have employed membrane-electrode assemblies (MEA) incorporated with bipolar membranes (BPM) or cation exchange membranes (CEM) to initiate (bi)carbonate reduction (Khiaarak et al., 2025; Zheng et al., 2025; Rong et al., 2026; Liu et al., 2025). Protons from the membrane react with (bi)carbonate to produce *i*-CO₂, and then reduced cathodically to yield products, like conventional CO₂RR process. Recent progress has demonstrated that performance can be substantially improved by regulating the local reaction microenvironment. Rong et al. (Rong et al., 2026) achieved a record-high CO partial current density of

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<https://doi.org/10.1016/j.ces.2026.124385>

Received 17 April 2026; Received in revised form 20 May 2026; Accepted 3 June 2026

Available online 3 June 2026

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