

00373

Influence of antimony doping on tin oxide nanoparticles for high current density electrochemical reduction of CO₂ to formate

C. Exploring emerging photo and electrochemical systems for CO₂ conversion to fuels and chemicals (II)

Digvijay Ghogare^{1, 2}, Sander Stulens^{1, 3}, Dries de Sloovere^{1, 3}, Deepak Pant², An Hardy^{1, 3}, Marlies K. Van Bael^{1, 3}

¹Institute for Materials Research (imo-imomec), DESINe Group, Hasselt University, Agoralaan Building D, Diepenbeek 3590 - Diepenbeek (Belgium),

²Electrochemistry Excellence Centre, Materials & Chemistry Unit, Flemish Institute for Technological Research (VITO), Boeretang 200, Mol 2400 - Mol (Belgium), ³EnergyVille, Thor Park 8320, 3600 Genk - Genk (Belgium)

Abstract

Electrochemical CO₂ reduction reaction (CO₂RR), when coupled with renewable electricity sources, offers a sustainable approach to producing chemicals while mitigating environmental challenges caused by CO₂ emissions. Electrochemical CO₂ reduction to formate is considered a techno-economically feasible pathway, with tin (Sn)-based electrocatalysts such as tin oxide (SnO₂) known to exhibit high selectivity toward formate. However, achieving high current density simultaneously with selective formate production remains challenging with these electrocatalysts due to high overpotential barriers. Thus, highly conductive electrocatalysts are paramount for efficient CO₂ reduction as the rate of electron transfer to CO₂ becomes crucial during CO₂RR. Herein, we propose highly conductive antimony-doped tin oxide (ATO) nanoparticles (NPs) for high current density CO₂ electroreduction. Monodisperse ATO NPs with controlled Sb content (1–10%) and particle sizes within approximate range from 10–30 nm were synthesized via colloidal hydrothermal treatment of Sn(IV) and Sb(III) in an aqueous alkaline solution, capped with the

cationic $\text{N}(\text{CH}_3)_4^+$ ligand. X-ray diffraction analysis of the ATO nanoparticles showed reflections characteristic of rutile tetragonal SnO_2 , with peak broadening upon Sb doping, indicating successful incorporation of Sb and a decrease in crystallite size. Increasing Sb doping in SnO_2 led to a reduction in NP size, thereby resulting in an increased electrochemical active surface area (ECSA), with 10% ATO NPs demonstrating up to a ca. 3-fold increase in double layered capacitance compared to undoped SnO_2 NPs. Initial electrocatalyst screening in H-cells revealed that ATO NPs exhibit a reduced onset potential and higher overall current density compared to undoped SnO_2 NPs. Specifically, the best-performing 4% ATO NPs remarkably reduced the overpotential by 150 mV at a current density of 10 mA/cm^2 compared to SnO_2 NPs. High current density at lower overpotentials was observed at optimal 2–6% Sb doping, attributed to reduced charge transfer resistance in ATO NPs, as confirmed by electrochemical impedance spectroscopy. Beyond optimal Sb doping (>6%), overall current density decreases, suggesting that the enhanced activity at optimal doping arises from a combination of improved intrinsic conductivity and reduced particle size. These findings highlight the potential of ATO NPs as promising electrocatalyst candidates for efficient and selective formate production at higher current densities.