RESEARCH ARTICLE

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Facile Synthesis of Cu_xS Electrocatalysts for CO_2 Conversion into Formate and Study of Relations Between Cu and S with the Selectivity

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The conversion of CO_2 into formate ($HCOO^-$), a techno-economically feasible product, can be achieved using earth-abundant Cu_xS electrocatalysts, but questions remain regarding how catalyst structure, composition, and reaction environment influence product selectivity. A novel synthesis method based on electrodeposition of Cu foam and its subsequent sulfidation via immersion in sulfur saturated toluene solution resulted in Cu_xS foams. Catalytic activity studies found that $HCOO^-$ selectivity is dependent on electrochemical activation at higher overpotentials. To understand the effects of activation, determine the active forms of the catalysts, and identify the role of sulfur, the electrodes are carefully characterized as well as gaseous and sulfur dissolved in electrolyte. This included study of the effects of intentional addition of solution sulfur species, identification of the sulfur loss, determination of the electrode composition and relating sulfur speciation to observed product selectivity. It is found that residual sulfur stabilizes Cu^+ during electrolysis at potentials favoring $HCOO^-$ production, in contrast to pristine Cu that undergoes complete reduction and shows poor $HCOO^-$ selectivity. Sulfur in both the catalyst and dissolved in electrolyte are of dynamic nature, and surface residues of SO_4^{2-} species are identified in all activated catalysts which correspond with enhanced $HCOO^-$ production.

1. Introduction

The emission of the greenhouse gas CO_2 in the atmosphere is continuously increasing together with the energy demand that is still majorly derived from fossil fuels, caused by the development of the global society since the start of the industrial revolution.[1,2] Significant long-term measures are already taken in the past decades to mitigate the CO_2 emissions via decreasing the dependence from fossil fuels energy production,[3,4] however more immediate actions are necessary. A core component of a carbon-neutral economy will be efficient renewable energy driven CO_2 capture and its conversion into valuable products for use as fuels and chemicals in the existing industry, substituting fossil-derived chemicals.[3,4] The electrochemical conversion of CO_2 (CO_2EC) is a promising approach for CO_2 recycling into value-added products,[4] and among the wide range of possible products, to date the 2 e^- CO_2EC

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