



Bulk pH contribution to CO/HCOO[−] production from CO₂ on oxygen-evacuated Cu₂O electrocatalyst

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ARTICLE INFO

Article history:

Received 22 July 2016

Received in revised form

11 September 2016

Accepted 17 September 2016

Available online 22 September 2016

Keywords:

CO₂ reduction

Bulk pH effect

Local pH effect

Product selectivity

Cu₂O catalyst

ABSTRACT

Controlling product selectivity is regarded as one of the main barriers in the application of Cu-based electrodes to electrochemical CO₂ reduction and hence significant studies on experimental factors to improve the selectivity towards desired products. In particular, two pH parameters appear to be important in controlling product selectivity of the CO₂ reduction process. We study how both bulk and local pH conditions affect product distributions during CO₂ reduction on oxygen-evacuated Cu₂O electrode. In contrast with previous studies of local pH effect on CO₂ reduction using metallic Cu, our results suggest that not always is the preferential production of C₂ compounds (C₂H₄ + C₂H₆) achieved by high local pH condition irrespective of catalyst materials, but rather bulk pH condition could contribute to ability to control product selectivity. It is finally demonstrated that the bulk pH effect, often underestimated but related to carbonate speciation, is associated with the direct reduction of HCO₃[−] to HCOO[−].

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1. Introduction

Increased interest in environmental remediation and alternative energy resources has led to intensive research into CO₂ conversion processes because such an approach can mitigate greenhouse gas emissions while simultaneously storing energy through chemical synthesis [1–3]. Among various conversion methods developed to date, the electrochemical reduction of CO₂ to value-added organic products is attracting considerable attention because of its simple system configuration and mild operating conditions [3,4]. The type of products mainly depends on the catalyst metal (e.g. Pb, Sn, Ag, Au or Cu) [5–9]. In particular, Cu has been extensively studied because various hydrocarbons such as methane (CH₄), ethylene (C₂H₄) and ethane (C₂H₆) can be uniquely synthesised on Cu-based electrodes; in contrast, reaction products on other metals are primarily limited to carbon monoxide (CO) and formate (HCOO[−]) [1,2,10–13]. Although many researchers have contributed to the development of Cu and Cu-based electrodes for CO₂ reduction, their catalytic performance remains unsatisfactory.

The ability to control product selectivity towards the desired organic compound is one of the main barriers in the application

of Cu-based electrodes to CO₂ reduction. Several experimental parameters such as CO₂ pressure, nature of electrolyte ions and electrolyte pH have been demonstrated to be critical factors that affect product selectivity [14–16]. Recent experimental and computational studies have reported that relatively higher local pH can lead to the preferential formation of C₂H₄ over CH₄ via a CO dimerization pathway [17,18]. Such interesting phenomena have driven many researchers to investigate the effects of local pH rather than the possible effects of bulk pH on product selectivity. An increase in local pH is due to the generation of OH[−] via the hydrogen evolution reaction and CO₂ electroreduction; moreover, an increase in local pH can be controlled by buffer strength depending on electrolyte concentration [19]. This approach has been recently studied using Cu nanoparticles obtained from the reduction of cuprous oxide (Cu₂O) and using mechanically polished Cu foil [20,21]. The reports demonstrated that local pH, in addition to the intrinsic catalytic properties of electrodes, appears to be critical for selective C₂H₄ production.

With regard to product selectivity towards CO₂ reduction on various electrodes, bulk pH can also play an important role by determining carbonate equilibria among carbon dioxide (CO₂), bicarbonate (HCO₃[−]) and carbonate (CO₃^{2−}) species [22]. Since the beginning of CO₂ reduction studies, an electrolytic process has typically been performed under neutral or near-neutral bulk pH conditions to prevent the hydrogen evolution reaction that is easily activated under acidic condition. Among the carbonate species,

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