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journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)Bulk pH contribution to CO/HCOO<sup>−</sup> production from CO<sub>2</sub> on oxygen-evacuated Cu<sub>2</sub>O electrocatalystSeunghwa Lee<sup>a</sup>, Sujik Hong<sup>a</sup>, Jaeyoung Lee<sup>a,b,\*</sup><sup>a</sup> Electrochemical Reaction and Technology Laboratory (ERTL), School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), South Korea<sup>b</sup> Ertl Center for Electrochemistry and Catalysis, RISE-CHESS, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea

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## ABSTRACT

Controlling product selectivity is regarded as one of the main barriers in the application of Cu-based electrodes to electrochemical CO<sub>2</sub> 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 CO<sub>2</sub> reduction process. We study how both bulk and local pH conditions affect product distributions during CO<sub>2</sub> reduction on oxygen-evacuated Cu<sub>2</sub>O electrode. In contrast with previous studies of local pH effect on CO<sub>2</sub> reduction using metallic Cu, our results suggest that not always is the preferential production of C<sub>2</sub> compounds (C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>) 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 HCO<sub>3</sub><sup>−</sup> to HCOO<sup>−</sup>.

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## 1. Introduction

Increased interest in environmental remediation and alternative energy resources has led to intensive research into CO<sub>2</sub> 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 CO<sub>2</sub> 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 (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>) 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<sup>−</sup>) [1,2,10–13]. Although many researchers have contributed to the development of Cu and Cu-based electrodes for CO<sub>2</sub> 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 CO<sub>2</sub> reduction. Several experimental parameters such as CO<sub>2</sub> 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 C<sub>2</sub>H<sub>4</sub> over CH<sub>4</sub> 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<sup>−</sup> via the hydrogen evolution reaction and CO<sub>2</sub> 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 (Cu<sub>2</sub>O) 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 C<sub>2</sub>H<sub>4</sub> production.

With regard to product selectivity towards CO<sub>2</sub> reduction on various electrodes, bulk pH can also play an important role by determining carbonate equilibria among carbon dioxide (CO<sub>2</sub>), bicarbonate (HCO<sub>3</sub><sup>−</sup>) and carbonate (CO<sub>3</sub><sup>2−</sup>) species [22]. Since the beginning of CO<sub>2</sub> 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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