

Understanding the Roles of Hydroxide in CO₂ Electroreduction on a Cu Electrode for Achieving Variable Selectivity

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Hydroxide-derived copper (OH/Cu) electrodes exhibit excellent performance for the electrocatalytic CO₂ reduction reaction (CO₂RR). However, the role of hydroxide (OH) in CO₂RR remains controversial and the origin of the selectivity enhancement emerging on OH/Cu has not been fully understood. The center of the debate has been what product selectivity can be improved by OH formation, not intrinsic natures of the electrode surface. Thus, in this study, we evaluated the influence of the OH on CO₂RR by preparing Cu electrode with different amount of surface OH.

We synthesized three electrodes characterized by significantly different OH amounts: small (**Cu foil**), moderate (**M-OH/Cu**), and large amounts of OH (**L-OH/Cu**), in which the **M-OH/Cu** and **L-OH/Cu** were prepared by electrooxidation method followed by reduction with different degree. The CO₂RR performance was evaluated at current densities from −10 to −80 mA cm^{−2} using a gastight H-type glass cell.

Scanning electron microscopy (SEM) suggested that the pristine **Cu foil** has a relatively flat surface, whereas needle-like nanostructures are formed on the surface of the **M-OH/Cu** and **L-OH/Cu**. The OH amount on the Cu surface was characterized by electroadsorption technique, which is the first time used for OH amount evaluation.¹ The electroadsorption suggested that the amount of OH and the OH-to-Cu⁰ ratio on **L-OH/Cu** were 4.7 times and 2.7 times, respectively, larger than those on **M-OH/Cu**, whereas obvious adsorption was not observed on **Cu foil**. Fig. 1 presents Faradaic efficiencies (FE) for CO₂RR on prepared Cu electrodes. **Cu foil** showed a high CH₄ selectivity with an average CH₄ FE of 67% and **M-OH/Cu** provided a C₂₊ FE of 71%. **L-OH/Cu** having large OH amount exhibited a lower C₂₊ FE (54%) than **M-OH/Cu** (71%) but the ratio of C₂₊-to-CH₄ on **L-OH/Cu** is higher than 355 (Fig. 1). Density functional theory calculation conducted by Prof. A. Staykov represented that the OH coverage modifies the work function (WF) of Cu surfaces (Fig. 2) and the reaction energetics for the formation of *CHO and *COCHO, which are deeply related to the variable selectivity observed on the Cu electrodes.¹

1) M. Sun, A. Staykov, M. Yamauchi, *ACS Catalysis* **2022**, *12* (24), 14856.

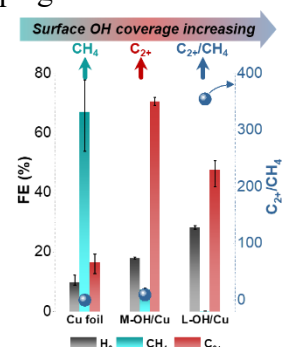


Fig.1. Faradaic efficiency (FE) and the ratio of C₂₊-to-CH₄ in CO₂RR.

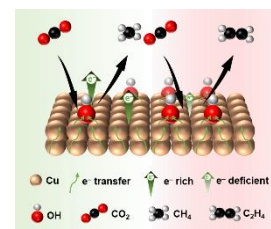


Fig.2. Roles of OH with low (left) and high coverage (right) on Cu electrodes.