Ultrasonication-assisted Preparation of Oxygen-vacancy-rich CuO/CF Monolith Electrode: BoostingSelective Oxidation of Alcohols to Value-added Chemicals

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Introduction

Low-molecular-weight aliphatic alcohols like methanol and ethanol are good fuels for direct alkaline alcohol fuel cells (DAAFCs). Selective oxidation of these alcohols to carboxylate offers both decent power output and value-added chemicals, which is environmentally and economically more desirable than their full oxidation to CO_2. Herein, we report the in-situ fabrication of oxygen-vacancies-rich CuO nanosheets on copper foam (CF) via a simple ultrasonication-assisted acid-etched method. The CuO/CF monolith electrode enables an efficient and selective electrooxidation of ethanol (274 mA cm^{-2} at 1.82 V *vs*. RHE) and methanol (247 mA cm^{-2} at 1.82 V *vs*. RHE) into value-added acetate and formate with ~100% selectivity. First principle calculations reveal that oxygen vacancies in CuO nanosheets efficiently regulate the surface chemical and electronic structure, provide abundant active sites, and enhance charge transfer that facilitates the adsorption of reactant molecules on the catalyst surface. The selective oxidation of alcohols to value-added chemicals in DAAFCs without CO_2 emission is highly favorable to power electrical equipment with decent current densities. The generation of value-added chemicals will sufficiently lower the overall cost of DAAFCs.

Characterization, Results and discussion

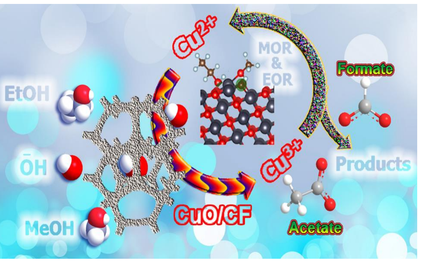

Figure 1. A simple ultrasonication-assisted acid-etched method enhance the electrocatalysis performance of inert copper foam: greatly lowered the charge transfer, increase the surface area and boosted redox nature, along with the distinct porous nanosheets structure and copious oxygen vacancies, provide the CuO/CF outstanding electrocatalytic efficiency against alcohols and carbon monoxide oxidation

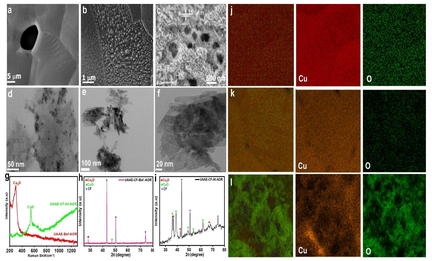

Figure 2. a) SEM images of the B-CF b) SEM images of UAAE-CF before the AOR stability test. c) SEM images of UAAE-CF after the AOR stability test. d) TEM images of UAAE-CF before the AOR stability test. e,f) images of UAAE-CF after the AOR stability test g) Raman spectra of B-CF and UAAE-CF before and after the MOR stability test. h) XRD patterns of B-CF and UAAE-CF. i) XRD patterns of UAAE-CF before and after the MOR stability test. j) Element mapping of B-CF k) Element mapping of UAAE-CF before AOR stability test. l) Element mapping of UAAE-C after AOR stability test

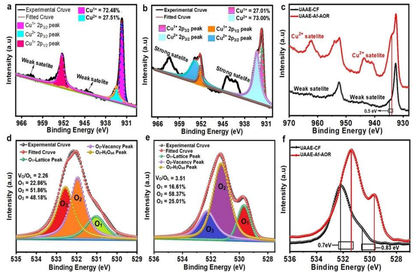

Figure 3. Core level of XPS spectrum of UAAE-CF. a) Cu 2p spectrum of UAAE-CF before AOR stability test. b) Cu 2p spectrum of UAAE-CF after AOR stability test. c) Comparison of Cu 2p spectra of UAAE-CF before and after AOR stability test, d) O 1s spectrum of UAAE-CF before AOR stability test. e) O 1s spectrum of UAAE-CF after AOR stability test. f) Comparison of O 1s spectra of UAA-CF before and after the AOR stability test.

Sustainable Development Goals

This work supports the following SDGs

Goal 7: Ensure access to affordable, reliable, sustainable, and modern energy
Goal 6: Ensure availability and sustainable management of water
Goal 13: Climate safe energy and protected Ecosystem

Characterization, Results and discussion

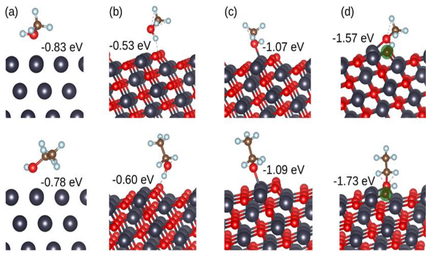

Figure 4. Ball-stick model for methanol and ethanol adsorption on (a) Cu(111), (b) pristine CuO(111) for interaction with the H atom, (c) pristine CuO(111) for interaction with the O atom, and (d) O-vacant CuO(111) for interaction with the O atom. The position of the O vacancy is highlighted by green color. The binding energy is given in each case. The blue, gray, red, and black spheres represent the H, C, O, and Cu atoms, respectively.

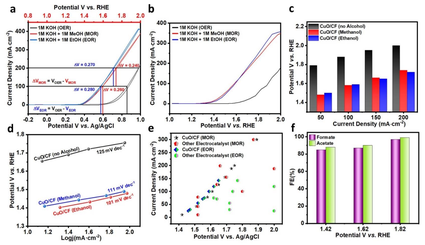

Figure 5. a) CV curves collected over the as-prepared CuO/CF in nitrogen-purged 1M KOH with and without 1M ethanol or methanol. b) SCV curves collected over the as-prepared CuO/CF in nitrogen-purged 1M KOH with and without 1M ethanol or methanol c) Summaries of anodic potentials at 50, 100, 150, and 200 mA·cm^{-2} for the as-prepared CuO/CF in 1M KOH with and without 1M ethanol (EtOH) or methanol (MeOH). d) Comparison of EOR, MOR, and OER Tafel plots obtained from their respective SCVSs collected over the as-prepared CuO/CF. e) Comparison with recently reported non-noble metal-based MOR and EOR catalysts, star data represents activity of the as-prepared CuO/CF f) Summaries of Faraday's efficiencies for acetate and formate.

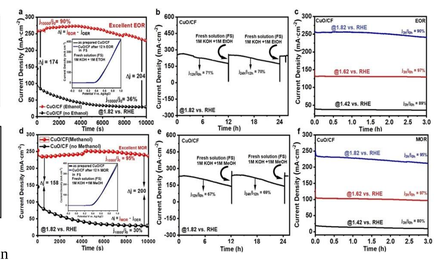

Figure 6. Long-term stability test over the as-prepared CuO/CF at 1.82 V *vs*. RHE in nitrogen-purged 1M KOH with and without 1M EtOH or MeOH. e.) Chronoamperometric cyclic stability test of the as-prepared CuO/CF for two consecutive cycles at 1.82 V *vs*. RHE in nitrogen-purged 1M KOH with 1M EtOH or MeOH. c,f) Chronoamperometry test for 3 hours at different potentials in nitrogen-purged 1M KOH containing 1M EtOH or MeOH.

Conclusion

In conclusion, the obtained Vo-rich ultrathin CuO/CF nanosheets exhibit an outstanding activity for the selective oxidation of ethanol and methanol into value-added acetate and formate with a reasonably higher Faraday efficiencies ~ 99% at an applied potential of 1.82 V *vs*. RHE. DFT calculation reveals that Vo enhances charge transfer and efficiently tunes the electronic structure of the surface, facilitating the adsorption of reactant molecules on the surface of as-prepared CuO/CF, which results in exceptionally boosted MOR and EOR kinetics. The outstanding CO tolerance ability as well as the in-situ grown active sites bestow the as-prepared CuO/CF with significantly enhanced stability for an exceptionally long time. So, this study not only signifies the vital role of Vo in enhancing the AOR kinetics at the atomic level but also encourages exploring other transition metal-based catalysts for stable and selective oxidation of alcohols. Meanwhile, adding ultrasound energy with acid-etching is a simple and promising path for the large-scale fabrication of other transition metal-based oxide/hydroxide catalysts for DAAFCs.

Acknowledgment

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References

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