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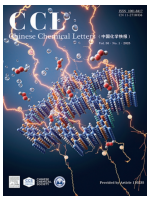

Editorial

Topologically close-packed intermetallic alloy electrocatalysts for CO_2 reduction towards high value-added multi-carbon chemicals

The continuous combustion of unsustainable carbon-based fossil fuels has dramatically accelerated the increase in carbon dioxide (CO_2) concentration in the atmosphere (from approximately 278.3 ppm in 1750 to 417.9 ppm in 2023), which would exacerbate environmental problems such as greenhouse effect [1]. The effective electrosynthesis of high value-added multi-carbon (C_{2+}) chemicals (*e.g.*, ethanol, ethylene) from CO_2 reduction reaction (CO_2RR) is a promising strategy to mitigate these environmental issues mentioned above but remains highly challenging due to the competition of hydrogen evolution reaction (HER) and low selectivity of target products. Cu-based catalysts have been widely studied because of the optimal adsorption of *CO intermediates and thus promoting C–C coupling. However, the low selectivity, deficient Faraday efficiency (FE) and unsatisfactory partial current densities of target products still cannot meet industrial requirements.

In order to enhance the selectivity and activity of Cu-based catalysts to C_{2+} chemicals, heterogeneous elements have been introduced to construct bimetallic alloys with redistributed electronic structures and optimized binding energies of intermediates. Compared to common disordered alloys, Cu-based structurally ordered intermetallic alloys have been reported to exhibit superior selectivity and activity as well as stability in CO_2RR towards C_{2+} products (*e.g.*, acetate) owing to the unique electronic structures originating from ordered atomic arrangement and more negative formation energy [2]. Therefore, constructing intermetallic alloy *via* phase engineering may be a promising strategy to achieve efficient and stable CO_2RR towards C_{2+} products. Currently, most of researches focus on developing electrocatalysts based on conventional body-centered cubic (*e.g.*, PdCu, NiCu with B2 phase) and cubic close-packed ordered structures (*e.g.*, Cu_3Pt, Cu_3Au with $L1_2$ phase), there is still a lot of room for performance improvement [3]. Since catalytic activity/stability is closely related to atomic distribution, bond strength, coordination environments, electronic structures, *etc.*, which are determined by phase structures, it is significant to investigate and rationally design innovative catalysts with unconventional crystal phases. Among various unconventional phases, topological close-packed Frank-Kasper phases (A15, C15, C14, σ, *etc.*) with higher coordination numbers (*e.g.*, 8 for body-centered cubic structures, 12 for cubic close-packed structures and 12, 14, 15, 16 for topological close-packed structures), lager packing densities (>0.74), unique electronic structures, larger corrosion energy barriers (*e.g.*, 0.84, 1.07, and 2.77 eV for $L1_2$-Pt_3Ni, $L1_0$-PtNi, and C14-Fe_2Ni, respectively) and more negative formation energy (*e.g.*, −0.566, −1.022, and −1.084 eV for $L1_0$-PtZn, $D0_{24}$-Pt_3Zr, and C15-Pt_2Y, respectively) may exhibit promoted activity and stability towards CO_2RR to C_{2+} chemicals [4].

Recently, Prof. Gengfeng Zheng *et al.* proposed a phase engineering strategy to develop the topological close-packed C15 Cu_2Mg intermetallic alloy with high-density ordered active Cu sites, which achieved high $FE_{C_2H_5OH}$, current density and stability in CO_2RR simultaneously [5]. The C15 Cu_2Mg possesses a space group of Fd3m and lattice spacing of 0.405 nm corresponding to the (111) planes, differing from the disordered cubic close-packed solid solution Mg-doped Cu ($Mg_{0.1}Cu$, Fm3m space group, 0.219 nm lattice spacing corresponding to the (111) planes) and pure Cu (Fm3m space group, 0.21 nm lattice spacing corresponding to the (111) planes) (Figs. 1a and b). Additionally, two types of Mg atoms are embraced by Cu_6 and Cu_3 rings in C15 Cu_2Mg, which allows to expose abundant Cu edges and provide more active sites for CO_2RR. Compared with pure Cu and disordered $Mg_{0.1}Cu$, due to the difference in electronegativity and phase structure, more electrons can transfer from Mg to Cu in C15 Cu_2Mg, thereby leading to a negative shift of d-band center of Cu and optimization of electronic distribution (Fig. 1c). The negative shift of d-band center of Cu can reduce the energy barriers of *CO-*CO coupling, thus enhancing the selectivity of C_{2+} products. During the CO_2RR tests, the C15 Cu_2Mg catalyst exhibits much lower overpotential (only −0.84 V to achieve j_{total} of −600 mA/cm^2), much higher $FE_{C_2H_5OH}$ (76.2% ± 4.8%) and cathodic energy efficiency (42.1% ± 2.6%), far exceeding the disordered $Mg_{0.1}Cu$ (main product is CH_4 with FE_{CH_4} no >60%). Moreover, the C15 Cu_2Mg displays durable $FE_{C_2H_5OH}$ (>80%) in the j_{total} range from −200 mA/cm^2 to −600 mA/cm^2 and maintains its high $FE_{C_2H_5OH}$ (61%) after 15 h of continuous reaction at −600 mA/cm^2.

To further investigate the reaction mechanism, density functional theory (DFT) calculations were performed. The variation of energy from *CHCOH to *CHCHOH or *CCH was used as a descriptor to explore the ethanol and ethylene pathways. The C15 Cu_2Mg possesses a lower energy barrier from *CHCOH to *CHCHOH than to *CCH, thus exhibiting high selectivity for ethanol. In contrast, pure Cu and disordered $Mg_{0.1}Cu$ prefer the ethylene pathway (Fig. 1d). Furthermore, the CH_4 pathway was also researched by comparing energy difference from CO_2 to *COOH and from *CO to *CHO. The C15 Cu_2Mg displayed a higher energy barrier than its counterparts (pure Cu and disordered $Mg_{0.1}Cu$), thus showing lower FE_{CH_4}. The above experimental results and theoretical calculations verify the superior activity, selectivity and stability of C15

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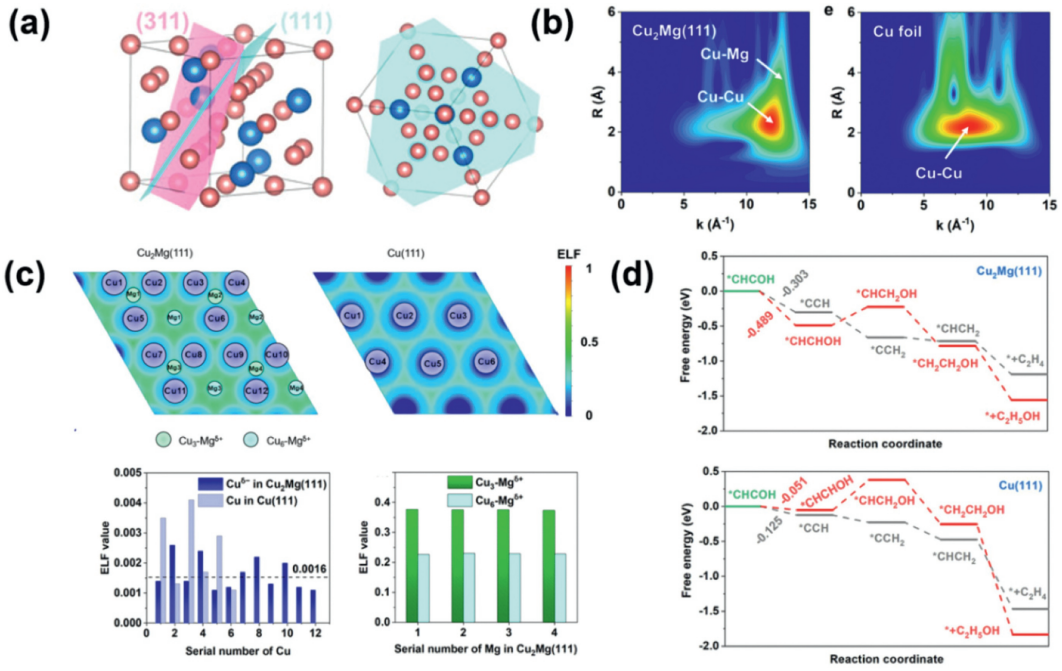

Fig. 1. (a) Schematic of C15 Cu_2Mg intermetallic compound. (b) Wavelet-transform of the k^2-weighted of Cu K-edge extended X-ray absorption fine structure (EXAFS) data of C15 Cu_2Mg and Cu foil samples. (c) Electronic localization function (ELF) and extracted ELF value of C15 Cu_2Mg and Cu model. (d) Energy diagrams of hydrogenation of *CHCOH intermediate to form ethanol and ethylene on C15 Cu_2Mg and Cu models. Reprinted with permission [5]. Copyright 2024, Wiley-VCH.

Cu_2Mg catalysts in CO_2RR towards ethanol to commercial Cu and disordered $Mg_{0.1}Cu$.

Prospectively, the performance of unconventional intermetallic alloys for CO_2RR should be further evaluated in real devices, especially in proton-exchange membranes (PEM) based devices due to their prominent thermodynamic stability and corrosion resistance. Additionally, more unconventional phases with optimal atomic distribution, coordination environments and electronic structure should be explored and applied as electrocatalysts in CO_2RR. Moreover, the correlations between crystal phases and electrocatalytic performance remain ambiguous. It is of significance to build bridges among the phase structure, electronic distribution and electrocatalytic performance *via* rationally designing and comparing catalysts with different crystal phases.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Qiyan Wu: Methodology, Investigation, Data curation, Conceptualization. **Qing Li:** Supervision, Resources, Methodology, Formal analysis, Conceptualization.

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