

## Rational Design of Intermetallic Electrocatalysts for CO Reduction via Electronic Structure Engineering

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The electrochemical reduction of CO<sub>2</sub> enables carbon-neutral fuels and chemicals to be produced directly from renewable electricity. Unfortunately, Cu is the only electrocatalyst capable of catalyzing this chemistry and it is neither active nor selective enough to enable industrial implementation.<sup>1,2</sup> It has been hypothesized that the dimerization of neighboring CO\* intermediates is the rate-determining step for multi-carbon product formation.<sup>3</sup> Thus, methods for enhancing the stability of OCCO\* relative to CO\* must be identified. However, a linear scaling relationship exists between CO\* and OCCO\* since both species bind to the electrode surface through carbon atoms. Interestingly, the stability of OCCO\* is more significantly influenced by the local electric field strength than CO\*, providing a viable route toward breaking this scaling relationship. The CO adsorption energy of transition metals depends on the energetics of their d-band, which can be systematically modified through intermetallic bonding.<sup>4</sup> The strength of the electric field present at the surface of a polarized electrode depends primarily on the difference between the applied potential and the potential of zero charge of the electrocatalyst, which shifts to more anodic potentials as the work function increases. Interestingly, Pd forms intermetallic bonds of similar strength with many post-transition metals, despite the significant differences in their work functions. Thus, we hypothesize that intermetallic alloying will enable surface reactivity (d-band) and electric field strength (work function) to be independently and systematically tuned through variation of alloy composition and post-transition metal constituent identity. Initial electronic structure measurements indicate that PdGe exhibits Cu-like d-band energetics but a significantly elevated work function, the combination of which should yield superior intrinsic activity for CO reduction. However, accurately measuring the electrocatalytic activity of intermetallic materials is challenging due to their susceptibility to segregation upon air exposure. To address this challenge, we have designed an electrochemical reactor setup that enables intermetallic alloys to be electrochemically synthesized and tested without ever breaking potential control. Validation experiments demonstrate that this reactor also exhibits superior mass transfer to other contemporary reactors utilized to investigate CO<sub>2</sub> reduction electrocatalysts. Finally, an electrochemical approach for producing PdGe near-surface intermetallic alloys has been developed based upon prolonged polarization at potential sufficient to underpotentially deposit Ge onto the Pd surface. Ge incorporated into the Pd surface using this method exhibits unusual oxidative stability in alkaline electrolytes and preliminary XPS analysis demonstrates that it exhibits significant electronic structure differences compared to bulk Ge. This irreversible Ge incorporation is hypothesized to be a result of the stabilizing effects of intermetallic bond formation and a reduction of surface energy.

## References:

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