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New alloy systems for the electrochemical conversion of CO₂ to multicarbon products

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The electrochemical reduction of aqueous CO₂ provides an attractive path for the production of fuels and bulk chemicals. To make this approach economically viable, electrode systems need to be developed that are stable, operate at low overpotential, and are produce specific. Despite a significant research effort to develop these systems only a limited number of systems based on indium or tin electrodes have come close to commercial application.¹⁻⁶ These materials reduce CO₂ by two electrons to formate with excellent selectivity, reasonable overpotential, and good stability.

In contrast to the systems noted above, the only single element electrode material reported to carry out the reduction of CO₂ to highly reduced C1 products (methanol or methane), as well as, generate carbon-carbon bonded organic products from aqueous CO₂ is copper.^{4,7}

Recently, Lewis reported that C1 and C2 products can be obtained from aqueous CO₂ electrolytes when an electrode composed of a Ni-Ga alloy supported on highly ordered pyrolytic graphite (HOPG) is used.⁸ Similarly, we have found that a Ni₃Al electrocatalyst on glassy carbon generates C1-C3 products including methanol, ethanol, acetone and propanol.⁹ The Ni₃Al system was found to be quite stable with reasonable overpotential. These reports are the first indication that non-copper based metal electrodes can be catalytic for the formation of carbon-carbon bonded products. Building on these results we have found that CO is obtained as a key intermediate in the reduction of CO₂ in these Ni based alloy systems. Support for this conclusion comes from the observation that introduction of ¹³C into the reactant mixture gives rise to ¹³C incorporated organic products.

Perhaps the most interesting outcome of this work is the observation that aqueous CO₂ can be reduced to oxalate using an appropriate alloy electrode. This appears to be the first report of oxalate from CO₂ using an aqueous electrolyte and a metal electrode. Prior reports on the electrosynthesis of oxalate have employed highly negative electrode potentials that have required the use of nonaqueous electrolytes.¹⁰ The observations reported here indicate that oxalate can be synthesized through a CO intermediate at modest potential, opening up a water-based process for the electrosynthesis of oxalate.

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