Electrochemical and Photoelectrochemical Conversion of CO_2 to C-C Coupled Products

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Electrochemical and photoelectrochemical conversion of CO_2 (EC-CO_2R and PEC-CO_2R) to chemical precursors and/or fuels is of fundamental and technological interest. If driven by renewable power sources, such a technology could slow the rate of carbon dioxide emissions into the atmosphere by replacing chemicals obtained from oil with sustainably generated alternatives. However, CO_2R is complex and challenging. Indeed, the multi-electron reduction of CO_2 to products such as ethanol (12 e^-), ethylene (12 e^-), and propanol (18 e^-) represents the most ambitious synthetic chemistry to be performed with electrocatalysis. Formation of these products involves a corresponding number of surface bound intermediates linked by proton-coupled electrons transfers, chemical steps, and interactions with the solvents. Identification of the elementary steps in these complex chemical conversion processes is obviously crucial for developing more selective catalysts.

Recent experimental work aimed at identifying selectivity-determining steps in multi-electron CO_2 reduction will be presented. In a process that was never previously predicted or observed, $C^{16}O$ reduction in $H_2{}^{18}O$ electrolyte produces oxygenate products (ethanol, acetate, propanol) containing ^{18}O which must have originated from the solvent. As a result of this discovery, previously proposed mechanisms for CO and CO_2 reduction on Cu under aqueous conditions require reexamination [1]. Electrochemical reduction of isotopically labeled $^{13}CO/^{12}CO_2$ mixtures is used to identify product-specific active sites for ethylene, ethanol and acetate, and 1-propanol. The existence of such sites implies that it should be possible to create Cu-based electrocatalysts which will be much more selective than what is available today [2]. Tandem cascade electrocatalysis has been realized using CO at the intermediate species on micropatterned Ag/Au and Cu. This approach allows tuning of the CO activity at the surface of Cu during CO_2R; increasing CO activity boosts oxygenate production at the expense of ethylene [3,4].

Coupling of selective catalysts to light absorbers enables PEC-CO_2R. Charge selective contacts can be used to direct photo-generated carriers to catalytic sites that perform CO_2 reduction in an integrated photocathode. When this concept is implemented with a Si absorber, current densities (>30 mA cm^{-2}) and photovoltages (>600 mV) similar to those of PV devices can be achieved. By coupling photocathodes to series-connected semi-transparent halide perovskite solar cells, we have demonstrated stand-alone, "no-bias," CO_2 reduction with a 1.5% conversion efficiency to hydrocarbons and oxygenates [5]. In a related, "PV+electrolyzer" approach, we have shown that that C-C coupled products such as ethylene and ethanol can be produced with solar light using Cu-based electrocatalysts at an overall efficiency of over 5%, which is ca. 10x the efficiency of natural photosynthesis [6].

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Biography

Joel W. Ager III is a Staff Scientist in the Materials Sciences Division of Lawrence Berkeley National Laboratory and an Adjunct Full Professor in the Materials Science and Engineering Department, UC Berkeley. He is a Principal Investigator in the Electronic Materials Program and in the Joint Center for Artificial Photosynthesis (JCAP) at LBNL and in the Berkeley Educational Alliance for Research in Singapore (BEARS) where he serves as Co-Lead PI of the eCO_2EP project with Cambridge University. He graduated from Harvard College in 1982 with an A.B in Chemistry and from the University of Colorado in 1986 with a PhD in Chemical Physics. After a post-doctoral fellowship at the University of Heidelberg, he joined Lawrence Berkeley National Laboratory in 1989. His research interests include the discovery of new photoelectrochemical and electrochemical catalysts for solar to chemical energy conversion, fundamental electronic and transport properties of semiconducting materials, and the development of new types of transparent conductors. Professor Ager is a frequent invited speaker at international conferences and has published over 300 papers in refereed journals. His work is highly cited, with over 30,000 citations and an h-index of 87 (Google Scholar).