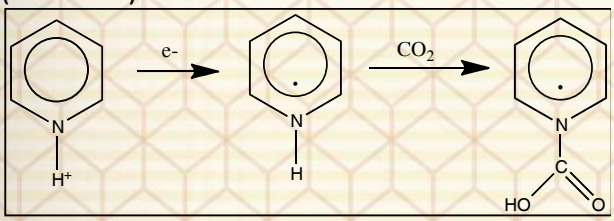
MATERIALS CHEMISTRY SEMINAR

The visible light driven photoelectrochemical production of energy rich liquids from carbon dioxide is appealing, both in terms of climate change issues and new sustainable energy resources. To this end, we have proposed the electrosynthesis of alcohols from CO_2 as an energy conversion and storage approach, which recycles carbon that would otherwise end up as an atmospheric greenhouse gas. The thermodynamically uphill nature of this reaction coupled with the large activation energy associated with this multielectron, multiproton reduction makes conversion of CO_2 problematic. Alternative energy schemes for this conversion only become possible if the typically observed system activation overpotentials (≤1V) can be significantly reduced. Thus, key to a successful process is the development of a stable catalytic system.

We have discovered the pridinium catalyzed electrochemical reduction of CO_2 to methanol at illuminated p-GaP photocathodes, where we find that faradaic efficiencies are <95%, when run at several hundred millivolts of underpotential. The observed reduction involves a mediated charge transfer process, which is initiated by the one electron reduction of pyridinium leading to the formation of formic acid through the reduction of a carbamate intermediate (***Scheme I***).



Scheme I: Initial pyridal reduction to form a radical carbamate.

Professor Andrew Bocarsly

Princeton University

"Designing Interfaces to Achieve the Light-Driven Electrochemical Conversion of CO_2 to Alcohols: Materials and Interfaces that Generate Efficient Reverse Combustion"

Thursday,
May 3, 2012
12:15 p.m.
Seminar Hall