

# Tuesday Afternoon, October 29, 2013

## Energy Frontiers Focus Topic

Room: 101 A - Session EN+AS+PS-TuA

## Water Splitting and Carbon Dioxide Conversion

Moderator: D. Lutterman, Oak Ridge National Laboratory

2:00pm EN+AS+PS-TuA1 Turning CO<sub>2</sub> into Liquid Fuel, *M. Kanan*, Stanford University **INVITED**

The longstanding reliance on fossil fuels as the principal energy source for society has boosted the atmospheric CO<sub>2</sub> concentration to a level that is unprecedented in modern geological history. Since the use of carbon-containing fuels is entrenched in society, controlling the atmospheric CO<sub>2</sub> concentration may ultimately require recycling CO<sub>2</sub> into liquid fuels and commodity chemicals using renewable energy inputs. Arguably the greatest challenge for this vision is to develop efficient CO<sub>2</sub> reduction catalysts. This talk will describe our development of "oxide-derived" metal nanoparticles as electroreduction catalysts. Oxide-derived metal nanoparticles are prepared by electrochemically reducing metal oxide precursors. This procedure results in highly strained metal nanocrystals, as determined by grazing incidence synchrotron x-ray diffraction. I will describe examples of these catalysts that electrochemically reduce CO<sub>2</sub> to CO with exceptional energetic efficiency as well as a catalyst that selectively reduces CO to two-carbon oxygenates. The catalysts operate in water at ambient temperature and pressure and are remarkably robust. The reduction mechanisms will be discussed based on electrokinetic measurements. Metal oxide reduction represents a "top-down" approach to metal nanoparticle synthesis that can result in unique surface structures for catalysis.

2:40pm EN+AS+PS-TuA3 Efficient Conversion of CO<sub>2</sub> to Fuels using Inexpensive Cathode Materials, *J. Rosenthal, J. DiMeglio, J. Medina-Ramos*, University of Delaware

The wide-scale implementation of solar and other renewable sources of electricity requires improved means for energy storage. An intriguing strategy in this regard is the reduction of CO<sub>2</sub> to CO, which generates an energy rich commodity chemical that can be coupled to liquid fuel production using Fischer-Tropsch methods. To this end, we have developed an inexpensive Bismuth Carbon Monoxide Evolving Catalyst (Bi-CMEC) that can be formed upon cathodic polarization of an inexpensive carbon or metallic electrode in acidic solutions containing Bi<sup>3+</sup> ions. This catalyst can be used in conjunction with ionic liquids and other weak organic acids to effect the electrocatalytic conversion of CO<sub>2</sub> to CO with appreciable current density at low overpotential. The systems to be described are selective for production of CO, operating with very high Faradaic efficiency for conversion of CO<sub>2</sub> to this valuable product. As such the ability of this electrocatalyst system to drive production of CO from carbon dioxide is on par with that which has historically only been observed using expensive silver and gold cathodes.

4:00pm EN+AS+PS-TuA7 Power Curves of the Artificial Leaf, *D. Nocera*, Massachusetts Institute of Technology **INVITED**

An artificial leaf can perform direct solar-to-fuels conversion via water splitting. The artificial leaf is a buried junction, in which the rectifying junctions are protected from solution or "buried". Whereas water splitting catalysis is combined with charge separation, current rectification, and photovoltage generation in a solution junction PEC device, in a buried junction device, catalysis is separated from the current rectification, charge separation, and photovoltage generation, which occur at the internal junction. The buried junction photoelectrochemical (BJ-PEC) cell is free from many of the design limitations of a traditional solution junction photoelectrochemical (SJ-PEC) cell. First and foremost, in a SJ-PEC, water splitting catalysis is combined with charge separation, current rectification, and photovoltage generation. Accordingly, most candidate materials are based on metal-oxides. Decades of research have shown that it is extremely difficult to produce a competent photovoltaic (PV) material that at the same time is capable of facilitating the demanding four-electron, four-proton chemistry of water splitting. Second, in a SJ-PEC, the band edges of the flatband potentials of the semiconductor must straddle the thermodynamic potentials of OER and HER under the conditions of operation. These foregoing limitations are circumvented in a buried junction device. In a BJ-PEC, water-splitting catalysis is separated from the internal junction where current rectification, charge separation, and photovoltage generation occur. Accordingly, the OER and HER catalysts may be optimized independently from the PV device such that the maximum power characteristics of the PV and catalyst may be matched independently. Of equal significance, in a BJ-PEC, the potential drop across the outer Helmholtz layer will adjust

automatically to move the Fermi levels to energetic positions that allow the water splitting reaction to proceed. For this reason, the photovoltages produced at buried junctions need not be fixed relative to a specific material flatband potential and consequently there is no requirement for the flatband potentials of the semiconductors to straddle the thermodynamic potentials of the OER and HER. There simply has to be sufficient potential generated by the PV device to enable water splitting. This talk will focus on the analysis of Tafel and photovoltaic power curves. The presented analysis highlights the importance of matching the electrochemical load of the water splitting catalyst to the onset of maximum current of the PV component, drawing a clear link between the kinetic profile of the water splitting catalyst and the SFE of devices such as the artificial leaf.

4:40pm EN+AS+PS-TuA9 Transient Plasma for Green Technologies: Reduced Emissions, Greenhouse Gas Reduction, and Improved Combustion Efficiencies, *M. Gundersen*, University of Southern California **INVITED**

Transient plasma, that is, plasma during a formative, short time period prior to equilibration of a plasma electron energy distribution, is studied for applications to the fundamental improvement of fuel-burning engine efficiency in fuel-air mixtures, and in exhaust streams. This transient plasma requires operation with short (<100ns) pulsed high voltage, and typically requires only small pulse energy (10mJ to <1J). Transient plasma has been demonstrated shows promise for improving engine efficiency through improved combustion efficiency, and has been demonstrated to be efficient for NO<sub>x</sub> conversion. Results for studies of engine types including internal combustion engines, pulse detonation engines, will be discussed, and ideas for future directions will be presented. This work has been supported by the AFOSR, ARO, and the TCC Corp.

5:20pm EN+AS+PS-TuA11 Activation of CO<sub>2</sub> using Non-equilibrium Plasma: Mechanisms and Power Efficiency, *M.C.M. van de Sanden, A.P.H. Goede, M. Graswinkel, W. Bongers*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands, *F. Brehmer, S. Welzel, R. Engeln*, Eindhoven University of Technology, Netherlands **INVITED**

Sustainable energy generation by means of, either photovoltaic conversion, concentrated solar power or wind, will certainly form a significant part of the energy mix in 2025. The intermittency as well as the temporal variation and the regional spread of this energy source, however, requires a means to store and transport energy on a large scale. In this presentation the means of storage will be addressed of sustainable energy transformed into fuels and the prominent role plasma science and technology can play in this great challenge.

The storage of sustainable energy in these so called solar fuels, e.g. hydrocarbons and alcohols, by means of *artificial photosynthesis* from the feedstock CO<sub>2</sub> and H<sub>2</sub>O, will enable a CO<sub>2</sub> neutral power generation infrastructure, which is close to the present infrastructure based on fossil fuels. The challenge will be to achieve *power efficient* dissociation of CO<sub>2</sub> or H<sub>2</sub>O or both, after which traditional chemical conversion (Fischer-Tropsch, Sabatier, etc.) towards fuels can take place.

Most of the research efforts are directed at the splitting of water in hydrogen and oxygen. However, no efficient catalytic or traditional chemical alternative is yet available. A promising route is the dissociation or activation of CO<sub>2</sub> by means of plasma, possible combined with catalysis. Taking advantage of non-equilibrium plasma conditions to reach optimal energy efficiency the FOM institute DIFFER has started its solar fuels program at the beginning of 2012 focusing on CO<sub>2</sub> plasma dissociation into CO and O<sub>2</sub>. The plasma is generated in a low loss microwave cavity with microwave powers up to 10 kW using a supersonic expansion to quench the plasma and prevent vibrational-translational relaxation losses. New ideas on the design of the facility and results on power efficient conversion (more than 50%) of large CO<sub>2</sub> flows (up to 75 standard liter per minute with 11% conversion) as determined from calibrated mass spectrometry measurements at low gas temperatures will be presented.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Bongers, W.: EN+AS+PS-TuA11, 1  
Brehmer, F.: EN+AS+PS-TuA11, 1

## — D —

DiMeglio, J.: EN+AS+PS-TuA3, 1

## — E —

Engeln, R.: EN+AS+PS-TuA11, 1

## — G —

Goede, A.P.H.: EN+AS+PS-TuA11, 1  
Graswinkel, M.: EN+AS+PS-TuA11, 1  
Gundersen, M.: EN+AS+PS-TuA9, 1

## — K —

Kanan, M.: EN+AS+PS-TuA1, 1

## — M —

Medina-Ramos, J.: EN+AS+PS-TuA3, 1

## — N —

Nocera, D.: EN+AS+PS-TuA7, 1

## — R —

Rosenthal, J.: EN+AS+PS-TuA3, 1

## — V —

van de Sanden, M.C.M.: EN+AS+PS-TuA11, 1

## — W —

Welzel, S.: EN+AS+PS-TuA11, 1