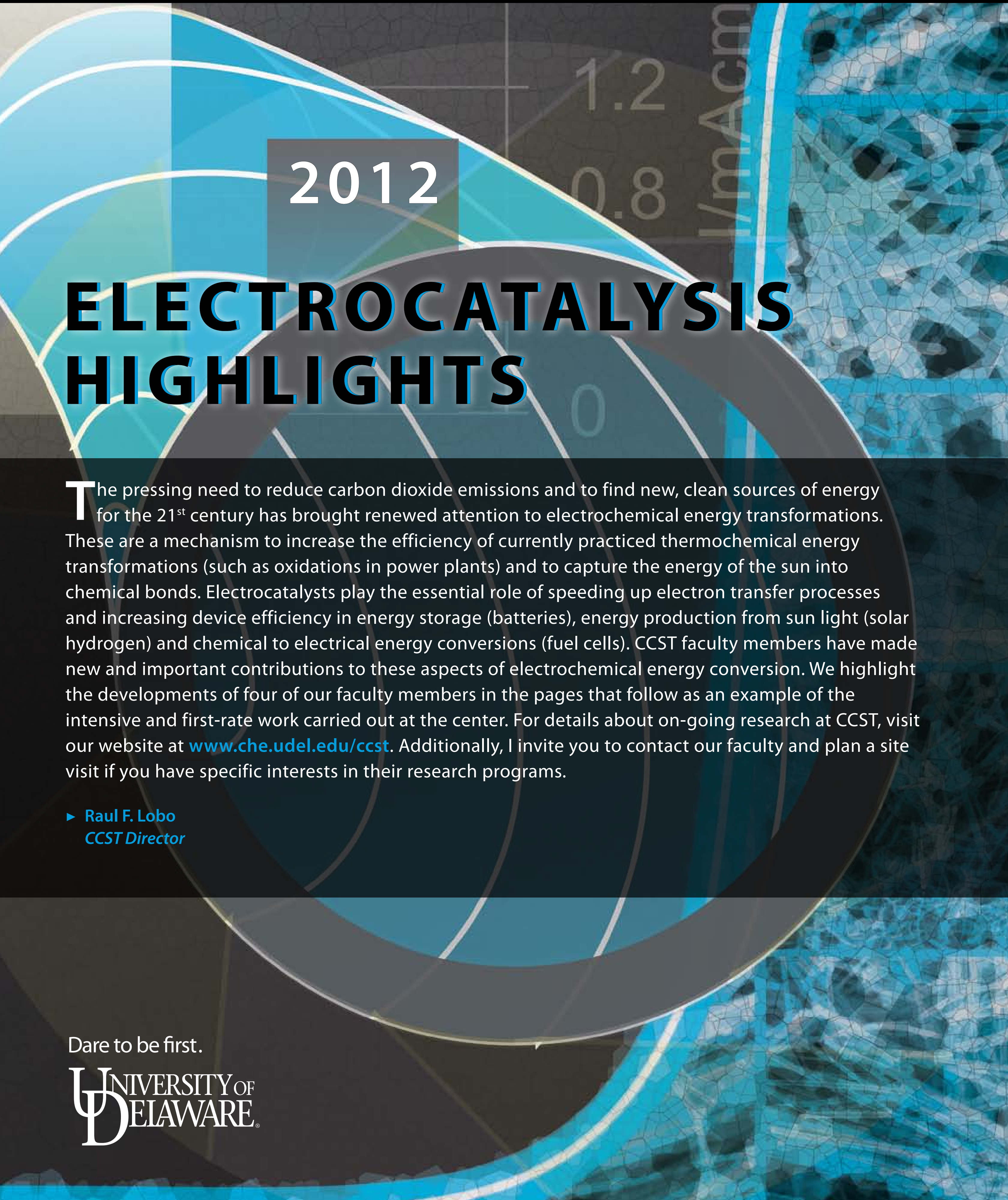


2012

ELECTROCATALYSIS HIGHLIGHTS

The pressing need to reduce carbon dioxide emissions and to find new, clean sources of energy for the 21st century has brought renewed attention to electrochemical energy transformations. These are a mechanism to increase the efficiency of currently practiced thermochemical energy transformations (such as oxidations in power plants) and to capture the energy of the sun into chemical bonds. Electrocatalysts play the essential role of speeding up electron transfer processes and increasing device efficiency in energy storage (batteries), energy production from sun light (solar hydrogen) and chemical to electrical energy conversions (fuel cells). CCST faculty members have made new and important contributions to these aspects of electrochemical energy conversion. We highlight the developments of four of our faculty members in the pages that follow as an example of the intensive and first-rate work carried out at the center. For details about on-going research at CCST, visit our website at www.che.udel.edu/ccst. Additionally, I invite you to contact our faculty and plan a site visit if you have specific interests in their research programs.

▸ **Raul F. Lobo**
CCST Director

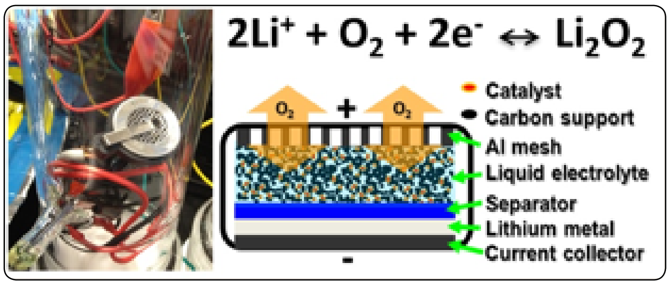
Dare to be first.

UNIVERSITY OF DELAWARE

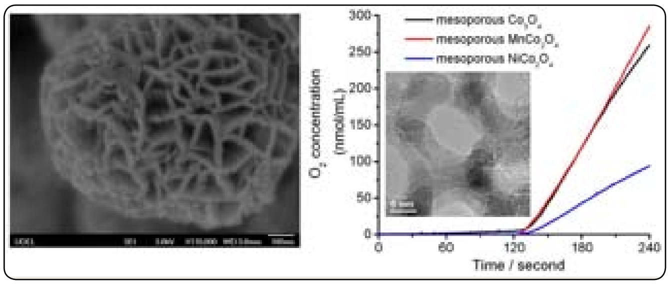
NEXT GENERATION RECHARGEABLE LITHIUM-OXYGEN BATTERIES

- Feng Jiao: Chemical and Biomolecular Engineering

Next generation rechargeable lithium-oxygen batteries offer the potential of ten fold increase in energy density over current generation by replacing cathode intercalation compounds with a carbon/oxygen/catalyst composite electrode. The current state-of-the-art cathode catalyst is α-MnO_2 nanowires, but the origin for its high performance is not fully understood: using our expertise in nanomaterial synthesis, structural characterization and novel in situ spectroscopy we have made important inroads towards solving this puzzle. Our results suggest that an intercalation mechanism causes a change in the surface oxidation state of catalytic sites at the beginning of cell charge and discharge, which accounts for both the increase in discharge capacity and reduction of charging overpotential. We are using this new information to develop improved high performance advanced battery systems.



Oxygen evolution from water is the critical reaction for solar fuel production, because water is the only inexpensive, clean and abundant raw material that is capable of completing the redox cycle for producing either hydrogen (from H_2O) or carbonaceous fuels (from CO_2) on a terawatt scale. We recently demonstrated that morphology and crystal structure have negligible effect on the photocatalytic properties of MnO_2-based oxygen evolution catalysts, while the turnover rate is proportional to the number of surface sites. To further enhance the turnover frequencies (TOFs) that are limited by surface area, new surface sites with a higher TOF rate compared with Mn^{4+} are required. To this end we have introduced K^+-doped MnO_2 catalysts into oxygen evolution reaction. This creates Mn^{3+} sites on the surface of mixed manganese oxides leading to more than ten times higher oxygen evolution rates per surface Mn. Detailed structural characterization investigations indicate that Mn^{3+} sites generated by K^+ doping may be responsible for the high TOFs.



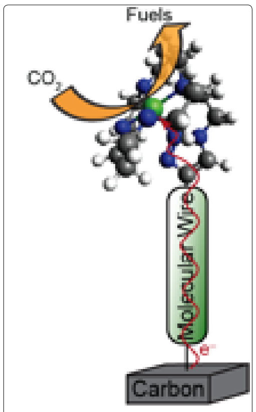
Reference:

Boppana, V. B. R.; Jiao, F. Nanostructured MnO_2: an efficient and robust water oxidation catalyst. Chem. Comm. 47, 8973-8975, 2011.

ELECTROCATALYTIC CONVERSION OF CARBON DIOXIDE TO FUELS

- Joel Rosenthal: Chemistry and Biochemistry

The widespread implementation of intermittent renewable energy sources such as solar and wind requires the efficient storage of electron equivalents. The development of methods to store energy via the generation of chemical fuels in a carbon-neutral fashion represents one strategy to address this issue. A major thrust of our research program is dedicated to the catalytic conversion of stable substrates such as CO_2 and H_2O to versatile, energy-rich fuels via energetically uphill chemical processes. We are particularly interested in the development of systems for the sequestration and reduction of carbon dioxide to generate reactive small molecules and liquid fuels.



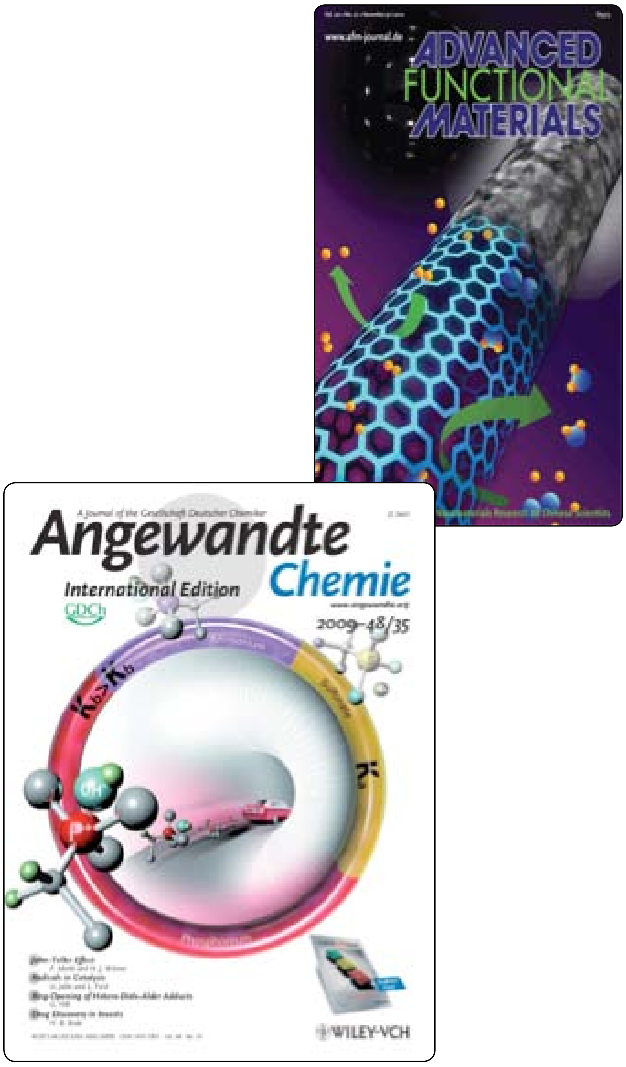
Engineered electrode assembly for conversion of CO_2 to fuels.

We have placed particular emphasis on the development of homogeneous and hetereogeneous electrocatalyst platforms for the efficient uphill conversion of CO_2 to carbon monoxide. These architectures show large current densities and good faradaic efficiencies for CO production and are based on earth abundant materials. Moreover, we have developed a robust chemistry that allows these electrocatalyst materials to be supported/anchored on inexpensive conducting carbon supports. In carrying out this work, we are also developing general methods to engineer monolayers of easily adapted molecular wires (MWs) linked to catalytic platforms for CO_2 conversion. This approach allows us to control the molecular topology of electrode–catalyst interface, which is a critical factor in engineering devices with specific electron transport kinetics and catalytic efficiencies.

INEXPENSIVE AND ABUNDANT CLEAN ENERGY

► Yushan Yan: Chemical and Biomolecular Engineering

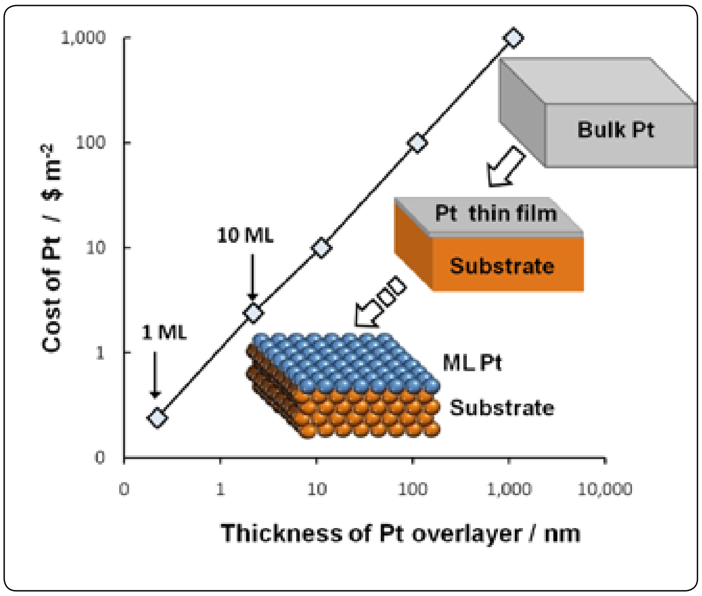
The availability of inexpensive and abundant fossil energy is primarily responsible for the fastest ever human progress in the past 100 years. With the depletion of fossil energy, the increase of world population, the improvement of living standard in large population centers, and the concern of the air quality and climate change, one of the grand challenges facing humanity today is the development of an alternative energy system that is safe, clean and sustainable and where combustion of fossil fuels no longer dominates. Fuel cells coupled with solar hydrogen represent a safe, clean and sustainable energy system that can help significantly alleviate or eliminate the energy supply and CO_2 problem. We have been focusing on **developing catalyst and membrane materials** that will help to solve the cost problem, the most significant commercialization barrier for fuel cells. We have explored the concept of using platinum nanotubes (PtNTs) catalysts that have shown significantly improved catalyst durability and activity for oxygen reduction reaction in proton exchange membrane fuel cells (PEMFCs). This catalyst platform has the potential to meet the mass and specific activity targets for vehicle applications specified by the US Department of Energy. We have also investigated a new class of **fuel cell membranes**, **hydroxide exchange membrane** (HEMs). HEMs, when used in fuel cells (HEMFCs), allow the platinum catalysts to be replaced by non-platinum-group-metals such as nickel and silver while the fluorinated membrane is substituted by an inexpensive hydrocarbon membrane drastically reducing the cost of fuel cells and making them potentially economically viable. HEMs can also be used in electrolyzers or flow batteries for large-scale solar/wind electricity storage and for solar hydrogen generation.



FUEL CELLS

- Jingguang Chen: Chemical and Biomolecular Engineering

Fuel cells, electrolyzers, and photoelectrochemical cells are electrochemical devices that are commonly touted as core technologies in a clean energy future. Central to the operation of all of these devices are catalysts, more specifically **electrocatalysts**, which **mediate charge transfer processes** between the electrolyte and device electrodes with minimal losses in efficiency. Unfortunately, many state-of-the-art catalysts are comprised of expensive Pt-group metals (Pt, Ru, Rh, Ir, and Pd). The high prices and limited supplies of these precious metals create potentially prohibitive barriers to market penetration and scale-up production of electrochemical devices. Research in our group focuses on decreasing **Pt loading by utilizing one atomic layer** (ML) of Pt on low-cost carbide substrates.[1] As shown in the figure, a reduction of Pt film thickness from 10 nm to 1 ML provides more than a ten-times reduction in Pt costs. Such a large reduction in Pt loading, without compromising catalytic activity, may overcome the catalyst-cost-barriers in commercial applications. We have verified similar electrocatalytic properties between ML Pt/carbide systems and bulk Pt for several electrochemical reactions.



Low-cost electrocatalysts for hydrogen evolution reaction (HER): Our research approaches involve parallel efforts in density functional theory (DFT) calculations, surface science experiments on model systems, and synthesis and characterization of porous catalyst particles under electrochemical conditions. DFT results predicted the possibility of using ML Pt on tungsten carbide (WC) to achieve the same HER activity as bulk Pt, which was verified experimentally on model surfaces of ML Pt/WC. We also synthesized Pt-WC core-shell structures to extend model surfaces to more realistic, porous catalysts. [2] Comparing to the leading Pt electrocatalyst, the ML Pt/WC catalysts represent a reduction by a factor of ten in Pt loading. We also obtained a volcano relationship between DFT calculated hydrogen binding energy and experimentally measured electrolysis activity to identify other metal-modified carbide systems as potential low-cost electrocatalysts [3].

References:

[1] D.V. Esposito and J.G. Chen, "Monolayer Platinum Supported on Tungsten Carbides as Low-Cost Electrocatalysts: Opportunities and Limitations", Energy and Environmental Science, (Perspective), 4 (2011) 3900-3912.

[2] D.V. Esposito, S.T. Hunt, A.L. Stottlemyer, K.D. Dobson, B.E. McCandless, R.W. Birkmire and J.G. Chen, "Low-Cost Hydrogen Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide (WC) Substrates", Angewandte Chemie International Edition, 49 (2010) 9859-9862.

[3] D.V. Esposito, S.T. Hunt, Y.C. Kimmel and J.G. Chen, "A New Class of Electrocatalysts for Hydrogen Production from Water Electrolysis: Metal Monolayers Supported on Low-Cost Transition Metal Carbides", Journal of the American Chemical Society, 134 (2012) 3025-3033.