Fundamental Research Underpinning Hydrogen and Fuel Cells
Office of Basic Energy Sciences
U.S. Department of Energy

U.S. DEPARTMENT OF ENERGY | Office of Science

Basic Energy Sciences (BES)

Mission

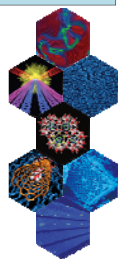
To understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular level.

BES fulfills its mission through:

Supporting **basic research** to discover new materials and design new chemical processes that underpin a broad range of energy technologies.

Operating **world-class scientific user facilities** in X-ray, neutron, and electron beam scattering as well as in nanoscale research.

Managing **construction and upgrade projects** to maintain world-leading scientific user facilities.



Organization

Office of Basic Energy Sciences
Harriet Kung, Director

Materials Sciences and Engineering Division	Scientific User Facilities Division	Chemical Sciences, Geosciences, and Biosciences Division
Linda Horton, Director	James Murphy, Director	Bruce Garrett, Director

Funding Motifs

Increasing scope and size

- Core Research (>1,000 projects, ~$550M/year)
  Single investigators ($150K/year) and small groups ($500K-$2M/year) engage in fundamental research related to any of the BES core research activities. Investigators propose topics of their choosing. Includes awardees under the SC Early Career Research Program.
- Energy Frontier Research Centers ($110M/year)
  $2-4 million/year research centers for 4-year award terms; focus on fundamental research described in the Basic Research Needs Workshop reports.
- Computational Chemical and Materials Sciences ($26M/year)
  - Up to $2-4 million/year research centers for 4-year award terms; focus on delivering open source, experimentally validated software and the associated data for predictive materials and chemical sciences in preparation for exascale computing.
- Energy Innovation Hubs ($39M/year)
  Research centers, established in 2010 ($15-25 million/year), engage in basic and applied research, including technology development, on a high-priority topic in energy that is specified in detail in an funding opportunity announcement (FOA). Project goals, milestones, and management structure are a significant part of the proposed Hub plan.

User Facilities

Access available **at no cost** for non-proprietary research, through a merit based peer review of brief proposals.

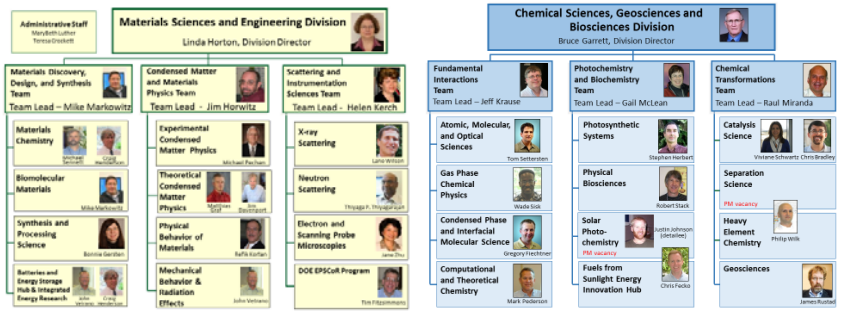
Strategic Planning

BES reports, workshops, and roundtables seek to **encourage transformative, basic science breakthroughs** by tapping the creative imagination of the research community.

Recent Basic Research Needs (BRNs) Workshops

Grand Challenge Reports

BES Research is Grouped by Scientific Topic



- As with all technology areas, there is no Hydrogen and Fuel Cell-specific Funding Opportunity Announcements in FY 2018 though it is one of the topics in the current Energy Frontier Research Center solicitation
- BES funding for fundamental research underpinning fuel cells and hydrogen has remained steady between $20,000k and $25,000k for the past several years.
- Research topics include hydrogen storage, nanoscale catalysts, membranes/separations, bio-inspired hydrogen production and solar hydrogen production
- Annual solicitations applicable for basic research in these areas are our "open" core FOA and our Early Career Research Program. The Energy Frontier Research Center Program supports research in these areas as well.
- BES coordinates with other DOE Offices through the internal working group, and with other Government Agencies through participation in the Interagency Working Group
- Recent Basic Research Needs workshop on Catalysis Science was held in 2017 and the report is available on the BES web site

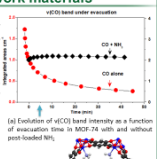
Highlights of BES-Funded Basic Research

Role of hydrogen bonding on transport of co-adsorbed gases in metal-organic framework materials

Scientific Achievement
Post-loading NH_3 and H_2O can strongly trap weakly adsorbed molecules such as CO and CO_2 inside metal-organic framework (MOFs) through cooperative effects.

Significance and Impact
Provides a new way to retain weakly adsorbed molecules inside MOFs for storage by tuning the diffusion barrier instead of the binding energy at the adsorption site.

Research Details
- MOF-74 contains a high density of open metal sites that bind with guest molecules (NH_3, H_2O, CO, CO_2, C_2H_4, etc) and its 1D channels provide the only diffusion pathway for molecules.
- NH_3 (or H_2O) first displaces a certain amount of pre-adsorbed molecules (CO, CO_2) in the outer portion of MOF-74 crystallites and then hinders the diffusion of the remaining molecules trapped deeper inside the MOF channels.
- Combination of *in situ* infrared spectroscopy and first-principles calculations shows that the hydrogen bonding interaction between NH_3 (or H_2O) is responsible for an increase of a factor of 7 or 8 in diffusion barrier of CO or CO_2 through the channel.



(a) Evolution of ν(CO) band intensity as a function of evacuation time in MOF-74 with and without post-loaded NH_3 molecules.

(b) CO diffusion through the channel (along c axis) hindered by hydrogen bonding (dashed lines) with post-loaded NH_3 molecules.

Kui Tan, et al., J. Am. Chem. Soc., 2018, 140, 836

Work was performed at UTD, Wake Forest, and Rutgers

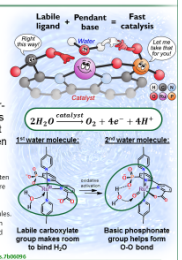
ENERGY Office of Science | UTD | Wake Forest University | RUTGERS

Fast Single-Site Water Oxidation Catalyst

Scientific Achievement
Scientists designed a single-site molecular water oxidation catalyst that has the highest activity at low pH that has been achieved to date.

Significance and Impact
Water oxidation is a source of protons and electrons for fuel-forming reactions in artificial photosynthesis. Single-site catalysts are potentially important for solar-fuels devices, but have been slow. The new catalyst is 100x faster at low pH than the best previous, and first to match the rate of a site of the photosynthetic oxygen evolving complex in green plants.

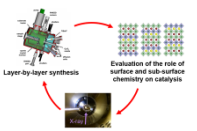
Research Details
- Immobilized catalysts in devices are hampered in bimolecular steps and often function at low pH. Thus, single-site catalysts for low pH are desired, but are typically slow due to high oxidation potentials and high H^+ loss barriers.
- The new catalysts are Ru complexes with multifunctional ligands designed with computational insights to accelerate reactions with two water molecules.
- A labile carboxylate group allows initial H_2O binding, lowering the oxidation potential by releasing H^+. A basic phosphonate group accelerates O-O bond formation by accepting H^+ from the incoming second H_2O molecule.



D.W. Shaffer, Y. Xie, D.J. Szalda, J.J. Concepcion, J.Am. Chem. Soc. (2017) DOI: 10.1021/jacs.7b00896

ENERGY Office of Science | BROOKHAVEN NATIONAL LABORATORY

Tailoring oxide surfaces at the atomic level to increase catalytic reactivity



Scientific Achievement
The influence of surface and sub-surface atomic placements on the oxygen reduction catalysis was investigated on perovskite oxides using a layer-by-layer synthesis ('digital' synthesis).

Significance and Impact
The ability to program the catalyst structure at the atomic level provides an opportunity to establish the catalytic form-to-function and a roadmap toward rationally designed catalytic structures. In this work, the placement of a reactive atom in the sub-surface layer instead of on the surface shows an opportunity for improving the reactivity beyond controlling only the bulk catalyst composition.

Research Details
Perovskite oxide catalysts were synthesized using layer-by-layer depositions to demonstrate that a rational selection of atoms in the surface and sub-surface layers can be used to improve the oxygen reduction activity. A strategy to reap the benefit of a reactive dopant atom while avoiding unintended surface poisoning reaction was shown by placing the reactive dopant atom in the sub-surface layer.

Layer-by-layer synthesis was used to prepare perovskite oxide catalysts with well-defined surface and sub-surface chemistries. By rotating the surface and sub-surface layer chemistries, information on the catalytic form-to-function was obtained. Identifying why certain chemistries were beneficial to the oxygen reduction was then investigated using the Advanced Light Source.

C.J. Eom, D.Y. Kuo, C. Adamo, E.J. Moon, S.J. May, E.J. Crumlin, D. G. Schlom, J. Suntivich, *Nat. Commun.* 2018, 4034. DOI: 10.1038/s41467-018-06503-9

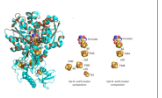
ENERGY Office of Science | ALS | Cornell University

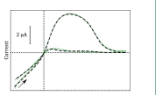
Electrochemical Definition of Unusual Catalytic Properties of [FeFe]-hydrogenase II from *Clostridium pasteurianum*

Scientific Achievement
Defined the potentials in which CpII is catalytically active. The range is much narrower than for other [FeFe]-hydrogenases suggesting that the protein can tune active site chemistry over a broader range than expected.

Significance and Impact **The work shows that subtle changes in the secondary coordination sphere, or even farther, can have dramatic impact on the active site chemistry. The potentials at which CpII is catalytically active are shifted by almost 400 mV relative to CpI.**

Research Details
- Enzyme is immobilized on a graphite electrode so that potential dependence of activity can be directly observed
- Kinetic and thermodynamic information can be obtained by modeling electrochemical data
- Potential dependence of both activation and inactivation has been observed for the first time. This is likely a property of all [FeFe]-hydrogenases but difficult to measure for others.





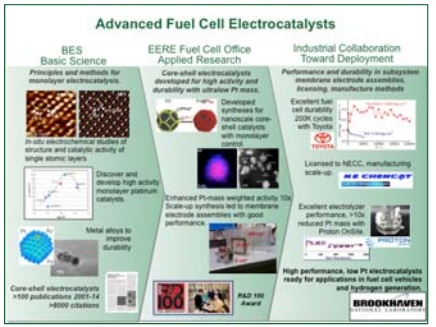
Cyclic voltammogram from CpII immobilized on an electrode showing rapid inactivation at oxidizing potentials.

Williams et al., 2018, Chem. Commun. in review

Work was performed at ASU, WSU, MSU, and NREL

M G W ASU Duke NREL BETCy

Science to Technology



BES Funding Opportunities

General Core Proposal Information

Annual Funding Opportunity Announcement (FOA):
http://science.energy.gov/grants/foas/open/

Contact the program manager for the program of interest to discuss your idea (**email** is usually best).

Consider submitting a **pre-application** (or white paper) to the DOE program (2-3 pages)
- The process for submitting the white paper can vary by CSGB program, so contact the program manager prior to submission.
- Pre-applications are evaluated internally for appropriateness and with regard to program scope and needs
- Encourage/Discourage decision is communicated to the PI

Early Career Research Program (since FY10)

- 5-year awards, $150,000/yr for University researchers
- **Eligibility:** Within 10 years of receiving a Ph.D., either untenured assistant or associate professors on the tenure track

Tips

1. Familiarize yourself with what types of projects are funded in CSGB and what program(s) fit your proposed work.
2. Contact the program manager of the relevant program before submission with any questions.
3. Adhere to all guidelines in the Funding Opportunity Announcement.

Workforce Development for Teachers and Scientists (WDTS)

Office of Science Graduate Student Research (SCGSR) Program
3-12 month supplemental support to conduct research at a DOE laboratory

Science Undergraduate Laboratory Interns (SULI) Program
Supports ~750 undergraduates at one of 17 DOE labs or facilities

Summer School Programs
Nuclear Chemistry, Applied Geophysics, and Particle Accelerator Schools

Important Links and Resources

General Links

BES: http://science.energy.gov/bes
Early Career: http://science.energy.gov/early-career/
User Facilities: http://science.energy.gov/bes/suf/user-facilities
WDTS: http://science.energy.gov/wdts

Resources

Funding Opportunity Announcement (FOAs):
http://science.energy.gov/grants/foas/open/
Reports: http://science.energy.gov/bes/community-resources/reports/
PAMS (grant management system):
http://pamspublic.science.energy.gov/