5th Annual CCAC Student conference
AUGUST 8 & 9, 2013, YMCA OF THE ROCKIES
PROCEEDINGS

Proceedings also available online at
http://ceramics.mines.edu/5th_annual_proceedings_2013.pdf
A photomacrograph (1:1) showing the stress-induced fracture surface of a single crystal gallium arsenide film. Colors were enhanced.
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The Office of Research and Technology at the Colorado School of Mines

Dr. John Poate, Vice President

The Renewable Energy Materials Research Science and Engineering Center

Prof. Craig Taylor, Director

Prof. Ivar Reimanis, Herman F. Coors distinguished professor of ceramic engineering
Welcome to the meeting!

It is my pleasure to welcome one and all to the 5th Annual CCAC Student Conference, organized by the members of the Colorado Center for Advanced Ceramics, Colorado School of Mines, Golden, Colorado. This year, we have preserved all the popular elements from the previous years and also have included several new elements to the conference that we believe will make the conference much more enjoyable. One such addition is the online abstract submission and conference registration. My sincere thanks go to Ms. Alison Gorman for helping us with the student conference webpage.

Another valuable addition is a special tutorial on the fundamentals of Density Functional Theory by Dr. Vladan Stevanovic. My thanks to Vladan for accepting our invitation to teach the tutorial. As we all know, more than ever, it is becoming very essential to have expertise in both theoretical and experimental science. We expect this tutorial to be highly beneficial to all the participants, especially our CCAC student members, a majority of who are experimentalists.

Another exciting addition is a new session on career discussion. I would like to extend my very sincere thanks to our career discussion panelists: Dr. Carole Graas (IBM), Dr. David Ginley (NREL), Prof. Craig Taylor (CSM), Prof. Corinne Packard (CSM), Dr. Josh White (LANL), and Dr. Kristin Kiriluk (Abengoa Solar) for agreeing to provide career suggestions to the students. We also have two invited speakers this year - Dr. John Poate and Dr. David Ginley. I’m grateful to both of our invited speakers for accepting our invitation in spite of their very busy schedules.
I'd like to thank our conference sponsors: Dr. John Poate from the Office of research at Colorado School of Mines, Prof. Craig Taylor from REMRSEC (Renewable Energy Materials Research Science and Engineering Center) and Prof. Ivar Reimanis, Herman F. Coors distinguished professor of ceramic engineering for their financial support.

Personally, I owe my deepest gratitude to our center director Prof. Ivar Reimanis for his trust and confidence in us. He has provided full freedom, which allowed us to pursue our thoughts and ideas to improve the conference experience. I'm very thankful to Alice Jensen for her help in all the financial and travel work associated with the conference. I’m grateful to the rest of the committee members: Amy Morrissey, Ann Deml and Wan Zheng for their interest, efforts and support throughout the eleven months of preparation. I appreciate their help.

I also would like to thank my fellow CCAC graduate students for their active contribution to the conference.

Looking forward to meeting all of you at Estes Park. We sincerely believe every one of us will find this conference educational and rejuvenating.

Regards,
Archana Subramaniyan
PhD candidate
Organizing Committee Chair, 5th Annual CCAC Student Conference

5th Annual CCAC Student Conference Planning Committee

Archana Subramaniyan  Ann Deml  Amy Morrissey  Wan Zheng

A special thanks to Kelly Hummel for photographing our committee members!
## Schedule Overview

### Thursday, August 8, 2013

10:00a  Introduction, welcome, and instructions by Archana Subramaniyan

10:15a  Introduction to CCAC by Prof. Ivar Reimanis

10:30a  *“Research at Mines: Fun, Factoids, and the Future”* by Dr. John Poate (Invited)

11:00a  Break

11:15a  **Session One: “Thin films for photovoltaic applications”**  
   Yi Ke, Cassi Sweet, Archana Subramaniyan  
   Session chair: Prof. Ryan O’Hayre

12:15p  Lunch

1:30p  **Poster preview presentations**  
   Daniel Clark, Ann Deml, Amy Morrissey, Matt Musselman, Stefan Nikodemski, Kevin Wood, Wan Zheng  
   Session chair: Dr. Michael Sanders

1:45p  Group photo

2:00p  *“A brief introduction to density functional theory and simulations of properties of real materials,”* tutorial by Dr. Vladan Stevanovic

3:00p  Break

3:15p  *“Why renewable energy can’t work and why it is your job to change that”* by Dr. David Ginley (Invited)

3:45p  **Session Two: “Processing and properties of organic materials”**  
   Yunjiang Jiang, Liangju Kuang, Taylor Wilkinson  
   Session chair: Dr. Jianhua Tong

4:45p  Break, check-in for YMCA lodging

5:00p  Dinner and networking

7:30p  Poster presentations and networking
Schedule Overview

Friday, August 9, 2013

8:00a  **Session Three: “Innovations in oxide ceramics”**
Yachao Chen, Aaron Miller, Chuancheng Duan
Session chair: Dr. Ivan Cornejo

9:00a  Break, check-out for YMCA lodging

9:15a  **Career discussion panel (Invited)**
Dr. David Ginley, National Renewable Energy Laboratory
Dr. Josh White, Los Alamos National Laboratory
Dr. Carole Graas, IBM
Dr. Kristin Kiriluk, Abengoa Solar PV Inc.
Prof. Craig Taylor, Colorado School of Mines (Moderator)
Prof. Corinne Packard, Colorado School of Mines

11:00a  Announcement of scientific art winners and awards

11:15a  Closing remarks

12:00p  Lunch (provided)
Mines has the broadest portfolio of energy related research of any university in the US. Materials research is at the core of our endeavors. Three examples of materials related energy research will be given which are at center stage; electronic materials (photovoltaics); light weight structural materials (ferrous alloys) and unconventional fossil fuels (methane clathrates). The success of those research areas depends on many factors but close coupling to industry is key. Research at Mines is flourishing but the question for the future is how do we maintain this momentum?

John M. Poate (Ph.D. Australian National University, 1967) is Vice-President for Research and Technology Transfer at the Colorado School of Mines. He previously served as a Harwell Fellow of the UKAEA, Head of the Silicon Processing and Interface Physics Research Departments at Bell Laboratories, Dean of the New Jersey Institute of Technology and CTO of Axcelis Technologies. Dr. Poate has published extensively in several areas of nuclear physics solid state physics, materials science and engineering. He is a Fellow of the American Physical Society and Materials Research Society, MRS Past-President and the John Bardeen award winner of the TMS. He has served on advisory panels or councils for NATO, US and overseas universities, NSF, NRC, and DOE. He currently serves as Chair of the Director’s Review Committee for Physical and Life Sciences at Lawrence Livermore National Laboratory and is on the Board of the National Renewable Energy Laboratory.
“A brief introduction to density functional theory and simulations of properties of real materials” by Dr. Vladan Stevanovic

Thanks to both theoretical developments and the availability of massively parallel computers we are currently witnessing the transformation of quantum mechanics from purely scientific into a powerful engineering discipline. We are now able to dig deep into the intrinsic properties of many classes of materials with quantitative accuracy and find ways to improve their performance in a wide range of relevant applications, including, at present, the very important applications related to renewable energy. In this lecture I will provide an overview of the computational techniques frequently used in simulating properties of real materials and discuss several examples from my current research. This includes a brief description of Density Functional Theory (DFT), its numerical implementations, as well as the description of related methods constructed to improve some of the shortcomings of DFT. The examples, on the other hand, will reveal how this whole machinery works in practice and how we can deliberately design materials for a given application using quantum mechanics, DFT, and large-scale computations.

Vladan Stevanovic (Ph.D. EPFL, 2009) currently holds a joint Research Assistant Professor position between the CSM Dept. of Physics and NREL and is one of the PIs of the Center for Inverse Design, an Energy Frontiers Research Center of the US Department of Energy. Vladan graduated from the Faculty of Physics, University of Belgrade, Serbia, and earned his Ph.D. degree from Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland. Vladan has a background in theoretical condensed matter physics and experience in numerical techniques and computer simulations based on DFT and related methods that he applied to investigate properties of bulk materials, oxide surfaces, gas-phase and supported metallic clusters. Current work focuses on materials for renewable energy applications and includes developing and applying high-throughput theoretical tools for predicting existence of new materials, studying the influence of the cation disorder on materials properties, and searching for new water splitting semiconductors. Vladan has published his work in top journals and has been invited to present at numerous conferences and workshops.
“Why renewable energy can’t work and why it is your job to change that” by Dr. David Ginley

Renewable energy especially solar is rapidly becoming cost competitive with conventional power generation but at the same time the overall impact of renewables is still small. Making a real change in the mix requires new science, new technology, social change and political change. This will enable production at levels that matter and approach to adoption at large scale. Thus there are many roles for all of you. How do you choose - is advocacy a role a responsibility the talk will briefly present the big picture and then talk about opportunities for careers in this space.

David Ginley (Ph.D. Massachusetts Institute of Technology, 1976) is a Research Fellow and Group Manager at the National Renewable Energy Laboratory. He is currently leading activities in the applications of nanotechnology/nanomaterials, organic electronics, transition metal oxides (ferroelectric materials, rechargeable Li batteries, fuel cells, and transparent conductors) and ink jet printing for solar cells. Current work focuses on the development and basic science of very high quality materials (transparent conducting oxides, ferroelectric materials, organic materials and nano-materials) and the development of next generation process technology for materials and device development (combinatorial methods, direct write materials, composite materials and non-vacuum processing).

Dr. Ginley has published more than 400 papers, received 30 patents, and been honored with a Department of Energy Award for Sustained Research in Superconducting Materials, R&D 100 awards for novel chemical etches, for nanoparticle technology, for ferroelectric frequency agile electronics, for alumina based nanofibers, and hybrid photovoltaics. He has also received three FLC technology transfer awards. He is also an adjunct Professor of Physics at CU Boulder and of Research Professor of physics at the Colorado School of Mines. He received the Presidents Service Award in 2007.
**Dr. David Ginley**, National Renewable Energy Laboratory
See profile on previous page.

**Dr. Josh White**, Los Alamos National Laboratory

Josh T. White (Ph.D. Colorado School of Mines, 2011) received a B.S. from the Colorado School of Mines in Metallurgy and Materials Engineering in 2006, after which he was accepted into the Materials Science graduate program at CSM under Dr. Ivar Reimanis. His work at CSM focused on magnetometry of NiO doped Y₂O₃ stabilized ZrO₂ for which he received a M.S. in 2008 and Ph.D. in 2011. Currently he is a postdoctoral research associate in the Materials Science and Technology division of Los Alamos National Laboratory where he works on thermophysical transport properties and reduction-oxidation kinetics of nuclear fuels. He has 5 peer-reviewed publications and has presented in multiple conferences.

**Dr. Carole Graas**, IBM

Carole Graas (Ph.D. Colorado School of Mines, Materials Science, 1989) manages the technology reliability engineering team and is the reliability strategist for the IBM Microelectronics Division. In this capacity, she leads the qualification of IBM’s most advanced semiconductor technologies, while also driving key strategic innovation programs. She has held this and other senior technical and management positions in the field of technology and product reliability since joining IBM in 2003. Prior to this, she held progressively broader responsibilities both in the US and in Europe, as an engineer and then a manager in technology development successively for Texas Instruments and Siemens Microelectronics (a.k.a. Infineon Technologies). She has published extensively in the field of semiconductor interconnect reliability, served on numerous industry and professional committees, including as general chair and chairman of the
board of the IEEE International Reliability Physics Symposium. Carole also holds a Research Associate Professor appointment with MME at Colorado School of Mines, where her work focuses on physics-based simulations of degradation mechanisms. She also founded the IEEE Conference on Reliability Science for Advanced Materials and Devices, held for the first time on the Mines campus earlier this year. When not in her IBM office in Vermont, or Mines office in Colorado, you will find Carole training and competing with her horse on the New England Hunter/Jumper circuit.

**Dr. Kristin Kiriluk**, Abengoa Solar PV Inc.

Kristen Kiriluk (Ph.D. Colorado School of Mines, 2011) did her undergraduate work at University of MD, College Park in physics. Her master's was completed at University of Colorado, Boulder in High Energy Nuclear Physics. Her PhD was at the Colorado School of Mines in condensed matter physics in materials characterization. She currently works at Abengoa Solar in Lakewood, CO as a research engineer and project manager and work with photovoltaic technologies.

**Prof. Craig Taylor**, Colorado School of Mines (Moderator)

P. Craig Taylor received the A. B. degree from Carleton College, Northfield, Minnesota, in 1964 and the Ph.D. degree from Brown University, Providence, Rhode Island, in 1969. He was a Research Associate at Brown University and a National Academy of Sciences Postdoctoral Research Associate at the Naval Research Laboratory between 1969 and 1971. From 1971 to 1982 Dr. Taylor was employed at the Naval Research laboratory where he performed research on the electronic and structural properties of crystalline and amorphous semiconductors. He spent a sabbatical year at Heriot-Watt University, Edinburgh, Scotland and Cambridge University, Cambridge, England (1976-1977). In 1982 Dr. Taylor joined the Physics Department at the University
of Utah as a Professor. He was the Chairman of the Physics Department from 1989 to 1998 and appointed to the rank of Distinguished Professor in 2001. He was also for many years the Director of the John A. Dixon Laser Institute at the University of Utah. Currently Dr. Taylor is a Professor in the Physics Department and in the Department of Metallurgical and Materials Engineering at the Colorado School of Mines and the Scientific Director for the Center for Revolutionary Solar Photoconversion, the Associate Director of the Colorado Energy Research Institute, and the Director of the Renewable Energy Materials Research Science and Engineering Center. Dr. Taylor has written over 400 scientific papers including several book chapters and review articles. He is a Fellow of the American Physical Society and a member of the American Association for the Advancement of Science, the Materials Research Society, and the American Association of Physics Teachers. Selected honors include the Research Publication Award from the Naval Research laboratory in 1975, Department of Energy Certificates for Outstanding Contributions to Photovoltaic Research in 1990 and 1995, a Citation and Medal for Outstanding Professorial Contributions from Brown University in 1992, the Distinguished Scholarly and Creative Research Award from the University of Utah in 2003, and the Mott Lecture in 2005.

**Prof. Corinne Packard**, Colorado School of Mines

Corinne Packard (Ph.D. Massechusset Institute of Technology, 2008) is an Assistant Professor in the Metallurgical and Materials Engineering Department at CSM and holds a joint appointment at the NREL in the National Center for Photovoltaics. She earned her Ph.D. in Materials Science & Engineering from MIT for her research on the nanomechanics of metallic glasses and the development of high temperature nanoindentation techniques. Her post-doctoral research focused on the control of interfacial and intermolecular forces to fabricate large-area MEMS and pattern materials for OLEDs and organic photovoltaics. At Mines, she explores the fundamentals of plasticity and stress-assisted failure mechanisms in materials used in energy applications.
Improving the mobility through defect pairing in wide-band-gap conductive Zn$_{0.7}$Mg$_{0.3}$O:Ga

Yi Ke$^{1,2}$, Stephan Lany$^2$, Joseph J. Berry$^2$, John Perkins$^2$, Andriy Zakutayev$^2$, Tim Ohno$^3$, Brian Gorman$^1$, Ryan O’Hayre$^1$, David S. Ginley$^2$

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$^2$ National Renewable Energy Laboratory, Golden, CO, USA
$^3$ Department of Applied Physics, Colorado School of Mines, Golden, CO, USA

Alloying MgO into ZnO substantially increases the band-gap energy but reduces the conductivity and effectiveness of donor-doping. While the increased band gap makes it attractive for energy-level-tunable transparent conducting contacts, the conductivity reduction limits its practical application. By combining high quality material synthesis, characterization and theory, we attribute the major limitation on the electrical conductivity of epitaxial Ga-doped Zn$_{0.7}$Mg$_{0.3}$O to intrinsic acceptors, such as zinc vacancies (V$_{Zn}$), which both trap carriers and increase the ionized impurity scattering. In addition, it shows that V$_{Zn}$ can form defect complexes with Ga substituted on a Zn site (Ga$_{Zn}$) during annealing, and this can increase the mobility by reducing the number of ionized impurity scattering centers. In particular, a Zn$_{0.7}$Mg$_{0.3}$O:Ga (1%) sample annealed for 2 hours in vacuum ($P_{O_2} = 10^{-7}$ Torr) at 400°C leads to an increase in mobility from 12 cm$^2$/Vs to 18 cm$^2$/Vs. This results in an electrical conductivity of 475 S/cm, a 50% increase over 320 S/cm from our previous best as-deposited conductivity to date. This work establishes that enhancing defect pairing is an effective strategy to increase mobility in semiconductors where ionized impurity scattering limits the transport.

Changes in defect densities during annealing fitted based on carrier concentration and mobility. It shows that there are less scattering centers as the isolated V$_{Zn}$ pairing up with Ga$_{Zn}$.
Exfoliation of GaAs flexible thin films by controlled spalling fracture

Cassi Sweet\textsuperscript{1}, David Young\textsuperscript{2}, Aaron Ptak\textsuperscript{2}, Corinne Packard\textsuperscript{1,2}

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\textsuperscript{2}National Renewable Energy Laboratory, Golden, CO, USA

As part of a larger project to significantly reduce the cost of III-V semiconductor-based photovoltaic production, this study addresses key issues regarding the reuse of GaAs wafers as seed layers for epitaxially grown thin film solar cells. We employ a repeatable process to remove thin, flexible GaAs foils from a crystalline host wafer by controlled planar fracturing. Controlled fracture is achieved through the application of an electrochemically deposited stressed film, which generates a stress field within the GaAs substrate and induces a spalling fracture at a specified depth. The depth-controlled fracture propagates across the substrate on crystallographically weak planes to exfoliate a thin layer the size of the entire substrate. Fabrication of GaAs foils less than 10 \( \mu \text{m} \) thick is demonstrated for both (100) and (110) crystal orientations with little to no waste material. This rapid and repeatable process shows promise for enabling the production of efficient III-V photovoltaic devices at lower cost.
Non-equilibrium thin-film growth of Cu$_2$O via combinatorial PLD

Archana Subramaniyan$^{1,2}$, Vladan Stevanovic$^1$, John D. Perkins$^1$, Ryan P. O’Hayre$^2$, David S. Ginley$^1$, Stephan Lany$^1$ and Andriy Zakutayev$^1$

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Cuprous oxide, Cu$_2$O, is an earth abundant, low cost and non-toxic material that is widely used in several applications including solar cells, gas sensors, and thin film transistors. In this work, we study the non-equilibrium growth of Cu$_2$O thin films via combinatorial PLD from a CuO target as a function of oxygen partial pressure (p$_{O_2}$) and total pressure (P$_{tot}$ = p$_{Ar}$ + p$_{O_2}$) with a temperature gradient of 300 – 600 °C. Unlike conventional PLD oxide growth studies where either O$_2$ or Ar is used, here we simultaneously utilize both gases to deposit copper oxide thin films. A phase mixture of Cu$_2$O and CuO was formed with increasing p$_{O_2}$ while Cu$_2$O and Cu was formed with increasing temperature. Phase pure Cu$_2$O was formed at intermediate p$_{O_2}$ (0.25 mTorr) and lower temperature (310 °C). The formation of oxidizing or reducing second phases with varying p$_{O_2}$ and T$_s$ are consistent with the oxygen chemical potential relation derived from the ideal gas law. But, the coexistence of phases contradicts the Gibbs phase rule and the formation of phase pure Cu$_2$O (at the p$_{O_2}$-T$_s$ studied) does not coincide with the equilibrium phase diagram indicating that the resulting films are in a non-equilibrium state.

To gain a large processing window where phase pure Cu$_2$O can be obtained, we varied the total pressure in the chamber from 10 – 100 mTorr (p$_{O_2}$ fixed to an optimized value). It was found that phase pure Cu$_2$O can be formed both at lower (300 °C) and higher (375 – 600 °C) end of the temperature range studied depending on the P$_{tot}$ value. Therefore, total pressure is a key processing parameter that alters the plume dynamics and the kinetic rates during deposition. This enables the synthesis of phase pure Cu$_2$O at lower temperatures, an important criteria for many practical applications.
Synthesis and activity of antimicrobial polymer molecular brushes

Yunjian Jiang, Wan Zheng, Liangju Kuang, Hongjun Liang

Colorado Center for Advanced Ceramics, Colorado School of Mines, Golden, CO, USA

A new generation of antibiotics is urgently needed to battle against nonstop evolution of antibiotics-resisting pathogens. Among all candidates, antimicrobial peptides (AMPs) and their synthetic analogues are considered the forerunners because they function by attacking bacterial cell membrane, hence evading the typical DNA-based counteracting mechanisms of the pathogens. So far, most of the research focuses on small molecules. Few, if any, have tried to investigate the structure-activity relationship of complex superamolecules. Inspired by the common structural characteristics of antimicrobial protein, we synthesized a series of polymer molecular brushes with different size and different degree of amphiphilicity and electronpositivity, and examined their structure-dependent antimicrobial activities. The antimicrobial activity of polymer molecular brushes depends on the size of the backbone molecule, the size of brushes, as well as the degree of electronpositivity of these brushes. Generally, the activity increases with the increasing backbone molecular size and brush size, but shows a maximum at moderate degree of electronpositivity, indicating that a balanced amphiphilicity is necessary for their optimum activity. When compared with free linear polymers of the same structure as the brushes, polymer molecular brushes exhibit much higher activity, suggesting the antimicrobial activity of small antimicrobial polymers can be improved by assembling them into spatially-defined superamolecules. Further studies on the toxicity of polymer molecular brushes showed that they are safe to human red blood cell, with no appreciable hemolysis up to 500μg/mL. Finally, the polymer molecular brushes can be designed to selectively kill the gram-negative bacteria, but not gram-positive bacteria. This is usually unachievable by small synthetic AMPs. Based on the fact that not all of bacteria are harmful, selectivity among different types of bacteria is of great significance to human health, and our study may reveal a novel family of synthetic antibiotics for future development.
Microalgae are widely regarded as promising feedstocks for next-generation biofuels production. However, due to their small specific density of microalgal cells and their like-charge repulsion, microalgae dewatering is one of the key processes that limit a microalgae-based biofuel production at an industry scale. We consider the microalgae dewatering problem can be understood in the context of colloidal stability, where inter-algal potential is tunable via surface engineering of novel coagulation agents, hence cost-effective microalgae harvesting can be directed to occur spontaneously. We propose to harvest microalgae using nanoparticle-pinned polymer brushes. By designing a solid-state paramagnetic core, the nanoparticle-pinned polymer brushes allow the use of magnetic force to not only modulate inter-algae pair potentials, but also facilitate retrieval of the coagulation agents to be re-used after algal oil extraction. Both fresh water and marine microalgae species are tested to show high coagulation efficiency. Our preliminary data on the preparation of well-defined nanoparticle-pinned polymer brushes, their structure-dependent coagulation performance on both fresh water and marine microalgae species, and their re-suability for continuous cycles of microalgae farming and harvesting will be discussed.
High resolution mechanical property mapping in oil shales

Taylor Wilkinson¹, Saeed Zargari², Manika Prasad², and Corinne Packard¹

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² OCLASSH (Organic, Clay, Sand, Shale) Research Group, Colorado School of Mines, Golden, CO, USA

Oil shales are naturally occurring materials composed of clays, organic matter, calcite, quartz, and other minerals that can produce oil through the use of hydraulic fracturing. The typical microstructure of these materials is a composite network with organic matter in open and closed pores tucked between mineral phases, with individual phases ranging in size from sub-micron to several-micron sized pockets. Extraction of the organic matter is controlled by the fracture of these composites and the resulting flow characteristics. In this study, we explore high resolution topographic and modulus mapping using new nanoindentation techniques. Dynamic modulus mapping allows for data to be recorded across grains and intragranular regions of organic matter known as kerogen, providing substantially higher spatial resolution of properties than achievable by previously employed indentation techniques. In performing the data analysis, we further refine the collected data by filtering extreme and sudden changes in topography, which would not be accurately resolved with the indenter tip. This work provides a detailed understanding of how the materials are arranged on this scale and their mechanical properties, which is necessary to populate microstructure-based models of shale fracture behavior and oil recovery predictions.
Understanding interfacial phenomena in proton conductors using atom probe tomography

Daniel Clark\textsuperscript{1}, Sandrine Ricote\textsuperscript{2}, Jianhua Tong\textsuperscript{1}, Dave Diercks\textsuperscript{1}, Ryan O’Hayre\textsuperscript{1}

\textsuperscript{1} Colorado Center for Advanced Ceramics, Colorado School of Mines, Golden, CO, USA
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In proton-conducting ceramics many of the bulk material transport properties are dominated by interfacial transport at grain boundaries, which are highly resistive for \( \text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta} \) (BZY10), and at heterogeneous interfaces, which have been shown to increase protonic conductivity by over an order-of-magnitude. At these interfaces, space-charge regions are believed to form, which dramatically alter the local ionic transport properties causing an enhancement or degradation in the overall proton conductivity of a material. Atom probe tomography (APT) is a powerful technique that can be used to characterize these interfaces with sub-angstrom spatial resolution and parts-per-billion chemical resolution, allowing for further understanding of what is happening at these interfaces. APT will be demonstrated as a tool to connect the local chemistry of these interfaces to the overall electrochemical properties of the material to gain insight in how to better engineer these materials to achieve more desirable protonic transport.

A bright-field TEM image of \( \text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta} \) with a grain boundary at the tip and an atom probe reconstruction showing nickel accumulation at the grain boundary.
Solar thermochemical (STC) fuel production, a process which utilizes solar radiation to thermochemically split H₂O and/or CO₂, is a candidate technology for the clean and renewable generation of alternative chemical fuels. In a typical two-step thermochemical redox cycle, a metal oxide is reduced at high temperature and then reoxidized at a lower temperature by reaction with H₂O and/or CO₂. Despite potential for efficiencies in excess of 50%, current materials systems commonly exhibit slow reaction rates, material degradation, limited fuel production capacity, and/or complex cycling requirements resulting in efficiencies less than 10%. New materials systems which exhibit enhanced performance must be identified.

With this aim, we report a high-throughput first principles method for screening nonstoichiometric metal oxides based on thermal redox behavior. Our method includes a) assessment of material stability with respect to decomposition into other phases as a function of T and P_{O₂} and b) prediction of oxygen vacancy formation energetics to obtain oxygen nonstoichiometry δ as a function of T and P_{O₂}. We have applied this method to several basic perovskites structures including the (La,Sr)MnO₃ family which has received much attention for its effectiveness for oxygen reduction in solid oxide fuel cells. We validate our results against experimental data and present plans to implement this tool as a guide for the development of promising new materials for STC fuel production.
Internal reduction of transition metal doped oxides and perovskites

Amy L. Morrissey¹, Jianhua Tong¹, Ivar E. Reimanis¹, Jim R. O’Brien²

¹ Colorado School of Mines, Golden, CO USA
² Quantum Design, Inc., San Diego, CA USA

Transition metal (M = Ni, Co, Fe) doped Y₂O₃-stabilized ZrO₂ (YSZ) is widely used in oxygen pumps, oxygen sensors, and solid oxide fuel cells (SOFCs). These electrochemical devices can be operated in reducing and oxidizing environments. In the present study, specimens containing small concentrations of M dopant (0.01 to 1 mol%) dissolved in the YSZ matrix are chemically synthesized using a high purity methods. Reduction experiments are conducted in a custom-built, environment-control furnace. The extent of internal reduction which occurs at variable times (up to 500 h) and temperatures is monitored with SQUID VSM magnetometry. The microstructural development of the internal reduction process of each M dopant is confirmed with microscopy techniques. Magnetometry is shown to be useful for distinguishing between M ions present in solution, as a second phase, or as metal particles of various sizes. The investigation is repeated on M doped yttrium-doped barium zirconate (BZY), a proton conducting perovskite.

Arrows indicate Ni⁰ precipitates along a 10YSZ grain boundary after 20 hours at 1000°C in hydrogen.
Micro-scale mechanical properties of lithium ion battery cathodes
Mukesh Kumar\textsuperscript{1,2}, Matt Musselman\textsuperscript{1,3}, Kandler Smith\textsuperscript{2}, and Corinne Packard\textsuperscript{1,2}

\textsuperscript{1} Colorado School of Mines, Golden, CO, USA
\textsuperscript{2} National Renewable Energy Laboratory, Golden, CO, USA
\textsuperscript{3} Renewable Energy Materials Research Science and Engineering Center (REMRSEC), Golden, CO, USA

Lithium ion battery cathodes are a composite material with ceramic particles as the active material, PVDF (polyvinylidene difluoride) for adhesion, and carbon particles for conductivity. The ceramic provides scaffolding allowing for the repeated insertion and removal of lithium ions in the intercalation process providing recharging capabilities, one of the major benefits of lithium ion battery technology. Intercalation produces mechanical strains that cause a significant change in volume of the ceramic, alternating between shrinking and swelling when charging and discharging, respectively. Repetitive cycling of the batteries may result in mechanical degradation of the particles and their connection to other composite materials, isolating sections of the cathode thereby reducing the batteries overall capacity.

Transportation industries seek to update current lithium ion battery lifetime models to provide more accurate predictions on batteries for use in electric and hybrid cars. New physics-based models for battery lifetime will require knowledge of the mechanical degradation of ceramic particles and the properties of each component over the life span of the battery. Measuring the mechanical properties of individual particles using nanoindentation will help develop a better understanding of the fundamental material physics behind battery degradation. Critical techniques were established in order to make these measurements including sample preparation of a composite material containing particles of varied hardness and grinding and polishing using non-aqueous media. Nanoindentation methods have been developed to probe individual particles with the ability to analyze the same particles after indentation using scanning electron microscopy (SEM) for fracture toughness measurements and electron backscatter diffraction (EBSD) to determine particle orientation. Mechanical property variations between fresh and cycled material will be discussed.
Engineering nanoionic interfaces by pulsed laser deposition for energy conversion and storage

Stefan Nikodemski\textsuperscript{1}, Dave Ginely\textsuperscript{2}, Philip Parilla\textsuperscript{2}, Jianhua Tong\textsuperscript{1}, Ryan O’Hayre\textsuperscript{1}, Joseph Berry\textsuperscript{2}

\textsuperscript{1} Colorado School of Mines, Golden, CO USA
\textsuperscript{2} National Renewable Energy Laboratory, Golden, CO USA

The present work is concerned with harnessing the nanoionics phenomena, which can be induced by engineering interfaces on the nanometer length scale. This effort aims to study some of the fundamental physics and scaling behavior of ionic transport in nanometric heterostructures/composites by using pulsed laser deposition (PLD) to fabricate geometrically well-defined ion-conducting oxide nanostructures. All heterostructures investigated in this study were grown by PLD technique using KrF excimer laser with a 248 nm wavelength and 10 Hz repetition rate. The proton conducting material used in this study, BaCe\textsubscript{0.6}Zr\textsubscript{0.3}Y\textsubscript{0.1}O\textsubscript{3-δ} (BCZY), was deposited from a target whose powders were prepared via a modified sol-gel method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to examine sample morphology. X-ray diffraction (XRD) experiments were conducted concurrently with sample annealing in order to determine crystallization temperatures of the materials present in the films as well as to assess the formation of any non-conducting/undesirable phases. Ionic transport properties at various operating temperatures are examined via electrochemical impedance spectroscopy (EIS).

A FESEM image showing a BCZY/TiO\textsubscript{2} multilayer heterostructures fabricated by pulsed laser deposition with layer thickness on the order of 10 nm.
Electrocatalysis of graphene-supported PtRu for direct methanol fuel cells

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Significant advances in catalytic activity and durability of electrocatalytic materials are still needed for commercialization of direct methanol fuel cells. Further development of this technology also requires improved utilization of the noble metal catalysts, such as Pt and Ru. Changing the carbon structure has been shown to affect the catalyst support interactions and potentially benefiting the catalyst utilization, catalytic activity and durability. The unique structure and properties of graphene nanosheets make them a very promising alternative to carbon black supports. The effects of graphene on electrocatalytic performance have been the subject of intensive interrogation. It is clear that one of the biggest challenges associated with the graphene supports is poor dispersion of this material during electrode preparation.

Graphene oxide was synthesized by modified Hummer’s method. Further reduction of graphene oxide was performed by means of hydrazine at room temperature. Functionalization of graphene sheets with nitrogen is performed using nitrogen ion implantation. This technique was previously employed to incorporate nitrogen functional groups onto the surface of HOPG substrates and carbon black supports with both types of functionalized substrates demonstrating improved PtRu nanoparticle stability. Deposition of Pt-Ru is conducted by sputtering from an alloyed (50:50) Pt-Ru target onto the carbon support material.

Methanol oxidation cyclic voltamograms for PtRu electrocatalysts obtained in 0.5 M NaOH + 0.5 M MeOH, at room temperature, 10 mV/s.
Directed assembly of nanoparticles by “click” reactions

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Complex and hierarchically organized arrays of nanoparticles show enhanced properties originated from their collective interactions. However, the structures formed by self-assembly approaches are usually hard to predict and control. We report here a novel strategy to achieve directed assembly of nanoparticles through “click” reactions, which represent a highly specific and efficient synthetic methodology to create sharply defined nanostructures. For example, complex architectures formed through the reaction between alkyne- and azide-functionalized nanoparticles are not only quantitative predictable, but also stable, because the nanoparticles are linked via covalent bonds. Our preliminary data show this method can be applied to organize a wide range of different nanomaterials with different sizes and shapes, such as silica nanospheres and gold nanorods with different architectures.
Lithium aluminum silicates such as β-eucryptite (LiAlSiO₄) are well-suited for thermal shock resistant structures, precision optics platforms, and various other applications where low or negative coefficient of thermal expansion (CTE) is required. Particularly, β-eucryptite has potential use in many of these applications because it exhibits an average negative CTE. β-eucryptite is also known to undergo a reversible pressure-induced phase transformation at ~0.8 GPa to ε-eucryptite. The present study investigates the effect of doping with Mg on the CTE and pressure-induced phase transformation. Dilatometry is used to measure the CTE of doped and un-doped β-eucryptite synthesized from chemical precursors while In situ DAC-Raman spectroscopy is used to investigate pressure induced phase transformations in both.
Enhancing the mechanical properties of materials transparent in the infrared is desirable for applications such as ceramic armor and radome casings. A potential method for increasing the hardness of these materials is the use of nanocomposite oxide ceramics. In this study, the hardness of Y$_2$O$_3$ to several Y$_2$O$_3$-based nanocomposites are compared to a commercially available powder. It was found that the macro hardness increased from 6.3 GPa for pure Y$_2$O$_3$ to 10.6 GPa for the commercial 50-50 vol% MgO-Y$_2$O$_3$ composite, while the maximum transmission from 400cm$^{-1}$ to 4000cm$^{-1}$ decreased from 85% to 70%. Micro and macro hardness data will be presented, and the mechanisms controlling the hardness of the composites at different length scales will be discussed.
Oxygen production using a proton-conducting perovskite-structured ceramic membrane

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In this work, we demonstrate for the first time the use of a proton-conducting perovskite-structured ceramic membrane \((\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta})\) for oxygen production. This approach makes use of the protonic transport and water splitting capabilities of the membrane—oxygen is produced from water decomposition and proton transport rather than oxygen ion transport through the membrane. The oxygen flux increases with increasing steam concentration on the sweep gas (Helium) side of the BCZYb membrane (feed side is dry air). This behavior is attributed to the decomposition of water. If pure steam is used as the sweep gas, pure oxygen can be produced (with steam separation accomplished by condensation).

Dependence of oxygen flux of BCZYb membrane vs. temperature under various conditions.
CCAC News

New Researchers

Prof. Ivan Cornejo joined the CCAC as a Research Professor in the Department of Metallurgical and Materials Engineering. Dr. Cornejo has over 20 years of experience in glass, glass-ceramics, and ceramic research and development.

Chuancheng Duan has recently joined the O’Hayre research group as a graduate student working on mixed conducting oxides. He has his BS from the Dalian University of Technology in China.

Cassi Sweet has joined the Packard research group as a graduate student working on a project to improve efficiency and lower cost of one-sun PV by new growth and processing methods with III-V materials. She has her B.S. in Engineering Physics and M.S. in Materials Science from CSM.

Graduate students Adam Stokes and Lauren Vitti have joined the Gorman group.

Recent Graduates & Advancements

Postdoctoral associate Dr. Mukesh Kumar has accepted a position as an Applications Engineer at Hysitron, Inc.

Dr. April Corpuz defended her Ph.D. in Chemistry in the fall of 2012 and is currently working as a postdoctoral researcher with Prof. Will Medlin's group in the Department of Chemical and Biological Engineering at CU Boulder conducting research on surface catalysis.

Dr. Harvey Guthrey defended his Ph.D. in Materials Science in March 2013 and is currently working as a research scientist at NREL.

Dr. Badri Narayanan defended his Ph.D. in Materials Science in June 2013.

Dr. Robert Pasquarelli defended his Ph.D. in Materials Science in the fall of 2012 and is currently serving as a postdoctoral researcher at Technische Universitat Hamburg-Harburg (TUHH) conducting research into the thermal stability of photonic structures as part of a SFB.
Dr. Prakash Periasamy defended his Ph.D. in Materials Science in October 2012 and is currently an advisory engineer/scientist at IBM.

Dr. Subramanian Ramalingam defended his Ph.D. in Materials Science in March 2013. He is currently working as a postdoctoral researcher with the Reimanis group while applying for industry positions.

Dr. Michael Sanders successfully defended his Ph.D. in Materials Science in March 2013 and was awarded a postdoctoral researcher position in the Advanced Energy Materials Laboratory under Prof. Ryan O’Hayre. He is conducting research on ceramics for solar thermochemical hydrogen production.

Dan Clark defended his M.S. in Materials Science in October 2012 and has continued research for his Ph.D. thesis in the O’Hayre group.

Sarah McMurray (M.S. Materials Science, 2012) is currently employed as an engineer at ADA Carbon Solutions.

Amy Morrissey defended her M.S. in Materials Science in March 2013 and has continued research for her Ph.D. thesis in the Reimanis group.

Kory Riskey defended her M.S. in March 2013 and is currently conducting research in Prof. Taylor’s group while job searching.

Anthony Martinez accepted a position at Honeywell Aerospace as a Material and Process Engineer.

Kayla Raddant Rankin accepted a position at Timken Company as a Steel Business Associate.

Awards, Honors, & Achievements

Prof. Brian Gorman has been elected as a Director on the Microanalysis Society Executive Council.

Prof. Brian Gorman was appointed Director of the Interdisciplinary Materials Science Program.

Prof. Hongjun Liang has received NSF funding for a project to develop nanoparticle-pinched polymer brushes for cost-effective microalgae harvesting and biofuel production. Profs. David Wu and Matthew Posewitz from Chemistry will be participating in the study.
Prof. Ryan O'Hayre was awarded a Chinese Academy of Sciences Visiting Professorship for Senior International Scientists. This competitive and prestigious appointment allowed him to spend his sabbatical at the Dalian Institute of Chemical Physics, which is one of the largest and most well-known CAS labs in China (similar to the US National Lab system). He was involved with fuel cell, catalyst and membrane research.

Prof. Ryan O'Hayre is serving on the organizing committee for the Solid State Ionics-20 Conference to be held June 15-19, 2015 in Keystone, CO.

Prof. Ryan O’Hayre, Prof. Jianhua Tong, Dr. Michael Sanders, Jason Fish, Ann Deml, Dan Clark, and Stefan Nikodemski all attended and presented at the Solid State Ionics-19 Conference in Kyoto, Japan.

Prof. Corinne Packard gave an invited talk at the TMS Annual Meeting in March 2013 on tuning electronic tunneling using depth-controlled nanoindentation. A publication detailing this work has been accepted at the Journal of Materials Research.

Prof. Ivar Reimanis has been selected as the third Herman F. Coors Distinguished Professor of Ceramic Engineering in the Department of Metallurgical and Materials Engineering at the Colorado School of Mines.

Prof. Svitlana Pylypenko has been elected as a board member for the local AVS chapter.

Dan Clark and Jason Fish were recipients of the SSI-19 Young Researcher Supporting Program funds to attend the Solid State Ionics-19 Conference in Kyoto, Japan.

Ann Deml and Dr. Subramanian Ramalingam received sponsorship to attend a workshop on Ethnic Diversity in Materials Science and Engineering in Arlington, VA in December 2012.

Ann Deml was featured in a REMRSEC promotional video "Inside REMRSEC: Advancing the Frontiers of Renewable Energy Materials Research" which also included Archana Subramaniyan, Meng Shang, Korey Riskey, and Dan Clark.

Jason Fish spent a year as a guest PhD student in the Department of Energy Conversion and Storage at the Risø Campus of the Technical University of Denmark (DTU) from Aug. 2011 through November 2012. During his stay he
synthesized and characterized novel ceramic composite materials for hydrogen gas separation membranes, in particular exploring the spark plasma sintering technique. Also while abroad, Jason forged a collaboration with electron microscopists at the University of Lund in Sweden to study the phase distribution and microstructure of these composite membrane materials.

**Jason Fish** was awarded best poster in the MME Department at the 2nd annual Conference on Earth and Energy Resources hosted by CSM's Graduate Student Association in February 2013.

**Prakash Periasamy** received third prize for his poster presentation at the Rocky Mountain Region American Vacuum Society in 2012.

**Kevin Wood** was selected as a fellow to attend the Joint US/Africa Materials for Sustainable Energy School in Ethiopia in December 2012. Prof. Ryan O’Hayre also acted as an invited lecturer at the same School.

**Scott Harper** received the school-wide Waltman Award. The Waltman Award winner is recognized by CSM for his/her school and community activities, academic excellence and promise in the future. Scott also spent last summer in India conducting studies on yttria-stabilized zirconia at the Indian Institute of Science in Bangalore facilitated by contacts of Prof. Ivar Reimanis.

**Matt Musselman** was featured in the CSM Energy and the Earth 2013 publication.

**Ray Oberbroeckling** accepted a position at Paterson & Cook for a summer internship.

**Paul Wilson** was part of the CSM MME team to win the 2013 TMS Materials Bowl held during the annual TMS Conference.

**New Equipment**

The Thermal Analysis Lab has recently acquired new Setaram SETSYS Evolution Simultaneous Thermal Analysis (STA) equipment using funds from sources across the MME department and the campus at large. This purchase greatly improves the capabilities of the lab with an increased mass resolution for thermogravametric analysis and greatly simplified gas control.
The Advanced Energy Materials Laboratory recently purchased a four-channel gas chromatography instrument with resolution on the order of 10 ppm. The instrument, housed in HH 371, is being used for hydrogen permeation and water-splitting studies.

Publications


J.S. Fish, S. Ricote, T. Holgate, F. Lenrick, R. Wallenberg, R. O’Hayre, and N. Bonanos, “Synthesis by Spark Plasma Sintering of a BaCe0.2Zr0.7Y0.1O3-δ/Sr0.95Ti0.9Nb0.1O3-δ (BCZY27/STN95) Composite Material for Hydrogen Separation Membranes”, Journal of Materials Science, 48, 6177-6185 (2013).

P. Joghee, S. Pylypenko, T.S. Olson, A.A. Dameron, A.R. Corpuz, H.N. Dinh, K. Wood, K. J. O’Neill, K. E. Hurst, G. Bender, T. Gennett, B. S. Pivovar,


M. Shang, J. Tong, and R. O'Hayre, “A Promising Cathode for Intermediate Temperature Protonic Ceramic Fuel Cells: BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-δ}”, in press, RSC Advances.

M. Shang, J. Tong, and R. O’Hayre, “A Novel Wet-Chemistry Method for the Synthesis of Multicomponent Nanoparticles: A Case Study of BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-δ}”, Materials Letters, 92, 382 (2013).


“Tribal Adornment” by Cassi Sweet
Microscopic image showing a (100) fracture surface of a flexible gallium arsenide flake on a thin nickel substrate. Ornate reflection patterns originate from the serrated topology.