2012 Internal Conference

ccac

COLORADO CENTER FOR ADVANCED CERAMICS

Thursday & Friday, August 9-10

PROCEEDINGS

PROGRAM & PROCEEDINGS

COLORADO CENTER FOR ADVANCED CERAMICS
4th Annual Meeting

Estes Park, Colorado

AUGUST 9-10, 2012

Organized by
Amy Morrissey
Liangju Kuang
Taylor Wilkinson
Sarah McMurray


Amy Morrissey


Liangju Kuang


Taylor Wilkinson


Sarah McMurray, Chair

Welcome to the meeting,

I'm very pleased to welcome all of you to this year's CCAC Student Conference, our 4th annual. I hope you will enjoy the variety of scientific research, speakers, and this beautiful setting.

I'd like to begin by thanking the NSF, CoorsTek, and FEI for their generous sponsorship of this event. I sincerely hope research collaborations, and sharing between academia and industry will continue to grow from these promising relationships. I look forward to hearing our guest speaker, Ozan Ugurlu from FEI.

Additionally, I'd like to thank our Center Director, Prof. Ivar Reimanis. His guidance and mentoring throughout this process has been superb. I hope you all will join me in thanking him, and congratulating him on becoming the third Herman F. Coors Distinguished Professor and Endowed Chair of Ceramics. A great deal of thanks also goes to Alice Jensen for her help with all the tedious financial and travel issues. I also owe a debt of gratitude to the rest of my committee: Amy Morrissey, Liangju Kuang, and Taylor Wilkinson. The support of these ladies has been invaluable.

Last but not least, thanks to all of you for your hard work. I happily anticipate hearing about your research, and getting to know you better in this lovely venue.

Warm Regards,
Sarah McMurray
Conference Organizing Chair, CCAC 2012 Student Conference.

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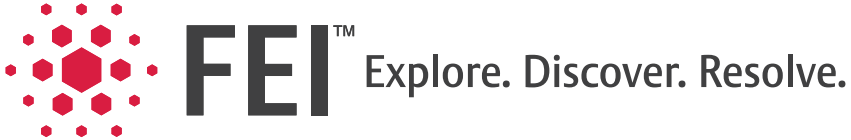

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Thursday's Overview

3.00p Opening remarks from the Chair

3.05p CCAC Introduction, Ivar Reimanis

3.20p FEI Guest Presentation

Ozan Ugurlu will speak on EDS and STEM, and present case studies on on SrTiO3-PbTiO3 intfaces and InAlAs-InP.
Chair, Dr. Dave Diercks

4.00p FEI Q&A

4.15p Break for check-in

4.30p Poster Showcase

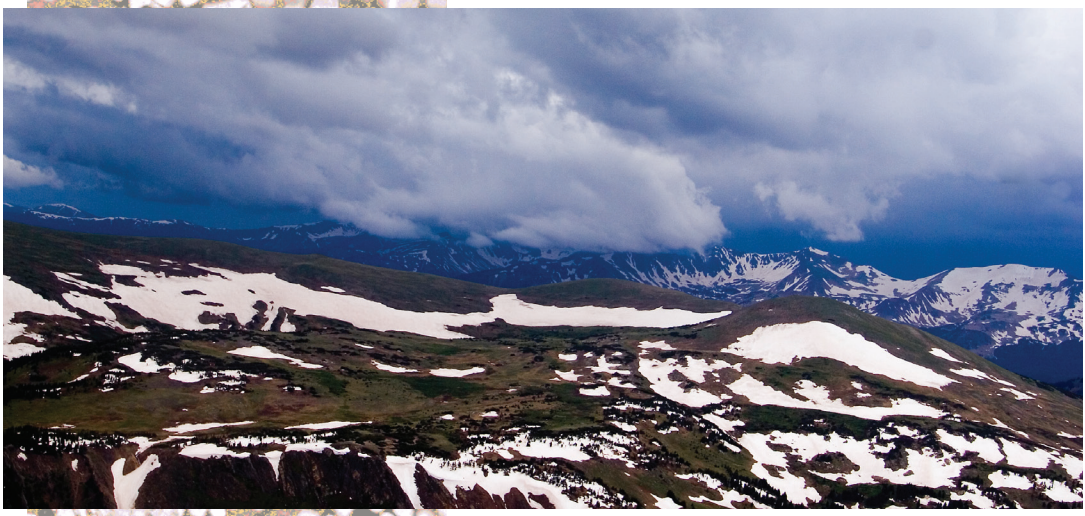
Daniel Clark, Brian Davis, Ann Deml, Harvey Guthrey, Sarah McMurray, Matt Musselman, Stefan Nikodemski, Prakash Periasamy, Subramanian Ramalingam, Archana Subramaniyan, and Logan Ward.
Chair, Dr. Jianhua Tong

5.00p Group photo

5.15p Dinner

Dinner served from 5-7.30p in common dining room.

7.15p Poster Session & Dessert



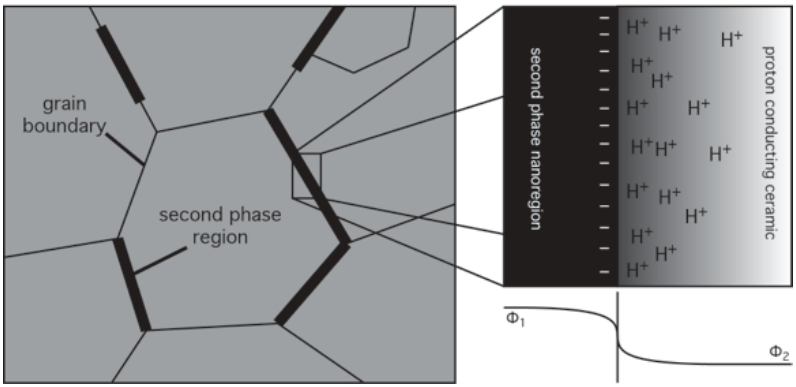
Friday's Overview

7.00a	Breakfast served until 9a
9.00a	Oral Session 1
	Mukesh Kumar, Taylor Wilkinson, Wan Zheng, and Liangju Kuang. *Chair, Corinne Packard.*
10.00a	The Daniel Clark Memorial T-shirt Snack Break
10.15a	Oral Session 2
	Aaron Miller, Badri Narayanan, Michael Sanders, and Yi Ke *Chair, Ryan O'Hayre.*
11.15a	Snack Break & Faculty discussion
11.30a	Thank you
11.35a	Closing Remarks & Awards
11.50a	Check-out
12.00p	Closing lunch provided!

Nanoionic enhancement of $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_3$-δ using reduced nickel

D Clark[1], J Tong[1], A Morrissey[1], I Reimanis[1], and R O'Hayre[1]

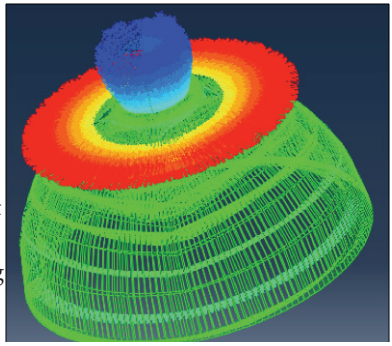
[1]Colorado School of Mines, Golden, Colorado



Over the past several decades, it has been shownthat interfaces can drastically change the ionic transport properties in many solid-state ion conducting systems, leading to a change in bulk material behavior. Using nickel oxide in the proton conducting $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_3$-δ(BCZYYb) not only dramatically increases the sinter ability, but upon reduction ,causes the formation of nickel nano-regions oriented along the grain boundaries. These nickel regions cause a space charge layer to form, having profound effects (up to 30x enhancement) on the BCZYYb's conductivity, especially at lower temperatures (50-350 °C). The conductivity has been examined via electrochemical impedance spectroscopy, along with concentration cell and isotope measurements to examine the dominant charge carriers. The nickel has been characterized via scanning and transmission electron microscopy as well asmagnetometry experiments to define the state of the nickel.

Mechanical Properties of the SiC Shell in TRISO-Coated Particles

BC Davis[1], L Ward[1], B Gorman[1], I Reimanis1, J Youngsman[2], D Butt[2], B Fillery[3]
[1] Colorado School of Mines, Golden, Colorado [2]Boise State University, Boise, Idaho [3]Coffey Mining, West Perth, Australia



Direct conversion of a hydrocarbon feedstock (e.g. natural gas) to electricity in a fuel cell system, either by pre-reforming or direct reforming in a solid oxide fuel cell (SOFC), is a major objective of the fuel cell community. However, carbon formation and the resultant catalyst deactivation of reforming catalysts is a significant problem in hydrocarbon reforming and direct reforming of hydrocarbon gases in SOFC systems. Carbon formation on catalysts has been studied extensively for many years and much effort is being put into developing catalysts that are resistant to carbon formation. Although many promising catalysts have been developed, catalyst deactivation by carbon formation remains a major obstacle to developing robust SOFC systems operating on natural gas and logistics fuels.

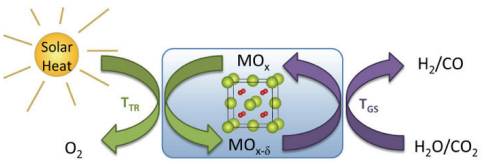
The objective of this project is to develop a low cost sensor for detection of carbon formation (coking) on reforming catalysts in SOFC systems. The device will seek to detect the onset of carbon coking before it begins to take place on the reformer; preventing damage and/or reduced effectiveness of the catalyst. The sensor will detect the presence of carbon formation by measuring the electrical impedance across a thin catalyst layer. Carbon formation on the catalyst layer increases electrical conductivity across the catalyst, leading to a response from the sensor that alerts the system operator or control system that a coking condition exists. Prototype sensors have been built and demonstrated in the Colorado Fuel Cell Center (CFCC). Once developed and initially tested, the sensors will be tested in SOFC reforming environments at the CFCC.

The current sensor design employs a Nickel catalyst supported by a partially stabilized zirconia substrate. The substrate is uniaxially pressed into a circular disk, and a Dimatix “drop on demand” printer is used to deposit the catalyst layer onto the substrate surface. These prototype sensors are then inserted into a tube furnace for conductivity measurements, where both the temperature and gas environment can be precisely controlled.

First-principles thermodynamic materials screening for solar thermochemical fuel production: The example of nonstoichiometric ceria

A Deml[1,2], J Tong[1], Charles Musgrave[2], Ryan O'Hayre[1]

[1]Colorado School of Mines, Golden, Colorado, [2]University of Colorado at Boulder, Boulder, Colorado



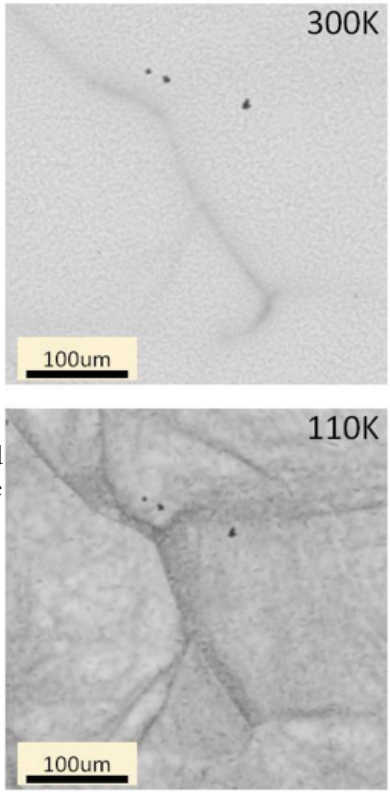
Solar thermochemical (STC) fuel production, a process which utilizes concentrated solar radiation to thermochemically split water and/or carbon dioxide molecules, is a viable, new technology which may provide clean and sustainable fuels and chemical precursors for commercial applications[1,2]. In a typical two-step thermochemical redox cycle, a metal oxide is thermally reduced at high temperatures and then reoxidized at lower temperatures by reaction with water and/or carbon dioxide to produce hydrogen, carbon monoxide, or syngas. Several material systems have been demonstrated to be effective in this application; however, these systems commonly exhibit slow reaction rates, material degradation, limited fuel production capacity, and/or complex cycling requirements[3,4].

In order to rapidly and cost effectively identify improved materials for STC fuel production, we attempt to implement a first-principles screening methodology developed by Meredig and Wolverton5 which identifies favorable changes in thermodynamic properties for both the thermal reduction and gas-splitting redox reactions. We apply this computational approach first to the example of nonstoichiometric ceria (CeO2-x) which has been demonstrated to yield high-rate STC fuel production6 and remains an attractive material choice for this application.

We report progress toward first-principles calculations of the structural and thermodynamic properties for ceria using conventional and high-level hybrid density functional theory (DFT) functionals. We emphasize the complexity of the ceria system and propose further studies to elucidate understanding of the compositions and experimental conditions which lead to favorable thermodynamic properties for STC fuel production using ceria.

A Model for Electron Beam Induced Current Analysis of mc-Si Addressing Defect Contrast Behavior in Heavily Contaminated PV Material

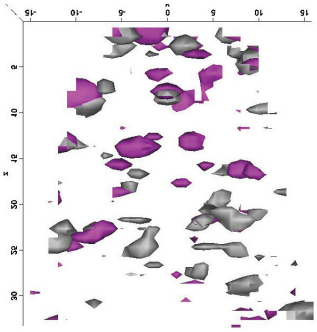
H Guthrey[1,2], B Gorman[1], G Coletti[3], M Al-Jassim[2]
[1]Colorado School of Mines, Golden, Colorado, [2]National Renewable Energy Laboratory, Golden, Colorado [3]ECN Solar Energy, Petten, Netherlands



Much work has been done to correlate electron beam induced current (EBIC) contrast behavior of extended defects with their character and degree of impurity decoration. However the existing models fail to fully account for recently observed contrast behavior of defects in heavily contaminated mc-Si PV cells. We have observed large increases in defect contrast with decreasing temperature for all electrically active defects regardless of their initial contrast signatures at ambient temperature. This negates the usefulness of the existing models in identifying defect character and levels of impurity decoration based on the temperature dependence of the contrast behavior. Through considerations of the interactions of transition metal impurities with the silicon lattice and extended defects we attempt to provide an explanation for these observations. Our findings will enhance the ability of the PV community to understand and mitigate the effects of these types of defects as the adoption of increasingly lower purity feedstock for mc-Si PV production continues.

3D Atomic scale imaging of dopants in quantum structed Si

SG McMurray[1], B Simonds[1], D Diercks[1], I Perez-Wurfl[2], Y Heng-So[2], R Kirchhofer[1], PC Taylor[1], BP Gorman[1]
[1]Colorado School of Mines, Golden, Colorado, [2]The University of New South Whales

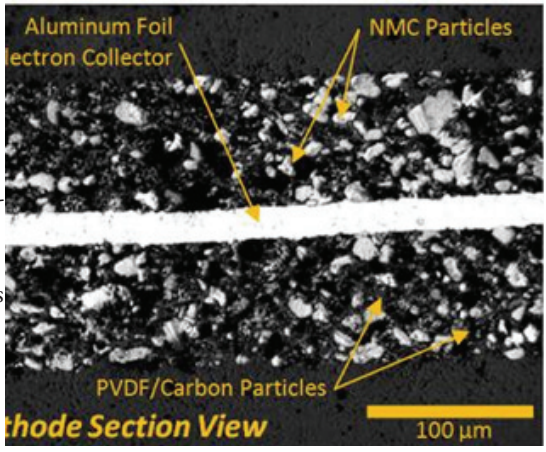


Atom Probe Tomography (APT) has lately been coming to the forefront of characterization techniques, as several developments have made for robust, commercial instruments, with the capability of high throughput. A timed laser pulse evaporates a positively biased needle-shaped specimen one surface atom at a time. This thermally activated evaporation is key to obtaining data on less conductive materials, as it reduces the stress caused by a traditional voltage pulse [1]. Here, the potential of APT is explored in analyzing phosphorous doped silicon quantum dots in an SiO_2 matrix. Silicon (Si) quantum dots (QD) are an important technological material for the future of many semiconducting devices, including light-emitting diodes and photovoltaic (PV) cells [2]. A common need for any of these devices is a p-n junction to separate carriers, which requires impurity doping of single QDs. Successful doping of dots is more problematic than in the bulk due to unfavorable thermodynamic conditions [3] and studying the location of these dopants is experimentally challenging. APT has a distinct advantage over other analytical techniques in that in can spatially resolve single dopants on single QDs. In this study, phosphorous was chosen as a dopant because at the preferred annealing temperature (~1100 C), it has a high solid solubility in Si, and is a well-known shallow dopant in c-Si [4]. Electron paramagnetic resonance (EPR) data suggests that P is not present within the as-grown QD. A reasonable explanation for this is that P is passivating the surface defects, which is more energetically favorable than substitutional doping inside the QD. Subsequent analysis of the SiO2 / Si QD samples using APT provides direct evidence of P atmospheres formed around the QDs.

[1] D.N. Seidman et al. MRS Bulletin. 34 (2009) 717-724
[2] G. Conibeer et al., Thin Solid Films. 516 (2008) 6748-6756.
[3] G. Polisski et al., Physica, B, 273 (1999) 951
[4] Eun-Chel Cho et al., Nanotechnology. 19 (2008) 245201.
[5] This research was supported by the Renewable Energy Materials Research Science and Engineering Center at the Colorado School of Mines. BS would like to acknowledge The National Science Foundation East Asia and Pacific Summer Institutes program for travel support for the preparation of the materials used in this study (award# OISE-1108007). BPG gratefully acknowledges the support of the National Science Foundation grant #DMR-1040456 for support of the atom probe facilities at CSM

Micro-Scale Mechanical Properties of NMC Lithium Ion Cathodes

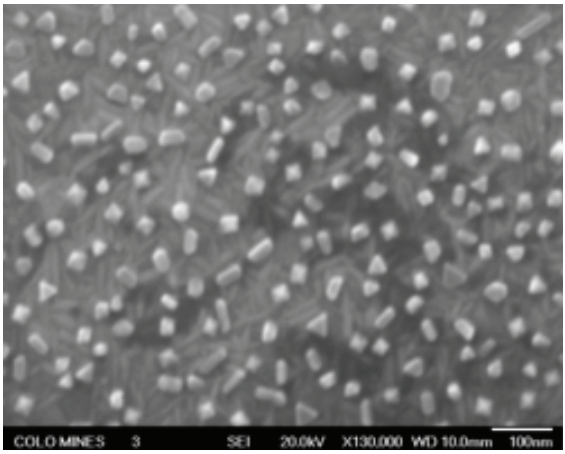
M Musselman[1], TM Wilkinson[1], K Smith[2], CE Packard[1,2]
[1]Colorado School of Mines, Golden, Colorado, [2]National Renewable Energy Laboratory, Golden, Colorado



$Li[Ni_{1/3} Mn_{1/3} Co_{1/3}] O_2$ (or NMC) is used as the active component in cathodes of some lithium ion batteries. The cathodes are a composite material, also containing PVDF (polyvinylidene difluoride) for adhesion and carbon particles for conductivity. NMC provides scaffolding allowing for the insertion and removal of lithium ions in the intercalation process, providing recharging capabilities. This is one of the major benefits of lithium ion battery technology. Intercalation produces mechanical forces that can cause a 10% to 40% change in volume of the NMC due to shrinking and swelling. Cycling of the batteries results in a mechanical degradation of NMC particles and their connection to other composite materials, 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 lifetime will require knowledge of the mechanical degradation of NMC 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 that need to be established in order to make these measurements include sample preparation of a composite material containing particles of varied hardness, grinding and polishing using non-aqueous media, and specialized nanoindentation methods to determine the overall mechanical properties. The relevance of these activities to obtaining accurate mechanical property values for lithium ion battery lifetime prediction will be discussed.

Engineering Nanoionic Interfaces by Pulsed Laser Deposition for Energy Conversion and Storage

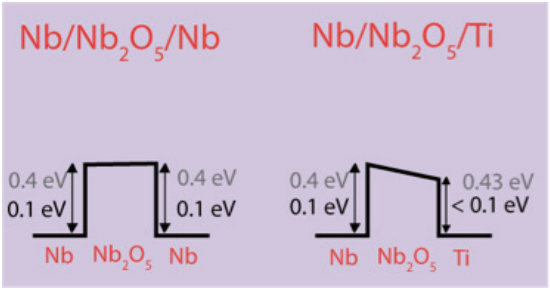
S Nikodemski[1], D Ginely[2], P Parilla[2], J Tong[1], R O'Hayre[1], J Berry[2]
[1]Colorado School of Mines, Golden, Colorado, [2]National Renewable Energy Laboratory, Golden, Colorado



The present work is concerned with harnessing the nanoionics phenomena which can be induced by engineering interfaces on the nanometer length scale. A disordered space-charge layer associated with these interfaces gives rise to high concentrations of charged defects, which can significantly enhance local ionic conductivity by up to eight orders of magnitude. These dramatic effects can, if appropriately harnessed, spark a paradigm shift in the design of electrochemical devices and materials including fuel cells, batteries, and membranes. Structures with well-defined interfaces including highly oriented and polycrystalline multilayer stacks as well as nanocomposite configurations were proposed in order to investigate the nanoionics effect in proton conducting ceramics. The deposition conditions required in order to produce high quality metal oxide and metallic films were first optimized by synthesizing thin layers via pulsed laser deposition utilizing a variety of temperatures and gas pressures. Thus far, the crystal structure, composition, morphology, and surface roughness characteristics of various ceramic and metallic thin films and nanocomposites have been characterized by XRD, FESEM, and AFM.

Barrier height measurement at metal/insulator interfaces

P Periasamy[1], J Gassman[2], K Rachut[2], J Berry[3], D Ginley[3], R O'Hayre[3], P Parilla[3], A Klein[2]
[1]Colorado School of Mines, Golden, Colorado, [2]Technische Universitat Darmstadt, Petersenstraße 32, Darmstadt, D-64287, Germany, [3]National Renewable Energy Laboratory, Golden, Colorado

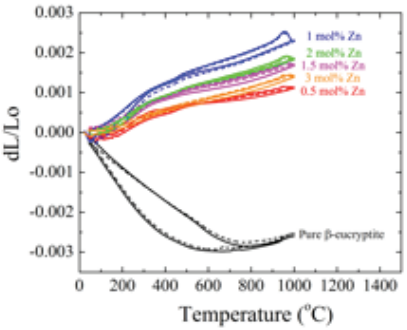


Electronic barrier heights in metal/insulator/metal rectifying structures are investigated via x-ray photoelectron spectroscopy by sequential deposition of the insulator (or metal) over-layer on top of metal (or insulator) under-layer in an ultra-high vacuum environment. Measured barrier heights are in good agreement with the material design criteria for MIM rectifiers, proposed by some of these authors in an earlier study. Electronic barrier height values for Nb_2O_5 (under-layer) and Nb, Ti, Cu and Pt as the over-layers are 0.1 (Nb2O5/Nb), 0 (Nb2O5/Ti), 0.6 (Nb_2O_5 /Cu) and 0.6 eV (Nb_2O_5 /Pt), respectively. The barrier height values for Al_2O_3/Nb and Al_2O_3/Pt are 4.6-6.1 and 5-5.3 eV, respectively. These reported values, first of its kind in MIM community, can be of high importance for high-frequency MIM device modeling efforts and for practical applications such as infrared detection, sensing and energy harvesting applications based on rectenna.

*Schematic representation of the experimentally measured (in bold) and theoretical barrier (in grey) height values for Nb/Nb_2O_5/Nb and Nb/Nb_2O_5/Ti interfaces. Photoemission interface experiments are used to measure the barrier height values.

Effect of Doping on the Thermal and Mechanical Behavior of β-eucryptite

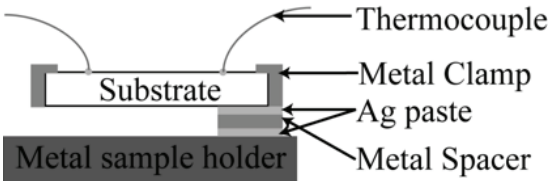
S Ramalingam[1], CE Packard[1], IE Reimanis[1]
[1]Colorado School of Mines, Golden, Colorado



The thermal expansion behavior of pure β-eucryptite and Zn-doped β-eucryptite (substituting Zn for Li), prepared by sol–gel methods and hot pressing, were investigated. β-eucryptite exhibits an anisotropic negative coefficient of thermal expansion (CTE) which leads to microcrack formation in sintered polycrystalline samples. This is manifested by the presence of a hysteresis in the thermal expansion curves. The hysteresis disappears when a small amount of Zn (0.5 mol% – 3 mol% Zn) is present. Furthermore, the bulk CTE increases significantly in magnitude (from –4 x 10-6 /°C for pure β-eucryptite to 1 x 10-6 /°C to 2 x 10-6 /°C) and is slightly positive in the range from 25°C to 1000°C. No difference in grain size was observed between the pure and doped samples, and all the ceramics exhibited high relative densities. It is likely that Zn substitutes for Li in the β-eucryptite structure and reduces the c-axis thermal expansion, thereby lowering the CTE anisotropy and lowering the tendency for microcracking.

Combinatorial temperature gradient for Cu-O thin film synthesis

A Subramaniyan[1,2], A Zakuyatev[1], V Stevanovic[1], J Perkins[1], D Ginley[1], R O'Hayre[2], S Lany[1]
[1]National Renewable Energy Laboratory, Golden, Colorado, [2]Colorado School of Mines, Golden, Colorado



Combinatorial thin film deposition explores wide spatial distribution of stoichiometries in one deposition through composition gradient. However, in a conventional combinatorial synthesis, the accessible phases are restricted to a single temperature point on a phase diagram. Introducing temperature gradient orthogonal to the compositional gradient on a substrate has the advantage of accessing a temperature region (as opposed to a single point) of a phase diagram.

In this work, temperature gradient across the substrate was achieved via a modified sample holder setup in such a way that it can be incorporated as a plug-in module into almost any existing thin film deposition chamber. Cross-sectional schematic view of the modified sample holder set up is shown in Figure 1. One end of the substrate was glued to the metal spacer mounted on top of a metal sample holder using Ag paste. The metal spacer was used to establish temperature gradient from the glued to the free end of the suspended substrate. A metal clamp holds securely the suspended substrate. The actual temperature at different spatial locations of the substrate was measured in-situ in a vacuum chamber using k-type thermocouples. Using this setup, temperature gradient of 300°C (from 300 – 600°C) across the 50 mm long substrate was observed. Based on the measured temperature profile and the fitted power law, the substrate temperatures at 44 different spatial locations were calculated.

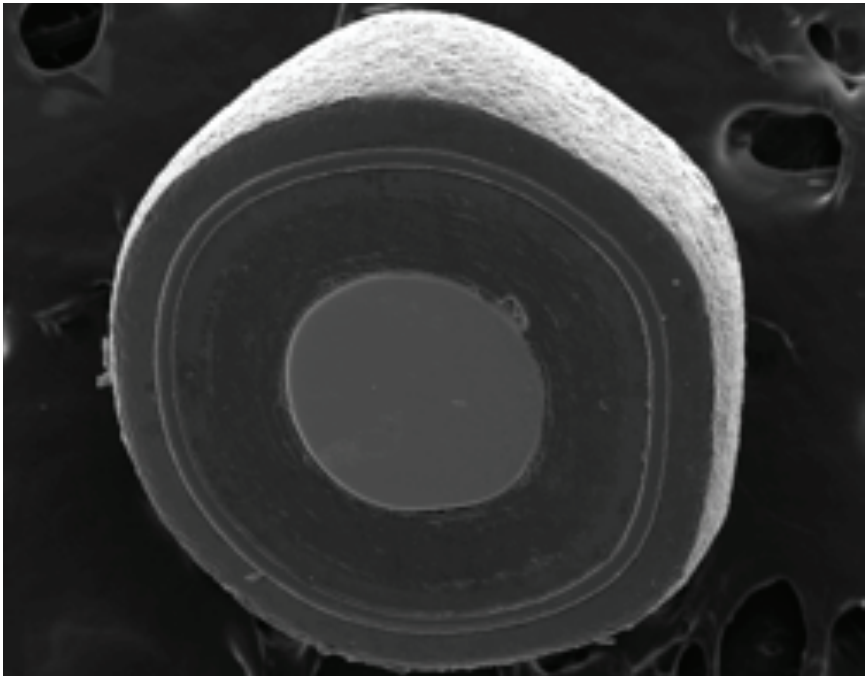
To demonstrate the advantage of employing a temperature gradient across the substrate, we investigated a pO_2 vs. T phase diagram of Cu-O system at a temperature range of 300 – 600°C. Cu2O films were deposited using Pulsed Laser Deposition from CuO target, and 400mJ laser energy at various oxygen partial pressures (0.01 – 10 mtorr). The resulted films testified the formation of various copper oxide phases including Cu_2O, CuO and mixture of CuO and Cu_2O in one deposition. In addition to temperature and oxygen partial pressure, it was found that there are other significant parameters including total pressure and target surface that determines the resulting phase composition.

This research is supported by the U.S. Department of Energy, office of Energy Efficiency and Renewable Energy, as a part of a Next Generation PV II project within the SunShot initiative.

Figure: Cross-sectional schematic view of the modified sample holder set up to facilitate temperature gradient across the substrate.

Composite Nanoparticle-Directed Cost-Effective Microalgae Harvesting for Biodiesel Conversion

LJ Ward[1], BC Davis[1], I Reimanis[1], B Gorman[1], JM Youngsman[2], DP Butt[2]
[1] Colorado School of Mines, Golden, Colorado [2]Boise State University, Boise, Idaho



Tristructural-isotropic (TRISO) particles are used as nuclear fuel for very high temperature reactors. One particle consists of a uranium-dioxide sphere TRISO-coated with two forms of carbon and dense SiC. The SiC layer functions as a containment vessel for fission products created by the uranium core. This study investigates the mechanical properties of the SiC layer and the practicality of using crush testing. Crush tests were performed to calculate the failure stress for SiC hemisphere shells. Fracture mechanics, statistical analysis and computer modeling were used to investigate stress concentrations within the shell and the impact of geometrical features that influence the fracture behavior. The results reveal the advantages and important considerations that must be made using crush tests for characterizing the mechanical properties of SiC in TRISO-coated nuclear fuels.

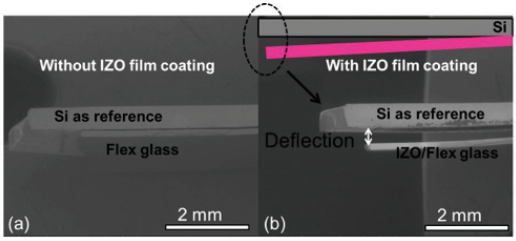
In-situ SAXS Analysis for Catalyst Durability

[1]K Wood
[1]Colorado School of Mines, Golden, Colorado

In situ small-angle x-ray scattering (SAXS) is used to investigate the electrochemical durability of Pt-Metal (Pt-M) catalysts sputtered onto nitrogen-modified high surface area carbon powder. The results demonstrate that nitrogen modification promotes catalyst durability through reduction of nanoparticle dissolution and coarsening. Although particle sizes of Pt-M on high surface area carbon supports can be difficult to determine with transmission electron microscopy (TEM), a novel SAXS method has been employed to calculate particle size. SAXS analysis shows that the Pt-M nanoparticle size distribution remained stable for 3000 electrochemical cycles after nitrogen modification, whereas the unmodified support material leads to Pt-M nanoparticle instabilities. These results for industrial-relevant catalyst/support architectures underscore the potential of nitrogen-modified carbon support structures for enhanced Pt-M catalyst durability.

Measuring residual stress in Indium Zinc Oxide thin films for next generation flexible electronics

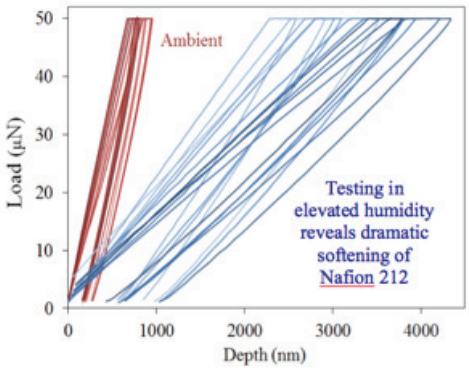
M Kumar[1], T Gennette[2], JD Perkins[2], DS Ginley[2], CE Packard[1,2]
[1]Colorado School of Mines, Golden, Colorado [2]National Renewable Energy Laboratory, Golden, Colorado



Low residual stress in transparent conducting oxides (TCO's) thin films is required for the mechanical reliability of next generation flexible devices and is intimately associated with the film's microstructure resulting from growth parameters. Variations in growth parameters have also been shown to affect the optoelectronic properties of TCO's thin film. In this study, we apply design of experiment (DOE) principles to investigate the influence of several growth parameters and their interactions: sputtering power, growth pressure, oxygen partial pressure (PO_2) and RF/DC. Residual stress is measured using a beam deflection technique in an attempt to establish a correlation with electrical conductivity in the indium-zinc-oxide (IZO; In_2O_3:ZnO = 87:13 wt%) thin film system. The result reveals that the residual stress and electrical conductivity in IZO thin film spread over a wide range of +2 GPa (tensile stress) to -4.9 GPa (compressive stress) and 0.6 S/cm to 2600 S/cm, respectively. The power, pressure and RF/DC are observed the main input parameters affecting the residual stress while all four input parameters; power, pressure, RF/DC and PO_2 have significant effect on electrical conductivity. The DOE approach allows us to write a generalize model equation not only including the main effect of growth parameters but also their two-way interactions. These results may not only help to establish a correlation between residual stress and electrical conductivity in IZO thin film but also to support better reliability prediction and better performance for flexible TCO thin films for next generation flexible electronics.

Using a variable humidity environment to test the mechanical properties of polymer electrolyte membranes via nanoindentation

TM Wilkinson[1] and CE Packard[1]
[1]Colorado School of Mines, Golden, Colorado



While polymer electrolyte membrane (PEM) fuel cells continue to develop as a means of alternative energy, the need for quick, high through-put screening to test the reliability of the membranes becomes more important. One of the most crucial aspects of environment simulation for these materials is humidity due to the fact that water causes the polymer to swell and ultimately affects the mechanical properties and failure point of these energy sources.

By using modified nanoindentation techniques, the mechanical properties of materials can be characterized in a way that mimics the humidified conditions experienced during fuel cell operation. Nanoindentation is a technique that applies small loads with a diamond tip to a sample while tracking the displacement of the tip into the sample (within the nanometer range). The loading and unloading curves (a function of force and displacement) allow for the modulus and hardness of the sample to the calculated. Accuracy of the measurements however are dependent on the stability of the testing environment; both humidity stability as well as drift must be monitored.

Directed assembly of nanoparticles through "click reaction"

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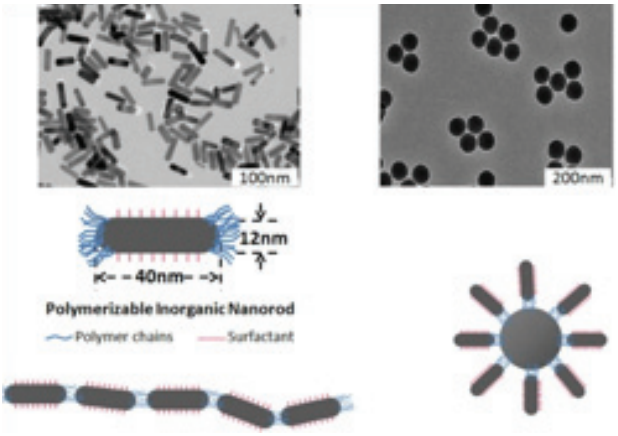

Organized arrays of nanoparticles show optical, electronic, and magnetic properties that are originated by collective interactions of individual nanoparticles. Self-assembly has been studied widely as an efficient method for producing nanostructures with complex, hierarchical architectures. However, the structures formed by this strategy are hard to be predicted and controlled. We are developing a novel strategy to achieve directed assembly of nanoparticles through "click reaction". Complex architectures formed through the reaction between azide- and alkyl-terminated NPs are not only stable, but also quantitative predictable, because the NPs are assembled by high fidelity covalent bond formation. We show that this method is applicable to organize nanoparticles with different sizes and shapes, such as silicon nanospheres and gold nanorods. We expect that individual nanoparticles can be directed to form different architectures, such as linear, branched, and cyclic nanostructures by simply controlling the conditions of click reactions between functionalized nanoparticles. The successful outcome of this study will open a new bottom-up avenue to fabricate nanomaterials-based devices.

Synthesis and characterization of polymer membranes to support membrane protein functions

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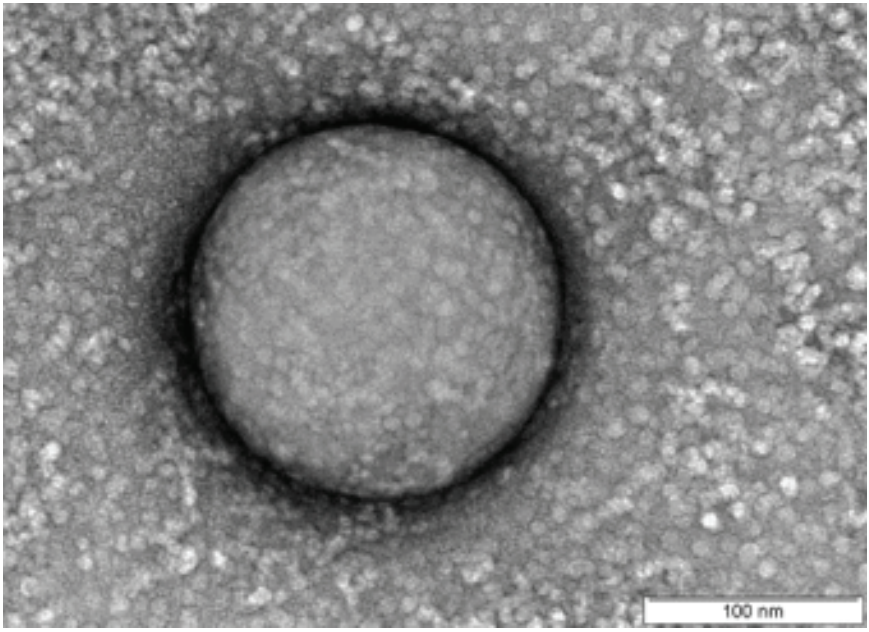

It is well known that membrane proteins are Nature's examples of nanoengineering for matter transport, energy conversion, and information processing. Harnessing MP functions directly in engineering systems has the potential to create extraordinary biotechnological opportunities, but the lability of biomembranes makes them unsuitable for use in a broad range of harsher, non-biological conditions. To study the effect of polymer glass transition temperature (T_g) on the self-assembly behavior of membrane proteins, a series of lipid-mimicking polymer membranes (PDMS, PMA, and PS) were synthesized by controlled/living free radical polymerization with well-defined structures. Both cationic and anionic polymer membranes were synthesized to study the effect of charge interactions. The resultant products were characterized by Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC), Electron Microscopy Transmission (TEM), and Dynamic Light Scatting (DLS).

Using X-Ray Diffraction to Characterize Ceramic

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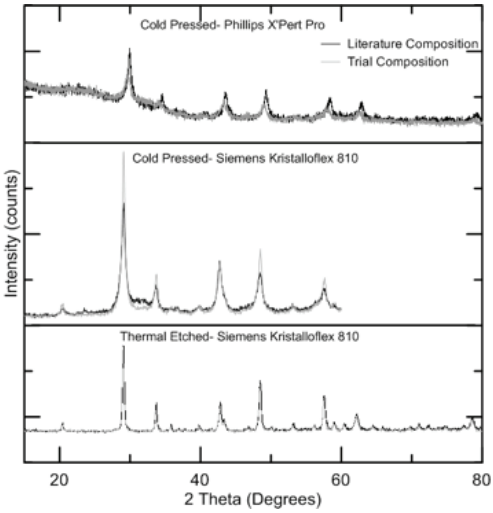

X-Ray Diffraction (XRD) is a technique commonly used in many fields of research, and can provide a wide range of valuable information essential to the characterization of ceramic materials. Understanding the capabilities of XRD and how to properly analyze the generated data can offer insight to the crystal structure and confirm the chemical makeup of a material. This information is often critical in explaining material behavior such as mechanical, optical, or electrical properties. In this presentation, a brief background of XRD will be provided, followed by a description of proper procedure to follow and common errors to avoid in order to produce reliable results. Analysis of experimental results obtained from the diffraction of MgO-Y_2O_3 spinel samples will be discussed. These experimental results will be used to show the characterization capabilities of X-Ray Diffraction, including phase identification and quantification. Other commonly used characterization capabilities, such as stress analysis and determination of single crystal orientation, will also be discussed.

Radiation effects and tolerance mechanism in β-eucryptite

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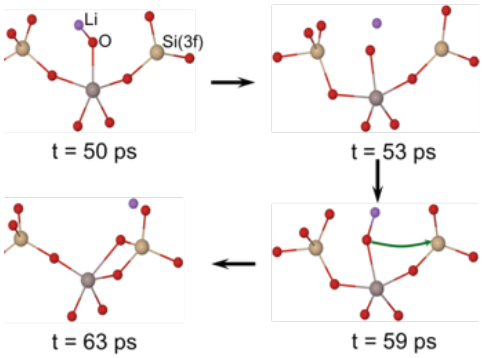

Recent electron microscopy studies have revealed that solid solutions based on β-eucryptite ($LiAlSiO_4$) exhibit low sensitivity to neutron radiation, which makes them promising candidate materials for reactor blankets and solid state breeders in nuclear fusion reactors. Apart from the radiation tolerance, β-eucryptite has exceptional thermal shock resistance owing to its near-zero (slightly negative) coefficient of thermal expansion. This unique thermal property makes it suitable for use in fuel coatings in order to avoid cracking during thermal cycling. It has been empirically observed that high lithia content in lithium aluminum silicate (LAS) ceramics is associated with improved tolerance to radiation. The atomic scale mechanisms responsible for the radiation tolerance in LAS ceramics are however, largely unknown. In this study, we employ atomistic simulations to characterize the radiation induced structural damage in β-eucryptite, and gain a fundamental understanding of the atomic-scale phenomena that occur in response to radiation. Using molecular dynamics simulations based on a reactive force field, we have found that upon radiation dosage of 0.21 displacements-per-atom (dpa) or less, the structure largely retains its long-range order while exhibiting (a) disordering of the Li atoms, (b) distortion of the Si and Al tetrahedra defined as the change in their oxygen-coordination number, and (c) tilting of the Si and Al tetrahedra with respect to one another. We find that Si tetrahedra that distort to SiO_3 during irradiation recover significantly upon thermal relaxation, and provide the mechanism for this recovery (as shown in the figure). This mechanism consists in the tilting of AlO_5 polyhedra formed by irradiation so as to satisfy the oxygen-coordination of distorted Si tetrahedra. Large dosage (0.43 dpa) results in significant increase of the concentration of Si-Al antisite defects, which renders the tolerance mechanism inefficient and leads to amorphization. These results have implications in designing radiation tolerant materials based on LAS ceramics.

Numerical modeling of multi-species transport permeation in proton conducting membranes

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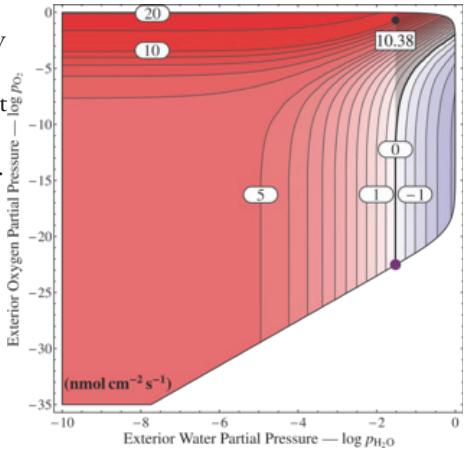

To understand conduction and permeation phenomena in many important solid-state ionic systems, the effects of multiple charged defect species (e.g., both mobile ions and electronic defects) must be captured. Analytically modeling this multi-species transport behavior typically requires a number of limiting assumptions that restrict the circumstances under which the model can be applied. However, the problem can also be formulated and solved computationally, greatly reducing the number of assumptions that must be made. In the present work, a numerical approach is therefore implemented to model multi-species permeation in proton-conducting perovskite systems and is used to explore multicomponent permeative transport across a very wide range of operating conditions. A mapping method is developed that allows the large amounts of information produced by the model to be presented in a graphical manner that allows for the rapid analysis of a wide range of possible experimental conditions. This method provides detailed insight into the fundamental nature of permeative chemical transport in these materials and also serves to delineate the conditions under which unusual effects such as "uphill" chemical transport occur in these systems. Validation of results can be done with permeation experiments using atmospheric mass spectroscopy.

The Influences of Defects on Carrier Generation and Transport in ZnMgO

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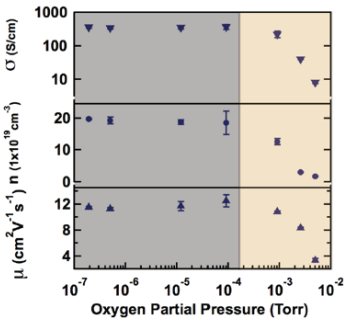

Wide-bandgap metal oxides such as Zn(Mg)O have the potential to enhance the performance of many optoelectronic devices. Here, we report on record-high conductivities (480 S/cm) in $Zn_{0.7}Mg_{0.29}Ga_{0.01}O$ (with 3.9 eV optical band gap) and present detailed studies on carrier generation and transport as influenced by the defect structure controlled by oxygen pressure during deposition and anneal, yielding insights needed to optimize the properties of this complex mixed-metal oxide for specific applications. Films were grown as a function of oxygen partial pressure and subsequent controlled-atmosphere anneals.

Obtaining high conductivity in wide-bandgap ZnMgO is historically difficult. While band gap increases with increasing Mg content, this is generally accompanied by decreased conductivity σ, mobility μ, and carrier concentration n. To address this issue, Ga-doped ZnMgO thin films with 30 at. % Mg were grown using Pulsed Laser Deposition on sapphire in an Ar/O2 atmosphere. Oxygen partial pressure (PO_2) during the deposition was varied between 1×10^{-7} Torr to 5×10^{-3} Torr for different samples while keeping the total pressure constant. PO2 had a significant influence on both electron concentration (n) and Hall mobility (μ). A maximum conductivity (σ) of 350±14 S/cm, was found in films deposited at PO_2 below 1×10^{-4} Torr. When films were subsequently annealed in low oxygen pressure (1×10^{-7} Torr), μ increased by ~36% while n remains effectively constant ($1.9\times10^{20}\pm0.1\times10^{20}$ cm^{-3}), leading to a maximum conductivity (σ) of 480±25 S/cm. The fundamental absorption onset of these ZnMgO:Ga samples was at 3.9 eV, which is 0.4 eV larger than the baseline ZnO:Ga samples. The combination of high conductivity and wide band gap is desirable for many optoelectronic devices such as OPV, OLED, and thin-film solar cells.

Photoluminescence, FTIR, and temperature-dependent Hall measurements were performed on the as-deposited and annealed films in order to understand how oxygen concentration (PO_2) during processing influences ultimate carrier concentration and transport. Temperature-dependent Hall showed little variation of μ or n for samples with conductivities higher than 200 S/cm, suggesting that the doping is degenerate. A broad photoluminescence peak centered at ~2 eV was universally presented in all films. This peak's intensity was inversely coupled with carrier concentration. HRTEM images were also taken on as-deposited samples and indicate that the samples are structurally similar, thus differences in PL emission and electrical properties may correlate to point defects.

CCAC News

Awards, Honors & Achievements

Professor Ivar Reimanis has been selected as the third Herman F. Coors Distinguished Professor and Endowed Chair of Ceramics in the Department of Metallurgical and Materials Engineering at the Colorado School of Mines. Ivar will continue to serve as the Director of CCAC.

Dan Clark won a NSF graduate student fellowship and also won a travel award to the 4th International Congress on Ceramics, where he presented an interactive poster on his work on nanoionics. Dan also won the CCAC t-shirt design contest & has a snack break named in his honor.

Robert Pasquarelli and April Corpuz successfully defended their PhD theses this summer.

Kevin Wood, Stefan Nikodemski, and Archana Subramaniyan successfullydefended their masters theses.

Ryan O'Hayre will be going on sabbatical to the Dalian Institute of Chemical Physics in Dalian, China as a Chinese Academy of Sciences Visiting Professor starting Aug 16th, 2012. He'll be coming back to CSM a few times in the fall and the spring to catch up with his students anddepartment activities.

Josh White successfully defended his PhD thesis in November 2011.

Robert Pasquarelli and Prakash Periasamy also just successfully defended their PhD dissertations.

Rita Kirchhofer obtained her Professional Engineering License from the State of Colorado in "Materials Science". License Number: 45977.

Sarah McMurray, Seth Griffiths, and Rachel Madland defended their Masters theses.

Sarah McMurray won funding to attend the Ettore Majorana Foundain and Center for Scientific Culture's school on Materials for Renewable Energy in Erice, Sicily, this summer.

Liangju Kuang won the Chevron-C2B2 Graduate Fellowship(2012-2013).

Wan Zheng won the Materials Science Fellowship.

Prof. Liang research group received a NSF-REMRSEC seed grant on the development of biohybrid polymer membranes with solar-driven proton-pumping performance.

Prof. Liang research group received a grant from Colorado Bioscience Association on the pilot studies to commercialize their patented technology on cost-effective microalgae harvesting.

Prof. Hongjun Liang's research project on the development of artificial cells for anti-cancer drug delivery has been designated by the CSM Proof of Concept Board for special funding. The Board recognizes projects that could bring technology to the commercial marketplace.

New Researchers

Yunjiang Jiang will be joining Prof. Hongjun Liang's group as a graduate student working on drug delivery system. He got his BS from Sichuan University, China, in 2011 and then worked as a research assistant in University of Science and Technology of China for one year.

Aaron White is working on transparent ceramics with Prof. Reimanis

Yachao Chen is working on mechanical behavior of ceramics with Prof. Reimanis

Brian Campbell Davis is working on finite element modeling of mechanical behavior of ceramics.

Einar Vollsted from the University of Oslo, Norway, will be joining Ryan O'Hayre's group as a visiting student for ~3 months starting Sept 2nd, 2012. He will be working with Michael Sanders on permeation measurements in protonic ceramics.

New Equipment

Brian Gorman's group has the LEAP 4000XSi up and running. The Dynamic Atom Probe is currently being built. And the FIB/SEM unit now as an in-situ AFM attachment, and is soon to have NSOM capabilities as well.

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