

2010

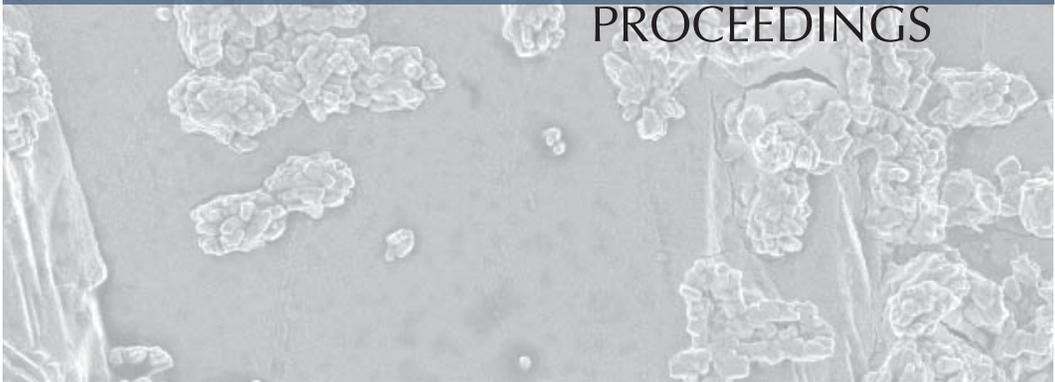
Internal Conference

ccac

COLORADO CENTER FOR ADVANCED CERAMICS

Thursday, August 26

PROCEEDINGS



PROGRAM & PROCEEDINGS

COLORADO CENTER FOR ADVANCED CERAMICS
2010 Internal Conference

Golden, Colorado

JULY 2010

Edited by

Michael Sanders
Prakash Periasamy
Liangju Kuang
Sarah McMurray



Michael Sanders, Chair



Liangju Kuang



Prakash Periasamy



Sarah McMurray

Welcome to the meeting

Welcome students, faculty, and guests, to the 2010 Colorado Center for Advanced Ceramics Internal Conference. The goal of this meeting is to foster an exchange of information and ideas within CCAC as well as with members of the greater ceramics community. Our research area is vast and often insights and solutions to a research problem may lie in the office next door.

On behalf of the entire planning committee, I would like to thank Dr. Grover Coors for giving our plenary talk – he and the entire CoorsTek/Ceramatec family are very good friends of the ceramics department. I would also like to thank the other external guests present today – your participation is invaluable to this exchange. We gratefully acknowledge the true rock upon which this endeavor is based, the National Science Foundation. Funding for this conference is provided by the Ceramics Program at NSF (grant #DMR-1003030).

Even small one day conferences such as ours do not put themselves together. I would first like to thank Professor Reimanis for giving us the opportunity to cut our teeth in the conference planning game. Thank you to all of this year's presenters as well. And last but certainly not least, Alice Jensen has been an invaluable resource – we couldn't have done it without you.

Michael Sanders
2010 CCAC Internal Conference Planning Chair

2010

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Thursday, August 26

Day's Overview

8.00a Opening remarks

8.15a Alternative energy

Jason Fish, Chung Min An, Aimee Queen, Lianju Kuang (Discussion led by Dr. Liang)

9.30a Microstructures & defects

Marc Rubat du Merac, Tim Jochum, Sarah McMurray, Josh White (Discussion led by Dr. Gorman)

10.45a Ionics

Dan Clark, Archana Subramanyan, Ann Deml, Michael Sanders, Daoben Hua (Discussion led by Drs. Sammes & Tong)

12.15p Plenary lecture & lunch

Dr. Grover Coors

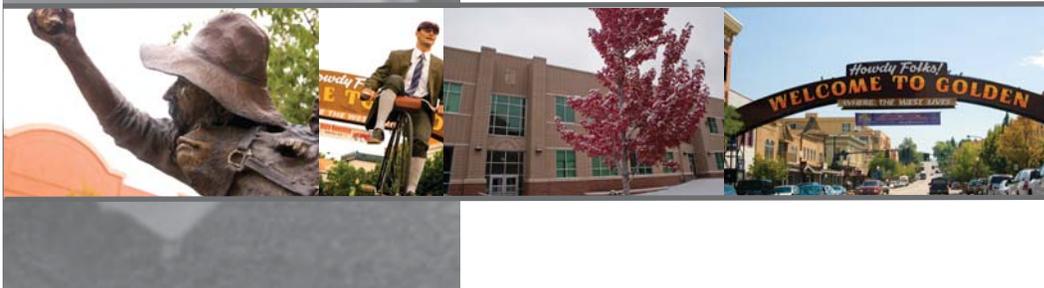
1.00p Light harvesting

Harvey Guthrey, Prakash Periasamy, Robert Pasquarelli, Yi Ke (Discussion led by Dr. O'Hayre)

2.15p Mechanical properties

Badri Narayanan, Subramanian Ramaling, Brian Hansford, Emily Mieritz (Discussion led by Dr. Reimanis)

3.30p Closing remarks



Synthesis and Characterization of a Novel Cathode Material for Solid Oxide Electrolysis Cells (SOEC)

Jason Fish and Nigel Sammes

Department of MME, Colorado School of Mines, Golden CO

A novel cathode material for solid oxide electrolysis cells (SOEC) has been synthesized by solid state reaction: tantalum-doped strontium titanate (STT). A composition of $\text{Sr}_{0.95}\text{Ti}_{0.9}\text{Ta}_{0.1}\text{O}_3$ was found to produce a phase-pure material upon calcination and sintering. Dense samples of sintered STT were machined into cone electrodes and tested in a custom-built electrochemical rig. Electrochemical Impedance Spectroscopy (EIS) was used

to analyze the impedance response of the cones in various gas atmospheres from 650 – 1000 °C, under both 0 bias and with an applied load (polarization sweeps). Nyquist and i-V plots were created from the data and compared with results for similar materials in the literature. Dense bars and discs of sintered STT were also made, and the conductivities of these samples were measured with the 4-point DC and AC methods for bars and discs, respectively. Synthesis characterization, details of the electrochemical test rig, and electrochemical and conductivity data for STT will be discussed further in the paper.

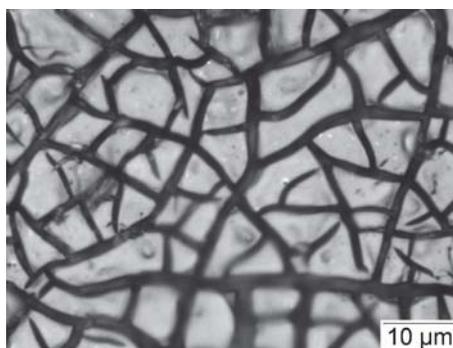


Fabrication of Ti/IrO₂-Ta₂O₅ anode electrode for increasing resistance of acid corrosion and electrode efficiency via painting coating

Chung Min An, Yong Wook Sin, and Nigel Sammes

Department of MME, Colorado School of Mines, Golden CO

The anode electrode should be resistant to a strong acid and have high electrochemical reaction efficiency during electrolysis in electrochemical systems. IrO₂-Ta₂O₅ coated titanium electrodes are a candidate for anodes in electrolysis systems. Experiments were carried out in which painting coating was used to coat IrO₂-Ta₂O₅ on Ti. A Ti electrode was coated with 50 mol% IrO₂ and 50 mol% Ta₂O₅ to find the optimization anneal-



ing temperature within the range of 400 to 800 °C. The optimum IrO₂(mol%)/Ta₂O₅(mol%) coating composition was established by fabricating and testing four different compositions; 50 mol%/50 mol%, 60 mol%/40 mol%, 70 mol%/30 mol%, and 80 mol%/20 mol%. The structure and morphology of the IrO₂-Ta₂O₅ layer were determined by Scanning electron microscopy (SEM) and X-ray diffraction (XRD). Resistance of the electrode to acid corrosion was measured in a H₂SO₄ solution with a pH of less than 0.5 during electrolysis over a 7-day period. The efficiency of electrode was calculated by the ratio of applied electrical power to used electrical power during electrolysis.

The electrochemical reaction during electrolysis increases as the surface between solution and electrode becomes wider. The “mud-cracked” appearance increases the surface area. Increasing the concentration of IrO₂ in the coating resulted in more of a “mud-cracked” appearance. However, at a coating concentration of 80 mol% IrO₂ the “mud-cracked” appearance was not observed. Though electrode efficiency of the electrode coated with 70 mol% IrO₂ was highest, the difference was small compared to the 60 mol% IrO₂ coated electrode. Thus, since Ir is expensive, the electrode coated with 60 mol% IrO₂ was measured for acid corrosion resistance. The 60 mol% IrO₂ coated electrode was operated for 7 days in a solution of pH less than 0.5, with little degradation. This suggests that this coating can be used for commercial electrolysis applications, which typically operate at a pH of 4.0.

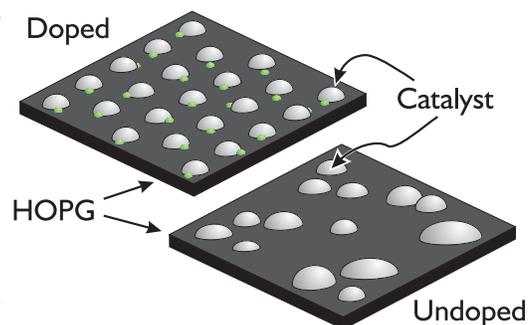
The effect of nitrogen doping levels on the structure, composition and durability of a PtRu/HOPG model catalyst system

Aimee Queen^{†‡}, Svitlana Pylypenko[†], Tim Olson[‡],
Arrelaine Dameron[‡], Kevin O'Neill[‡], Huyen Dinh[‡],
Tom Gennett[‡], and Ryan O'Hayre[†]

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[‡]National Renewable Energy Laboratory, Golden CO

Before direct methanol fuel cells (DMFCs) can become commercially viable, an improvement in the performance of the catalyst used for the methanol oxidation reaction is necessary. By investigating the effect of nitrogen doping levels on the structure, composition and durability of a PtRu/HOPG model catalyst system, this study extends previous



efforts which suggest nitrogen doped carbon supports in a Pt/C system improve the catalytic activity and durability by promoting the desired catalyst characteristics of small particle size and good dispersion. Because several steps in the methanol oxidation reaction (MOR) can lead to the formation of CO, poisoning the fuel cell, a transition has been made to a PtRu/C catalyst system which increases the CO tolerance and rate of direct methanol electro-oxidation. Nitrogen doping is achieved through ion beam implantation used to enhance Highly Oriented Pyrolytic Graphite (HOPG) which serves as the geometrically well defined carbon substrate. After which, magnetron sputtering with a single target allows for the deposition of Pt-Ru nanoparticles with a controlled composition independent of nucleation site density. The implantation time was varied to study structural and chemical modification as well as changes in morphology as a function of nitrogen ion implantation dosage. XPS and Raman spectroscopy are being utilized to understand structural and chemical modifications while completing TEM imaging before and after electrochemical cycling shows changes in the PtRu nanoparticle size distribution and coverage. It has been observed that samples with dosage levels resulting in saturation, as shown by the elemental concentrations and D to G-band intensity ratios, have smaller and more well dispersed PtRu nanoparticles after 300 cycles as compared to undoped samples.

Harvesting Microalgae with Magnetic Nanoparticles for Biofuel Production

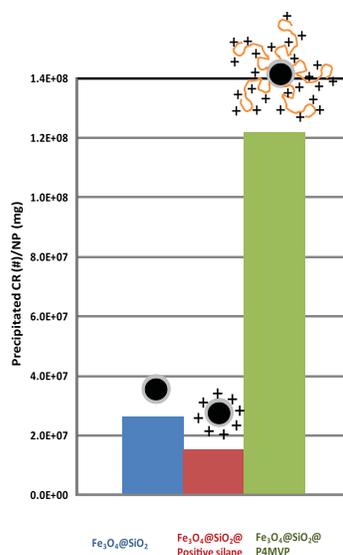
Liangju Kuang[†], Patrick Eduafo[‡], Daoben Hua[†],
Matthew Posewitz[‡], and Hongjun Liang[†]

[†] Department of MME, Colorado School of Mines, Golden CO

[‡] Department of Chemistry, Colorado School of Mines, Golden CO

Microalgae are considered as promising feedstocks for next-generation biofuels production. However, harvesting microalgae is one of the key processes that limit the microalgae-based biofuel production at an industry scale due to the small specific density of microalgal cells and their like-charge repulsion. We propose a magnetic coagulation method to harvest microalgae using magnetic nanoparticles grafted with polyelectrolytes. Magnetic coagulation involves the use of both chemical and physical mechanisms to separate microalgal mass from their aqueous growth medium. The paramagnetic nanoparticles of Fe_3O_4 were first prepared by a solvothermal reduction method. Then polyelectrolytes were grafted to the surface of Fe_3O_4 nanoparticles by the method of both 'graft to' and 'graft from' method.

Both positive and negative polyelectrolytes were synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization with controlled chain lengths. The resultant products were characterized by fourier transform infrared spectrometer (FT-IR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), Zeta potential, and gel permeation chromatography (GPC). Preliminary results on the coagulation efficiency suggest our novel strategy is a very viable method to harvest microalgae.



Chemical Interactions and Effect of Impurities in Transparent Magnesium Aluminate Spinel Hot Pressed with LiF

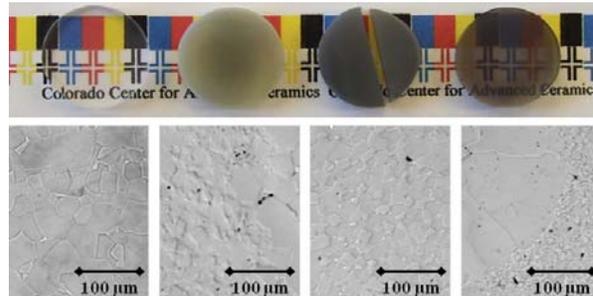
Marc Rubat du Merac[†], Ivar Reimanis[†], Charlene Smith[‡], and Hans Joachim Kleebe^{*}

[†] Department of MME, Colorado School of Mines, Golden CO

[‡] Corning Inc., Corning NY

^{*} Technical University of Darmstadt, Germany

Transparent polycrystalline magnesium aluminate spinel (MgAl_2O_4) has potential application as infrared missile windows, transparent armor, and scratch-resistant windows for consumer goods. 1 wt. % lithium fluoride (LiF) is used as



a sintering aid during hot-pressing to promote densification at lower temperatures and to achieve a fully dense, transparent material. However, this processing technique is expensive and not automatable. Moreover, the sintering kinetics of spinel and the role of LiF are still not fully understood. Experiments have been designed to gain a better understanding of the sintering behavior of this system, particularly the role of LiF and the effect of impurities during the late stages of sintering. Transparent spinel samples were hot-pressed under various conditions and examined with optical spectroscopy, optical microscopy, SEM/EDS, SEM/WDS, TEM/EDS, STEM/EDS, laser ablation ICP-OES/MS, STA-MS, Raman spectroscopy, and impedance spectroscopy. Changes in transparency were related to microstructural features and microstructure was related to processing parameters and interactions between spinel, LiF, and impurities present in the starting powders. A brief discussion of this work will be presented.

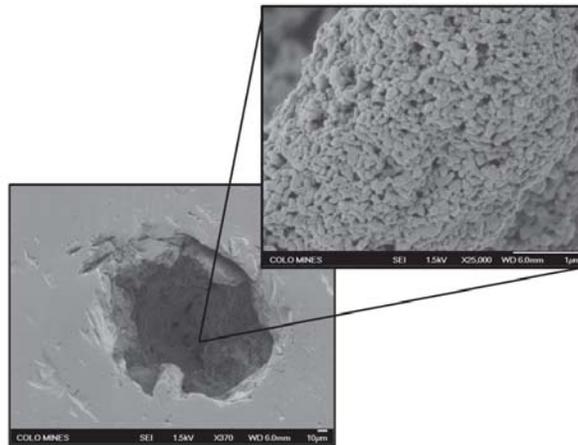
The Effect of Impurities on Grain Growth in Magnesium Aluminate Spinel

Timothy Jochum and Ivar Reimanis

Department of MME, Colorado School of Mines, Golden CO

The ability to use traditional methods for the sintering of transparent spinel, MgAl_2O_4 , can be described as a balance between densification and grain growth. Transparent materials must contain a very low degree of porosity, less than one percent. Additionally, excessive grain growth will degrade the physical properties of a ceramic material.

Therefore, acquiring a transparent material with desirable mechanical properties without pressure-assisted sintering demands a control over both densification and grain growth. The goal of this project is to determine the effect of impurities on grain growth behavior in spinel powder. Removing existing impurities in the as received powder will allow for controlled contamination with specific impurities for study. Drawing conclusions from the effects of various impurities on the densification and grain growth will allow for better sintering control over spinel.

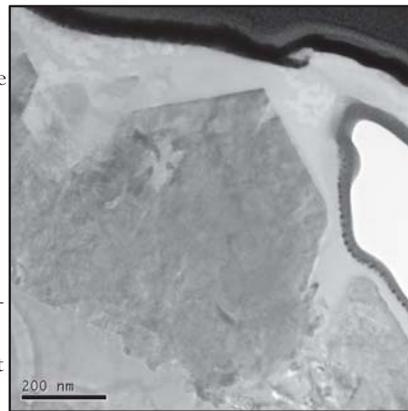


Investigation of Calcium Carbonate Formation in Seawater

Sarah McMurray, Brendan Foran, and Brian Gorman

Department of MME, Colorado School of Mines, Golden CO

As p_{CO_2} rises in the atmosphere, there is a concurrent rise of p_{CO_2} in the upper ocean waters. This results in a decrease in carbonate ion concentration, leading to a decrease in the saturation state of seawater with respect to carbonate minerals. A better understanding of CaCO_3 precipitation and dissolution reaction kinetics and solubility behavior is needed. Over the last 50 years, aragonite precipitation has been observed to act unpredictably in relation to simple thermodynamics. There is substantial indirect evidence that a phase on the surface with different solubility properties causes this unusual behavior.



SEM analysis of carbonate precipitation for different times illustrated the evolution of carbonate growth morphology on natural aragonite and calcite substrates in natural seawater. It was observed that aragonite growing on an aragonite substrate happens in a complex fashion that does not follow the Kossel crystal kink and step movement model. Aragonite growth is observed to start with small rounded overgrowths, on a submicron scale, increasing with time until a “resting period”, where a continuous layer of small precipitates exists. Low current and low angle FIB specimen preparation combined with high accelerating voltage and low dose STEM techniques are successfully utilized to minimize beam damage. HRTEM revealed an amorphous calcium carbonate (ACC) surface layer tens of nm in thickness above an aragonite overgrowth. Electron diffraction and HRTEM determined that $\langle 111 \rangle$ aragonite planes had the highest growth rate, presumably precipitating from the ACC. STEM-EELS illustrated a large change in Ca/C ratio between the amorphous and crystalline regions. Analysis of the Plasmon edges also verified a change in bonding and structure. Mg (present as a secondary cation in the seawater) was determined to be of equal concentration in both regions, and may play a role in the precipitation of the ACC.

This and prior work indicates the possibility that as p_{CO_2} rises, and ion concentration in the upper ocean waters decreases, carbonate precipitation may be limited by the formation of ACC. Further studies are currently ongoing to understand the thermodynamic forces behind the formation of this metastable phase.

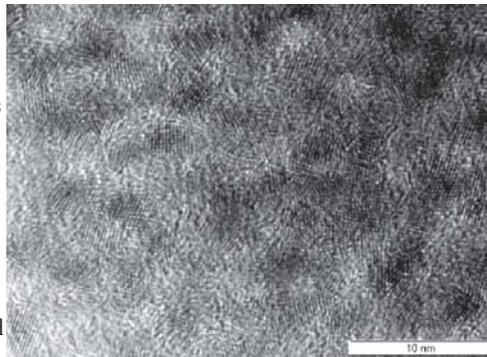
Phase stability and grain growth kinetics in the nano-scale NiO-Y₂O₃-ZrO₂ system

Josh White[†], Ivar Reimanis[†], and Grover Coors[‡]

[†] Department of MME, Colorado School of Mines, Golden CO

[‡] Ceramtec, Inc., Salt Lake City UT

Y₂O₃ stabilized ZrO₂ (YSZ) is commonly utilized for its unique structural, thermal, and electrical properties. The addition of NiO has been used to decrease the processing temperature and time to stabilize ZrO₂ in the presence of Y₂O₃. To understand the mechanism of this enhanced stabilization, powder samples of varying composition were created by the Pechini method at different temperature and cooling rates. The grain size and composition of the powders was measured by XRD with Rietveld refinement and TEM. Highly sensitive SQUID based magnetometry was used in conjunction with the previous measurements to determine the solubility limit of the Ni²⁺ ions. Results are discussed in terms of NiO influence on grain growth and kinetics in the YSZ and ZrO₂ system.



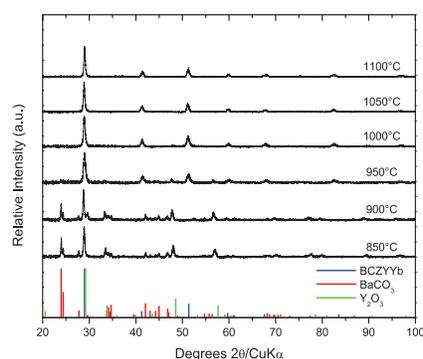
Characterization of $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ synthesized using polymeric sol-gel method

Daniel Clark, Jianhua Tong, and Ryan O'Hayre

Department of MME, Colorado School of Mines, Golden CO

The recently reported co-ionic conductor of $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb) shows high coking and H_2S poisoning resistance and looks to be promising for applications such as SOFC anodes and electrolytes, steam/hydrogen/oxygen permeation membranes, and sensors etc. In current work, the high-quality BCZYYb powder was first synthesized by polymeric sol-gel method under optimized calcination temperatures.

The optimized powder was pressed into pellets and sintered at different temperatures to find the best sintering conditions for the preparation of high-quality BCZYYb ceramic pellets. The crystal structure, composition, morphology, and grain size of the as-fabricated BCZYYb ceramic pellets were characterized by XRD, XRF, FESEM, and EBSD. After that, the electrical conductivities were investigated using AC impedance in the temperature range of $100^\circ\text{-}750^\circ\text{C}$ under different atmospheres for some representative pellets.



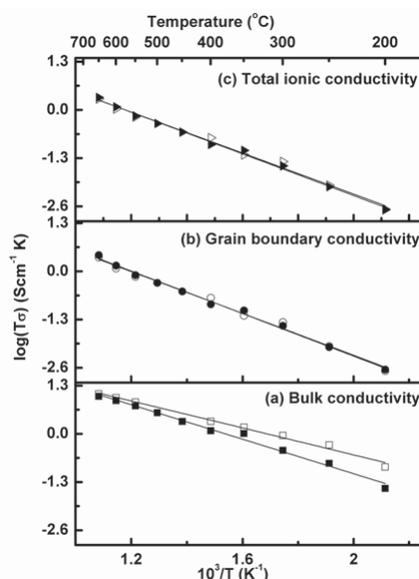
Proton Conductivity in BCY20-Pd Ionic Hybrid Material

Archana Subramaniyan, Jianhua Tong, Ryan O'Hayre and Nigel Sammes

Department of MME, Colorado School of Mines, Golden CO

Proton conducting oxides are widely popular for its applications such as hydrogen sensor, fuel cells and other electrochemical reactors. Among the several different efforts going on to improve the protonic conductivity, implementing nanoionics in proton conducting ceramic is one of them. By impregnating nanometal (hydrogen permeable) particles into the bulk of the proton conducting ceramic develops space charge layer which would increase the charge carrier concentration and therefore it is expected to increase the protonic conductivity. 20 mol% yttria doped barium cerate ceramic (BCY20) is mixed with nano-palladium particles to fabricate a superionic hybrid pellet. Fabrication of superionic hybrid pellets involves

several challenges such as (a) phase pure BCY20 without palladium agglomeration or BCY20-Pd solid solution and (b) closely located palladium particles to develop overlapped space charge layer. This work aims to address the first challenge in fabrication by characterizing superionic hybrid pellets for its structure and micro-structure. Electrical characterization via EIS will also be discussed.



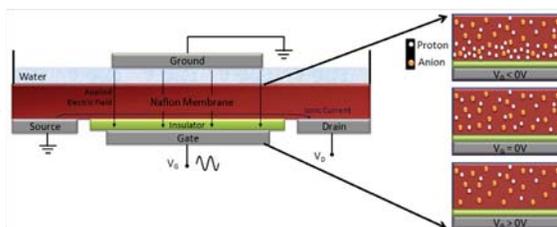
A Novel Solid State Ionic Transistor Configuration to Probe Ionic Space Charge Phenomena

Ann Deml[†], Annette Bunge[†], Michael Reznikov[‡],
Alex Kolessov[‡], and Ryan O'Hayre[†]

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Nanoionics, the study and manipulation of ionic space charge regions at ionic material surfaces and/or interfaces, is a nascent yet rapidly emerging field which is expected to play an innovative role in electrochemistry



through energy conversion and storage applications. The drive to advance our understanding of nanoionic phenomena has led to investment in this solid state ionic field effect transistor (IFET) configuration which may provide gatable ion transport as well as valuable insight into ionic space charge fundamentals.

Ionic space charge regions develop at interfaces between ionic materials or at the free surfaces of ionic materials. The resulting possibility of a localized relative enhancement (or depletion) of mobile ionic defects becomes evident as material characteristic dimensions reach the nanometer scale and become comparable to fundamental length scales such as the Debye length. Consequently, we suggest a solid state IFET configuration using polymeric Nafion to attain gatable ion transport. To this point, measurements of ionic current modulation in proton conducting Nafion by electrostatic gating have proven to be challenging. Although carrier concentrations and, therefore, conductivities are likely enhanced and depleted with the applied gate voltage, the resistance modulations have proven to fall below instrument sensitivity. Calculations utilizing double layer models indicate that thinner films, on the order of nanometers, are necessary. This approach is currently under further examination.

If successful, this system will be extended to high temperature proton conducting oxides such as yttrium doped barium cerate (BCY). Development of such devices may provide for applications in electrochemical switches, ionic logic components, and electrochemical logic operations.

Coupled transport and uphill permeation of steam and oxygen in a dense ceramic membrane

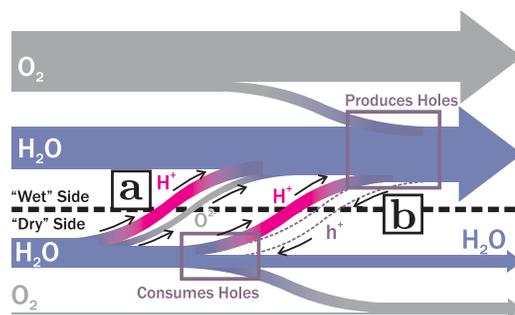
Michael Sanders and Ryan O'Hayre

Department of MME, Colorado School of Mines, Golden CO

Coupled transport membranes utilize the flux of one species to help drive the flux of another species, in some cases even against its own chemical potential gradient. These membrane processes are exploited in both natural systems, (where, for example, they underpin cellular membrane signal transduction) and in man-made systems,

(where, for example, they have been applied to a number of multi-component solvent or metal separations processes). To date, however, coupled transport membrane studies and applications have been almost exclusively confined to aqueous or liquid membrane media. While these systems have provided remarkable insights and have enabled novel separations approaches, both scientific understanding and commercial application have been limited because of the challenges associated with liquid membranes. These challenges include instability of the membrane and/or the carrier chemistry.

Using the coupled defect transport inherent in a proton conducting perovskite ceramic, we have developed a membrane capable of simultaneously transporting water and oxygen, including the uphill transport of either chemical species. This is the first known example of a solid-state coupled transport membrane and is the first of any type to operate at high temperatures. The unique features of this system alleviate many of the drawbacks associated with liquid membranes and opens up the possibility of new membrane separation applications, including air separation or natural gas reforming using waste steam and heat streams, as well as the ability to controllably “pump” or “gate” the permeation of select gas species using conjugate chemical potential gradients.

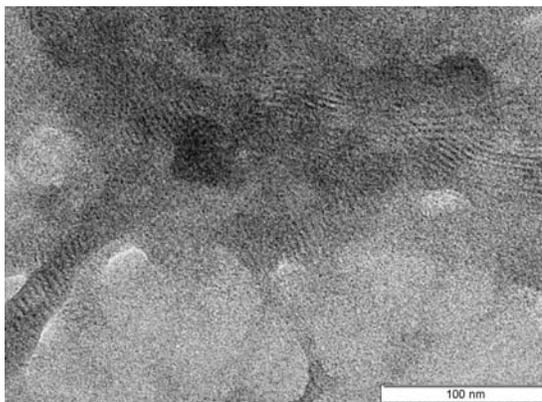


Self-assembly of membrane protein with synthetic polymersomes

Daoben Hua, Liangju Kuang, Laura Pate, and Hongjun Liang

Department of MME, Colorado School of Mines, Golden CO

It is well known that membrane proteins fulfill many vital roles in all living cells, such as matter exchange and energy conversion. However, the biological lipid bilayers used by living organism to accommodate membrane protein functions are oftentimes fragile and subject to disintegration when exposed to air, which limit the utilization of membrane protein



functions in practical devices. Using proteorhodopsin – a light powered proton pump as a prototype, we report here the directed spontaneous reconstitution of membrane protein with synthetic polymer membranes for the first time. The samples were characterized by dynamic laser scattering (DLS), electron microscopy (TEM), confocal microscope, and x-ray diffraction (XRD). This work may open a new door to the promising application of membrane proteins in a robust polymeric thin film format.

Origins of Spatial Non-uniformity in Distributions of Minority Carrier Properties in Directionally Solidified Silicon

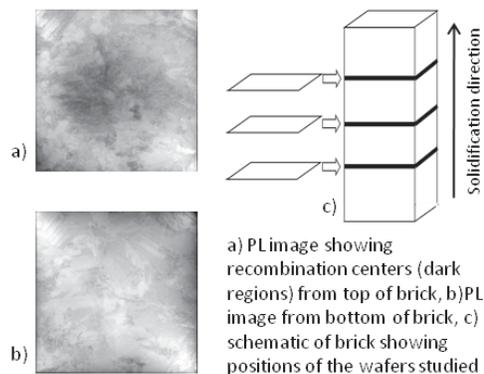
Harvey Guthrey^{†‡}, Brian Gorman[†], and Mowafak Al-Jassim[‡]

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The majority of photovoltaic cells are based on directionally solidified polycrystalline silicon (poly-Si) due to the lower cost of required feedstock and the ability to produce cells with conversion efficiencies up to 16%. The casting process introduces conditions which result in non-uniform grain structure, defect densities, and minority carrier lifetimes throughout the solidified ingot.

Understanding the origins of the non-uniform spatial distributions of these characteristics and how they are related to the casting process is necessary in order to modify the casting conditions to produce the highest quality ingots and thus solar cells with the highest conversion efficiencies. This study employs large-scale mapping (PL, EL, LIT, μ -PCD, Reflectometry, LBIC) of ascut wafers and processed cells from adjacent positions within a directionally solidified silicon ingot to obtain information on the spatial distributions of defects and minority carrier properties. Small scale techniques (SEM, EBIC, CL, ICP-MS, SIMS, STEM) are used to study the structural and chemical phenomena associated with defects and regions with poor minority carrier properties. It is shown that from the bottom of the ingot to the top of the ingot (direction of solidification) the density of defects increases and the important minority carrier properties such as diffusion length and lifetime decrease.



A Novel Approach to Deposit Ultra-thin Insulator Layer in MIM Device via Anodic Oxidation and UV Exposure

Prakash Periasamy^{†‡}, Philip Parilla[‡], Adrian Podpirka^{*},
Shriram Ramanathan^{*}, Ryan O'Hayre[†]

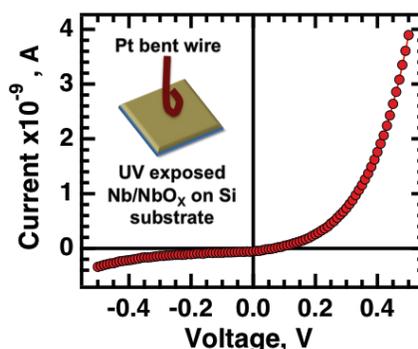
[†]Department of MME, Colorado School of Mines, Golden CO

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^{*}Harvard University, Cambridge MA

Metal-Insulator-Metal (MIM) devices are a promising rectifier candidates for applications such as optical rectenna (convert sunlight to DC), infrared detectors/imaging and other high-speed electronics. A successful metal-insulator-metal device will have a low turn-on voltage (close to zero bias), very high asymmetry, non-linearity and responsivity at low biasing voltage (< 0.5 V). One of the main challenges in MIM devices is the fabrication of ultra-thin (< 5 nm) insulator layer, which influences the barrier parameters.

In this paper, we report a novel method to deposit thin and high quality insulator layers in a facile manner without the use of any vacuum related deposition techniques. First a metal layer in the MIM device was sputtered on to a Si substrate, which is then anodized to a thickness of 1-4 nm. Then the anodized substrate is subjected to ultra-violet (UV) exposure at room and high temperatures for 1 hour in a flowing oxygen environment. A bent platinum wire is the metal 2 component in the MIM device. The contact of the Pt bent wire on the UV treated substrate defines the active area and hence forms a point-contact MIM device. The devices are characterized for their current-voltage (I-V) response. The UV treated samples when compared with non-UV treated samples, shows a significant improvement in their I-V responses. One of the important improvements is the reduction or complete elimination of the hysteresis in the I-V response, which is an indication of elimination of defects in the insulator layer. The best device performance was achieved in sample anodized to 3 nm and subjected to UV exposure at 300°C. The device had a turn-on voltage of close to 0.1 V and asymmetry and non-linearity value of 12 and 3, respectively at 0.5 V. In addition, experiments are currently underway to parse the influence of UV exposure, exposure temperature and atmosphere on the quality of the insulator layer. This detailed analysis is expected to arrive at a defect reaction that explains the hysteresis behavior.



Solution Deposition of Nb:TiO₂ Transparent Conducting Thin Films

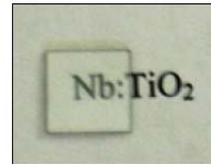
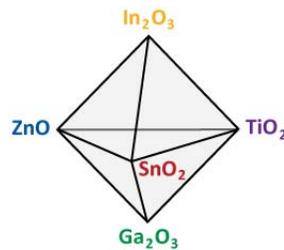
Robert Pasquarelli^{†‡}, Maikel van Hest[‡], Alexander Miedaner[‡], Calvin Curtis[‡], John Perkins[‡], David Ginley[‡], Ryan O'Hayre[†]

[†]Department of MME, Colorado School of Mines, Golden CO

[‡]National Renewable Energy Laboratory, Golden CO

Transparent conducting oxide (TCO) thin-films play a critical role in many current and emerging opto-electronic devices. Their unique combination of high transparency in the visible region of the spectrum and tunable electronic conductivity is ideal for applications in displays, transparent thin-film transistors, and as collection layers for photovoltaics. Niobium-doped titanium dioxide (Nb:TiO₂) has recently gained interest due to its high index of refraction and the fact that is composed of more abundant, and thus lower cost,

elements than conventional indium-based TCOs. Here we report on the solution deposition and properties of Nb:TiO₂ thin-films. Atmospheric-pressure solution deposition is an attractive alternative to conventional vacuum-based TCO deposition techniques due to its ease and potential to lower device manufacturing costs. Ti_{0.95}Nb_{0.05}O₂ films were deposited by spin-coating from solutions of Ti(isopropoxide)₂(acetylacetonate)₂ and Nb(ethoxide)₅ in isopropanol/THF onto glass and lattice matched LaAlO₃ substrates. Films were annealed under O₂ and Ar-4%H₂ from 400-800°C. The anatase phase of TiO₂ is desired due to its higher electronic mobility and thus higher conductivity. The phases formed as a function of temperature, substrate, and processing conditions were investigated using X-ray diffraction. The optical and electronic properties of the films will also be presented.



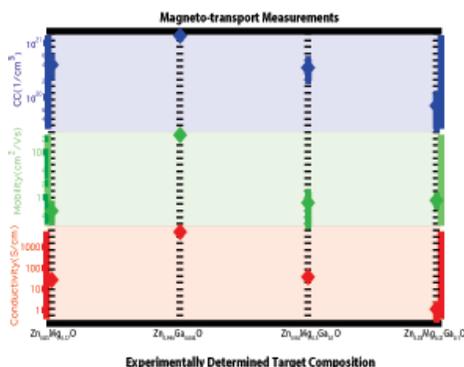
Structure and Chemical Considerations for Doping in ZnMgO: A Path Towards Conductivity-Bandgap-Tunable TCO System

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The bandgap tuning of ZnMgO by modulation of Mg concentration coupled with independent engineering of the materials conductivity is highly desirable for numerous device applications but remains a subject of intense research. We present our work in investigating the influence of grain size and grain boundaries on the structural stability and the efficiency of carrier generation in ZnMgO. We have prepared single wurzite-phase polycrystalline $Zn_{1-x}Mg_xO$ ($0.05 < x < 0.20$) on fused silica by pulsed laser deposition (PLD), which were observed to develop a measurable fraction of what appears to be a MgO phase when stored in air after 3 months. While these films are reproduced and stored under different conditions to test the possible mechanism for phase separation, we have also successfully stabilized this decomposition by changing depositing conditions. Correlation between XRD data and stability indicates that the phase separation is likely caused by inhomogeneous MgO distribution along the grain boundaries. Hall effect measurement results shows for the same chemical composition system different crystal structure cause more one magnitude order difference in doping efficiency and transport properties respectively, which can be explained by electrostatic potential barrier between grains. We will also report on our efforts to eliminate the influence of grain boundaries by deposition of epitaxial ZnMgO films via PLD on sapphire substrates. We will compare epitaxial and polycrystalline films to quantify the importance of how well Mg incorporate into this system in relation to the electrical properties (e.g. the doping efficiency) in ZnMgO system. Within the considerations relating to the detailed crystal structure, we will report our results on the doping efficiency of Ga in $Zn_{1-x}Mg_xO$ ($x=0, 0.05, 0.1, 0.2$) tested in high quality epitaxial ZnMgO films designed to control the crystal qualities and de-convolute the influence of different chemistry. We will also discuss our efforts to use novel n-type dopant in ZnMgO.



Parameterization of the Reactive Force Field for Elastic Properties of Eucryptite Phases

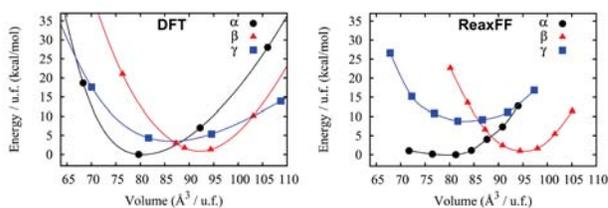
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The reactive force field (ReaxFF) is a new generation of force fields developed to bridge the gap between quantum chemical/mechanical and empirical



cal interaction models. In the present work, the ReaxFF has been parameterized for the Li/Al/Si/O system by fitting against equations of state obtained by density functional theory calculations for oxide, silicate and aluminate phases. While the ReaxFF parameters were found to give a somewhat poor description of the Li-aluminate phases, they give a good description of the structural properties of other oxides, silicate and aluminate phases. The parametrization also provides a reasonably good description of the lithium aluminosilicate phases, in particular, the elastic constants of β-eucryptite are within ~30 % of the experimental values except C₁₂. The elastic properties of α-eucryptite are predicted using ReaxFF. The results are discussed in the context of application and utility of the present force field parameters for eucryptite phases.

Determination of Crack Growth Parameters Using the Dynamic Fatigue Indentation Technique

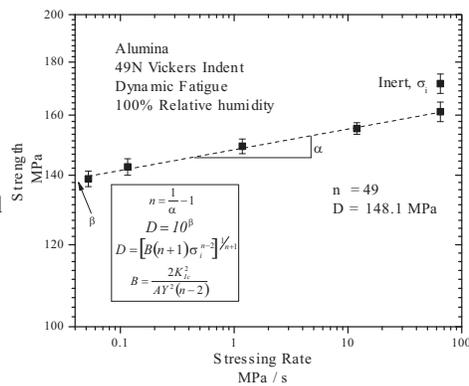
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A method to determine the sub-critical crack growth (SCG) parameters by the dynamic fatigue (constant stress rate tests) indentation technique is described. A Vickers indenter was used to introduce the flaws and the samples are then tested in a conventional four point bending apparatus. All the fatigue tests were carried out at 100 percent relative humidity conditions. Inert strength tests were carried out in dry nitrogen environment. Regression analysis of the dynamic fatigue data yields 'apparent' fatigue parameters which are converted to 'true' fatigue parameters via the transformation equations. Fractography was carried out on samples after the testing to characterize differences in the type of fracture. In the present study, the SCG behavior of platelet reinforced zirconia toughened alumina (PR-ZTA), which exhibits a rising R-curve behavior, is studied and the results are compared with that of a high purity medical grade alumina and a 99.5% alumina.



Sample Preparation of SiC Shells from TRISO Fuel Particles

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The Department of Energy (DOE) is currently conducting research on Next Generation Nuclear Power Plants (NGNP) to meet the energy needs of the future. One proposed design is the Very High Temperature Reactor (VHTR). The VHTR can provide electricity and because of the high operating temperatures greater than 1000°C hydrogen can be generated for transportation needs.

The design and licensing of the VHTR requires validation of all of the reactor systems. The VHTR uses triisotropic (TRISO) fuel particles as a fuel source. These fuel particles consist of a nuclear fuel kernel, buffer carbon layer, dense carbon layer, silicon carbide layer and another dense carbon layer. The overall size of the fuel particle is about 1 mm. The SiC layer acts as a pressure vessel to contain the fission product gases released during irradiation. The goal of this project is to study the mechanical properties of the 35 μm thick SiC layer.

Working with radioactive materials presents significant challenges when trying to perform any type of testing. This presentation focuses on the TRISO fuel currently being studied at Idaho National Lab (INL) and what it takes to isolate the SiC layer of an irradiated TRISO fuel particle.

After irradiation the compacts are placed in a cooling cannel for a minimum of 60 days. The particles are then transported to from the Advanced Test Reactor (ATR) to the Materials and Fuels Complex (MFC) at INL via a containment cask on a flat bed truck. At MFC the cask is unloaded at the Hot Fuel Examination Facility (HFEF) where the compact is removed from their experimental casing. The compacts are then sent to an analytical lab where the TRISO particles are removed from the compacts and cold mounted. The cold mounts are then sent back to the HFEF for grinding and polishing. After grinding and polishing the mounts are sent to electron microscopy lab (EML). At the EML the particles undergo a process to remove the uranium kernel, burn off the carbon layers, and remove the particles from the mount. The remaining SiC shell is now ready for mechanical testing.

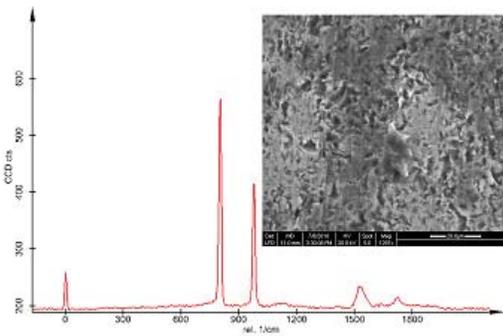


Planar CVD SiC as a Surrogate for TRISO Particles

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TRISO particles, from the word tri-isostructural, are spheres which have a SiC layer between two graphite layers surrounding a ceramic nuclear fuel kernel. The purpose of the SiC layer is to act as a mm-scale pressure vessel that retains fission products. This layer is deposit-



ed by chemical vapor deposition (CVD) in a pebble bed reactor in order to achieve a homogeneous, spherical coating. In CVD, the factors of pressure and temperature can affect the choice of chemicals to vaporize, the concentration of impurities in the system, and the thermodynamics and kinetics of the deposition, all of which affect the performance of the SiC. Unfortunately, testing spherical geometries is not always straightforward, and planar surrogates are highly desirable. In this work, spherical and planar CVD-deposited carbide layers are compared in terms of their microstructure, strain, and mechanical properties to determine the applicability of planar geometries to TRISO surrogates.

