# Monday Morning, October 30, 2017

## Actinides and Rare Earths Focus Topic
## Room 22 - Session AC+MI+SA+SU-MoM

### Magnetism, Complexity, and Superconductivity in the Actinides and Rare Earths

**Moderator:** Tomasz Durakiewicz, Los Alamos National Laboratory

**8:20am AC+MI+SA+SU-MoM-1 Magnetic and Transport Characteristics in the Uranium Intermetallic Compounds with the $HoCoGa_5$-type Structure**, *Yoshinori Haga,* Japan Atomic Energy Agency, Japan  **INVITED**
Physical properties of actinides compounds are mainly dominated by the 5f electrons behavior. The spatial extent of the 5f wave function and resulting hybridization with the neighboring atoms lead to itinerant characters. On the other hand, well isolated 5f electrons carry magnetic moment. Competition between those two characteristics often bring about peculiar electronic properties. Among a series of actinides compounds, so-called 115 compounds crystallizing in the tetragonal $HoCoGa_5$-type structure have extensively been studied because of unusual correlated electronic states, including heavy effective mass of conduction electrons, magnetic orderings and heavy fermion superconductivity. Those compounds are also good cases to study electronic transport properties in detail because of availability of extremely high quality samples. Among them, we discuss electronic properties of $URhX_5$ (X = Ga and In). While $URhIn_5$ orders antiferromagnetically at fairly high tempearture 98 K, isostructural and formally isoelectronic analogue $URhGa_5$ is a nonmagnetic semimetal[1,2,3]. Detailed transport measurements as well as the de Haas-van Alphen experiment revealed Fermi surface characteristics. We discuss origin of magnetism of uranium 5f electrons and its relationship between superconductivity realized in Pu-analogues.

[1] Y. Matsumoto et al., Phys. Rev. B 88, 045120 (2013).

[2] S. Ikeda et al., Physica B 359-361, 1039 (2005).

[3] Y. Matsumoto et al, JPS Conf. Proc. 3, 011097 (2014).

**9:00am AC+MI+SA+SU-MoM-3 Magnetic Structures of Layered $U_nRhIn_{3n+2}$ Materials**, *Attila Bartha, M Klicpera,* Charles University, Prague, Czech Republic*; P Čermák,* Forschungszentrum Juelich GmbH, Germany*; B Ouladdiaf,* Institut Laue Langevin, France*; P Javorský, J Custers,* Charles University, Prague, Czech Republic
Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronics. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivial metal. Another example is high temperature superconductors being quasi-2D materials as well.

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series $Ce_nT_mIn_{3n+2m}$($n$=1, 2; $m$=0, 1, 2; $T$=transition metal) of layered compounds, which can be viewed as $m$ $TIn_2$–layers alternating with $n$–layers of $CeIn_3$ along the $c$-axis, has been extensively investigated. $CeIn_3$ is cubic (3D) and orders antiferromagnetically (AFM) at $T_N$ = 10.2 K [1] with a propagation vector $k$ = (0.5, 0.5, 0.5) [2]. Under hydrostatic pressure superconductivity appears with highest $T_c$ = 0.3 K at $p$ = 2.5 GPa. In $CeRhIn_5$, the anisotropic crystal structure leads to an incommensurate magnetic structure described with $k$ = (0.5, 0.5, 0.297). The AFM order is reduced ($T_N$ = 3.8 K) while superconductivity is supported, $T_c$ increases to 1.9 K at $p$ = 1.77 GPa [3-4].

We report on the magnetic structures of $URhIn_5$ and $U_2RhIn_8$, two new members of this intriguing $R_nT_mX_{3n+2m}$($R$= Lanthanide, Actinide, $X$ = In, Ga) family of compounds. Neutron diffraction measurements were performed on structurally well-defined single crystals. Both, $URhIn_5$ and $U_2RhIn_8$, adopt the tetragonal $Ho_nCoGa_{3n+2}$-type structure (P4/*mmm*) typical for this group of compounds. $URhIn_5$ orders antiferromagnetically below $T_N$ = 98 K. The propagation vector equals $k$ = (0.5, 0.5, 0.5) and we obtained a value of 1.65 $\mu_B/U^{3+}$ for the size of the ordered magnetic moment. The antiferromagnetic transition temperature of $U_2RhIn_8$ is higher yielding 117 K. We found that the magnetic structure can be described by propagation vector $k$ = (0.5, 0.5, 0). The respective ordered magnetic moment amounts 1.7 $\mu_B/U^{3+}$. In both materials the ordered magnetic moments are aligned along the tetragonal $c$-axis. Comparison with isostructural compounds and general conclusions for the series will be presented.

[1] C. Pfleiderer, Rev. Mod. Phys. 81 (2009) 1551

[2] A Benoit *et al.*, Solid State Commun. 34 (1980) 39

[3] H. Shishido *et al.* J. Phys. Soc. Jpn. Vol. 71 Suppl. (2002) 276

[4] H. Hegger *et al.,* Phys. Rev. Lett. 84 (2000) 4986

**9:20am AC+MI+SA+SU-MoM-4 $U_3Si_2$ – Physical Properties and Resistance to Hydrogen**, *Silvie Maskova,* Charles University, Prague, Czech Republic*; K Miliyanchuk,* Ivan Franko National University of Lviv, Lviv, Ukraine*; S Middleburgh,* Westinghouse Electric Sweden AB, Vasteras, Sweden*; L Havela,* Charles University, Prague, Czech Republic
$U_3Si_2$ (tetragonal structure with the space group of P4/*mbm* and two different U-positions, U1 and U2, in the unit cell) is considered to be promising material (due to its high density of uranium) as an accident-tolerant nuclear fuel [1] with rather high melting point (1938 K) indicating a high thermodynamic stability. From this point of view, it is very important to study its resistance to oxygen or hydrogen, as it can significantly influence the integrity of the material. $U_3Si_2$ was reported to oxidize at elevated temperatures [2].

We studied the H absorption and concomitant changes of basic electronic properties. We found that $U_3Si_2$ reversibly absorbs hydrogen (H can be released again by heating up to approx. 700 K) to the level of approximately 1.8 H/f.u., i.e. yielding $U_3Si_2H_{1.8}$. The H absorption proceeds at very low H pressures (kPa range) already, resulting in 10 % volume expansion. The temperature-induced desorption experiment showed that the hydrogen atoms are located in one specific position only. The crystal structure arrangement suggests that two different positions should be considered - $U_3Si$ tetrahedra (similar to $U_3T$ tetrahedra in $U_2T_2X$ compounds [3] crystallizing in an ordered ternary derivative of the $U_3Si_2$ structure) and a split position in the $U_6$ octahedra consisting of 4 U1 and 2 U2 atoms (H atom shifts from the central position into the tetrahedra formed by 2 U1 and 2 U2 atoms. As H generally does not occupy two adjacent tetrahedra, we can assume only two from the 4 tetrahedra occupied). The later was confirmed as more plausible option by ab-initio calculations using Vienna Ab-initio Simulation Package (VASP) with the PBE-GGA exchange correlation.

Magnetic studies of $U_3Si_2$ confirmed that it is a Pauli paramagnet, as reported previously [4]. The volume expanded hydride reveals a Curie-Weiss behavior and a weak and inhomogeneous ferromagnetism arising gradually below $T$ = 100 K. The low-temperature specific heat of $U_3Si_2H_{1.8}$ shows an upturn and a dramatic enhancement of the Sommerfeld coefficient of electronic specific heat $\gamma$, which reaches 440 mJ/mol f.u. $K^2$ ($\gamma$ = 88 mJ/mol f.u. $K^2$ for $U_3Si_2$).

This work was supported by The Czech Science Foundation under the Grant No. 15-01100S.

[1] K.D. Johnson, A.M. Raftery, D.A. Lopes, J. Wallenius, J. Nucl. Mater. 477 (2016) 18-23.

[2] E. Sooby Wood, J.T. White, A.T. Nelson, J. Nucl. Mater. 484 (2017) 245-257.

[3] K. Miliyanchuk, L. Havela, A.V. Kolomiets, A.V. Andreev, Physica B 359–361 (2005) 1042-1044.

[4] T. Miyadai, H. Mori, T. Oguchi, Y. Tazuke, H. Amitsuka, T. Kuwai and Y. Miyako, J. Magn. Magn. Mater. 104-107 (1992) 47-48.

**9:40am AC+MI+SA+SU-MoM-5 Understanding Surface Chemistry of f-element Oxides using First-principle Methods**, *Ping Yang,* Los Alamos National Laboratory  **INVITED**
Interfacial chemistry for f-element materials is critical for nuclear waste management and to address the environmental concerns associated with actinides. Cerium is often used as a surrogate for more radioactive actinide elements for thorough characterization using advanced spectroscopic techniques. Herein, we will present recent progress in characterizing interfacial interactions of ligands with $CeO_2$ and $ThO_2$ in both surface and nanoparticle forms. We will demonstrate how the synergy between theory and experiment has accelerated the progress in this field. The theoretical results are validated by spectroscopic characterizations. A better molecular-level understanding of the interfacial chemistry including coordination, energetics and reaction mechanisms will pave the way to a better strategy for waste management and environment remediation.

**10:40am AC+MI+SA+SU-MoM-8 Inelastic X-ray Scattering Study of the Crystal Dynamics of Neptunium and Uranium Dioxide**, *Roberto Caciuffo*, European Commission, Joint Research Centre, Karlsruhe, Germany; *P Maldonado*, Uppsala University, Sweden; *L Paolasini*, European Synchrotron Radiation Facility, France; *P Oppeneer*, Uppsala University, Sweden; *T Forrest*, European Synchrotron Radiation Facility, France; *A Prodi*, Consiglio Nazionale delle Ricerche, Italy; *N Magnani*, European Commission, Joint Research Centre, Karlsruhe, Germany; *A Bosak*, European Synchrotron Radiation Facility, France; *G Lander*, European Commission, Joint Research Centre, Karlsruhe, Germany **INVITED**

The energy-wavevector dispersion relations for normal modes of vibration propagating along high-symmetry lines in $NpO_2$ and $UO_2$ have been determined by measuring the coherent one-phonon scattering of X-rays from single-crystal specimens with mass varying from a few µg to ~1 mg. The inelastic X-ray scattering (IXS) experiments were carried out using the ID28 beamline at ESRF with an incident energy E=17.794 keV. The results are compared against *ab initio* phonon dispersion simulations computed within the first-principles density functional theory in the generalized gradient approximation plus Hubbard U correlation (GGA+U) approach, taking into account third-order anharmonicity effects in the quasiharmonic approximation.

In the case of $NpO_2$, the sample of dimension of $0.4x0.3x0.3mm^3$ was oriented with the specular direction along the (100) crystal axis and the (011) axis in the scattering plane. We have investigated different Brillouin zones in order to optimize the inelastic structure factor for the different optic branches. Optic phonons arise mainly from oxygen vibration modes and are very weak. Thermal expansion, heat capacity, thermal conductivity, phonon linewidth, and thermal phonon softening are calculated and compared with experimental data available for both $NpO_2$ and $UO_2$ [1]. We show that optical phonons contribute significantly to the heat transport due mainly to their large velocities and short lifetimes. Compared with $UO_2$, the main differences in the phonon density of states of $NpO_2$ are a softening of the optical modes and an increase of the peak centred around 55 meV, whereas the acoustic modes in $NpO_2$ are shifted to higher frequencies. The calculated value at 0 K of the bulk modulus in $NpO_2$ is in agreement with the experimental value and slightly smaller than the one determined by high-pressure X-ray diffraction for $UO_2$. $NpO_2$ has a smaller thermal conductivity than $UO_2$, at least in the temperature range 600 to 1000 K for which experimental values are available.

The lattice dynamics of $UO_2$ have been extensively investigated by neutron scattering both at low and high temperature. In this study we focussed our attention to the low temperature region, searching for vibronic contributions to the vibrational-magnetic-quadrupolar mixed modes that appear in $UO_2$ because of magnetoelastic and multipolar superexchange interactions. The situation is cleaner than with neutrons, as the latter see both magnons and phonons – the IXS spectra just the phonons. This observation opens a new window on these "hidden excitations", which drive much of the physics of $UO_2$.

[1] P. Maldonado *et al.,* Phys Rev B **93**, 144301 (2016)

**11:20am AC+MI+SA+SU-MoM-10 Emergent Phenomena in 4f Heavy-Fermion Systems: from Bulk to Thin-Films**, *Priscila Rosa*, Los Alamos National Laboratory **INVITED**

The interplay between magnetism and unconventional superconductivity in bulk materials has been one of the central topics in condensed matter physics for the past 40 years. In particular, the family of compounds $CeMIn_5$ (*M* = Co, Rh, Ir) provides an ideal platform for such investigation due to the small energy scales involved, and the high sample quality. In this talk, I will first discuss novel insights provided by substitution studies in bulk $CeRhIn_5$ under pressure. I will then present recent efforts to fabricate hybrid superlattices consisting of alternating superconducting $CeCoIn_5$ and antiferromagnetic $CeRhIn_5$.

## Actinides and Rare Earths Focus Topic
## Room 22 - Session AC+AS+SA+SU-MoA

### Chemistry and Physics of the Actinides and Rare Earths
**Moderator:** David Shuh, Lawrence Berkeley National Laboratory

**1:40pm AC+AS+SA+SU-MoA-1 Oxidation and Crystal Field Effects in Uranium**, *James G. Tobin,* University of Wisconsin-Oshkosh*; S Yu,* Lawrence Livermore National Laboratory*; C Booth,* Lawrence Berkeley National Laboratory*; T Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley*; D Shuh,* Lawrence Berkeley National Laboratory*; G van der Laan,* Diamond Light Source, UK*; D Sokaras, D Nordlund, T Weng,* Stanford Synchrotron Radiation Lightsource*; P Bagus,* University of North Texas
An extensive investigation of oxidation in uranium has been pursued. [1] This includes the utilization of soft x-ray absorption spectroscopy, hard x-ray absorption near-edge structure, resonant (hard) x-ray emission spectroscopy, cluster calculations, and a branching ratio analysis founded on atomic theory. The samples utilized were uranium dioxide ($UO_2$), uranium trioxide ($UO_3$), and uranium tetrafluoride ($UF_4$). A discussion of the role of nonspherical perturbations, i.e., crystal or ligand field effects, will be presented. The conclusions are as follows. (1) The hypothesis of the potential importance of CF effects in the XAS branching ratio (BR) analysis of 5f states was incorrect. (2) Both $UO_2$ and $UF_4$ are $n_{5f} = 2$ materials. The combination of the 4d XAS BR and RXES analyses is particularly powerful. (3) CF broadening in the $L_3$ RXES spectroscopy does not preclude a successful analysis. (4) The prior experimental result that $n_{5f}$ ($UO_2$) = 3 and the proposed causation by covalent bonding was incorrect. $UO_2$ is an n5f = 2 material and analysis within a simple, ionically localized picture provides the correct result. (5) $UO_3$ appears to be an $n_{5f} = 1$ material. (6) While the 4d XAS BR analysis is blind to CF effects, crystal field and covalence remain important. (7) For localized actinide systems, the 4d XAS BR analysis founded upon the utilization of the intermediate coupling scheme remains a powerful tool. (8) For delocalized actinide systems, the BR analysis is problematic.

[1] J. G. Tobin, S.-W. Yu, C. H. Booth, T. Tyliszczak, D. K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, Phys. Rev. B **92**, 035111 (2015)

**2:00pm AC+AS+SA+SU-MoA-2 Electron Spectroscopy Studies of U and U-Mo Hydrides**, *Ladislav Havela, M Paukov, M Dopita, L Horak, M Divis, I Turek,* Charles University, Prague, Czech Republic*; T Gouder, A Seibert, F Huber,* European Commission, Joint Research Centre, Karlsruhe, Germany*; D Legut,* VSB - Technical University of Ostrava, Czech Republic
U hydride was the first material indicating that 5*f* states can yield ferromagnetism analogous to 3*d* metals. However, the electronic structure of $UH_3$ is not yet well understood, and it is not clear to which extent it can be described by conventional band structure calculations. We have been studying structure and electronic properties of $UH_3$ and $(UH_3)_{1-x}Mo_x$ films synthesized by reactive sputtering. Primary diagnostics was performed by in-situ XPS. The U-4*f* core level spectra exhibit a development as a function of partial pressure of $H_2$ in Ar ($p_{Ar} = 8*10^{-3}$ mbar). Their intensity gradually decreases, they shift by 0.2 eV towards higher binding energies (BE) and an extended (9 eV wide) satellite structure develops on the high BE side of both 4*f* peaks. This tendency saturates at 5% $H_2$ concentration, and we assume that this pressure is sufficient to form $UH_3$. XRD and X-ray reflectivity proved indeed the β-$UH_3$ structure of deposited films, which were polycrystalline, but highly textured. Ferromagnetism of the $UH_3$ films has the correct Curie temperature $T_C \approx 165$ K. Magnetic coercivity of the films is enormous, the width of hysteresis loop exceeds 10 T at low temperatures. Details of the valence band observed in UPS reveal a transformation of the triangular emission of the U metal into a sharp feature at the Fermi level accompanied by a broad shoulder around 0.5 eV for the hydride. A distinct development was noticed also for the U-6*p* states, which become narrower and shift by 1.2 eV to higher BE in the hydride, which can be interpreted as an impact charge transfer from U towards H. Besides photoelectron spectroscopy, the variations of electronic states were monitored also by BIS spectra collected for the 1486.6 eV photon energy. The spectroscopy results are confronted with different types of in-initio calculations.

As U-Mo alloys tend to form nanocrystalline β-$UH_3$ based hydrides, we were curious about reactive sputter deposition of the U-Mo alloys. We found that the tendency to form hydrides is fast suppressed by Mo for room temperature sputtering (γ-U alloy without H is the product), but

cooling the substrate to 77 K helps to maintain the hydride phase even for even higher Mo concentrations.

**2:20pm AC+AS+SA+SU-MoA-3 Comparative Structural Studies of Tetravalent f ions in Solids and in Aqueous Solutions**, *Lynda Soderholm,* Argonne National Laboratory **INVITED**
Predicting a metal ion's aqueous chemistry – including its stability, reactivity, and solubility – requires molecular-level knowledge of the various factors influencing speciation and complex formation. This chemistry is particularly complicated for f-ions, where the electrostatic, non-directional bonding provides flexibility to their coordination environments, which can vary widely depending on the ligating species. This presentation will focus on our efforts to establish trends in f-ion solution behavior and to provide a direct link between metal correlations in solution and the thermodynamic stability constants that are used to derive relative free energies of available metal-ligand complexes. Although several examples will be provided, the discussion will center on a comparison between the behaviors of tetravalent Th, Pu, and Ce and how differences in the complexes formed in solution impact the composition and structure of precipitates that form. High-energy X-ray scattering (HEXS) experimental results will be used to demonstrate how changing conditions can influence solution chemistry, with a specific emphasis on the role of the anion. X-ray surface-based techniques will be used to provide a link between solution speciation and the complexes that form on mineral surfaces. The structures of molecular species isolated as single-crystals from these solutions will be directly compared with the solution and surface-adsorbed species. This work is supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Biosciences and Geosciences, Heavy Element Chemistry, under contract No. DE-AC02- 06CH11357.

**4:00pm AC+AS+SA+SU-MoA-8 Interfacial Dynamics in Radiation Environments and Materials: An Energy Frontier Research Center**, *Sue Clark,* Pacific Northwest National Laboratory **INVITED**
The US Department of Energy's Office of Environmental Management (EM) is faced with remediating millions of liters of highly radioactive wastes that resulted from the production of nuclear weapons during the Cold War. These legacy wastes are stored in large, underground tanks at former nuclear weapons production sites in the US. Not only are these wastes radioactive, but they are also highly alkaline and concentrated in electrolytes. Using currently available technologies and approaches. EM estimates that processing these wastes into waste forms for disposal in a geologic repository will take at least 5 decades and over $300 billion dollars. Basic research on the chemical and physical behavior of these materials in such extreme conditions is needed to provide a foundation of innovation to accelerate processing and reduce aggregate costs.

IDREAM is an Energy Frontier Research Center (EFRC) conducting fundamental research to support innovations in processing high-level radioactive wastes (HLW). Activities in IDREAM are designed to support the transformation of HLW processing by elucidating the basic chemistry and physics required to control and manipulate interfacial phenomena in extreme HLW environments (e.g., non-equilibrium, heterogeneous, and chemically complex). This foundational knowledge is required to achieve IDREAM's vision to master molecular–to–mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing (g,b) radiation. Further, understanding these processes will enable prediction of waste aging over the many decades required to complete this difficult cleanup task.

Currently, IDREAM activities focus on the aluminate anion in alkaline solutions, and its nucleation into boehmite (aluminum (oxy)hydroxide, AlO(OH)) and gibbsite (aluminum hydroxide, $Al(OH)_3$) , as they are key principal components of bulk waste materials to which a variety of other metal ions and radionuclides partition. In this presentation, initial results on interfacial reactivity between aluminate, boehmite, and gibbsite will be discussed. The impact of g and b radiation on boehmite and gibbsite will also be presented.

**4:40pm AC+AS+SA+SU-MoA-10 Real Structure of Nanocrystalline Uranium based Hydrides Studied By the X-ray Scattering Methods**, *Milan Dopita, L Havela, L Horak, M Paukov,* Charles University, Prague, Czech Republic*; Z Matej,* MAX-IV, Lund, Sweden
Interaction of hydrogen with uranium is not only an important issue for its nuclear and military applications but also contributes to understanding of

the 5$f$ magnetism. Uranium hydrides provide a unique tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. However, the electronic structure of uranium hydrides is not fully understood yet. Especially, the role of the real structure, i.e. the influence of the lattice defects, particle size in the nanocrystalline bulk materials and the preferred orientation of crystallites – the texture, the strains and stresses in the case of films is not well described, but can significantly influence electronic and magnetic properties of materials.

In our contribution we report the real structure of bulk and powder Mo- and Zr-alloyed uranium hydrides, prepared by rapid (splat) cooling and high pressure synthesis, and Mo alloyed uranium hydride films synthesized by reactive sputtering, using X-ray scattering methods. The sample series with different alloying element concentration as well as at different hydrogen pressure were prepared. Since the classical powder diffraction methods, as the profile analysis and/or Rietveld method, reach the limits of their applicability for the nanocrystalline uranium hydrides alloys in terms of the real structure description, the use of more advanced methods is necessary. Here we describe the total scattering method – pair distribution function analysis, and Debye equation calculation for simulations of the intensity scattered from nanocrystalline clusters.

The key results of our study were the determination of the phase composition and its evolution, as well as detailed atomic positions, which can influence the U-U spacings in individual phases, tuning the 5$f$ magnetism. The methods are able to describe the particle size and defect distributions, the stress, strains, and textures in the films. In addition, the depth profiles and evolution of above mentioned parameters can be determined. Such X-ray analysis provides useful characterization of the sputter-deposited films, which are also used for fundamental electron spectroscopy studies of $UH_3$-based films, exhibiting much lower surface contamination by oxygen than comparable bulk material.

## Sustainability Focus Topic
## Room 5 & 6 - Session SU+AC+MI+MS-TuM

### Critical Materials and Energy Sustainability

**Moderators:** Erik B. Svedberg, The National Academies, Robert Lad, University of Maine

**8:00am SU+AC+MI+MS-TuM-1 How Critical Materials Affect Emerging Technologies**, *Alexander King,* The Ames Laboratory **INVITED**
We live in a golden age for the development of technologies that have potential for clean and efficient production, storage or use of energy. Many, if not all of these technologies, however, depend on the properties of specific materials that may have low availability, or produce environmental challenges of their own during their production. We will look at the impact of materials supply challenges on the adoption of some recent clean energy technologies, consider possible impacts on some emerging technologies, and describe what efforts must be undertaken to ensure that fragile materials supply-chains do not prevent the adoption of technologies that promote a sustainable energy future.

**9:20am SU+AC+MI+MS-TuM-5 The Role of Oxidation and Charging Rates on Li Electrochemical Deposition in Solid State Batteries**, *Alexander Yulaev,* University of Maryland*; V Oleshko,* NIST*; P Haney,* NIST Center for Nanoscale Science and Technology*; A Talin,* Sandia National Laboratories*; M Leite,* University of Maryland*; A Kolmakov,* NIST Center for Nanoscale Science and Technology
The recent progress in all-solid-state Li-ion batteries (SSLIBs) allowed a significant reduction of overall dimensions of stand-alone medical and micro-electronic devices. Owing to their compatibility with microfabrication process, high specific power, energy densities, and reduced safety risks of the thermal runaway, SSLIBs are likely to compete with their liquid counterparts in the near future. However, the large-scale implementation of SSLIBs requires further characterization during their fabrication and operation. Particularly, spatially resolved *in-operando* techniques probing electrochemical processes at the interfaces are needed. In the present work, we quantify the effects of oxidizing environment and charging rates on a lithium plating morphology using UHV electron microscopy and spectroscopy in correlation with electrochemical characterization. To conduct these measurements, we fabricate a model thin-film planar battery with $LiCoO_2$ cathode, LiPON electrolyte, and an ultra-thin carbon anode. Our experimental data reveal a strong dependence of plated Li morphology on presence of oxidation species at the surface and a gas phase. Under UHV conditions a linear correlation between the nucleation density of lithium clusters and a charging rate is observed. We show that the 2D nucleation model adequately describes the obtained dependence. The plated lithium morphology drastically changes from the in-plane clusters to out-of-plane whisker growth when ~$10^{-7}$ Pa of oxygen is admitted to the UHV chamber. The in-plane cluster growth resumes when oxygen pressure increases from $10^{-7}$ to $10^{-5}$ Pa. We envision that our findings will contribute to whisker-free safer SSLIB performance under realistic operating conditions.

**9:40am SU+AC+MI+MS-TuM-6 Unique Super-Ionicity Achieved on the Nanoscale with Applications in Next-Generation Lithium Ion Batteries**, *Progna Banerjee, D Dumett Torres, P Jain,* University of Illinois at Urbana-Champaign
Lithium-ion (Li-ion) batteries have been dominating the global market for consumer electronics and power vehicles. However, significant safety concerns arise from degradation reactions (reduction/decomposition) of the electrolyte during cycling, potentially causing dendrite formation resulting in leakage and fires. A potential solution is the replacement of the flammable organic electrolyte with an inorganic solid electrolyte with superior electrochemical, mechanical and thermal stability, absence of leakage, long shelf-life, enhanced electrochemical stability and the possibility of battery miniaturization.

A promising candidate for these solid electrolytes are super—ionic materials which exhibit high ionic conductivities matching those of liquid electrolytes. In these materials, past a phase transition, one sub-lattice (often the cationic) melts, resulting in a disordered cation network, wherein cations can transport in a manner reminiscent of that of a liquid. Known superionic materials, such as AgI, $Cu_2Se$ etc. in their bulk form, display this phase transition at high temperatures and/or pressures, making them unsuitable for many applications. In our recent study, we examined $Cu_2Se$ nanocrystals (NCs) prepared from their magic-sized CdSe counterparts using a synthetic topotactic method called cation exchange. In these NCs, the superionic disordered "liquid-like" behavior was observed under ambient conditions. Larger NCs prepared under similar conditions interestingly display ordered layers of $Cu^+$ ions and vacancies similar to bulk solid. We investigate the origin of this nanoscale effect using arguments based on lattice strain, cationic occupancies obtained from crystallography, and density functional theory (DFT) calculations.

We are extending this work to investigate the possible mechanism of ionic transport in these NCs using a.c. impedance measurements. We are investigating size and dimensionality effects on the transport behavior of cations and the superionic phase transition. We will also investigate the effect of cation vacancies in terms of their profile and density on the phase transition behavior and ionic conductance. This study will pave the way to fundamental understanding on ion transport behavior in solids, and applications as solid-state electrolytes, thermoelectrics and ultrafast electronic switches.

**11:00am SU+AC+MI+MS-TuM-10 Electric Cell Potential Driving Changes in Perovskite Surface Termination and Enabling Catalysis**, *Monika Backhaus,* Corning*; L Gregoratti, M Amati,* Elettra-Sincrotrone Trieste, Italy **INVITED**
Dynamic segregation processes in perovskite electrodes have been studied in operando in electrochemical model cells with thin zirconia electrolyte and mixed perovskite catalyst by spatially resolved scanning photoelectron microscopy (SPEM) in combination with impedance spectroscopy and gas analysis in the goal to gain better understanding of electrode surface chemistry and its key drivers. We focused on the oxygen reduction reaction at perovskite electrodes and electrochemically driven reactions, such as redox reactions in chemical reactors or sensors. The current overview summarizes our synchrotron in-operando surface spectroscopy in various technical areas.

Our electrochemical cells are built of a thin zirconia electrolyte and mixed perovskite catalyst. They were studied by SPEM at the Elettra synchrotron. The experimental set up allowed operating temperatures up to 700C, mixtures of unreactive or reactive gases at chamber pressure up to $10^{-5}$ mbar and local pressure above the sample of 1mbar (gas jet). Electrochemical measurements, such as monitoring of i-V behavior or impedance were realized simultaneously.

The surface termination of $(La,Sr)MnO_3$ (LSM) electrodes was studied as a function of cell potential, oxygen partial pressure and temperature. The surface chemistry reversibly changed with applied potential, exhibiting Mn-termination in highly oxygen-rich environment and increasing strontium segregation in oxygen-poor environment and under reducing cell potential. Cathode termination changed not only with applied cell potential, but also with cell current. LSM cathode pump cells operating at high current densities preserved an "oxygen-rich" surface chemistry under high cell potential, while low current cells exhibited large changes in surface chemistry.

The response of perovskite electrodes to reactive gas environment was also investigated. Model cells with LSM electrodes were studied in oxygen-propene gas mixtures at different cell potentials under oxygen flux at 400-600°C. Oxygen ion flux and cell potential, both were found to drive dynamic changes of catalyst and electrolyte surface chemistry, including redox reaction, surface segregation and long range surface diffusion. Strongly positive cell potential drove an interaction of hydrocarbon with the mixed oxide catalyst surface, yielding adsorbed carboneous species with epoxy-type bonding at a strongly Sr-enriched surface. The carboneous surface complexes reversibly formed and decomposed with cell potential, suggesting it to play the role of an intermediate in an oxide-electro-catalyzed partial oxidation of propene.

**11:40am SU+AC+MI+MS-TuM-12 Possibilities of Hydrogen Energy Utilization in Kazakhstan: Preparation of TiCrMn Hydrogen Storage Alloys and Investigation of Their Absorption Properties**, *Saule Zholdayakova, H Uchida, Y Matsumura,* Tokai University, Japan
The society of Kazakhstan has been becoming strongly dependent on fossil fuels, which results in facing serious environmental problems. Kazakhstan is a Central Asian country with rich natural resources, such as Mn, Cr and Ti and energy self-sufficiency is 200% including exportation. Most of the consumption is fossil resources, mainly dependent on coal. The power configuration of Kazakhstan is 70% coal, 19% natural gas, 1% oil, and 10% hydraulic power. With a background of rich production of fossil fuels, Kazakhstan exports most of its oil and domestically dependent on coal. By 2020, Kazakhstan government planning to reduce the amount of green house gas produces by 15% of that in 1992. For these reasons, the development of renewable energy is significant. In this study we focus on

the application of hydrogen as an energy carrier for spreading renewable energy, especially hydrogen energy to solve the environmental problems in Kazakhstan. Hydrogen has more energy per unit of mass, flexible storage options, and it is clean energy. Hydrogen can be stored as a gas, a liquid and as a solid. The other side, for realization hydrogen energy system we need to think more concretely about a manufacture of hydrogen, storage, transportation and utilization. The main manufacture method for hydrogen is electrolysis. The electricity consumption per capita is 5000 kWh/year. If hydrogen energy become a conductor of energy, $1.13m^3$/year of water will necessary to source of hydrogen. After utilizing renewable energy for product hydrogen from water, storage, transport and change to electric power. In the end of consumption, we get the same amount of water. In this study, especially conditions necessary for the renewable energy in Kazakhstan are summarized and trained to preparing hydrogen storage ally using the metals of Mn, Cr and Ti available in Kazakhstan.

## Actinides and Rare Earths Focus Topic
## Room 22 - Session AC+MI+SA+SU-TuA

### Actinide and Rare Earth Theory
**Moderator:** Ladislav Havela, Charles University, Czech Republic

2:20pm **AC+MI+SA+SU-TuA-1 Magnetic Susceptibility, Magnetic Resonance, and Bonding in Actinide Complexes: Ab-initio Calculations**, *Jochen Autschbach,* University of Buffalo, SUNY **INVITED**
Actinide complexes exhibit fascinating magnetic properties and interesting chemical bonding. An on-going research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, and other spectroscopic parameters of actinide complexes in relation to their chemical bonding, in particular regarding the involvement of the 5f shell in metal-ligand bonding. We will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods.

References: Gendron, F. et al., 'Puzzling lack of temperature dependence of the $PuO2$ magnetic susceptibility explained according to ab-intio wavefunction calculations', J. Phys. Chem. Lett. 2017, 8, 673-678. 'Ligand NMR chemical shift calculations for paramagnetic metal complexes: 5f1 vs. 5f2 actinides', J. Chem. Theory Comput. 2016, 12, 5309-5321. 'Magnetic properties and electronic structure of neptunyl(VI) complexes: Wavefunctions, orbitals, and crystal-field models', Chem. Eur. J. 2014, 20, 7994-8011. Knecht, S. et al, 'A nonorthogonal state-interaction approach for matrix product state wave functions', J. Chem. Theory Comput. 2016, 12, 5881-5894. Silver, M. et al., 'Characterization of berkelium(III) dipicolinate and borate compounds in solution and the solid state', Science 2016, 353, aaf3762.

3:00pm **AC+MI+SA+SU-TuA-3 Combining DMRG with Standard Relativistic Multireference Methods to Probe the Properties of Strongly Correlated Systems: Plutonium Oxides**, *Valérie Vallet, S Kervazo,* CNRS / University of Lille, France*; F Réal,* University of Lille, France*; A Severo Pereira Gomes,* CNRS / University of Lille, France*; F Virot,* IRSN, France **INVITED**
Actinide-containing complexes present formidable challenges for electronic structure methods due to the large number of degenerate or quasi-degenerate electronic states arising from partially occupied 5f and 6d shells. In particular, we focus our study here on volatile forms of plutonium such as $PuO_2$, $PuO_3$ or $PuO_2(OH)_2$, for which spectroscopic and thermodynamics properties are of interest.

To attain an accuracy comparable to that of experiments, highly accurate calculations including static and dynamic correlation effects as well as relativistic effects are required. Conventional multi-reference methods, however, can treat active spaces that are often at the upper limit of what is required for a proper treatment of species with complex electronic structures and large number of valence orbitals involved in chemical bonds, leaving no room for verifying their suitability.

In this work, we address first the issue of properly defining the active spaces in such calculations, and introduce a protocol to determine optimal active spaces based on the use of the Density Matrix Renormalization Group algorithm and concepts of quantum information theory.[1]

The guidance offered by this protocol allows us to define the suitable active space to compute the electronic structures

and the nature of the ground states with the desired accuracy, i.e. the clear multi-reference character of the wave-function of those compounds requires that the energies of formation to be computed with multi-configurational quantum chemical methods like CASSCF and CASPT2 and with spin-orbit interaction, treated here *a posteriori* with the state-interaction RASSI method. Specifically, our results illustrate the complex multi-configurational character of $PuO_3$. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.

5:00pm **AC+MI+SA+SU-TuA-9 The Thermal Expansion of UC and $UO_2$ from First Principles Calculations - The Importance of Correlations Effects and Spin-orbit Coupling**, *Dominik Legut,* IT4Innovations Center, VSB - Technical University of Ostrava, Czech Republic*; U Wdowik,* Pedagogical University, Poland*; P Piekarz,* Polish Academy of Sciences, Poland*; G Jaglo,* Pedagogical University, Poland*; L Havela,* Charles University, Prague, Czech Republic
Uranium monocarbide, a potential fuel material for the generation IV reactors, is investigated within density functional theory. Its electronic, magnetic, elastic, and phonon properties are analyzed and discussed in terms of spin-orbit interaction and localized versus itinerant behavior of the 5f electrons. We demonstrate that the theoretical electronic structure, elastic constants, phonon dispersions, and their densities of states can reproduce accurately the results of x-ray photoemission and bremsstrahlung isochromat measurements as well as inelastic neutron scattering experiments only when the 5f states experience the spin-orbit interaction and simultaneously remain partially localized [1]. The partial localization of the 5f electrons could be represented by a moderate value of the on-site Coulomb interaction parameter of about 2 eV. The results of the present studies indicate that both strong electron correlations and spin-orbit effects are crucial for realistic theoretical description of the ground-state properties of uranium carbide. This is even more pronounced considering the thermal expansion and thermal conductivity of UC, where for the latter the optical phonon branches may cause a significant contributions [2]. We compare the novel material UC to the experimental data and to the presently used nuclear fuel material, $UO_2$ oxide. Here our calculations show that considering the exchange and electron correlations effects the generalized gradient approximation was successful in describing the phonon dispersion spectrum, thermal expansion, and heat capacity w.r.t to the recorded data [3]. For both materials the so-called direct method, based on the harmonic and quasi-harmonic approximation, was used [4]. To study the pressure dependence of the phonon frequencies of $UO_2$ we calculated phonon dispersions for several lattice constants. Our computed phonon spectra demonstrate the opening of a gap between the optical and acoustic modes induced by pressure. Taking into account the phonon contribution to the total free energy of $UO_2$ its thermal expansion coefficient and heat capacity have been computed from first-principles [3].

1. U. D. Wdowik, P. Piekarz, D. Legut, and G. Jaglo, Phys. Rev. B **94**, 054303 (2016).

2. P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander, and R. Caciuffo,

Phys. Rev. B 93, 144301 (2016).

3. Y. Yun, D. Legut and P. M. Oppeneer, J. Nucl. Mat. **426**, 109 (2012).

4. K. Parlinski, Z.-Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997); K. Parlinski, Software PHONON, ver. 6.15, Krakow, Poland, (2015).

## Sustainability Focus Topic
## Room 5 & 6 - Session SU+2D+MS+NS-TuA

### Membranes, Thin Films, and Sensors
**Moderators:** Keith Brown, Boston University, Roya Maboudian, University of California at Berkeley

2:20pm **SU+2D+MS+NS-TuA-1 Protecting Food and Water Quality: Considerations for Materials Innovation**, *Susan Duncan,* Virginia Polytechnic Institute and State University **INVITED**
Innovation in materials and membranes provides opportunity for enhancing water and food safety, diversifying and expanding water and food sources, protecting nutrient quality and bio-availability, and improving human health and well-being. Food and water are transitioned from their original sources into resources for animal feed and human food through production, processing, packaging, and distribution/retail stages. Throughout these stages, membranes and materials for physical and chemical separations, microbiological control, analysis and measurement, capture and containment are required.

Synergistic partnerships, among scientific disciplines and between private-public entities, encourage innovation in the design and applications of materials and membranes for discoveries and advancements in water and food processing and packaging. The objective of this discussion is to showcase the engagement of chemists, engineers, and food scientists in approaching and resolving challenges relating to water and food processing, safety, and quality and the relationship to the consumer. Three featured examples, relating to membranes and materials, include:

1. Aquaculture: Recirculating water for the purpose of raising fish has high economic and global impact by increasing sustainable supply of high quality food proteins for feeding the growing global population. Challenges include the need for removing biosolids, small molecular weight molecules, and bacteria that influence fish health and quality of the fish as a food source.

2. Water Safety from Source and Supplier to the Consumer: Protecting public health is the primary role of water treatment. Changes in water disinfectant treatment, e.g. chlorine to chloramine, affect material stability, safety and performance and can lead to significant economic impacts and consumer concerns.

3. Food Packaging Functionality: Protecting food and beverage freshness from processing to purchase requires understanding of the food system, the process, and storage conditions. Innovative materials that interfere with light energy can protect beverage and food quality for retaining freshness and nutrient retention for enhancing human health.

Expanding our scientific continuum from molecule to materials through process, package and consumer perspective enriches and guides scientific discovery.

**3:00pm SU+2D+MS+NS-TuA-3 Real-time Detection of Water Contaminants Using a Graphene-based Field-Effect Transistor Sensing Platform**, *Junhong Chen,* University of Wisconsin - Milwaukee **INVITED**
The National Academy of Engineering identified "providing access to clean water" as one of the top 10 grand challenges for engineering in the 21st century. A central requirement for safe drinking water is the availability of low-cost and real-time water quality monitoring. Current detection methods for critical analytes in water are often too expensive or unsuitable for in-situ and real-time detection (*an unmet need*). As a result, there is a lack of water quality monitoring along the water distribution line and at the point of use, which is inadequate because of potential deterioration in water quality within water distribution systems (e.g., Flint Water Crisis). This talk will unveil a powerful approach to real-time water sensors through a graphene-based field-effect transistor platform. The working principle of the sensor is that the conductivity of 2D nanomaterial channel (usually measured in resistance) changes upon binding of chemical or biological species to molecular probes anchored on the graphene surface. As such, the presence and the concentration of analytes, such as heavy metals, bacteria, and nutrients, can be rapidly determined by measuring the sensor resistance change. The talk will introduce the performance of the sensor for detection of various water contaminants and focus on the molecular engineering aspects of the sensor device through both theoretical and experimental approaches. The talk will end with a brief introduction on the translation of the platform technology from concept to prototype product through partnership with industries.

**5:00pm SU+2D+MS+NS-TuA-9 Nanocellulose Thin Films and Nanocellulose Aerogels**, *Kenneth Carter,* University of Massachusetts - Amherst*; A Chang, K Martin, Y Li,* University of Massachusetts – Amherst **INVITED**
Nanocellulose is an interesting material with unique properties and chemistry. We have worked to exploit these characteristics to develop new functional thin films and aerogels. We have developed a new method for the preparation of well-dispersed cellulose nanofibrils and nanocrystals. Advantageously, the method does not require the use of harsh acids and excludes the use of catalytic oxidants such as 2,2,6,6-tetramethyl-1-piperidine-N-oxy (TEMPO) . Furthermore, the nanofibrils and nanocrystals produced by the method are easily re-dispersible and give stable aqueous dispersions. Transparent, robust nanocellulose thin films were prepared with outstanding anti-fogging properties. Most recently, nanocellulose was used to prepare aerogel/foam materials using a new fabrication method. The aerogels are mechanically stable and robust. Our new aerogel fabrication process obviates the need to use freeze-drying or low pressure solvent removal. We will present data on new nanocellulose aerogels with densities ranging from 5-100 mg/cm$^3$.

**5:40pm SU+2D+MS+NS-TuA-11 Fabrication and Characterization of Thermal Treated Si/Si+Ge Thin Films For Energy Harvesting**, *S Budak, Z Xiao, Michael Howard, B Rodgers, M Alim,* Alabama A&M University
Thermoelectric thin film devices were prepared from the alternating nanolayers of Si and Si+Ge to form the Si/Si+Ge thin films structures using DC/RF magnetron sputtering system. Fabricated thermoelectric devices were treated at different temperatures for an hour for each case to form quantum (nano) structures in the alternating nanolayers of Si and Si+Ge to increase both the Seebeck coefficients and the electrical conductivity and decrease the thermal conductivity. The prepared Si/Si+Ge thin film thermoelectric devices were characterized using the Seebeck coefficient measurement; the four probe van der Pauw resistivity measurement and the laser thermal conductivity systems for in-plane geometries. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS). Thermal treatment showed positive effects on the thermoelectric properties of Si/Si+Gethin films on the selected temperatures. The findings will be presented during the meeting.

**Acknowledgement**

6:00pm **SU+2D+MS+NS-TuA-12 Thermoelectric Properties of Bi$_2$Te$_3$/Sb$_2$Te$_3$ Thin Films Annealed at Different Temperatures**, *S Budak, Z Xiao, M Howard, Breonna Rodgers, M Alim,* Alabama A&M University
Thermoelectric devices were prepared from Bi$_2$Te$_3$/Sb$_2$Te$_3$ thin films using DC/RF magnetron sputtering system. Fabricated devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thermoelectric devices were characterized using Seebeck coefficient measurement system; four probe van der Pauw measurement resistivity system and the laser thermal conductivity system. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM/EDS).

**Acknowledgement**

## Nanometer-scale Science and Technology Division
## Room 19 - Session NS+SS+SU-WeM

### Nanotechnology for Renewable Energy

**Moderator:** Robert Ilic, National Institute of Standards and Technology (NIST)

**8:40am NS+SS+SU-WeM-3 Can "Photovoltaic" Halide Perovskites (MAPbI₃ & MAPbBr₃) be Ferroelectric?**, *David Cahen,* Weizmann Institute of Science, Israel **INVITED**
Ferroelectricity, well-known in oxide perovskites, was suggested as possible reason for the outstanding solar-to-electrical energy conversion of MAPbI$_3$ & MAPbBr$_3$-based halide perovskite PV cells, esp. because ferroelectric domain wall conduction was thought to keep photogenerated charges separated.( à low carrier recombination rate à high photovoltage efficiency).

Contradicting e xperimental evidence, relevant to ferroelectricity, is based on structural diffraction, electric field vs. polarization plots, second harmonic generation and piezoelectricity measurements . To resolve this debate we first asked if

· the materials are pyroelectric, direct evidence for *spontaneous polarization*, a necessary condition for ferroelectricity.

· polar-domains exist in the structure, as often found in many ferroelectric materials.

Using home-grown, well-characterized single crystals, we find the cubic phases of MAPbI$_3$ (>330K) and MAPbBr$_3$ (>236K) phase to be non-polar, excluding ferroelectricity in them. The tetragonal phase of MAPbI$_3$, however, shows clear evidence of pyroelectricity when probing the potentially-polar, [001], crystallographic orientation, proving its polar nature. By adding low-temperature electric field vs. polarization and room temperature SHG studies and optical observations of polar domains, we arrive at a clear-cut conclusion that MAPbI3 is ferroelectric in the tetragonal phase. I will briefly dwell on the remaining question, i.e., "does that really matter?".

\* work done by Yevgeny Rakita, Dr . David Ehre, Omri Bar-Eli, Elena Meirzadeh, Hadar Kaslasi, Yagel Peleg, with Profs. Gary Hodes, Igor Lubomirsky, Dan Oron, all from the Weizmann Inst.

**9:20am NS+SS+SU-WeM-5 NSTD-Recognition Award Talk: Mixed-Dimensional Nanomaterial Heterostructures for Electronic and Energy Applications**, *Mark Hersam,* Northwestern University **INVITED**
Layered two-dimensional (2D) nanomaterials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, the emerging layered 2D nanomaterials can be integrated with a diverse range of other materials, including those of different dimensionality, to form van der Waals heterostructures. This talk will explore mixed-dimensional combinations of 2D + n-D (n = 0, 1 and 3) materials, thus significantly expanding the van der Waals heterostructure concept [1]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly [2]. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, and boron nitride) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [3]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic and energy applications can be enhanced including digital logic circuits [4] and lithium-ion batteries [5]. Furthermore, by integrating multiple nanomaterial inks into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [6], gate-tunable photovoltaics [7], and neuromorphic memristors [8]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across previously unexplored mixed-dimensional heterointerfaces.

[1] D. Jariwala, *et al.*, *Nature Materials*, **16**, 170 (2017).

[2] J. Zhu, *et al.*, *Advanced Materials*, **29**, 1603895 (2017).

[3] J. Kang, *et al.*, *Accounts of Chemical Research*, DOI: 10.1021/acs.accounts.6b00643 (2017).

[4] M. Geier, *et al.*, *Nature Nanotechnology*, **10**, 944 (2015).

[5] K.-S. Chen, *et al.*, *Nano Letters*, **17**, 2539 (2017).

[6] D. Jariwala, *et al.*, *Nano Letters*, **15**, 416 (2015).

[7] D. Jariwala, *et al.*, *Nano Letters*, **16**, 497 (2016).

[8] V. K. Sangwan, *et al.*, *Nature Nanotechnology*, **10**, 403 (2015).

**11:00am NS+SS+SU-WeM-10 Magnetron Sputtered Nanostructured TiO₂ Thin Films for Dye Sensitized Solar Cells Applications**, *Pierre-Antoine Cormier, J Dervaux,* ChIPS, University of Mons, Belgium*; Y Pellegrin, F Odobel,* CEISAM, University of Nantes, France*; R Snyders,* ChIPS, University of Mons, Belgium
Among the many advantages of Dye Sensitive Solar Sells (DSSCs), their non-toxic and low cost components, their lightweight and their high performances under diffuse light and high temperatures are very interesting. DSSCs are therefore considered as a promising alternative to conventional Si and chalcogenide based solar cells. In DSSCs, the light is absorbed by dye molecules inducing an electron injection into a TiO$_2$ nanoparticles (NPs)-based photo-anode. Although this allows a high photon collection, the charge transport is limited by charge recombination at the NPs boundaries limiting the solar to conversion efficiency [1]. Many efforts have been devoted to rule this problem such as replacing NPs by nanofils, nanotubes or hierarchical nanostructured thin films which offer a direct path way to electrons [1]. We previously shown that such hierarchical structure can be obtained by reactive magnetron sputtering (RMS) at grazing incidence which allows to tune the film morphology from slanted nanoculmns, to zigzag or pillars [2].

In this work, such films were synthesized and annealed during 2h at 773 K under atmospheric pressure in order to obtain nanocolumns composed by a single anatase crystal as verified by TEM. These films were used as photo-anode in liquid DSSCs, which were characterized under simulated AM1.5 Global spectrum and 1sun illumination. Different morphologies (slanted columns, zigzag and pillars) and different thicknesses of slanted columns based films were studied. In addition, the dye grafting efficiency on these structures was evaluated by absorbance measurements performed by UV-Visible spectrophotometry.

The slanted columns-based cells present the best performances followed by zigzag and pillar based ones. This result is directly related to the corresponding specific surface area which is the highest for the slanted columns films. By increasing the thickness of the slanted films from 1.2 to 4.3 μm, the cell efficiency increases from 1.2 to 2.6 %. As the short-circuit current density also increased while the open circuit voltage was not affected, it was concluded that the critical parameter limiting the cell efficiency is the adsorbed dye density, which is enhanced for thicker films

To overcome this limitation still using thin films, the slanted columns films were impregnated by TiO$_2$ NPs (~20nm). This allows for an enhancement of the cell efficiency by 2.2% attributed to a synergetic effect between: (i) a higher dye adsorption and (ii) and the very good charge transport through the single crystalline columns.

[1] A. Hagfeldt et al. "Dye-Sensitized Solar Cells," 2010

[2] J. Dervaux et al., Vacuum, vol. 114, pp. 213–220, Nov. 2014.

**11:20am NS+SS+SU-WeM-11 Spectroscopic Evolution of Halide Perovskite Growth on Graphene Oxide Surfaces for Photovoltaics**, *Muge Acik,* Argonne National Laboratory*; G Lee,* Ulsan National Institute of Science and Technology, Korea*; R Rosenberg,* Argonne National Laboratory
High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. Hybrid organic-inorganic methylammonium lead halides, MAPbX$_3$ (X=I, Br, Cl)/mixed-halides (I$_{3-x}$Cl$_x$, I$_{3-x}$Br$_x$) have been reported as light harvesting layers with tunable bandgaps, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination (1). Graphene-derived hybrids has recently emerged as an ETL/HTL replacement in these devices. Graphene/perovskite structure-property relationships are, however, not well understood due to unclear chemistry at the ETL/perovskite/HTL interfaces (2). Moreover, effect of film thickness, lead content, stoichiometry control, and overlayer/underlayer morphology/composition ought to be examined for better charge transport at the graphene/perovskite interfaces. Stability factors also need to be

studied for charge mechanisms to unravel device performance challenges. Indeed, underlayer ETLs (TiO₂/Al₂O₃) and overlayer HTLs (spiro-OMeTAD) were rarely studied with graphene. To address scalability and stability issues, we investigated degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature (≤600°C, Ar(g)) *in situ* spectroscopy (infrared absorption and micro-Raman). Controlled perovskite formation was achieved at room temperature for bromide-based perovskites resulting in improved chemical stability (vs. iodide/chloride derivative). Perovskite decomposition was observed at ≥150°C on RGO surfaces. Oxygen-induced chemical reactions occurred at ≤150°C, initiated at room temperature because of precursor interactions forming carbonyls upon perovskite deposition (3), and eliminated hydroxyls reducing GO during perovskite growth. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O₂, H₂O). Film morphology was explored by SEM, XRD, XPS, AFM, and the reaction mechanisms were studied by first principles calculations that bring insights for solar cell design principles.

Acknowledgement

**11:40am NS+SS+SU-WeM-12 2D Material Laminates for Ultra-fast and Selective Molecular-scale Separation**, *Saeed Moghaddam,* University of Florida

Due to their intrinsic properties, 2D materials have provided a unique opportunity to develop membranes with ultrafast and highly selective permeation capability. Graphene oxide (GO) is among 2D materials that has garnered significant attention in the past several years and numerous studies have been conducted on transport characteristics of its laminates. However, a comprehensive understanding of the effect of synthesis conditions on physicochemical conditions of GO that dictate transport characteristics of its laminates is lacking. In this study, the effect of oxidation conditions during the synthesis process of GO flakes on transport characteristics of GO laminates are investigated. Transport properties of the GO laminates are observed to be significantly different. It is determined that i) mean-flake size, ii) surface defects, and iii) inter-layer spacing are the key parameters.

The fundamental knowledge gained has been utilized to developed membrane separators for energy and water applications. To enhance performance of DMFCs, it was determined that at a constant oxidation level methanol permeability decreases linearly with increasing the GO mean flake size while changes in proton conductivity remain insignificant. This behavior is attributed to difference in adopted conduction pathways of protons and methanol molecules. With increasing the oxidation level, proliferation of surface defects is deductively reasoned to be the dominant factor responsible for a large increase in the measured methanol permeability. The proton conductivity is also significantly increased with increasing the oxidation level because of greater number of ion exchange sites, shortened transport pathway and increased GO flakes inter-layer spacing. The observed transport characteristics are attributed to either different adopted conduction pathways or surface mobility of protons and methanol molecules. The findings imply that the GO nanoplatelets contain atomic formations that are more selective to protons than to methanol molecules.

We have also utilized the superior water selective transport properties of GO laminates as filtration membranes for Endocrine Disrupting Compounds (EDCs) with high permeate flux rates. A layer-by-layer (L-b-L) approach was utilized to prepare thin film composite membranes with a polymer support and a few layers of GO interlinked via poly(allylamine hydrochloride) (PAH).

The prepared membrane showed a fourfold increase in the permeate flux in comparison to the commercially available nanofiltration (NF) membranes. The rejection performance of the membrane was evaluated by studying the permeation of ibuprofen and a rejection rate of 75% was obtained.

## Sustainability Focus Topic
## Room 5 & 6 - Session SU+AS+EM+MS-WeM

## Piezoelectrics, Thermoelectrics, and Superconductors

**Moderators:** George Nolas, University of South Florida, Kimberly Cook-Chennault, Rutgers University

8:20am **SU+AS+EM+MS-WeM-2 Investigation into Novel p-type Thermoelectric Materials**, *Dean Hobbis, K Wei, G Nolas,* University of South Florida

Novel thermoelectric materials are in high demand due to the ability to directly convert waste heat into electrical power, a process that has limitless applications both privately and commercially. Currently n-type thermoelectric materials have been more vastly studied than p-type and have been optimized to higher Figures of Merit (ZT). A thermoelectric module requires both n-type and p-type materials, therefore the efficiency of the module is characterized by the combination of ZT values. This means the optimization of p-type thermoelectric materials is extremely important to the commercial viability of thermoelectric technology. Furthermore, the particular synthesis method is also of importance for applications in industry. In skutterudites, for example, methods of fractional filling are typically used to improve thermoelectric efficiency by promoting phonon scattering to reduce thermal conductivity in the material, but most of the elements used as filler are electron donors. Nevertheless, Br is an electron acceptor when used as a filling atom [1]. In quaternary chalcogenides, thermal conductivity can be intrinsically low due to the crystal structure so methods to improve electrical transport is often employed through alloying and substitution on different atomic sites. Certain antimonides also possess intrinsically low thermal conductivity. Furthermore, differing processing conditions can influence the transport properties significantly, resulting in different ZT values. In this talk we present our latest work on these material systems, including new data that shows substantial improvement In ZT with composition and processing conditions.

[1] Nolas et al. *Mat. Res. Soc. Symp.* 626, **2001**, Z10.1.1

8:40am **SU+AS+EM+MS-WeM-3 Thermoelectrics for Sustainable Energy Harvesting**, *Mary Anne White,* Dalhousie University, Canada **INVITED**
Thermoelectrics can convert heat to power. The key to this process is the combined electrical (high electrical conductivity and Seebeck coefficient) and thermal (low thermal conductivity) properties. Although thermoelectrics have been used commercially for more than 50 years, new materials with higher efficiency could make their use more widespread. A large fraction of energy consumed is actually wasted as heat, so efficient conversion of this waste heat to useable power would be a great advantage to humanity. After a general introduction to thermoelectrics, this presentation will focus on improvement of thermoelectrics via sustainable approaches, including consideration of sustainability of the elements, and recent work focusing on elements with high availability.

9:20am **SU+AS+EM+MS-WeM-5 Toward a Greener World: The (Re)search for Lead-Free Piezoelectrics**, *Xiaoli Tan,* Iowa State University **INVITED**
Piezoelectricity refers to the linear coupling, in the direct effect, between mechanical stress and electric displacement, and in the converse effect, between mechanical strain and applied electric field. The proportionality constants are the piezoelectric coefficients which are equivalent between the direct and the converse effects. For the past six decades ceramics based on Pb(Zr₁₋ₓTiₓ)O₃ (PZT) perovskite oxides have been the workhorse of piezoelectric technology due to their excellent properties, ease of processing, and low cost. The high piezoelectric performance of PZT is primarily resulted from the intrinsic lattice distortion and the ferroelectric domain switching. However, environmental concerns with lead have stimulated worldwide intensive efforts in the search for lead-free piezoelectric ceramics.

The research efforts on lead-free piezoelectric ceramics have been largely concentrated on three solid solution families: BaTiO₃-based, (K₀.₅Na₀.₅)NbO₃-based, and (Bi₁/₂Na₁/₂)TiO₃-based compositions. BaTiO₃-based ceramics exhibit excellent piezoelectric coefficients, but their applications are limited by their low Curie points (~100 °C). (K₀.₅Na₀.₅)NbO₃-

based compositions possess high piezoelectric coefficients and relatively high Curie points (> 200 ºC), but have stringent requirements on the processing conditions. $(Bi_{1/2}Na_{1/2})TiO_3$-based polycrystalline ceramics develop giant electrostrains (up to 0.70%), but usually require a very high electric field.

In this presentation, an overview of the recent development in the search and research on lead-free piezoelectric ceramics will be given. Their chemical compositions, structure evolutions, and mechanisms for property optimization will be discussed. In addition, two specific investigations will be presented. The first one is on the microstructural response to poling electric fields in the $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ solid solution. With the *in situ* transmission electron microscopy technique, it is directly observed that poling fields can either destroy or create morphotropic phase boundaries and the associated strong piezoelectric property. The second investigation is on the development of a giant electrostrain of 0.70% at 50 kV/cm at room temperature in $\{[Bi_{1/2}(Na_{0.84}K_{0.16})_{1/2}]_{0.96}Sr_{0.04}\}(Ti_{0.975}Nb_{0.025})O_3$. This polycrystalline ceramic with randomly oriented grains is even better than some single crystals in terms of some electromechanical properties. *In situ* transmission electron microscopy examination indicates that the giant electrostrain is originated from the reversible phase transitions under applied electric fields.

}

11:20am **SU+AS+EM+MS-WeM-11 Thermal Annealing Effects on the Thermoelectric Properties of Si/Si+Sb Thin Films**, *Satilmis Budak, Z Xiao, M Curley, M Howard, B Rodgers, M Alim,* Alabama A&M University

Thermoelectric devices were prepared from multi-nanolayered Si/Si+Sbthin films using DC/RF magnetron sputtering system. Thermoelectric devices were annealed at different temperatures to form quantum (nano) structures in the multilayer thin films to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The prepared devices were characterized using Seebeck coefficient measurement; four probe van der Pauw measurement resistivity and the laser thermal conductivity systems. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS).

**Acknowledgement**

11:40am **SU+AS+EM+MS-WeM-12 Critical Current by Design**, *George Crabtree, U Welp,* Argonne National Laboratory; *K Kihlstrom,* University of Illinois at Chicago; *A Koshelev,* Argonne National Laboratory; *A Glatz,* Northern Illinois University; *I Sadovskyy, W Kwok,* Argonne National Laboratory **INVITED**

We introduce a new approach for rational design of superconducting critical currents, using time-dependent Ginzburg-Landau simulation to predict the critical current produced by an arbitrary mixed pinning landscape. Time dependent Ginzburg-Landau simulations automatically take into account vortex flexibility, the variation of coherence length with temperature and field, the mutual interaction of vortices and the interaction of vortices and defects. Core pinning by an arbitrary mixed pinning landscape is included by lowering the superconducting condensation energy at points, along lines and within finite nanoscale regions corresponding to specific pinning defects. We show results for several real-world cases that verify predictive ability, outline a program for unfolding the interaction of multiple pinning defects and for maximizing the critical current in targeted temperature and field ranges

*Vortices in High Performance High Temperature Superconductors*, W. K. Kwok et al., Reports on Progress in Physics. 79, 116501 (2016)

*Toward Superconducting Critical Current by Design,* Ivan A. Sadovskyy et al, Advanced Materials 28(23), 4593-4600 (2016)

# Author Index

## Bold page numbers indicate presenter