

## 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<sub>2</sub> 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  $\sim 10^{-7}$  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, *Pragna 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<sub>2</sub>Se 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<sub>2</sub>Se 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<sup>+</sup> 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<sub>3</sub> (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 carbene species with epoxy-type bonding at a strongly Sr-enriched surface. The carbene surface complexes reversibly formed and decomposed with cell potential, suggesting it to play the role of an intermediate in an oxide-electrocatalyzed 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

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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<sup>3</sup>/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.

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