SESSIONS AND ABSTRACTS

Thursday

8:00: **Oak Ridge National Laboratory Management Welcome**,
Thom Mason, Oak Ridge National Laboratory (ORNL)

8:10: **Symposium Overview**,
Jason Zhang, Pacific Northwest National Laboratory (PNNL), Jack C. Wells, ORNL, and Winfried Wilcke, IBM Research

Session 1: Perspective on the Future of Energy Storage Research I
Session Chair: Jason Zhang, PNNL

8:20: **Energy Storage Materials: Past and Future,**
Stan Whittingham, SUNY-Binghamton

This introductory lecture will discuss chemical energy storage from the 1970's into the future putting today's and tomorrow's research into perspective. All of today's rechargeable lithium-ion batteries use the intercalation concept of the 1970's. Intercalation allows for high power and long-life, because little or no structural change occurs; however, it does constrain the capacity to around 250 Ah/kg for a one-electron redox reaction. Capacities exceeding 300 Ah/kg may be achievable when more than one electron is involved. In contrast, conversion reactions, in which the crystal structure is destroyed and rebuilt each discharge/charge cycle, allows for significantly higher storage capacities. However, this comes at the cost of power capability and cycle life. Moreover, such reactions are inherently volume-intensive and it is not clear at this time if they can achieve higher volumetric energy storage than the next generation intercalation reactions. A third group of batteries utilizes liquid electrodes and a solid electrolyte and might enable the use of pure metal anodes, such as lithium or sodium. These are likely to operate at elevated temperatures, and might find use in large-scale batteries, but less likely in consumer applications. Rechargeable metal-air batteries, in particular lithium-air, face the challenges of both the fuel cell and lithium battery, are likely to need the use of solid protective electrolytes and probably need to be sealed. In all the above cases, it is essential that we understand the electrochemical and chemical reactions occurring and that these be studied *in-situ*.

9:10: **Directions for Energy Storage R&D in the Vehicle Technologies Program,**
Tien Duong, Department of Energy, Office of Vehicle Technologies

10:00: **Comfort Break**

Session 2: Perspective on the Future of Energy Storage Research II

Session Chair: Jack C. Wells, ORNL

10:20: **Present Research and Future Focus of the Batteries of Advanced Transportation Technologies Program,**
Venkat Srinivasan, Lawrence Berkeley National Laboratory (LBNL)

This talk will introduce the Batteries for Advanced Transportation Technologies (BATT) Program, a $16M per year Program run by the Lawrence Berkeley National Lab (LBNL) for the US Department of Energy. BATT is the premier program in the Office of Vehicle Technologies that is charged with performing the research needed to identify the next generation batteries for use in hybrid-electric, plug-in hybrid, and electric vehicle applications. The Program presently funds 31 PIs from across North America with participants in universities, national labs and industry. LBNL is the lead Lab that performs the technical management of BATT.

This talk will describe the structure of BATT, the recent success stories, and the focus of the Program in the coming years. The emphasis of the program in working on short-term goals while simultaneously nucleating research projects that will ensure success in the long-term will be discussed.

11:10: **Moving Away From Conventional Lithium-ion Battery Electrodes – Recent Materials Developments at Argonne National Laboratory,**
Michael M. Thackeray, Argonne National Laboratory (ANL)

Rechargeable lithium-ion batteries have had a profound and revolutionary impact on the battery market and the consumer electronics industry since their launch by Sony Corporation in 1991. These batteries offer at best an energy density of approximately 200 Wh/kg at the cell level. For transportation applications, in particular all-electric vehicles, this energy density is too low to make electric power competitive to the internal combustion engine for providing an acceptable driving range. Concerted research efforts are therefore being made to investigate the possibility of exploiting Li-O_2 and Li-S electrochemical couples that offer, at least in principle, significantly higher energy densities. In this presentation, recent progress made at ANL in designing and exploiting electrocatalytic materials that participate in the charge and discharge reactions at the oxygen electrode of Li-O_2 cells will be discussed.

12:00: **Lunch**
(Speaker, TBD)

1:00: **Materials Science and Materials Chemistry for Large Scale Energy Storage,**
Jun Liu, PNNL

This talk aims to discuss important cross-cutting, fundamental materials science and materials chemistry challenges that are applicable to a range of technologies encountered in electrochemical storage. This talk will attempt to highlight the critical materials problems using specific examples and results from recent efforts to reduce the cost and improve the performance of electrochemical energy storage devices. Specifically, this talk discusses 1) the characterization and understanding of the complex solution chemistry and redox reactions in concentrated, aggressive electrolyte solutions;

2) approaches to develop new battery designs and new chemistry combinations to reduce the cost; and, 3) limitations and challenges of the electrode materials, nanoporous materials and ion selective membranes. In addition, the paper discusses the prospect of emergent technologies with ultralow costs on new energy storage materials and mechanisms.

Session 3: Lithium-air Batteries I

Session Chair: Alan Luntz, IBM Research

1:50: **Electrode Processes in the Nonaqueous Lithium-air Battery,**

Kuzhikalail M. Abraham, Northeastern University

The rechargeable Li-air battery utilizing nonaqueous electrolytes, in which the active positive electrode, O_2, is accessed from the atmosphere (1,2), has received significant attention recently as it is the highest energy density battery theoretically possible after the Li/F_2 couple. The specific energy of the battery calculated for a discharge reaction involving the reduction of O_2 to O_2^{2-} at an average voltage of 2.9 V is 5200 Wh/kg. The presently available data suggest that this battery is rechargeable although only a limited number of cycles have so far been demonstrated. The four-electron reduction of O_2 required to achieve the full energy capability of the Li/air battery suggests that the multi-step O_2 reduction processes involved in the discharge and charge processes must be elucidated in order to transform it into a long cycle life practical battery. To this end, we have studied the electrochemistry of O_2 in a series of organic electrolytes in order to determine the kinetics and mechanism of O_2 reduction, the products thus formed, and their rechargeability. We have found that O_2 reduction reactions in organic electrolytes are unique and different from those observed in aqueous electrolytes. The first product of oxygen reduction in nonaqueous electrolytes is superoxide, O_2 (eqn. 1). In electrolytes containing tetrabutyl ammonium (Bu_4N^+) salts, the superoxide, is extremely stable as Bu_4NO_2, whereas in Li ion-conducting electrolytes, the LiO_2 formed is unstable and decomposes to Li_2O_2 and O_2 (eqn.3). The LiO_2 that survives decomposition is reduced to Li_2O_2 (eqn.4). These finding can be explained using the Hard Soft Acid Base theory of Pearson (3).

$$O_2 + Li^+ + e^- = LiO_2 \qquad [1]$$
$$2\,LiO_2 = Li_2O_2 + O_2 \qquad [2]$$
$$LiO_2 + Li^+ + e^- = Li_2O_2 \qquad [3]$$

Li_2O is probably formed as the ultimate reduction product of O_2 via the reaction in equation 4.

$$Li_2O_2 + 2Li^+ + 2e^- = 2\,Li_2O \qquad [4]$$

We have identified the main discharge product of the Li-O_2 battery to be Li_2O_2 from the Raman Spectrum, and X-ray diffraction pattern and SEM-EDX analyses of the discharged electrodes. Factors affecting the rechrgeability of the Li-air battery, as we presently understand, will be discussed.

References:

1. K. M. Abraham and Z. Jiang, J. Electrochem. Soc., 143, 1 (1996)
2. C. O' Laoire, S. Mukerjee and K .M. Abraham, E. Plichta and M.A. Hendrickson, J. Phys. Chem C, 113, 20127 (2009).
3. C. O' Laoire, S. Mukerjee and K .M. Abraham, E. Plichta and M.A. Hendrickson, J. Phys. Chem C, 114, 9178 (2010).

2:40: **Investigating the Electrochemistry of Lithium-O_2 Battery Using DEMS and Surface Characterization Techniques,**

Girish Gopalakrishnan and Bryan McCloskey, IBM

Two complementary studies of lithium-oxygen electrochemistry were performed. The first of these focused on the use of Differential Electrochemical Mass Spectrometry (DEMS) combined with isotopic labeling to probe the gases evolved during the discharge and recharge of lithium-oxygen cells. Carbonate-based electrolyte solvents (*e.g.*, ethylene carbonate/dimethyl carbonate mixtures) were found to mostly produce CO_2 during recharge, indicating that irreversible solvent decomposition occurs. To better understand the solvent's role in producing the desired rechargeable chemistry (*i.e.*, $Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$), DEMS and isotopic labeling were used to also study other aprotic solvents. Two ethereal solvents, dimethoxyethane and tetraglyme, were found to evolve oxygen upon cell recharge, albeit at a rate lower than expected from the amount of oxygen consumed during discharge. Similar behavior was observed with dimethyl sulfoxide.

In the second study, lithium-oxygen discharge electrodeposits formed on smooth, glassy carbons electrodes were characterized by both electrochemical and surface analytical techniques. In addition to using common galvanostatic discharge and cyclic voltammetry methods to independently produce and characterize the deposits, Ferrocene was used as an internal electrochemical redox probe to track *in-situ*, the changes in electron conductivity with the formation of reaction products. These studies revealed that a critical thickness of the electrodeposit was coincident with exponentially decreasing electron transport and cell failure. E*x-situ* analysis of the electrodeposit using focused ion beam micromaching combined with conductive atomic force microscopy yielded results consistent with the *in-situ* findings. Additional *ex-situ* analysis of the electrodeposits using scanning electron microscopy, X-ray photoelectron spectroscopy, and Auger microscopy revealed the presence of lithium carbonates, lithium alkyl carbonates, and lithium oxides when such deposits were formed with the use of carbonate-based electrolyte solvents.

3:30: **Afternoon Break**

Session 4: Lithium-air Batteries II

Session Chair: David Wesolowski, ORNL

3:50: **Status of Nonaqueous Lithium-air Battery Technology and Remaining Technological Barriers,**

Lonnie Johnson, Excellatron Solid State LLC

Improve the performance characteristics of the Lithium-oxygen/Lithium-air battery by focusing on the implementation of a solid state, Lithium ion conductive electrolyte barrier to provide a stable interface with both the anode and cathode to control

passivation phenomena at the electrodes, promote good morphology of re-deposited Lithium metal during charging, and protect the anode from chemical reaction with the cathode reactant.

4:30: **Fundamental Study on Rechargeable Reaction of Lithium-oxygen Battery,**
Fuminori Mizuno, Toyota

Rechargeable Li-air battery is a promising candidate for post lithium-ion battery with high energy density. Using carbonate-based liquid electrolytes, we have already confirmed the rechargeability of Li-O_2 batteries over 100 cycles and their capacity retention of over 60 %. However, a large voltage gap of about 1.4 V was observed in the discharge and charge profiles, resulting in low energy efficiency of the batteries. In order to clarify the reason for the large voltage gap, discharge and charge reactions on a cathode were investigated in detail. It was found that a carbonate solvent was first decomposed by one-electron reductant, O_2 radical, and then carbonate species, X-O-(C=O)-OLi were deposited on a cathode during discharge. After recharging, the carbonate species decomposed and CO_2 gas evolved. It was, thus, suggested that the electrolyte solvents would play an important role in controlling the cathode reaction due to O_2 radical. In this presentation, we will propose the electrolyte solvents to control the rechargeable reaction as indicated in $2Li^+ + x/2O_2 + 2e^- = Li_2O_x$.

5:10: **O_2 Electrocatalysis for Li-air Batteries**,
Yang Shao-Horn, Massachusetts Institute of Technology (MIT)

Session 5: Posters
Session Chair: Larry Curtiss, ANL

5:50: **Posters** (Hors D'oeuvres Served)

Friday

Session 6: Lithium-air Batteries III
Session Chair: Winfried Wilcke, IBM Research

8:00: **Rechargeable Aqueous Li-air Battery Development at EDF: Problems, Solutions, and Future Challenges**,
Philip Stevens, Electricite de France (EDF)

8:40: **Water Stable Lithium Metal Electrode for Lithium-air Rechargeable Batteries,**
Osamu Yamamoto, Mie University, Japan

A water stable multilayer lithium-metal anode consisting of a lithium metal, a PEO based polymer electrolyte, and a NASICON-type lithium-ion conducting solid

electrolyte was proposed as the lithium anode for lithium-air secondary batteries. This type lithium electrode could be used as the anode for aqueous lithium-air batteries and also is quite effective to protect the water contamination from air in organic electrolyte lithium-air batteries.

The stability of the NASICON-type solid electrolyte, Li2-x-yTi1-xAlx(P1-ySiyO_4)3,in aqueous solutions was examined and found that the electrolyte is unstable in strong acid and basic solutions, but stable for a long period in a neutral solution with lithium-ions. The interface resistances of the water stable lithium metal electrode were measured using an ac impedance technique. The significant resistance was observed between the lithium metal and the polymer electrolyte. These resistances and a dendrite formation of lithium in a lithium deposition were improved by addition of a nano-size inorganic filler and a ionic liquid into the polymer electrolyte.

In this talk, we will discuss the possibility of the aqueous lithium-air secondary batteries using the water stable lithium metal electrode.

9:20: **High Energy Density Li-Air and Li-CFx Batteries: A Reaction Mechanism Study,**
Yong Yang, Xiamen University, China

10:00: **Comfort Break**

Session 7: Alternative Battery Technologies I
Session Chair: Gao Liu, LBNL

10:20: **Developing Lithium-Sulfur Chemistry for High Energy Rechargeable Batteries,**
John Affinito, Sion Power

Lithium-sulfur (Li-S) batteries offer the highest specific energy and volumetric energy densities of any electrochemical couple involving only solid elements – more than four times that of the highest energy Li-ion battery chemistries in use today. However, commercialization has been hampered due to cycle-life limitations. The major failure mechanisms/cycle life issues are traceable to solvent reactions with the metallic lithium anode, while the dominant safety issues involve sulfur reacting with the metallic lithium anode. The fundamental aspects of Li-S cell chemistry are reviewed, the primary Li-S cell failure mechanisms are discussed and Sion Power's approach to increase cycle life, increase energy density and improve safety of Li-S cells is presented.

At Sion, the cycle life and safety issues are each addressed by protecting the lithium anode by a variety of methods, including: doped, vacuum deposited lithium, utilizing a sputtered current collector; a combination of vacuum deposited Lithium-ion conducting ceramic/polymer multi-layer coatings; a slot-die coated polymeric gel layer; and uniaxial pressure applied to the packaged cell. A limited amount of data on the effects of these protection methods on the metallic lithium will be presented.

11:00: **Solid-state Batteries with Lithium Metal Electrodes,**
Nitash Balsara, LBNL

Nanostructured block copolymer electrolytes comprising soft conducting channels embedded in a hard insulating matrix were developed for rechargeable lithium batteries.

In contrast to both current liquid and solid electrolytes, the ionic conductivity of the electrolyte increased with increasing molecular weight, thus enabling optimization of both its electrical and mechanical properties. The ability of block copolymer electrolytes to slow down the formation of lithium dendrites in demonstrated. The structure of the electrode-electrolyte interface before and after cycling was studied by electron microscopy.

11:40: **Ionic Liquids, Lithium Salts, Solvents and Water: Phase Behavior and Molecular Interactions,**
Wesley A Henderson, North Carolina State University

Significant attention has been devoted in recent years to the use of ionic liquids as electrolyte materials for lithium batteries – the latter include not only Li-ion, but also lithium metal and perhaps lithium/air batteries. Ionic liquids (ILs) are salts or mixtures of salts (composed solely of ions) which melt at low temperatures - frequently below room temperature. The negligible volatility of these liquid salts, combined with other properties such as high ionic conductivity, low flammability and high electrochemical/thermal stability, suggests that ILs may be well suited as candidates for battery electrolyte materials. Much remains unknown about the properties of ILs when mixed with lithium salts and how such mixtures interact with solvents (which may be contaminants or utilized as additives). In particular, certain ILs are known to phase separate from water and are frequently dubbed "hydrophobic." This trait has resulted in many advocates for the use of ILs in lithium/air batteries to limit the corrosive reaction between lithium metal and water. This presentation will therefore explore the phase behavior of IL-lithium salt mixtures, the influence of solvent on this phase behavior and the validity regarding IL hydrophobicity.

12:20: **Lunch**

12:40: **Lunch Presentation: Advanced Li-ion Battery and Beyond at Samsung,**
Mark Lefebvre, Samsung Electronics

Session 8: Alternative Battery Technologies II
Session Chair: Ray Bair, ANL

1:20: **Task-specific Ionic Liquids for Energy-related Applications,**
Sheng Dai, ORNL

Conventional synthesis of electrode materials and electrolytes in energy storage devices relies heavily on molecular solvents. Alternatively, the synthesis of functional electrode and electrolyte materials using, or in the presence of, ionic liquids represents a burgeoning direction in materials chemistry. Ionic liquids are a family of non-conventional molten salts that can act as both templates and precursors to functional materials, as well as solvents. They offer many advantages, such as negligible vapor pressures, high ion conductivities, wide liquidus ranges, good thermal stability, tunable solubility of both organic and inorganic molecules, and much synthetic flexibility. The unique solvation environment of these ionic liquids provides unique media for controlling ion transport and synthesizing electrode materials. Challenges and opportunities in this research area will be discussed.

2:00: **Mapping the Diffusion and Electrochemical Reactivity of Ions in Solids on the Nanoscale,**
Sergei V. Kalinin, ORNL

2:40: **Lithium-ion Conductive Glass Ceramics: Properties and Application in Lithium Metal Batteries,**
Kousuke Nakajima, Ohara Inc., Japan

3:20: **General Discussions and Conclusion Remarks,**
Jason Zhang, PNNL, Jack C. Wells, ORNL, and Winfried Wilcke, IBM Research