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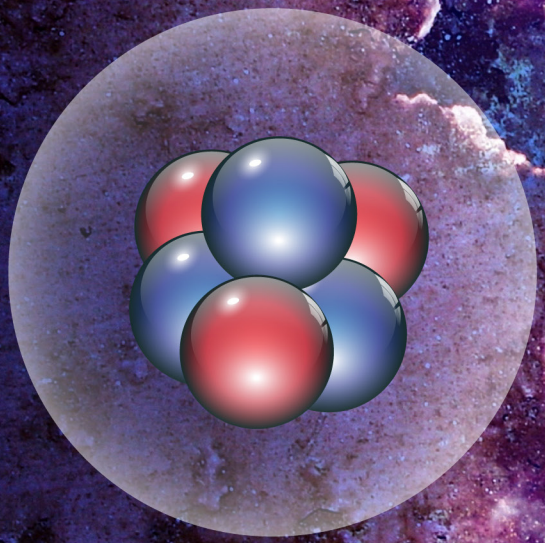

Poster Session

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Come see the outstanding poster session at the

5th Symposium on Energy Storage: Beyond Lithium Ion.

This is a list of the posters that will be featured in the session.

1 The effect of nanocomposite anode microstructures on electron and ions transport, volume and stress evolution during charging: A phase-field model

Shenyang Hu,* Yulan Li, Maria L. Sushko, and Kevin M. Rosso

Pacific Northwest National Laboratory, Richland, WA

A meso-scale phase-field model was developed to simulate electron and ion transport, volumetric and stress evolution during charging in model porous nanocomposites of carbon and titania. The model is informed by thermodynamic and kinetic properties such as electro-chemical potentials, anisotropic dielectric constants of titania crystals, the anisotropic mobility of charged particles, lattice and elastic constants, obtained from classical density function theory (cDFT), molecular dynamics simulations, and experimental measurements. Using this model we have studied the charging process in two- and three-dimensional networks of carbon coated titania grains. Electron and ions diffusion, local charge segregation, electric potential evolution, volume and stress changes, and charge rates were simulated. The effect of nanocomposite morphology including nanoparticle sizes, their relative orientations and arrangements on ion and electron transport efficiency and stress distribution are investigated. The results demonstrate the capability of the phase-field model to study the effect of composite structures on charge transport, deformation and stresses with implications for the overall battery performance.

* Corresponding author: Shenyang.hu@pnnl.gov

2 One-step synthesis of sulphur-impregnated graphene cathode for lithium-sulphur batteries

Min-Sik Park,[1] Young-Jun Kim,*[1] Ji-Sang Yu,[1] and Shin Kang[2]

[1]Advanced Batteries Research Center, Korea Electronics Technology Institute, Republic of Korea; [2]Technology Innovation Center, SK Holdings, Seoul, Republic of Korea

A practical route is introduced for synthesizing sulphur-impregnated graphene composite as a promising cathode material for lithium-sulphur batteries. Sulphur particles with a size of a few microns are successfully grown in the interior spaces between randomly dispersed graphene sheets through a heterogeneous crystal growth mechanism. The proposed route not only enables the control of the particle size of active sulphur but also affords quantitative yields of composite powder in large quantities. We investigate the potential use of sulphur-impregnated graphene composite as a cathode material owing to its advantages of confining active sulphur, preventing the dissolution of soluble polysulphides, and providing sufficient electrical conduction. A high discharge capacity of 1237 mAh g-1 during the first cycle and good cyclic retention of 67% after 50 cycles are attained in a voltage range of 1.8 to 2.6 V *vs.* Li/Li^+. These results emphasize the importance of tailoring cathode materials for improving the electrochemical properties of lithium-sulphur batteries. Our results provide a basis for further investigations on advanced lithium batteries.

* Corresponding author: yjkim@keti.re.kr

3 Materials modeling challenges for future energy storage technologies

Ram Devanathan* and Michel Dupuis

Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, Richland, WA

The development of energy storage technologies that go well beyond the capabilities of current Li-ion batteries calls for revolutionary materials advances, especially in the area of chemically stable, safe, and inexpensive electrolytes that are compatible with new battery chemistries under consideration. Currently available materials for Li-air and Li-S batteries are beset with numerous challenges, such as

- Flammability of the electrolyte, poor ionic conductivity, and low cycle life
- Irreversible processes: capacity fading, internal resistance, and loss of active S
- Electrolyte decomposition when exposed to H_2O or CO_2
- Unstable solid electrolyte interphase (SEI)
- Loss of contact between active electrode particles and current collector
- Formation of Li dendrites with adverse implications for safe device operation.

Experimental studies of novel battery materials are limited in their ability to probe transient processes that occur at the nanoscale in active energy storage devices. This presentation will outline our multiscale, data-driven modeling approach to understand battery materials from the molecular level to the mesoscale as part of a fundamental science-based effort to overcome the materials development challenges for energy storage. At the most fundamental level, we employ density functional theory (DFT) to study the structure and energetics of model electrolytes. We also use ab initio molecular dynamics (AIMD) simulations to obtain information about ion transport pathways and solvation structures. We will showcase results from our AIMD and classical molecular dynamics (MD) simulations of polymer membranes and ionic liquids (ILs).

* Corresponding author: ram.devanathan@pnnl.gov

4 Electrochemical stability of nonaqueous electrolytes for rechargeable lithium-air batteries

Yuyan Shao,* Wu Xu, Fei Ding, Zimin Nie, Mark Engelhard, Jie Xiao, Jiguang Zhang, Yong Wang, and Jun Liu

Pacific Northwest National Laboratory, Richland, WA

Rechargeable lithium air (oxygen) battery is emerging as a transformative energy storage technology due to its potentially high energy density/specific energy. However, the use of oxygen cathode and lithium metal anode also presents significant challenges for nonaqueous electrolytes. For a practical nonaqueous Li-air battery, the requirements of electrolytes, in addition to those for Li-ion battery, should at least include: 1) high stability in oxygen-rich electrochemical conditions, 2) compatibility with Li metal anode, and 3) high boiling point. Currently, the "high stability in oxygen-rich electrochemical conditions" is the priority to meet. Due to the high reactivity of oxygen reduction/oxidation intermediates (O, O_2^-, LiO_2, etc.) in Li-air battery, traditional organic electrolytes are decomposed during discharge and charge. This leads to the formation of lithium (alkyl) carbonates and lithium hydroxide, instead of the desired Li_2O_2 as discharge product, only which can make Li-air battery sustainably rechargeable. Therefore, a stable electrolyte which can exclusively form Li_2O_2 is very important. In this work, we developed a protocol for fast screening of stable electrolytes for Li-air battery. The stability study of various nonaqueous electrolytes (including solvents and lithium salts) in oxygen-rich electrochemical conditions will be presented.

* Corresponding author: yuyan.shao@pnnl.gov

5 Implications of the formation of small polarons in Li_2O_2 for Li–air batteries: First-principles study

Joongoo Kang,* Anne C. Dillon, and Su-Huai Wei

National Renewable Energy Laboratory, Golden, CO

Lithium-air batteries (LABs) have recently been revitalized as a promising electrical energy storage

system due to their exceptionally high theoretical energy density. However, its usage is limited by poor rate capability and large polarization in the cell voltage primarily due to the formation of Li_2O_2 in the air cathode. Here, by employing hybrid density functional theory, we show that the formation of small electron polarons in Li_2O_2 limits the electron transport in Li_2O_2.[1,2] Consequently, the low electron mobility, $\mu = 10^{-10}$–10^{-9} cm^2/V s at room temperature, contributes to both the poor rate capability and the polarization of LABs. We suggest that p-type doping of Li_2O_2 and/or designing alternative carrier conduction paths for the cathode reaction could improve the performance of LABs at high current densities.

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* Corresponding author: joongoo.kang@nrel.gov

6 Structural and mechanistic revelations on an iron conversion reaction from pair distribution function analysis

Badri Shyam,* Karena W. Chapman, Mahalingam Balasubramanian, Robert J. Klingler, George Srajer, and Peter J. Chupas

X-ray Science Division, Argonne National Laboratory, Argonne, IL

Nanoscale electrodes (1–100 nm) are expected to play a significant role in the next-generation of high-performance batteries.[1,2] However, due to the nano-size of both starting materials and products during operation, characterizing their structure and behavior presents a challenge that is yet to be fully addressed. High energy X-ray Pair Distribution Function (PDF) methods are capable of providing direct, atomic-level structural insights into nanomaterials, greatly enabling the understanding of their complex phase-behavior.[3–5] As such, the technique is well-suited to investigate conversion electrode materials and the multiple phases that form and coexist during battery operation. Here, we present an *ex situ* PDF study on the complete electrochemical lithiation of α-Fe_2O_3, revealing new details regarding the local structure of the intermediate phases and the formation of iron nanoparticles during discharge. An emphasis will be laid on the merits of using PDF analysis to characterize and study nanoscale electrode materials for energy storage applications.

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* Corresponding author: shyam@aps.anl.gov

7 Lithium/sulfur liquid cell with exceptionally high capacity density

Sheng S. Zhang*

U.S. Army Research Laboratory, Electrochemistry Branch, Adelphi, MD

In this presentation, we disclose a lithium/sulfur liquid cell that has exceptionally high capacity density. In such a cell, the cathode is composed of a highly porous carbon cloth (CC) as the current collector and a porous sulfur paper as the source of active material. In the first discharge, sulfur is reduced on the CC surface into high-order lithium polysulfide (PS), which dissolves into liquid electrolyte and serves as the catholyte of the so-called "Li/S liquid cell". With protection of Li anode employing a $LiNO_3$–contained electrolyte, the Li/S liquid cell is shown to cycle reversibly between 1.7 V and 2.8 V with an initial capacity density of 10.1 mAh cm^{-2} CC, which could be the highest value among the rechargeable Li/S batteries reported ever. This work reveals that the initial mixing state of sulfur and carbon in the cathode is not important since sulfur eventually dissolves into liquid electrolyte in the form of soluble PS, and that the high capacity density Li/S batteries can be made through a "Li/S liquid cell" by employing a highly porous carbon electrode to accommodate the insoluble sulfur reduction products (Li_2S_2/Li_2S) with appropriate protection of the Li anode.

* Corresponding author: shengshui.zhang.civ@mail.mil

8 SEI slow formation by stabilized lithium metal powder in Li-ion batteries

Lei Wang,* Vince Battaglia, and Gao Liu

Lawrence Berkeley National Laboratory, Berkeley, CA

With current Li-ion technology, the lithium in the cell is provided by the cathode material, like $LiCoO_2$, which leads to limitations in performance. In the process of Solid-Electrolyte Interphase (SEI) formation, part of lithium was consumed resulting in the first cycle capacity loss. The incorporation of stabilized lithium metal powder (SLMP) developed by FMC corporation into anode has been suggested to overcome the irreversible capacity loss, which can increase the capacity by 5~10%. Moreover, non-lithiated cathode materials tend to have much higher specific capacities than lithiated cathode materials. When the fully lithiated anode is used together with the high capacity of non-lithiated cathode, the full cell capacity can significantly increase.

In this report, we demonstrated the application of SLMP in the anode materials. Two different strategies have been applied: either the SLMP was homogenized together with anode materials to cast film, or the SLMP was applied directly on top of the anode films. The prelithiated anode was resting for different time periods before cycling without any low C-rate formation. The cycling data suggest that the anode prelithiation can help the development of SEI.

The metallic Li content in SLMP was measured by the Li stripping. SLMP was first weighted precisely, then spread on top of copper disk and crushed by calendar machine to expose the Li out. The crushed SLMP was assembled into a 2325 coin cell with the Li sheet reference/counter electrode. SLMP was electrochemically stripped off the copper surface with the rate of C/20. The metallic Li content is at least 93%, considering the reaction of Li with EC/DEC electrolyte.

CGP-G8 graphite from Conoco Phillips was homogenized with styrene-butadiene rubber (SBR), acetylene black (AB) and SLMP in toluene to make slurry as the ratio of (88% CGP-G8, 5% SBR, 5% AB, 2% SLMP). With the incorporation of SLMP, the open potential dropped quickly from 2.3V to 0.1 V, which indicated the partial lithiation of graphite anode. The capacity dropped quickly at first 10 cycles when no resting. The capacity was increasing up to 10% with the resting time and became stable after 4 days, which reveals the SEI formation process. With the enough resting time, the prelithiated graphite anode can have the SEI developed, which is equivalent to the slow SEI formation while anode lithiation and delithiation.

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* Corresponding author: wanglei@lbl.gov

9 Probing the effects of atomic surface modifications of Li-air electrode

Isaac Scott,*[1,2] Chunmei Ban,[2] Feng Lin,[2,3] Andrew Cavanagh,[1] Yoon Seok Jung,[2,4] Steven George,[1] Anne Dillon,[2] and Se-Hee Lee[1]

[1]University of Colorado at Boulder, Boulder, CO; [2]National Renewable Energy Laboratory, Golden, CO; [3]Colorado School of Mines, Golden, CO; [4]Ulsan National Institute of Science and Technology, Ulsan, South Korea

Rechargeable lithium-air batteries (LABs) are an attractive electrochemical power source due to their high theoretical specific energy density (520 Wh/kg). In theory, a LAB should lead to a four-electron reduction of O_2 to Li_2O, but generally the major product formed has been identified as Li_2O_2 and to a much lesser extent Li_2O. The current study elucidates on the mechanisms that lead to the formation of these final products and investigates the effects of various catalysts deposited by atomic layer deposition (ALD) and their promise for reducing the over-potential that is observed because of the formation of Li_2O_2 (Li_2O). Using ALD allows for the catalyst to be deposited on very high aspect ratio structures and on very high radii of curvature particles, as well as infiltrating very porous high surface area structures. As a process, ALD is a thin film growth method based on sequential, self-limiting surface reactions that can deposit extremely conformal thin films with atomic layer control, ~1.0 Å/cycle. Using this technique, carbon composite electrodes may be

coated with various catalysts including: MnO, Pd, and Pt. Using three different film thicknesses (1cyc, 2cyc, 4cyc) we are investigating the change in the charge/discharge voltage profiles using our standard LAB cell. After cycling the LAB cell, X-ray diffraction patterns of the discharged carbon electrodes reveal the products formed and various potentials (2.0 V for Li_2O_2 and 1.0V for Li_2O). Recently, via a collaborative effort with the Stanford Synchrotron Radiation Light Source, we also have data that suggests that a NiO_X-based catalyst may be very useful in promoting in the breakdown of Li_2O_2. Finally, using a rotating ring disk electrode, we examine the products formed from the catalyst coated disk at the ring electrode. This provides us with information about the products formed, their relative amounts, if they are electrochemically active, and whether or not they are stable. Understanding these mechanisms will allow us to overcome current obstacles facing the development of LABs. These results will all be discussed in detail.

* Corresponding author: Isaac.Scott@colorado.edu

10 Prototype primary Li-air batteries

Owen Crowther,* Lin-Shu Du, David M. Moureau, Michael Morgan, Idajet Bicaku, Benjamin Meyer, and Mark Salomon

MaxPower, Inc., Harleysville, PA

Lithium air (Li-air) batteries are an ideal power source for applications requiring long life because of their high theoretical energy density. Despite the high theoretical energy density and excellent performance of lab cells in pure oxygen, practical Li-air batteries discharged in wet air suffer from poor energy and power densities. The poor energy density is caused by the large amount of aprotic organic electrolyte required to flood a highly porous air electrode. The poor power density is related to the current density being limited by oxygen transport into the battery and through the flooded air electrode.

Ideas to reduce the mass of electrolyte and increase the oxygen transport rate will be presented. The effect of temperature and relative humidity for ambient discharge of lab cells will also be presented. Finally, the performance of single prototype cells with 40 cm^2 area will be shown.

* Corresponding author: Owen.Crowther@MaxPowerInc.Com

11 Precipitate in separator shortens the Li-O_2 battery's lifespan

Jiang-Lan Shui,[1] John S. Okasinski,[2] Jonathan D. Almer,[2] and **Di-Jia Liu***[1]

[1]Chemical Sciences and Engineering Division; [2]X-Ray Science Division; Advanced Photon Source, Argonne National Laboratory, Argonne, IL

Research on Li-O_2 battery has generated a great deal of attentions due to its high energy storage capacity for future vehicular technology application. Ample amount of studies have been reported on the understanding of the impact of catalysts, cathode structures and electrolytes to the battery performance. At present, the cell stability has become a major challenge. The side-reactions at individual battery sections and their contributions to the overall cell durability are yet to be fully understood. One particularly important issue is the electrolyte stability during the charge and discharge processes in the presence of oxygen. Several recent investigations have linked the shortened battery lifespan to the instability of electrolytes. Oxidative decomposition was attributed as the root cause of the electrolyte loss and detected products included H_2O, CO_2, lithium alkyl carbonates and Li_2CO_3. Since the decomposition would most likely to be catalyzed by the cathode catalyst, the studies so far have mainly focused in this region.

At Argonne National Laboratory, we developed a holistic approach in studying the deactivation mechanism of the lithium-oxygen battery containing carbonate and ether based electrolytes. Various characterization techniques, such as SEM, TEM, FTIR, XRD, were used to analyze the structure, morphology and chemical species at the electrodes and separator regions of the operating battery. Particularly, we introduced a newly-developed, spatially-resolved microfocused synchrotron X-ray diffraction (μ-XRD) technique which enabled us to probe the phase and concentration distributions of individual solid components at the spatial resolution of 20 μm through the entire cell. High spatial resolution and

deep penetration by focused hard x-ray beam render this method a unique tool to investigate the layer-by-layer compositions in the cathode, anode and separator region of the Li-air battery under both *ex situ* and *in situ* conditions. For example, we collected a series of X-ray diffraction patterns progressively from anode-separator interface through the separator and cathode regions of failed Li-O_2 battery cells. We found unexpectedly that there was significantly higher concentration (almost 2×) of Li_2CO_3 in the separator than in the cathode. SEM revealed that the precipitates grew on the separator fiber surface, ultimately obstructing the pores serving as the ion-transport channel. "Refurbished" battery, using a spent separator from a failed battery, showed much higher overpotentials and shorter cycle life as compared to that found in the new one. A model of "precipitation through diffusion" was built which explained the observed carbonate distribution across the separator.

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* Corresponding author: djliu@anl.gov

12 Fundamental research on rechargeable non-aqueous Li-air battery

F. Bardé,*[1] Y. Chen,[2] S. Freunberger,[2] and P.G. Bruce[2]

[1]Toyota Motor Europe, Advanced Technology, Technical Center, Zaventem, Belgium; [2]School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, Scotland

In the last decennia, a lot of effort was dedicated to rechargeable Li-Air batteries, as attested by the constant increase of number of publications. Although this technology might be a solution to develop Hybrid / Electric Vehicles with long cruising range thanks to its high energy density, it remains at the moment a very immature technology.[1] Several problems need to be addressed. Among them, the role of the cathode constituents (carbon, catalyst) and properties (porosity...) in the reaction mechanism is not so clear. Therefore, we have been conducting fundamental research in view to understand the reactions mechanisms at the air cathode. Thanks to a combination of analysis techniques, we could identify the reaction products formed during the discharge and verify which gas was formed during the charge process. We demonstrate that a key issue in the non-aqueous system was to find an electrolyte stable against O_2 radicals. For example, both linear and cyclic carbonates based electrolytes proved to be very unstable in presence of O_2 radicals, leading to the formation of lithium carbonate (Li_2CO_3) as main discharge product, instead of the expected lithium peroxide (Li_2O_2).[2,3] A second study performed in ether-based electrolytes proved that it was possible to form Li_2O_2 as main discharge product during the first discharge. Unfortunately, while cycling, side reactions products issued from the decomposition of the solvent by O_2 radicals were also formed.[4] Finally another class of electrolyte was investigated and proved to be slightly more stable while cycling.[5] Based on the results of our investigations in various types of solvents, we will discuss about possible new classes of candidate electrolytes for future Li-Air battery system.[6]

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* Corresponding author: Fanny.Barde@toyota-europe.com

13 Aqueous sodium ion batteries for grid applications

Mona Shirpour,* Jordi Cabana, and Marca Doeff

Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA

The drastic increase in demand for Li-ion batteries in electronics and automotive industries is expected to be even steeper over the coming years. The increased

demand has already caused an enormous pressure on limited sources of Li and resulted in price rise of Li_2CO_3.[1] For grid applications, sodium ion batteries are interesting alternative to lithium ion batteries. The well-established understanding of lithium based electrochemical system helps the fast replacement/development of Na based components. Aqueous, or water-based, sodium ion batteries would have the extra advantage of being even safer and less expensive.

Identification of suitable materials for sodium insertion/intercalation is the first necessary step in order to develop aqueous Na ion batteries. As sodium intercalation into crystalline graphite[2] (the most common anode in Li ion cells) is very difficult, selection of anode composition is the most challenging part. Furthermore, in aqueous electrolyte systems, both the anode and cathode must undergo redox processes approximately within the voltage stability region of water.

Ternary oxides in the Na-Ti-O system (stepped layered or tunnel structures), and NASICON[3] (Na Super Ionic Conductor) structure tested in Na-half cells with organic electrolyte will be discussed as anode material. $Na_{0.44}MnO_2$[4] and Na_2FePO_4F[5] cathode materials and their performance paired with our selected anode composition will be presented.

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* Corresponding author: MShirpour@lbl.gov

14 *In situ* imaging studies of Li-S and Li-Ge batteries using transmission X-ray microscopy

Johanna Nelson,*[1] Sumohan Misra,[1] Nian Liu,[2] Yuan Yang,[2] Ariel Jackson,[2] Joy C. Andrews,[1] Yi Cui,[2] and Michael F. Toney[1]

[1]SSRL, Stanford Synchrotron Radiation Light Source, SLAC National Accelerator Laboratory, Stanford University, Menlo Park, CA; [2]Stanford University, Menlo Park, CA

We will present recent transmission X-ray microscopy (TXM) work on two Li-ion battery materials. High resolution X-ray imaging allows for direct studies of morphology changes during operation. Additionally, using *in situ* 3D microscopy, volume and density changes can be tracked on the same particle over time.

With its high specific capacity (1673 $mAhg^{-1}$), sulfur is an attractive Li-ion battery cathode material. However, due to the solubility of the higher order polysulfides, Li-S batteries suffer from capacity fading and loss of active material. We will present results from *in situ* TXM studies showing the localization of higher order polysulfide on the cathode throughout the discharge cycle despite their high solubility in the electrolyte. These results contradict *ex situ* SEM and EDS studies on similarly prepared cathodes.

The theoretical capacity (1600 $mAhg^{-1}$) of germanium is more than four times higher than existing commercial anode materials. Nevertheless, with a theoretical volume increase of around 370% due to Li-ion insertion, the Ge anode is believed to crack and pulverize leading to capacity fading. With 3D *in situ* TXM studies, we can quantify this volume change and visualized the formation of cracks in micron-size Ge particles due to the insertion/removal of Li-ions.

* Corresponding author: jlnelson@slac.stanford.edu

15 Pore filling in lithium-air gas diffusion electrodes

Alexander Struck,* Daniela Fenske, and Ingo Bardenhagen

Fraunhofer Institute for Manufacturing Technology and Advanced Materials—IFAM, Oldenburg, Germany

Lithium-oxygen batteries are promising candidates for next generation rechargeable energy storage devices in automotive applications. Expected energy densities higher than 1000 Wh/kg would let them easily outperform conventional Lithium-ion cells.

A typical aprotic Lithium-oxygen system consists of a Li containing anode, an organic electrolyte and a carbon-based gas diffusion electrode (GDE). For now, such cells show a rather disappointing discharge-charge cycling behaviour. This is partially attributed to an electrochemical instability of the electrolytes towards the Lithium-carbon electrode arrangement. Moreover, products of the Lithium-oxygen reactions, both reversible and irreversible, depose on the electrode surface during discharge. This results in a less active surface as well as in a reduced pore volume hampering the oxygen transport and thus preventing the effective distribution of active material in the electrode. Therefore, a description of the pore filling can help to optimize the GDE design with respect to improved performance.

In this contribution, we use a simple mathematical model to describe the pore filling during galvanostatic discharge coupled to oxygen transport in the electrolyte and demonstrate the behaviour of pores with different geometries. In particular, electrodes with meso- and microporous areas are investigated, as for instance found in carbon aerogel based GDEs.

First results based on diffusion-limited transport are compared to the discharge characteristics of carbon aerogel GDEs and support them as well performing electrodes for aprotic Lithium-air cells.

* Corresponding author: alexander.struck@ifam.fraunhofer.de

16 Impact of GDE-design and electrolyte/catalyst couple for lithium-oxygen battery stability

D. Fenske,*[1] O. Yezerska,[1] M. Augustin,[1,2] I. Bardenhagen,[1,3] J. Derendorf,[1,4] T. Plaggenborg,[2] J. Parisi,[2] M. Bäumer,[3] and G. Wittstock[4]

[1]Fraunhofer Institute for Manufacturing Technology and Advanced Materials—IFAM, Oldenburg, Germany; [2]University of Oldenburg, Energy and Semiconductor Research Laboratory, Oldenburg, Germany; [3]University of Bremen, Institute of Applied and Physical Chemistry, Bremen, Germany; [4]University of Oldenburg, Department of Pure and Applied Chemistry, Oldenburg, Germany

Metal-oxygen batteries are of great interest as next generation energy storage devices. In particular, the lithium-oxygen system opens the way to energy densities expected to be much higher than 1000 Wh/kg, which would be well beyond the performance of conventional Li-ion cells.

In general aprotic lithium-oxygen systems include a Li containing anode, an organic electrolyte and a carbon-based gas diffusion electrode (GDE). The structure and composition of the GDE can be modified to improve the insufficient cell performance. To overcome the current GDE limitations regarding e.g. cycle stability caused by deficient kinetics of recharging process and destruction of porous structures during cycling, different carbon materials and catalysts have been tested. It has been shown that the efficiency and re-chargeability of lithium-oxygen cells are not only determined by the nature of the catalyst but also by the decomposition of the electrolyte and degradation of the system itself. In order to distinguish these two aspects that may effect the degradation behaviour, more promising electrolyte systems will be presented as an initial step on the way towards stable and practical Li-oxygen batteries. Beyond that, our future developments focus also on novel designs for the gas diffusion electrodes and different concepts will be presented for discussion.

* Corresponding author: Daniela.fenske@ifam.fraunhofer.de

17 Thin film lithium ion conducting electrolyte for Li metal cells

Joong Sun Park,*[1] Lei Cheng,[1] Jordi Cabana,[1] Guoying Chen,[1] Marca M. Doeff,[1] Thomas J. Richardson,[1] and Wan-Shick Hong[2]

[1]Lawrence Berkeley National Laboratory, Environmental Energy Technologies Division, University of California, Berkeley, CA; [2]Department of Nano Science and Technology, University of Seoul, Seoul, Korea

Batteries based on lithium metal as a negative electrode could potentially bring about significant increases in both specific energy and energy density over current lithium-ion technologies. However, several concerns including stability, safety, and cycling efficiency have limited development. The tendency of lithium metal to form mossy deposits or dendrites upon cell recharge lead to unsafe cells with short lifetimes. The use of

solid state protective layers, which conduct ions but are electronically insulating, has been proposed as a potential solution to enable long cycle life and can enable use with high energy air and sulfur cathodes.[1] Several phases such as LISICON ($Li_{1+x+y}Al_xTi_{2-x}SiyP_{3-y}O_{12}$) and $La_{0.5}Li_{0.5}TiO_3$, among others, are being investigated for this purpose.[2,3] However, these compounds are not stable with respect to reduction by lithium and form electronically conducting phases. To prevent this, an interlayer between the lithium electrode and solid ionic conductor is required. Phases that do not contain redox active transition metals are preferable to avoid the use of an interlayer. We have recently studied the lithium ion-conducting phosphosilicate phase, $Li_{3.4}Si_{0.4}P_{0.6}O_4$ (60%Li_3PO_4-40% Li_4SiO_4), which meets this criterion. $Li_{3.4}Si_{0.4}P_{0.6}O_4$ forms a stable interface against lithium and has an ionic conductivity of 4.5×10^{-6} S/cm at room temperature.[4]

Because this value is about four orders of magnitude smaller than that of a liquid electrolyte, approaches for preparing thin pinhole-free dense layers are needed. The goal is to minimize the ceramic electrolyte impedance while preventing contact between the lithium metal anode and a liquid electrolyte, which wets the cathode. Such a thin ceramic membrane must be prepared on a porous support to provide physical strength. To this end, we are investigating the fabrication of $Li_{3.4}Si_{0.4}P_{0.6}O_4$ thin films using the pulsed laser deposition (PLD) technique. The PLD targets have been synthesized by solid state reaction of Li_4SiO_4 and Li_3PO_4. A 248 nm KrF excimer laser with energy density of 1.5~3 J/cm^2 per pulse was used for ablating the target using an oxygen gas environment in the deposition chamber. For this presentation, we will discuss the physical and electrochemical properties of $Li_{3.4}Si_{0.4}P_{0.6}O_4$ films fabricated with different PLD parameters such as the laser fluence, the laser frequency, the distance between target and substrate, and the substrate temperature.

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* Corresponding author: joongspark@lbl.gov

18 Discharge product control of non-aqueous lithium-oxygen batteries to overcome capacity fading

K. Takechi,*[1] F. Mizuno,*[2] H. Nishikoori,*[3] H. Iba,[3] S. Higashi,[1] T. Shiga,[1] and T. Asaoka[1]

[1]Toyota Central R&D Labs., Inc., Advanced Battery Laboratory, Nagakute, Japan; [2]Toyota Research Institute of North America, Materials Research Department, Ann Arbor, MI; [3]Toyota Motor Corporation, Battery Research Division, Shizuoka, Japan

High energy rechargeable devices beyond lithium ion batteries are of considerable interest to realize a sustainable society. Li-air batteries are one of the promising candidates among them and have been extensively studied worldwide. Since Abraham's group first demonstrated the rechargeability, there have been many efforts to improve the cell capacity, energy efficiency, cycleability and rate capability, focusing on carbon, catalyst, electrolyte and lithium metal. To our knowledge, the cathode reaction mechanism in the conventional carbonate-based system is concluded as follows. During discharge, the carbonate solvent is decomposed mostly caused by O_2 radicals, generated as intermediates of electrochemical reduction of O_2, in spite of the presence of any catalysts. During recharge, the carbonate species deposited on the cathode are further decomposed electrochemically to evolve CO_2 gas.

To overcome the above-described side reaction, we have focused on the electrolyte stability against O_2 radicals i.e. O_2- and LiO_2, and electrochemical and non-electrochemical screenings of electrolyte solvents have been done to find out the alternative of carbonate solvents. As a consequence, we reached a conclusion that *N*-methyl-*N*-propylpiperidinium bis-tri(fluoromethansulfonyl)amide (PP13TFSA) was a good candidate for the highly stable electrolyte against the active radicals. According to our analyses, the main discharge product was Li_2O_2, and O_2 gas was mostly generated during charging. These facts implied that the

electrolyte solvent brought about the reversible reaction on an cathode due to the high stability against the radicals and played an indispensable role to establish the non-aqueous Li-air rechargeable battery.

We, however, faced a serious issue that was a formation of μm-sized discharge products for a further improvement of the battery. According to our results, the aggregates were difficult to be decomposed during recharging because of their insulative nature, and then more aggregates were found to decrease the cell performance, especially for coulomb efficiency as well as cycleability. This should be a fundamental issue to achieve the rechargeability during hundreds of cycles.

In this study, we focused on the cathode architecture and electrolyte viscosity to understand why the discharge products were formed up to μm size and how the discharge products were agglomerated. A CNT based cathode structure was applied to a Li-O_2 battery cathode and the discharge products were carefully observed. Furthermore, to evaluate the effect viscosity for the formation of the aggregates, dimethylsulfoxide (DMSO) as an alternative of PP13TFSA was applied to the electrolyte, and the morphology of discharge product was discussed.

* Corresponding author: e1088@mosk.tytlabs.co.jp

19 *In-situ* observation of Li deposition process in room temperature ionic liquids using optical microscope

Hikari Sakaebe,*[1,2] **Hikaru Sano**,[1,2] and Hajime Matsumoto[1,2]

[1]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST); [2]Japan Science and Technology Agency, Osaka, Japan

Li metal electrode is an important candidate for battery system with high-energy density, and almost indispensable in order to achieve energy density over 500 Wh/kg. In the past, quite a lot of paper was published concerning the improvement in cycling efficiency and morphology of deposited Li in organic electrolyte. These properties were closely related to the chemical state of surface film formed on Li in an electrolyte, and thus to the electrolyte composition. Sakaebe, *et al.* have applied room temperature ionic liquids (RTILs), that are in a liquid state without any solvent, to Li metal electrode and cycling efficiency was evaluated.[1] In that report sufficiently high cycling efficiency of Li in PP13[TFSA] (*N*-methyl-*N*-propylpiperidinium bis(trifluoromethylsulfonyl)amide) electrolyte was confirmed and it was found that the surface of Li counter electrode after cycling test was smooth.

In order to understand the mechanism of dendrite suppression, authors have tried to investigate the effect of electrolyte on the morphology of Li in initial deposition using conventional two-electrode cell.[2] Unfortunately, morphology was altered during the sample preparation procedure and strongly depended on the separator in that case, then importance of *in-situ* observation technique was recognized for this purpose.

From our past study on *in-situ* observation, using PP13[TFSA], PP13[FSA] (*N*-methyl-*N*-propylpiperidinium bis(fluorosulfonyl)amide), EMI [TFSA] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide), and EMI[FSA] (1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide) with/without VC (vinylene carbonate), it was revealed that morphology of electrodeposited Li on Ni depended on the combination of RTIL system and additives.[3] Electrolyte containing PP13[TFSA] and VC suppressed the dendrite formation of Li. Viscosity, cathodic limit potential, and chemical interaction between Li^+, cation, and anion in RTIL may be responsible for the difference described above. In order to see what parameter could be greatly dominant, further observation was carried out using more RTILs with the same number of carbon as $PP13^+$ in this study.

Py14[TFSA] (*N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl) amide) and TMHA[TFSA] (trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl) amide) were chosen for this study. After vacuum dried, electrolyte was prepared mixing 0.32 mol dm^{-3} Li[TFSA] in the dry environment. *In-situ* cell was set up following our previous report.[3] 3 C cm^{-2} of Li was electrodeposited at the current density of 50 μ A cm^{-2}. With VC, both electrolyte brought Li to be electrodeposited in round shape. Dendritic Li was entirely found without VC, however, round shape deposit was also contained in both

cases. The two electrolytes possess relatively higher viscosity and cathodic stability.[4] These properties seem to be indispensable to suppress dendrite with VC. On the other hand, round shape Li was partly obtained without VC. Some more additional parameter should have affected in this case, and further study is now underway.

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* Corresponding author: hikari.sakaebe@aist.go.jp

20 Analyzing cell resistance with electrochemical impedance spectroscopy in lithium-air batteries

J. Højberg*

Haldor Topsøe A/S and Technical University of Denmark, Kgs. Lyngby, Denmark

From a theoretical point of view, Lithium-Air batteries are currently the most promising battery system. The technology is however still in a premature state and commercialization is still years ahead. A further development of Lithium-Air batteries are depending on an improved understanding of the actual mechanisms involved during charge and discharge—both the desired and the undesired ones.

The electrochemical characterization of Lithium-Air battery systems are dominated by charge-discharge curves and cyclic voltammetry. Both methods are well suited as screening tools to distinguish different materials, but in complex systems like the Lithium-Air battery both methods are incapable of determining the reaction and degradation mechanisms and need to be complemented by other techniques. One promising supplement is the Electrochemical Impedance Spectroscopy (EIS) and although this technique is used widely within Lithium-Ion batteries, only few research groups have used it to characterize Lithium-Air batteries.[1,2]

This poster will introduce different EIS measurement series adapted to Lithium-Air batteries. The methods may be used to distinguish between different sources of internal resistance in the battery, differentiate cathode and anode reactions from each other and enable a quantitative description of relevant degradation mechanisms. Certain important features in the EIS spectra will be highlighted and examples of measurements, conducted at a Swagelok-setup, will be discussed.

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* Corresponding author: jhoj@topsoe.dk

21 Improved layered oxide cathodes for lithium-ion batteries

Kinson C. Kam,*[1] Apurva Mehta,[2] John T. Heron,[3] and Marca M. Doeff[1]

[1]Lawrence Berkeley National Laboratory, Environmental Energy and Technologies Division, University of California, Berkeley, CA; [2]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA; [3]Department of Materials Science and Engineering, University of California, Berkeley, CA

One approach to raise the practical capacities of lithium ion batteries involves modifying common layered oxide materials, e.g. NMC, or $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$. While higher capacities can be achieved by raising the charge voltage limit of lithium cells containing unmodified NMCs beyond the usual cutoff of 4.3V, this is detrimental towards cycle life, possibly due to structural changes that occur at high states-of-charge (for example, loss of oxygen). In contrast, we have found that Ti-substituted NMCs, where Co^{3+} is replaced by Ti^{4+}, demonstrate higher capacities and better cycling retention when they are used as cathodes in lithium batteries charged to 4.7V compared to the unsubstituted analogs. In some cases, improvements in practical capacities as high as 15% were observed. The origins of this improvement arise from improved first cycle efficiencies, which result in higher discharge capacities after the initial charge. In this poster, we will discuss the physical and electrochemical properties for several series of NMCs where the Ti content was varied, as well as the origins of the cycling and practical capacity improvements.

* Corresponding author: kckam@lbl.gov

22 Poly(ethylene oxide)-coated graphite as an anode material for lithium ion batteries

Sang-Jae Park* and Gao Liu

Environmental Energy Technology Division, Lawrence Berkeley National Laboratory, Berkeley, CA

Poly(ethylene oxide) (PEO) has a strong interaction with metal ions through the coordination of the ions and the oxygen atoms in the polymer chain and exhibits the ion conduction at room temperature through the continuous PEO segment rearrangement. Compared with the widely used poly(vinylidene fluoride) (PVDF) as a binder, the comparability with Li metal salts and the ion conductance suggests that PEO be used as a binder material for lithium ion batteries. However, the high solubility can increase the dissolution of PEO into the electrolyte for charging/discharging cycles and it would cause the instability of the battery performance during long cycling. In this study, PEO was cross-linked and coated on the surface of graphite via reverse phase synthetic method in order to ensure the uniform coating of PEO onto graphite and prevent the PEO precursors from being homogeneously polymerized in the solution without being coated onto the surface. The as-modified graphite was applied as an anode material and the result shows the high adhesion to the electrode material and copper collector and the electrochemical stability over long cycling.

* Corresponding author: sangjaepark@lbl.gov

23 *In-situ* TEM observation of delithiation/lithiation in $LiFePO_4$ nano-battery

Jun Jie Niu,*[1] Akihiro Kushima,[1] Liang Qi,[1] Jian Yu Huang,[2] and Ju Li[1]

[1]Department of Nuclear Science and Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA; [2]Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, NM

Lithium ion phosphate cathode material stimulates wide interest recently based on its high battery performance and low cost. Researchers have developed lots of different methods including carbon coating and transition metal doping to improve the Li-ion and electron conductivity. Here we present a novel electrospinning method to synthesize one-dimensional $LiFePO_4$ nanowires, which is composed of crystal $LiFePO_4$ core and amorphous carbon shell. A single $LiFePO_4$ nanowire is picked up to form a nano-battery configuration for the delithiation/lithiation observation inside high-resolution TEM. The Li^+ diffusion process is monitored and a slightly swelled volume is found. The data analysis shows that the reaction interface between two end-member phases plays an important role on phase transition.

* Corresponding author: jjniu@mit.edu

24 Parallax in Li-air systems

Katharine R. Ryan,* Anthony K. Burrell, Lynn Trahey, and Brian Ingram

Electrochemical Energy Storage Department, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL

The theory behind Li-Air batteries is elegant and deceptively simple. In reality they are highly complex systems with a prodigious number of parameters to optimize and side reactions to minimize. For such matters to be addressed efficiently, it is essential to have a better understanding of the Li-Air system as it stands.

Due to the complexity of the Li-Air system experiments require very careful planning to ensure observations actually arise from the process of interest. And indeed, that the measurement itself is not destroying that which you wish to observe, for example radiation damage.

A series of fundamental measurements on post cycled Li-Air cell have been made to examine electrolyte decomposition and Li_2O_2 formation. The primary techniques used were IR for the electrolytes and XRD for the peroxide. Both sets of experiments revealed some surprising results about the Li-Air system. In the first set electrolyte decomposition was observed even in cells cycled in the absence of O_2. In the second set, discharge rate was found to have a significant impact on whether Li_2O_2 could be detected by XRD.

* Corresponding author: ryank@anl.gov

25 Characterization of the discharge products in Li-O_2 batteries by non-resonant inelastic X-ray scattering

Naba K. Karan,*[1] Mahalingam Balasubramanian,[1] Timothy T. Fister,[2] and Peng Du[2]

[1]X-ray Science Division; [2]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL

Identifying the discharged products in Li-O_2 batteries is important for understanding the subsequent charging behavior, which in turn is critical for successful rechargeability of Li-O_2 batteries. At present, the understanding of the working principles of Li-O_2 batteries is incomplete and is under continuous evolution. It is now generally accepted that while using conventional carbonate based electrolytes, Li-O_2 activity is dominated by electrolyte decomposition instead of formation/decomposition of Li_2O_2 and/or Li_2O. Spectroscopic techniques, which are elemental specific, are expected to give useful information on the discharged products in Li-O_2 cells, particularly for situations where the discharged products are not formed in well crystalized "bulk" like states. However, such techniques that have been used so far (XPS and soft x-ray absorption) are prone to be affected by surface contamination. In the present work non-resonant inelastic x-ray scattering (NIXS) technique has been employed to obtain bulk sensitive information on the discharged products in Li-O_2 batteries. Li-O_2 coin cells were discharged to 2.2V (*vs.* Li^+/Li) in 1NM3, TEGDME, CH_3CN based electrolytes using low current (0.025 mA/cm^2). NIXS measurements at O and Li K-edges were performed on the discharged Li-O_2 cathodes at sector 20ID, APS using the LERIX spectrometer. A comparison of the characteristic Li_2O_2 feature in the O K edge spectra (at ~532 eV) showed that in all cases the discharged cathodes contain at most 3-5% Li_2O_2. Present NIXS results reveals that at the end of first discharge oxygen in the discharged products is bound predominantly to species other than that in peroxide. Details of NIXS measurements at O and Li K-edges on the discharged Li-O_2 cathodes using various electrolyte solvent/salt combinations will be presented.

* Corresponding author: nkaran@aps.anl.gov

26 Identifying performance-limiting phenomena in Li-air batteries via first-principles simulation

Maxwell D. Radin,[1] Feng Tian,[2] Jill F. Rodriguez,[2] and Donald J. Siegel*[2,3,4]

[1]Department of Physics, [2]Mechanical Engineering Department, [3]Applied Physics Program, and [4]Michigan Energy Institute University of Michigan, Ann Arbor, MI

Thanks to their high theoretical specific energy densities, Li-air batteries are attracting increasing attention as a potentially transformative energy storage technology. However, despite this potential, Li-air technology remains in its infancy, and attaining a viable secondary Li-air battery will require that several challenges be overcome. To accelerate the development Li-air batteries, we employ density functional theory calculations to elucidate those factors that limit performance in this system. Our work addresses the surface and bulk thermodynamics of Li-O discharge phases, and explores mass and electron transport limitations in Li_2O_2 in the bulk and at surfaces. Regarding surface conduction, we examine the competition between band conduction of holes *vs.* that of small hole polarons localized at Li_2O_2 surfaces. Our results suggest that the conductivity of low-energy {0001} surfaces can be several orders of magnitude larger than in the bulk, regardless of the conduction mechanism. Regarding bulk transport, we examine how point defects impact the concentration and conductivity due to hole polarons. Although polarons could be quite mobile in Li_2O_2, our results suggest that the conductivity due to polaron hopping is low as a result of their low concentration.

* Corresponding author: djsiege@umich.edu

27 X-ray diffraction of α-MnO_2 in lithium-oxygen battery cathodes

Lynn Trahey,*[1] Zhenzhen Yang,[2] Chi-Kai Lin,[1] Naba K. Karan,[2] Mahalingam Balasubramanian,[2] Yang Ren,[2] and Michael M. Thackeray[1]

[1]Electrochemical Energy Storage Department, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL; [2]X-ray Sciences Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL

Lithium-oxygen batteries offer extremely attractive theoretical energy densities and therefore represent a rapidly emerging area of research. Numerous technical barriers to realizing efficient, long-lasting cells exist, chief among them being electrolyte instability, charge hysteresis, and anode corrosion. Our research has focused on developing electrocatalytic materials that can lower the charge hysteresis and potentially impact the nature of the discharge products. Specifically, we have synthesized and characterized transition metal oxide electrocatalysts that have natural affinities to the ultimate discharge product in nonaqueous Li-O_2 cells, Li_2O. The most widely recognized charge electrocatalyst at this time is α-MnO_2. However, the discharge/charge reaction mechanisms at work and catalytic efficacy retain a large degree of uncertainty. Herein we present *in situ* high-energy X-ray diffraction (HE-XRD) experiments performed on Li-O_2 cells at the Advanced Photon Source of Argonne National Laboratory. Electrochemical cycling has been performed using three different electrolyte solvents, two different MnO_2-based electrocatalysts, and varying XRD conditions. The results highlight the changes observed in the electrocatalyst and the presence or absence of crystalline discharge products.

* Corresponding author: trahey@anl.gov

28 Freestanding all-carbon electrodes for Li-O_2 batteries

Betar M. Gallant,*[1] Robert R. Mitchel,[1,2] Carl V. Thompson,[2] and Yang Shao-Horn[1]

[1]Electrochemical Energy Laboratory, Massachusetts Institute of Technology, Cambridge, MA; [2]Materials for Micro and Nano Systems Lab, Massachusetts Institute of Technology, Cambridge, MA

Lithium-oxygen (Li-O_2) batteries are receiving increasing attention owing to their high theoretical gravimetric energy densities (~3–5 times higher than lithium-ion).[1] However, despite recent development of carbon-only electrodes achieving a ~4-fold increase relative to $LiCoO_2$ cathodes at the laboratory scale,[2] significant and fundamental challenges remain for development of practical Li-O_2 systems. First, the chemical and electrochemical stability of the electrolyte/electrode system, which has been widely investigated recently, will play a critical role in the selection and design of materials as surfaces for Li_2O_2 formation and growth in order to avoid parasitic reactions. Recently, reports of undesired byproducts such as lithium carbonate and alkyl carbonate formed in carbon-based electrodes during discharge in tetraglyme,[3] and of CO_2 generated during charge even when Li_2O_2 is shown to be the predominant discharge product,[4] have raised important questions regarding the reversibility and overall stability of Li_2O_2 in ether-based electrolytes such as DME. Another open question regards the design of electrodes and surfaces to optimize electrode performance provided a stable electrolyte can be identified. While significant research efforts have focused on the development of catalysts to target both ORR and OER voltages and improve the round-trip efficiency, relatively fewer reports have systematically investigated the influence of the electrode structure on the discharge performance. However, tuning of the electrode structure, which includes active surface area, surface structure, pore volume, pore size distribution, and active material morphology, has been shown to substantially influence the maximum attainable capacity in Li-O_2 electrodes.

Free-standing electrodes consisting entirely of vertically aligned carbon nanotubes (VACNTs), with no binder, substrate or other additives, are used as "clean" model cathodes to study the formation of Li_2O_2 formation during the first and subsequent discharges. First, the

morphology of Li_2O_2 is investigated with respect to parameters such as gravimetric current and depth of discharge, where distinct growth mechanisms can be identified depending on the current regime, leading to clearly observable and distinct morphological trends. The morphology of the discharge product is compared to that formed on aligned carbon nanofibers on a porous alumina substrate reported previously,[2] indicating a surprisingly different morphology at comparable gravimetric currents and which may influence the subsequent charging behavior. Next, we study the cycling behavior of VACNTs by investigating the chemical and structural nature of the product formed on the first and subsequent discharges, as well as the "regenerated" carbon surfaces after charging. We also discuss the charging voltages of freestanding VACNT electrodes and their dependence on parameters such as the cycle number, carbon structure, and discharge product morphology.

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* Corresponding author: bgallant@mit.edu

29 Alternative ion systems: Energy storage in secondary sodium-ion batteries

Michael D. Slater,*[1] Eungje Lee,[1] Donghan Kim,[1] Dehua Zhou,[1,2] Lynn Trahey,[1] and Christopher S. Johnson[1]

[1]Electrochemical Energy Storage Department, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL; [2]University of Rochester, Rochester, NY

Energy storage in non-aqueous sodium-ion electrochemical systems is poised to advance rapidly in the coming years by leveraging the advances in technology driven by lithium-ion battery commercialization. Theoretical energy densities of 150–200 Wh/kg are possible in Na-ion batteries, comparable to current Li-ion technology, using known layered sodium transition-metal oxide cathodes and hard carbon or intermetallic composite anodes (e.g. SnSb/C). A major advantage of replacing lithium with sodium in analogous systems is that sodium is cheaper and, as an unconstrained resource, is not subject to price fluctuations that already affect the lithium market – a problem that will only become worse as Li-ion deployment is broadened. We have examined several experimental Na-ion full cell designs, pairing high capacity layered oxide cathodes with state-of-the-art carbon, titanate, or intermetallic anodes using various electrolyte formulations. Despite being in an early stage of development, Na-ion batteries are attractive for their potential to offer similar performance to Li-ion systems at lower cost.

* Corresponding author: mslater@anl.gov

30 Strategies for lithium stabilization in novel electrochemical systems

Cormac Ó'Laoire,* Jaroslaw Syzdek, and Robert Kostecki

Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA

In order to achieve high energy density batteries for future applications, improvements in the anode performance are necessary. Lithium metal anodes display as much as 3860 mAh g^{-1} in Li-air batteries compared to conventional graphite anodes 372 mAh g^{-1}. In the past, lithium metal anodes were beset with issues such as poor cycle life due to electrode surface morphological changes during deposition/dissolution cycles. Formation of mossy and dendritic growth on Li can compromise cell integrity and lead to short circuits. To overcome this effect, our studies focus on the development of ceramic membranes and cross-linked siloxane containing polymers acting as coatings to protect lithium

A study of Lithium electrodes coated with siloxane polymers in bis(trifluoromethanesulphonyl)imide (LiTMFSI) electrolyte within aprotic gylme solvents have been carried out. Spectroscopic tools such as *in situ* FTIR demonstrate that lithium metal quickly decomposes conventional carbonate-based electrolytes to form a complex SEI layer. Siloxanes varied according

to alkyl group and glymes varied according to n = 1, 2, 3, and 4 ($CH_3O(CH_2CH_2O)_nCH_3$). Using techniques such as AFM, Raman, FTIR and standard electrochemical spectroscopy, the electrode/coating and coating/electrolyte interfaces were probed. The relationship between the surface structural and morphological changes, the surface interfacial behavior, and the electrochemical performance of Li-metal anodes was determined.

Solid state inorganic electrolytes such as OHARA® glass ($Li_{1+X+3Z}Al_x$ $(Ti,Ge)_{2-X}Si_{3Z}P_{3-Z}O_{12}$) were also investigated as promising candidates for the development of artificial interfaces in lithium batteries due to its chemical stability and relatively high Li-ion conductivity ($<10^{-4}$S/cm) at room temperature. Impedance spectroscopy was used to measure the lithium-ion transfer in an OHARA® glass membrane and across the solid/liquid electrolyte interface. Lithium ion solvation and desolvation processes at the solid/liquid glyme electrolyte interface were investigated using a four-electrode Devanathan-Stachurski symmetrical AC impedance cell used for the solid/liquid electrolyte measurements (all lithium electrodes). Gold and aluminum electrodes were deposited directly onto commercially available OHARA® glass by e-beam sputtering in order to characterize the sample independent of electrolyte. RF sputtering was used to deposit thin films of lithium cobalt oxide (LCO) on OHARA® glass. LCO provides a source and sink for lithium ions, allowing an accurate measure of Li ion transport in the glass membrane. The impedance spectra distinguish the contributions from bulk and interfacial regions. These results show that the composition of the solid/liquid interface greatly affects the Li-ion transfer process.

* Corresponding author: cmolaoire@lbl.gov

31 Applications of light element X-ray raman spectroscopy and hard X-ray emission spectroscopy to the electronic structure of energy storage materials under *in-situ* conditions

Dimosthenis Sokaras,* Dennis Nordlund, and Tsu-Chien Weng

Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA

In situ conditions for energy related science applications—and beyond—require the development and implementation of demanding characterization techniques. Hard x-ray based spectroscopies exhibit some unique advantageous properties for providing structural and electronic information under *in situ* environments. Modern high brilliance beamlines in synchrotron radiation facilities and developments in hard-x-ray optics render high energy- resolution x-ray spectroscopy as a state-of-the-art analytical tool.

Recently, we have designed and built a high-resolution and large solid angle spectroscopy end-station at beamline 6-2 at Stanford Synchrotron Radiation Lightsource. Three multicrystal high energy-resolution x-ray spectrometers (a 40-crystal low-q x-ray Raman spectrometer, a 14-crystal high-q x-ray Raman spectrometer and a 7-crystal x-ray emission spectrometer) coupled on a single end-station provide non resonant and resonant inelastic x-ray scattering, as well as x-ray emission and high resolution x-ray absorption (XANES) and extended x-ray absorption fine structure (EXAFS) capabilities.

Both the energy resolution and the high throughput of the instruments enables the real-time characterization of *in-situ* processes towards addressing outstanding scientific questions for a wide range of scientific cases.

Here, we present the applicability of x-ray Raman spectroscopy of light elements and hard x-ray emission to probe the electronic structure of energy storage materials under *in-situ* conditions. In particular, the recent advances in resolution and throughput of x-ray raman spectroscopy (XRS) offer the capability to measure 1s x-ray absorption profiles of light elements such as lithium, boron, carbon, nitrogen and oxygen with less than 0.3eV resolution in the order of 10s of minutes.

Initial results from the Spectroscopy program at SSRL and collaborations with groups in various energy storage fields will be presented, with an emphasis on Lithium Ion/ Air Batteries and Hydrogen Storage applications.

* Corresponding author: dsokaras@slac.stanford.edu

32 Electrochemistry and transport limitations of non-aqueous Li-air batteries from first-principles

V. Viswanathan,[1] J.S. Hummelshøj,[1] A.C. Luntz,[1,2] and J.K. Nørskov[1]

[1]SUNCAT, Department of Chemical Engineering, Stanford University, Stanford, CA and SLAC National Accelerator Laboratory, Menlo Park, CA; [2]Almaden Research Center, IBM Research, San Jose, CA

Li-air batteries have much higher gravimetric energy storage density compared to all other battery chemistries, and this has led to a strong interest in seeing if such batteries could be developed for powering EVs, enabling driving ranges comparable to gasoline powered automobiles. However, many fundamental challenges exist in these batteries that need to be solved before these batteries can become practical.

In this work, we will discuss a detailed electrochemical model describing the discharge process of the growth of Li_2O_2 on terraces, steps and kinks. The different kinds of growth mode along the different kinds of sites have vastly different thermodynamic overpotential. This leads to an explanation of the high Tafel slope observed in the experiments. We will also discuss the effect of deep discharge and the origin of 'sudden death' in these lithium-air batteries and we will show that the origin of this 'sudden death' in flat electrode cells is due to the limitation imposed by electron transport to support the required electrochemistry. Using a simple metal-insulator-metal model, we show that discharge products beyond >10 nm, have serious transport limitations and this leads to a bias rise across the film. In addition, we discuss a model incorporating details from some of the recent experiments that show the presence of a carbonate layer. We conclusively show that the origin of potential rise during recharge of the lithium-air batteries is due to a rising concentration of carbonate impurities at the Li_2O_2-electrolyte interface. This rise in the overpotential leads ultimately to the decomposition of the electrolyte and limits the rechargability of lithium-air batteries.

* Corresponding author: venkvis@stanford.edu

33 Self-breathing polymer framework for Li-S batteries

Lifen Xiao, Yuliang Cao, **Jie Xiao**,* Ji-Guang Zhang, and Jun Liu

Pacific Northwest National Laboratory, Richland, WA

Li/S battery with low cost and high energy density is one of the most promising technologies for the next generation of energy storage systems. However, the practical application of Li-S cells has been plagued by a poor cycling ability caused by soluble polysulfide intermediates. Herein, a flexible interwoven sulfurized polyaniline (referred as SPANI hereafter) is designed to imbed sulfur in the form of S/SPANI composite. The soluble long chain polysulphides produced during repeated cycling are effectively constrained within the SPANI spatial network through both physical and chemical interactions. After 500 cycles a capacity retention rate of 76% is observed in the S/SPANI composite with a reversible capacity of around 432 mAh g^{-1}(at 1C). Compared with the conventional carbon matrix, the framework of the elastic SPANI polymer functions very differently in that the volume of SPANI varies in the same pace as that of S addressing the dislocation issue of sulfur appropriately. The amine groups and/or imine groups decorated on SPANI surface further interacts or attracts the soluble polysulfides anions leading to the superior electrochemical performances. The attractive behavior exhibited by the SPANI/S composite not only underlies a new concept for designing sulfur-based electrode material but also can be applied into many other different applications.

* Corresponding author: jie.xiao@pnnl.gov

34 Sandwiched MWCNT@TiO_2-C nanocables for ultrafast lithium storage

Jianli Cheng* and John B. Kerr

Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA

TiO_2 has emerged as an alternative material to the carbonaceous anode owing to its superior safety, chemical stability, non-toxicity and low price. However, TiO_2, has intrinsically low Li-ion diffusivity (~10^{-12} *to* 10^{-9} $cm^2\ s^{-1}$) and electronic conductivity (~10^{-12} *to* 10^{-7} $S\ cm^{-1}$) which are not conducive to reversible lithiation capacity as well as rate capability. One of the effective ways to improve the electronic conductivity of the TiO_2 material is to interconnect nanostructured TiO_2 materials with highly conductive materials. One-dimensional MWCNT is an ideal conducting substrate. Although MWCNT-TiO_2 based anode materials have been synthesized, the reported method usually contain complex synthetic procedure. It is highly desirable to generate hybrid metal oxide/MWCNT material by a straightforward synthetic route.

In this report, MWCNT@TiO_2-C coaxial nanocables were synthesized by a one-pot hydrothermal reaction by using glucose as a carbon precursor, MWCNT as a structure template and TiO_2 nanoparticle as an inorganic precursor. The prepared MWCNT@TiO_2-C nanocable exhibits superior rate capability, with the capacity of 134 mA h g^{-1} at 10C, 112 mA h g^{-1} at 20C, and 85 mA h g^{-1} at 50C (discharge and charge in 72s). More importantly, a stable capacity of 200 mA h g^{-1} can be delivered when the rate is reduced back to 0.5C, suggesting the good structural stability of the nanocable.

In summary, by a simple synthesis method and low cost starting material, it is now possible to prepare relatively large quantities and high yield of MWCNT@TiO_2-C nanocables for high performance of LIBs. This talk will further describe testing and capabilities of these materials.

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* Corresponding author: Jcheng@lbl.gov

35 Kynar® Waterborne Binder for LIB electrodes

Ramin Amin-Sanayei, PhD,*[1] and Rosemary Heinze

Arkema, Inc., King of Prussia, PA

Polyvinylidene Fluoride is a preferred binder among fluoropolymers for lithium ion battery applications because of its excellent electro-chemical resistance and its superb adhesion. In conventional methods, Polyvinylidene Fluoride is used with large amounts of N-Methyl-2- pyrrolidone (NMP) to produce electrode slurries. The NMP-based slurry presents safety, health and environmental dangers that are not present in an aqueous system; costly manufacturing controls are required to mitigate these risks.

The intent of Kynar® Waterborne Binder is to significantly reduce volatile organic compounds in electrode slurry formulations by replacing most or all of the NMP with water and not compromise battery performance. Kynar® Waterborne Binder is composed of submicron particles of Polyvinylidene Fluoride (PVdF) that are dispersed in water; after drying, it leaves only PVdF with purity of well over 99%.

This waterborne binder has been designed so that it provides the desired properties of the intermediate and the final products. The design considerations include: a) stability of the waterborne fluoropolymer dispersion for having sufficient shelf-life, b) stability of the slurry after admixing the powdery material, c) an appropriate viscosity of the slurry to facilitate good aqueous casting d) no foaming, and e) superb interconnectivity within the electrode after drying.

Kynar® Waterborne Binder has been successfully used to fabricate cathodes using water instead of NMP as the media for the slurry. These cathodes were used to make 18650 cells that subsequently exhibited excellent coulombic efficiency and capacity fade characteristics; the results were equivalent to standard cells made with solvent cast electrodes over 130 cycles. The poster shows a chart for several different discharging voltage profiles versus discharge capacity for $LiCoO_2$ cells made using Kynar® Waterborne Binder and for $LiCoO_2$ cells made using a conventional NMP slurry method, at room temperature.

Additional tests conducted at room temperature and at 60C show that the cyclability of cells made with Kynar® Waterborne Binder is at least as good as that of cells made with solvent cast electrodes. Since the cathode is the most moisture-sensitive part in the cell, the good performance demonstrated here suggests that waterborne fluoropolymer processes can be compatible with overall cell fabrication. These results indicate that a Kynar® Waterborne Binder process in the cathode can be developed to be at least equivalent to a solvent cast process for cell performance and calendar life.

Kynar® is a trademark of Arkema, Inc.

* Corresponding author: ramin.amin-sanayei@arkema.com

36 Cost-effective ionic liquids enable next-generation electrochemical storage

Jerry L. Martin* and Joseph C. Poshusta

Boulder Ionics Corporation, Arvada, CO

New electrode chemistries promise to dramatically improve battery energy capacity, however, conventional organic electrolytes may not meet the requirements for advanced batteries. Room temperature ionic liquids, salts with melting points below room temperature, exhibit both excellent stability over wide electrochemical windows and high conductivity, key parameters for use in high voltage batteries and ultracapacitors. In addition, ionic liquids lack a measurable vapor pressure and therefore possess low flammability, providing a path to increased safety, even with high-energy density batteries.

Although the benefits of ionic liquids as electrolytes have been successfully demonstrated in a number of new battery chemistries, high cost in electrochemical grades has limited their commercial adoption. Conventional synthetic routes to ionic liquids involve complex, multi-step syntheses followed by time- and energy-intensive purification steps. It is unlikely that this approach will ever be successfully scaled to cost-effective production on the ton scale.

Boulder Ionics Corporation is commercializing ionic liquid electrolytes for advanced batteries. These electrolytes are produced using a novel, patent-pending approach with the potential to dramatically improve the cost/performance ratio over current offerings. By applying novel synthetic routes and process intensification methods, significant improvements in both product purity and cost can be obtained. A novel solvent-free and continuous reactor produces virtually pure ionic liquid in a single step. Halide-free synthesis dramatically reduces the need for extensive and costly cleanup. While less flexible than general laboratory methods, the new processing methods have been specifically tuned to continuous manufacturing of high purity ionic liquids in dedicated equipment with low labor costs. Raw material costs are further reduced by applying process intensification principles to their manufacture as well. The result is a processing facility that is easily scalable to tens of metric tons per year, with additional capacity achievable by simply duplicating the process equipment. Combined with advanced chemistry batteries, Boulder Ionics' technology could enable production of ionic liquid electrolytes at costs directly competitive with lower-performing organic electrolytes.

Ionic liquid electrolytes are of particular interest to metal-air batteries, as they do not evaporate and can be made hydrophobic, key features in batteries where the electrolyte can be exposed directly to air. Availability of ionic liquid-based electrolytes and novel metal salts for advanced batteries at competitive prices is expected to accelerate the introduction of battery technologies beyond lithium-ion. In this poster, Boulder Ionics describes its current research into ionic liquid electrolytes and provides recent data on purity and performance from scalable industrial production processes.

* Corresponding author: Jerry.Martin@boulderIonics.com

37 Direct determination of the thickness and composition of electrode-electrolyte interface during electrochemical reaction

Gabriel M. Veith,*[1] Jim Browning,[2] Loïc Baggetto,[1] Wyatt A. Tenhaeff,[1] and Jong K. Keum[2]

[1]Material Science and Technology Division and [2]Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN

Understanding the formation of resistive solid-electrolyte interphase (SEI) layers as a function of potential, time, and electrolyte composition is critical to developing new approaches to reduce deleterious lithium and solvent consumption. To date most approaches to understand SEI formation have been performed ex-situ over a large area with little to no identification of the film thickness, composition as a function of depth, or changes with chemical potential or washing of the electrode. The critical lack of information concerning the SEI structure can be solved by the application of chemical specific neutron reflectometry (NR) to directly measure the thickness, chemical composition and density of the formed SEI layer on electrodes with nanometer resolution.

NR is a neutron scattering technique highly sensitive to morphological and compositional changes occurring across surfaces and interfaces, including buried interfaces. It can be used to study such changes over lengths scales extending 1 nm to hundreds-of-nanometers. Neutrons, by virtue of their nature, are deeply penetrating and therefore ideally suited as a probe to study materials in complicated environments, such as electrochemical cells. Unlike x-rays, neutrons interact with the nuclear potential of constituent element and are sensitive to light elements like Li and H.

This presentation will describe the first experimentally determined interface thickness and composition between the high voltage cathode material ($LiMn_{3/2}Ni_{1/2}O_4$) and the electrolyte ($LiPF_6$ in ethylene carbonate/dimethycarbonate 3:7 by weight) as a function of state-of-charge. Figure 1 shows a representative model of the layer thicknesses experimentally determined for $LiMn_{3/2}Ni_{1/2}O_4$ thin films supported on Pt current collectors. This data shows the formation of a 3 nm Li-rich interface at the electrode-electrolyte junction. In addition, the interfacial properties between the same electrolyte and the anode $Li_4Ti_5O_{12}$ will be reported as a function of Li content.

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* Corresponding author: veithgm@ornl.gov

38 Discharge rate capability of Li-O_2 batteries

David G. Kwabi,*[1] Yi-Chun Lu,[1] Koffi P.C. Yao,[1] Jonathon R. Harding,[1] Jigang Zhou,[2] Lucia Zuin,[2] Betar M. Gallant,[1] and Yang Shao-Horn[1]

[1]Electrochemical Energy Laboratory, Massachusetts Institute of Technology, Cambridge, MA; [2]Canadian Light Source Inc, University of Saskatchewan, Saskatoon, Canada

The O_2 electrode in Li–O_2 cells has been shown to exhibit gravimetric energy densities (considering the total weight of oxygen electrode in the discharged state) four times that of $LiCoO_2$ with comparable gravimetric power, but one major challenge remains its low rate capability (typically 0.1 to 1mA/cm^{-2} We investigate whether catalysts already shown to enhance oxygen reduction reaction kinetics at low current densities can increase the discharge rate capability of Li-O_2 batteries, by comparing Au-catalyzed Vulcan carbon and pure Vulcan carbon (VC) O_2 electrodes in the current range of 100 to 2000 mA g_{carbon}. It was found that Au- catalyzed electrodes had a higher discharge voltage than pure Vulcan electrodes at all currents studied. From X-Ray diffraction (XRD) and X-ray absorption near edge structure (XANES) O and Li K edge data, we hypothesize that higher discharge voltages of cells with Au/C than VC at low rates could have originated from higher oxygen reduction activity of Au/C while at high rates, higher discharge voltages with Au/C than VC could be attributed to faster lithium transport in nonstoichiometric or structurally defective lithium peroxide formed upon discharge. In order to further explore the nature of discharge product formed in Li-O_2

cells, carbon nanofiber O_2 electrodes discharged to varying capacities were analyzed by XANES. While bulk peroxide is detected consistent with other reported studies, the surface structure/chemistry was found to vary with depth of discharge. Deviations from reference lithium peroxide powder in both surface and bulk regions of discharged and cycled electrodes were also observed, suggesting different surface and bulk electronic structures exist for electrochemically formed lithium peroxide.

* Corresponding author: dkwabi@mit.edu

39 Windable lithium-ion conducting electrolyte for Li/air

Qiang Wei,[1] Binod Kumar,[2] and **Yuhong Huang***[1]

[1]Chemat Technology Incorporated, Northridge, CA; [2]University of Dayton Research Institute, Dayton, OH

For developing rechargeable lithium metal batteries, such as Li-S and Li/Air, a mechanically strong separator which can prevent dendrite penetration is essential. Solid lithium ion conductors such as single crystals of Li_3N[1] and glasses from the LiI-Li_2S-B_2S_3 system,[2] and polymer electrolytes[3,4] exhibit high ionic conductivity. However, their poor electrochemical and chemical stability in air have limited interest in these materials for lithium cells. Solid ionic conductors based on a $LiM_2(PO_4)_3$, where M is a metal structure (analogous to a Nasicon type structure[5]) are among the most promising group of oxide-based solid lithium ion conductors investigated in recent years as they possess certain advantages in terms of electrical conductivity, mechanical strength, and stability in air compared to other solid electrolytes.

During an earlier sponsored research program, we have developed derivatives of the lithium analog of Nasicon - lithium aluminum titanium phosphate (LATP) and lithium aluminum germanium phosphate (LAGP) glass-ceramic solid electrolytes having conductivities in the 10^{-3} to 10^{-4} S/cm range at room temperature.[6–8]

In this research, we focus on developing a windable glass ceramic dense LAGP membrane for used as solid electrolyte separator membrane for Li/air battery application. Thin glass (~30 µm or thinner) have reported to be flexible when laminated with polymer.[9] In this work, dense LAGP dense membrane was developed via tape-casting process with porosity of <4.5% and thickness of ~22 µm. The LAGP membrane is partially windable. By laminating polyethylene oxide, the glass-ceramic membrane can be bended on 3 cm cylindrical object without cracking. The conductivity of the membrane was 4.23×10^{-3} S/cm at 27 °C.

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* Corresponding author: yhuang@chemat.com

40 Protection strategies for lithium metal anodes

J.T. Vaughey, D. Schroeder, B. Key, **B.J. Ingram**,* S. Neuhold, and A. Hubaud

Chemical Science and Engineering Division, Argonne National Laboratory, Argonne, IL

Metallic lithium electrodes have exhibited well documented problems with stability, safety, and cycling efficiency that continue to block their implementation into advanced lithium batteries for PHEVs and next generation technologies (e.g., Li-air, Li-sulfur). We investigated two approaches to stabilize lithium metal. First, ceramic phases have been considered as physical protection barriers between the lithium metal electrode and liquid electrolyte. High density, chemical stability, and high lithium ionic conductivity are critical considerations. We present results describing

synthesis-properties relationship as it relates to the densification and phase evolution of lithium conducting ceramics. Second, organic materials that produce interfacial coatings which stabilize lithium metal in a liquid electrolyte environment have been investigated and shown to increase the safety and stability of lithium-based batteries. This work was funded by the Integrated Lab/Industry Research Project of the Batteries for Advanced Transportation Technologies (BATT) program of the DOE.

* Corresponding author: ingram@anl.gov

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