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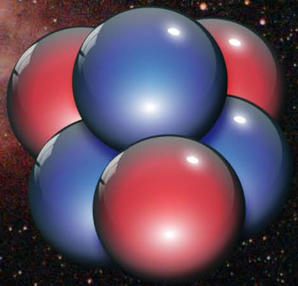
4th Symposium on Energy Storage

BEYOND LITHIUM ION



POSTER SESSION

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Come see the outstanding poster session at the 4th Symposium on Energy Storage: Beyond Lithium Ion. This is a list of the posters that will be featured in the session.

1 Possibility and aspect of lithium-air-water rechargeable batteries

O. Yamamoto,* N. Imanishi, T. Zhang, Y. Takeda, Mie University, Japan

During the past few years, lithium/air rechargeable batteries are paying great attention, because of a possibility to develop a high energy density battery for electric vehicles. Two types of lithium/air battery systems have been studied, namely, non-aqueous electrolyte system and aqueous electrolyte systems. The reversible cell reactions for non-aqueous and aqueous systems are

$$2Li + O_2 \rightleftharpoons Li_2O_2 \qquad (1),$$

and

$$4Li + 6H_2O + O_2 \rightleftharpoons 4(LiOH \cdot H_2O) \qquad (2),$$

respectively. The energy density including oxygen of 3,456 Wh kg^{-1} is calculated from the reaction (1) and that of 2,450 Wh kg from the reaction (2). The energy density of the aqueous system is about 30% lower than that of the non-aqueous system, but the non-aqueous system has some disadvantages compared to the aqueous system. The product of the discharge reaction, Li_2O_2, is insoluble in the aprotic solutions which deposits on the pore orifices or surface of the air electrode, hence decreasing the usable pore volume for O_2 intake and stopping the discharge process, And in the charging process, a high polarization was observed. The moisture in air penetrates into the cell to contaminate the aprotic electrolyte and reacts with the lithium metal and the lithium salt, which makes the pore cycling performance. These obstacles could be removed by using an aqueous electrolyte.

The proposed lithium-air-water battery is constructed of a water stable lithium anode of Li/PEO_{18}LiTSFI-PP13TFSI/LTAP, a LiCl saturated aqueous solution, and a perovskite-type oxide air electrode $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$. The water stable lithium conducting solid electrolyte, $Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}Si_yO_{12}$, (LTAP), is stable in a LiCl and LiOH saturated aqueous solution and PEO_{18}LiTFSI and ionic liquid of N-methyl-N-propylpiperidinum bis(trifluoromethanesulfonyl)imide (PP13TFSI) composite electrolyte suppressed the dendrite formation by lithium deposition process. A charge-discharge performance of the proposed cell at 60 °C showed an open-circuit voltage of 2.8 V and lower polarizations compared to those of the non-aqueous system under air.

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2 Design of electrolyte solvents for rechargeable lithium-oxygen batteries

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Li-air batteries are of considerable interest because of their high energy density. Since Abraham's group first reported the rechargeability, many researchers have examined the influence of carbon, catalyst and electrolyte on the discharge capacity and rate capability. Several studies on cycleability have been also performed. Bruce's group already reported that Li-O_2 cells with MnO_2 catalyst and carbonate-based electrolyte were discharged and recharged during 50 cycles.

At first, we focused on the reversibility of Li-air batteries with carbonate-based electrolytes. As a result, we confirmed that the Li-O_2 cell operated repeatedly for 100 cycles and maintained the capacity retention of 60% or more. 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 cause of the large voltage gap, discharge and charge reactions on a cathode were examined in detail. We 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 the cathode during discharge. After recharging, the carbonate species decomposed and CO_2 gas generated. Therefore, we have proposed that the electrolyte solvents would play an important role in controlling the cathode reaction due to O_2 radical.

Here, we will report the electrolyte solvents to control the rechargeable reaction as indicated in $2Li^+ + x/2O_2 + 2e^- = Li_2O_x$. We adopted the non-electrochemical screening test of solvents with KO_2 material, because it is very convenient method to pick out the candidates. Compared with propylene carbonate (PC), N-methyl-N-propylpiperidinium bis-trifluoromethansulfonylamide (PP13TFSA) and acetonitrile were considerably stable against O_2 radical to afford Li_2O_2 generation. Dimethyl sulfoxide was also more stable than PC in spite of slight decomposition. In this presentation, we investigated the cathode reaction mechanism in the PC and

PP13TFSA-based systems. Furthermore, we evaluated the battery performances using the DMSO-based electrolyte.

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3 Identification of discharge products from Li-air cells

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Raman, infrared and x-ray photoelectron spectroscopies were used to characterize the thick coating of reaction products on carbon and MnO_2 coated carbon cathodes produced during discharge of Li-air cells. The results show that neither Li_2O_2 nor Li_2O are major components of the insoluble discharge products; instead the products are composed primarily of fluorine, lithium, and carbon, with surprisingly little oxygen. The complex reaction chemistry also appears to involve the formation of ethers or alkoxide products at the expense of the carbonate solvent molecules (ethylene carbonate and dimethyl carbonate). The irreversible discharge reaction is likely electrochemically promoted with Li-anion species and dissolved oxygen. Exactly how the molecular O_2 participates in the reaction is unclear and requires further study. The addition of a conformal coating of MnO_2 on the carbon lowers the cell's operating voltage, but does not alter the overall discharge chemistry.

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4 Alternative to metal-air batteries: Sugar-air abiotic batteries

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A novel sugar-air battery has been demonstrated in our laboratory recently that has achieved a superior performance characteristic than anything we know to date in the pursuit of harnessing the chemical energy of sugar into electricity. Commonly metallic or biological catalysts are used to promote the energy conversion in any form of sugar-air configurations. We, however, showed that in our device we do not need to use any of these conventional catalysts to facilitate the sugar oxidation, at least in the initial partial oxidation step in the transformation of sugar to lactone. What we need is just the presence of mediators to facilitate the charge transfer in alkaline solutions. The reaction is specific that we also do not need to use a separator (e.g., Nafion in most configurations reported to date) to separate the two reaction chambers for oxidation and reduction reactions. We were able to achieve about 3 mW/

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cm^2 at 0.3 V and 10 mA/cm^2 in a primitive cell design without any optimization at room temperature. With this success, we illustrated a viable power source that employs renewable chemical energy source of reducing sugars with relatively low-cost and benign mediators to harness the energy into electric power directly. The power density is comparable to what metal-air batteries have achieved so far; thus, promises an alternative to metal-air system for unique power source applications. We will present our understanding of how this sugar-air battery works, limitations it experienced, and current investigation on the mechanism.

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5 Performance of MnO_2 crystallographic phases in rechargeable lithium air cathode

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Manganese dioxide (MnO_2) has been shown to be effective for improving the efficiency of cathodes in lithium air cells. The different crystallographic phases (α, β and γ) of MnO_2 nanowires, α-MnO_2 nanosphere and α-MnO_2 nanowires on carbon were synthesized using the hydrothermal method. Their physical properties were examined using XRD, BET, SEM & TEM and found to be in agreement with literature. Electrochemical properties of the synthesized catalyst particles were investigated by fabricating cathodes and testing them in a lithium air cell with lithium hexafluorophosphate in propylene carbonate ($LiPF_6$/PC) and tetra (ethylene glycol) dimethyl ether (LiTFSi/TEGDME) electrolytes. α-MnO_2 had the highest discharge capacity in the LiTFSi/TEGDME electrolyte with 2500 mAh/g whilst α-MnO_2/Carbon in $LiPF_6$/PC showed a significantly higher discharge capacity of 11,000 mAh/g based on total mass of catalytic cathode. However the latter showed low capacity retention compared to γ - MnO_2 nanowire, which were for up to 30 cycles. This result shows a higher discharge capacity than recorded in previous studies on lithium air cells.

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6 The facts influencing rechargeability of lithium/air batteries

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Li/air batteries draw great attention and research effort recently due to their high theoretic energy density and potential low cost. In past decades, various metal/air batteries have been investigated; however, several major challenges prevent Li/air batteries from practical application. The oxygen reduction and evolution both take place on the cathode and the effective and long-lasting bifunctional cathodes have not been developed yet. In order to reduce the products of the discharge, such as Li_2O_2 and Li_2O, effective catalysts have to be used. To prevent volatile reaction of Li with water, the Li/air batteries have to use non-aqueous electrolyte or use dual electrolyte with membrane separator that limits current rate at very low level. The products of discharge, Li_2O_2 and Li_2O are not soluble in the non-aqueous electrolyte currently used by researchers. Updated reports indicated that the carbonate-based electrolytes are attacked by intermediate specie such as Li_2O_2 resulting in formation Li_2CO_3 that seals the pores of the cathodes and eventually kill the cell. Focusing on these issues, we have conducted our investigation on cathode architecture, catalyst, electrolyte and anode in regarding of the performance of the Li/air batteries. We will discuss our results and share our vision for the future of this technology.

7 High-power nanostructured carbon electrodes for lithium batteries

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Large scale commercialization of electric and plug-in hybrid vehicle technologies require energy storage systems that can demonstrate high-power, high-energy, and longer cycle life. Among the commercialized rechargeable systems, lithium-ion batteries exhibit high energy densities on both gravimetric and volumetric bases, but have relatively low power capabilities. Alternatively, electrochemical capacitors have much higher power capabilities but lower energy densities than lithium-ion batteries. Considerable research efforts have been focused on increasing the power capabilities of high-energy rechargeable lithium-ion batteries by employing nano-scaled materials with lower lithium diffusion time, and increasing the energy capabilities of electrochemical capacitors by utilizing the high surface areas of the electrodes for faradaic charge storage (pseudocapacitance). However, the performance gap between batteries and electrochemical capacitors remains to be bridged by developing materials that can combine the advantages of both devices.

We report here a novel class of electrodes for lithium storage, which are based on functionalized multiwalled carbon nanotubes (FMWNTs) that include stable pseudo-capacitive functional groups. These additive-free electrodes exhibit high rate capability with a gravimetric capacity of ~200 mAh/$g_{electrode}$ at low rates in Li/FMWNT cells. They deliver specific energies of ~200 Wh/$kg_{electrode}$ at an exceptionally high power of 100 kW/$kg_{electrode}$, in the voltage range of 1.5 - 4.5 V vs. lithium, which could be attributed to Faradaic reactions between the lithium ions and the surface functional groups on FMWNT electrodes. Additionally, they can also be cycled up to a thousand cycles with minimal loss in stored energy. These additive-free FMWNT electrodes, which exhibit specific energy comparable to lithium rechargeable batteries, and the specific power and cycle life of electrochemical capacitors, are promising materials for the development of new high-energy and high-power storage technologies.

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8 Tracking Li-ions on the nanoscale

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The development of the capability for probing ion transport on the nanometer scale is a key challenge for development of energy storage and generation systems including Li-ion batteries, and can potentially unravel complex interplay between structure, functionality, and performance in these systems. However, the existing electrochemical methods invariably utilize slow and large scale ion electrodes, limiting these studies to ~10 micron scale, well above the characteristic size of grains and sub-granular defects. Consequently, the nanoscale mechanisms underpinning Li-ion battery functionality remain unexplored, precluding developing strategies for improvement of energy and power densities and life times of these devices. Here we introduce 'Electrochemical Strain Microscopy' for mapping the local ionic current in Li-ion batteries and cathode materials based on 'Scanning Probe Microscopy.' The lithium diffusivity is mapped on a level of a single grain and grain-boundary like defects in electrode materials and solid state electrolytes (e.g., LiSICON) using time and voltage spectroscopies. The evolution of Li-ion diffusivity during charging is observed and correlated with macroscopic measurements. Finally, the bias-dependence of response is used to explore the critical bias required for the onset of electrochemical transformation, potentially allowing the deconvolution of reaction and diffusion processes. This poster will present ESM results conducted on Li ion battery anodes (Si) and cathodes (LiCoO$_2$) and electrolyte (LiPON, Lisicon).

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9 Nanoscale mapping of lithium ion currents on lithium ion conducting glass ceramic by electrochemical strain microscopy

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Electrochemical Strain Microscopy (ESM) was developed as a probe for detecting and mapping ionic currents in solids on the nanoscale. In ESM, a high-frequency periodic bias is applied between the tip and an electrochemically active material surface (tip-electrode). The SPM tip acts as a probe of local periodic strains generated due to bias-induced ion redistribution and associated changes in molar volume of the material. The intrinsic high sensitivity of AFM to small (~2-5 pm level) oscillatory surface displacements combined with high (10-20 nm) lateral resolution allows Li-ion motion to be probed in ~ 106 smaller volumes than possible by current-based electrochemical methods. ESM has been successfully deployed to investigate Li-ion conduction in Li-ion battery materials such as LiCoO$_2$ cathodes and Si anodes. Here we will demonstrate that ESM is a useful tool to investigate Li-ion conduction in solid-state electrolytes as well. Commercially available LISICON (product AG-01, Ohara Inc.) is an ideal candidate for ESM as it exhibits high Li-ion conductivity and is a polished glass ceramic consisting of three phases, all of which may yield a slightly different ESM signal, hence giving rise to spatial contrast.

This poster will describe our ESM observations for various ESM imaging and spectroscopic modes, including Band Excitation Piezoresponse Spectroscopy (BEPS), First Order Reversal Curves (FORC), and current measurements. These SPM modes produce nanoscale maps of Li-ion current and further the understanding of electrochemical processes (reversible and irreversible) on single particles. These results are necessary for understanding of origins of high charge-discharge hysteresis and

polarization losses in Li-ion batteries and suggest pathways for material optimization.

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10 Modeling electrochemical performance and degradation in high temperature electrochemical devices

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Macro-scale modeling of electrochemical cells and devices is critical to understanding the long-term performance and degradation of electrochemical storage devices. With electrochemical storage devices being considered for stationary and transportation storage it is important to understand the effects of operating conditions, outside environmental factors and contaminants on the structural integrity and electrochemical performance of these devices over their designed operating lifetime. In this poster we present two computational models capable of considering electrochemical storage devices at the cell and device scales. A three-dimensional cell level distributed electrochemistry model is developed to simulate the overall cell performance and resolve the local operating conditions within the electrodes. At the device scale, a multi-physics model is developed to simulate the temperature and species distributions as well as the overall electrochemical performance of the multi-cell stack. These models resolve the temperatures, pressures, species concentrations and potentials in the system and can be used to examine the effects of operation-induced localized degradations, and to optimize the design and operational conditions of the system.

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Both energy dense and environmentally friendly, the lithium-air battery holds great promise for reducing transportation's dependency on fossil fuels.

11 Probing structural and chemical evolutions in lithium ion battery using in-situ TEM

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Lithium ion batteries, as similarly with other electrochemical energy storage devices, are complex multi-component systems that incorporate widely dissimilar phases in physical and electrical contact. Repeated charging and discharging of the Lithium ion battery induces microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode. Although it has been established that this microstructural evolution is responsible for the failure of the battery, the mechanisms of the microstructural changes as a function of charging/discharging are not well understood. Transmission electron microscopy (TEM) and spectroscopy have been evolved to a stage such that it can be routinely used to probe into both the structural and chemical composition of the materials with a spatial resolution of a single atomic column, a direct in-situ TEM observation of structural evolution of the materials in lithium ion battery during the dynamic operation of the battery has never been reported. This is related to three factors: high vacuum operation of a TEM; electron transparency requirement of the region to be observed, and the difficulties dealing with the liquid electrolyte of lithium ion battery. In this paper, we report the results of exploring the in-situ TEM techniques for observation of the interface in lithium ion battery during the operation of the battery. The objective of this presentation is to illustrate recent in-situ TEM capability development that enables direct probing of the structural and chemical composition of electrode materials in lithium ion battery. In perspective, we also pin point the future research directions.

12 All-carbon-nanofiber electrodes for high-energy rechargeable Li-O$_2$ batteries

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Lithium-Air batteries have received renewed attention in the last several years owing to an increasing need for high-density energy storage for electric vehicle applications. In this study hollow carbon fibers with diameters on the order of 30 nm were

grown on a ceramic porous substrate, which was used as the oxygen electrode in lithium-oxygen (Li-O_2) batteries. These all-carbon-fiber (binder-free) electrodes were found to yield high gravimetric energies (up to 2500 Wh/$\text{kg}_{\text{discharged}}$) in Li-$O_2$ cells, translating to an energy enhancement ~4 times greater than the state-of-the-art lithium intercalation compounds such as $LiCoO_2$ (~600 Wh/$\text{kg}_{\text{electrode}}$). The high gravimetric energy achieved in this study can be attributed to low carbon packing in the grown carbon-fiber electrodes and highly efficient utilization of the available carbon mass and void volume for Li_2O_2 formation. The nanofiber structure allowed for the clear visualization of Li_2O_2 formation and morphological evolution during discharge and its disappearance upon charge, where Li_2O_2 particles grown on the sidewalls of the aligned carbon fibers were found to be toroids, having particle sizes increasing (up to ~1 μm) with increasing depth-of-discharge. The visualization of Li_2O_2 morphologies upon discharge and disappearance upon charge represents a critical step toward understanding key processes that limit the rate capability and low round-trip efficiencies of Li-O_2 batteries, which are not currently understood within the field.

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13 Li_4SiO_4-Li_3PO_4 system as protective layer in Li-metal batteries

Liying Zhang,* Lei Cheng, Jordi Cabana-Jimenez, Guoying Chen, Marca M. Doeff, and Thomas J. Richardson, Lawrence Berkeley National Laboratory, Environmental Energy Technologies Division, Berkeley, CA

The application of Li-metal batteries is plagued with issues associated with the cycling of the Li electrode, such as dendrite formation and high reactivity with other cell components. The use of protective layers in the solid state that conduct ions but are electronically insulating has been proposed as a possible solution. It is preferable to work with phases that do not contain redox active transition metals, which can form electronically conductive products upon reduction by lithium. For this reason, we have selected the Li_4SiO_4-Li_3PO_4 system for further study.

Li_4SiO_4-Li_3PO_4 system can form two different solid solution structures over the full composition range. Both structures are reported to be more ionically conductive than Li_4SiO_4 or Li_3PO_4. Borate-based phases are commonly used as sintering agents, with some formulations such as 42.5 Li_2O·57.5 B_2O_3 (mol%) (LB) reported to have good ionic conductivity.

Li_4SiO_4-Li_3PO_4 solid solutions were prepared by solid state reaction. X-ray diffraction (XRD) was used to characterize the phases. Die-pressed pellets from different compositions containing 40, 50 and 60 mol% Li_3PO_4 (40LP, 50LP and 60LP) and 60LP with the addition of various amount of LB were sintered at different temperatures (700-1000°C) and their morphologies, conductivities and activation energies were analyzed. 60LP pellets sintered at 900°C showed the highest conductivity with 4.5x10-6 Ω-1cm-1 and an activation energy of 0.49 eV. The addition of 0.5 wt% LB into 60LP decreases the sintering temperature significantly without any deterioration in ionic conductivity or activation energy.

Various methods such as sol-gel and radio frequency sputtering were used to deposit thin films with the compositions such as 60LP with 0.5wt% LB onto Al_2O_3 substrates. Heat-treatment was carried out in order to get dense or crystalline films. The films have been characterized by XRD, scanning electronic microscope (SEM)/energy dispersive X-ray Spectroscopy (EDS). The amorphous and crystalline thin films were compared in terms of morphology and conductivity.

The electrochemical stability of the prepared phases against lithium was studied in Li-Li symmetric cells with well-sintered pellets from 60LP and 60LP with 0.5wt% LB as electrolyte. The symmetric cell was heated at 90°C for 4 hours to improve the interfacial contact between lithium and solid electrolyte. After heating, the contact resistance remained stable. Both Li-Si-P-O and Li-Si-P-B-O solid electrolytes were found to have a stable voltage profile during cycling, with no deleterious reactions observed. Additional confirmative insight on the electrochemical stability of the phases was obtained from Li/liquid electrolyte/60LP cells.

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14 Characterization of energy storage systems using nuclear magnetic resonance spectroscopy

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Large-scale stationary energy storage is needed for the widespread use of intermittent renewable energy and for improving the quality of power management in modern electrical grids. Electrochemical storage has been recognized as one of the top choices for large-scale energy storage devices. Stationary batteries usually involve aggressive electrochemical environments such as concentrated electrolyte solutions (redox flow battery (RFB)) and molten salts (Na-metal halide battery (Na-MH)) combined with rather complex electrochemical reactions have been optimized using empirical methods and thereby require greater understanding to meet performance and cycle life goals

to obtain market penetration. Using RFBs as an example, the detailed redox chemistry in the electrolytes and the associated performance degradation at temperatures, i.e., greater than ~50°C and lower than ~ -20°C, the mechanisms of undesirable ion cross-over and ion deposition in the membrane, are not well established. To tackle these fundamental scientific problems, an *in situ* molecular probe is ideally needed. Nuclear magnetic resonance (NMR) spectroscopy, a non-invasive technique that is capable of providing detailed molecular structure information (i.e., bonds lengths, bond angles, and coordination) as well as molecular dynamics, including diffusivity, is ideally suited for understanding the scientific questions in stationary batteries provided some practical issues are carefully addressed. During the past three years, we have carried out comprehensive NMR investigations to understand the ion transport mechanisms in Lithium-ion battery, and piloted NMR studies on the electrolytes and membranes in V-flow battery, including development of NMR computational modeling that have provided significant progress in these areas. In this poster, we will report our recent findings in (a) the studies of the electrolytes of V-flow battery containing mixed acids, i.e., H_2SiO_4 and HCl, (b) the studies of the electrode materials from Li-Air battery; and (c) the development of the fast-MAS (40 kHz) probe at 7.05 T magnetic field for investigating electrode materials containing paramagnetic species.

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15 Carbon assisted electrocatalytic activities of $La_{0.6}Ca_{0.4}CoO_3$ toward oxygen reduction reaction in concentrated alkaline electrolytes

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Metal-Air rechargeable batteries, in particular Zinc-Air Rechargeable Batteries (ZARBs), have drawn attention in recent years due to their advantages of high specific energy, low cost, and safe operation in several possible application areas such as portable, backup power, and automobiles. However, the major challenge of relatively low performance and insufficient stability of the bi-functional air-electrode hinders further progress in current ZARB technology.

As a promising catalyst candidate, perovskite $La_{0.6}Ca_{0.4}CoO_3$ powder was prepared and characterized. The electrocatalytic properties of $La_{0.6}Ca_{0.4}CoO_3$ (LCCO) and $La_{0.6}Ca_{0.4}CoO_3$-carbon composite (LCCO-C) layers towards oxygen reduction reaction (ORR) were studied using rotating ring-disk electrode technique (RRDE) in 1, 4, and 6 M KOH electrolytes. Koutechy-Levich theory and Tafel slope analysis were applied to acquire the overall electron transfer number and kinetic parameters, such as the kinetic currents, rate constant, and the exchange current densities. The overall electron transfer number was measured to be almost 4 for both LCCO and LCCO-C. A synergetic effect toward ORR in the presence of carbon in the LCCO layer was observed and explained with an assumed 2+2-electron transfer pathway.

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16 Ambient operation of primary Li-air battery

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Novel O_2 selective membranes based on commercially available Teflon-coated fiberglass cloth are used to discharge primary Li-air batteries in ambient conditions. The membranes allow O_2 into the cell where it is reduced to Li oxides at the air electrode while preventing the ingress of water vapor into the cell that would corrode the Li anode. The membranes transport O_2 into the cell at a rate high enough to support a current density of at least 0.2 mA cm^{-2}. The Li anode shows no visible corrosion after discharge in ambient conditions, i.e., air at 40% relative humidity. Cell failure is caused by the air electrode and not passivation of the Li anode by water. Electrochemical impedance spectroscopy is used to investigate the reason the air electrode capacity decreases with increasing relative humidity.

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17 Oxygen reduction catalyst for Li/air batteries based on a heat-treated metal phthalocyanine complex

Sheng S. Zhang,* Xiaoming Ren, and Jeffrey Read, U.S. Army Research Laboratory, Adelphi, MD

Examine the feasibility of a heat-treated metal phthalo-cyanine complex as an oxygen reduction catalyst for non-aqueous electrolyte Li/air batteries.

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18 Oxygen reduction catalyst for Li/air batteries based on a heat-treated metal phthalocyanine complex

Sheng S. Zhang,* Xiaoming Ren, and Jeffrey Read, U.S. Army Research Laboratory, Adelphi, MD

In this presentation, we will report our results on the heat-treated FeCu-phthalocyanine complexes (FeCuPc) as an oxygen reduction catalyst for non-aqueous electrolyte Li/air batteries. A FeCu/C catalyst was prepared by first absorbing a Fe- and Cu-Pc mixed solution onto a high surface area Ketjenblack EC-600JD carbon and then heating the mixture at 800-900 ºC in argon atmosphere. We show that the resulting FeCu/C catalyst not only catalyzes the two-electron reduction of oxygen as "$O_2 + 2Li^+ + 2e \rightarrow Li_2O_2$", but also promotes the chemical disproportionation of Li_2O_2 as "$2Li_2O_2 \rightarrow 2Li_2O + O_2$". In Li/air cells, the former reduces cell polarization while the latter increases the open-circuit voltage (OCV) recovery rate. By measuring the charge-transfer resistance (Rct) of Li/air cells at various temperatures, we show that above 10 ºC, the FeCu/C catalyst reduces apparent activation energy of Li/air cells from 50.2 KJ/mol to 41.4 KJ/mol. In addition, we show that the FeCu/C catalyst induces solvent decomposition at ~1.7 V. Due to the catalytic effect on Li_2O_2 disproportionation and the difficulty in electrochemically oxidizing Li_2O to O_2, we consider that FeCu/C catalyst would not be a good choice for rechargeable Li/air batteries.

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19 Novel thermal battery anode of silicon nanocomposite

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Thermal batteries are single discharge reserve batteries that have been primarily used in a wide range of military applications. The technology, based on molten salt electrolyte, offers a long shelf life and high power performance. Activation of thermal batteries occurs in the time range of 0.1 – 1.0 sec with internal pyrotechnics that raise the battery internal temperature typically to >500°C and melt the electrolyte. Modern military applications call for advanced thermal batteries that provide higher power and capacity with a smaller footprint. We are focusing on improvement of the state of the art $Li(Si)/FeS_2$ system, particularly on the silicon-based anode. The overall objective of our research is to develop a novel nano-structured anode material for thermal battery with enhanced electronic conductivity and Li^+ ion storage capacity. We synthesized chemical vapor deposition (CVD) grown Si nanowires (Si NW) from 2nm thick Au seed films directly on stainless steel disk current collectors. We electrochemically tested the Si NW electrodes in a half cell setup with $LiPF_6$ electrolyte and Li metal counter electrode at room temperature. Providing enhanced electronic conductivity and maintained structural integrity with Li^+ intercalation, we also report the Li^+ ions storage capacity of 2.2 Ah/g and coulombic efficiency of 95%. Beyond thermal battery applications, we measured the intercalation process reversibility for 160 full cycles with capacity drop of 20% and more than 300 full cycles with capacity drop of 50%.

In order to increase utilization of silicon material and thus Li^+ ions storage capacity, we synthesized a Si nanocomposite material. The nanocomposite is based on CVD grown high surface area vertically aligned carbon nanotubes (∅ 30 nm, length: 500 μm) that serve as current collector. The current collector is then decorated with Si shell (thickness 100 nm) via low pressure decomposition of SiH_4. Such a nanocomposite has provided very high capacity of 4.0 Ah/g, and we expect higher power performance in comparison with Si NW and conventional anode material.

We tested the structural endurance in a high temperature environment of 600 ºC and did not observe any physical damage for both materials. For the Si NW material, we measured contact angle of both the eutectic mixture of LiCl and KCl (at 450 ºC) electrolyte and halide mixtures LiCl-LiBr-LiF (at 500 ºC) electrolyte. The measured contact angles were vastly different--134º versus 2º for the eutectic and halide mixtures respectively. This clearly identifies the selection of halide mixture electrolyte for the Si NW anode that readily wets and completely floods the Si nanowires.

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20 Improved Li-air batteries with nano-structured and ALD protected electrodes

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High risk Li-Air Batteries (LABs) are an intriguing technology due to their extremely high theoretical energy density, 11 kWh/kg, compared to the theoretical energy density of conventional Li-ion batteries ($LiCoO_2$/graphite) of only 0.4 kWh/kg. However, three significant challenging problems must be overcome to achieve reasonable performance. First, the charge discharge reaction requires a large activation energy resulting in large polarization that may only be decreased with a catalyst.

Second, the product of the discharge reaction, insulating solid Li_2O_2 or Li_2O, blocks the pores of the air cathode (AC) and prevents oxygen flow, which increases cell impedance. Third, dendrite growth as well as cross-over of H_2O and CO_2 on the Li metal anode causes degradation and severe safety concerns. NREL is uniquely poised to solve all of these problems, with a combination of atomic layer deposition (ALD) coatings and the formation of unique nanostructured carbons. The strategy follows: (1) Mesoporous carbon ACs are prepared using a template method where it is possible to control and optimize the pore structure. (2) Self-limiting ALD reactions with controlled nucleation is then employed to control and maximize the surface/weight ratio of the catalyst, resulting in higher energy density. (3) The Li metal anode is coated with an ALD protective layer that both protects the Li metal from H_2O or CO_2 cross-over and also prevents dendrite growth. (4) Finally advanced computation methods guide the experimental work and allow us to better understand the reaction mechanism. The results of the multi-scale, multi-physics modeling are enabling novel tailored design for charge transfer kinetics to be achieved.

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21 Investigation of electrolytes for lithium/oxygen and lithium/sulfur Batteries

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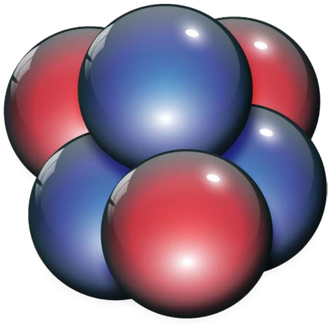
There is significant interest in the development of lithium batteries with greater energy density. One method to deliver more energy density while lowering the cost of the battery is to develop sulfur or oxygen-based cathode materials. However, there are many challenges related to the development of lithium-sulfur and lithium-air batteries. One of the critical problems with both of these systems is compatibility problems with the electrolyte. Thus, we have undertaken a details analysis of the solution behavior of common electrolytes and additives in the presence of Li_2O and Li_2S to develop a better understanding of the dissolution and solvation properties of these interesting materials.



22 Electrical energy storage R&D at PNNL for renewable integration and grid applications

Zhenguo (Gary) Yang,* Liyu Li, Soowhan Kim, Wei Wang, Zimin Nie, Baowei Chen, Qingtao Luo, Guan-Guang Xia, Amy Chen, Michael C. W. Kintner-Meyer, Xiaochuan Lu, Greg Coffey, Daiwon Choi, Wu Xu, JinYong Kim, Guosheng Li, Jun Cui, Dean Matson, Vince Sprenkle, John P. Lemmon, Yuliang Cao, Lifen Xiao, Vish Viswanathan, Birgit Schwenzer, Vijayakumar Murugesan, Gordon Graff, and Jun Liu, Pacific Northwest National Laboratory

The environmental consequences of burning fossil fuels and their resource constrains have spurred great interests in using electrical energy derived from renewable sources, such as wind and solar. However, the intermittency of the renewable sources makes the instantaneous solar and wind power uncontrolled and unreliable. To smooth out the intermittency and make dispatchable of the renewables demand the implementation of electrical energy storage (EES). EES has long been known as an effective approach to improve grid reliability, enhance value of transmission assets, and provide high quality power to a society that is increasingly being digitized. PNNL has conducted extensive research and development in the past few years in electrical energy storage for renewable integration and grid applications. The efforts have been supported by DOE-OE, ARPA-E and internal funding, with focus on development and demonstration of both existing technologies and emerging ones. These technologies include:

- Redox flow batteries
- Planar Na-metal halide batteries
- Low cost, long life Li-ion batteries
- Na-ion batteries and other new concepts.

The technology R&D efforts are guided by our grid analytics that help define applications and performance and economic requirements.

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23 Probing local structure, chemistry and electronic properties of lithium battery electrodes via TEM-EELS and synchrotron x-ray techniques

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The design of new electrode materials for safe, high energy-density lithium batteries requires a mechanistic understanding of the physical and chemical changes occurring on the surface and in the bulk of the electrodes during charge and discharge. However, the identification and characterization of nano-scale structural and chemical inhomogeneities, which often govern the thermodynamic and kinetic behaviors of the electrodes, remains a challenge. To better understand these structure-property relationships, we employ a synergistic approach, namely, a combination of electrochemistry, with ex-situ local structural/chemical studies via transmission electron microscopy and electron energy-loss spectroscopy (TEM-EELS), and in-situ bulk analysis via various synchrotron x-ray techniques. The results of investigation on nanostructured electrodes, including intercalation (e.g., $Li_4Ti_5O_{12}$, $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$), alloying (Si, Sn) and conversion (FeF_2, CuF_2) compounds, will be presented. We also report preliminary results in developing in-situ TEM-EELS capabilities. The nano-batteries fabricated from the full stack of the solid thin-film batteries, being used as model system, are suited for real-time imaging, diffraction and spectroscopy of the electrodes under the application of an external bias in the TEM. We expect to obtain critical information for understanding the kinetics and mechanisms associated with lithium transport through electrodes, electrolyte and interfaces.

24 Transport phenomena, and materials (EFRC-ETM) for innovative energy storage

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The objective of this project is to develop the basis for an entirely new high-density energy storage system combining the best properties of a fuel cell and a flow battery. The key novel components of the system are organic carriers, electro(de) hydrogenation catalysts, and compatible PEM. This will require advances in electrocatalysis, transport phenomena and membrane materials research aimed to attain the necessary properties of the three novel components.

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25 Understanding electrolyte stability from DFT calculations and double layer structure from MD simulations

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Ionic liquids at electrified interfaces exhibit a complicated response to the applied electric field. We will present molecular dynamics (MD) simulations on N-methyl-N-propylpyrrolidinium bis-fluorosulfonyl imide ($pyr_{13}FSI$) and $pyr_{13}TFSI$ room temperature ionic liquids confined between graphite electrodes and nanopores as a function of applied potential. The electric double layer (EDL) structure and differential capacitance (DC) of $pyr_{13}FSI$ as a function of applied potential will be compared with the results for $pyr_{13}TFSI$. Additionally, the limiting behavior of DC at large applied potentials will be discussed together with the electrode charging kinetics.

In the second part of the presentation, we will demonstrate how the presence of anions significantly reduces carbonate solvent oxidation stability, stabilizes the solvent-anion oxidation decomposition products and changes the order of the oxidation decomposition paths that influence not only the structure of SEI of cathode but also the toxicity of the decomposition products.

26 Investigating the electrocatalytic reactions in lithium-air battery

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In order to pave the way for the Li-air technology, enhancement of the reactivity oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in organic solvents in the presents of Li are of great importance. These reactions are known to be affected by both electrode material and solvent. Hence given fundamental understanding of the reaction mechanism, new catalysts can be tailored for activity, stability and selectivity in the future.

Our approach to gain further insight into these reactions is to firstly examine a well defined system, i.e., single crystals metals,

and metal-oxide, and establish electro catalytic trends for standard solvents (PC, DME, etc.). Using our new-developed air-sealed RDE setup, we have examined Pt and Au crystals of different facets as well as for GC towards both ORR and OER in PC and Siloxane solvents containing Li-salt. Additionally, a DEMS system is employed to verify the stability of solvents, salts and electrode materials in order to attribute the measured current to the correct reaction. The results show that both ORR and OER exhibit material dependence, i.e. structural and electronic properties, as well as dependence on the electrochemical interface, i.e., solvent and salt components.

27 Lithium peroxide surfaces and point defects: Relevance for Li-air batteries

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Because of their high theoretical specific energy density, rechargeable Li-air batteries are attracting increasing attention as a potentially transformative energy storage technology. However, to attain this potential a number of challenges must be overcome. One that is unique to Li-air systems is low efficiency, which results from high overpotentials during charging. During recharge, the primary product of the discharge reaction, lithium peroxide (Li_2O_2), decomposes into Li and O_2. As the decomposition of a solid phase can be rate limiting, we hypothesize that slow mass transport within Li_2O_2 may contribute to the overpotential. Although some catalysts moderately improve efficiency, further improvements are needed. Moreover, the mechanism of Li_2O_2 decomposition is poorly understood, even in the absence of catalysts. Towards revealing catalytic mechanisms and optimal catalysts, we use density functional theory to revisit the surface and bulk thermodynamics of the Li_2O_2/Li_2O discharge phases, and to calculate the formation and migration energies for all chemically-relevant intrinsic defects in Li_2O_2 as a function of applied potential. Regarding surface properties, we find that Li_2O_2 particles are dominated by two oxygen-rich {0001} and {1-100} surfaces. Despite the fact that Li_2O_2 is an insulator, our calculations reveal that its stable surfaces are metallic, suggesting that surfaces may play a role in electron transport. Regarding bulk properties, we find that lithium vacancies are the dominant defect across the range of potentials seen in a typical charge/discharge cycle. In contrast, oxygen defects play little role in mass transport due to their high formation energies. The mobility of low-energy defects along several directions was examined using nudged elastic band calculations, and is discussed in light of recent experiments probing Li_2O_2 microstructure. We conclude that slow mass transport in Li_2O_2 contributes to the high overpotentials observed during recharge.

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28 A rechargeable Al-MnO_2 battery in ionic liquid electrolyte

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Because modern battery technologies including state-of-the-art lithium ion batteries are not sufficient to meet the needs of using electrical energy efficiently in transportation and residential applications, new electrochemical cell chemistries and designs are highly desirable for capable batteries with high energy density, high power, reliable safety and low cost. Aluminum is a very attractive electrode material for batteries, due to its advantages in abundance, cost and theoretical energy density. However, rechargeable Al batteries remain a challenge to be a viable battery system until now.

In this work, a rechargeable Al-MnO_2 battery, consisting of reversible aluminum dissolution-deposition at anode (Al) and lithium insertion-extraction at cathode (λ–MnO_2) in a room temperature ionic liquid electrolyte (lithium chloroaluminate in 1-ethyl-3-methyl imidazolium chloroaluminate), has been demonstrated. This new battery shows an average discharge voltage of 2.0 V, very low self-discharge at charged state, and rechargeable capacity with tens of cycles. The feasibility of a hybrid aluminum-lithium ion battery increases the likelihood of using aluminum as active electrode material for cheaper and safer rechargeable batteries.

29 The effect of morphological modification of α-MnO_2 catalyst on the electrochemical properties of Li/air batteries

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Recently, the use of oxygen as an active reactant suggests the potential for a new type of advanced rechargeable batteries. Since the concept of Li/air batteries has been proposed by K. Abraham et al., it is of great interest owing to its theoretical specific energy of 11,972 Wh/kg, which is about ten times

higher than that of conventional lithium ion batteries. More attention has being aroused after the confirmation on the reversibility for the formation and decomposition of Li_2O_2 by P.G. Bruce et al in 2006. Recently, it is a quite fashionable and hottest research item in the field of energy storage and its formidable potential in various applications has ensured a rapid growth of interest in this new battery system.

For a proper operation of Li/air batteries, one of the most important concerns is to develop high performance air-electrodes, governing the redox reaction between Li and O_2. The air-electrode is generally composed of porous carbon and catalysts in which the discharge product, Li_2O_2, is reversibly formed and decomposed. The electrochemical reactions involved in the Li/air batteries are highly depending on the microstructure and morphology of catalysts as well as porous carbon frameworks. The influence of porosity of air-electrodes on the reversible capacity of Li/air batteries has recently been demonstrated by P. Albertus et al. based on the physical modeling. However, an exact relationship between the morphology and catalytic activity of catalysts has not been clarified yet.

In this regard, we will present the electrochemical performance of air-electrodes containing α-MnO_2 nanopowder and α-MnO_2 nanowire as catalysts to elucidate their morphological effects in the Li/air batteries. To fabricate air-electrode, the slurries containing Super-P and α-MnO_2 catalysts with different morphologies such as nanopowder and nanowire were spray-deposited on the porous Ni metal form at optimized conditions. For comparative purpose, the electrochemical properties of both catalysts were evaluated at various current densities. We found that nanowire form is more favorable to assist the redox reactions between Li and O_2 in the organic electrolytes. Our observation will be helpful to support the incomplete reaction mechanism of Li/air batteries.

30 Rationally-designed activated carbons for next generation energy storage applications

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EnerG2 engineers and produces advanced nano-structured carbon materials for energy storage breakthroughs. Starting with proprietary Polymer chemistry to control hydrolysis and condensation reactions, a carbon framework is created within the gelling process, allowing the materials' surface structures and pore-size distributions to be shaped, molded and customized for a variety of energy storage applications. Controlling molecular precursors and their assembly allows for optimization of physical (e.g., pore volume and/or surface area distribution) and chemical characteristics (e.g., presence of non-carbonaceous materials to achieve desired customization).

Control over physical properties such as specific area, pore volume, and the distribution of micropores and mesopores within the carbon enables optimization of energy storage capability (volumetric and gravimetric capacitance) and/or power performance (pulse power and frequency response). For example, we have demonstrated ability to produce carbons with specific surface area ranging up to about 500 to 3000 m^2/g, with pore volume ranging from about 0.5 to 2 cm^3/g, and fraction of pores <20 Angstroms ranging from about 50% to nearly 100%. In addition, other physical properties that can be customized include carbon particle size and particle size distribution. Finally, rational design of surface and/or bulk chemical compositions allows for specific functionalities tailored towards different energy storage needs, such as next-generation lead acid, lithium ion, sulfur, metal-air, and other future battery applications.

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31 Meso-scale phase-field modeling of charge and ion transport in titania nanocomposite anodes

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A meso-scale phase-field model was developed to simulate coupled charge and ion transport in model porous nano composites of carbon and titania. The model is informed by thermodynamic and microscopic kinetic properties such as electro-chemical potentials, anisotropic dielectric constants of titania crystals, and the anisotropic mobility of charged particles, obtained from classical density function theory (cDFT), molecular dynamics simulations, and experimentally measured values. With the model, electron and Li ion diffusion in porous nano composites of carbon and titania, local segregation of charged particles, and electric potential evolution were calculated for a simulated charging process. The effect of nano composite morphology including the nano particle sizes, relative orientations and arrangements on charged particle transport efficiency are investigated. The results demonstrate the capability of the phase-field model to study the effect of microstructure on charged particle transport and with implications for overall battery performance. The model is presently being adapted to simulate the conductivity of various nanocomposite configurations as a function of external applied potential.

32 Multiscale modeling of coupled ion and electron transport in nanostructured materials

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We have developed a novel hierarchical hybrid multiscale simulation technique for modeling coupled ion and electron transport in nanostructured energy storage materials. The model uses a multiphysics approach, in which instead of formal consecutive upscaling we introduce novel types of collective long-range interactions along with short-range effects of the finer scale models. The fine scale models take advantage of high accuracy such as from embedded cluster quantum mechanical simulations of elementary charge transport as well as state-of-the-art molecular dynamics free energy simulations of coupled ion and electron diffusion. The collective long-range electrostatic and excluded volume interactions are introduced on the mesoscale (10-300 nm) via classical Density Functional theory coupled with the Poisson-Nernst-Planck formalism for dynamic effects. The mesoscopic free energy, which includes contributions from short-range activation dynamics of ions and electrons derived from the atomistic models, is then used in a larger scale (microns) phase field model to simulate charge transport in a network of nano-sized grains. As a demonstration of the application of the model for elucidating the basic principles of charge transport in nanostructured energy materials, the fundamental physics of Li^+ and electron transport in nanostructured TiO_2 will be described.

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33 Oxygen permeable membrane for lithium air battery

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A Lithium-air (Li-air) battery is one of the most energy dense and environmentally friendly electrochemical power sources that offer great promise for applications including hybrid electric vehicle (HEV), portable electronic equipment and devices etc. The present work is aimed to design and fabricate a Li-air rechargeable battery that can provide much higher energy density than either Lithium ion (Li-ion) or nickel based battery. Lithium-air batteries have an anode made of lithium and an "air cathode" made of a porous material that draws in oxygen from the surrounding air. When the lithium combines with the oxygen, it forms lithium oxide and releases energy. Since the oxygen doesn't need to be stored in the battery, the cathode is much lighter than that of a lithium-ion battery, which gives lithium-air batteries their high energy density. However, their open cell structure causes some new problems such as evaporation of liquid electrolyte solvent and permeation of moisture into the cells. Thus, a microporous PTFE layer is normally added to the side exposed to the environment. However, such a cathode does not allow sufficient oxygen from the air to diffuse into the battery cathode due to the low oxygen permeability of the microporous PTFE membrane. Thus, for Lithium-air batteries to work at maximum potential, cathode (oxygen) is the limiting factor.

Michigan Molecular Institute has carried our synthesis and blending of nano-scaled hyperbranched polymers (HBPs) that possess excellent membrane-forming ability. Several membranes on a variety of support have been prepared and evaluated for O_2 permeability A *very high* O_2 *permeability* (~10^4 to $4x10^3$ Barrer), that depends on the support membrane and the thickness of the membrane. Evaluation of moisture permeability for the membranes exhibit very low moisture permeability (< 20 Barrer), while organic electrolyte permeability for the membranes is low. The prepared membranes show very good chemical resistance, especially towards the organic electrolytes. This membrane will subsequently be used in the construction of cathode for Li-air battery.

As feasibility study, all-solid lithium-air batteries have been assembled utilizing a composite air cathode, PEO based solid electrolyte and lithium metal anode. The rigid solid electrolyte will suppress dentrite formation on lithium anode during charging. The cells demonstrated excellent thermal stability and are being evaluated for charge/discharge efficiency, operation at different temperatures (low as well as high) under dry air. The performance of cells with and without oxygen permeable membranes under normal atmosphere is also under investigation. In addition, the developer will pursue the air cathode optimization and solid polymer electrolyte development to improve the cell performance.

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34 Electrochemical screening of solvents for non-aqueous rechargeable lithium air batteries

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Lithium air battery is an extremely attractive power source candidate for transportation application due to its high

theoretical energy density. Many studies have been carried out in the past a few years. Scientists have been taking advantage of the knowledge in the field of advanced lithium ion batteries and fuel cells in scientific investigation and engineering development of rechargeable lithium air batteries. However, non-aqueous lithium air battery has its own critical requirements, of which the non-aqueous electrolyte especially the organic solvent system is the most important one. The cathode reactions in a lithium air battery involve oxygen reduction and the formation of its active radicals (e.g. superoxide O_2^- and peroxide O_2^{2-}) during discharge, which may decompose the solvents via oxidation and reduction to produce some products that are not rechargeable. It has been reported that Li_2O_2 is chargeable at high efficiency but Li_2O is not chargeable, and the organic solvents play a critical role in the formation of discharge products. Therefore to make lithium air battery rechargeable, it is a prerequisite to form Li_2O_2 on the cathode during discharge. In this presentation, we will report our preliminary investigation on the screening of organic solvents in electrolytes for rechargeable lithium air batteries by electrochemical methods. Based on the stability of solvents/electrolyte in the presence of oxygen and oxygen radicals, we can speed up the screening of organic solvents and provide an insight on solvents selection for rechargeable lithium air batteries.

35 TM/N/C cathode catalyst for in Li-air battery application

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Carbon-nitrogen matrix metaled with low level transition metals such as Fe and Co has been studied as the catalyst for oxygen reduction reaction in proton exchange membrane fuel cell application. With atomically dispersed active site uniformly distributed throughout the carbon surface, such materials have unique morphology in promoting mass transport during discharging and charging reaction in Li-air battery. Herein we demonstrate for the first time the application of TM/N/C composite as the cathode catalyst in Li-air battery application. Several methods of preparation were explored with the transition metal loading typically less than 1%. The electrode catalysts were tested under $Li\text{-}O_2$ battery operating condition. We found that the discharge/charge capacities are in the range of 700~1000 mAh/g (total catalyst with carbon), which are among the highest reported in the literature. The discharge voltages are typically around 2.8V and the charges potentials generally start at 3.8V. The number of cycles is limited, however, at present mainly due to degradation of the electrolyte.

36 Sputtered noble metal catalysts for lithium-oxygen batteries

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Portable electronic devices and electric vehicles are important applications that need electric energy storage devices with high energy density. Today, lithium-ion batteries (LIBs) provide the highest energy density and numerous companies and research institutions are currently working on the further improvement of LIBs. However, the prospected increase of energy density is limited, mainly due to the limited specific capacities of positive electrode materials. Metal-air batteries, especially lithium-oxygen batteries, offer the possibility to enable energy densities 4- to 10-fold compared to state of the art LIBs.

Among the different concepts for lithium-oxygen batteries proposed in the literature, non- aqueous electrolyte based systems seem to be the most promising candidates for electrical rechargeable systems. Main challenges that have to be overcome are the weak cycling stability and the low electric efficiency, typically about 60%. One approach to increase the electrical efficiency is the incorporation of a catalyst in the positive electrode to both increase the discharge voltage and decrease the charge voltage. We prepared electrodes with different noble-metal catalytic layers and compare the effect on discharge and charge voltages.

Usually, the catalyst particles are incorporated in the paste that forms after drying the active layer. In our approach, the catalyst is deposited directly on the carbon-based substrate by Magnetron sputtering. Tuning of the sputtering process parameters allows us to modify the morphology of the deposited catalyst material. With an adequate set of deposition parameters, the material is deposited as highly porous particles, rather than a dense film. Such a catalyst layer was already reported in the literature for fuel cell applications and was found to be very reactive, due to its high specific surface area. We employed this method for the preparation of catalysts for lithium-oxygen batteries. With platinum and platinum-cobalt alloy material deposited on a porous carbon substrate, a significant reduction of charge voltage was observed. Increase of electric efficiency from 57% to a maximum of 73% was achieved.

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37 Investigation of the limited cyclability of $Li-O_2$ batteries using nonaqueous carbonate electrolytes

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$Li-O_2$ or Li-air batteries have been widely investigated in recent years due to their high specific energy that is required for many applications including electric vehicles. However, the cycle life of nonaqueous $Li-O_2$ batteries using carbonate electrolytes is poor, with a cycle life ranging from several to 100 cycles depending on the catalysts used. The mechanisms of the discharging and charging processes in $Li-O_2$ batteries with carbonate-based electrolytes are still not well understood. In this work, the nature of the cycleability of $Li-O_2$ cells with nonaqueous carbonate electrolytes and the reason for the limited cycle life and poor cycling efficiency for such $Li-O_2$ batteries have been fully investigated. The discharge products of the $Li-O_2$ cells at different depths of discharge were systematically analyzed via X-ray diffraction, with the electrolyte containing propylene carbonate and ethylene carbonate. The *in situ* gas chromatography/mass spectroscopy tests were employed to evaluate the chargeability of possible discharge products. The appropriate mechanisms for discharging and charging processes of a $Li-O_2$ battery using carbonate electrolytes have been proposed.

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38 Investigation on stable organic-solvents for rechargeable $Li-O_2$ batteries

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$Li-O_2$ or Li-air batteries have been widely investigated in recent years due to their high specific energy that is required for many applications including electric vehicles. However, the cycle life of nonaqueous $Li-O_2$ batteries using carbonate electrolytes is poor, with a cycle life ranging from several to 100 cycles depending on the catalysts used. The limited cycle life of the $Li-O_2$ batteries using carbonate-based electrolytes is caused by the discharge products that are primarily organic and inorganic carbonate species (Li_2CO_3 and lithium alkylcarbonate) from the reduction of carbonate solvent molecules rather than the desired Li_2O_2. The formation of these organic and inorganic carbonate species during discharge is based on the reductive decomposition of organic carbonate solvent molecules by the attack of superoxide radical anions ($O_2^{\bullet-}$) formed through single-electron reduction of O_2, while during charge these lithium alkylcarbonates are oxidatively decomposed to release CO_2, CO and other gases.

In this presentation, we address this topic by choosing different kinds of organic aprotic solvents to make nonaqueous electrolytes, conducting the discharge process of these electrolytes in $Li-O_2$ batteries, and systematically analyzing the discharged products on the carbon air electrodes from these batteries to identify appropriate solvent systems that can result in the formation of Li_2O_2 during discharge.

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39 In-situ fabrication of porous carbon supported α-MnO_2 nanoparticles: Application for rechargeable Li-air battery

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Lithium-air cells can be considered the 'holy grail' of lithium batteries because they offer a significantly superior theoretical energy density to conventional lithium-ion systems. In this study, porous carbon supported MnO_2 nanoparticles synthesized at room temperature have been explored as an electrocatalyst for rechargeable Li-air cells. Both high-energy X Ray Diffraction and XAFS analyses showed that the prepared MnO_2 exhibited tetrogonal crystal structure (α-MnO_2), which has been proved to be one of the most efficient catalysts to facilitate the charging reaction in the Li-air cell. Under the current synthetic approach, α-MnO_2 was uniformly distributed onto the surface of carbon support, while the porous structure and surface area of carbon were still well persevered. As a result, the as-prepared catalysts demonstrated a superior electrochemical behavior, which can deliver a capacity of 1000 mAh/g (carbon + electrocatalyst) using a current density of 0.05 mA/cm^2 during the initial discharge.

The charge potential has been significantly reduced to 3.7 V compared to most of the reported data, which are above 4.0 V. The mechanism of the capacity fade has also been investigated by analyzing the cathode electrode at different states of charge using X-ray photoelectron spectroscopy (XPS) technique.

40 Second use of transportation batteries

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Plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) are expected to gain significant market share in the next few decades. The economic viability for such vehicles is contingent upon the availability of cost-effective batteries with high power and energy density. Towards the end of battery life in the vehicle, the energy capacity left in the battery is not sufficient to provide the designed range for the vehicle. Typically, the automotive manufacturers recommend battery replacement when the remaining energy capacity reaches 70-80%. There is still sufficient power (kW) and energy capacity (kWh) left in the battery to support various grid ancillary services such as balancing, spinning reserve and load following. As renewable energy penetration increases, the need for such balancing services is expected to increase. This work explores optimality for the replacement of transportation batteries to be subsequently used for grid services. This analysis maximizes the value of an electric vehicle battery to be used as a transportation battery (in its first life) and then as a resource for providing grid services (in its second life). The results are presented across a range of key parameters, such as depth of discharge (DOD), number of batteries used over the life of the vehicle, battery life in vehicle, battery state of health (SOH) at the end of life in the vehicle and ancillary services rate. The results provide valuable insights for the automotive industry into maximizing the utility and the value of the vehicle batteries in an effort to either reduce the selling price of EVs and PHEVs or maximize the profitability of the emerging electrification of transportation.

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41 Fast ion conducting electrolyte based on $Li_7La_3Zr_2O_{12}$ garnet

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Lithium ion battery technology has advanced significantly in the last two decades. However, future energy storage demands will require safer, cheaper and higher performance electrochemical energy storage. While the primary strategy for improving performance has focused on electrode materials, the development of new electrolytes has been overlooked as a potential means to revolutionize electrochemical energy storage. This work seeks to explore a new class of ceramic electrolyte based on a ceramic oxide with the garnet structure that exhibits the unprecedented combination of high ionic conductivity (4×10^{-4} S/cm at 298 K) and chemical stability against metallic lithium and air. Examples of technologies that could be enabled by this class of electrolyte include: solid-state lithium ion batteries that are non-flammable and do not require hermetic packaging, lithium-air semi fuel cells and lithium-sulfur batteries.

This report summarizes recent progress towards the development of $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte membrane technology and the steps taken to evaluate its electrical and chemical properties. Two methods for synthesizing and stabilizing cubic LLZO are discussed to include solid-state reactions and a sol-gel process (non glycol-based). The sol-gel process is capable of synthesizing cubic LLZO at temperatures as low as 600 C. Hot pressing of cubic LLZO powders resulted in 98% dense coupons that were evaluated for ionic, electrical, chemical and mechanical properties. The ionic conductivity of densified LLZO membranes was 4×10^{-4} S/cm ionic conductivity at 298 K with electrical conductivity in the 10^{-8} S/cm range. The chemical stability against metallic lithium and interfacial impedance was evaluated as a function of temperature and stack pressure using AC impedance and DC polarization and cycling tests. Preliminary results indicate that metallic lithium can be plated and stripped in direct contact with cubic LLZO with no observable degradation. Additionally, several lithium ion electrode materials were tested for reactivity with cubic LLZO as a function of temperature to evaluate the potential integration into solid-state lithium ion cells. Some of the electrodes of interest include lithium cobalt oxide, lithium cobalt phosphate, lithium manganese oxide, lithium titanate and silicon.

Initial investigations indicate that LLZO has several key attributes that make it appealing for use in conventional and advanced electrochemical energy storage technology. Ongoing fundamental studies are focused on understanding the mechanisms that stabilize the cubic garnet phase and enable fast ionic conductivity. Of particular interest are the roles

that the synthesis conditions and dopants play in controlling defect concentrations.

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42 Theoretical study of peroxide nanoparticles in Li-air battery

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The Li-air battery may achieve a high practical specific energy, theoretically as much as 11 400 Wh/kg Li assuming lithium peroxide (Li_2O_2) is the product. To turn it into reality, numerous scientific and technical challenges have to be overcome. In addition, a fundamental understanding of the lithium peroxide (e.g. bulk crystals, nanoparticles, surfaces etc.) and their essential chemistry associated with appropriate electrolytes is necessary. To make progress towards this goal, a systematic theoretical study based on Density Functional Theory (DFT) has been carried out. To understand the basic differences between lithium oxide (Li_2O) and peroxide (Li_2O_2), we have computed a series of large nanoparticles of these two species up to 1500 atoms with DFT. Based on these results, the thermodynamic stability, energetics, and electronic properties of these systems in the gas phase are compared with their bulk crystalline phases. To further explore the stability of these nanoparticles in electrolyte, preliminary results on the interaction of Li_2O_2 with the new polyether-based silane electrolytes based on ab initio molecular dynamics are discussed.

43 The discharge rate capability of rechargeable Li-O_2 batteries

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The O_2 electrode in the Li-O_2 cells was shown to exhibit gravimetric energy densities (considering the total weight of oxygen electrode in the discharge state) four times that of $LiCoO_2$ with comparable gravimetric power. The discharge rate capability of Au-catalyzed Vulcan carbon and pure Vulcan carbon (VC) as the O_2 electrode was studied in the range of 100 to 2000 mA/g_{carbon}. The discharge voltage and capacity of the Li-O_2 cells were shown to decrease with increasing rates. Unlike propylene carbonate based electrolytes, the rate capability of Li-O_2 cells tested with 1,2-Dimethoxyethane was found not to be limited by oxygen transport in the electrolyte. X-ray diffraction (XRD) showed lithium peroxide as the discharge product and no evidence of Li_2CO_3 and LiOH was found. It is hypothesized 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. At high rates, higher discharge voltages with Au/C than VC could be attributed to faster lithium transport in nonstoichiometric and defective lithium peroxide formed upon discharge, which is supported by XRD and X-ray absorption near edge structure O and Li K edge data

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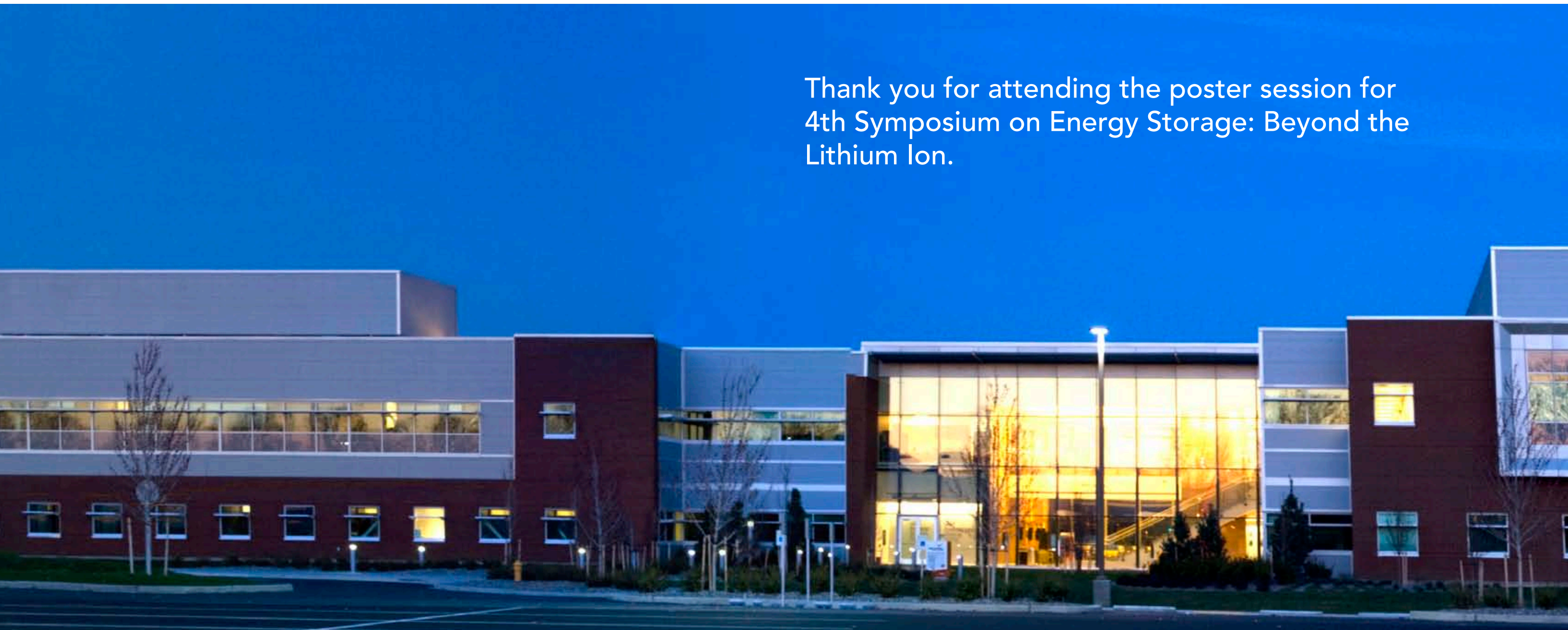

Thank you for attending the poster session for 4th Symposium on Energy Storage: Beyond the Lithium Ion.

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