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Characterization if Li-Air Batteries Influence of Cathode Degradation: Demonstration of Progress

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RESEARCH

CHARACTERIZATION OF LI-AIR BATTERIES

Demonstration of Progress

RESEARCH ODOT/OTREC

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CHARACTERIZATION OF LI-AIR BATTERIES
INFLUENCE OF CATHODE DEGRADATION

Demonstration of Progress

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by

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16. Abstract Li-air batteries are attractive candidates to be used in electric vehicles (EV) due to their high theoretical capacity, which results in an improved range, a requirement to make EV competitive against fossil fuel powered vehicles. However, Li-air battery technology is considered to be far from commercialization, due to its short lifespan. The decomposition of the electrolyte and its effect on cyclablity has been widely studied, no so much the cathode. The presence of undesirable reaction by-products at the cathode that affect the battery performance has been quantified through XRD and SEM. This work will make use of recently reported novel adaptation of titration techniques to study cathode degradation in Li-air batteries, along capacity, cyclability, and EIS studies, to characterize the effect of different carbon materials used as cathodes in Li-air batteries.		
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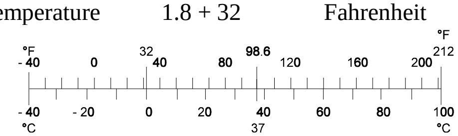
SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	millimeters squared	mm^2
ft^2	square feet	0.093	meters squared	m^2
yd^2	square yards	0.836	meters squared	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	kilometers squared	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	meters cubed	m^3
yd^3	cubic yards	0.765	meters cubed	m^3
NOTE: Volumes greater than 1000 L shall be shown in m^3.				
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9	Celsius temperature	°C

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	millimeters squared	0.0016	square inches	in^2
m^2	meters squared	10.764	square feet	ft^2
ha	hectares	2.47	acres	ac
km^2	kilometers squared	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	meters cubed	35.315	cubic feet	ft^3
m^3	meters cubed	1.308	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celsius temperature	1.8 + 32	Fahrenheit	°F



***** SI is the symbol for the International System of Measurement (4-7-94 jbp)

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DISCLAIMER

CHARACTERIZATION OF LI-AIR BATTERIES

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1.0 INTRODUCTION

1.1 BACKGROUND

Efforts for a wide implementation of electrical vehicles (EVs) have open several areas of opportunity on topics that would allow EV to be competitive with fossil fuel powered vehicles. Li-air batteries are promising candidates when considering lower battery pack weight and volume, resulting in higher vehicle efficiency, as well as increased capacity, which would improve EV range.

The principle of Li-air batteries is relatively new (*Littauer, 1976*). Generally composed of a lithium anode, an electrolyte and an air carbon cathode, this arrangement results in a lighter battery, therefore higher specific capacity is achieved when compared with other types of batteries. Promising theoretical values of specific capacity have been reported (*Linden, 1994*). However, the current stage of the technology still requires long-term actions to develop a commercial product. New chemistries are currently being developed and there is a need to develop proper characterization techniques to understand the degradation mechanisms within the components of Li-air batteries.

1.2 PROBLEM DESCRIPTION

The current project addresses the need to develop experimental capabilities at Oregon Institute of Technology for the study and characterization of Li-air batteries.

Li-air batteries are known to experience chemical stability issues that result in limited cyclabilty. Different composition of electrolyte salts and solvents react in diverse ways with the carbon air cathode and many combinations have yet been explored. (*Reed, 2002*) Most of the current research has been focus in the decomposition of the electrolyte, but new techniques have been developed that will allow the characterization of the cathode degradation due to the presence of undesirable byproducts, such as lithium peroxide. (*McCloskey, 2013*) This project will make use of recently reported novel adaptation of titration techniques to study cathode degradation in Li-air batteries through the quantification of lithium peroxide, along capacity, cyclability, and electrochemical impedance spectroscopy (EIS) studies, to characterize the effect of different carbon materials used as cathodes in Li-air batteries

1.3 OBJECTIVES

The current study addressed has two objectives. First, the focus of our work is the setup of experimental facilities that will allow the successful completion a battery characterization study. The achievement of the first objective is critical in the development future research projects.

1.3.1 Objective 1: Evaluation of the limitations and potentials of Li-air batteries through primary experimental testing

The establishment of an experimental station that will allow the preparation and characterization of Li-air batteries at Oregon Tech is the first goal of this project. Equipment constraints will be evaluated to determine the limitations and potentials of future characterization studies. The first battery cell successfully prepared and tested will mark the achievement of this objective.

1.3.2 Objective 2: Characterization of different compositions of Li-air batteries

Li-air batteries with different cathode compositions will be built and characterized by collecting capacity and electrochemical performance data with a potentiostat. Cathode performance will be also evaluated based on the reaction byproducts quantification through titration. Chemical and electrochemical results will be used to understand Li-air batteries reversibility based on cathode degradation.

1.4 APPROACH

The objectives of this project are achieved through two main tasks and several subtasks. Task 1 has currently a progress of 75% and Task 2 is on the initial stages.

1.4.1 Task 1: Laboratory setup

Objective 1: Evaluation of the limitations and potentials of Li-air batteries through primary experimental testing is achieved through this task.

Prior to experimental research, an extensive literature review on Li-Air batteries was performed. This literature review served to understand the technology and was reported in the MS thesis proposal that was presented by the graduate student working in the project. Additionally, such study of the literature served to focus the direction of the experimental research on cathode materials.

The laboratory setup work has consisted mostly in refurbishing an existing glove box to a working condition that serves for oxygen-sensitive materials. Due to the magnitude and relevance of this piece of equipment in the experimental work, specific details are given in section 2.1. Another critical section of the testing facility is the potentiostat, where battery cell capacity, cyclability, and EIS will be performed. In order to increase the laboratory capabilities an 8-channel potentiometer was acquired and a special setup was designed, based on the Swagelok design (*Beattie*, *2009*) that will be used for the Li-air batteries. Details on the potentiometer are given in section 2.2.

Task 1 also includes the acquisition of tools for electrode preparation, and the acquisition of oxygen-sensitive materials once the desired oxygen level was achieved in the glove box. Cathodes will be produced by mixing carbon with a solvent, which then will be applied to a stainless steel mesh and dried in a vacuum oven. The battery cells will be assembled in the glove box under argon environment. High purity oxygen will be provided to the cathode during testing with the potentiostat. Once electrochemical testing is done, samples will be disassembled in the glove box and cathode electrodes will be used for titration to determine the amount of lithium peroxide decomposition byproducts in the cathode.

Task 1 will be considered complete when the first Li-air battery is successfully built and characterized.

1.4.2 Task 2: Cell preparation and characterization

The samples for this experimental study will be prepared as described under Task 1. Different types of carbon will be used as cathode materials, while using same electrolyte and electrodes. A side-by-side comparison of the effect of cathode materials on battery performance will be done. Multiple batteries of the each cathode composition will be built and tested to ensure consistency.

The completion of task 2 is achieved when a complete set of cells with different carbon compositions are fully characterized. The results of this task will be documented in a MS thesis that will be defended over the summer.

2.0 LABORATORY SET UP

The majority of the time covered by this report has been devoted to complete the setup of the experimental capabilities for the characterization of Li-air batteries at Oregon Institute of Technology. Figure 5.1 shows the complete station that will allow cell preparation and characterization. In this figure can be seen several components of the system, including (from left to right) gas supply, glove box with automatic pressure controller and vacuum pump, vacuum furnace, and battery tester. The vacuum furnace will be used in the preparation of the battery cathodes. Two of these components, the glove box and the potentiostat, have been the main focus of our laboratory work during this period. It is worth mentioning that this laboratory setup will be useful not only to this project, but for several other projects in the future as well.

Figure 3.1: Laboratory station for the Li-air battery research project.

2.1 GLOVE BOX

A properly working glove is critical for the success of this project. This piece of equipment has two crucial roles:

1. To store consumables that cannot be exposed to moisture and oxygen.

2. To provide an environment to assemble the batteries.

While a glove box was available in the institution, the gas system had to be designed for the need. An argon gas supply was engineered to avoid introduction of impurities. Furthermore, an automatic pressure control sensor was incorporated in the design to maintain a positive pressure inside the glove box. That this custom-made gas system was designed to comply with the industry standard (gas system designs are usual performed and implemented by the glove box manufacturer).

Once a functional state was achieved in the glove box, oxygen sensitive chemicals have been acquired and stored inside of it. These chemicals will be used in the preparation of the Li-air batteries to be tested.

2.1.1 Issues affecting oxygen concentration in glove box

The oxygen concentration in the glove box has been closely monitored. The objective is to achieve a working environment with 10 ppm of oxygen or less. Undesirable amounts of oxygen that may react with lithium during cell construction would result in decreased cell performance. Two particular actions have been taken to address the challenges and to be able to achieve a low-oxygen environment.

2.1.1.1 Gloves material

A constant increase of oxygen concentration in the glove box was originally found. This was a concern because a high oxygen concentration will reduce the shelf life of chemicals stored inside the glove box. After purging the glove box down to 250 ppm O_2, the gas was monitored with the O_2 sensor over a week. The results showed a constant increase of around 100 ppm of O_2 per day. Since the leakage rate was very small, it was considered the possibility of gas diffusion, probably through the latex gloves. It was found that this material is not designed to reach this low of O_2 concentration. These gloves were replaced with gas-impermeable butyl material gloves. The change in glove material was crucial in the reduction of the oxygen penetration in the glove box, due to osmosis and partial pressure phenomenon.

2.1.1.2 Lack of gas purification recirculation system

Oxygen concentration inside the glove box was further tested. It was found that a 5 ppm/hr ingress was present. After discussing to multiple glove box suppliers, it was confirmed that this slow ingress is expected in systems without gas purification recirculation. Thus, it was concluded that the current state of this relatively aged glove box was improved to its optimum conditions, similar to an equivalent system coming out of the factory.

It was decided to use the glove box as a purge box as the most economical solution to overcome the oxygen ingress. With a constant slow purge, a working oxygen concentration can be obtained at the expense of more significant gas consumption.

2.2 POTENTIOSTAT STATION

An 8-channel battery tester has been acquired to allow the simultaneous characterization of multiple Li-air batteries in the Swagelok configuration. A structure was designed to hold and manipulate each cell independently. Figure 3.2 shows the potentiostat setup up where cells will be electrochemically tested. The brass design located at the top will provide a constant supply of pure oxygen to each cell while they are being tested.

Figure 3.2: 8-channel battery tester setup.

3.0 OUTCOMES

The original proposal application listed the following outcomes:

1. A report of experimental data regarding novel electrolyte compositions deemed to be presented to the research community.
2. An experimental laboratory setup and preliminary study that will serve as foundation for future students to build their projects on.
3. Qualified graduate students with skills in state-of-the-art research, quantitative data analysis and an extensive knowledge of battery testing techniques and characterization.

These outcomes have not been fully achieved up to date, and a no-cost extension is required for the completion of this project.

Outcome 1 has been modified to focus on the study of carbon electrodes rather than electrolytes. The decision was taken based on the relevance of the topic after careful study of the literature. This outcome will be achieved as during the no-cost extension period.

Outcome 2 has been partially completed. The experimental setup is functional and in place. Battery cells are currently being prepared, and will be used to test laboratory capabilities.

Outcome 3 has been completed, and is ongoing. Up to date, Jeremiah Deboever, MS in Renewable Energy Engineering, has been fully trained in the skills necessary to run the proposed study through his previous internship at PNNL. He is the main contributor in the setup of the experimental facilities. The topic of his master's thesis is the second objective of this study, the characterization of Li-air cathodes. The literature review and laboratory work sponsored by this project were the basis of his thesis proposal, which was presented to the members of his committee and approved. Other graduate and undergraduate students are currently being trained in the experimental setup and procedures.

Based on these milestones, the project is considered to be successful up to date, with great potential to be fully completed by July 2014.

4.0 CONCLUSIONS

The overall objective of this NITC small start grant was to provide the financial support for a new initiative targeting long-term actions on transportation emissions and climate change. Although the project has been delayed from the targeted timeline, its current development shows great promise to meet that objective. The establishment of the battery laboratory station is a major milestone in this long-term initiative at Oregon Tech. Not only is this project going to provide valuable knowledge to this research field, it is providing professional development for the principal investigator (tenure track portfolio) as well as academic development for the graduate research assistant (thesis research requirement). Although immediate benefits are apparent, the most valuable outcome that the NITC grant is providing with its positive support is the foundation of a research group at the institution. After presenting the project to the first-year graduate students, three to four students expressed interest in beyond-lithium-ion battery research and one student has already received partial funding for his project.

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