Lithium-Air Cell Development

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***Abstract*--Lithium-air (Li-air) primary batteries have a theoretical specific capacity of 11,400 Wh/kg, the highest of any common metal-air system. NASA is developing Li-air technology for a Mobile Oxygen Concentrator for Spacecraft Emergencies, an application which requires an extremely lightweight primary battery that can discharge over 24 hours continuously. Several vendors were funded through the NASA SBIR program to develop Li-air technology to fulfill the requirements of this application. New catalysts and carbon cathode structures were developed to enhance the oxygen reduction reaction and increase surface area to improve cell performance. Techniques to stabilize the lithium metal anode surface were explored. Experimental results for prototype laboratory cells are given. Projections are made for the performance of hypothetical cells constructed from the materials that were developed.**

I. Introduction

Very high specific energy batteries are required to address the requirements for a Mobile Oxygen Concentrator for Spacecraft Emergencies. The Mobile Oxygen Concentrator is being designed to operate onboard manned spacecraft, such as the International Space Station (ISS), to provide enriched oxygen for medical contingency operations. [1] The device is expected to operate continuously for 24 hours. In order to reduce the required stowage mass and volume on the resupply launch vehicle for the ISS, mass and volume of payloads must be minimized. The Mobile Oxygen Concentrator is designed to be reusable, however, in order to maximize the specific energy and energy density of the battery, primary battery technology is being targeted for this application. Since the batteries will need to be replaced after each use, reduction of the mass and volume of the batteries also becomes critical for the logistics of resupplying the batteries and for their storage onboard the spacecraft.

Specific energy requirements for the application are > 1800 Wh/kg, which is an order of magnitude greater than any commercial battery can offer. Li-air batteries were chosen for this application due to their potential to deliver extremely high specific energy. Since the batteries will be operating in a pressurized spacecraft environment, air will be available within the cabin for battery operation.

II. Lithium-Air Battery Technology

Lithium-air (Li-air) batteries have a theoretical specific energy of 11,400 Wh/kg, the highest of all common metal air technologies. Li-air technology development is currently in the early stages. Lithium metal is used as the anode and air is used as the cathode reactant. A porous carbon support is used on the cathode side to provide channels for air to infuse into the cell. Catalysts are incorporated into the carbon cathode structure to provide reaction sites for oxygen reduction during discharge. The theoretical open circuit voltage is 3.35 V and the practical operating voltage is 2.4 V,[2] however, these voltages may vary depending upon the catalyst used. The chemical formula for the reaction is shown below.[3]

$2Li + O_2 \text{--->} Li_2O_2 \qquad E° = 3.10V$
$4Li + O_2 \text{--->} 2Li_2O \qquad E° = 2.91V$, where E° is the calculated standard cell potential.

Numerous technical challenges exist that hinder the realization of a practical Li-air cell. The Li_2O_2 reaction product tends to clog the pores of the cathode and block reaction sites, which limits the performance of the cell. Other challenges include prevention of side reactions with the lithium metal surface, management of humidified air,

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development or optimization of electrolytes that are compatible with a system that contains lithium and humidified air, development of oxygen reduction catalysts, and development of an air cathode incorporating catalysts and other dopants that will collectively act to improve various aspects of battery performance. [2-4]

Ionova Technologies, Incorporated (Ionova) and Yardney Technical Products, Incorporated (Yardney) were tasked to develop Li-air technology for NASA Glenn Research Center (GRC) through the Small Business Innovation Research (SBIR) program. The aspects of Li-air technology each company chose to target its research efforts on are discussed in the sections below. Via their individual technical approaches, both companies developed air cathodes, experimented with different catalysts to improve the oxygen reduction reaction, and built experimental Li-air cells. Results of performance assessments conducted on these cells are discussed in this paper. These preliminary results are the culmination of short term developmental efforts and materials were not optimized prior to their use in the experimental cells. With continued development, other NASA applications could benefit in the mid-term from the high specific energy that could be achieved from these cells, particularly applications in which air or oxygen is already available and could be utilized without the need to provide ancillary tanks solely to provide reactants for the cells. Some of these applications require a fraction of the theoretical specific energy that Li-air batteries promise, but still require higher specific energy than aerospace-ready cells can offer today. Extravehicular activity (EVA) spacesuits, unmanned aerial vehicles (UAVs), and all-electric aircraft applications require 300-750 Wh/kg. In addition, portable devices or powered experiments onboard ISS, and pressurized habitats and rovers could potentially benefit from this technology.

III. 3-D Nanofilm Primary Li-Air Battery

Ionova recently completed a Phase I NASA SBIR contract entitled, “3-D Nanofilm Primary Li-Air Battery”.[5] The objective during the six-month period of performance was to demonstrate the feasibility of the proposed approach to develop Li-air cells utilizing a three-dimensional nanofilm structure that would serve the function of both an air cathode and a support for catalysts. The developed cathode was comprised of a networked mesoporous carbon structure, consisting of polymer aerogel supported by carbon microfiber mats, and was decorated with novel, highly reactive, ultra-high surface area catalysts. The approach was to optimize pore size, pore structure, and catalyst distribution to promote oxygen diffusion and to reduce pore clogging from reaction products, while maximizing reaction sites to increase capacity and current density.

A. Experimental

Ionova delivered three Li-air coin cells as final deliverables of the contract. Cells were tested at NASA to verify performance. Each cell contained a different catalyst, so no duplication of test results was possible. Cells were tested under identical conditions, discharged in room air at 22°C at a constant current density of ~ 15 mA/g (0.1 mA) of cathode until the voltage reached 1.5 V. Cells were then monitored for 8 hours following the test to observe voltage recovery.

Cells were activated with 0.2 M $LiPF_6$ in 1,2-dimethoxyethane (DME) electrolyte at Ionova and shipped in a sealed container to NASA GRC for testing. The container was opened in a dry room with less than 1% relative humidity. Cells were individually wrapped in an air-tight seal. Both the seal on the container and the seal on the individual cells appeared intact. The cells were brought into a glovebox that was purged with argon gas and placed into holders. The cells were then placed in a Nalgene bottle filled with argon gas and transferred to the test facility.

In the test facility, the cells were placed on test on an Arbin Instruments BT2000 Battery Cycler. Less than ten minutes elapsed between the cells’ initial exposure to room air in the dry room and the beginning of discharge. Cells were tested on a benchtop in room air with no forced flow. Figure 1 shows a representative coin cell delivered by Ionova. The coin cell is a 2325-type. A hole was drilled in the cell to allow air to flow into the cathode.

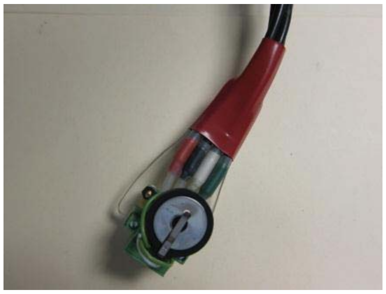


Figure 1: Representative coin cell by Ionova. Shown in holder and connected to current and sense leads.

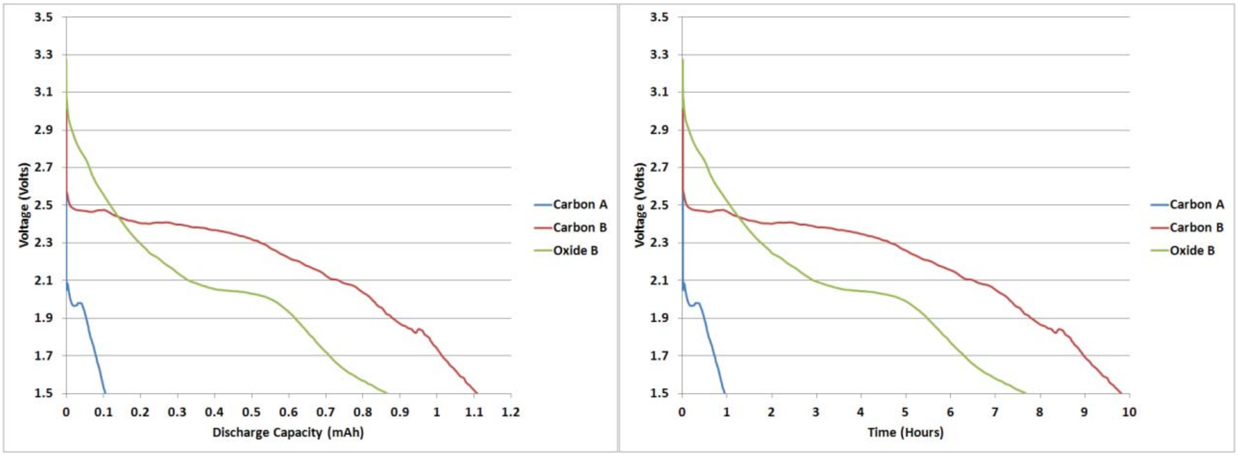
B. Results

Experimental results for the Ionova cells are shown in Figure 2 and are also summarized in Table 1. Catalyts were utilized in the carbon cathode to enhance the oxygen reduction reaction. A different catalyst was used in each of the three cells tested, designated Carbon A, Carbon B, and Oxide B. The Oxide B cell contained a cathode that had an oxide catalyst coating on the carbon structure.

The Carbon B cell yielded the highest capacity, delivering 1.1 mAh during an approximately 10 hour discharge. It delivered a specific capacity of 166 mAh/g of cathode. The specific capacity of the cathodes was calculated based on the current density, the discharge current, and the discharge capacity.

The Carbon A cell had a large voltage polarization which resulted in an instantaneous drop in voltage to 2.1 V upon discharge, hence no useable capacity was delivered until the cell voltage had dropped below a practical operating voltage. The Oxide B cell had the highest open circuit voltage at 3.27 V and exhibited the least amount of polarization upon initial discharge. However, the voltage declined steeply while discharging, so at 2.05 V, the midpoint discharge voltage was quite low as compared to the 2.27 V midpoint voltage for Carbon B. The voltage for the Carbon A and B cells recovered to peaks of 2.96 V at 3.75 hours post-discharge and to 2.94 volts at 4.5 hours post-discharge, respectively. After eight hours, the voltage for the Oxide B cell had recovered to 2.82 V and was still rising. Good OCV recovery is an indication that the cells remained well wetted during the discharge time.

Performance of the cells could possibly be limited due to side reactions from the organic electrolyte used in the cell. Further research in this area could include determining more suitable electrolyte formulations for this chemistry.



a) b)

Figure 2: Discharge profiles for Ionova cells: a) Discharge capacity versus voltage and b) Discharge time versus voltage.

Table 1: Summary of Test Results for Ionova Cells

Catalyst	Carbon A	Carbon B	Oxide B
OCV (V)	3.12	3.06	3.27
Mid-discharge Voltage (V)	1.91	2.27	2.05
Specific Capacity (mAh/g of cathode)	16	166	130
Discharge Capacity (mAh)	0.105	1.10	0.866
Energy Delivered (mWh)	0.193	2.41	1.80
Discharge time (hours)	0.93	9.8	7.7

These results were input into a model developed at NASA GRC to project the specific energy and energy density for a practical 45 Ah pouch cell with the voltage and specific capacity characteristics demonstrated by these cells.[6] A positive to negative ratio of 0.5, a 35% porous cathode, and 130% excess electrolyte were assumed. Separator and positive and negative collector thicknesses were taken into account. Irreversible capacity was neglected. When configured into a 45 Ah pouch cell, we project that the Carbon B cathode would result in a cell that delivers a specific energy of 196 Wh/kg and an energy density of 275 Wh/l.

IV. A Lithium-Air Battery with a High Energy Air Cathode

Yardney recently completed work on a NASA Phase I SBIR entitled, "A Lithium-Air Battery with a High Energy Air Cathode".[7] The main objective of this effort was to increase the energy of the air cathode by advancing its structure with new catalysts, formulations and processing. In addition, to increase the safety of the system, a new protective layer for the lithium metal anode was also investigated in conjunction with inorganic carbonate-based electrolytes.

A. Experimental

Yardney delivered several prototype Li-air cells as final deliverables of the contract. Three cells containing the same catalyst were tested at NASA to verify performance. Although Yardney experimented with stabilizing lithium metal during the effort, these cells did not contain an enhanced anode, but rather a pristine lithium metal anode. Cells were tested under identical conditions, discharged in room air at 24°C at a constant current of 2 mA until the voltage reached 1.5 V. Cells were then monitored for 8 hours following the test to observe voltage recovery.

Figure 3 shows a representative cell delivered by Yardney. The cell is contained in 3.75 inch x 3.75 inch fixture with an approximately 1.25 inch x 1.25 inch square hole that exposes the cathode to allow air flow. Cells were unactivated upon arrival and were activated in a dry room with less than 1% relative humidity using 1 M $LiPF_6$ in 1:1:1 EC:DMC:DEC electrolyte introduced using a syringe via an access port in the cell just prior to testing (see Figure 4). The cells were then immediately transferred to the test facility.

Once in the test facility, the cells were placed on test on an Arbin Instruments BT2000 Battery Cycler where they were monitored at open circuit for one hour to observe for voltage drops that might indicate the presence of shorts prior to the beginning of discharge. Cells were tested under a hood in room air with no forced flow directed at the cells, however, there was constant air flow in the hood. Since these cells were not designed for constant air flow over them, their operation within the hood environment could decrease their performance.

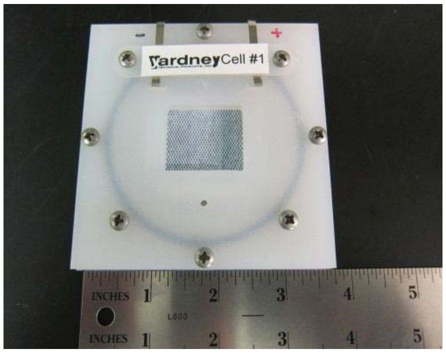


Figure 3: Representative experimental cell by Yardney

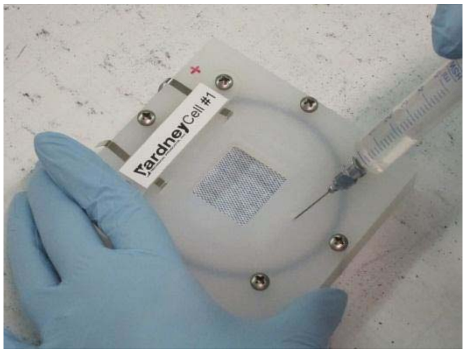
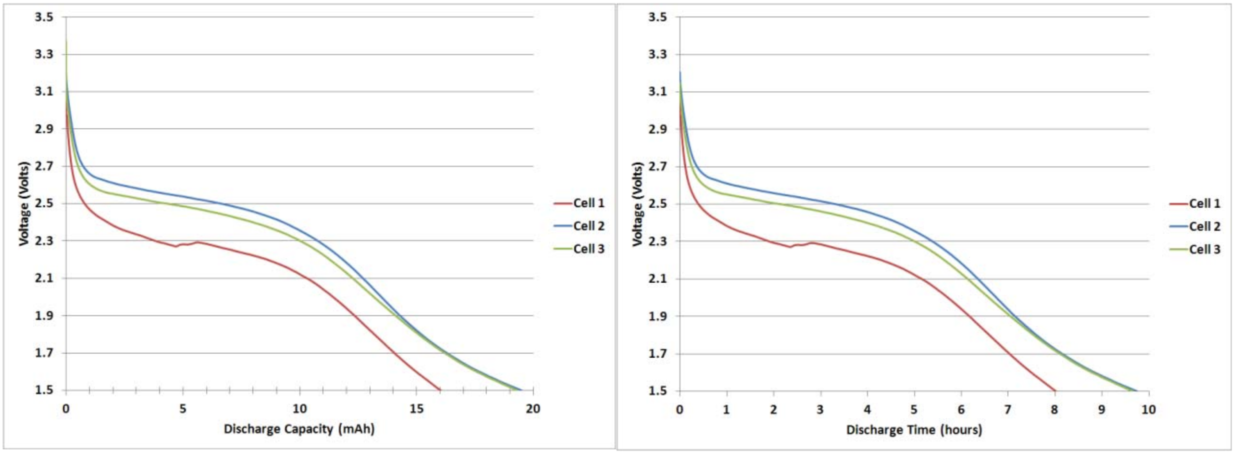


Figure 4: Activation of a Yardney cell with electrolyte

B. Results

Experimental results for the Yardney cells are shown in Figure 5 and are also summarized in Table 2. A manganese oxide-based catalyt is utilized in the cells. The cells had an open circuit voltage of 3.36 V. Cells 2 and 3 performed very similarly, both yielding about 19.5 mAh and discharging for almost 10 hours. Both cells delivered a specific capacity of 392 mAh/g of carbon. Since Cell 3 had a slightly lower voltage for most of the discharge, it delivered slightly lower energy than Cell 2. Cell 1 was out of family, likely due to expected variations in laboratory-scale electrode design. It delivered 16 mAh during its 8 hour discharge, which translates to a specific capacity of 370 mAh/g of carbon.

The voltages for all three cells recovered to 3.0 V at 8 hours post-discharge and were still rising. Such OCV recovery has been observed post-discharge in other Li-air cells developed and tested at Yardney, but we found that the cells could not support a load despite their high OCV. Upon dissection of those cells, we discovered that the cells contained minimal electrolyte - enough to maintain an OCV (therefore an OCV measurement could be made), but not enough electrolyte was present to sustain a voltage once current was applied. Although the cells reported on here were not dissected, based on this prior experience, we theorize that these cells lost electrolyte which decreased their available energy and adversely impacted their performance.



a) b)

Figure 5: Discharge profiles for Yardney cells: a) Discharge capacity versus voltage and b) Discharge time versus voltage.

Table 2: Summary of Test Results for Yardney Cells

Catalyst: MnO2-based	Cell 1	Cell 2	Cell 3
OCV (V)	3.36	3.36	3.36
Mid-discharge Voltage (V)	2.22	2.37	2.32
Specific Capacity (mAh/g of carbon)	370	392	392
Discharge Capacity (mAh)	16.0	19.5	19.3
Energy Delivered (mWh)	34.1	43.4	42.3
Discharge time (hours)	8.0	9.7	9.7

These results were input into a model developed at NASA GRC to project the specific energy and energy density for a practical 45 Ah pouch cell with the voltage and specific capacity characteristics demonstrated by these cells. Assumptions were the same as discussed above. When configured into a 45 Ah pouch cell, we project that the manganese oxide cathode discussed herein would result in a cell that delivers a specific energy of 361 Wh/kg and an energy density of 485 Wh/l.

V. Conclusion

New catalysts and carbon cathodes were developed for Li-air primary battery cells by Ionova Technologies, Inc. and Yardney Technical Products, Inc. under contract with NASA. Preliminary results from assessments on unoptimized laboratory cells indicate that feasibility of the technical approaches was achieved by the companies during the six month Phase I SBIR efforts. The best performing cathodes from both companies yielded specific capacities of 166 and 392 mAh/g, an order of magnitude lower than the specific capacity that would be required to meet NASA's aggressive goals for the Mobile Oxygen Concentrator. Nonetheless, all but one of the experimental cells displayed good voltage over a sustained discharge time of several hours. When modeled as 45 Ah pouch cells, we project that these cathodes would enable cells that can deliver specific energies of 196 and 361Wh/kg, respectively, and energy densities of 275 and 485 Wh/l, respectively. With continued research into new catalyst combinations, cathode structure, and compatible electrolytes, Li-air shows promise as a technology that, once mature, could enable the Mobile Oxygen Concentrator for Spacecraft Emergencies. Whereas approaching 1800 Wh/kg with Li-air batteries is a far-term goal, NASA applications that require specific energies on the order of 300 to 750 Wh/kg, such as EVA spacesuits, UAVs, and other electric aircraft applications could benefit from this technology in the mid-term. Li-air technology could also be enabling for other cross-cutting NASA applications and missions, and an unlimited number of other government and commercial applications that require primary battery technology.

Acknowledgments

This work was supported by NASA, Human Research Program, Exploration Medical Capabilities, Medical Oxygen Concentrator for Spacecraft Emergencies Technology Development Project and Game Changing Technology Development Program, Advanced Space Power Systems Project.

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