Characterization of Lithium Peroxide Formation on Lithium Air Electrode via Titration Techniques and EIS

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Abstract

Lithium-oxygen batteries have attracted attention in the last decade for their remarkable theoretical capacities. Valuable efforts have increased the initial discharge capacity for primary batteries to over 10 times that of conventional lithium-ion batteries. However, cells have yet demonstrated to be rechargeable as the internal reactions are highly unstable. The oxygen-rich environment in combination with a wide potential window and the presence of lithium encourage the chemical degradation of the electrolyte in the cell when cycled. Despite the obvious concern from the electrolyte, the carbon cathode has demonstrated to also be a factor in the overall reversibility of the cells as the properties of the carbon affect the formation of the sought discharge product – lithium peroxide. Here, the characterization of lithium peroxide formation in lithium air electrode via galvanostatic testing, titration techniques and Electrochemical Impedance Spectroscopy (EIS) is performed as a Master of Science Thesis study. This research evaluates various carbon materials with different surface area and pore volumes and analyze the findings to recognize any correlations. Three testing techniques, galvanostatic cycle testing, Li_2O_2 titration and EIS, provides different perspectives on the complex chemical mechanisms in lithium-oxygen batteries.

Background Information

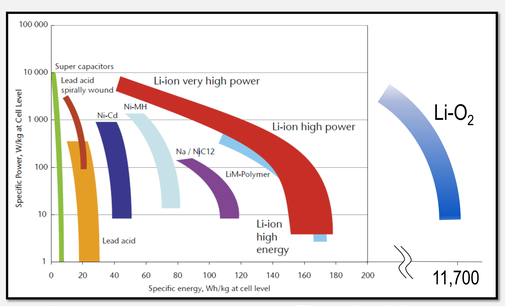


Figure 1: Theoretical Characteristics of Various Electrochemical Energy Storage .

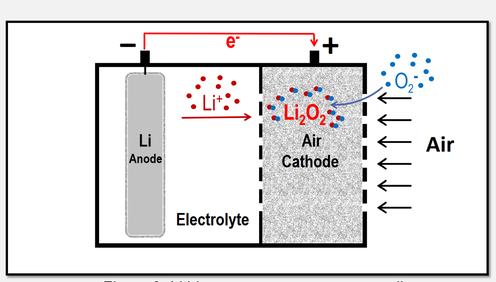
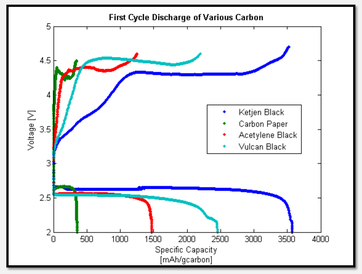


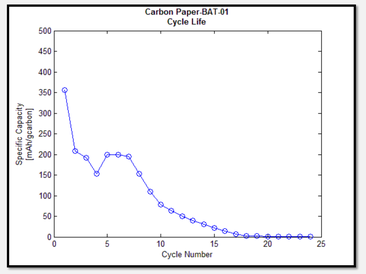
Figure 2: Lithium-oxygen non-aqueous cell.

Results:

Galvanostatic Cycling Test:

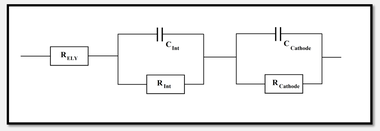
- Constant Current: 0.1mA/cm^2
- Assessment of the effect of carbon morphology on the performance of cells
- Five carbons with different structure properties:
  - Layered
  - Porous
  - Tubular

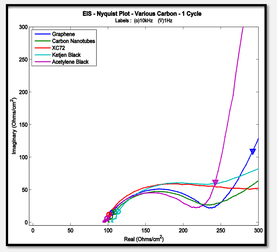




Electrochemical Impedance Spectroscopy:

- Estimate the internal equivalent circuit of a cell
- Provide insights on the chemical mechanisms of a cell
- Monitor the internal impedance of a cell to assess its life expectancy.





Iodometric Titration:

- Chemical characterization technique used to determine the quantity of Li_2O_2 (desired product of the reaction) present in a discharge cell.
- Determine the yield of lithium peroxide at various cycle number.
- Assess the effects of carbon structures on the evolution of lithium peroxide.

$$2\,Li^{(s)} + O_2 \rightarrow Li_2O_2$$

$$Li_2O_2 + 2H_2O \rightarrow 2LiOH + H_2O_2$$

$$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Carbon Material	Li_2O_2 Yield (%)
Graphene Nanoplatelets	72.0 ± 1.0
Carbon Nanotubes	71.7 ± 0.3
Volcan – XC72	75.2 ± 0.5
Ketjen Black	73.7 ± 0.2
Acetylene Black	71.3 ± 0.7

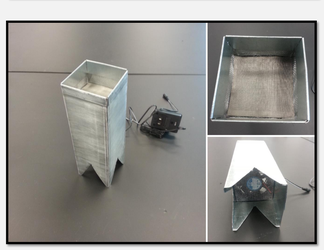
Laboratory Station:

Inert Environment System:

- High Purity Argon (99.995%)
- Oxygen Sensor: 0 - 9,999 ppm
- Moisture sensor: 0 – 999 ppm
- Scale: 0.1 mg – 100 g
- Automatic Pressure Controller (1 mBar control)
- Low Permeability Gloves
- High Vacuum for Transfer Chamber

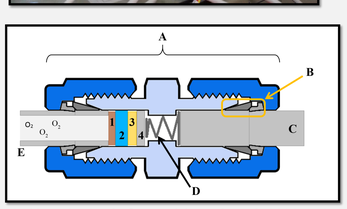
Battery Testing System:

- Ultra High Purity Oxygen (99.9995%)
- Oxygen Supply: 1 – 15 psig.
- 8 cells simultaneously, independent of one-another
- Voltage range: 0 – 5V
- Current Ranger: 0.05 – 5mA



Custom Purification System:

- Moisture: <20 ppm
- Desiccant: Molecular Sieves (4 Å)
- Capable to regenerate desiccant after use.



Swagelok Cells:

- Air-tight design
- Reusable
- Low-cost parts

1- Air cathode, 2- Spacer/electrolyte, 3- Lithium Anode, 4- Stainless Steel Spacer, A- Swagelok PFA Union, B- PFA ferrule set, C- Stainless Steel rod, D- Stainless Steel Spring, E- Stainless Steel Tubing.

Observation

A. The first discharge capacity is very dependent, as expected, on the carbon structure used in the cell. Furthermore, the capacity is directly related to the surface area of the carbon.
B. The cyclability of a cell is also dependent on the carbon structure as a higher surface area carbon has lower cyclability properties.
C. The impedance in the cell was found to vary from carbon to carbon. More specifically, the carbon affects the capacitance of the cell.
D. The lithium peroxide yield in Li_2O_2 cells is very dependent on the different carbons.

Future Work

A. Concerning specifically the lithium-oxygen battery study conducted in this work, a number of future directions has been discussed to be plausible:
   1. Expansion of the number of carbon studied
   2. Characterization of lithium peroxide formation due to various electrolyte composition.
   3. Cyclic Voltammetry study of carbon/electrolyte combination to further understand the reaction mechanisms.
   4. Study of the effect of catalysts and reaction mediators on the Li-O_2 reaction.
   5. Assessment of alternative non-carbon-based cathode material.

B. In addition, the results obtained from this study demonstrated a fully operational inert environment laboratory station that can be utilized for numerous projects in the supercapacitor, solar cells, fuel cells or in other battery fields.

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Oregon TECH