Design and Development of Advanced Air-Cathodes for Li-Air Battery

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Outline

- Introduction/NASA Energy Requirements
- Challenges for Li-Air Battery & Air-Cathode Development
- Design Parameters for Air-Cathode
- Result Summary
- Next Steps/Future Direction

Batteries: Important for NASA Missions

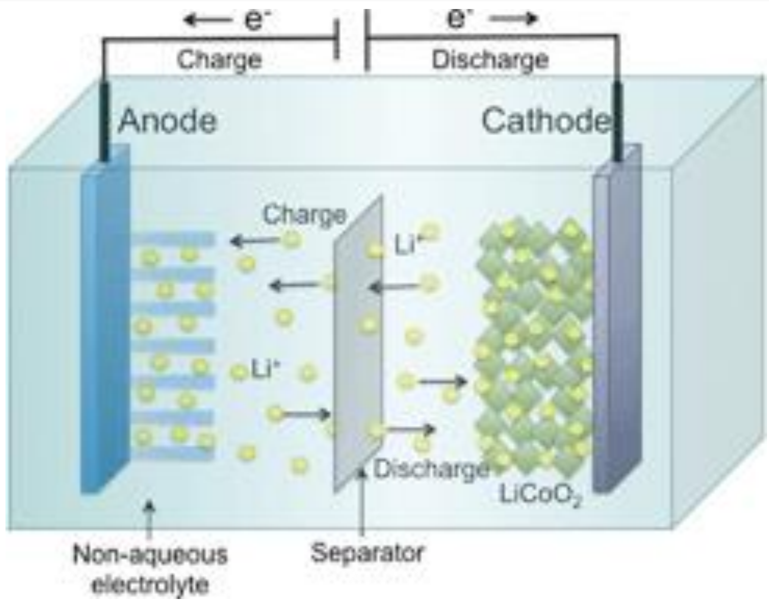
- **Batteries provide:**
  - a versatile, reliable, safe and portable energy source, and are an essential component of the power system of virtually all NASA missions
  - energy storage, serve as a power source such as during eclipses, and can provide peaking power, which are important electrical energy storage options for NASA space missions

Desired Battery Properties for NASA Missions

- **Safe**
- **High in specific energy**
- **Light in weight**
- **Compact in volume**
- **Long in shelf life**
- **Durable in wide temperature ranges and harsh environments**
- **Reliable in meeting mission requirements**

State-of-Art (SOA) Li-Ion Battery (LIB)

- **LIB Specs**:
  - Specific energy: 180-200 Wh/kg
  - Specific power: 300 W/kg
  - Temp range: -20^{o}C to 60^{o}C
  - Excellent rechargeability: (1000s cycles)



Poulomi, R. et al J. Mater. Chem. A 2015 (6)

Anode: Graphite
Cathode: $LiCoO_2$
Electrolyte: Li salt in organic carbonate

- **Limitations**:
  - Maximum of specific energy <250 Wh/kg
  - Flammable electrolyte and fire hazards

NASA Demands Very High Specific Energy Batteries

Electric Aviation

500 – 750 Wh/kg

- Green aviation – Less noise, lower emissions, high efficiency
- Hybrid / All-electric aircraft – Limited by mass of energy storage system
- Commercial aviation – Safe, reliable, lightweight on-board electric auxiliary power unit

Extravehicular Activities (Spacesuit power)

>400 Wh/kg

Required to enable untethered EVA missions lasting 8 hours within strict mass and volume limitations.

Astronaut life support
Safety and reliability are critical
100 cycles

Landers and Rovers, Robotic missions, In-space habitats

>500 Wh/kg

Batteries are expected to provide sufficient power for life support and communications systems, and tools including video and lighting

- >100 cycles

NASA future mission requirements far exceed the capabilities of SOA Li-ion chemistries

➢ Progress in these areas requires advances in safe, very high energy batteries

Advanced Safe, High Energy Batteries

- Improve Li-ion specific energy and safety
  - Advanced electrode materials development such as:
    - Si anode
    - NMC cathode
    - non-flammable additives in electrolyte
    - under NASA Advanced Space Power System (ASPS) project (2009-2014) and under NASA Advanced Energy Storage Systems (AESS) project (2014-2017)

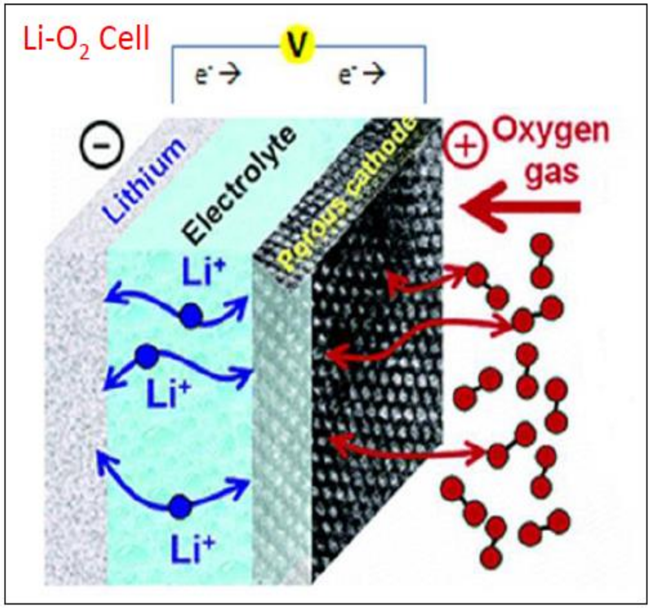
- Beyond Li-ion battery chemistries development
  - NASA Center Innovative Fund (CIF)
  - Independent Research and Development (IRAD)
  - Convergent Aeronautics Solutions (CAS)
  - NASA SBIR/STTR Program

Beyond Li-Ion Battery Chemistries

- **Battery chemistries with very high theoretical specific energy:**
  - **Li/S Battery Chemistry: 2680 Wh/kg**
  - **Metal-Air Battery chemistries, e.g. $Li/O_{2:}$ 5200 Wh/kg**
- **These high theoretical capacity battery chemistries have the potential to meet NASA's energy goal of >400 Wh/kg**

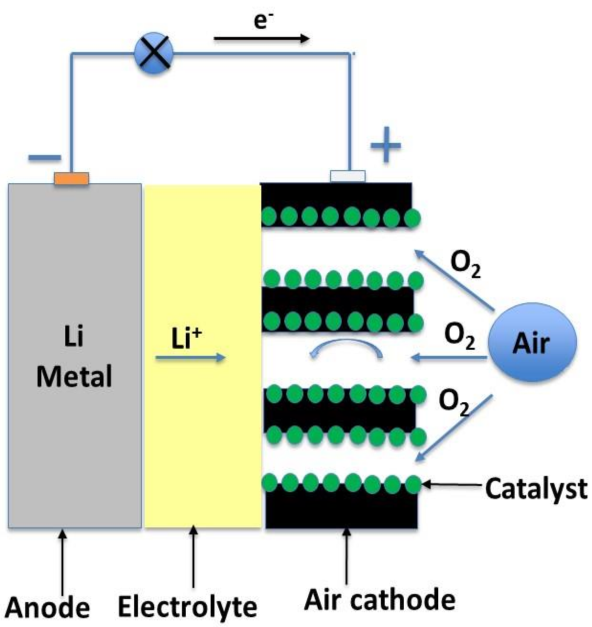
$Li\text{-}O_2$ Battery Chemistry: Challenges

- **Complex discharge intermediates/ products: LiO_2, Li_2O_2, Li_2O**
  - High overpotential during charge causing electrolyte decomposition
  - low cycle life
- **Low kinetics: poor rate capability**
- **air cathode is "open" to environmental**
  - environment e.g. CO_2, humidity, air flow, temperature impact the battery performance
- **Safety, Li dendrite growth**
- **Air cathode and electrolyte development – critical for $Li\text{-}O_2$ battery**



Air-Cathode Design

- **Requirement for the air-cathode:**
  - Permeable to air/O_2 – porous substrate
  - High catalytic reaction:
    - oxygen reduction reaction (ORR)
    - oxygen evaluation reaction (OER)
- **Substrates**
  - porous with adequate mechanical strength
  - good electronic conductivity
  - stable chemically to electrolyte an discharge intermediate/products
  - Stable at wider electrochemical window
  - Plus if the substrate has catalytical activity to O_2
- **Active materials of cathode**
  - High surface, high porosity and high catalytical activity to O_2
  - Stable chemically and at wider electrochemical window

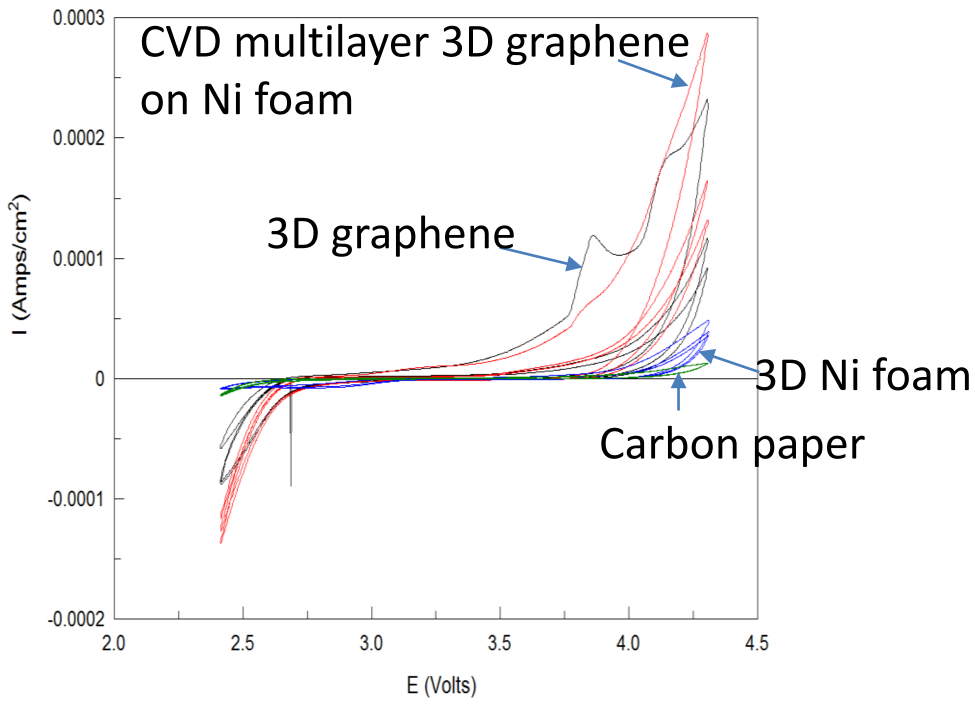


Air-Cathode Development

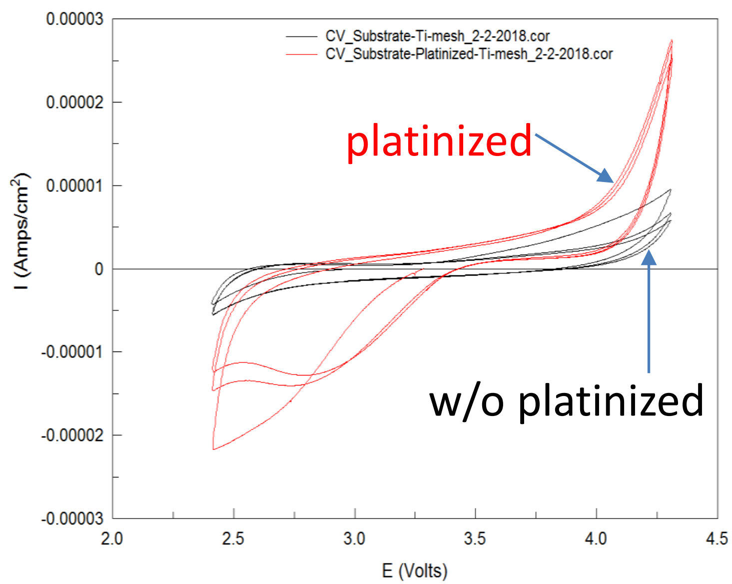
- **Different substrates**
  - 2D carbon: (carbon paper/cloth), 2D metal mesh (Ti, Pt/Ti)
  - 3D graphene, 3D Ni foam. 3D Ni foam with CVD multilayer 3D graphene
- **Different carbon as active materials**
  - Super P
  - KetjinBlack (KB) carbon
- **Catalyst in cathode**
  - Metal oxide
  - Nobel metal
- **Porosity of Ni Foam Substrate**
  - Different porosity
- **Additive in electrolyte**

Different Substrate Study

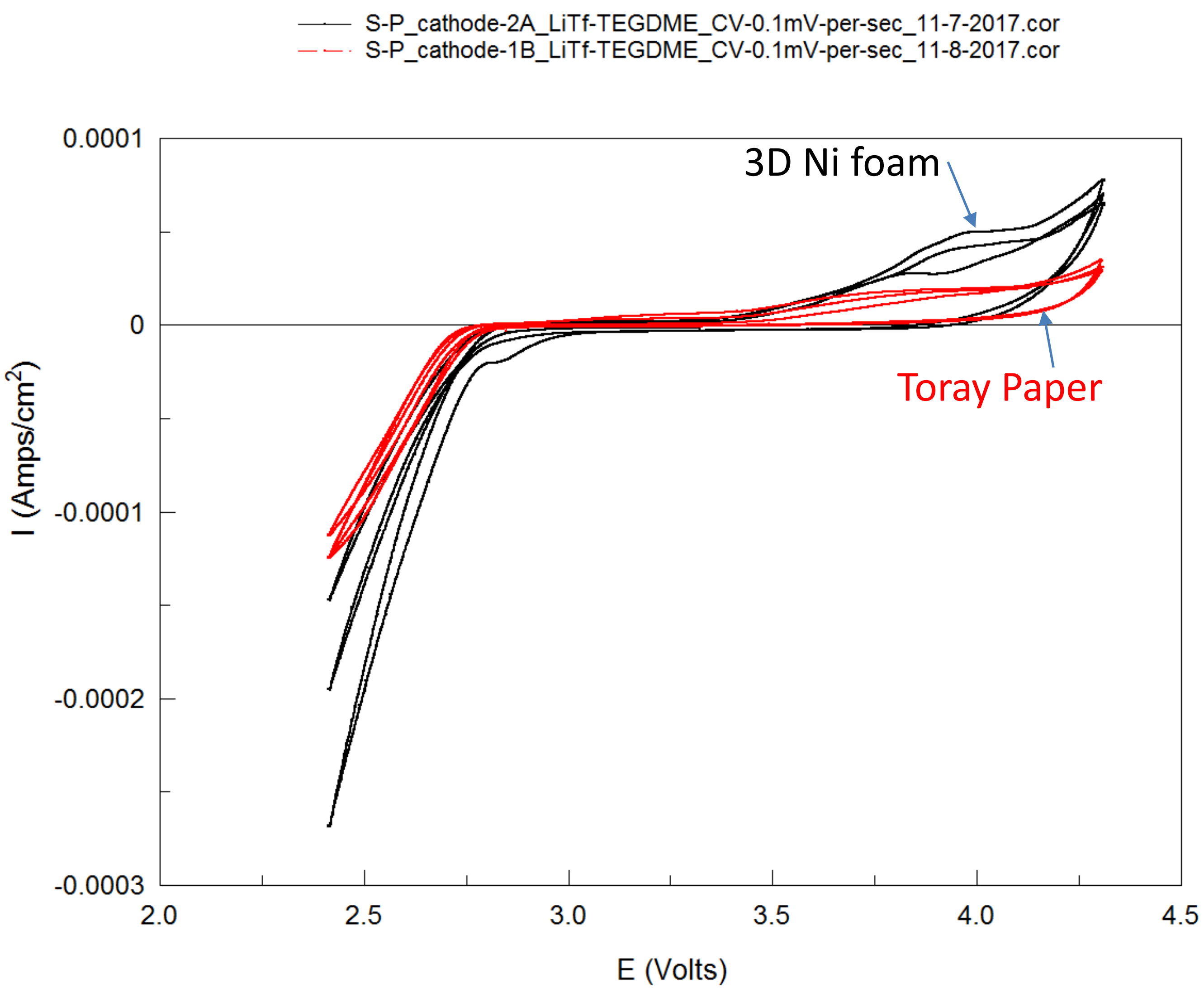
3D Graphene/3D Ni foam



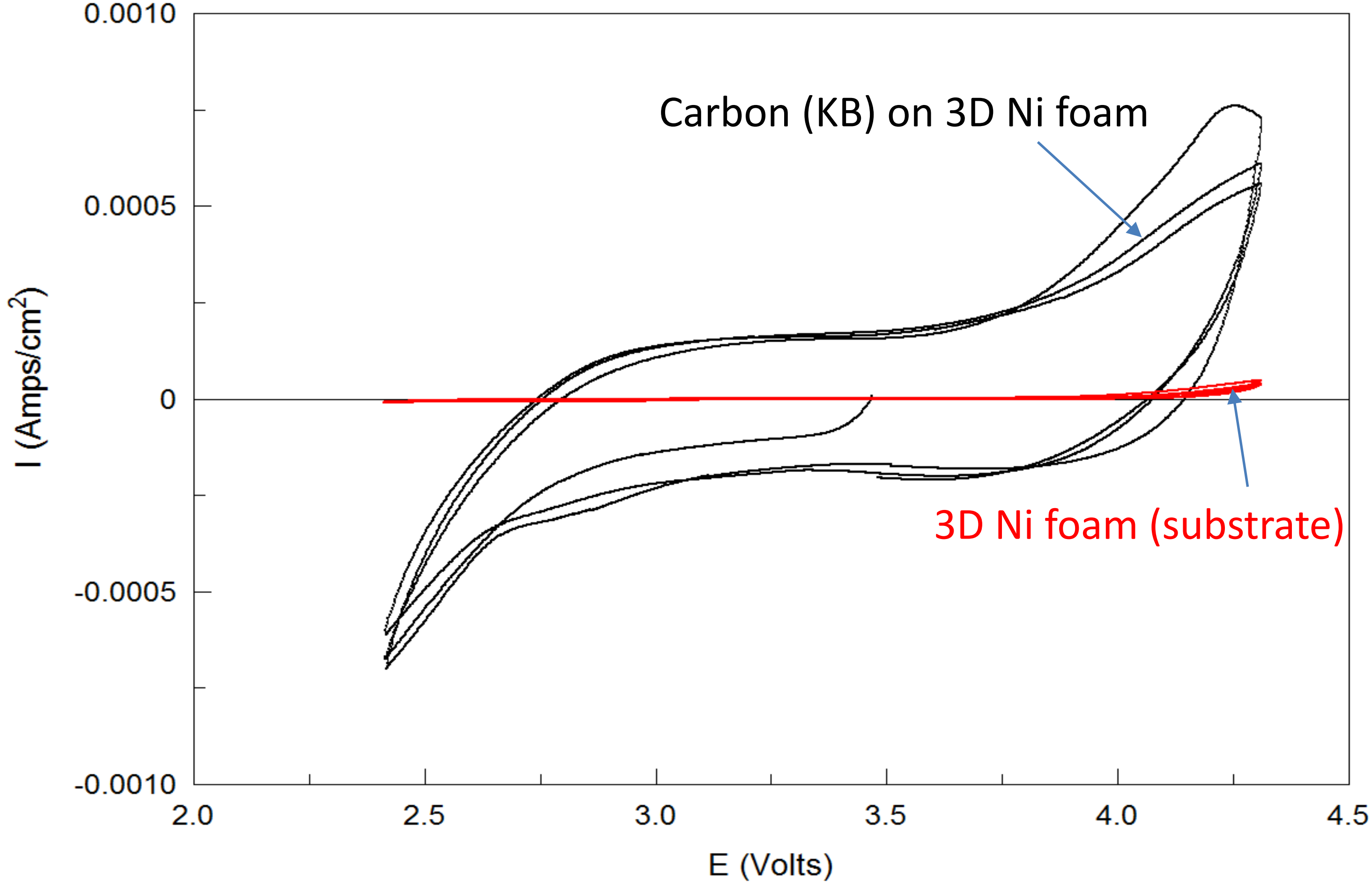
2D Ti mesh



Cyclic Voltammetry of Super P on Different Substrates



Cyclic Voltammetry of Carbon (KB) on Ni Foam



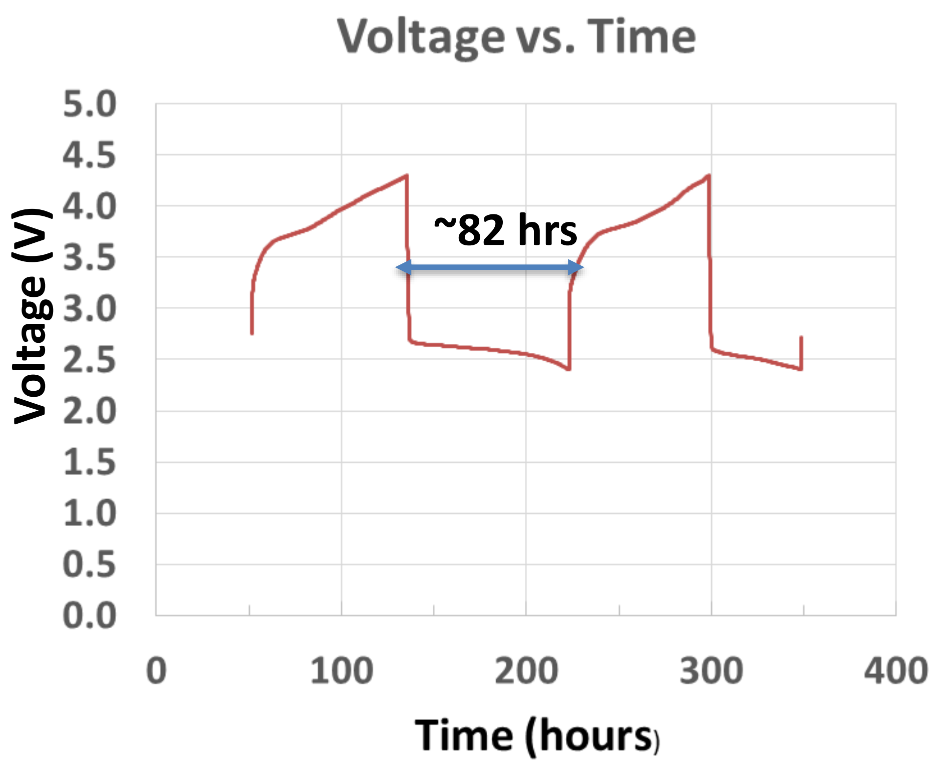
Substrates and Active Materials Study

- Platinized Ti mesh is better than Ti mesh w/o Pt treatment
- 3D Ni foam is better than 2D carbon/metal mesh
- Ketjin Black carbon is better than super P carbon
- 3D Ni foam and Ketjin Black are selected as cathode material

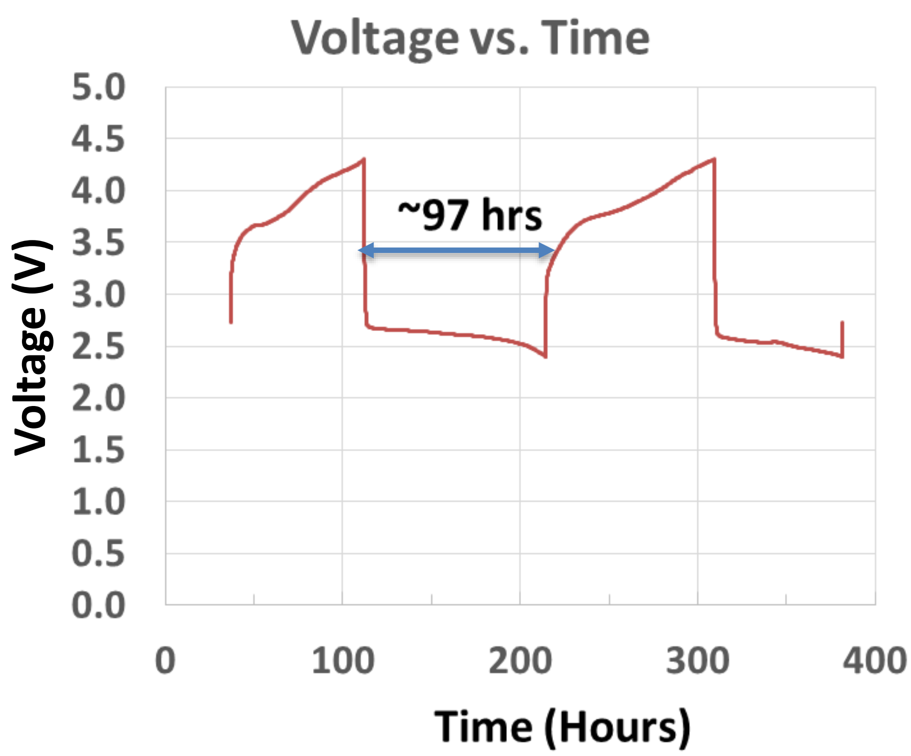
Porosity Impact

75 mA/g

Ni foam pore size: 450 um



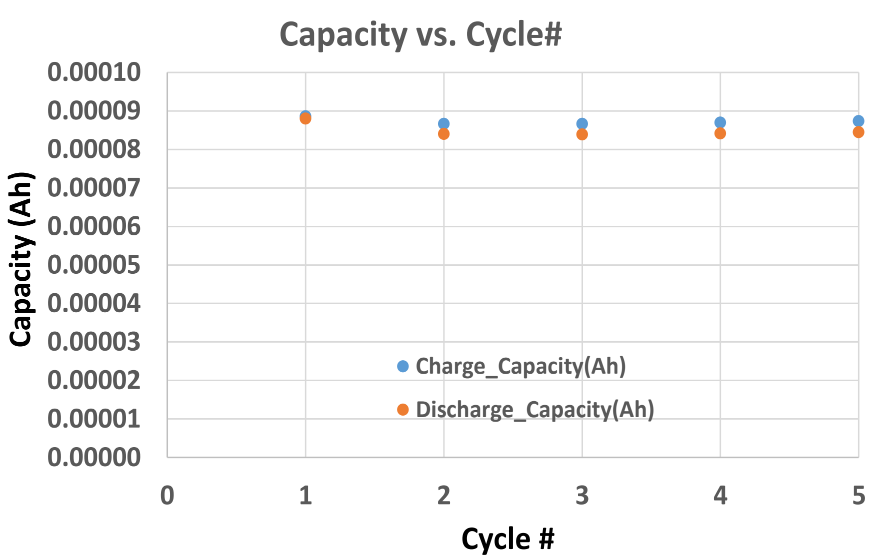
Ni foam pore size: 680 um



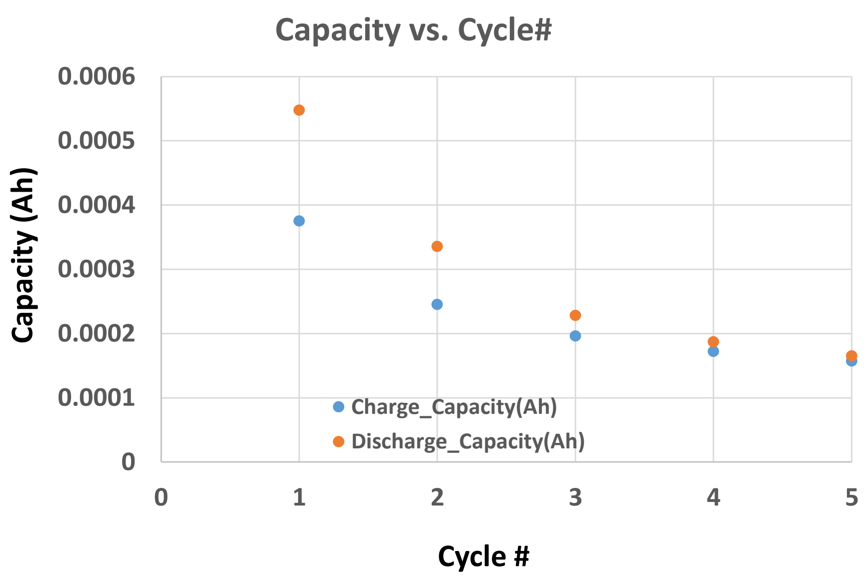
Cycling Performance at Different Cut-off Voltage

Current: 450 mA/g

4.3V – 2.4V



4.3V – 2.0V



Rate Capability Cycling of Li-Air Cell

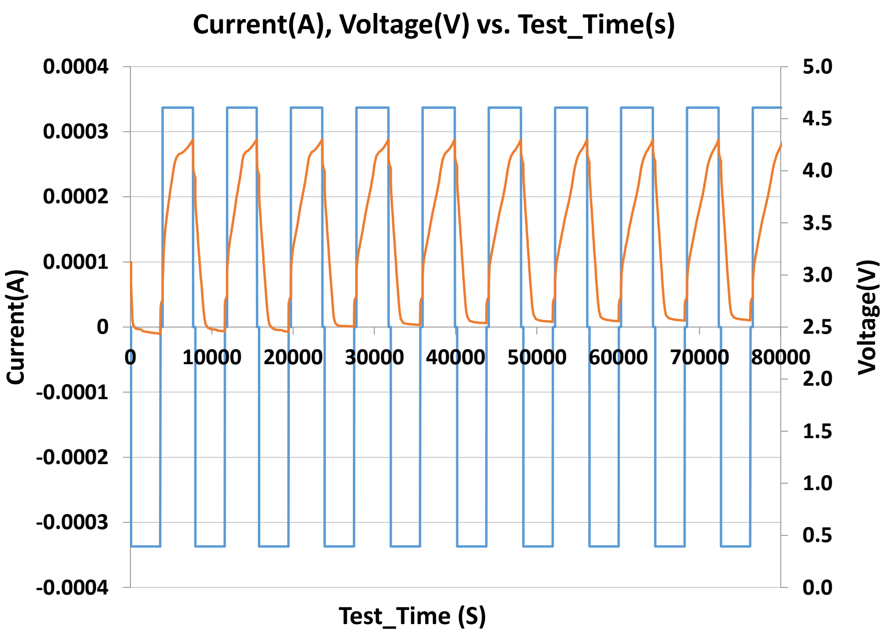
- KetjenBlack carbon on 3D Ni foam
- Loading: 3.2 mg/cm^2

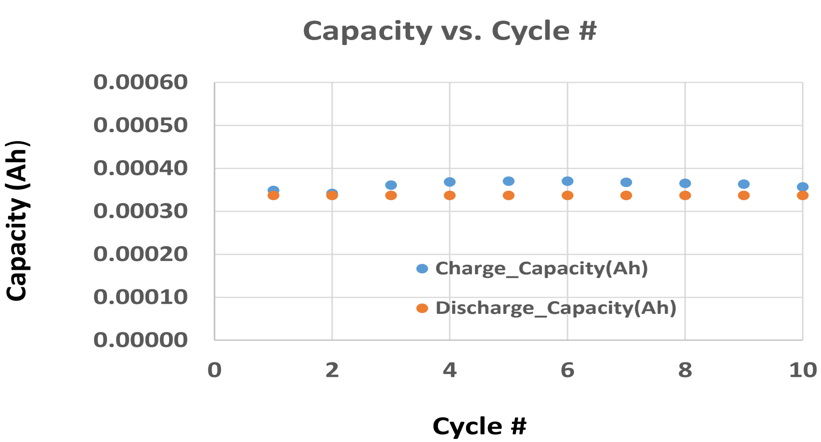
- Current density (mA/g):
  150 → 300 → 450 → 300 → 150
  150mA/g ---→ 0.47 mA/cm^2
  300mA/g ---→ 0.95 mA/cm^2
  450 mA/g --→ 1.42 mA/cm^2
- 4.3V – 2.4V
- Discharge: 1 hr or 2.4V

- High purity air (water <1 ppm in total contamination) environment

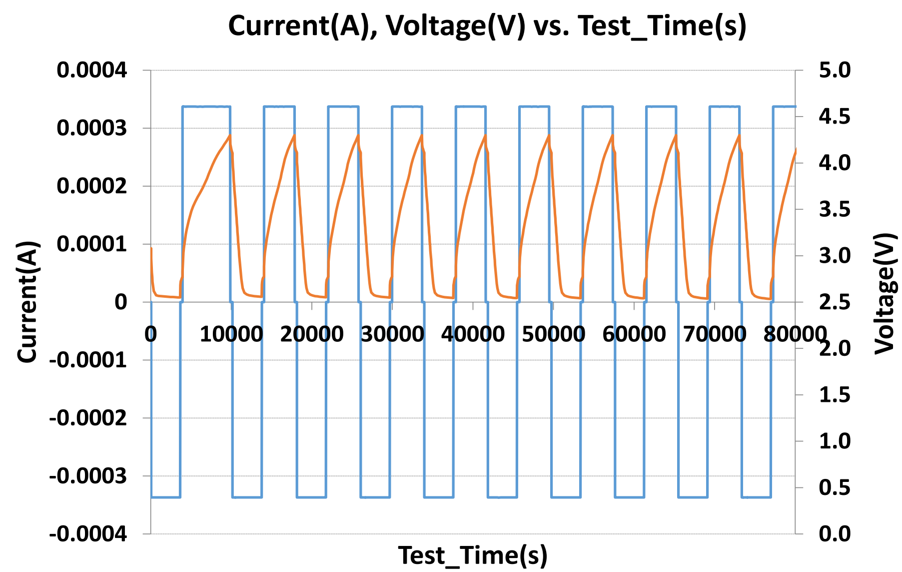
150 mA/g: Before and After Rate Capability Cycling

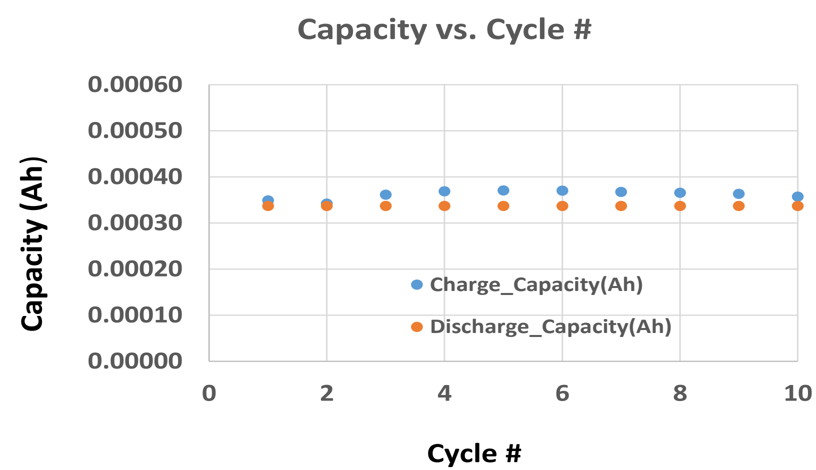
150 mA/g, initial





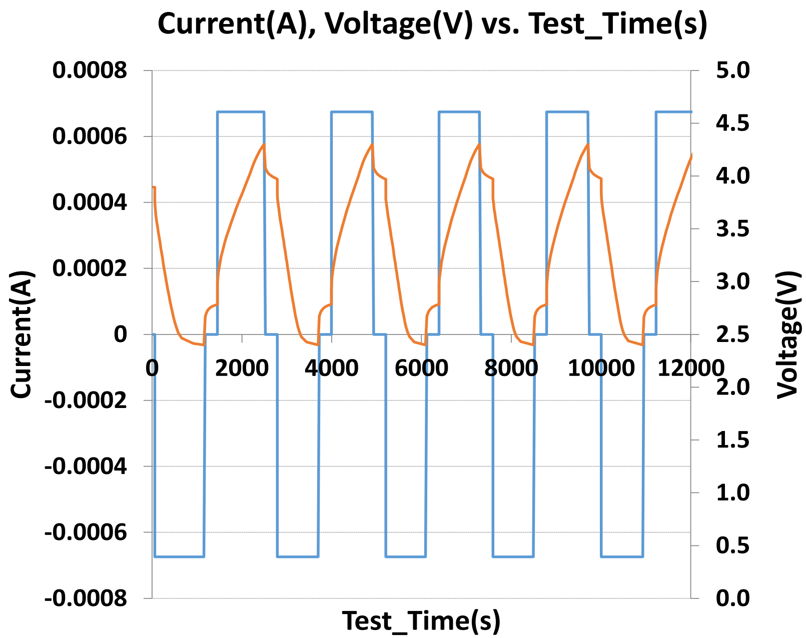
150mA/g, After 300, 450, 300 mA/g

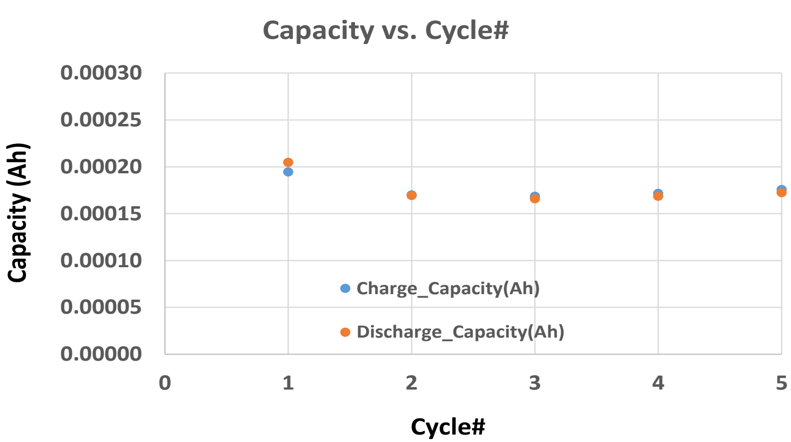




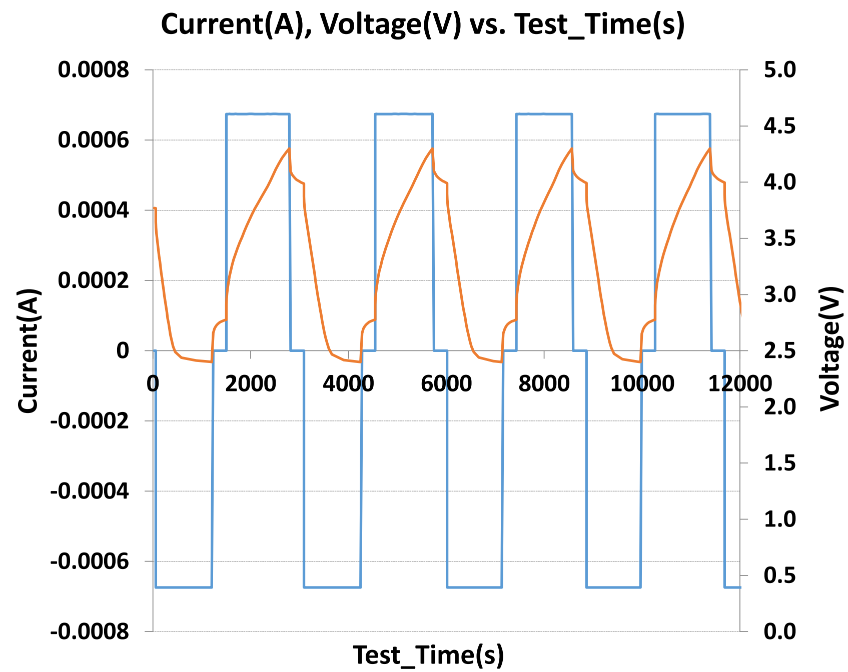
300 mA/g: Before and After Rate Capability Cycling

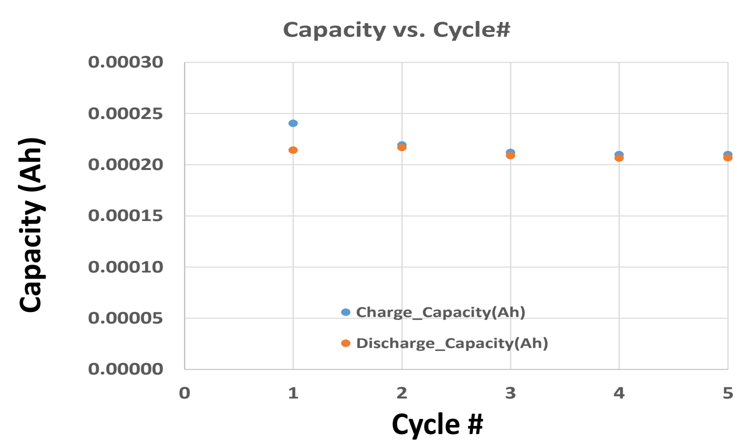
300 mA/g, Initial





300 mA/g, after 450 mA/g





Rate Capability Cycling vs. Commercial Air Cathode

Ketjen Carbon Black on Ni foam					
Loading: 4 mg/cm2		Discharge Condition	Discharge Time	W/kg	Wh/kg
Rate			(minutes)	vs. electrode coating	vs. electrode coating
mA/g	mA/cm2				
150	0.47	1 hour or 2.4V	60	401	401
300	0.95		18.2	815	247
450	1.42		5.2	1317	114
Commercial Air Cathodes					
CeTech (8 mg/cm2)	0.5	1 hour or 2.4V	12	45	9
	1		0.55	99	0.9
	1.5				
Elat (6 mg/cm2)	0.5	1 hour or 2.4V	26	51	22
	1		1.8	106	3.2
	1.5				

Result Summary/Next Steps

- The factors such as substrate type, carbon materials, porosity and discharge cut-off voltage impact air-cathode cycling performance

- Kenjet black carbon on 3D Ni foam substrate demonstrated excellent cycling performance and rate capability

- Current under Investigation/Next Steps:
  - Catalyst
  - Electrolyte with additive

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Thank you!

Any Questions?