Rechargeable Metal Hydride-Air Battery for EV and Stationary Applications

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Pros and Cons of State of Art Li-ion EV Batteries

Characteristics	State of Art EV (Li-ion) Battery
Cell Specific Energy (Wh/kg)	165-200
Cell Energy density (Wh/l)	400
Battery Specific Energy (wh/kg)	80-120 (50-60% of cell energy)
Battery energy density (Wh/l)	250
Electrical management	Essential to prevent over voltage/undervoltage
Thermal management	Essential to eliminate hot spots
Power, W/kg	400 W/kg
Cycle Life (100% DOD)	500-1000
Operating temperature	-30C to+ 50C
Cell Cost	$ 250/kWh
Battery Cost	$ 450/kWh (80% of additional cost from electrical, thermal management and mechanical containment
Safety	Likely to undergo go thermal runaway under abuse conditions and also due to unexpected internal shorts from either manufacturing/material contaminants
Reliability	Can develop problems (e.g., Li plating, internal shorts,) during use

- The specific energy of Li-ion batteries is only 50-60% of the specific energy at the cell level due to ancillary subsystems (thermal, electrical and mechanical) .
- A high energy aqueous rechargeable battery system may provide comparable (or higher) specific energy and energy densities as Li-ion (even with low cell-level energy densities) combined with inherent safety (ARPA-E's RANGE)

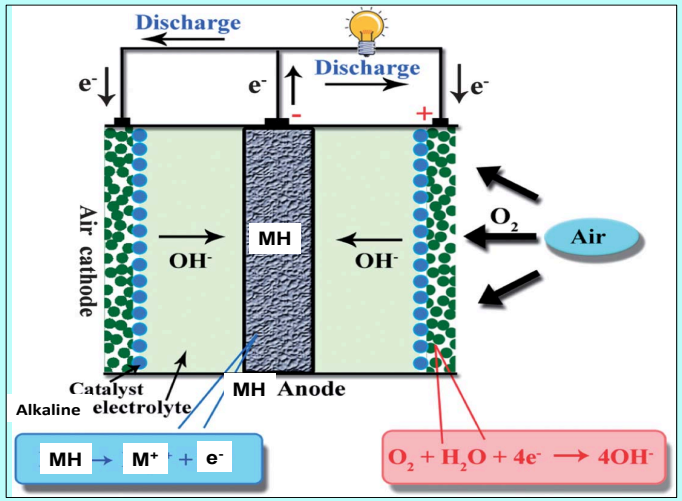
Metal Hydride - Air Cell Chemistry

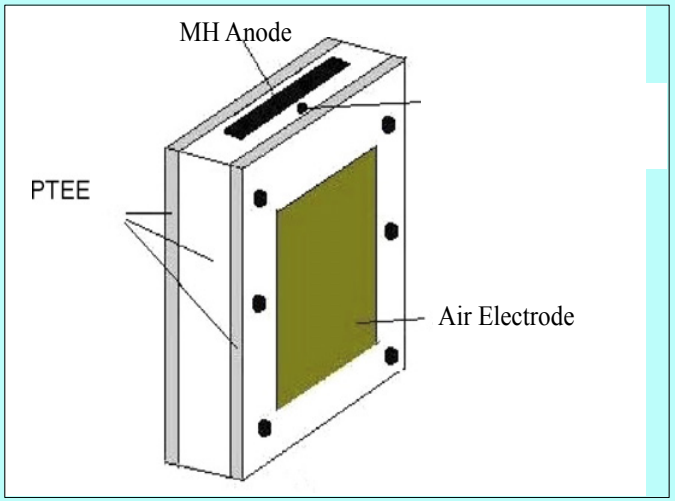
- Metal-air batteries have higher specific energies among the aqueous rechargeable systems.
  - Metal Hydride (in alkaline solutions) is probably the most stable anode upon cycling
- Chemistry
  - Anode: Intermetallic alloy that reversibly absorb and desorb hydrogen at ambient temperatures and moderate pressures.
  - Cathode: Catalyst-dispersed carbon (or other conducting substrate), where oxygen reduction (discharge) and oxygen evolution occurs reversibly either on one (bifunctional) or two cathodes.
  - Electrolyte: 31% KOH
- Leverage from existing technologies (MH alloy from the Ni-MH batteries and air cathode from fuel cells (regenerative).
- Cell reaction (Charging)

$$4\ OH^- = 2\ H_2O + O_2 + 4\ e^-\ (0.41\ V)\ \text{(+ve electrode)}$$

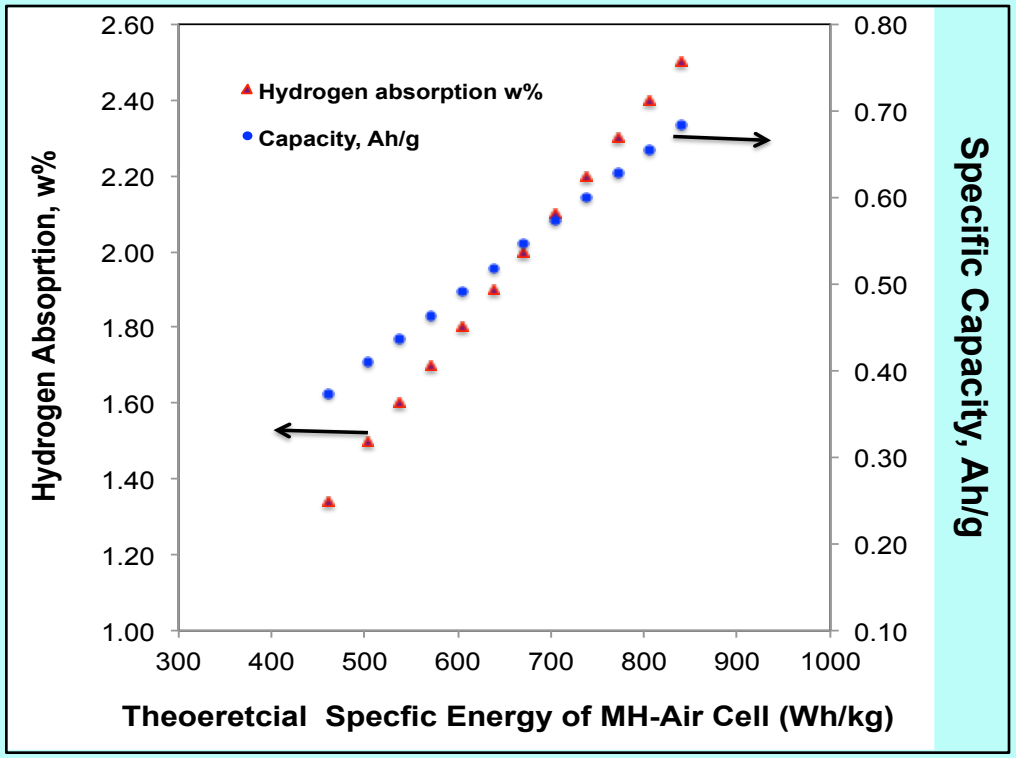
$$4M + 4\ H_2O + 4\ e^- = 4MH + 4\ OH^-\ (-0.82\ V)\ \text{(anode)}$$

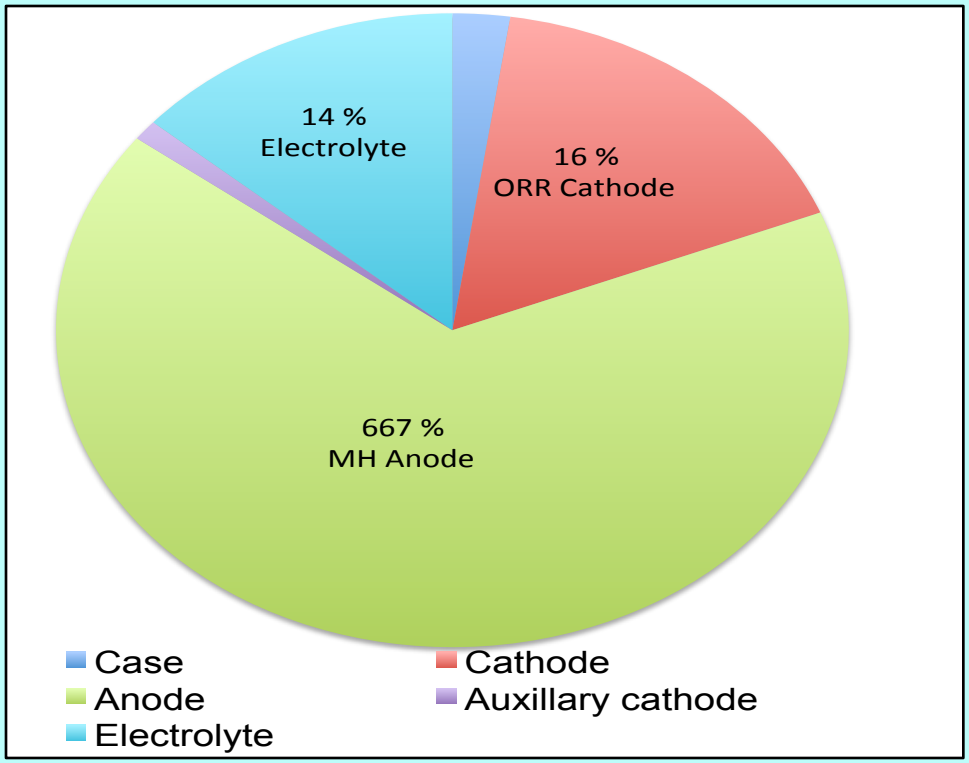
$$2\ H_2O + 4M = 4MH + O_2\ (1.23\ V)$$





Metal Hydride- Air Battery System

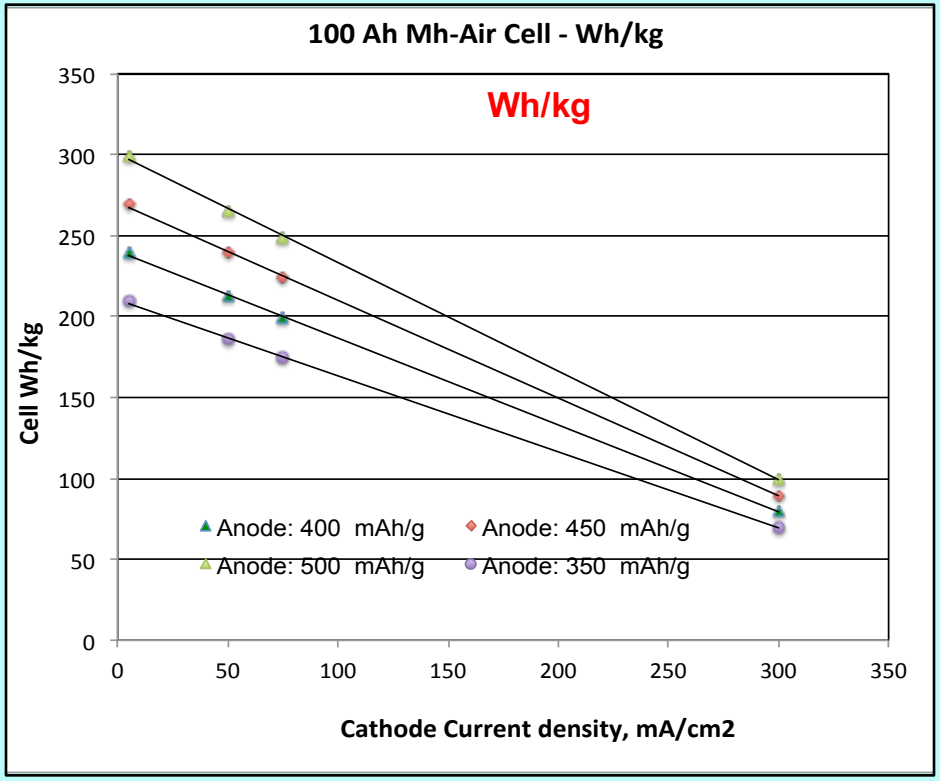


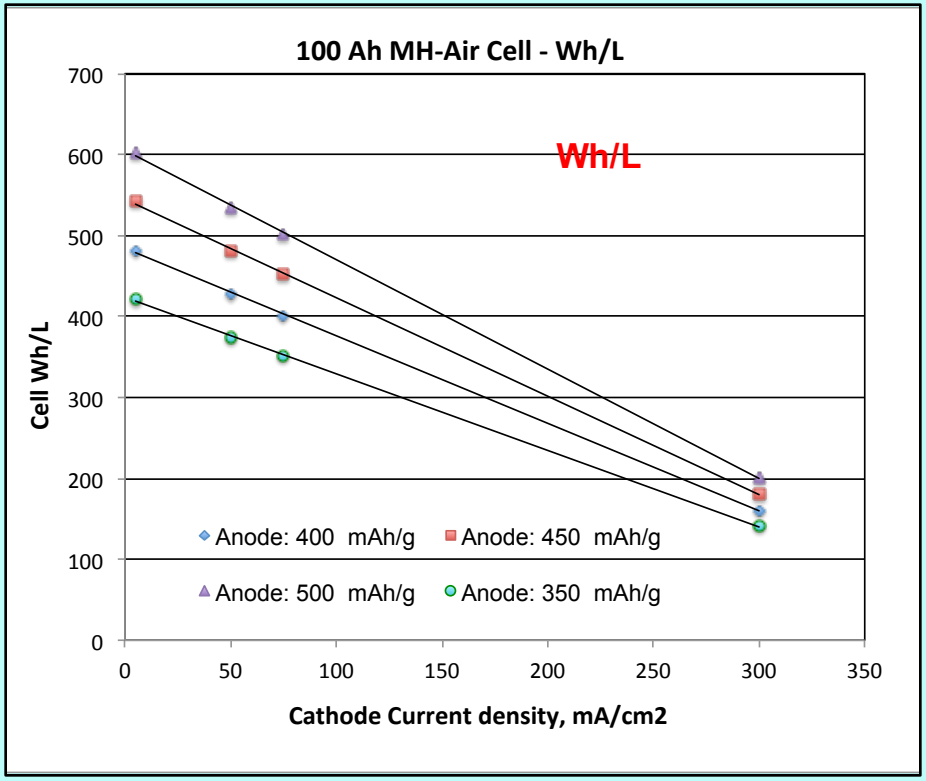


- Metal Hydride air system has the potential to offer high specific energy densities
  - Metal Hydride (in alkaline solutions) is probably the most stable anode upon cycling
  - A marginal improvement in the hydrogen absorption capability can result in significant increase in the MH-Air system.

Estimated Performance of MH-Air Cells

Anode Capacity and Cathode Kinetics vs Wh/kg and Wh/l





- Cell specific energy and energy densities improve significantly with an increase in the anode specific capacity as well as improvement in the cathode kinetics (which is rate-limiting).

Metal Hydrides Alloy Anodes

Type	Metal	Hydride	Mass%	P_{eq} and T
Elemental	Pd	$PdH_{0.6}$	0.56	0.020 bar, 298 k
AB_5	$LaNi_5$	$LaNi_5H_6$	1.37	2 bar, 298 k
AB2	ZrV_2	$ZrV2H_{5.5}$	3.01	10^{-8} bar, 323 k
AB	FeTi	$FeTiH_2$	1.89	5 bar, 303 k
A_2B	Mg_2Ni	Mg_2NiH_4	3.59	1 bar, 555k
Body centered cubic	TiV_2	TiV_2H_4	2.6	10 bar, 313k

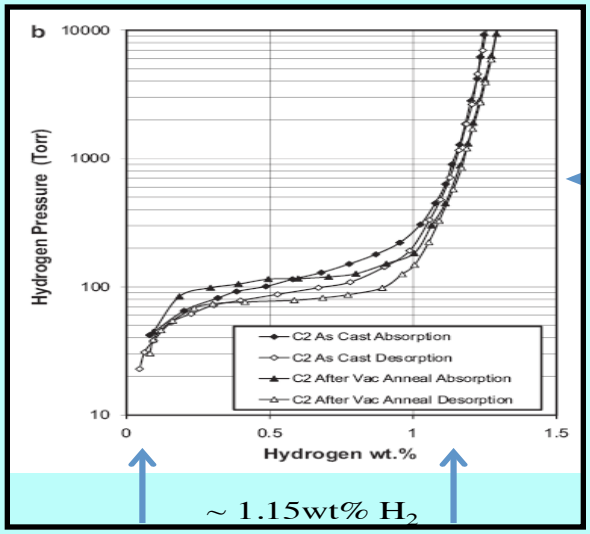
Peq is the absorption pressure and T is the desorption temp.

- State of art Ni-MH batteries use AB_5 alloys, which have low plateau pressures, facile desorption kinetics at ambient temperatures and good cyclic stability.
- AB_2 alloys are being actively pursued because of their higher hydrogen absorption capability, but their cyclic stability is still inadequate.

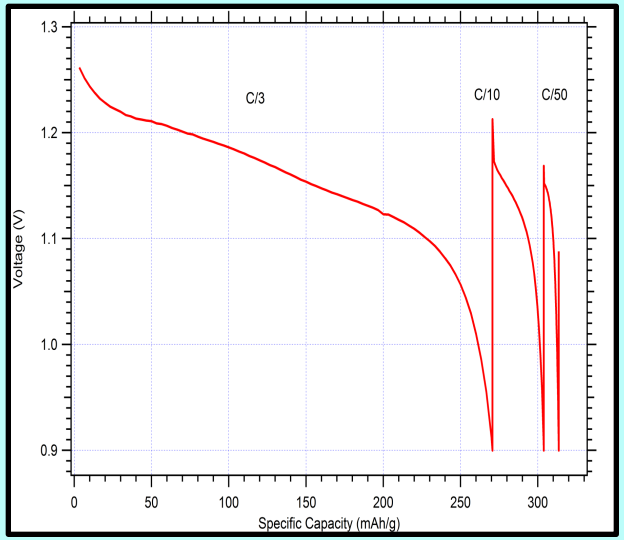
MH Alloy Anodes- AB_5 Alloys

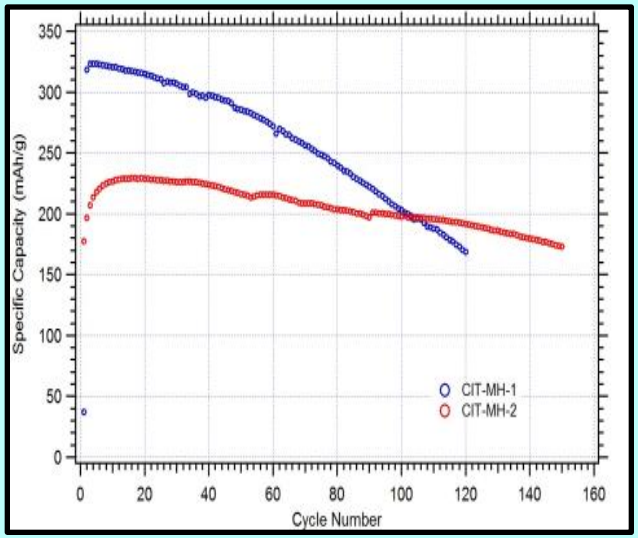
$La_{10.5}Ce_{4.3}Pr_{0.5}Nd_{1.4}Ni_{64.3}Co_{5.0}Al_{6.0}Mn_{4.6}Cu_{3.4}$ (from BASF)

Gas-Phase Isotherm



Electrochemical Testing



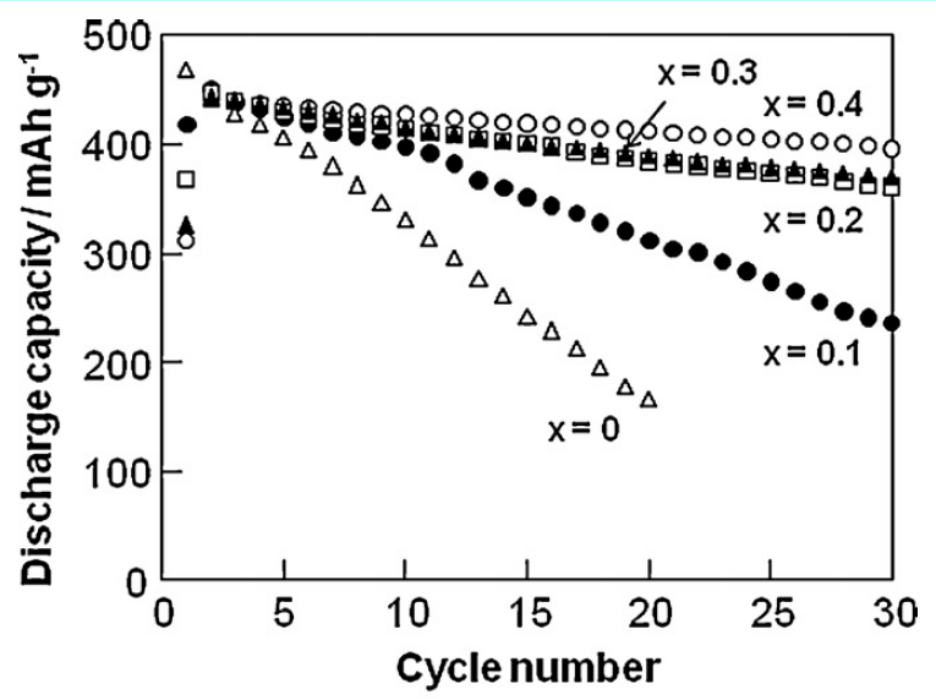


Young et al., J. Alloys Compounds (2011)

- Low absorption pressure with 1.1w% H_2 absorption.
- High initial capacity of 320 mAh/g against NiOOH cathode.
- Teflon-bonded electrodes with 20% Ni and 75% active material.
- AB_5 MH anode shows good cycle life, retaining 65% of capacity through 130 cycles (Charged to 330 mAh/g and discharged at high rate of 250 mA/g).
- Capacity retention and coulombic efficiency improve significantly if hydrided to $\leq$100% of the theoretical capacity

High Capacity MH Alloy (BCC) Anodes

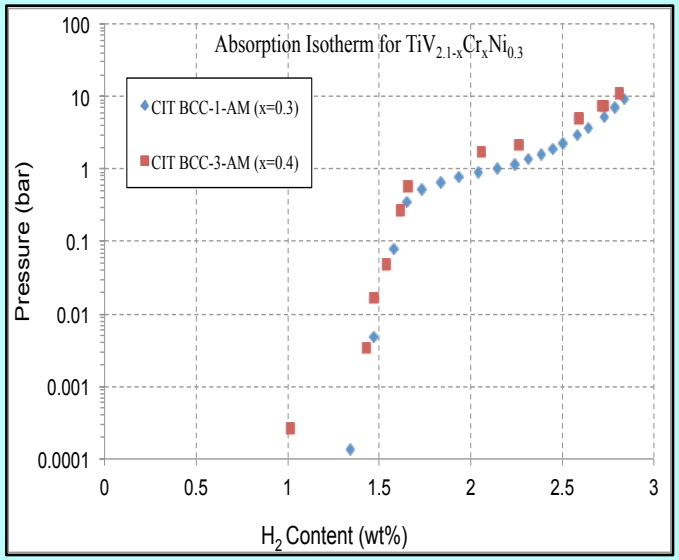
Ti-V-Ni-Cr BCC MH Alloys

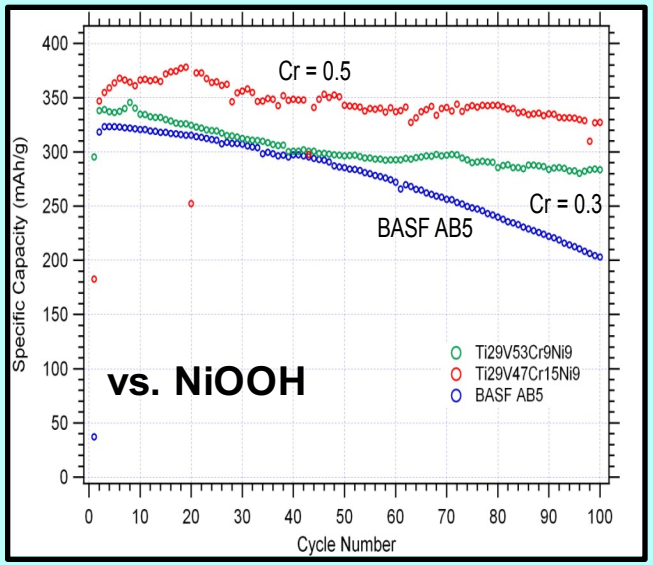


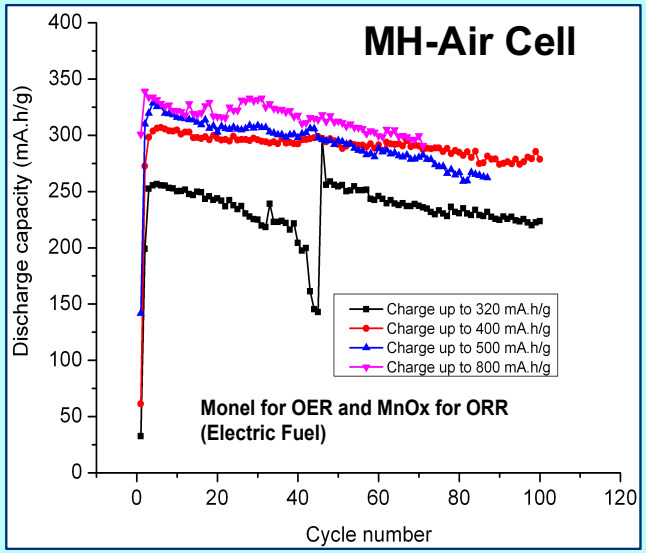
- Body-centered cubic (BCC) vanadium metal forms VH_2 at moderate pressures with 3.9 wt% of H_2
  - Alloyed with Ti Ni to increase or destabilize the lower plateau pressure
  - Lower cost from the absence of rare-earth metals
- Chromium addition improves the corrosion resistance (less severe than in AB_2 alloys) and hence the cycle life (cf: Inoue et al. *Electrochim. Acta* (2012))
  - Ti-V-Ni-Cr with a capacity of 450 mAh/g with 90% capacity retention over 30 cycles.

BCC MH Alloy Anodes

Ti-V-Ni-Cr BCC MH Alloys

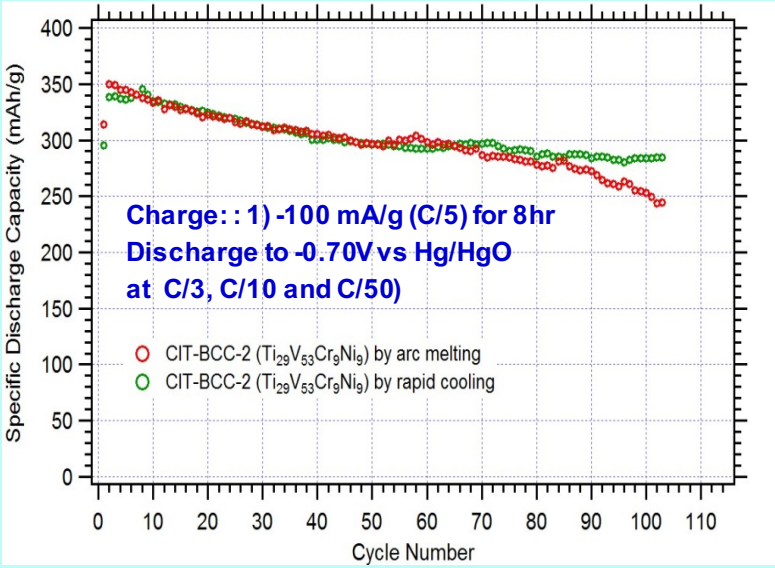


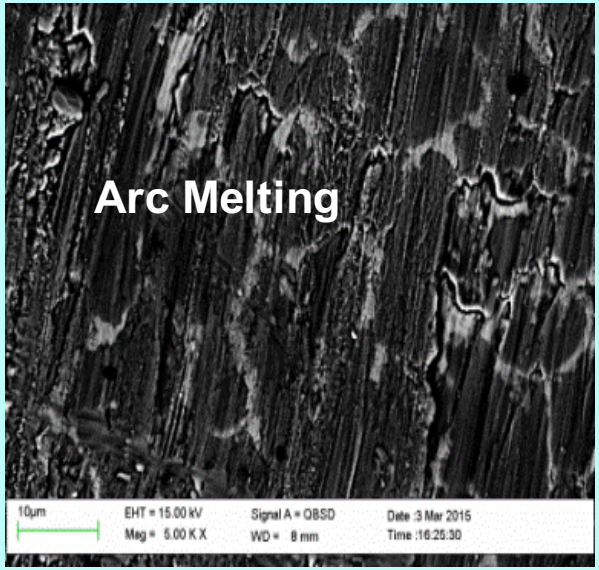


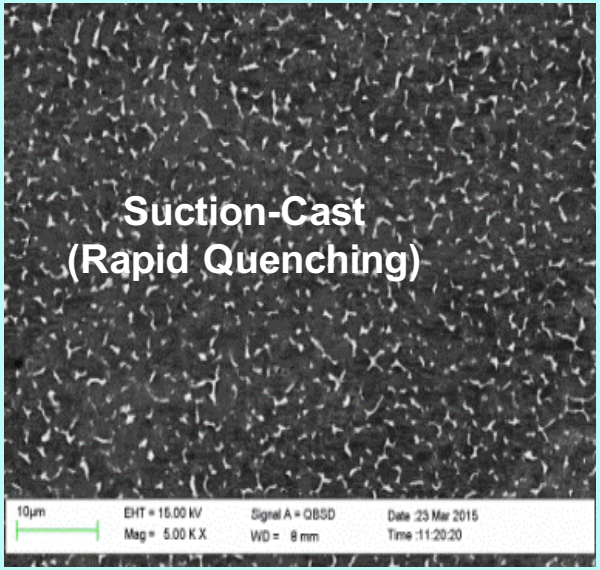


- **Reproduced (approximately) Osaka results for same compositions and processing**
- **Synthesized formulations with different chromium content using arc melting with and without rapid cooling (suction casting).**
  - **$TiV_{2.1-x}Ni_{0.3}Cr_x$ (x = 0.3, 0.4 and 0.5)**
  - **Characterized them through XRD for phase purity and microstructure.**
  - **Confirmed their high hydrogen absorption capacity of 1.5 w% from gas-phase isotherms. Plateau pressure increases linearly with increasing Cr content.**
  - **Higher capacity (>400 mAh/g) observed in half-cells.**
  - **Good cycle stability for Cr-containing alloys.**

Fast Quenching Refines Microstructure, Improves Kinetics



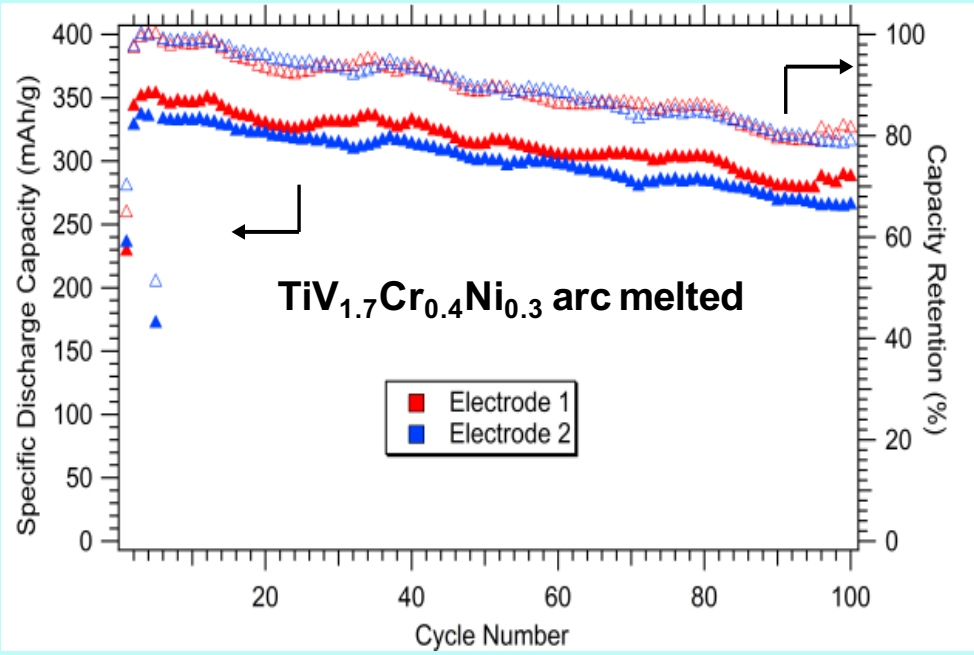


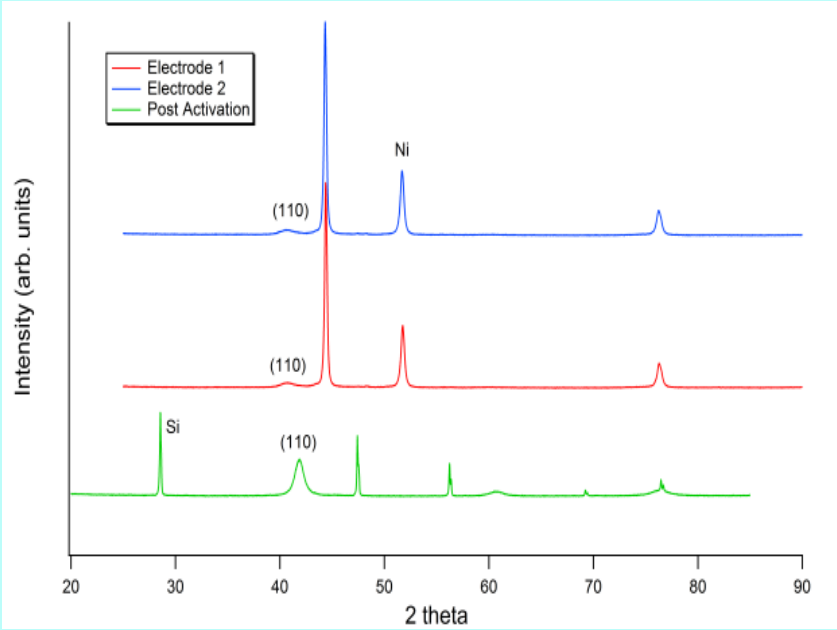


- V-Ti-Ni-Cr (BCC) metal hydride alloys show high capacities of >400 mAh/g and good cycleability both in Ni-MH and MH-air cells.
- Evaluated several formulations with different chromium content
  - $TiV_{2.1-x}Ni_{0.3}Cr_x$ (x = 0.2,0.3, 0.4 and 0.5)
- Modified the synthesis procedure (rapid quenching) to create 'Ti-Ni' sites for improved kinetics.

	High Rate Discharge (% capacity @ i_d = 250 mA g^{-1})	i_0 (mA g^{-1})	i_L (mA g^{-1})
Arc-melted	64	75	754
Suction cast	70	91	851

Capacity Fade is by Mechanical Loss





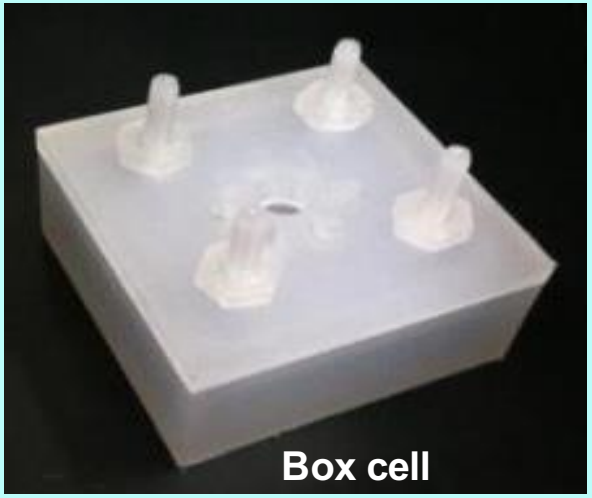
Electrode	%mass remaining	%max capacity @ cycle 100
1	83.7	79.4
2	78.1	78.3

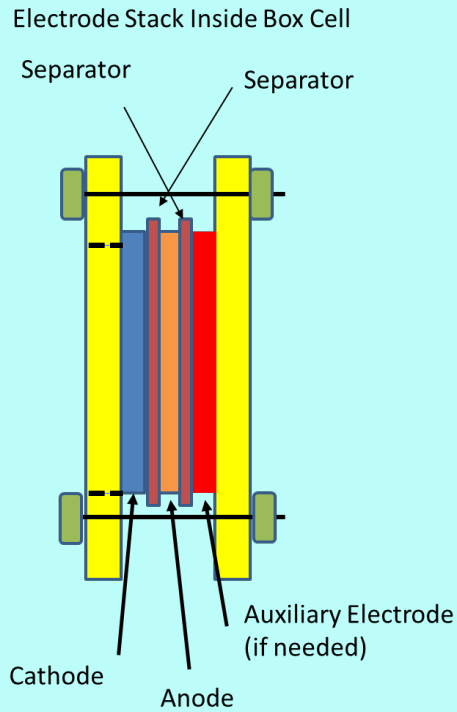
- Capacity loss matches the mass loss from mechanical deterioration. Powder found in separator.
- Primarily FCC peaks from Ni binder BCC 110 peak shift from pre-cycled material with residual hydrogen.
- Need more robust electrode fabrication and /or compaction in the cell.

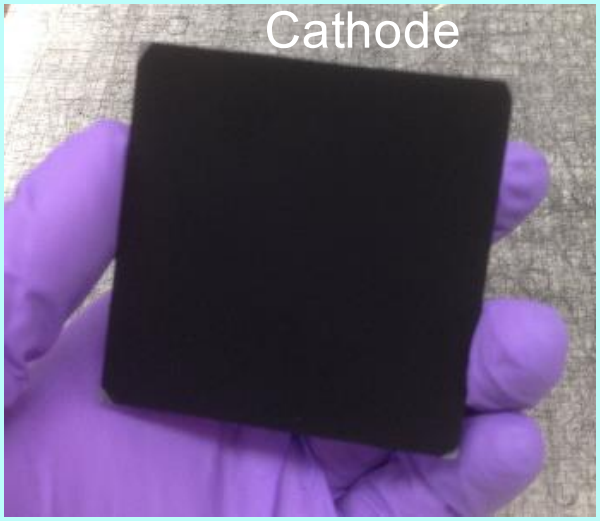
Catalysts for Air Cathode

- Noble Metal catalysts (for initial studies) (Pt, Ir based)
  - Conventional loading (4 mg/cm^2)
  - Thin-film noble metals (0.1 to 0.3 mg/cm^2)
- Non-Noble Metal Catalyst materials
  - LaBSCF perovskites
  - NiFeCo layered double hydroxides (LDH)
  - $CaMnO_3$ perovskites
    - Has good catalytic activity in 0.1 M KOH but poor activity in 6 M KOH
- Measurement of catalytic activity through RDE (rotating disc electrode) measurements
- Catalyst modifications through processing and compositional variations
- Assessment of catalysts in MH-air cells

Metal Hydride- Air Test Cells







FEATURES

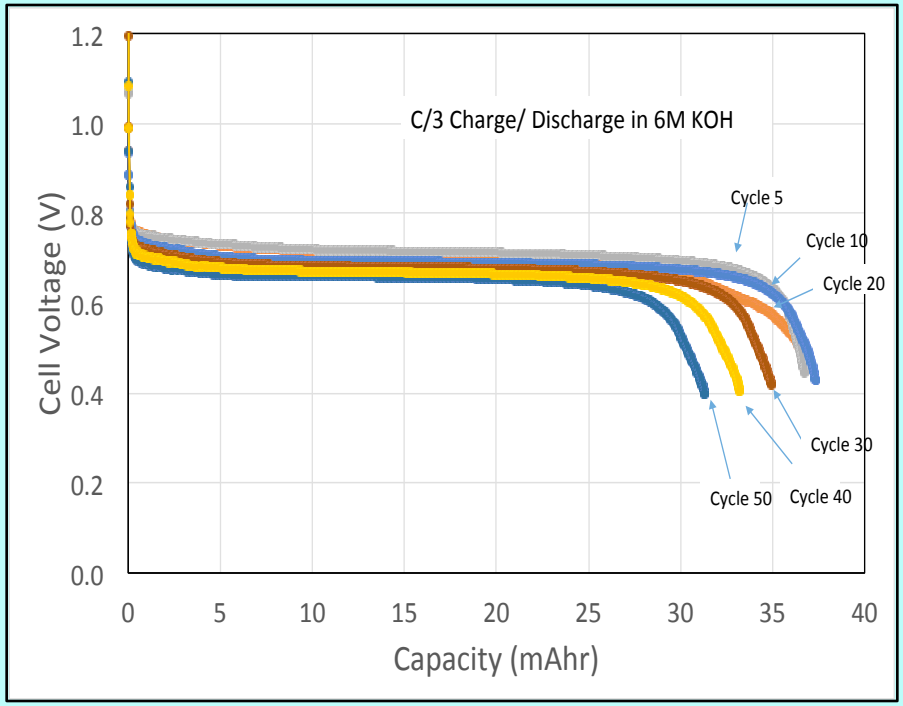
- More closely resembles a practical cell
- Applies adequate pressure on the electrodes
- Air electrode faces upward. avoids complicated seals
- Incorporates separators as in a practical cell-small inter-electrode gap
- Easy to assemble

- Toray 060 carbon paper as substrate
- Catalyst, conducting carbon, and PTFE binder are mixed to form an ink. The ink is sprayed on to a substrate at 80ºC
- Electrodes are pressed at 200psi and 120ºC to improve mechanical stability.

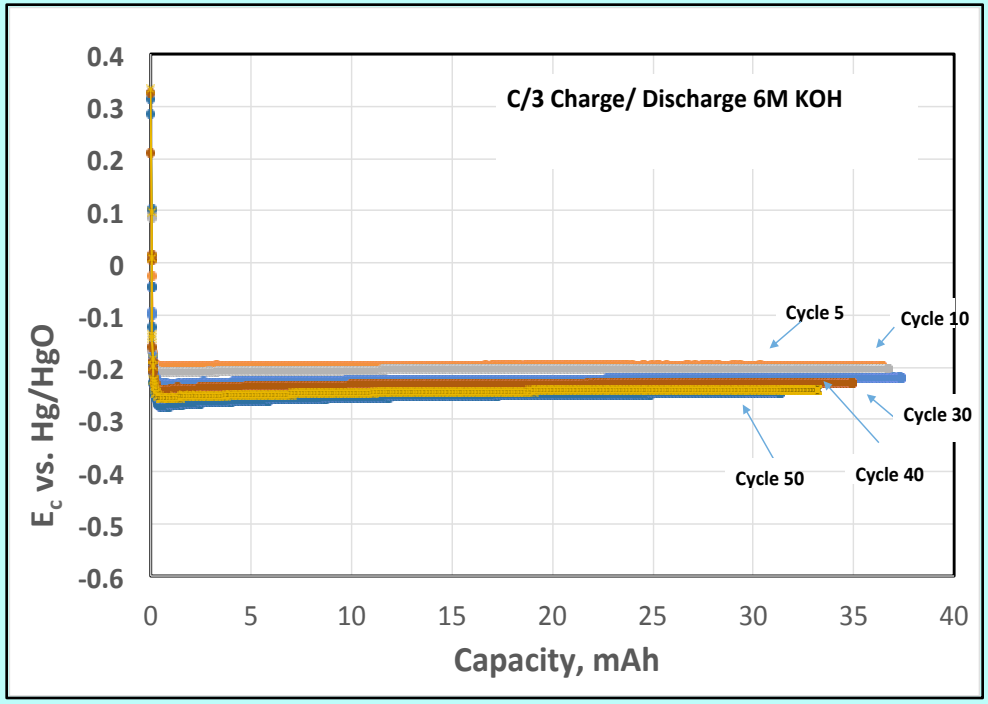
Cycling of MH-Air Cell with Bifunctional Air Cathode

(Noble metal Catalyst)

Discharge curves during Cycling



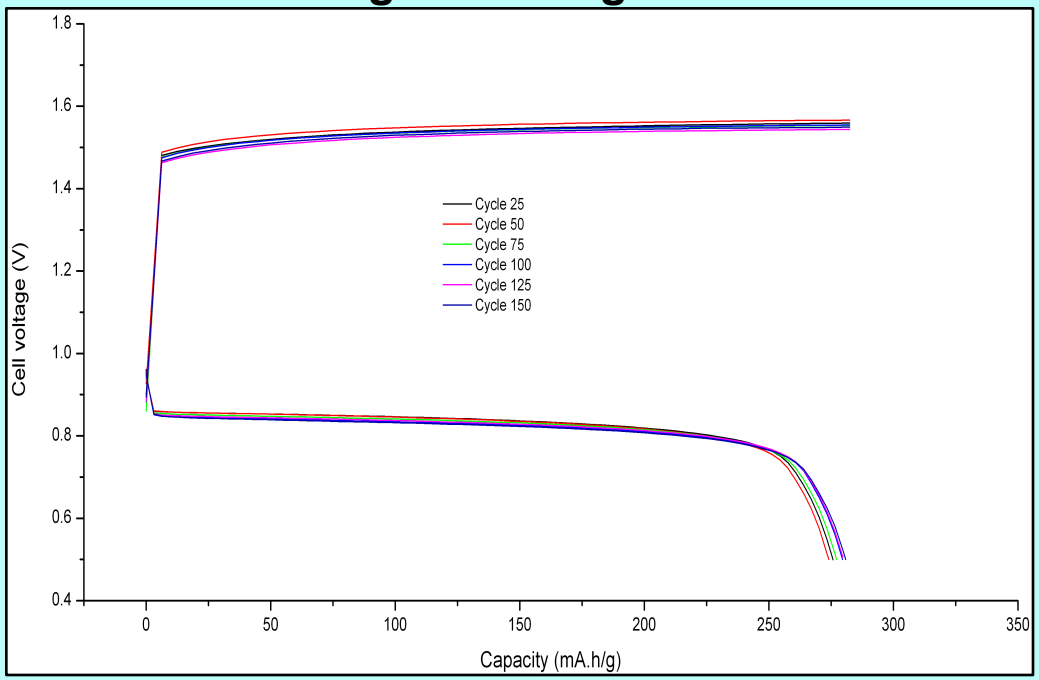
Cathode Potential during Cycling



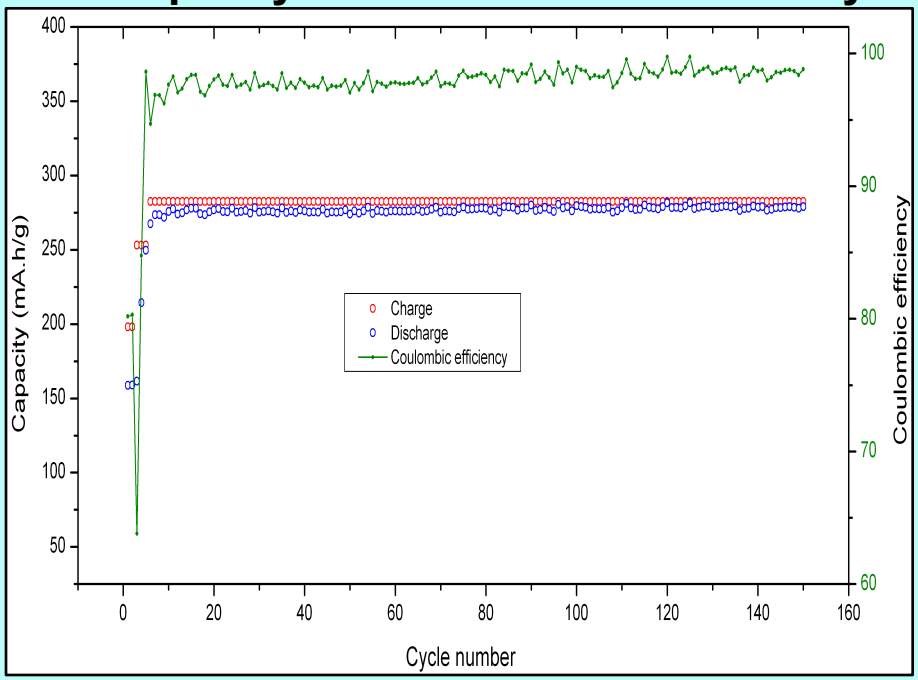
- Good cycle life (> 100 cycles) in a MH-air cell with a bifunctional air cathode.
  - Pt deposited (4 mg/cm^2) on a high surface carbon paper via a proprietary deposition process developed at JPL.
  - Charged to 115% capacity at C/3 and discharged at C/3 to -0.65 V vs. Hg/HgO.
  - Cell degradation attributed to MH anode failure (mechanical) (Active material shedding form MH anode fabricated without PTFE binder.

Cycling of MH-Air Cell with Dual Air Cathodes

Charge Discharge curves

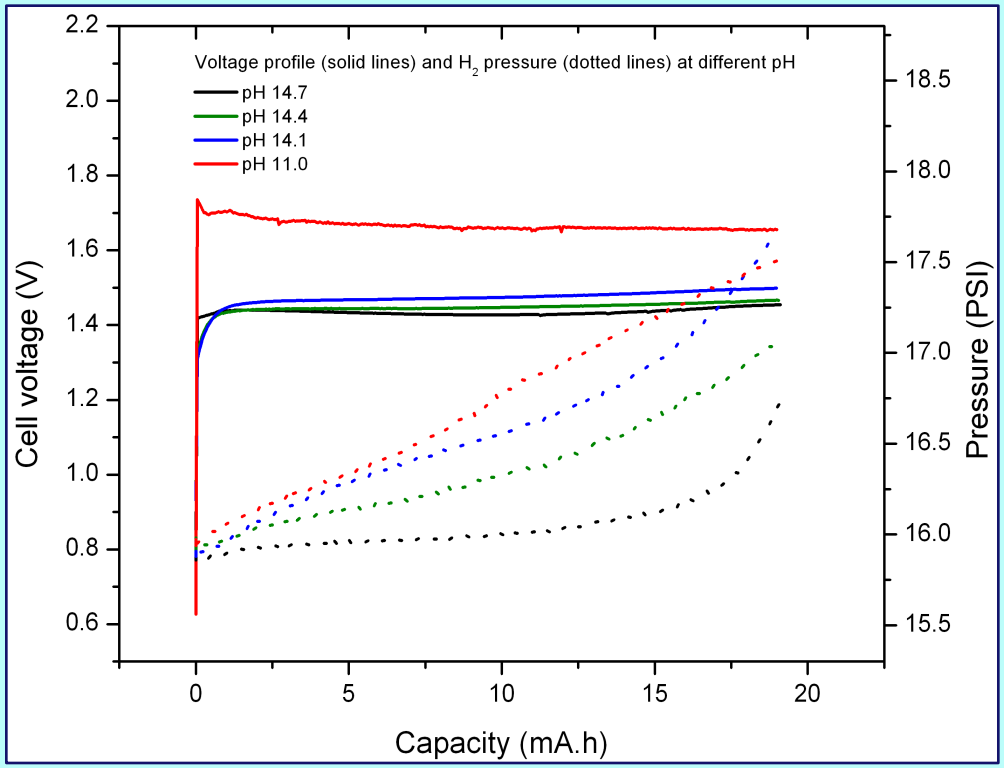


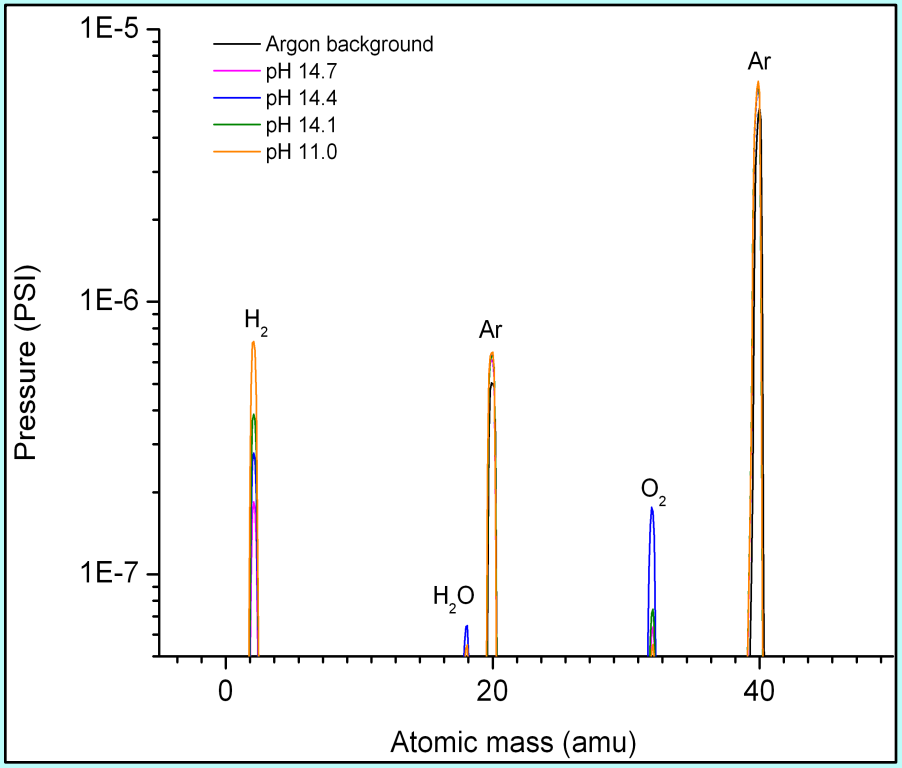
Capacity and Coulombic Efficiency



- OER electrode: Monel alloy(200 mesh) and ORR electrode: MnO_2 catalyst (Electric Fuel)
- Charged at C/1.5 (22.36 mA/cm^2) to 90% of the MH electrode capacity and discharging at C/3 (11.18 mA/cm^2) to 0.5 V.
- Remarkably stable voltage plateaus observed throughout all 150 cycles.
- High Coulombic efficiency of 97% for 150 cycles; Discharges at ~0.83 V and charges at ~1.5 V (voltage efficiency ~55% using non-precious metal catalysts for ORR and OER

Effect of Electrolyte pH: Gas Analysis of Ni/MH Cells



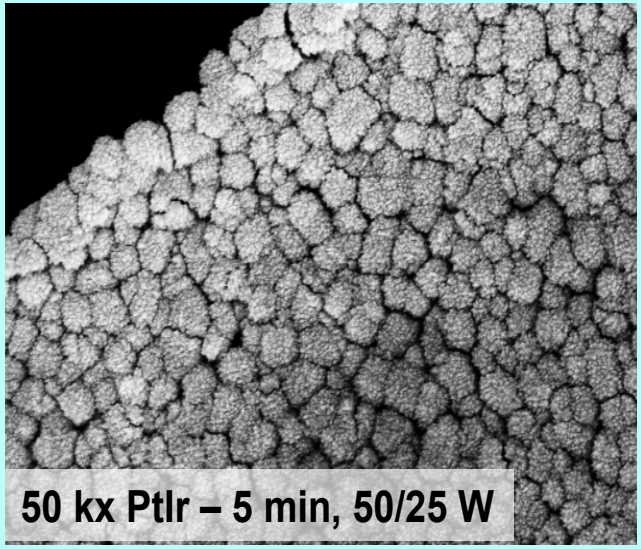


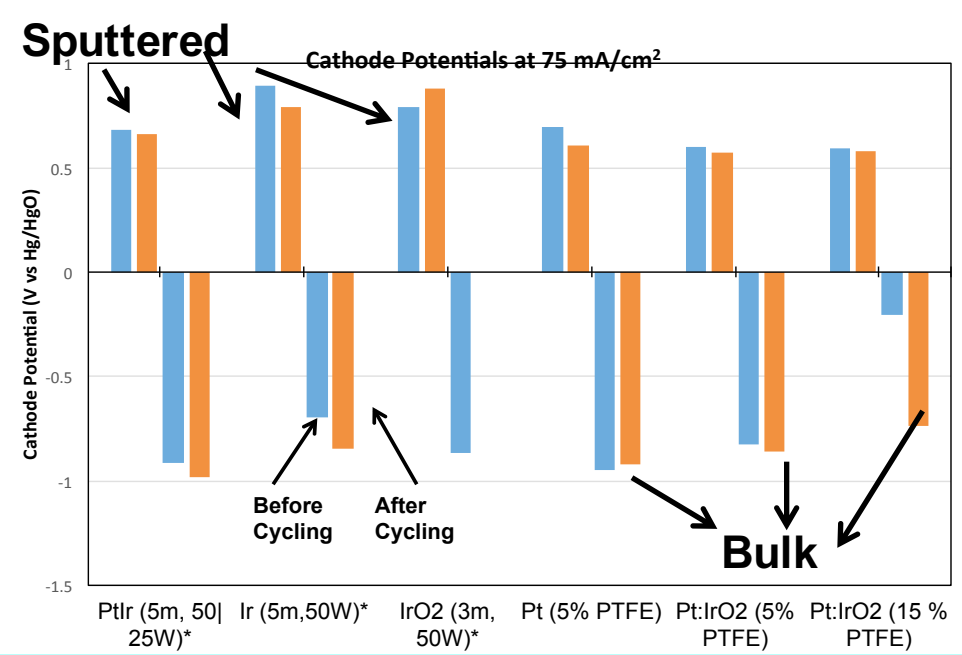
- Electrolytes of pH 14.7, 14.4, 14.1 and 11.0.
- Faster voltage and pressure increase during charging in low pH solutions.
- Subsequent discharges similarly indicate that discharge capacity is lower at lower pH.

- Mass spectrometry following charges indicates the partial pressure of H_2 is inversely related to electrolyte pH.

Thin-film Noble Metal Catalysts for Air Cathode

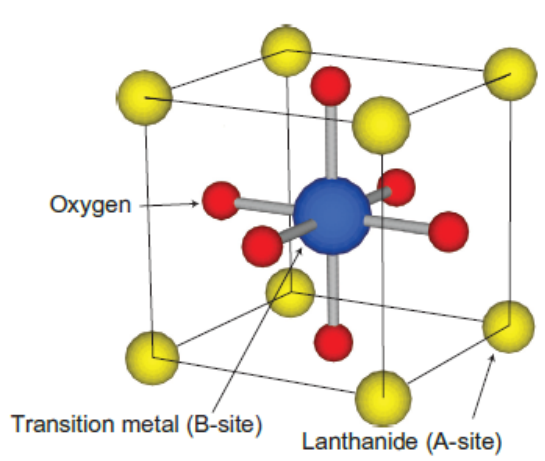
- Sputter-deposited thin-films (<0.3 mg/cm^2) of catalysts on carbon support and evaluated their catalytic activity
  - Sputtered particles cover entire surface of carbon paper.
  - Catalytic activity is comparable to the bulk materials in many cases
- Durability of the catalysts is tested in "Box" MH-Air cells (I-V curves before and after ten cycles)

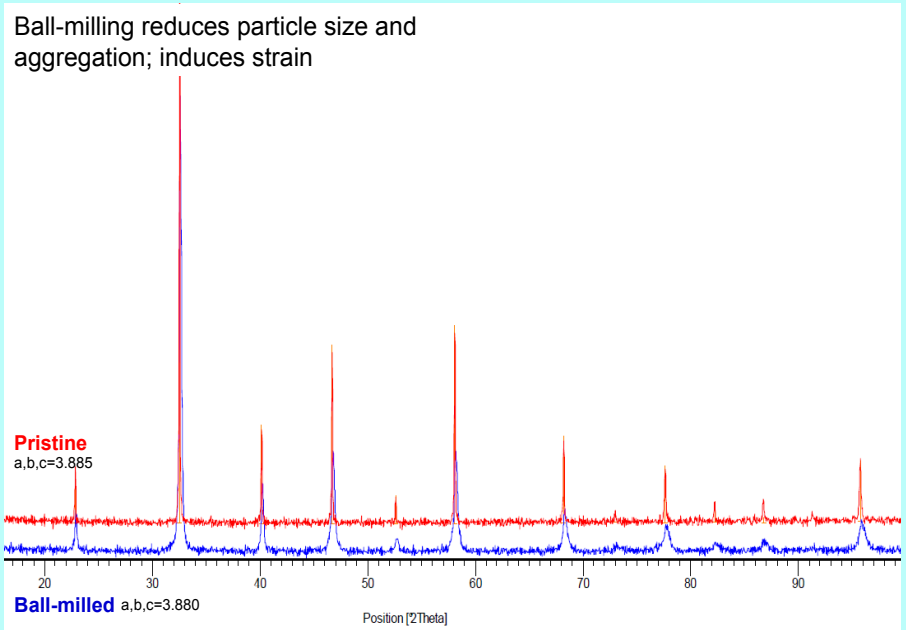


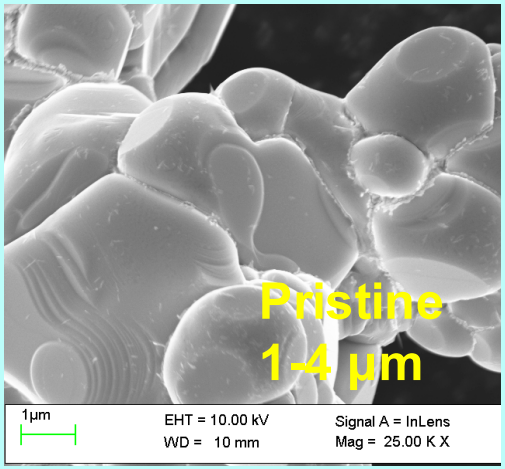


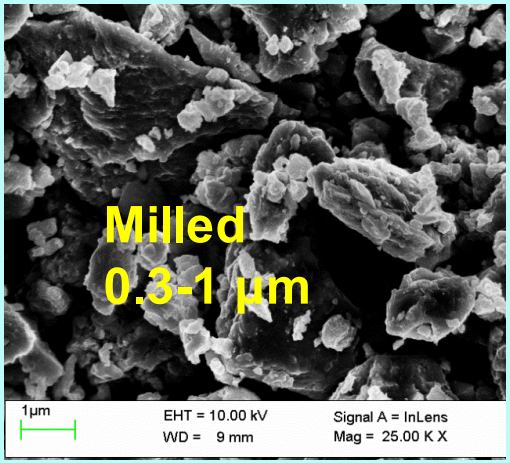
La-BSCF perovskites

- General formula: ABO_3, where B is electrochemically active transition metal and O_{3-d} denotes oxygen vacancies
- $La_{0.3}(Ba_{0.5}Sr_{0.5})_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is reportedly a bifunctional catalyst for OER/ORR reactions in 0.1 - 6 M KOH solutions (Jung, JI, *et al.*, *Angew. Chem.* 2014, *53*, 4582-6)





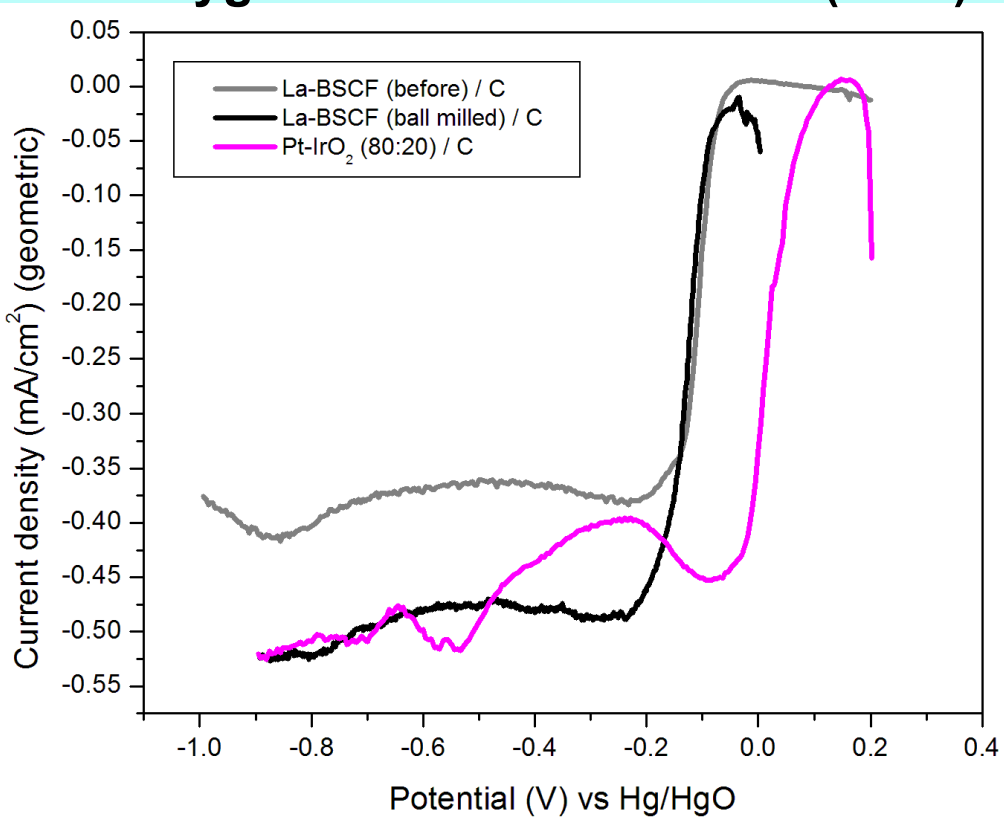




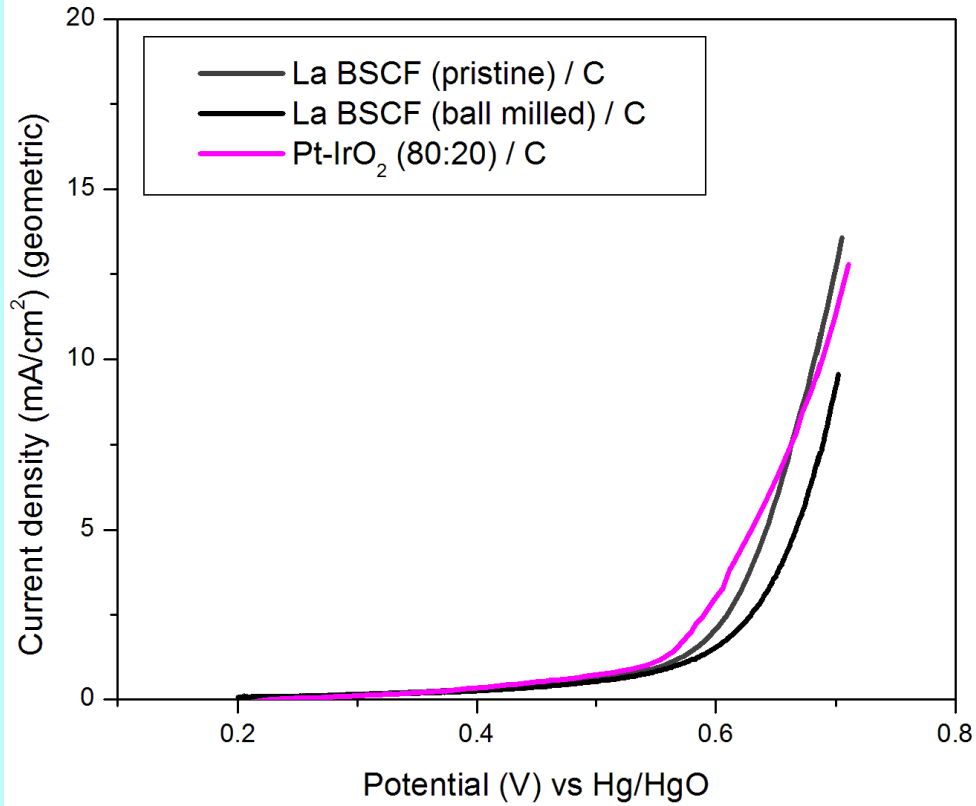
- Ball milling creates energetic sites and thus improve the catalytic activity; The particle size is noticeably reduced.

Catalytic Activity of La-BSCF for ORR and OER

Oxygen Reduction Reaction (ORR)



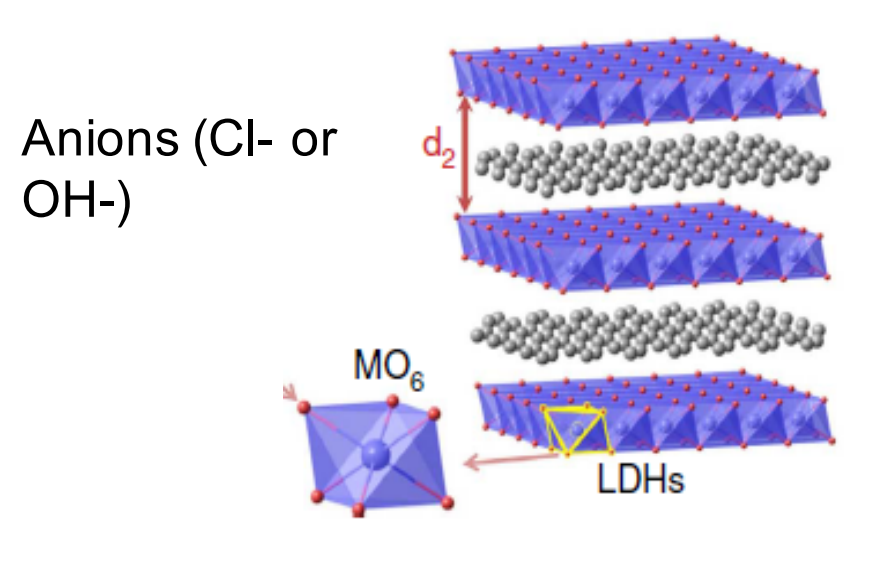
Oxygen Evolution Reaction (OER)



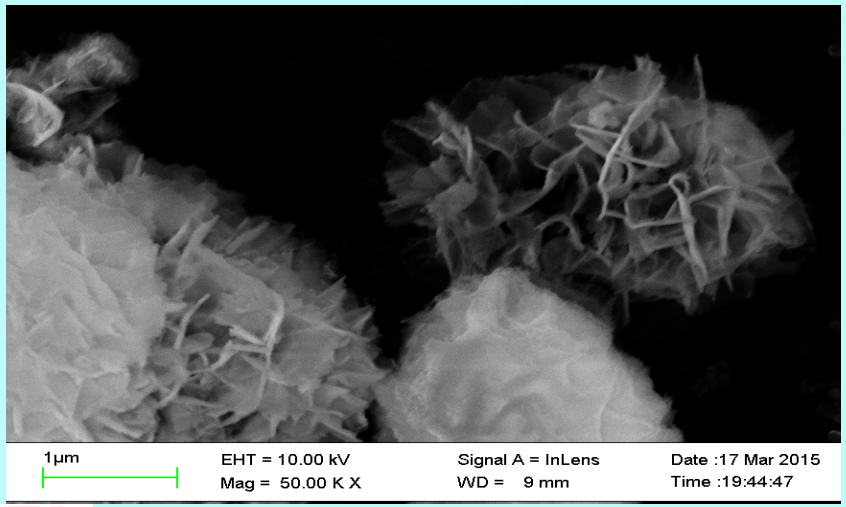
- La-BSCF is bifunctionally active in 6 M KOH
- Upon ball-milling, there is a slight increase in current density for ORR and slight decrease for OER.
- *j* (Rate Constant) is comparable to Pt/IrO_2 benchmark, with an additional 200 mV polarization for ORR.

NiFe Layered Double Hydroxides

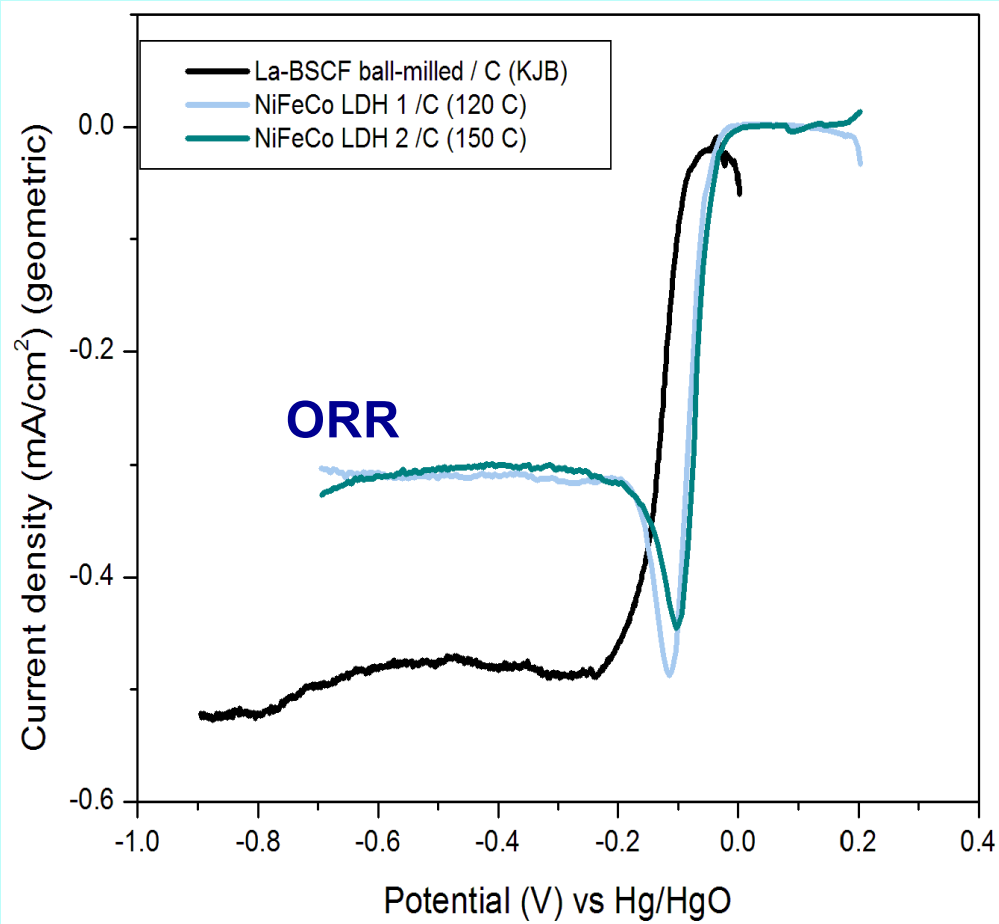
- Reported for OER only in 0.1 M KOH – with comparable kinetics as IrO_2
- Composition: NiFeCo (8:1:2)
- Hydrothermal synthesis: $Fe^{3+}(NO_3)_3$, $Ni^{2+}Cl_2$, $Co^{2+}Cl_2$ in H_2O, @ 120° C or 150° C.
  - Synthesized clusters of nanosheets

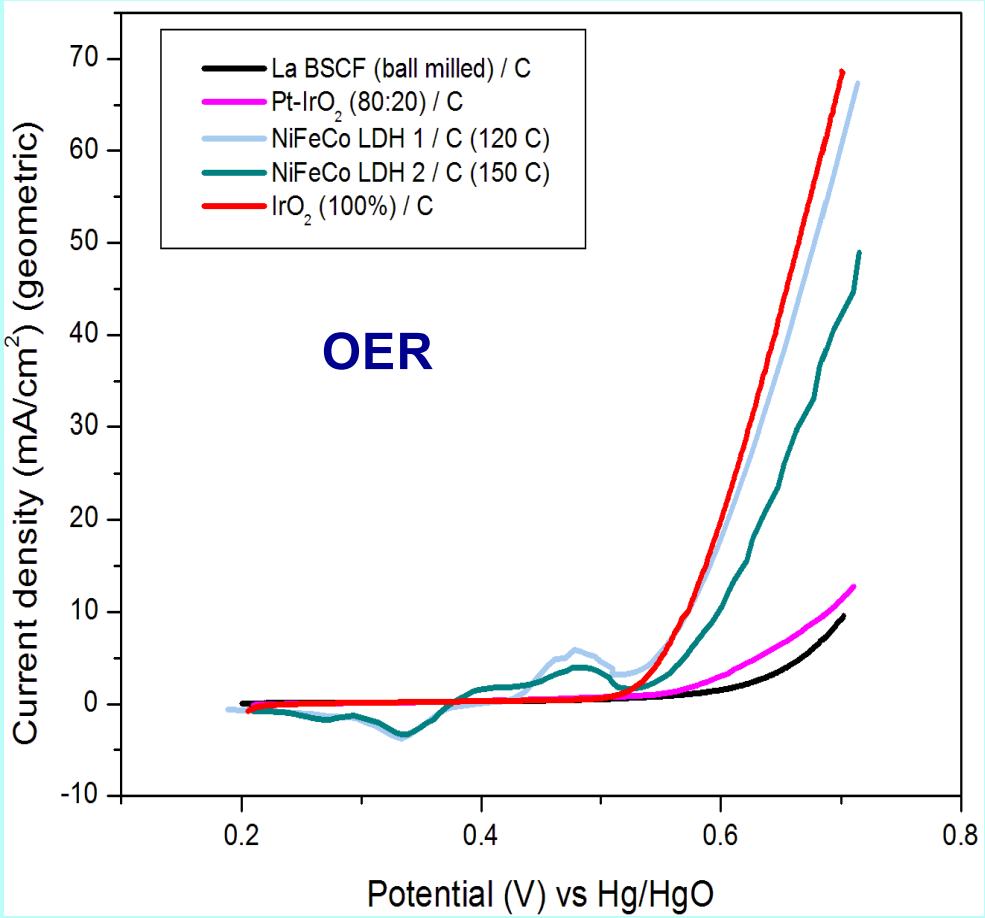


1. Long, X *et al.*, *Chem. Comm.* 2014, *51*, 1120–3
2. 2. Gong, M. *et al.*, *JACS* 2013, *135*, 8452–5
3. 3. Song, F.; Hu, X. *Nat. Comm.* 2014, *5*, 1–9



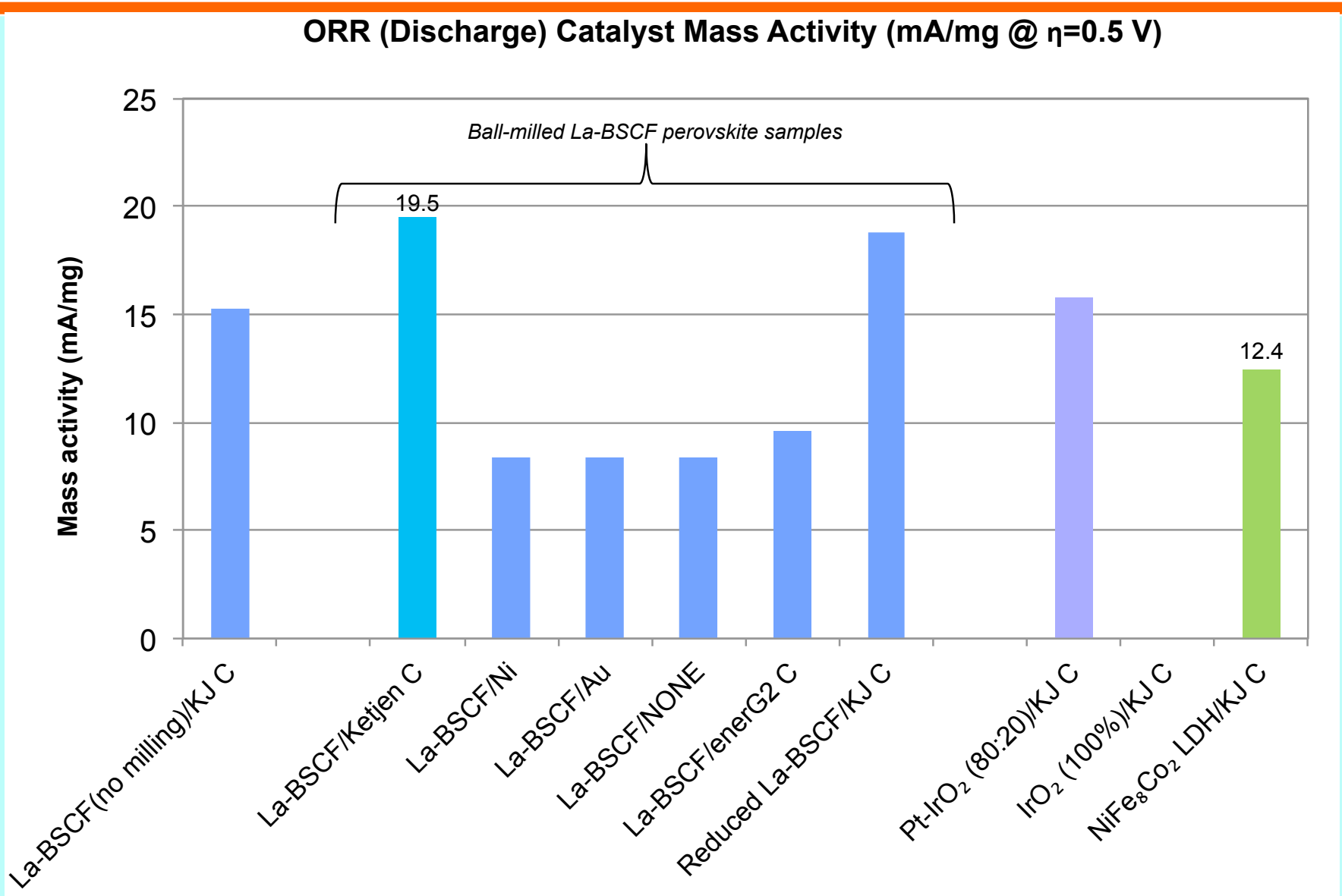
NiFe LDHs are active for OER in 6 M KOH





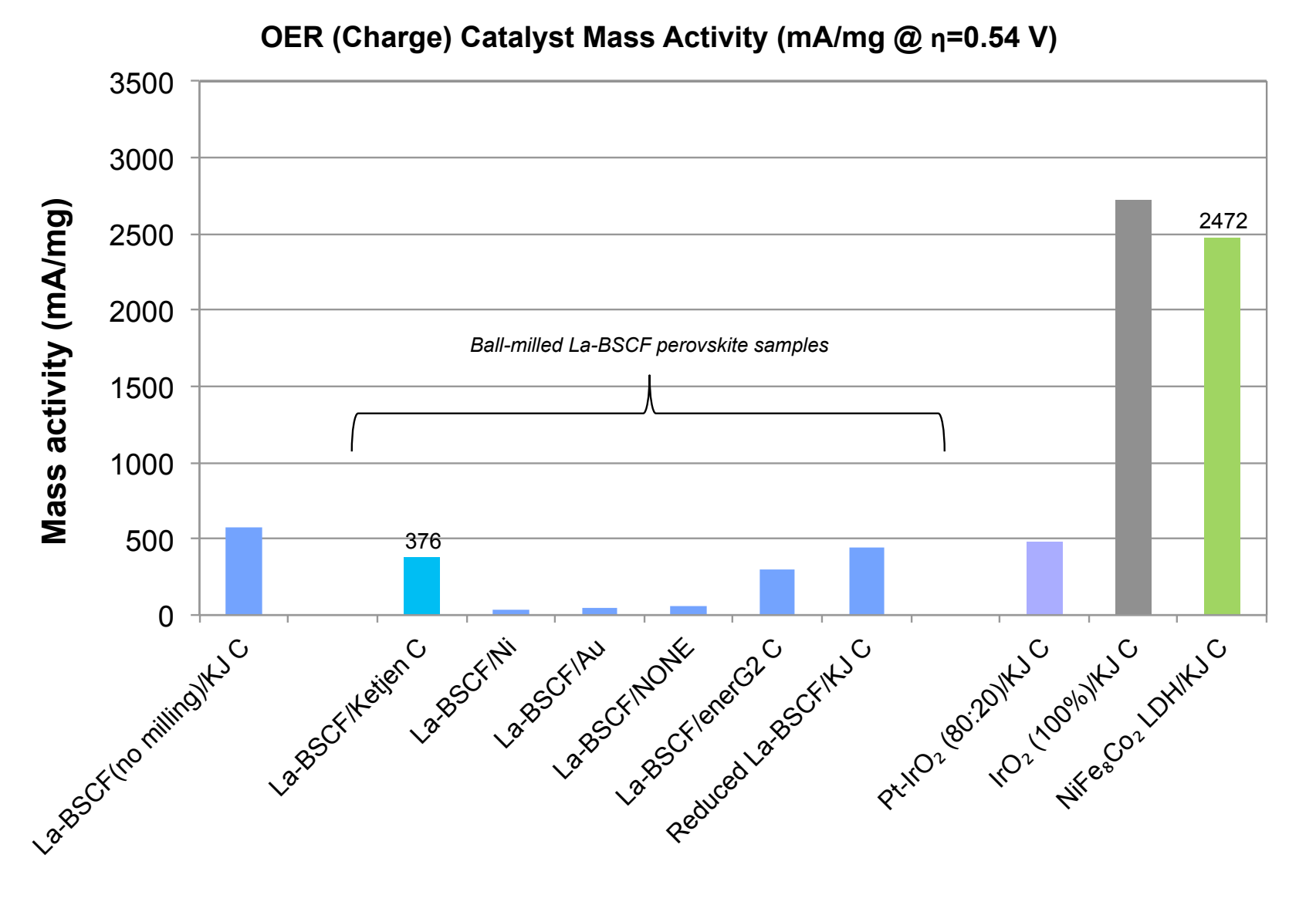
- Kinetics are more facile in 0.1M KOH for ORR compared to 6M KOH; NiFeCo layered double hydroxide is active, though not as much as La-BSCF.
- The OER kinetics are facile, better than La-BSCF and comparable to IrO_2

Comparison of catalytic activity - ORR



- For oxygen reduction La-BSCF > Pt-IrO2 > NiFeLDH

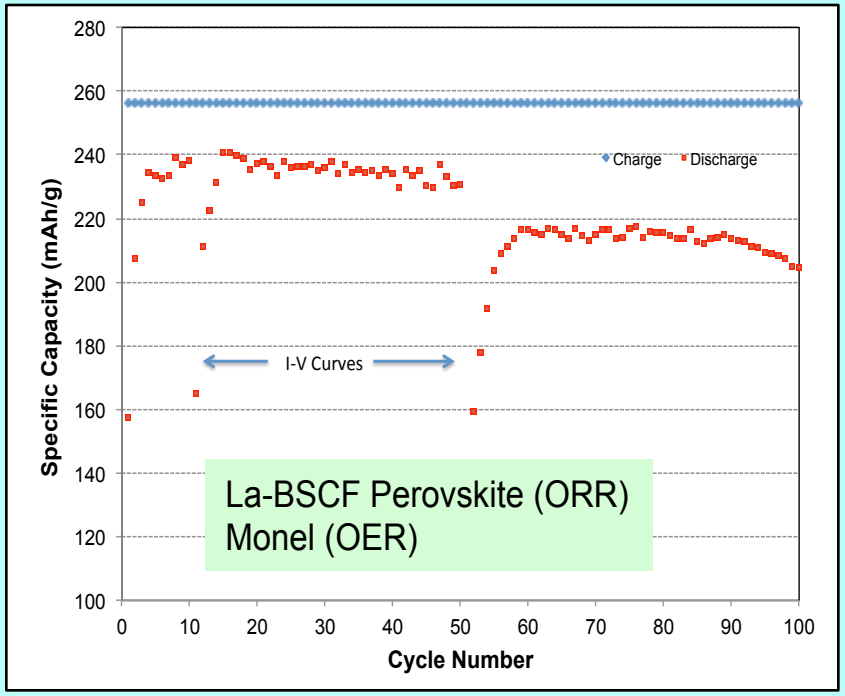
Comparison of catalytic activity - OER

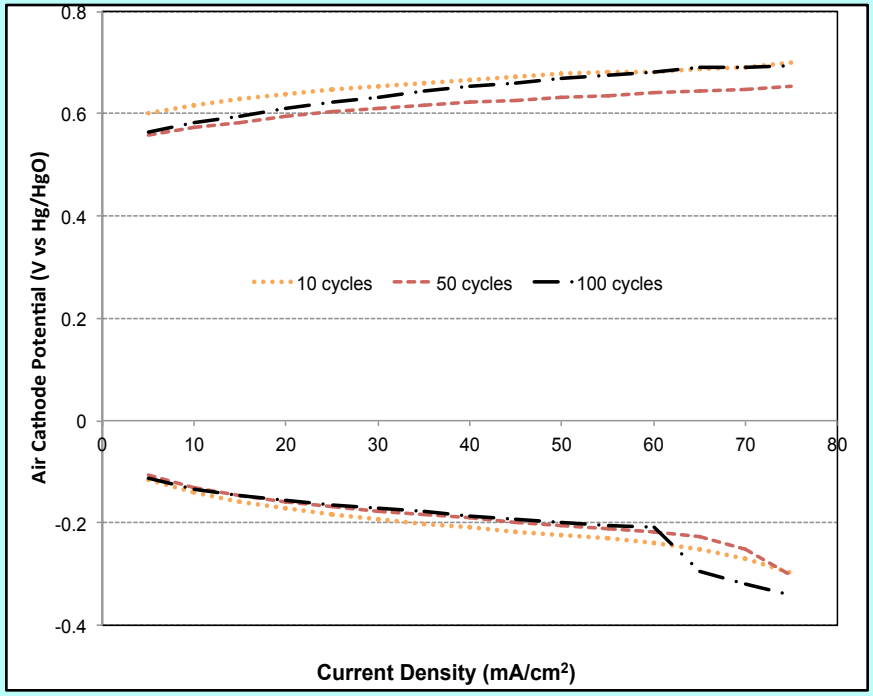


- For oxygen evolution IrO2 > NiFe-LDH >> La-BSCF

Dual Air Cathode: Perovskite (ORR) and Monel (OER)

Monel (OER), Perovskite-Ketjen Black (ORR) Cycling at C/3

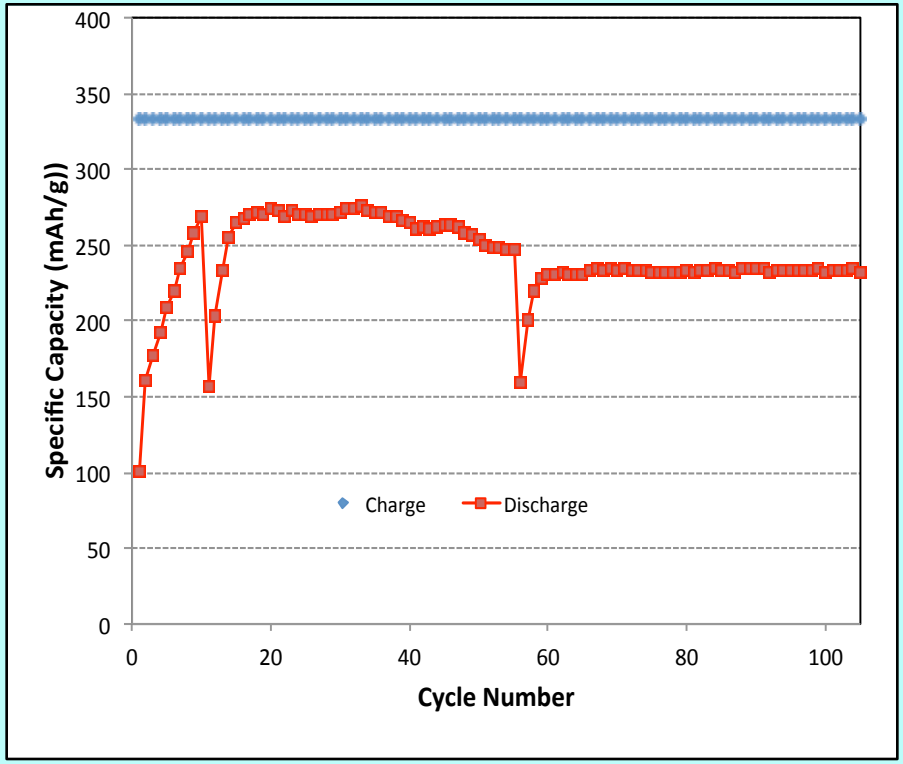


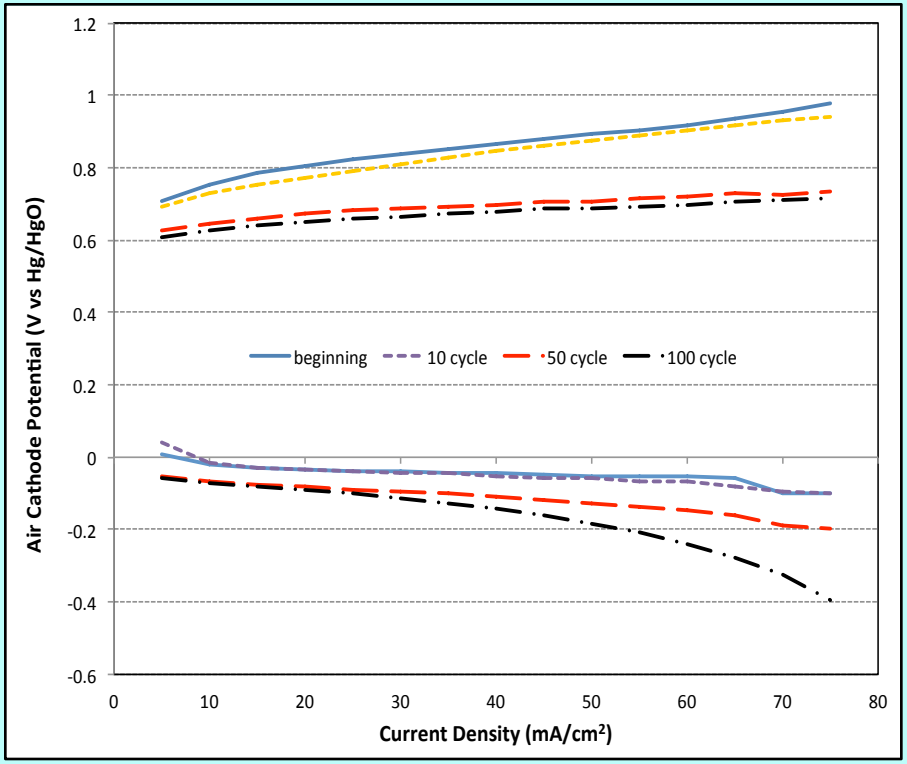


- MH-air Cell (box) with dual air cathodes with perovskite cathode for ORR and Monel for OER.
- The catalysts (La-BSCF for ORR and Monel for OER) showed good stability through 100 cycles.

Dual Air Cathode:MnO_2(ORR) and Monel (OER)

Monel (OER), MnO_2 (ORR) Cycling at C/3

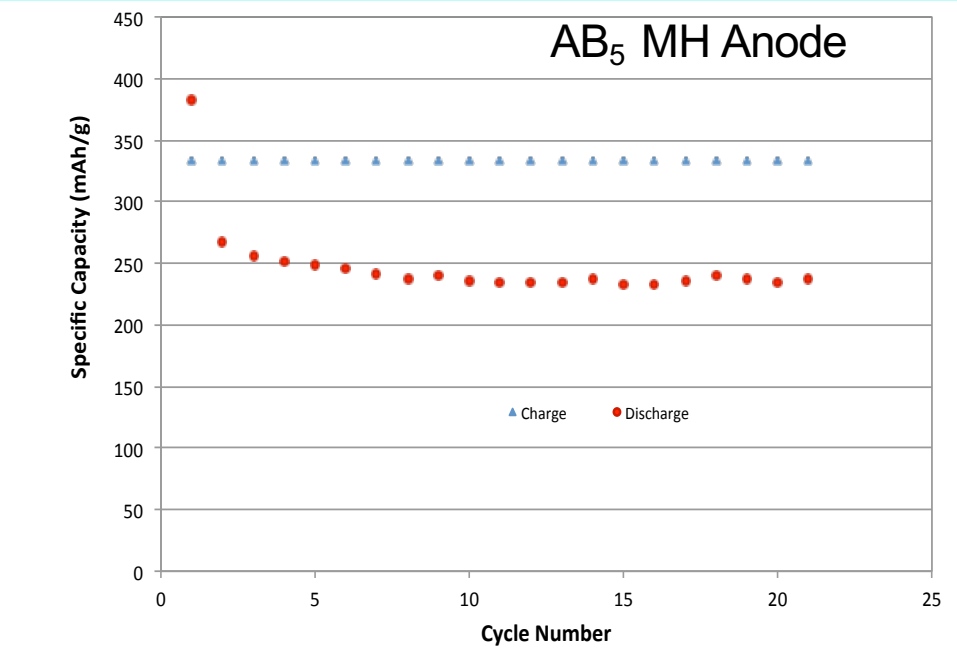


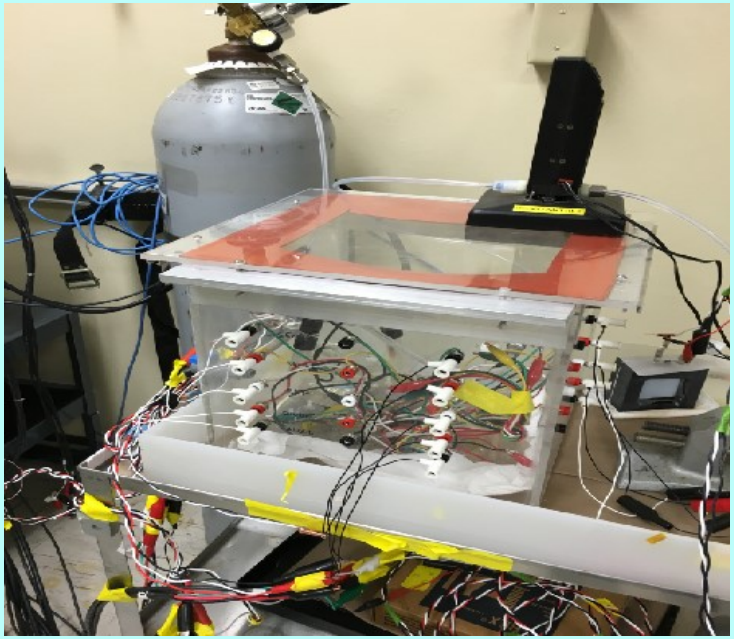


- MH-air Cell (box) with dual air cathodes with perovskite cathode for ORR and Monel for OER.
- The catalysts (La-BSCF for ORR and Monel for OER) showed good stability through 100 cycles.

Cycling in a humidified – CO_2-free Box

Monel (OER), Perovskite-Ketjen Black (ORR) Cycling at C/3





- **No water addition during cycling**

MH-Air EV Battery System Design

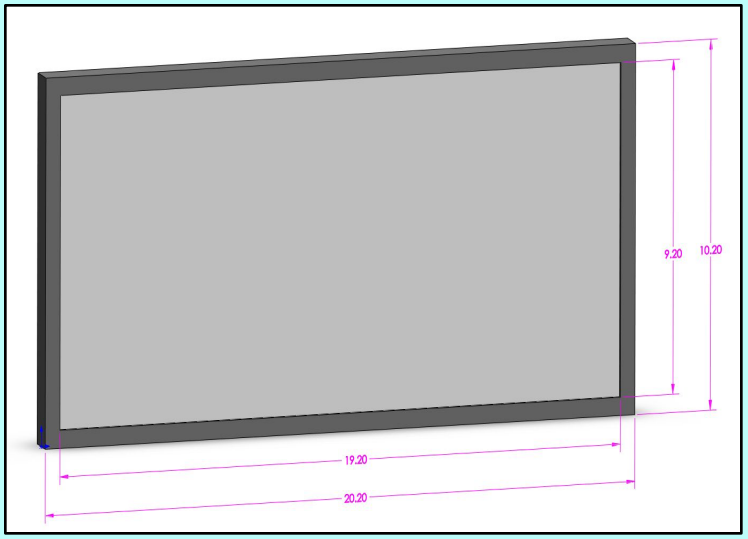
- Targeted Battery Energy: 85 kWh (same size as a Tesla battery)
  - Project Specific Energy:150 Wh/kg (goal) (C/3 at 25°C Beginning of Life)
  - Energy density : 225 Wh/l (project goal)
  - Voltage ~350 V
- MH-Air Battery Design
  - Battery voltage ~ 330 V;
  - Total number of cell 864; nine battery modules in series
  - Each module has 96 cells with two parallel strings of 48 cells in series (2p48s);
  - Cell characteristics
    - Capacity of 133 Ah;
    - Size: 20 cm x 10 cm;
    - Voltage: 0.75 V at 75 mA/cm^2 (cathode);
    - Anode specific capacity: 400 mAh/g
  - Cell Stack (from 864 cells); Stack mass: 427 kg; Stack Volume 180.6 liters

133 Ah MH-Air Cell 9 (Circulating Electrolyte)

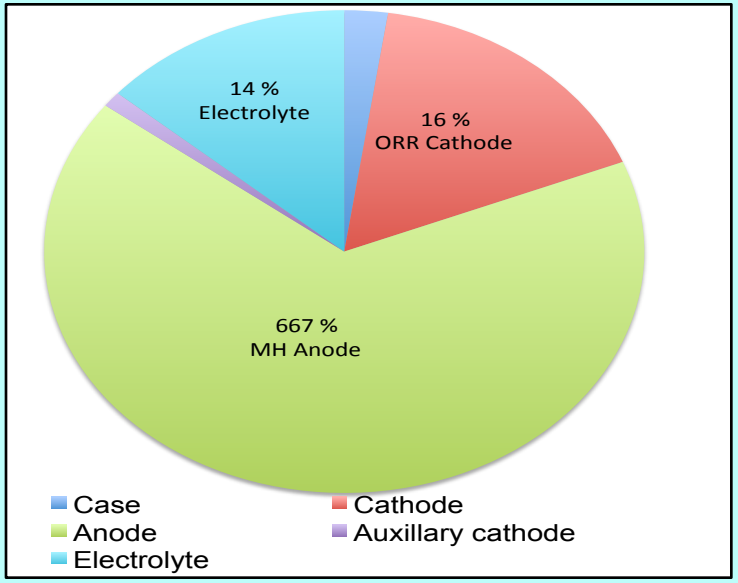
Physical Characteristics	
Whole cell width, cm	20.2
Whole cell length, cm	10.2
Whole cell thickness w/o frame, cm	0.8
Whole cell thickness including frame, cm	1.0
Frame area on air electrode, 1 side, cm2	29
Active area, 2 sides, cm2	342
Frame Volume, cc	10.8
Whole cell volume, cc	209
Frame weight, g	9.7
Cathode weight, g	80
Anode weight, g	333
Auxillary electrode weight, g	2.5
KOH:Anode volume ratio	1
Cell total weight w/ KOH at full charge, g	494

Electrochemistry	
Cathode normial current, mA/cm^2	75
Cathode normial potential vs. Hg/HgO, V	-0.10
Anode capacity, mAh/g	400
Anode normial potential vs. Hg/HgO, V	-0.85
Cell normial potential, V	0.75
Corresponding anode C-rate	0.2
Corresponding cell current, A	25.7
Cell Power, W	19.2
Cell capacity, Ah	133
Cell normial energy, Wh	100
Specific energy, Wh/kg	**202**
Volumetric energy, Wh/l	**478**

133-Ah MH-Air cell Cell



Cell Components Weight Distribution



- Critical parameters: i) Anode specific capacity, ii) Anode thickness, iii) Cathode thickness and iv) Cathode current density

MH-Battery Systems with Different Cooling Schemes at C/5

System Design Option ----->	KOH Cooled Option	Water Cooled Option	Air Cooled Option
Cell Size and Numbers			
Cell Size (m)	0.1 x 0.2 x 0.01	0.2 x 0.2 x 0.01	0.2 x 0.2 x 0.01
Number of Cells Across Width	1.00	1.00	1.00
Number of Cells Across Length	8.00	8.00	8.00
Number of Cells Across Height	12.00	12.00	12.00
Module Housing Internal Dimensions (m)			
Width (m)	0.11	0.21	0.21
Length (m)	1.91	1.64	1.85
Height (m)	0.21	0.14	0.39
Module Housing Mass	**80.80**	**68.68**	**132.83**
Air Flow System Mass	**42.11**	**44.61**	**44.70**
Cooling System Mass	**81.40**	**123.50**	**17.40**
Total Support Mass	**204.30**	**236.80**	**194.93**
Power Requirements (W)			
Air Flow Turbine (W)	1327	7777	7777
Coolant Pumps and Fans (W)	270	154	882
Power to Mass Factor (W / kg)	**39**	**39**	**39**
Total Effective Mass	**246**	**444**	**422**
Stack Mass (Electrochemistry)	**427**	**457**	**457**
Specific Energy, Wh/kg	**128.4**	**95.9**	**98.3**

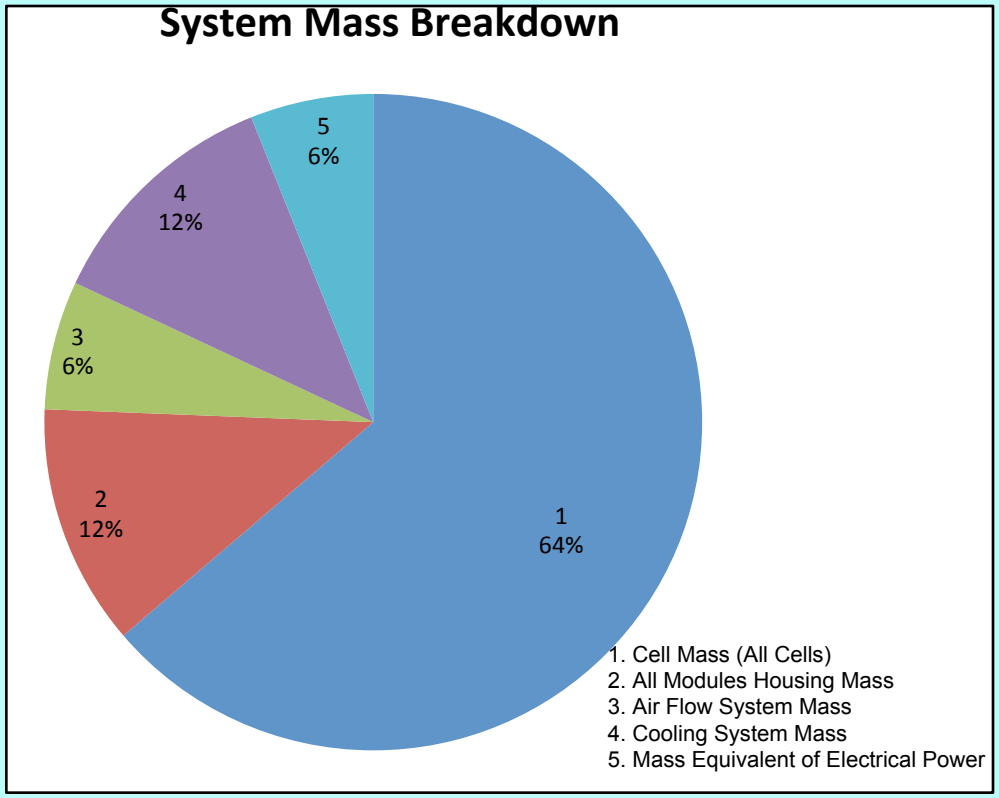
- Adequate margins in the components for Balance of Plant

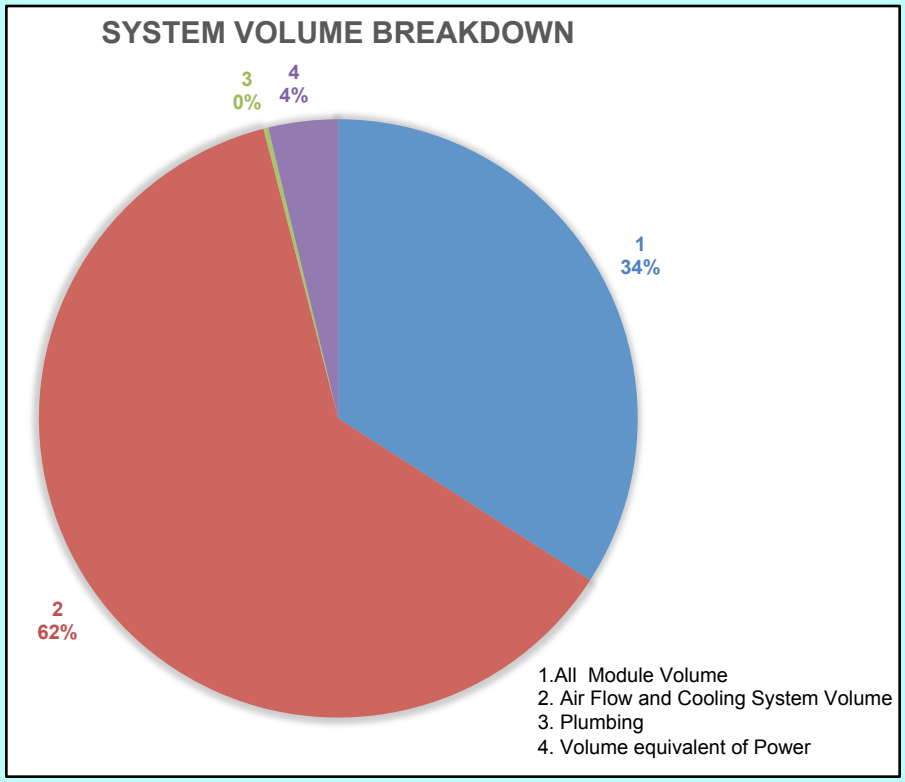
Energy Densities of 85 kWh MH-Air Battery

Battery and Balance of Plant	Circulating Electrolyte	Air-cooled
Module volume, lit	41.4	82.8
Volume of 9 modules, lit	372.4	744.8
Pumps and radiator, lit	75.0	75.0
Air flow plumbing, lit	0.3	0.3
Electrolyte container, lit	1.0	0.0
Total volume, lit	448	820
Energy Density, Wh/l	**193**	**105**

- **Air-cooled design has poor energy density because of the large gap for air channels**

MH-Air System (Circulating electrolyte) Mass and Volume





- About 64% of battery system mass is from the cells and 34% of battery volume is from the stack of cells

Summary

- Metal hydride air cells have the potential to provide high specific energy at the cell level and a good portion of this energy is also realized at the battery level.
- State of art rare-earth element based AB_5 alloys show high capacities of ~320 mAh/g combined with good cycle life in MH-air cells
- Higher specific capacity (~400 mAh/g) BCC alloys (V-Ti-Ni-Cr) have been synthesized with different Cr content, and demonstrated to have adequate cyclic stability in the alkaline electrolyte, due to Cr presence.
- Sputtered noble metal catalysts <0.1 mg/cm^2), e.g., Pt-IrO_2 seem to have comparable kinetics to bulk cathodes.
- Non-noble metal catalysts have comparable performance as noble metal (bulk) catalyst
  - LA-BSCF and NiFeCo-LDH are bifunctional, but have better kinetics in one direction, i.e., LaBSCF for reduction and NiFeCo-LDH for oxygen evolution.
  - The catalysts are durable upon cycling
- Good cycle life has been demonstrated in MH-air cells with dual air cathodes (for ORR and OER).
- High specific energy and energy density have been estimated from 85 kWh MH-air batteries with circulating electrolyte.

Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA), at the California Institute of Technology and Liox Pasadena. We acknowledge the financial support from the ARPA-E Range program (Drs. Ping Liu and Grigorii Soloveichik).