New High Energy Density Mg Battery Concepts for Electrical Energy Storage

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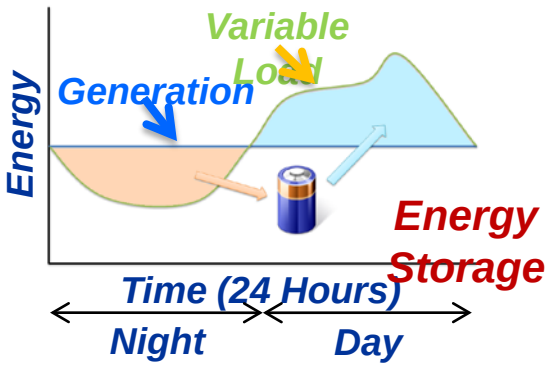
Outline

- **Introduction**
- **Objectives**
- **Approaches**
  - cathodes, electrolytes, current collectors
- **Results**
- **Summary**
- **Future work**

Introduction

Electrical Energy Storage and the Smart Grid

Electrical Energy Storage
A key enabler for the smart grid
www.netl.doe.gov/smartgrid



Advantages of the smart grid:

- Improve reliability and stability of the grid
- Provide responsive power to meet minute-to-minute fluctuations in electricity demand and increase margins against system upsets
- Provide capacity to "peak shave or load shift," enabling peak loads to be met during periods when generation, transmission and distribution assets can not yet be brought on line
- Improve efficiency of off-grid solar and wind power enabling the integration onto the grid of large scale renewable energy plants
- More stable and efficient delivery of electrical power <u>– including power generated from fossil fuel sources</u>

Electrical Energy Storage - result in more stable and efficient delivery of electrical power while reducing overall CO_2 emissions

Performance Targets and Needs for Electrochemical Energy Storage for Grid Applications*

Five year targets:

- **System capital cost: under $250/kWh**
- **Levelized cost: under 20 ¢/kWh/cycle**
- **System efficiency: over 75%**
- **Cycle life: more than 4,000 cycles**

Long term targets:

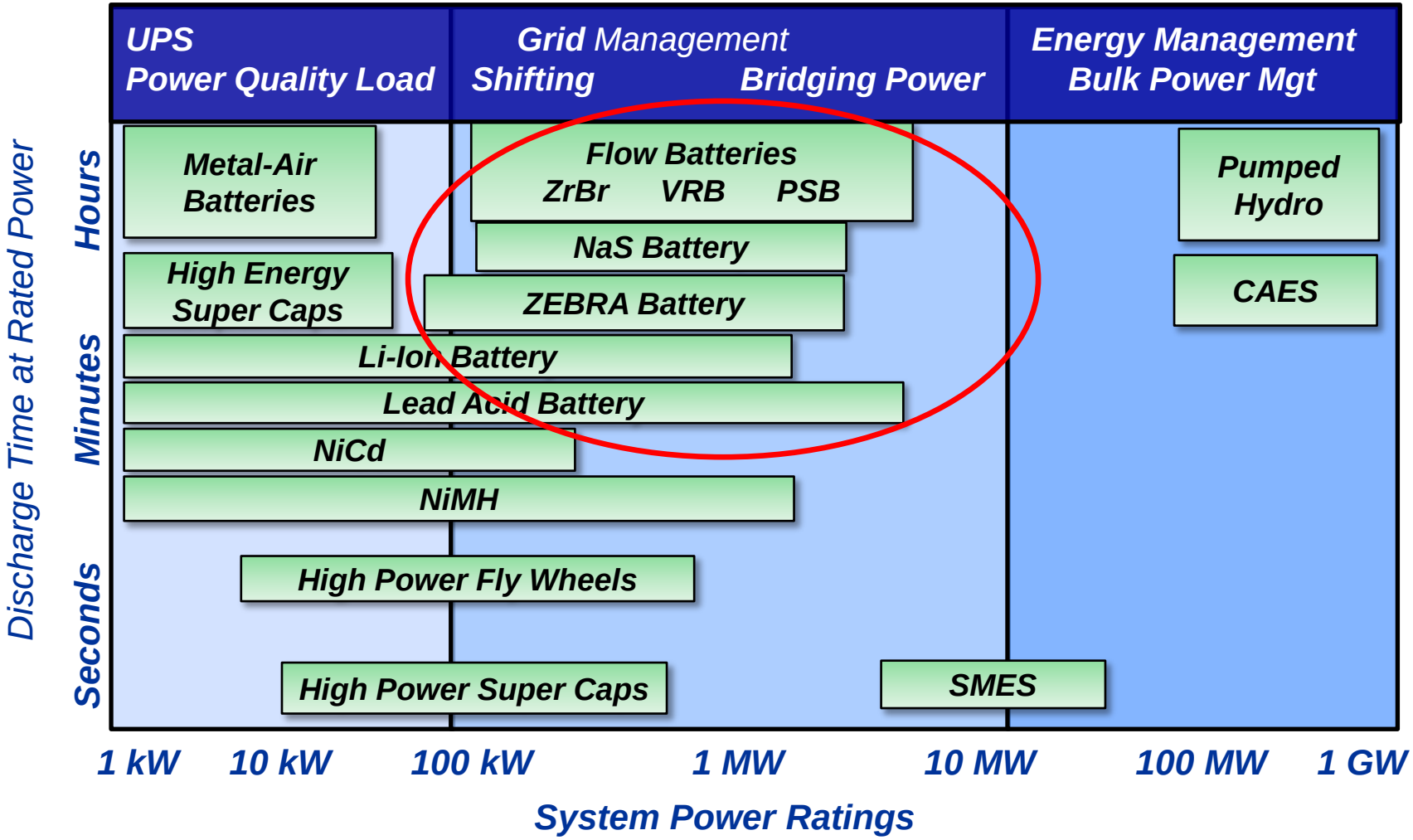
- **System capital cost: under $150/kWh**
- **Levelized cost: under 10 ¢/kWh/cycle**
- **System efficiency: over 80%**
- **Cycle life: more than 5,000 cycles**

NEEDS :

- ***Optimize materials and chemistries and modify current technologies to improve their performance and reduce costs.***
- ***Discover new materials and components that can lead to new technologies meeting the performance and cost requirements of grid storage applications.***

** Source: US DOE Office of Electricity Delivery & Energy Reliability (OE), Energy Storage Planning Document, February, 2011*

Current Grid Scale Batteries



Source: Figure adapted from EPRI report, "Integrated Distributed Generation and Energy Storage Concepts," (2003) Product ID 1004455.

State of the Art in Battery Technologies

Battery type	Cell voltage (V)	Energy per kg (Wh/kg)	Specific power (W/kg)	Direct use	Technical and cost barriers
Lead acid	2.1	30-40	180	Automotive engine ignition	Moderately expensive; Moderate energy density; Environmental hazard due to Lead.
Ni-Cd	1.2	40-60	150	wireless telephones, emergency lighting, aircraft starting & standby power	Inexpensive, Moderate energy density; memory effect; Environmental hazard due to Cadmium.
Ni-MH	1.2	30-80	250-1000	Portable electronic device, flashlights	High self-discharge rate
Lithium ion	3.6	180	250-340	Laptop computers, mobile devices, some modern automotive engines,	Reduced first-cycle capacity loss and volumetric expansion of intermetallic electrodes
Lithium-air		13,000		Portable electronic devices, electric vehicles	Poor cycle life times; Potential for formation of shorting dendrites when charged
Na-S	2.1	110	150	Electricity storage for grid support	High temp 350 ˚C
ZEBRA	2.6	100	150	Electric vehicles, energy storage for grid	High temp 270 ˚C

Current Battery Technologies for Grid Storage: Mg a possible solution to the grid-lock

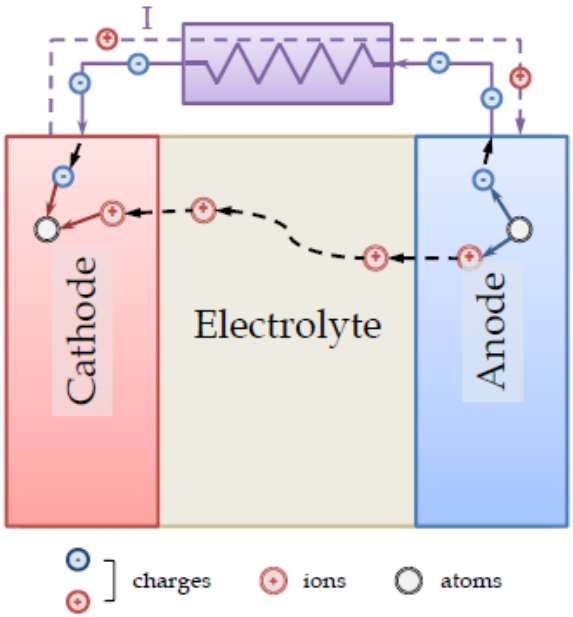
BATTERY	ZEBRA	NaS	Mg
Anode	Molten metallic Na	Molten Metallic Na	Solid Mg alloy
Cathode	$NiCl_2$ or $NaAlCl_4$	Molten S or Na_2S_x	$Mg_{1.03}Mn_{0.97}SiO_4$
Electrolyte	β''-Al_2O_3 solid electrolyte (BASE)	β''-Al_2O_3 solid electrolyte (BASE) membrane	$Mg(AlCl_2BuEt)_2$/THF (0.25 mol L^{-1})
Cell Voltage	2.58 V	2.1 V	1.1 V
Specific Capacity*	305 Ah/kg	377 Ah/kg	60-70 Ah/kg**
Specific Energy*	100 Wh/kg	110 Wh/kg	~60 Wh/kg
Operating Temperature	High 270°C	High 350°C	Room Temp (advantage)

**Theoretical **based on cathode*

Mg based Batteries for Grid Scale Electrical Energy Storage

Why Magnesium?

- **Mg batteries involve cycling Mg^{2+}**
  - Provides 2 electrons. Theoretical specific capacity: 2205 Ah/kg
- **Mg compounds are environmental stable "green" and non-toxic. Mg alloys can be readily stabilized.**
- **Mg as a raw materials is cheap and abundant**
  - Mg: ~ $2700/ton
  - Li: ~ $64,000/ton
  - Mg: ~ 13.9% earth's crust
  - Li: ~ 0.0007% earth's crust



Systems with Proper Designs and Architectures:

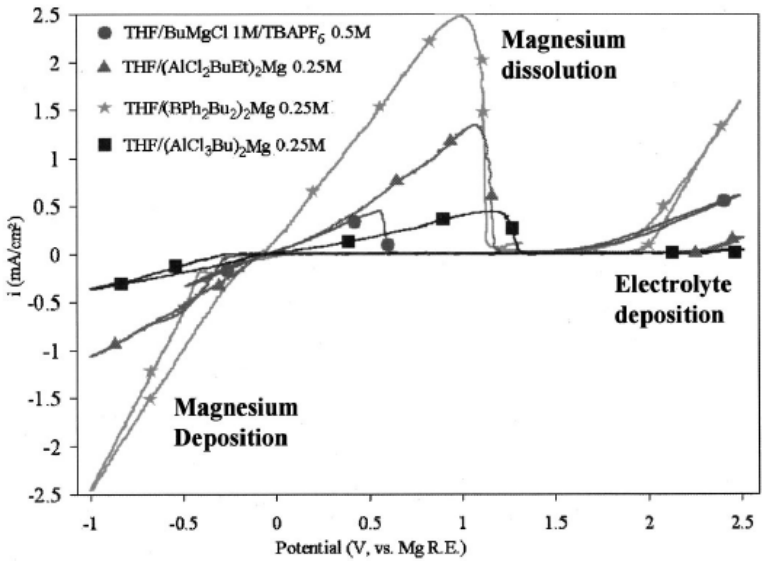
- **60-80 Wh/kg**
- **1-2 V**

Research Objectives

- Explore new electrolyte concepts for Mg batteries
  - Identify new non-aqueous liquid electrolytes (key)
- Explore new current collectors concepts
  - Anodic stability and electrochemical window (key)
  - Opportunities for cost effective concepts
- Explore new cathode concepts
  - New intercalation concepts (key)
  - Novel inorganic compounds
  - New insertion and Redox chemistries (key)

Prior arts in Mg based Rechargeable batteries

Non-aqueous Electrolytes developed by Aurbach and Co-workers (Bar Ilan University, Israel) shows high Mg cycling efficiency (~95%) & electrochemical window (~2.1 V)



CV performed using platinum WE, magnesium foil CE and RE with the electrolyte shows reversible Mg/Mg^{2+} deposition/dissolution occurs (within the electrochemical potential window of ~ 2.1 V with excellent Mg cycling efficiency

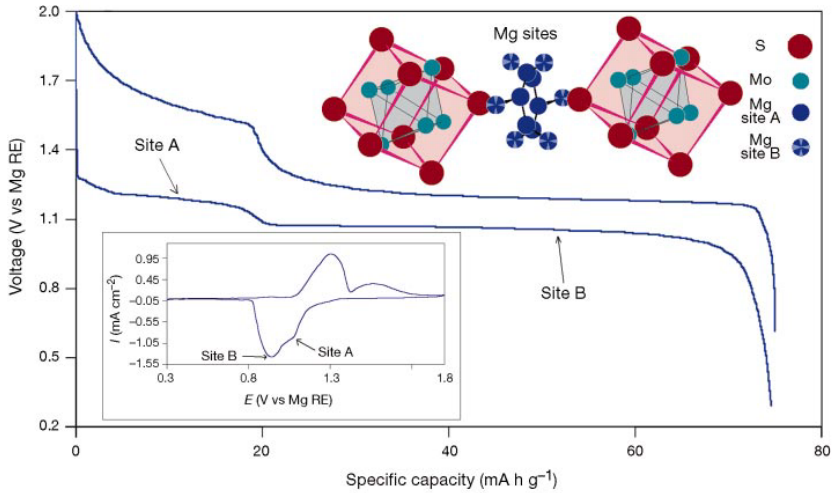
Table I. A summary of Mg cycling efficiency and oxidation potentials of THF solutions containing different combinations of Lewis bases and Lewis acids of the R_2Mg and $AX_{3-n}R'_n$ types, respectively, at different ratios as indicated.

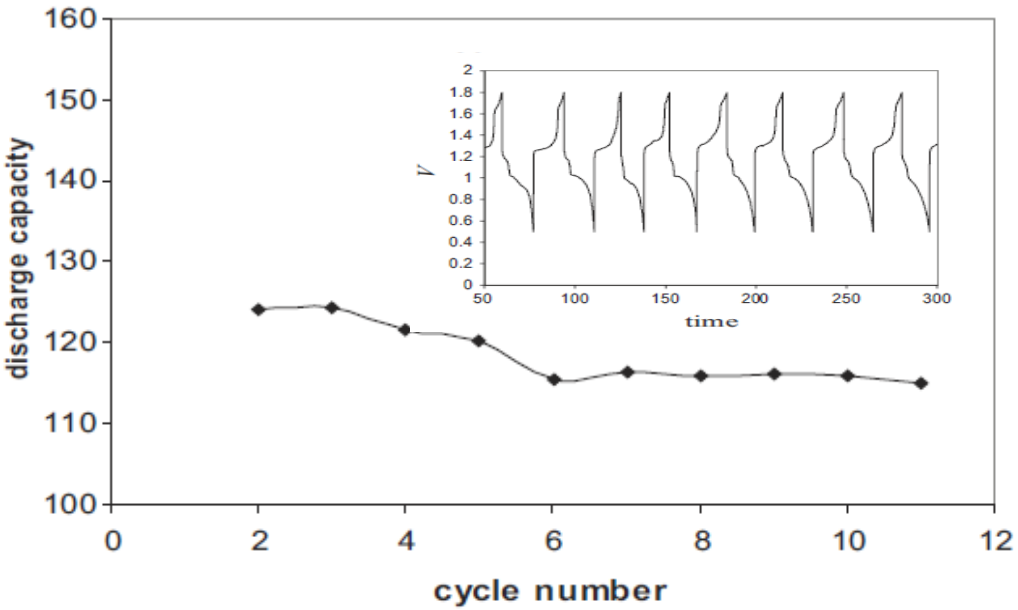
Lewis base	Lewis acid	Acid-base ratio	Mg cycling efficiency	Electrolyte decomposition potential
Bu_2Mg	$AlCl_2Et$	1-2.00	95	2.10
Bu_2Mg	$AlCl_2Et$	1-1.75	95	2.05
Bu_2Mg	$AlCl_2Et$	1-1.50	97	2.00
Bu_2Mg	$AlCl_2Et$	1-1.25	94	1.90
Bu_2Mg	$AlCl_2Et$	1-1.00	96	1.80
Bu_2Mg	$AlCl_2Et$	1-0.75	95	1.65
Et_2Mg	$AlCl_2Et$	1-2.00	92	2.25
Ph_2Mg	$AlCl_2Et$	1-2.00	80	2.08
Bz_2Mg	$AlCl_2Et$	1-2.00	88	2.15
Bu_2Mg	$AlCl_3$	1-2.00	75	2.40
Bu_2Mg	$AlCl_3$	1-1.75	74	2.30
Bu_2Mg	$AlCl_3$	1-1.50	74	2.25
Bu_2Mg	$AlCl_3$	1-1.25	83	2.15
Bu_2Mg	$AlCl_3$	1-1.00	86	2.10
Bu_2Mg	$AlCl_3$	1-0.75	92	2.00
Bu_2Mg	BPh_3	1-1.50	86	1.77
Bu_2Mg	BPh_3	1-1.00	68	1.60
Bu_2Mg	BPh_3	1-0.66	91	1.40
Bu_2Mg	BPh_3	1-0.50	93	1.30
Bu_2Mg	BCl_3	1-1.00	80	1.20
Bu_2Mg	BCl_3	1-0.50	93	1.75
Bu_2Mg	BCl_3	1-0.20	71	1.50

Aurbach *et al. J. Electrochem Soc.*, 149 (2), (2002), A115-21

New Intercalation cathode: $Mg_xMo_3S_4$ (0<x<1)

Chevrel phase cathode (Mo_6S_8) in $Mg(AlCl_2BuEt)_2$/THF (0.25 mol L^{-1}) electrolyte solution where reversible intercalation of Mg^{2+} occur





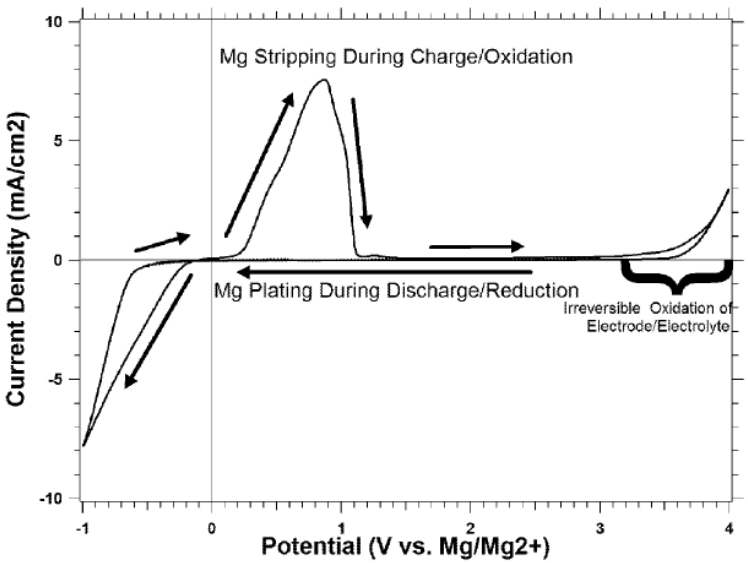
Maximum charge capacity 122 $mAhg^{-1}$ > 1000 cycles
Practical energy density ~ 60 $Whkg^{-1}$

Aurbach *et al*. *Nature*, 407 (10), (2000), 724-27

Chusid *et al*. *Adv. Mater*., 15, (2003), 627-30

Pellion Technologies shows current collector is a key factor for the anodic stability of the electrolytes

Anodic stability of the current collectors is a critical factor for the stability of the electrolyte and stable electrochemical window



Carbon sheet shows the highest stability ~ 3 V

PhMgCl : $AlCl_3$ = 2:1 (~ 3 V APC electrolyte developed by Aurbach *et al*.)

Current Collector Candidate	Anodic Stability Limit (I > 100uA/cm^2)
Pt	2.90
Au	2.61
Ni	2.01
Ti	2.58
Glassy Carbon	**2.85**
Carbon Sheet (Graphfoil and Fiber)	**2.99**

R. E. Doe, G. E. Blomgren, and K. A. Persson, "RECHARGEABLE MAGNESIUM ION CELL COMPONENTS AND ASSEMBLY," United States Patent, 2011

Results

Development and analysis of novel non-aqueous electrolytes

Development of 1st generation $Mg(AlCl_2BuEt)_2$/Tetrahydrofuran (0.25 mol L^{-1}) non-aqueous liquid electrolyte

Bu_2Mg (1 mol L^{-1} in heptane) + $AlCl_2Et$ (1 mol L^{-1} in hexane) mixed in the molar ratio of 1:2 at R.T. (transmetallation)

↓

A white solid precipitate

↓

Stir for 48 h to evaporate the heptane/hexane

↓

White solid, dissolved in anhydrous THF

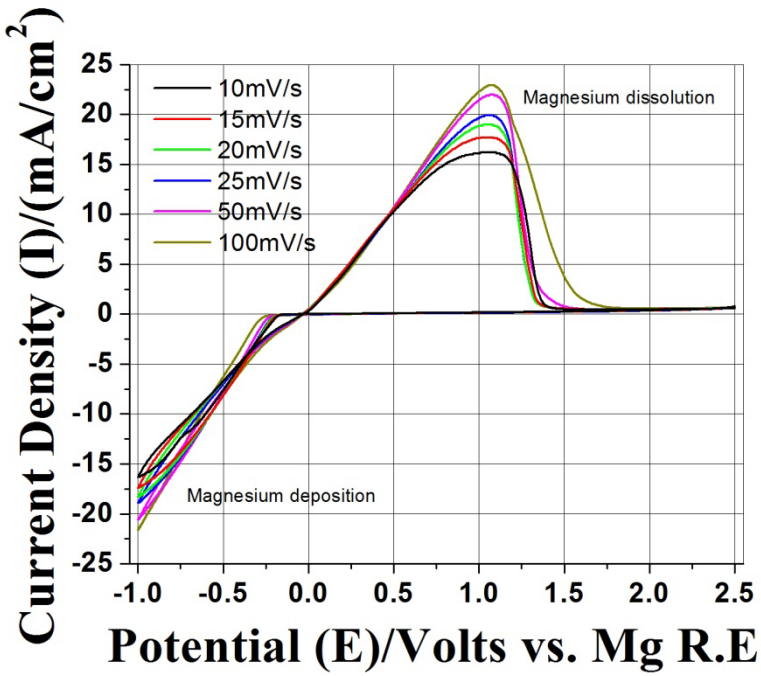
↓

Mg can be electrochemically deposited and dissolved reversibly from this solution

Aurbach *et al. J. Electrochem Soc.*, 149 (2), (2002), A115-21

Successfully synthesized $Mg(AlCl_2BuEt)_2$/(0.25 M THF) based BEC electrolyte (potential window ~ 2.1 V)

Scan rate (mV/s)	Onset deposition potential (V)	Anodic stripping peak potential (V)	Mg cycling efficiency (%)
10	-0.170	1.006	99.3
15	-0.180	1.006	98.3
20	-0.182	1.023	96.3
25	-0.193	1.032	95
50	-0.21	1.06	93.6
100	-0.23	1.051	94.3



Lewis base	Lewis acid	Acid-base ratio	Mg cycling efficiency	Electrolyte decomposition potential
Bu_2Mg	$AlCl_2Et$	1-2.00	95	2.10

Aurbach et al. J. Electrochem Soc., 149 (2), (2002), A 115-21

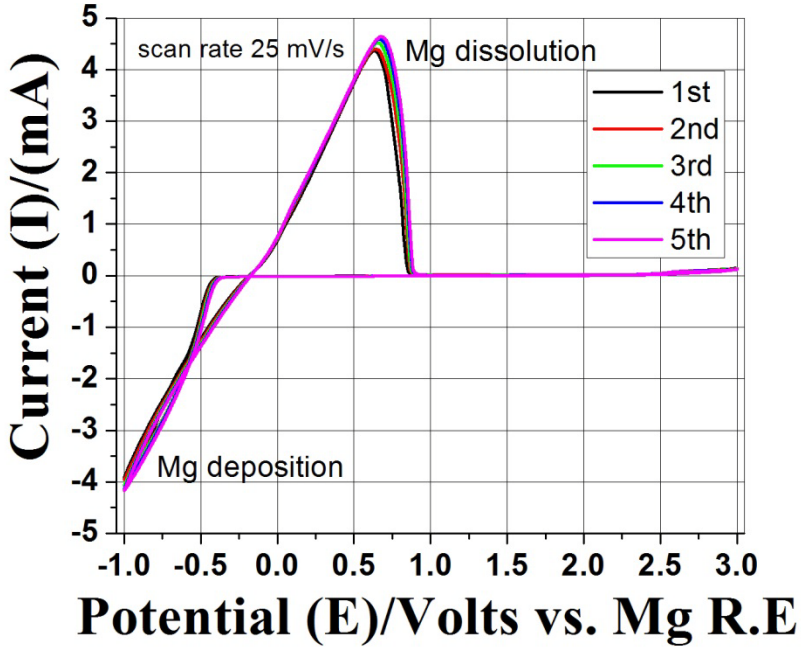
Mg/Mg^{2+} deposition/dissolution occurs within the electrochemical potential window of ~ 2V indicative of good electrolyte function as expected

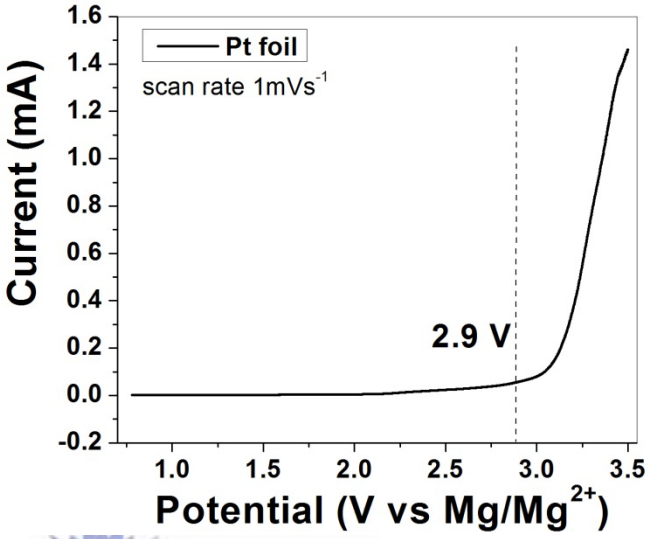
Successfully synthesized 2(PhMgCl)-$AlCl_3$/(0.4M THF) based APC electrolyte (potential window ~ 3 V)

LSV confirms the electrochemical window ~ 2.9 V (Pellion Tech also observed ~ 2.9 V)

Coulombic efficiency ~ 90%

Reversible electrochemical deposition/dissolution of magnesium observed within -1 V to 3 V potential window respect to Mg reference electrode

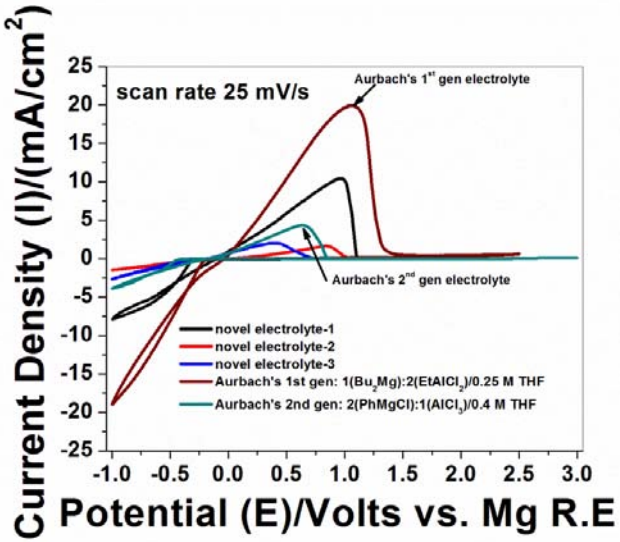


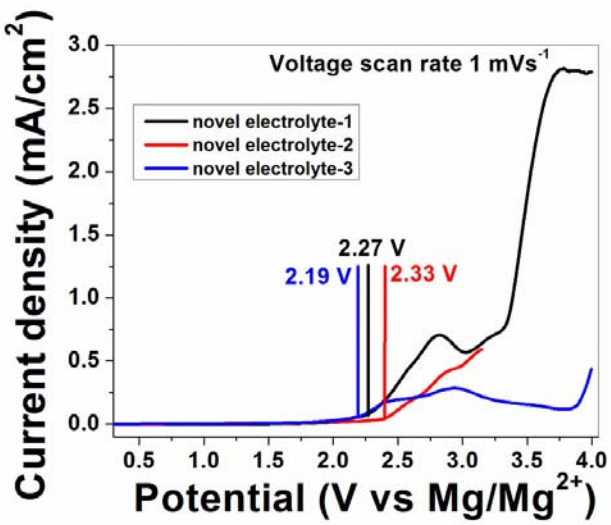


Scan rate (5mV/s)	Onset deposition potential (V)	Anodic stripping peak potential (V)	Mg cycling efficiency (%)
cycle 1	-0.37	0.643	85.5
cycle 2	-0.363	0.648	86.5
cycle 3	-0.355	0.66	87.1
cycle 4	-0.347	0.671	87.6
cycle 5	-0.333	0.681	88.0

Successfully synthesized amide based novel electrolytes

- Transmetallation of Lewis acid and Lewis base at various molar ratio
- A white solid precipitate, dissolved in THF
- Mg can be electrochemically deposited and dissolved reversibly from this solution
- Cyclic voltammetry performed in a 3-electrode cell using Pt foil as W.E. and Mg foil being C.E. and R.E.
- Mg deposition/dissolution occurs within the electrochemical potential window of -1 to 2.2 V vs. Mg/Mg^{2+}





Electrochemical performance of novel electrolytes at par with Aurbach's 1st generation electrolyte

Name	Onset deposition potential (V)	Anodic stripping peak potential (V)	Mg cycling efficiency (%)	Anodic stability limit in Pt, (I > 100 μAcm^{-2})
Novel electrolyte-1	-0.283	0.983	**93.2**	**2.27**
Novel electrolyte-2	-0.242	0.842	63.7	2.33
Novel electrolyte-3	-0.351	0.401	56.5	2.19
(Aurbach's 1stgen BEC)	**-0.193**	**1.032**	**95**	**2.2 (known)**
(Aurbach's 2ndgen APC)	**-0.37**	**0.643**	**90**	**2.9 (known)**

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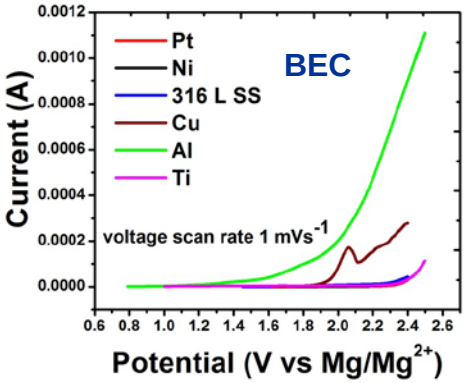
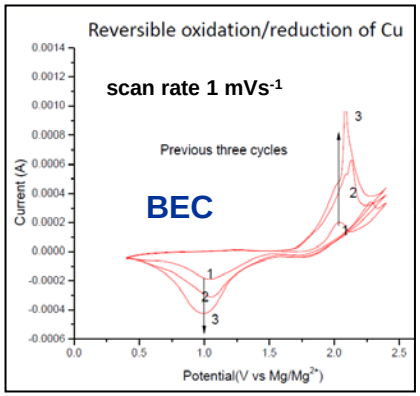
Analysis of current collectors

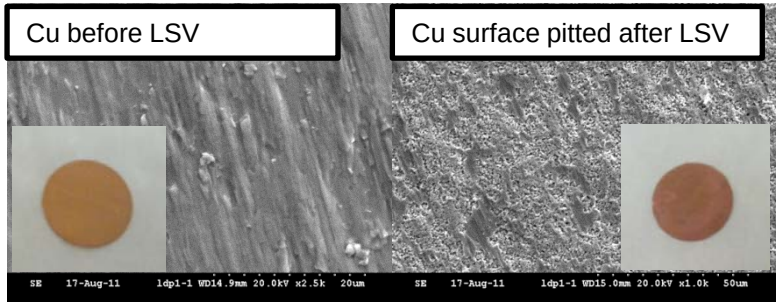
Electrochemical Stability of various current collectors in $Mg(AlCl_2EtBu)_2$/(0.25 M THF) BEC electrolyte

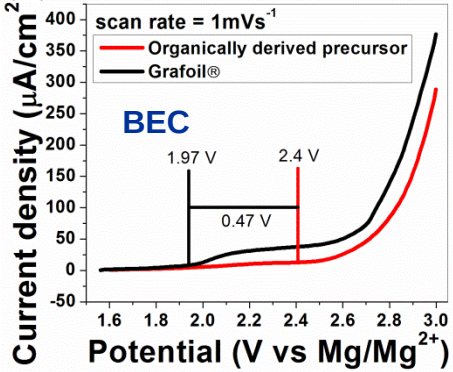
LSV on Cu, Ni, Al, Ti, 316 L SS and Pt.





Al, Cu and 316L SS are not stable enough in the Present electrolyte

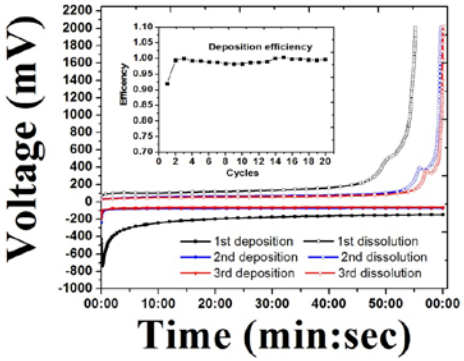


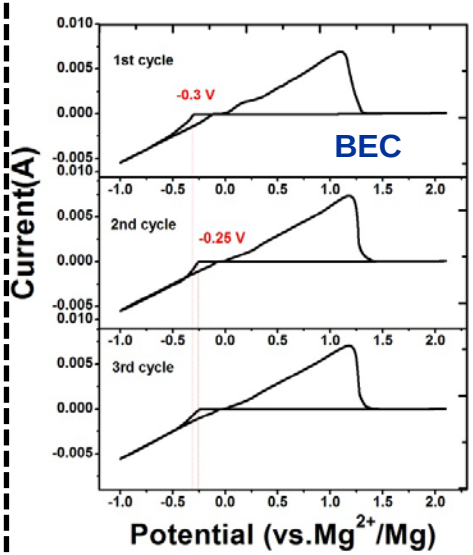


Anodic stability of organically derived precursor material is 0.43 V higher when compared to commercial Grafoil® make it an ideal candidate for current collector

Cycles	Scan between OCP to 3 V	Anodic stability limit (I > 100 mAcm^{-2})
Organically derived precursor	+ ive scan	**2.4**
Grafoil®	+ ive scan	1.97

Chronopotentiometry of Ni as current collector





Ni is also a good choice as current collector

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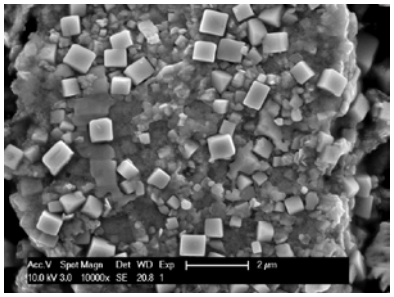
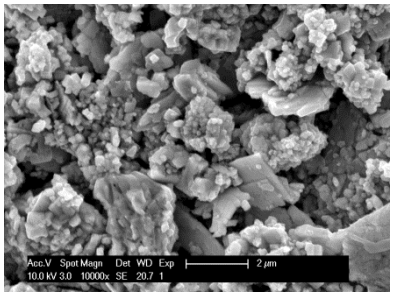
D. Lv, T. Xu, P. Saha, M.K. Datta, M. Gordin, A. Manivannan, P.N. Kumta, and D. Wang, J. Electrochemical Society 2(160), 2013, p-A351-55

Development of metal chalcogenide cathodes

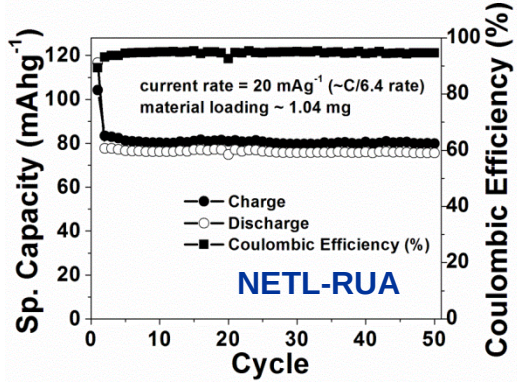
Galvanostatic performance of metal chalcogenide (MC-1) developed by modified low cost wet chemical route shows improved performance

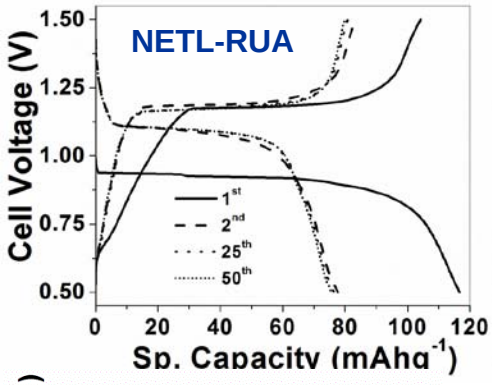


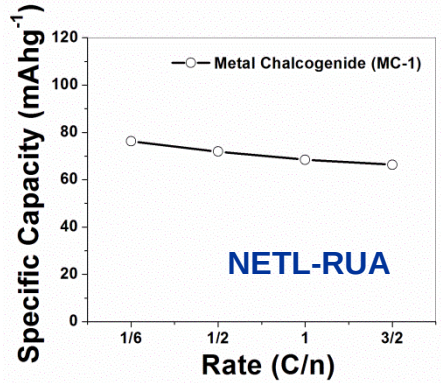
0.1-2 μm size rhombohedral shape particles (NETL-RUA)

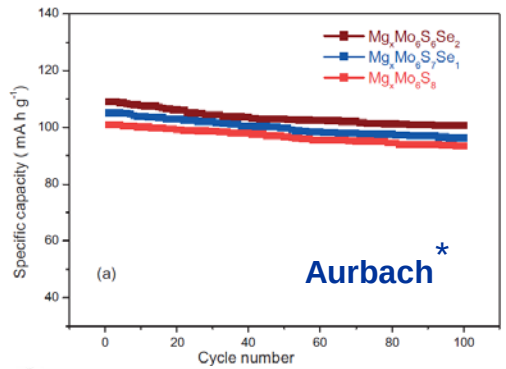


Irregular shape particles (Aurbach's)

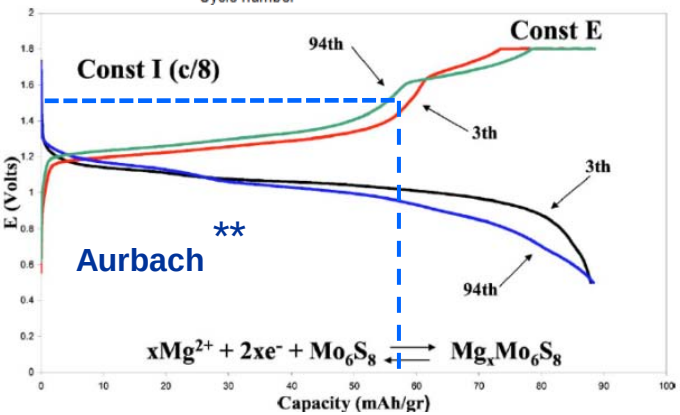


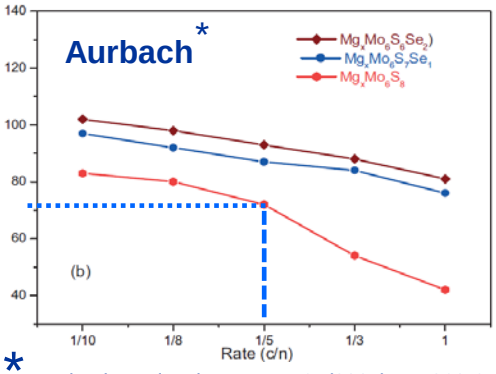






- discharge capacity ~ 76 mAhg^{-1} at ~C/6 rate
- coulombic efficiency ~ 99.3% at ~ 1.5C rate





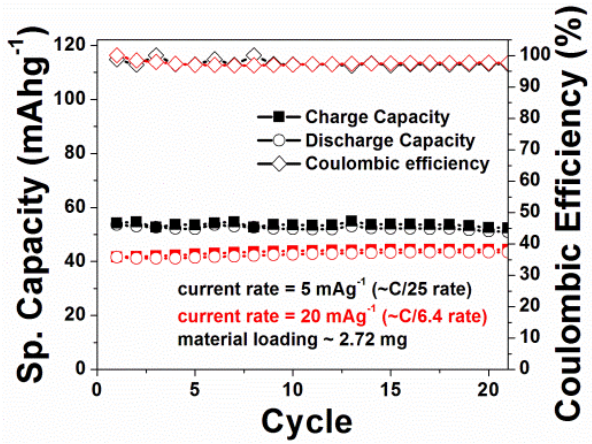
- Rate capability much better than Aurbach's material.

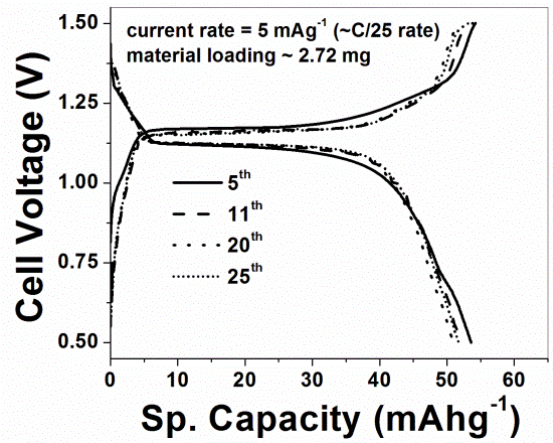
* Aurbach et al. Adv. Mater. 19, (2007),p.-4260-67

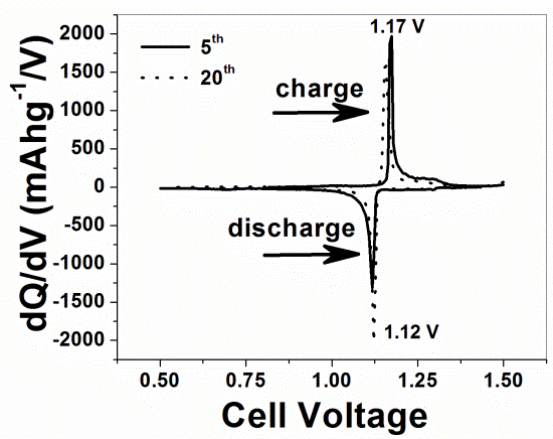
** Mizrahi et al. ECS. 155, 2 (2008), p.-A103-A109

(confidential)

Performance of MC-1 synthesized by Aurbach's molten salt synthesis (MSS) route tested with APC electrolyte





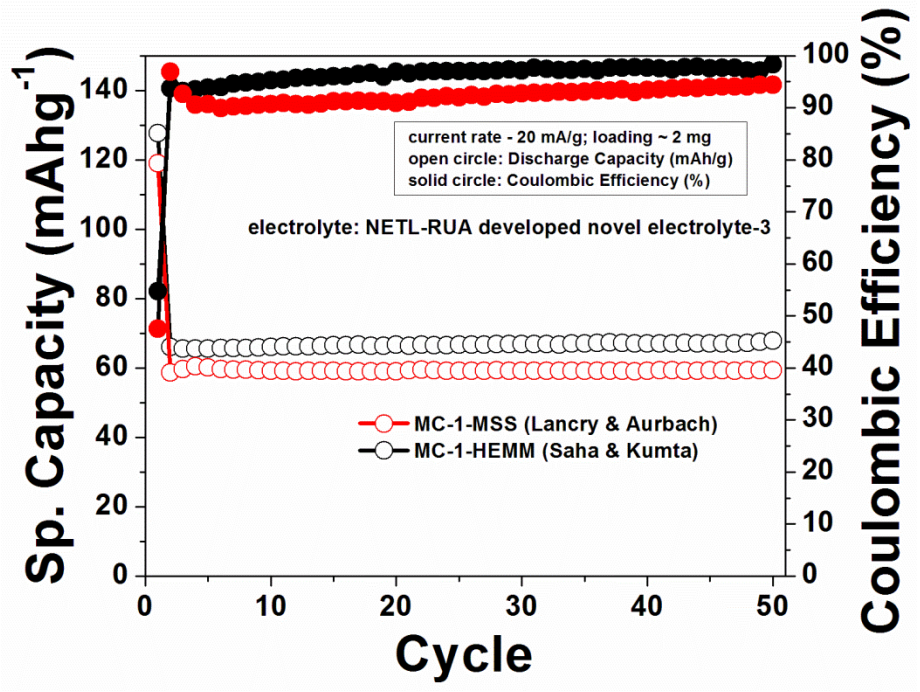


discharge capacity ~ 52 $mAhg^{-1}$ at ~C/25 rate and 40$mAhg^{-1}$ at ~ C/6 rate
coulombic efficiency ~ 97.4% at ~~C/25 rate and ~ 97.7% at ~C/6 rate

Note: MC-1made by Aurbach's MSS route tested with <u>organically derived precursor based current collector and APC electrolyte shows lower capacity</u> than published reports for C/6

(confidential)

Comparison of MC-1 prepared by High Energy Mechanical Milling (HEMM) route shows electrochemically improved performance with amide based novel electrolyte developed by NETL-RUA

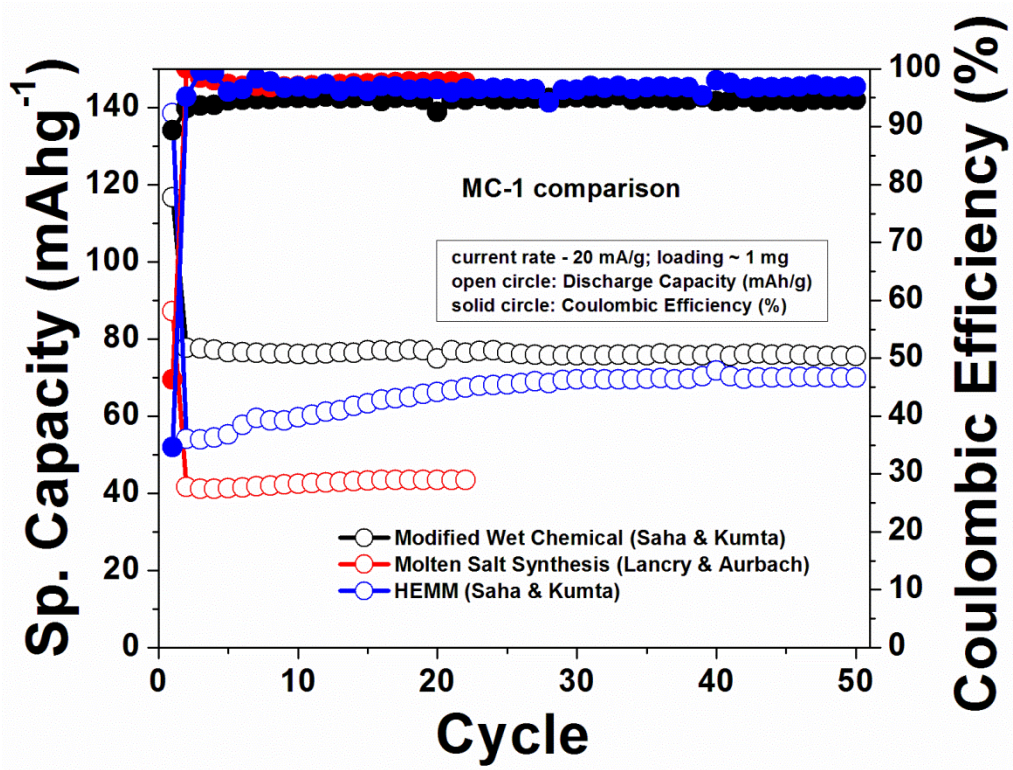


Material	1st cycle irreversible loss	Discharge capacity from 2nd cycle onwards	Coulombic Efficiency (%) from 2nd cycle onwards
HEMM derived MC-1	45.23%	67 mAh/g	97%
MSS derived MC-1	52.54%	59 mAh/g	93%

Note: NETL-RUA *developed cathode as well as electrolyte*
Synthesis of metal chalcogenides by HEMM first time ever achieved
HEMM- a convenient, scalable approach with high throughput

(confidential)

Performance comparison of MC-1 synthesized by various routes tested using APC electrolyte



Galvanostatic performance of HEMM and Modified Wet Chemical Approach derived MC-1 are same (Key Point)

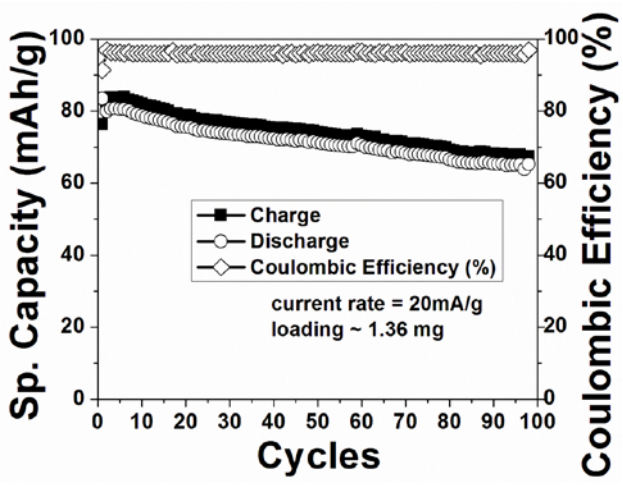
MSS (Lancry & Aurbach) derived MC-1 shows low discharge capacity

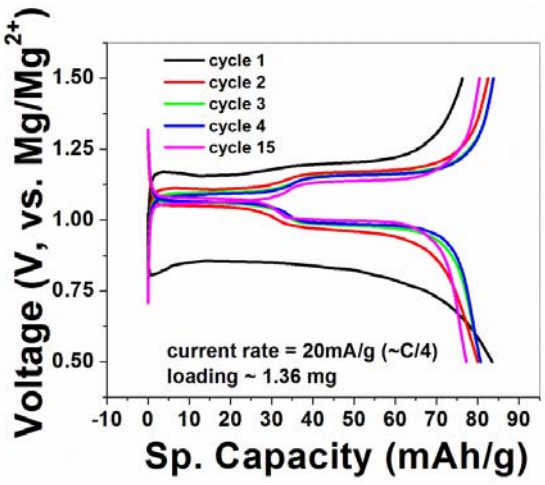
Coulombic efficiency are almost ~95-96% in all cases

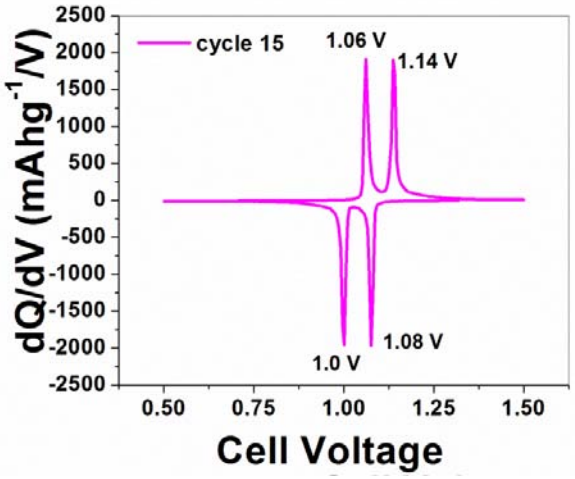
Note: improved electrochemical performance came from NETL-RUA *developed cathode as well as electrolyte*

(confidential)

Galvanostatic performance of MC-2 developed by HEMM route tested using APC electrolyte



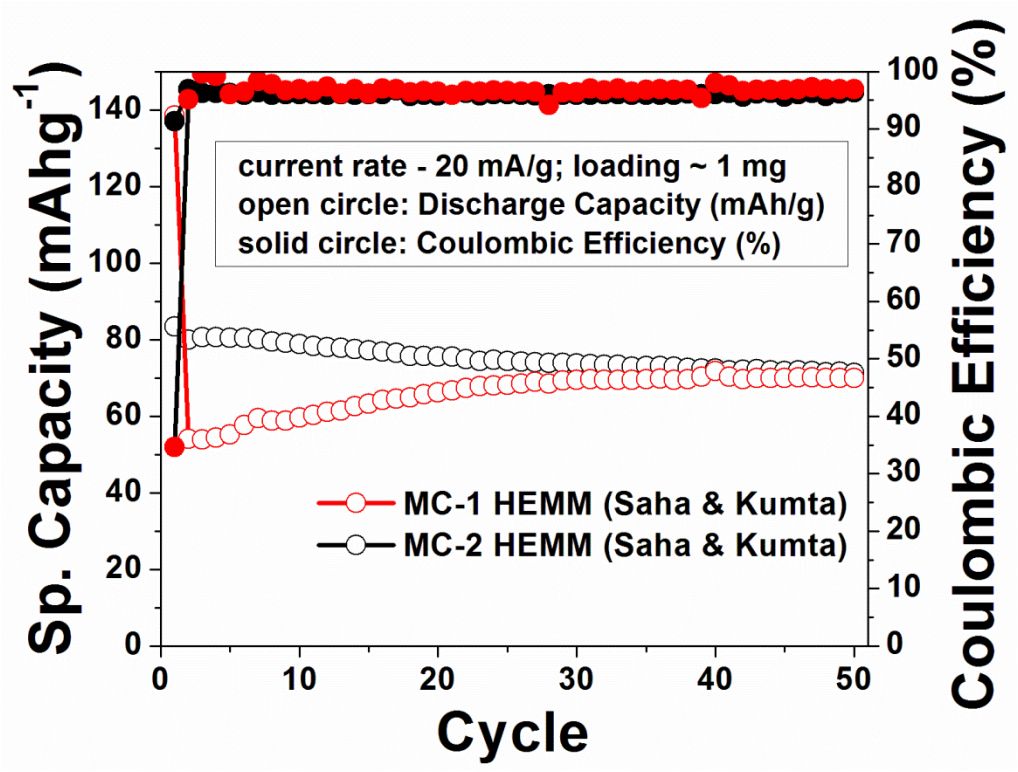




discharge capacity ~ 80 $mAhg^{-1}$ at ~C/4 rate
coulombic efficiency ~ 97% at ~C/4 rate
dQ/dV vs. voltage curve shows that magnesiation/demagnesiation occur in two-step.
78.25% capacity retention at 98th cycle from 1st cycle

(confidential)

Performance of MC-1 and MC-2 developed by HEMM route using 2(PhMgCl)-$AlCl_3$/(0.4 M THF) APC electrolyte



Note: HEMM approach is thus novel and indeed promising giving better response for both metal chalcogenides

HEMM derived MC-2 show initially higher discharge capacity than HEMM derived MC-1.

Discharge capacity are almost identical after 40 cycles.

Initial first cycle irreversible loss for MC-2 is also lower than MC-1 (~10% compared to 60%)

Slight modification of composition of MC-1 is underway to improve the 1st cycle irreversible loss

(confidential)

Key Technological advancement

- **Successfully synthesized $Mg(AlCl_2BuEt)_2$/THF (0.25 mol L^{-1}) based 1st generation electrolyte, coulombic efficiency close to 99% which is in excellent agreement with the literature value of 95% [**Aurbach et al. J. Electrochem Soc. 149(2), (2002), A115-121]

- **Successfully synthesized 2(PhMgCl)-$AlCl_3$ based 2nd generation electrolytes which show electrochemical stability upto 2.9 V vs. Mg/Mg^{2+} coulombic efficiency close to 90%**
- **Identified organically derived precursor materials and Ni foil as a potential current collector for Mg battery**

- **Developed three novel electrolytes by transmetallation of Lewis base and Lewis acid at different molar ratio**

  Electrochemical stability window ~ 2.2 V onto Pt

  Electrochemical performance at par with Aurbach's BEC electrolyte

- **Two different metal chalcogenides MC-1 and MC-2 already developed by low cost energy saving routes**

MC-1

Discharge capacity ~ 76 $mAhg^{-1}$ at ~ C/6 rate using APC electrolyte Coulombic efficiency ~ 99.3% at ~1.5C rate

MC-2

Discharge capacity ~ 80 $mAhg^{-1}$ at ~ C/4 rate using APC electrolyte Coulombic efficiency ~ 97%

-
- **All of the above make our technology unique and different from published literature.**

- **Patent Status: Invention disclosure already submitted with the above claims to Office of Technology Management at Pitt and NETL.**

Future Work

- **Develop novel electrolyte with improved electrochemical stability window (>3 V)**
- **Opportunities exist for breakthrough in electrolytes, cathodes, anodes and current collectors**
- **Explore metal/organometal based electrolyte systems for high Voltage electrolyte**

- **Ni and organically derived precursor has already been identified as suitable current collectors for Mg batteries which display excellent anodic stability. Electrochemical tests will be performed to check the feasibility an stability of the current collectors for long cycles (> 1000 cycles)**

- **Develop doped metal chalcogenides or solid solution of different chalcogenides to improve the specific capacity as well as operating voltage which will leads to improve energy density of the Mg based battery system**

Thank you for your Patience!!