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# New High Energy Density Mg Battery Concepts for Electrical Energy Storage

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# Acknowledgement and Disclaimer

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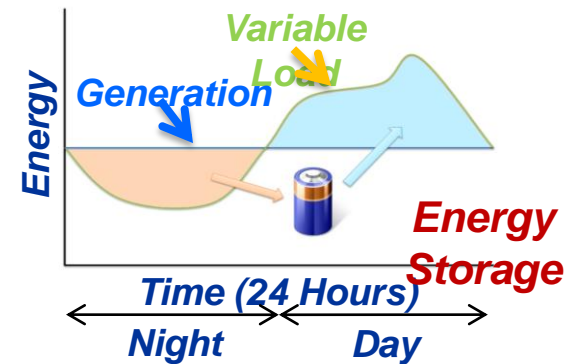
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# Outline

- **Introduction**
- **Objectives**
- **Approaches**
  - Anodes
  - Cathodes
  - current collectors
  - electrolytes
- **Results**
- **Summary**
- **Future work**

# Electrical Energy Storage and the Smart Grid

## **Electrical Energy Storage** **A key enabler for the smart grid** [www.netl.doe.gov/smartgrid](http://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 – including power generated from fossil fuel sources

**Electrical Energy Storage - result in more stable and efficient delivery of electrical power while reducing overall CO<sub>2</sub> 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:

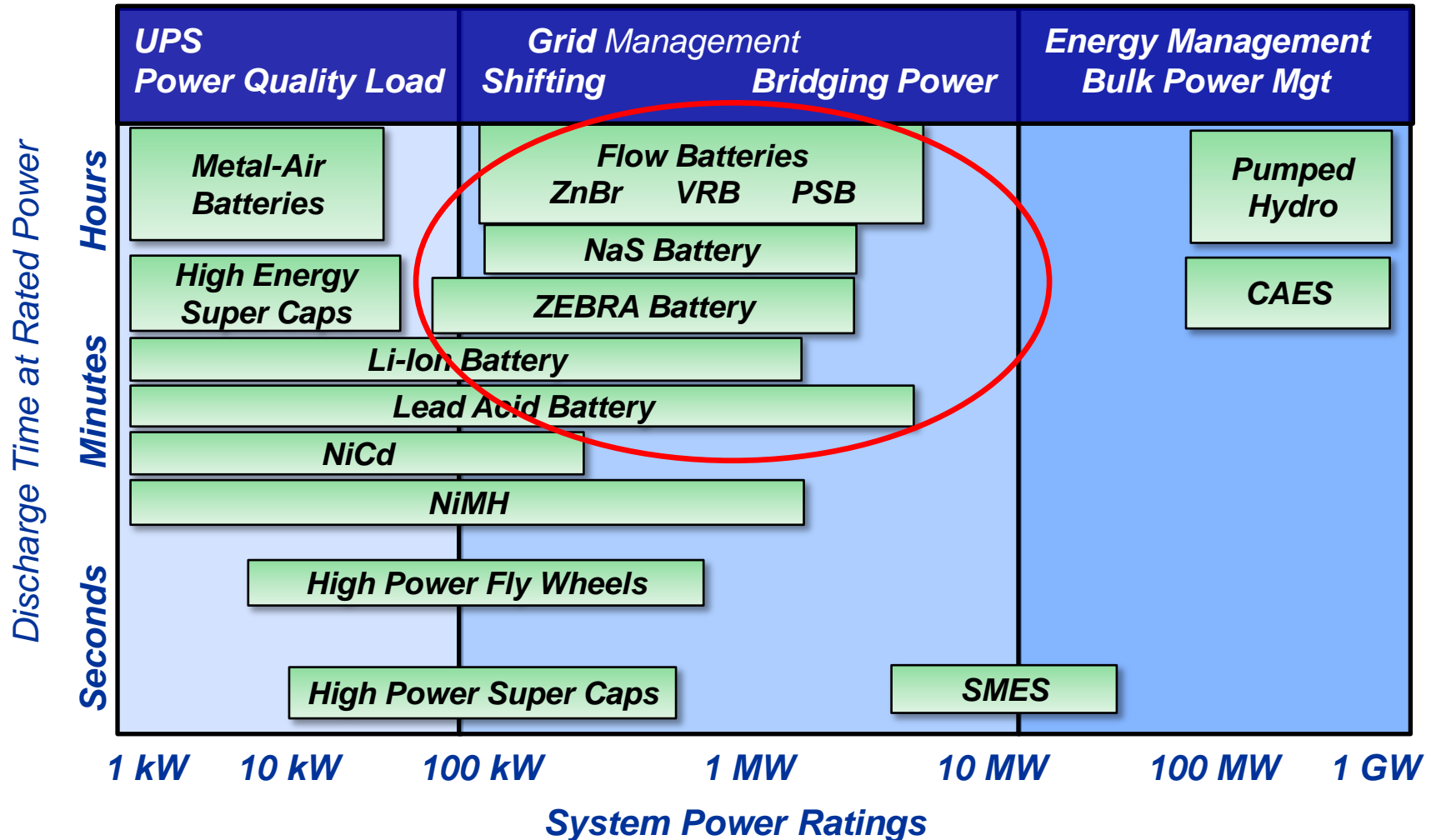
- System capital cost: under \$150/kWh
- Levelized cost: under 10 ¢/kWh/cycle
- System efficiency: over 80%
- Cycle life: more than 5,000 cycles

## **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; <b>memory effect</b> ; 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 | 3                | 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 <sub>2</sub> or NaAlCl <sub>4</sub>                          | Molten S or Na <sub>2</sub> S <sub>x</sub>                                 | Mg <sub>1.03</sub> Mn <sub>0.97</sub> SiO <sub>4</sub>                   |
| Electrolyte                  | $\beta'$ -Al <sub>2</sub> O <sub>3</sub> solid electrolyte (BASE) | $\beta'$ -Al <sub>2</sub> O <sub>3</sub> solid electrolyte (BASE) membrane | Mg(AlCl <sub>2</sub> BuEt) <sub>2</sub> /THF (0.25 mol L <sup>-1</sup> ) |
| Cell Voltage                 | 2.58 V  | 2.1 V  | 2.1 V  |
| Specific Capacity*           | 305 Ah/kg   | 377 Ah/kg  | 315 Ah/kg**  |
| Specific Energy*             | 100 Wh/kg   | 110 Wh/kg  | ~500 Wh/kg   |
| <b>Operating Temperature</b> | <b>High<br/>270°C</b>   | <b>High<br/>350°C</b>  | <b>Room<br/>Temp</b>   |

\*Theoretical

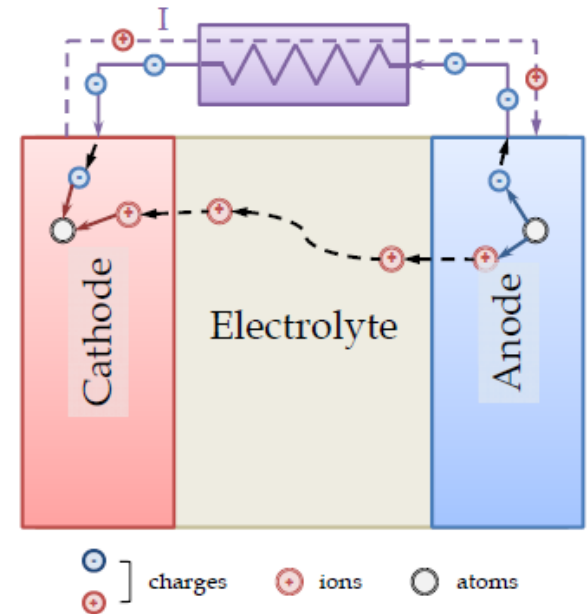
\*\*based on cathode



# Mg based Batteries for Grid Scale Electrical Energy Storage

## Why Magnesium?

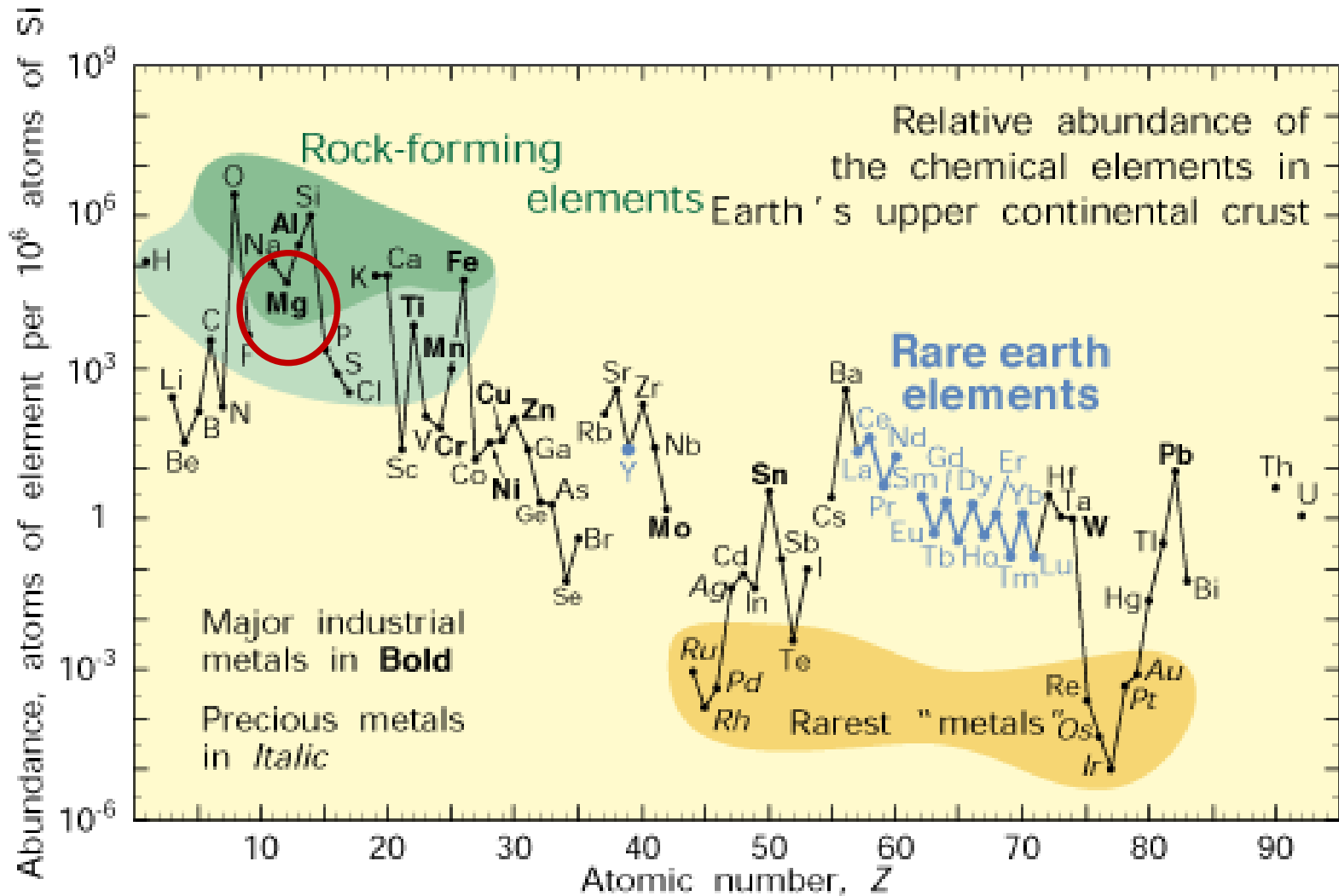
- **Mg batteries involve cycling  $Mg^{2+}$** 
  - Provides 2 electrons. Theoretical specific capacity: 2205 Ah/kg
- **Mg compounds are environmental stable “green” and non-toxic. Mg alloys can be readily stabilized.**
- **Mg as a raw materials is cheap and abundant**
  - Mg: ~ \$2700/ton
  - Li: ~ \$64,000/ton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



***Systems with Proper Designs and Architectures:***

- ***200-1000 Wh/kg***
- ***1-3 V***

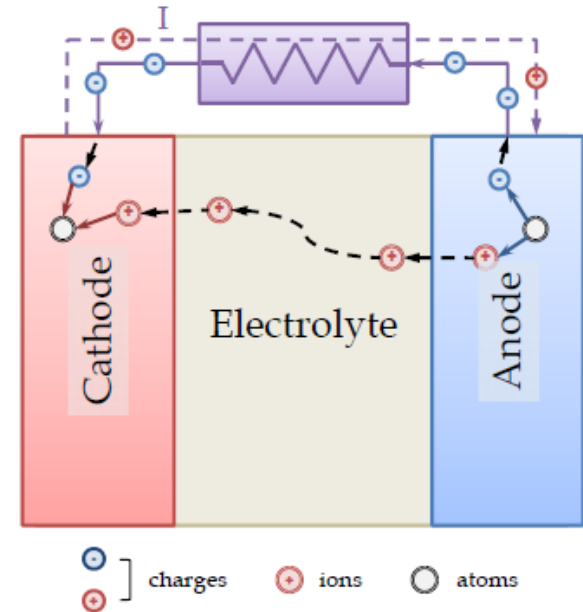
# Mg Abundance in Earth's Crust



# Mg based Batteries for Grid Scale Electrical Energy Storage

## Key Challenges

- **Electrolytes**
  - Solvents: neither donate or accept protons
  - Solvents: Not allow the formation of passivating surface films onto Mg anode
- **Cathodes**
  - Difficulty in intercalation of Mg ions
  - Cycling of Mg systems is quite poor
  - Cycling is a key requirement for a rechargeable battery



## Rechargeable Mg batteries recent work:

- **Electrolytes**
  - Aurbach et al <sup>1,2</sup>: Magnesium-organohaloaluminate salts
- **Cathodes**
  - Aurbach et al <sup>1,2</sup> :  $MgMo_3S_4$
  - NuLi et al <sup>3</sup>:  $Mg_{1.03}Mn_{0.97}SiO_4$
- **Anodes**
  - Aurbach et al <sup>1,2</sup> : Mg foil, AZ31

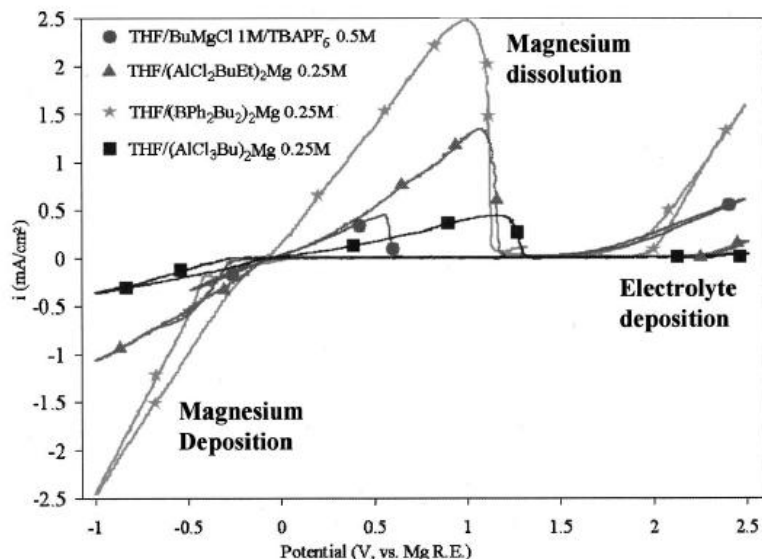
- 1) D. Aurbach et al, *Advanced Materials*, 2007, v19, p 4260
- 2) E. Levi et al, *Chem. Materials*, 2010., v22, p. 860
- 3) Y. NuLi et al. *Chem. Comm.* 2010, v46., p. 3794.

# Research Objectives

- **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)
- **Explore new anodic concepts for Mg**
  - Novel alloy design concepts for Mg anodes (key)
  - Explore corrosion resistant alloy designs
- **Explore new electrolyte concepts for Mg batteries**
  - Identify new non-aqueous liquid electrolytes (key)
  - Explore ionic liquids as potential electrolytes

# **Prior art in Mg Rechargeable batteries**

# Electrolyte shows high Mg cycling efficiency (~95%) & electrochemical stability window (~2.1 V)



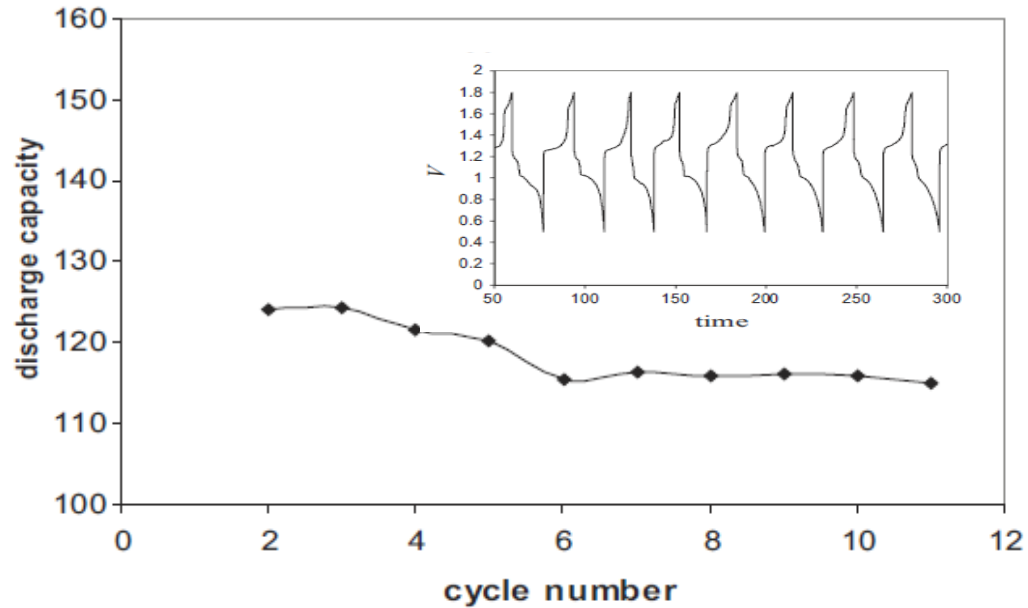
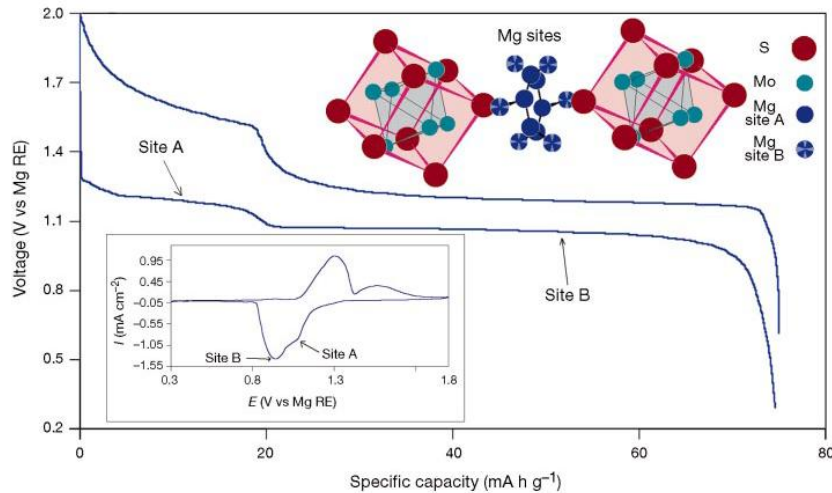
CV performed using platinum WE, magnesium foil CE and RE with the electrolyte shows reversible Mg/Mg<sup>2+</sup> deposition/dissolution occurs (within the electrochemical potential window of ~ 2.1 V with excellent Mg cycling efficiency

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<sub>2</sub>Mg and AX<sub>3-n</sub>R<sub>n</sub>' types, respectively, at different ratios as indicated.

| Lewis base         | Lewis acid           | Acid-base ratio | Mg cycling efficiency | Electrolyte decomposition potential |
|--------------------|----------------------|-----------------|-----------------------|-------------------------------------|
| Bu <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-2.00          | 95                    | 2.10                                |
| Bu <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-1.75          | 95                    | 2.05                                |
| Bu <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-1.50          | 97                    | 2.00                                |
| Bu <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-1.25          | 94                    | 1.90                                |
| Bu <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-1.00          | 96                    | 1.80                                |
| Bu <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-0.75          | 95                    | 1.65                                |
| Et <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-2.00          | 92                    | 2.25                                |
| Ph <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-2.00          | 80                    | 2.08                                |
| Bz <sub>2</sub> Mg | AlCl <sub>2</sub> Et | 1-2.00          | 88                    | 2.15                                |
| Bu <sub>2</sub> Mg | AlCl <sub>3</sub>    | 1-2.00          | 75                    | 2.40                                |
| Bu <sub>2</sub> Mg | AlCl <sub>3</sub>    | 1-1.75          | 74                    | 2.30                                |
| Bu <sub>2</sub> Mg | AlCl <sub>3</sub>    | 1-1.50          | 74                    | 2.25                                |
| Bu <sub>2</sub> Mg | AlCl <sub>3</sub>    | 1-1.25          | 83                    | 2.15                                |
| Bu <sub>2</sub> Mg | AlCl <sub>3</sub>    | 1-1.00          | 86                    | 2.10                                |
| Bu <sub>2</sub> Mg | AlCl <sub>3</sub>    | 1-0.75          | 92                    | 2.00                                |
| Bu <sub>2</sub> Mg | BPh <sub>3</sub>     | 1-1.50          | 86                    | 1.77                                |
| Bu <sub>2</sub> Mg | BPh <sub>3</sub>     | 1-1.00          | 68                    | 1.60                                |
| Bu <sub>2</sub> Mg | BPh <sub>3</sub>     | 1-0.66          | 91                    | 1.40                                |
| Bu <sub>2</sub> Mg | BPh <sub>3</sub>     | 1-0.50          | 93                    | 1.30                                |
| Bu <sub>2</sub> Mg | BCl <sub>3</sub>     | 1-1.00          | 80                    | 1.20                                |
| Bu <sub>2</sub> Mg | BCl <sub>3</sub>     | 1-0.50          | 93                    | 1.75                                |
| Bu <sub>2</sub> Mg | BCl <sub>3</sub>     | 1-0.20          | 71                    | 1.50                                |

# New Intercalation cathode: $\text{Mg}_x\text{Mo}_3\text{S}_4$ ( $0 < x < 1$ )

Chevreil phase cathode ( $\text{Mo}_6\text{S}_8$ ) in  $\text{Mg}(\text{AlCl}_2\text{BuEt})_2/\text{THF}$  ( $0.25 \text{ mol L}^{-1}$ ) electrolyte solution where reversible intercalation of  $\text{Mg}^{2+}$  occur



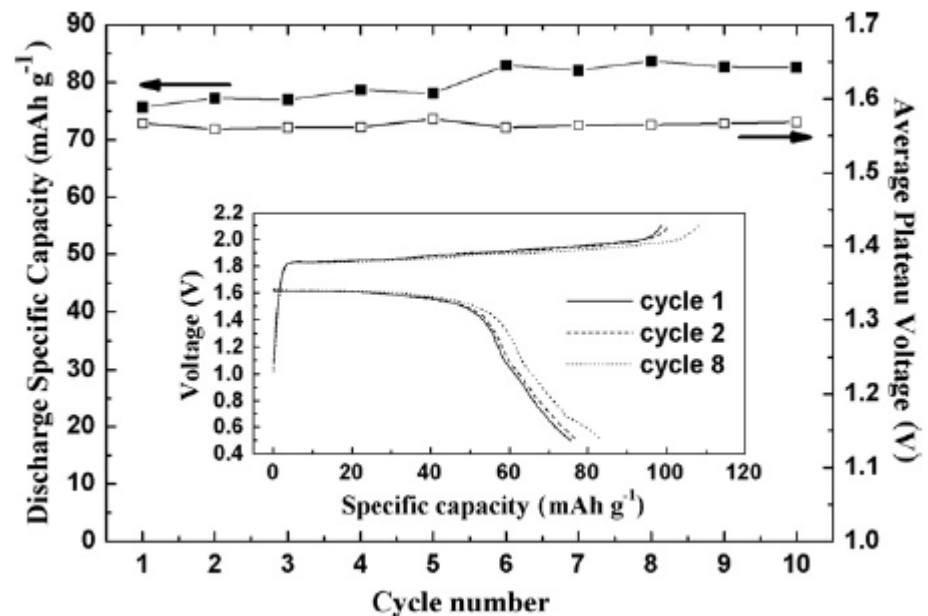
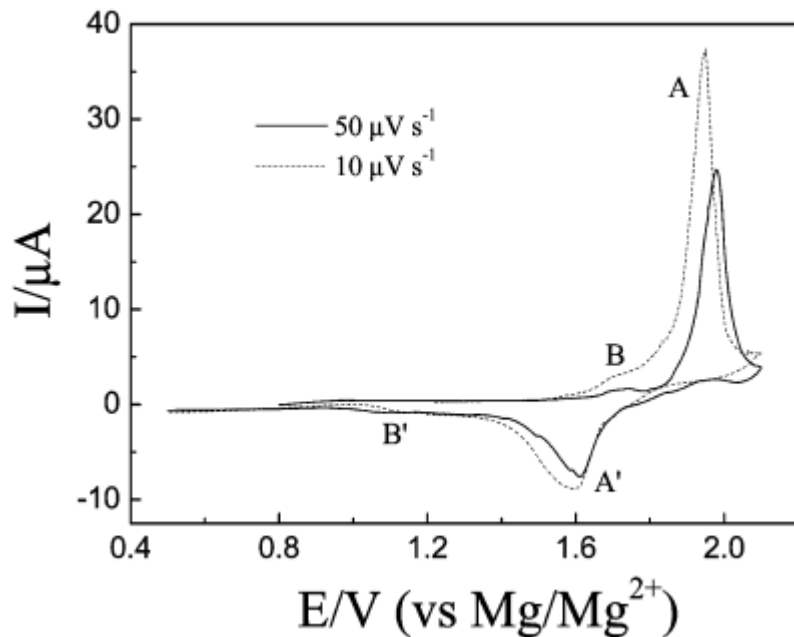
**Maximum charge capacity  $122 \text{ mA h g}^{-1} > 1000$  cycles**  
**Practical energy density  $\sim 60 \text{ Wh kg}^{-1}$**

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

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

# Mesoporous $\text{Mg}_{1.03}\text{Mn}_{0.97}\text{SiO}_4$ cathode

Mesoporous  $\text{Mg}_{1.03}\text{Mn}_{0.97}\text{SiO}_4$  synthesized by sol-gel route shows reversible intercalation of  $\text{Mg}^{2+}$  using  $\text{Mg}(\text{AlCl}_2\text{BuEt})_2/\text{THF}$  ( $0.25 \text{ mol L}^{-1}$ ) electrolyte



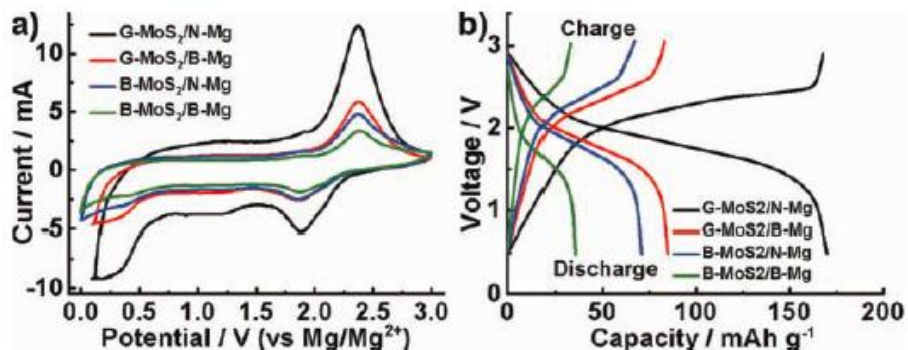
The reversible capacity  $\sim 80 \text{ mAhg}^{-1}$  up to 80 cycles

Nuli et al. *J.Phys. Chem.C.*, 113, (2009), 594-97

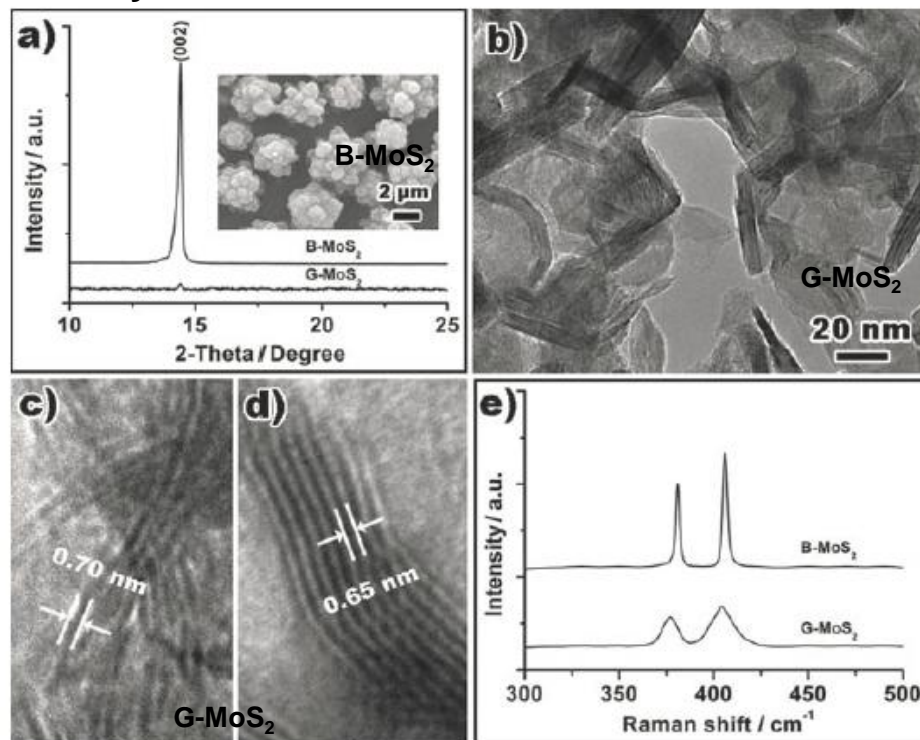
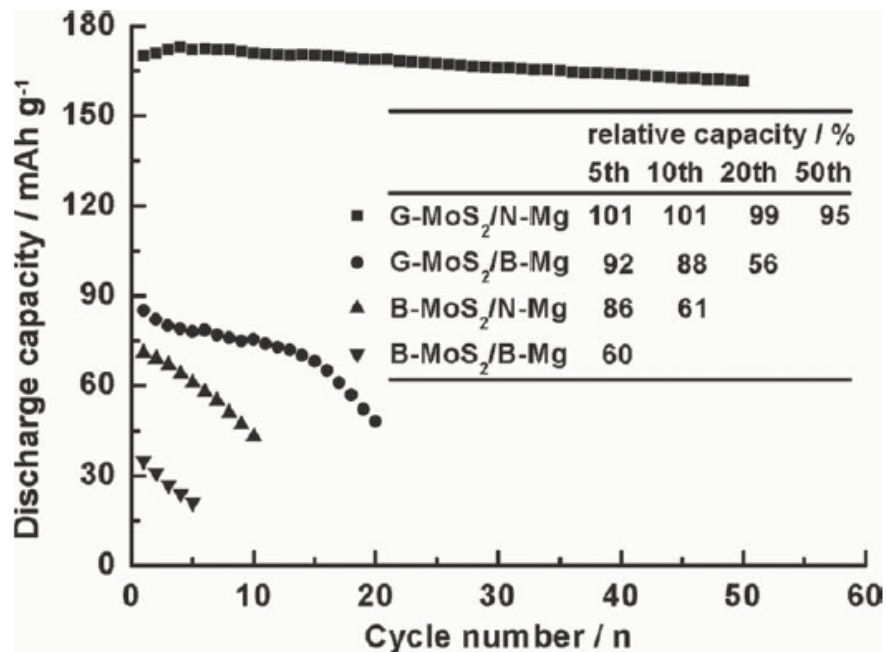
Feng et al. *J. Power* 184, (2008), 604-09



# Graphene like MoS<sub>2</sub> cathode and nano-Mg anode shows improved reversible capacity

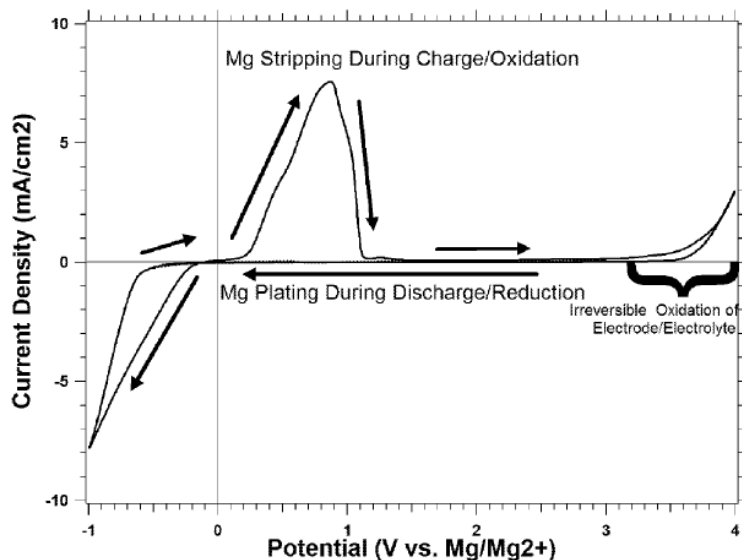


The combination of **G-MoS<sub>2</sub>** cathode and **N-Mg** anode has achieved operating voltage of 1.8 V and a 1<sup>st</sup> discharge capacity of 170 mAhg<sup>-1</sup> (95% is kept after 50 discharge – charge cycles) in Mg(AlCl<sub>3</sub>Bu)<sub>2</sub> electrolyte



# 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



## Pellion Technologies

PhMgCl : AlCl<sub>3</sub> = 2:1 (~ 3 V electrolyte developed by Aurbach *et al.*)

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

Carbon sheet shows the highest stability ~ 3 V

Need for improvement

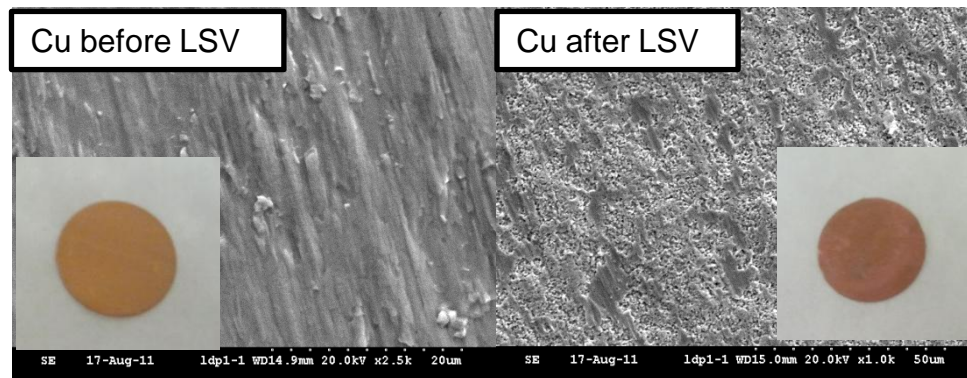
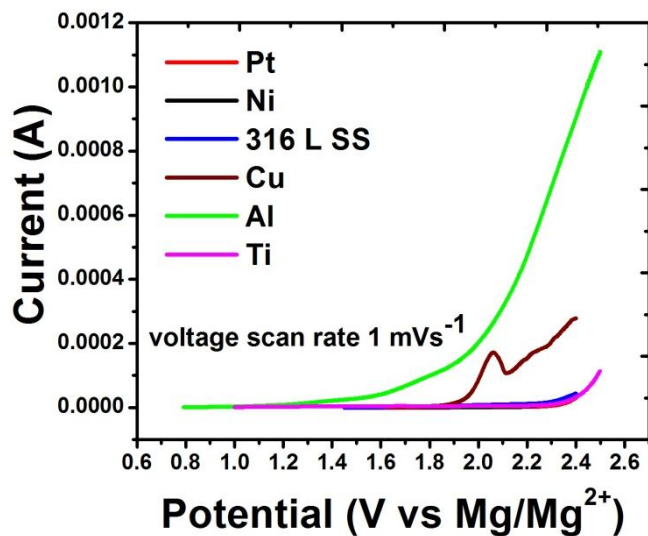
R. E. Doe, G. E. Blomgren, and K. A. Persson, "RECHARGEABLE MAGNESIUM ION CELL COMPONENTS AND ASSEMBLY," United States Patent, 2011

# Results and Accomplishments

# **Analysis of current collectors**

# Current collectors in $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/0.25 \text{ M THF}$ electrolyte

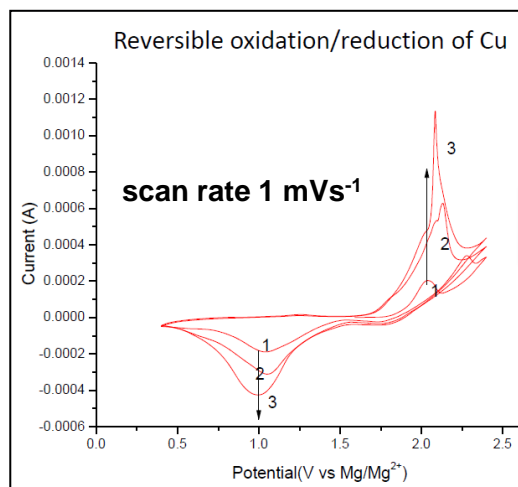
LSV on Cu, Ni, Al, Ti, 316 L SS and Pt.



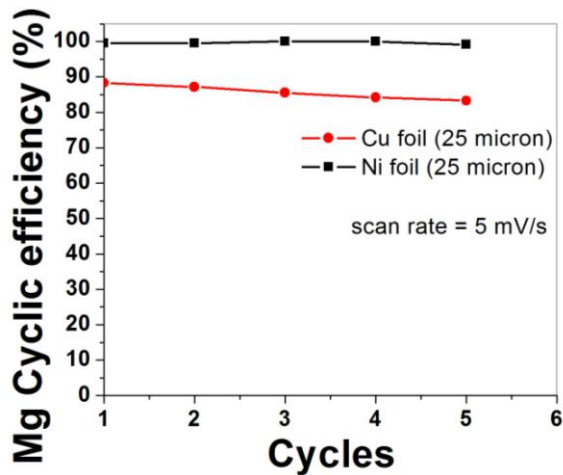
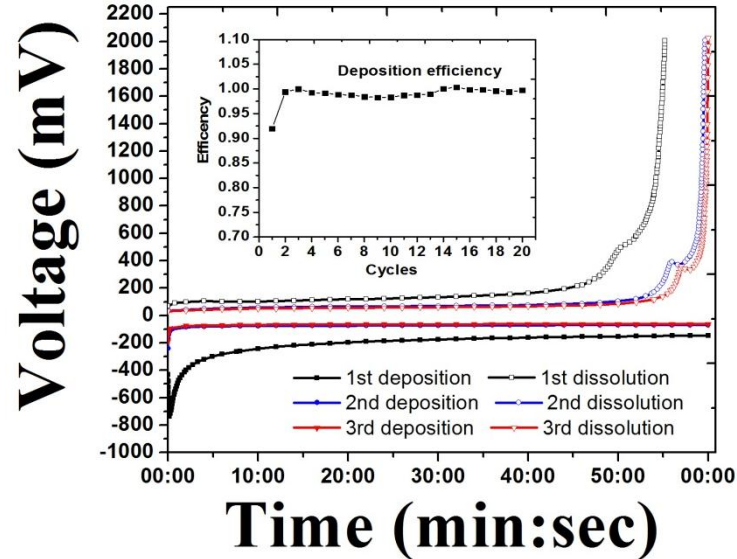
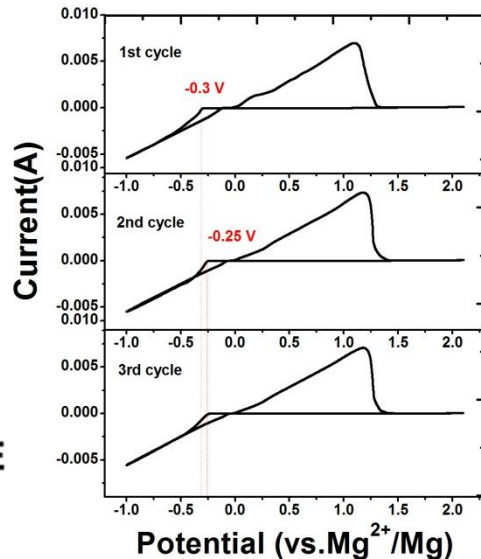
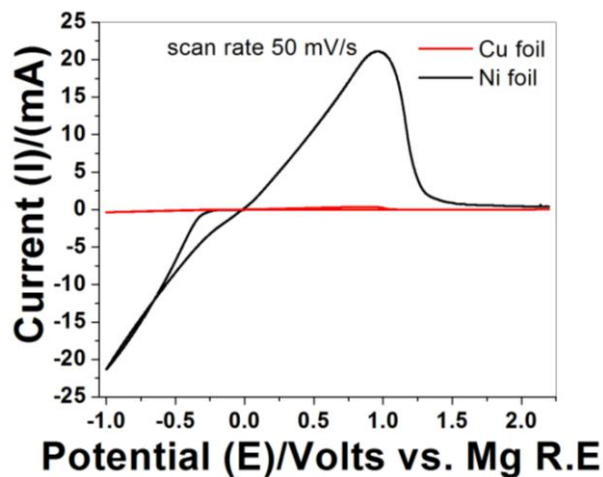
**Anodic stability of the current collectors (Cu, Ni, Al, Ti, 316L SS, and Pt) was tested in  $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/\text{THF}$  electrolyte**

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

***Commonly used current carriers do not work for Mg!!***

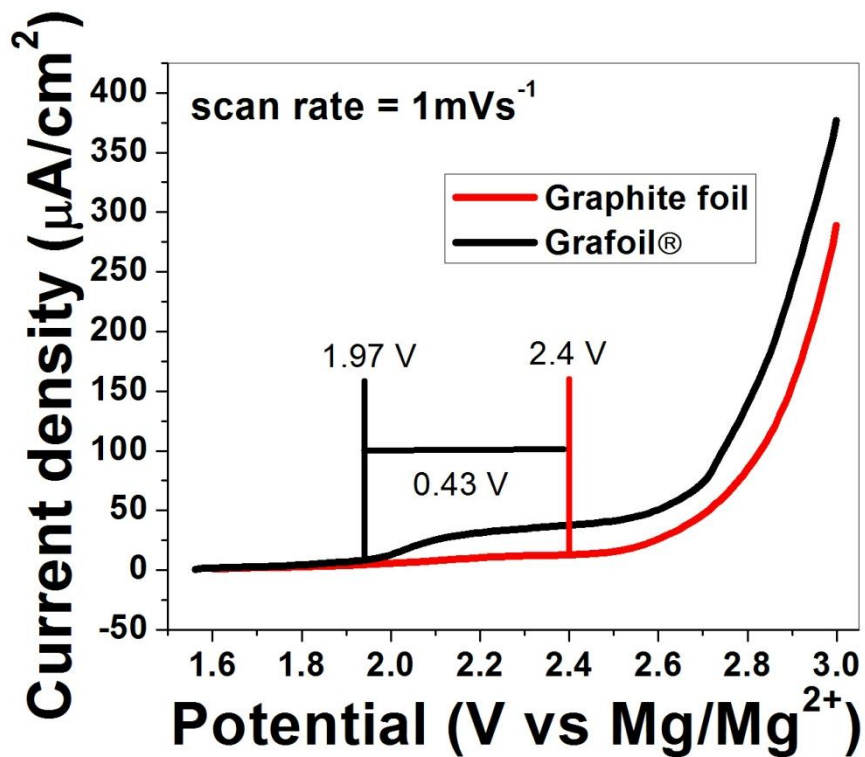


# Current collectors in $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/0.25 \text{ M THF}$ electrolyte



**Ni is a good choice as current collector with excellent stability and high deposition/dissolution efficiency**

# Carbon based Current collectors in $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/0.25 \text{ M THF}$ electrolyte



**Anodic stability of graphite foil is 0.43 V higher when compared to Grafoil®**

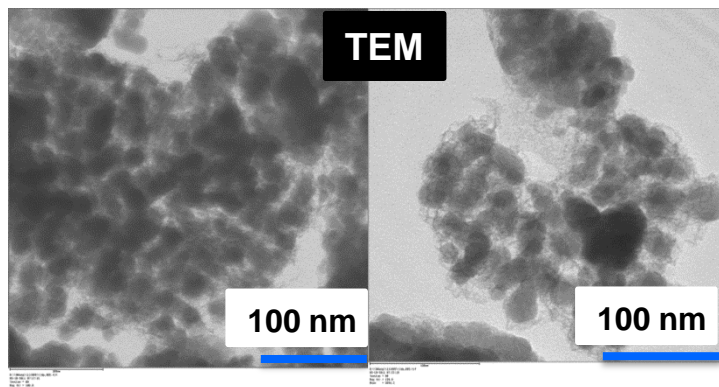
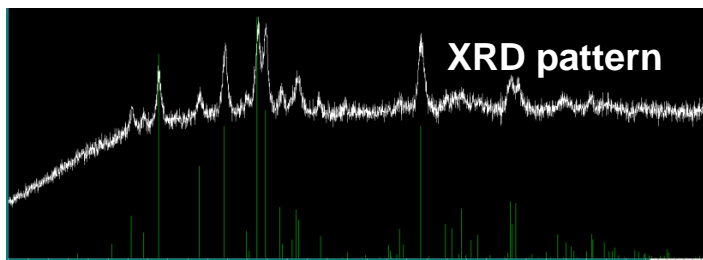
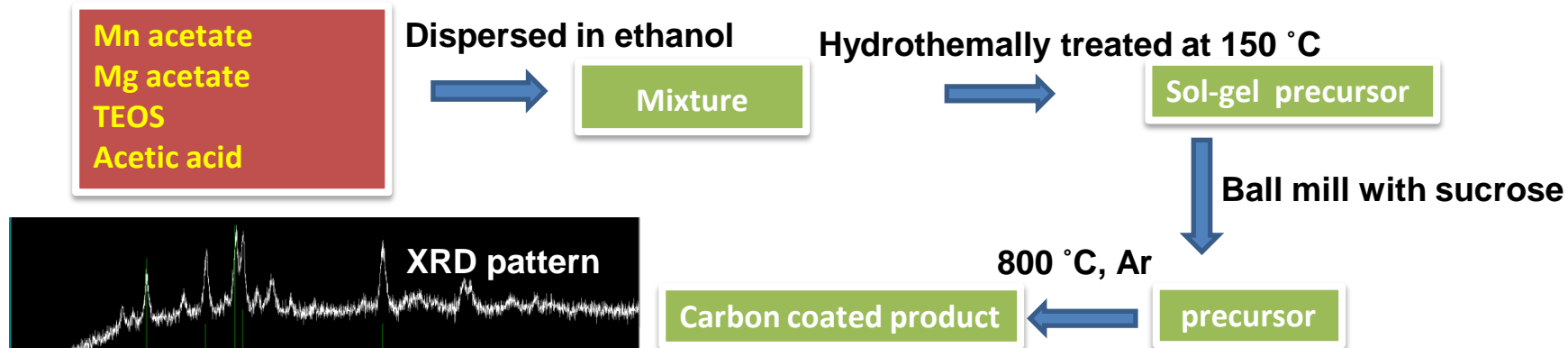
**Graphite foil is an ideal candidate for current collector**

| Cycles        | Scan between OCP to 3 V | Anodic stability limit ( $I > 10 \mu\text{Acm}^{-2}$ ) |
|---------------|-------------------------|--|
| Graphite foil | + ive scan              | 2.4  |
| Grafoil®      | + ive scan              | 1.97   |

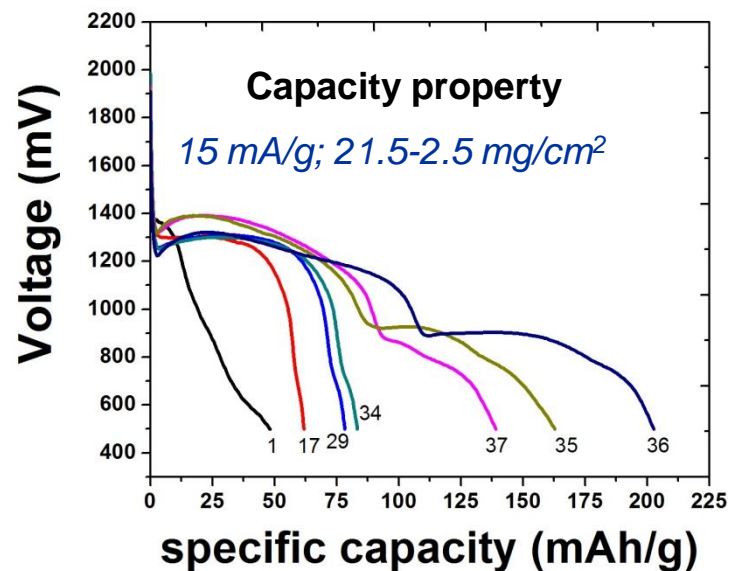
# Development of new cathodes



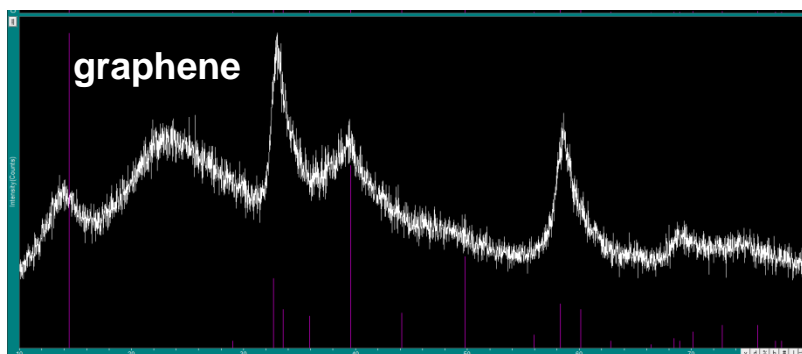
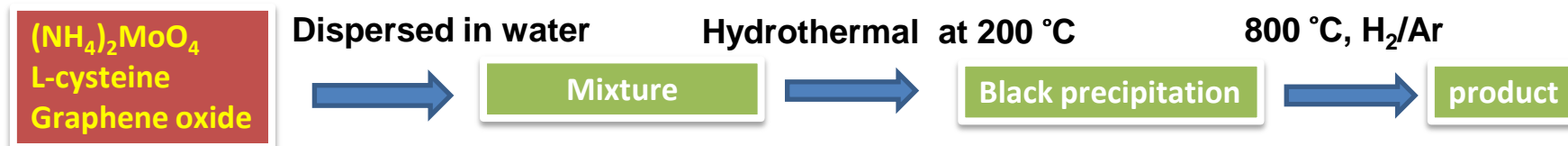
# Hydrothermal assisted sol-gel synthesis of $\text{MgMnSiO}_4$



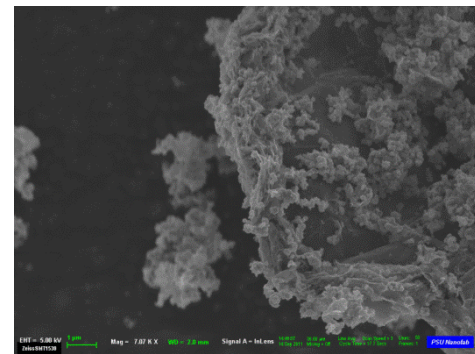
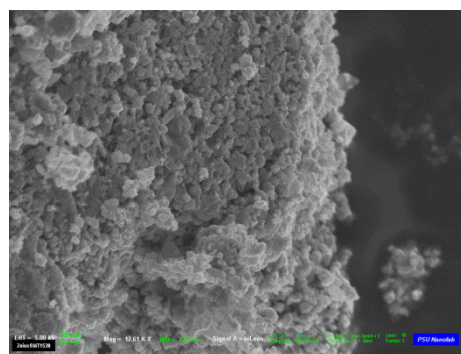
Nanosized carbon coated  $\text{MgMnSiO}_4$  particles was synthesized, characterized and electrochemically tested



# MoS<sub>2</sub>/Graphene composite



XRD pattern



SEM images

Nanosized MoS<sub>2</sub>/G composite was synthesized, characterized and electrochemically tested

# Synthesis and Galvanostatic cycling of Mg compound

Synthesized by Pechini's Route,

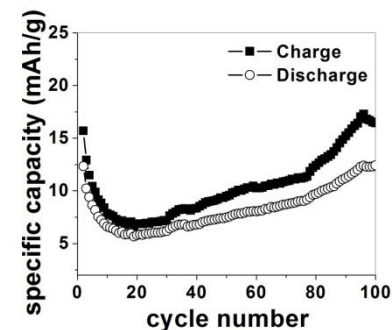
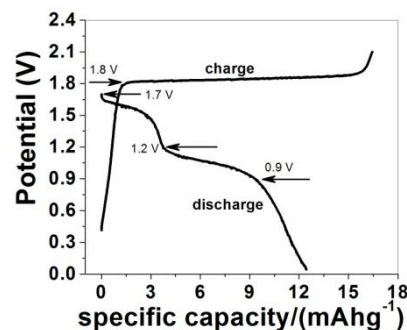
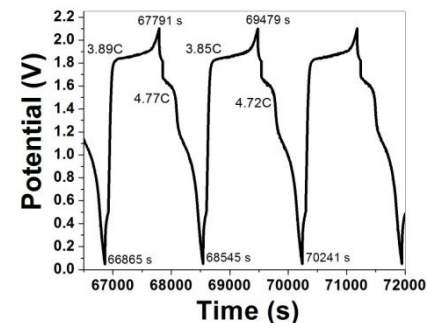
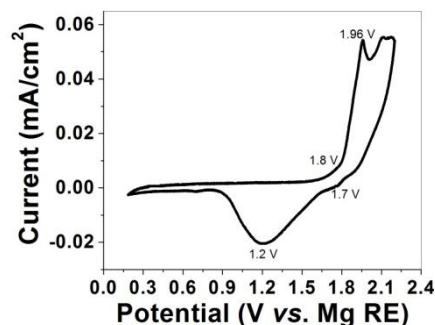
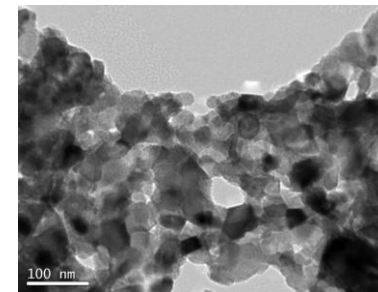
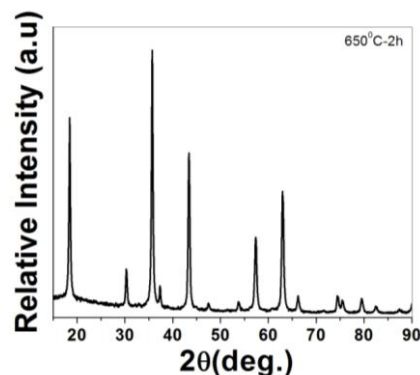
TEM shows ~ 50 nm particles

Mg<sup>2+</sup> intercalation occur at two different voltages ~ 1.7 V and 1.2 V (cyclic voltammogram)

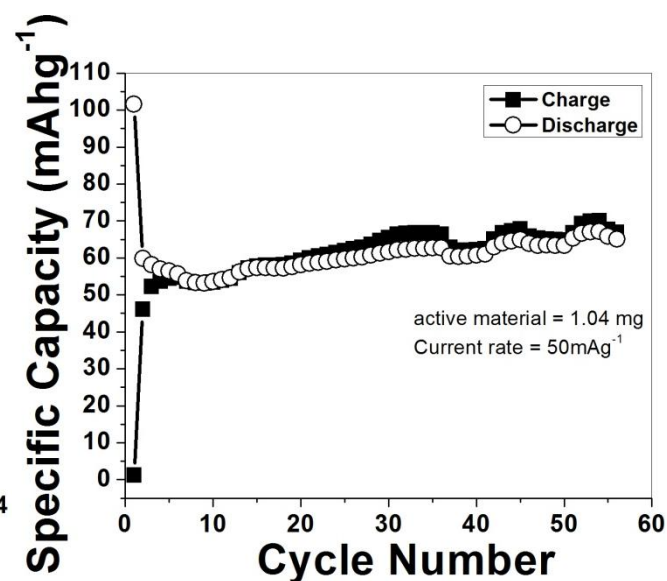
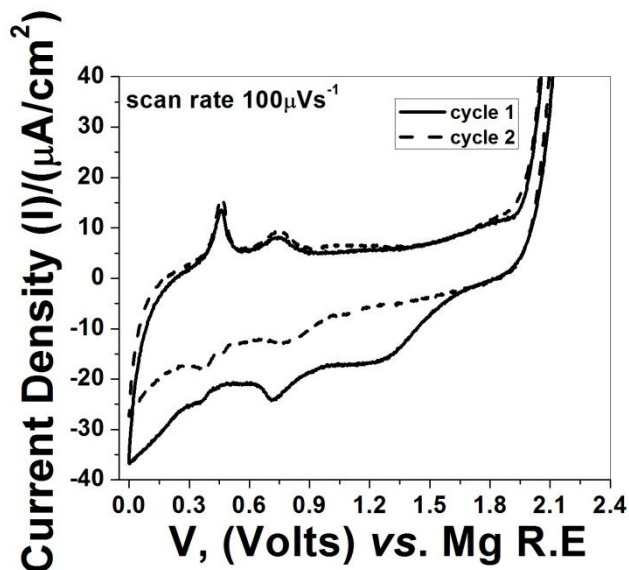
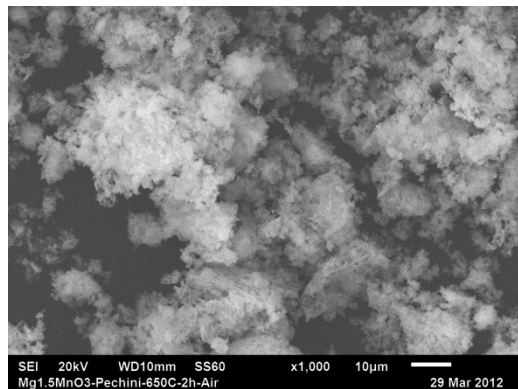
Maximum charge and discharge capacity at 2C rate ~ 18 mAhg<sup>-1</sup> and ~ 15 mAhg<sup>-1</sup> respectively

Sp. Capacity increases with increasing cycle number

Structural refinement needed



# Galvanostatic cyclic data of Mg compound



Raw powder prepared by Pechini's route and heated at  $650\text{ }^{\circ}\text{C}$  for 2 h

SEM shows the uniform sub-micron size spherical particles

Redox peaks: cathodic  $\sim 0.45\text{ V}$  and  $0.75\text{ V}$  and  
anodic  $\sim 0.71\text{ V}$  and  $\sim 0.37\text{ V}$

Max. charge & discharge capacity  $\sim 70\text{ mAhg}^{-1}$  and  $67\text{ mAhg}^{-1}$  (C/2 rate)

# Development of new anodes

# Theoretical sp. capacity of a new Mg compound is 26% more than pure Mg

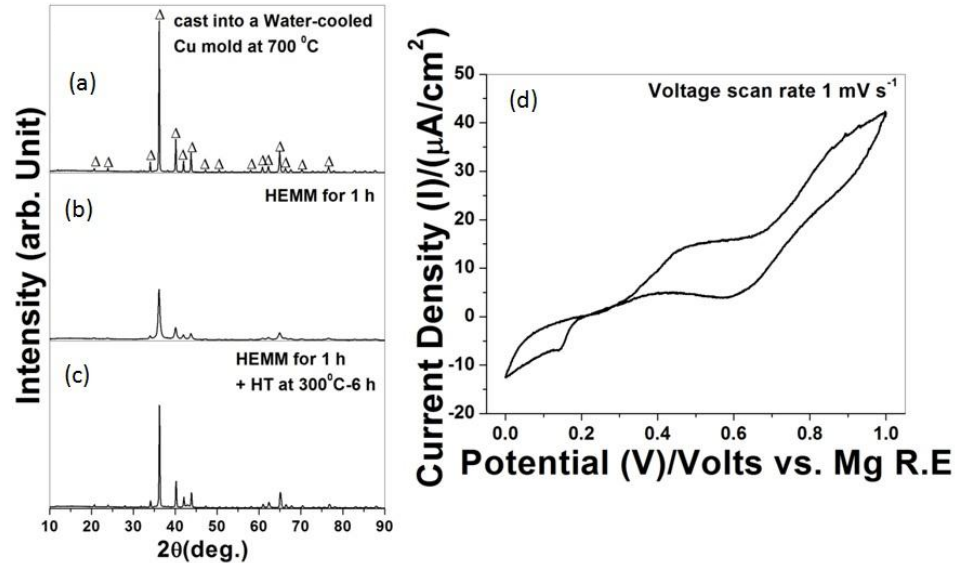
## Rapid Solidification Processing (RSP)

Stoichiometric amount of elemental shots melted in a steel crucible at 700 °C and cast into water-cooled Cu mold

Powder XRD-patterns confirm the formation of desired phase

Sample subjected to ball milling for a duration of 1 h

Ball-milled powder characterized by XRD to confirm presence of desired phase. Final powder was heated at 300° C -6 h and thereafter used for electrode preparations



Cyclic voltammogram shows material is active

During charging Mg leaves the parent structure (Mg de-alloying occurs ~ 0.45 V), further Mg de-alloying occur at ~ 0.85 V)

During discharge cycle Mg<sup>2+</sup> alloying occurs at ~-0.6 V and at ~ 0.12 V

Plans in place to form thin films (~ 50 nm) to test the intrinsic cycling capacity

|             | Theoretical Specific Capacity | Percent Improvement |
|-------------|-------------------------------|---------------------|
| Pure Mg     | 2233 Ah kg <sup>-1</sup>      | <b>26%</b>          |
| Mg compound | 2819 Ah kg <sup>-1</sup>      |                     |

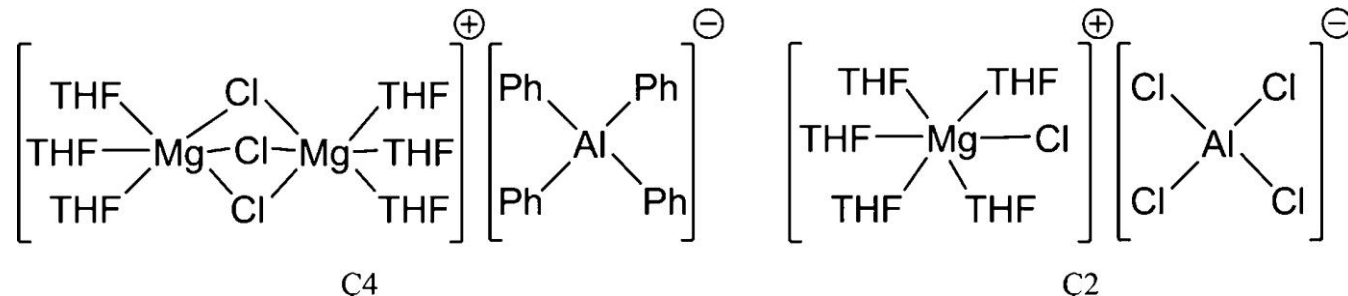
# **Development and analysis of novel non-aqueous electrolytes**

# Goals: Development of Electrolytes

- Identify and develop novel non-aqueous organic liquid as well as ionic liquid based electrolytes with potential window ( $\sim 4$  V) than state of the art electrolyte (maximum potential window  $\sim 3$  V)
- Use of non-flammable solvents for electrolytes
- Excellent cyclability of Mg dissolution/deposition process
- No side reactions



# State of the art in Electrolytes for Mg battery



- The equilibrium species are results of transmetallation reaction in this system
- Rapid ligand exchange between the Al and Mg core allows the reversible deposition and dissolution of Mg

## Drawbacks

- THF is highly flammable and difficult to handle (Safety issues)
- Potential window needs to be increased for next generation of Mg Batteries

# **Development of Organometal based Non-aqueous Mg Electrolytes**

# **Development of 1<sup>st</sup> generation Mg(AlCl<sub>2</sub>BuEt)<sub>2</sub>/Tetrahydrofuran (0.25 mol L<sup>-1</sup>) non-aqueous liquid electrolyte**

**Bu<sub>2</sub>Mg (1 mol L<sup>-1</sup> in heptane) + AlCl<sub>2</sub>Et (1 mol L<sup>-1</sup> 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**

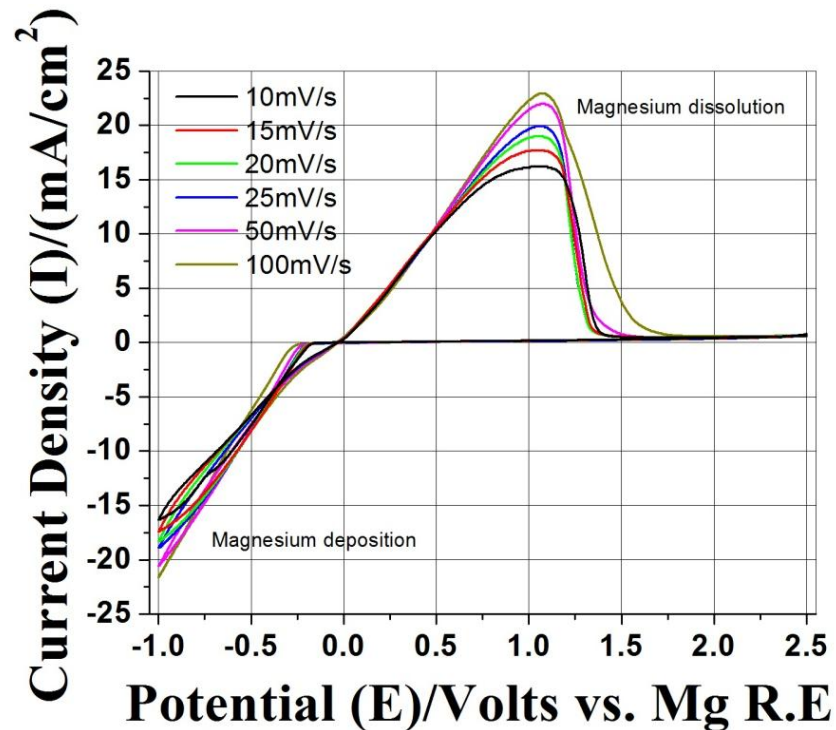
**Mg can be electrochemically deposited and  
dissolved reversibly from this solution**

# Successfully synthesized $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$ / (0.25 M THF) based 1<sup>st</sup> generation non-aqueous electrolyte (potential window ~ 2.1 V)

**Mg/Mg<sup>2+</sup> deposition/dissolution occurs within the electrochemical potential window of ~ 2V indicative of good electrolyte function as expected**

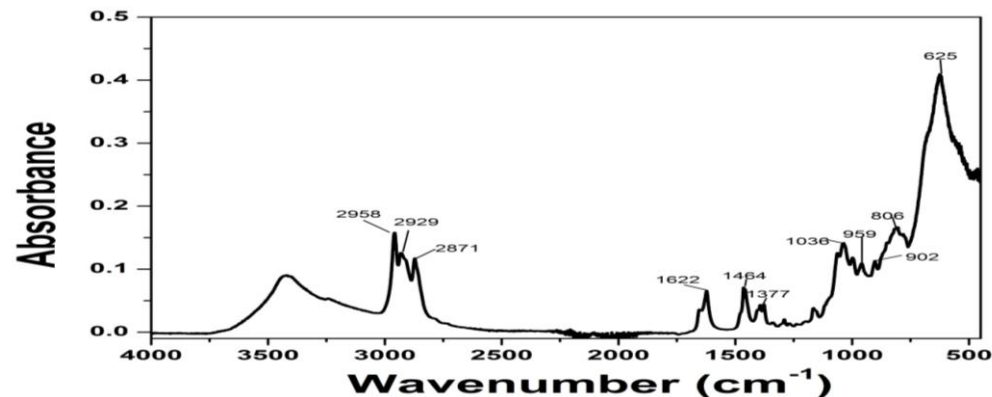
| Scan rate (mV/s) | Onset deposition potential (V) | Anodic stripping peak potential (V) | Mg cycling efficiency (%) |
|------------------|--------------------------------|-------------------------------------|---------------------------|
| 10               | -0.170                         | 1.006                               | 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 |
|------------------------|--------------------------|-----------------|-----------------------|-------------------------------------|
| $\text{Bu}_2\text{Mg}$ | $\text{AlCl}_2\text{Et}$ | 1-2.00          | 95                    | 2.10                                |



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

# Analysis of $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$ complex salt by FTIR and NMR



FTIR measurement was conducted using a Nicolet Model 6700 spectrometer

C-H stretch at 3000-2875  $\text{cm}^{-1}$  (alkyl groups/ alkanes)  
 $\text{CH}_2$  bending absorption at 1464  $\text{cm}^{-1}$  and  $\text{CH}_3$  bending at 1379  $\text{cm}^{-1}$   
 Mg-Cl bond  $\sim$  625  $\text{cm}^{-1}$

NMR spectra acquired using Bruker® 700 MHz NMR spectrometer

For NMR analysis  $\sim$  5 mg  $\text{Mg}(\text{AlCl}_2\text{BuEt})_2$  powder sample was dissolved into 0.5 ml deuterated THF ( $\text{d}_8$ ) solution

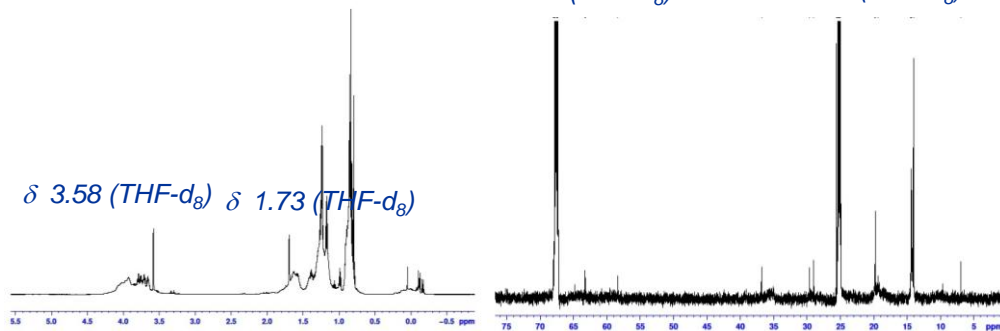
Chemical shifts of the alkyl function groups n-butyl:  
 $^1\text{H}$   $\delta$  -0.59, 0.9, 1.29, 1.57  
 sec-butyl:  $^1\text{H}$   $\delta$  -0.3, 0.99, 1.59, 1.67

Group of peaks observe due to spin-spin coupling of neighboring protons

Chemical shifts of the alkyl function groups  
 n-butyl:  $^{13}\text{C}$   $\delta$  7.98, 14.4, 32.29, 33.83  
 sec-butyl:  $^{13}\text{C}$   $\delta$  17.4, 20.63, 22.5, 34.11

$\delta$  67.57 (THF- $\text{d}_8$ )       $\delta$  25.37 (THF- $\text{d}_8$ )

$\delta$  3.58 (THF- $\text{d}_8$ )     $\delta$  1.73 (THF- $\text{d}_8$ )



**Proton ( $^1\text{H}$ ) NMR**

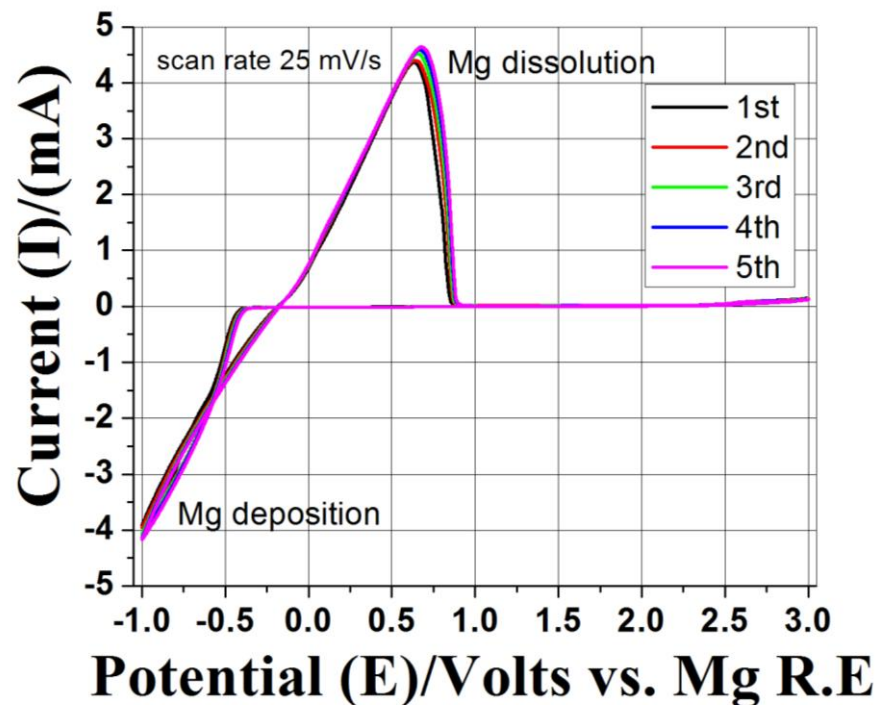
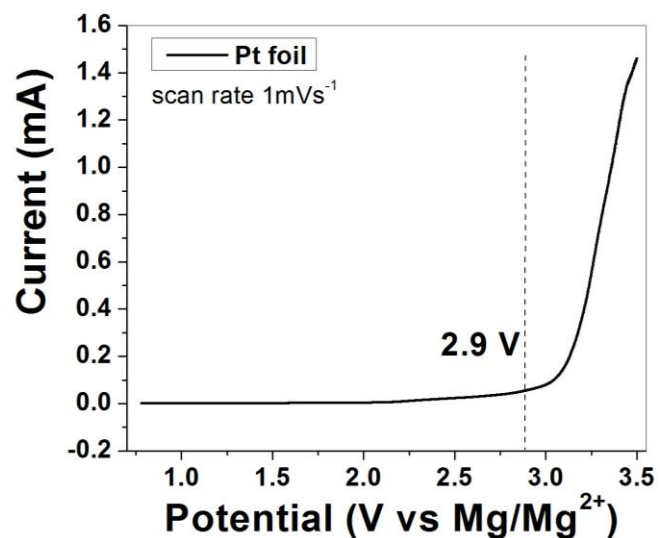
**Carbon ( $^{13}\text{C}$ ) NMR**

# 2(PhMgCl)-AlCl<sub>3</sub> based 2<sup>nd</sup> generation non-aqueous electrolyte (potential window ~ 3 V)

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

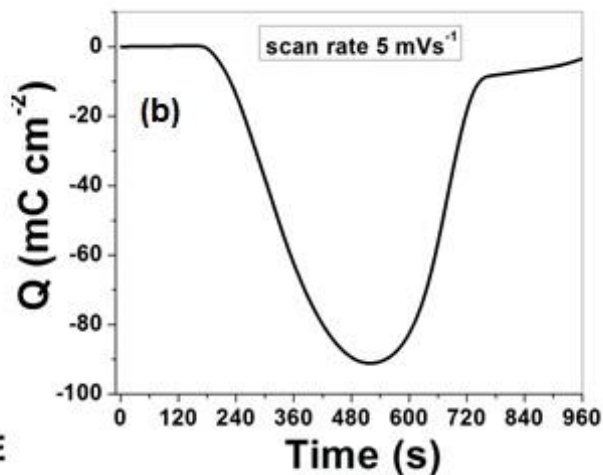
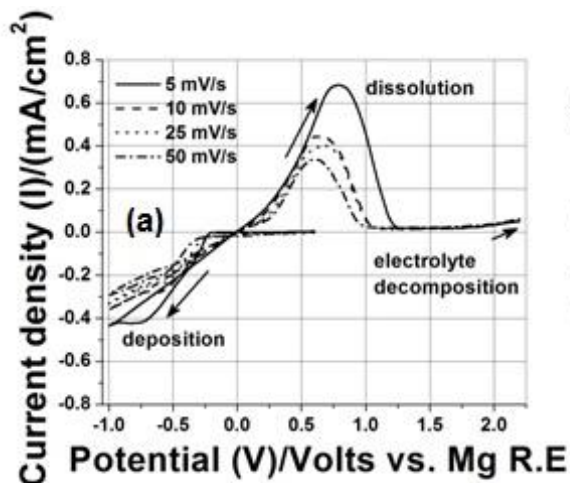
Coulombic efficiency ~ 90%

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                      |

# Developed novel electrolytes based on the amido metal-Mg halide complexes of Mg in 1.0 M THF



Transmetalation with a Lewis acid ( $\text{AlCl}_3$ ) will be performed to improve the anodic stability

The present Lewis base holds considerable promise and have the potential for developing high voltage ( $\sim 4$  V) next generation electrolytes

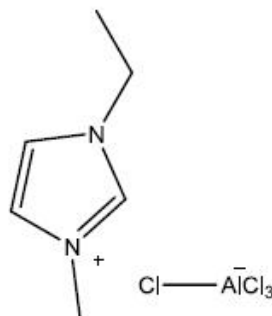
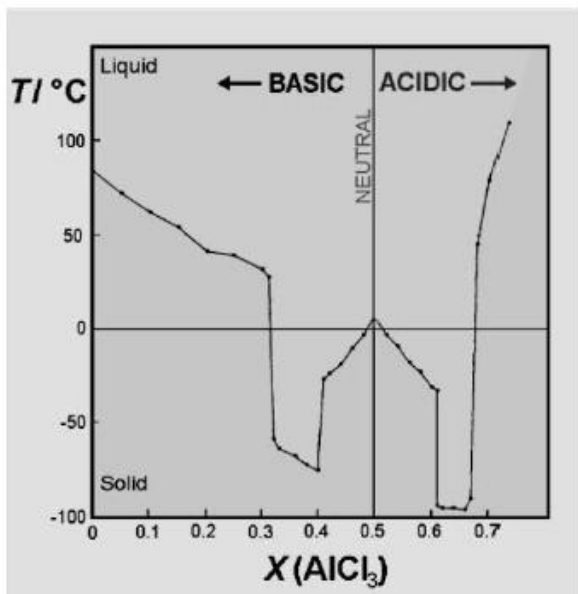
| Scan rate (mV/s) | Onset deposition potential (V) | Anodic stripping peak potential (V) | Mg cycling efficiency (%) |
|------------------|--------------------------------|-------------------------------------|---------------------------|
| 5                | -0.191                         | 0.682                               | 90.78                     |
| 10               | -0.192                         | 0.693                               | 64.29                     |
| 25               | -0.243                         | 0.686                               | 64.25                     |
| 50               | -0.293                         | 0.645                               | 56.89                     |

Electrochemical window/anodic stability  $\sim 2$  V

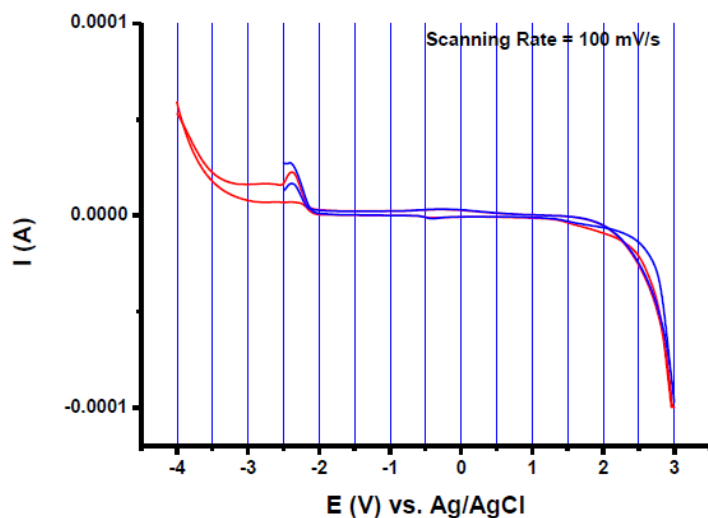
# **Development of Ionic Liquid (IL) based Mg Electrolytes**



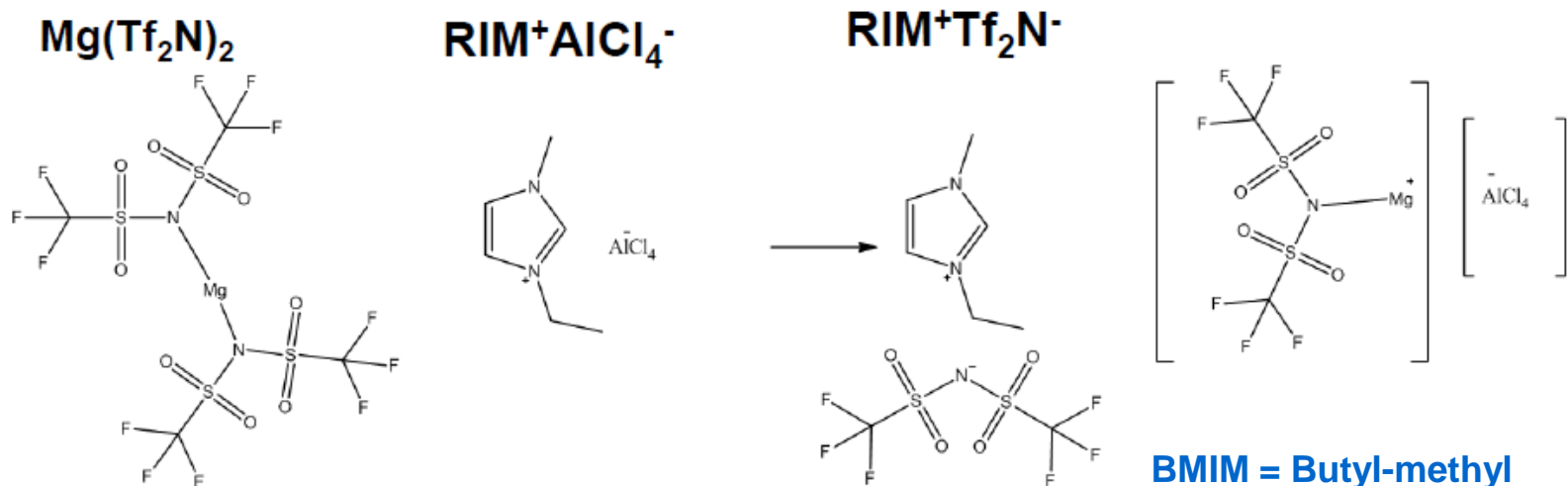
# Approach



- AluminioChlorate based ILs have the potential to perform transmetallation reactions with Mg
- AluminioChlorate can be basic, neutral or acidic ( $\text{AlCl}_3$  conc.)
- Large Potential window (4V)
- Excellent thermal stability ( $> 250\text{ }^\circ\text{C}$ )
- Excellent electrochemical stability



# Approach: IL assisted transmetallation reaction



**BMIM = Butyl-methyl imidazolium Chloroaluminate**  
(If it is an  $\text{AlCl}_4^-$  anion)

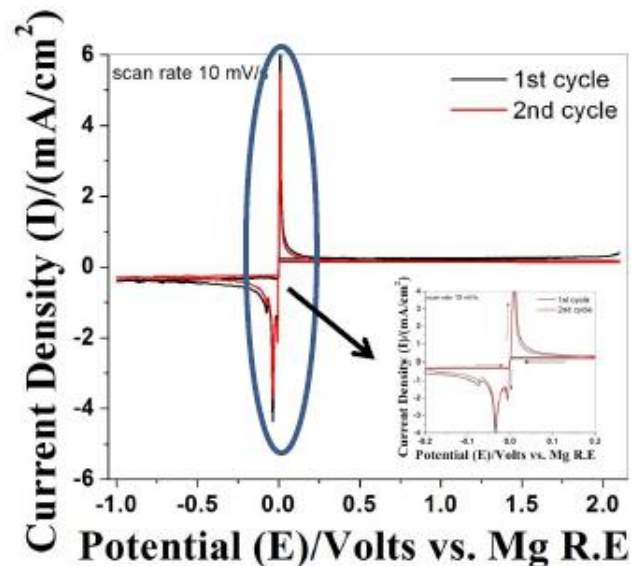
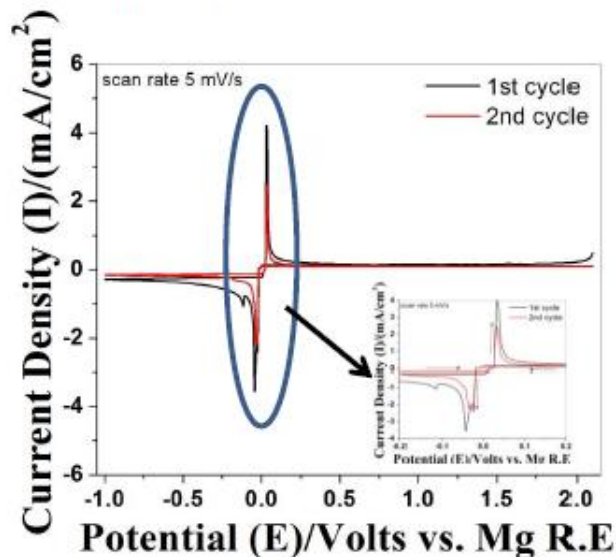
**$\text{Mg}(\text{Tf}_2\text{N})_2$  = Magnesium salt of Bis-trifluorosulfonamide**

- Ionic nature of ILs promotes transmetallation reaction
- Currently several types of ILs/solvent mixtures are being evaluated

# Cyclic voltammetry of Mg (TF<sub>2</sub>N)<sub>2</sub> in THF

Electrolyte prepared by dissolving the IL into dry THF (0.25 M<sup>-1</sup>basis )

Cyclic voltammetry conducted in a 3-electrode cell using Pt as W.E. and Mg foil being C.E. and R.E. (potential window of -1 to 2.1 V)

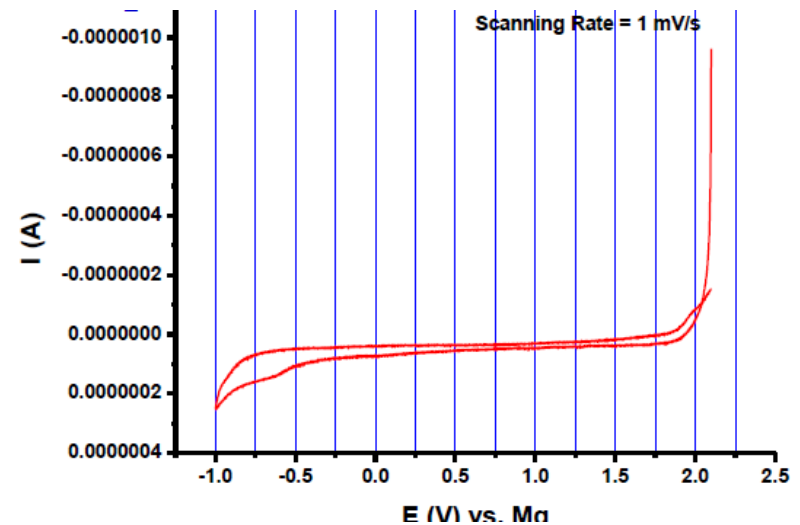
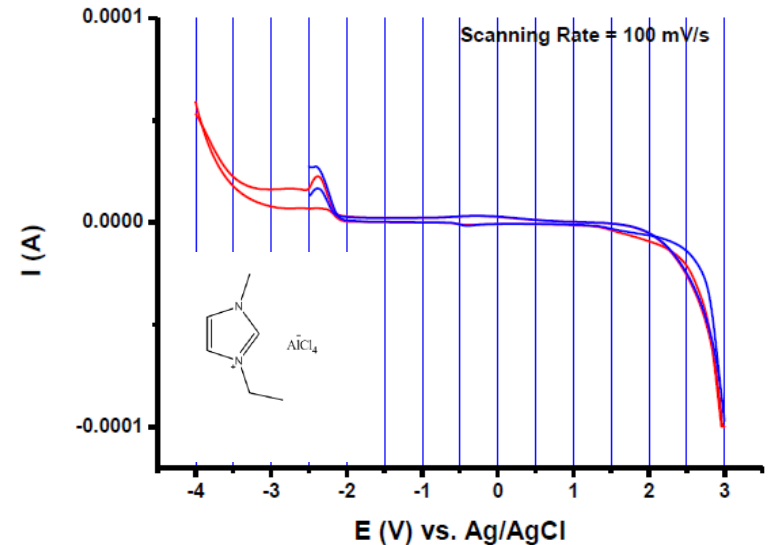


Initial test was performed on Mg (TF<sub>2</sub>N)<sub>2</sub> in THF.

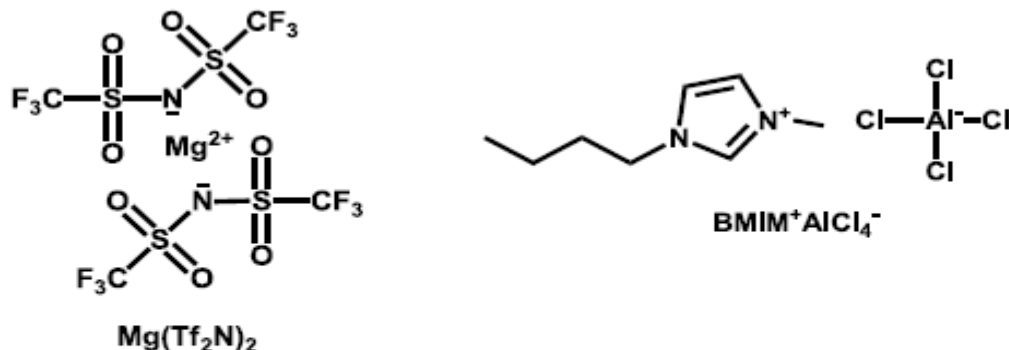
Reversible dissolution/ deposition of Mg was observed

# Results

- **BMIM<sup>+</sup> AlCl<sub>4</sub><sup>-</sup> has a potential window of 4V**
- 
- **No Mg deposition occurs with Mg(TF<sub>2</sub>N)<sub>2</sub> in BMIM TF<sub>2</sub>N ionic liquid**
- **Likely TF<sub>2</sub>N anion in IL binds tightly to the Mg in this system**



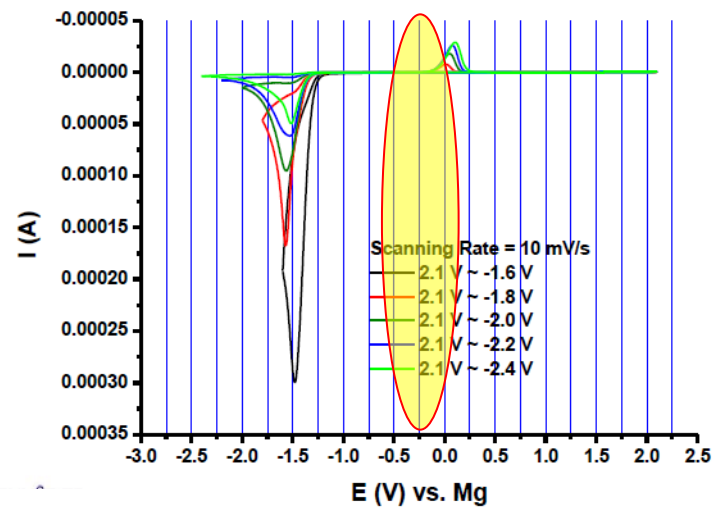
# Assisted transmetalation: Proof of concept



Molar ratio  $\text{Mg}(\text{Tf}_2\text{N})_{20} / \text{BMIM}^+\text{AlCl}_4^- = 1/50$   
 $[\text{Mg}(\text{Tf}_2\text{N})_2]_0 \sim 0.1 \text{ M}$

$[\text{Mg}(\text{TF}_2\text{N})_2] = 0.1 \text{ M}$  in  $\text{BMIM}^+\text{AlCl}_4^-:\text{THF}$  (1:1) shows deposition/dissolution

Solubility of  $\text{Mg}(\text{TF}_2\text{N})_2$  in  $\text{BMIM}^+\text{AlCl}_4^-$  is an issue



# Summary

- **Successfully synthesized  $\text{Mg}(\text{AlCl}_2\text{BuEt})_2/\text{THF}$  ( $0.25 \text{ mol L}^{-1}$ ) based 1<sup>st</sup> 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  $2(\text{PhMgCl})\text{-AlCl}_3$  based 2<sup>nd</sup> generation electrolytes which show electrochemical stability upto 2.9 V vs.  $\text{Mg}/\text{Mg}^{2+}$  Coulombic efficiency close to 90%**
- **Potential new electrolyte identified and will be further developed with potential window ~ 4 V**
- **Cyclic voltammetry of  $\text{Mg}(\text{Tf}_2\text{N})_2/\text{THF}$  IL based electrolyte shows Mg can be reversibly deposited onto the Pt electrode. Further improvements are needed**
- **Showed proof of concept for the assisted transmetallation reaction in  $\text{BMIM}^+\text{AlCl}_4^-$  :THF system**

# Summary

- Pt, Ti, Ni are the potential candidate which remain inert in the electrolyte
- Mg cyclic efficiency on Ni foil is close to 99% whereas Cu is close to 88%
- LSV study using 1<sup>st</sup> generation electrolyte onto commercial graphite foil (Alfa Aesar: 130  $\mu\text{m}$ ) show improved anodic stability ( $\sim 0.43$  V) than Grafoil<sup>®</sup>
- Developed novel Mg-compound by RSP (sp. capacity is 26% better than pure Mg), can act as potent alternative anode for Mg battery system. Cyclic voltammogram of the new Mg-anode shows the redox couple within 0-1 V
- Developed various Mg oxides, sulfides silicate compounds as potential insertion host for Magnesium. Few compounds are indentified as potential candidate where Mg<sup>2+</sup> ion can be reversibly cycled.
- Scope to improve the materials chemistry to reduce irreversible loss, capacity fading and discharge capacity. Attempt will be made to develop the in-situ carbon composite material to improve electronic conductivity and hence sp. capacity further

# Future Work

- Ni and graphite foil 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 and stability of the current collectors for long cycles (> 1000 cycles)
- Explore other novel corrosion resistant Mg-alloys with better sp. capacity than pure Mg as an alternatives for Mg anode system
- Various novel intercalation chemistries in 3-D, porous network will be explored via different synthesis routes (soft template, CVD, PLD, *in-situ* graphene composites etc.) in bulk form to improve Mg<sup>2+</sup> ionic transport, minimize the polarization effect and improve sp. capacity for longer cycles
- Develop novel electrolyte with improved electrochemical stability window (~ 4 V)
- Evaluate other Grignard based systems for generating novel, stable organic electrolytes
- New Lewis acid ionic liquids currently being synthesized will be targeted to have higher solubility for Mg(Tf<sub>2</sub>N)<sub>2</sub>





*"As Knowledge Increases, Wonder Deepens"*

*Charles Morgan; 1894-1958; English writer*

**Thank You For Your Attention**