# The Architectural Diversity of Metal Oxide Nanostructures: An Opportunity for the Rational Optimization of Group II Cation Based Batteries

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# Outline

Advantages and strategy of magnesium batteries

Current state of the art

Challenges of magnesium batteries

Our approach

- cathode
- anode
- electrolyte

Summary

Alternative energy sources may benefit from a well-conceived large scale coupling with appropriately designed secondary batteries.

# Magnesium Batteries

## Appeal of magnesium batteries

| | Mg | Li | Pb |
|---|---|---|---|
| Atomic mass | 24 | 6.9 | 207 |
| Ionic radius, Å | 0.72 | 0.76 | 1.19 |
| Melting point | 650 | 181 | 328 |
| mAh/g | 2205 | 3862 | 259 |
| mAh/cc | 3837 | 2047 | 2926 |
| $/lb | $1.12 | $28 | $1.68 |
| $/kWh | $2.5 | $58 | $31 |

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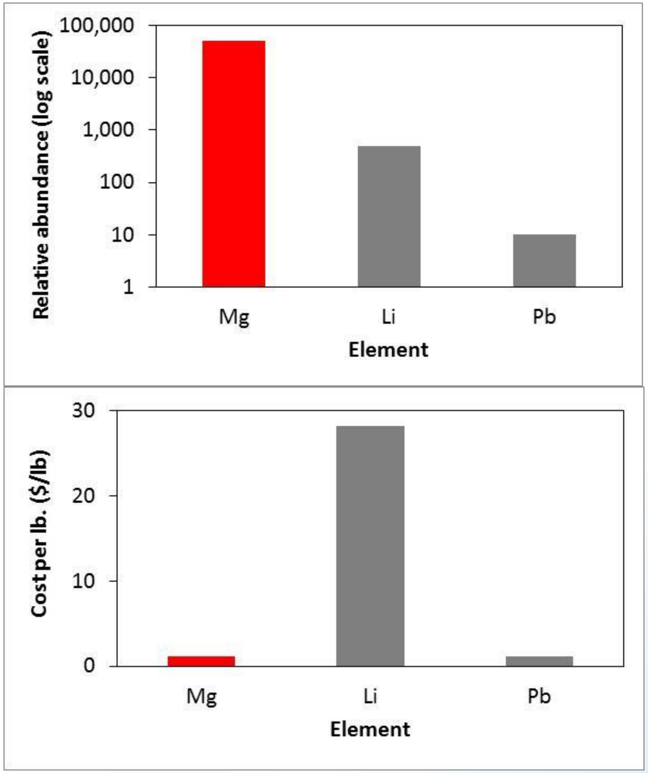
# Strategy

This project targets some of the unique needs of large scale power storage:

1) reduced cost
2) low environmental impact
3) scalability
4) reversibility
5) capacity retention




Utilize earth abundant, low cost elements with minimal environmental impact as battery materials.

Exploit magnesium due to ~1,000X higher natural abundance than lithium and ~5,000X higher abundance than lead.

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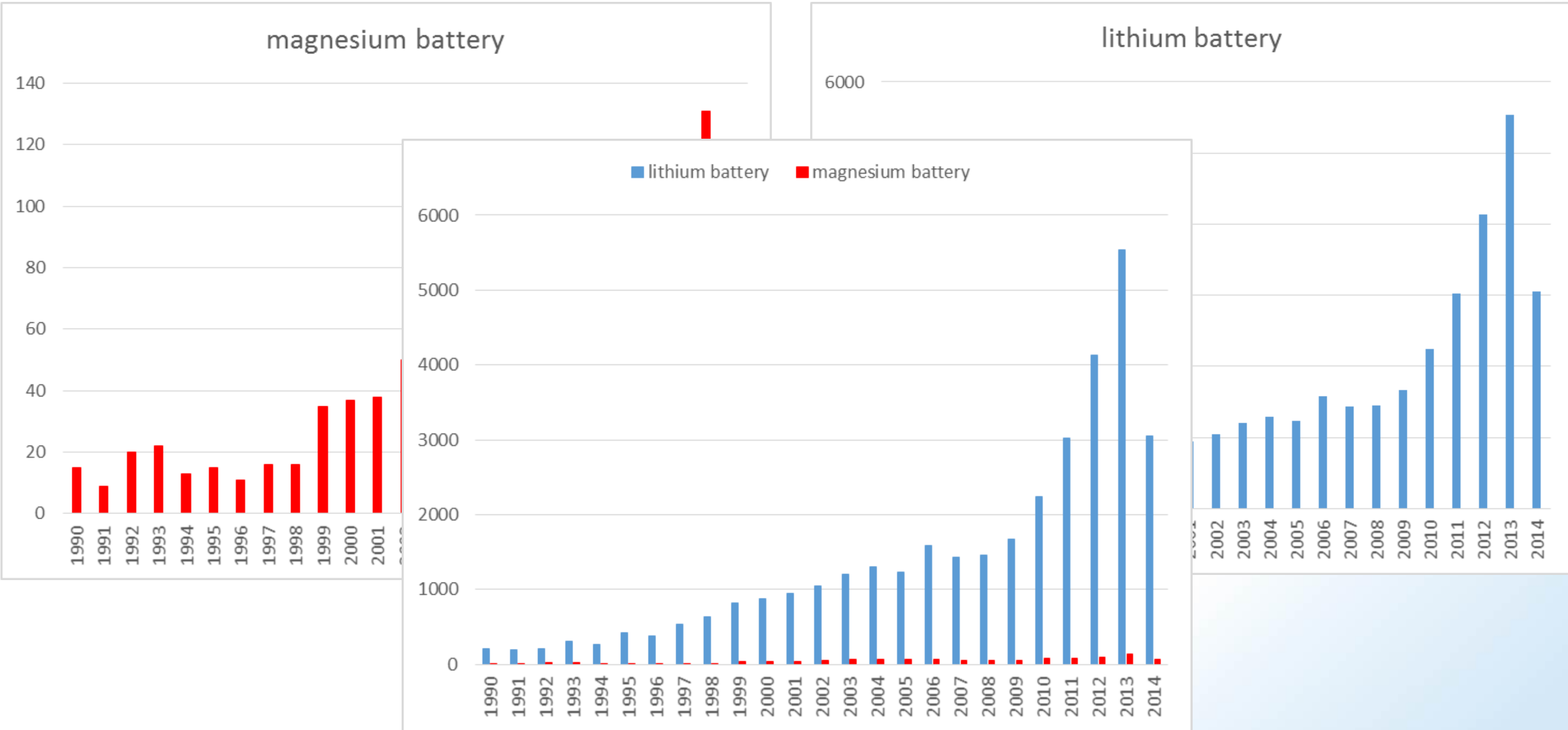
# State of the Art




Magnesium battery research is increasing, yet still in nascent stages

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# Magnesium Batteries

## Challenges with magnesium batteries

Passivation of Mg metal surface

reaction with oxygen, carbon dioxide, organic solvents

$Mg^{2+}$ ions can not migrate through surface film

Reversible plating of Mg requires reactive/corrosive electrolyte salts

For example: Grignard reagents, $Mg(AlCl_2RR')_2$ salts

often highly volatile flammable ether solvents

Migration of $Mg^{2+}$ in a solid host is kinetically slow

limits rate capability of battery systems

D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, *Ener. Envir. Sci.* **2013,** *6(8),* 2265-2279.

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# Approach to Mg Battery System

## The necessity of systems level understanding

Negative Electrode
reactions with Mg

Positive Electrodes
Mn, V

**Interactions**

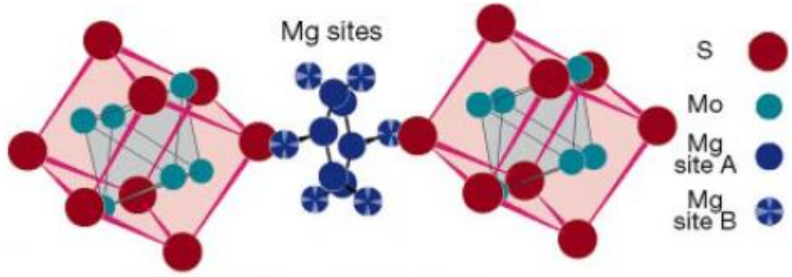
Electrolyte

Liquid, non-corrosive

Electrode- Electrolyte
Interfaces

# Cathode Investigations

## Chevrel Phase $Mo_6T_8$ (T=S or Se)




Cycle Life: Over 1,000 cycles with <10-15% capacity fade [1,2]
Capacity: 100-110 mAh/g [2-4] Voltage: 1-1.5 V [1-4]
Substituting Se for S improves capacity and rate [3,4]

Limitations: Low working voltage and modest capacity

1. D. Aurbach, Y. Gofer, Z. Lu, A. Schechter, O. Chusid, H. Gizbar, Y. Cohen, V. Ashkenazi, M. Moshkovich, R. Turgeman and E. Levi, *J. Power Sources,* **2001,** *97-98,* 28-32.

2. D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi, *Nature,* **2000,** *407(6805),* 724-727.

3. M. Levi, E. Lancri, E. Levi, H. Gizbar, Y. Gofer and D. Aurbach, *Solid State Ionics,* **2005,** *176(19-22),* 1695-1699.

4. G. S. Suresh, M. D. Levi and D. Aurbach, *Electrochim. Acta,* **2008,** *53(11),* 3889-3896.

# Cathode Investigations

## Vanadium oxide ($V_2O_5$)

First report of $V_2O_5$ electrochemistry with Mg, observed 0.5 equivalents $Mg^{2+}$ insertion[1]

Water in aprotic electrolytes helps “shield” the $Mg^{2+}$ ion for easier insertion and deinsertion,[2] increasing capacity to 170 mAh/g

Water in electrolyte forms passivation layers on Mg surface[3]

$V_2O_5$:CB (1:3 ratio) aerogel composite cathode showed ~300 mAh/g up to 35 cycles,[4] with noted change in interlayer spacing


1. J. P. Pereira-Ramos, R. Messina and J. Perichon, *J. Electroanal. Chem. Interfac. Electrochem.*, **1987,** *218(1-2),* 241-249.

2. P. Novak and J. Desilvestro, *J. Electrochem. Soc.,* **1993,** *140(1),* 140-144.

3. L. Yu and X. Zhang, *J. Colloid Interface Sci.,* **2004,** *278(1),* 160-165.

4. D. Imamura, M. Miyayama, M. Hibino and T. Kudo, *J. Electrochem. Soc.,* **2003,** *150(6),* A753.




M. Huie, D. Bock, E. Takeuchi, K. Takeuchi. *Coord. Chem. Rev. Submitted for publication, invited.*

# Cathode: $Mg_{0.1}V_2O_y \bullet 1.8H_2O$

## Material synthesis

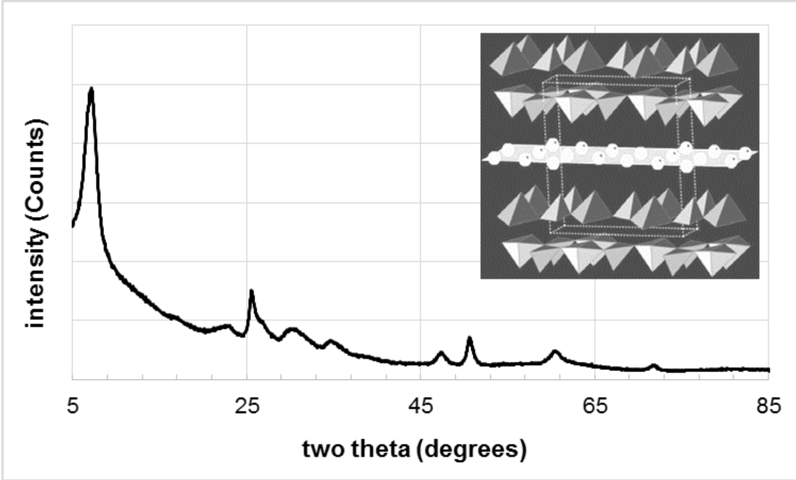
Two-Step Synthesis

Ion exchange

↓

Sol gel reaction

$Mg_xV_2O_y$ was prepared by a two-step scalable process where the first step was a ion exchange reaction of $MgV_2O_6$ followed by a sol gel reaction.




X-ray powder diffraction pattern of $Mg_xV_2O_5$ with schematic of $Mg_xV_2O_5$ structure

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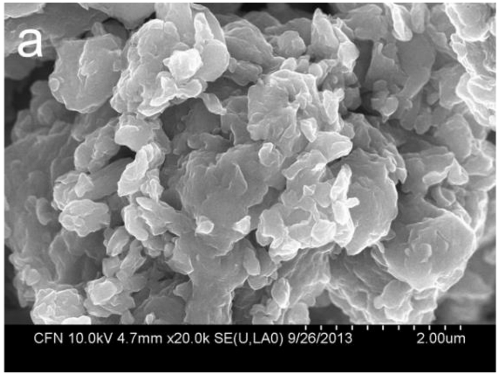
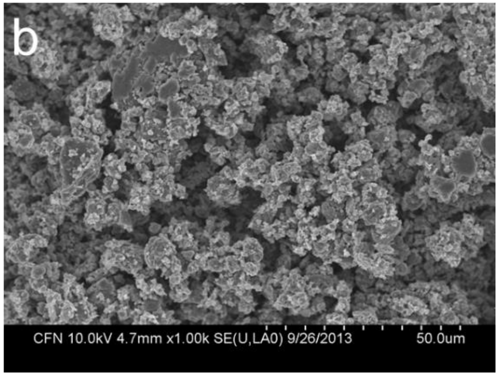
S. Lee, R. DiLeo, A. Marschilok, K. Takeuchi, E. Takeuchi, *ECS Electrochem. Lett.*, **2014**, *3(8)*, A87-A90.

# Cathode: $Mg_{0.1}V_2O_y$•$1.8H_2O$

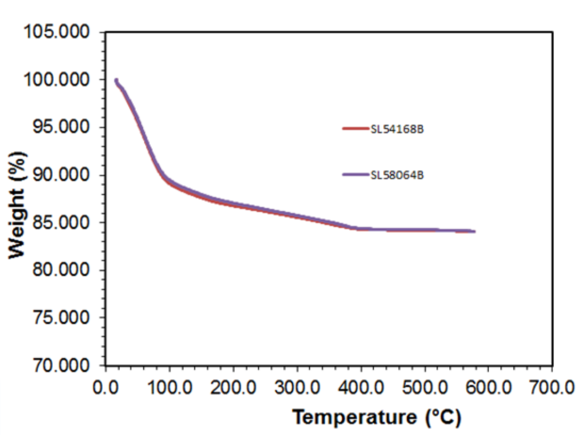
## Material characterization

ICP-OES used to determine Mg/V ratio of 0.05/1.0
TGA used to determine water content




(a) 20,000X (b) 1,000X.
Scanning electron micrographs of $Mg_{0.1}V_2O_5$•$1.8H_2O$




TGA of $Mg_{0.1}V_2O_5$ •$1.8H_2O$

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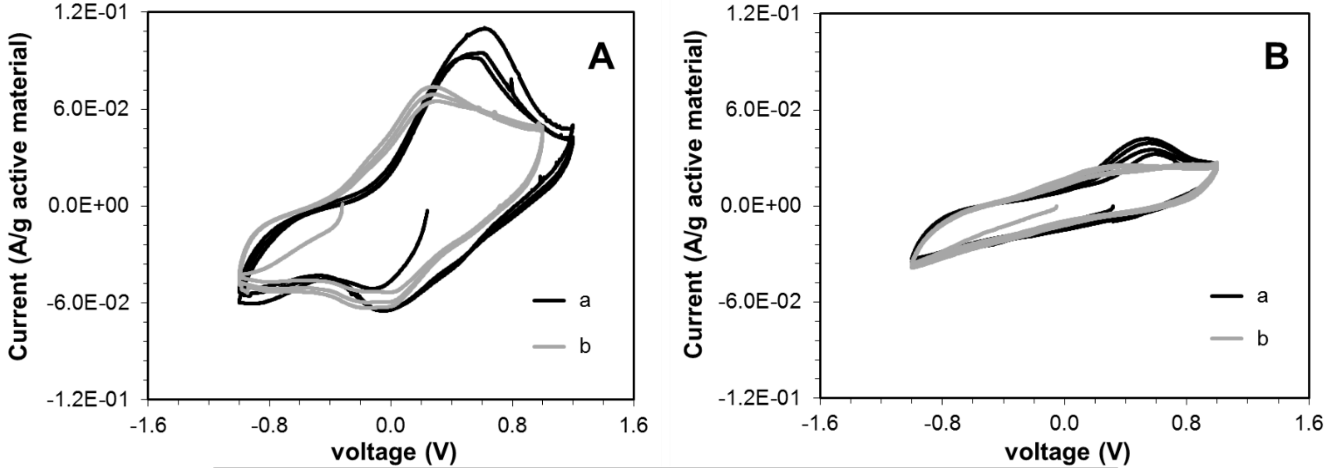
# Cathode: $Mg_{0.1}V_2O_y$•$1.8H_2O$

## Results of voltammetry




0.1M (a) $Mg(ClO_4)_2$ or (b) $Mg(TFSI)_2$

$CH_3CN$

EC:DMC (30:70)

Slow scan voltammetry at 1.00E-4 V/s.

working = $Mg_{0.1}V_2O_5$ , reference = $Ag/Ag^+$, auxiliary = Pt.

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S. Lee, R. DiLeo, A. Marschilok, K. Takeuchi, E. Takeuchi, *ECS Electrochem. Lett.*, **2014,** *3(8),* A87-A90.

# Cathode: $Mg_{0.1}V_2O_y{\bullet}1.8H_2O$

## Profound influence of electrolyte solvent

De-solvation energy of $Mg^{2+}$ is larger than $Li^{+}$ by 340-560 kJ/mol

Significant difference among solvents is predicted

Electrochemical results reflect difference in de-solvation energy

| Solvent | $Mg^{2+}$ De-solvation energy, kJ/mol | $Li^{+}$ De-solvation energy, kJ/mol |
|---|---|---|
| Acetonitrile | 490.8 | 189.6 |
| Ethylene carbonate | 552.9 | 211.3 |
| Propylene carbonate | 572.3 | 218.0 |
| Diethyl carbonate | 623.0 | 189.6 |

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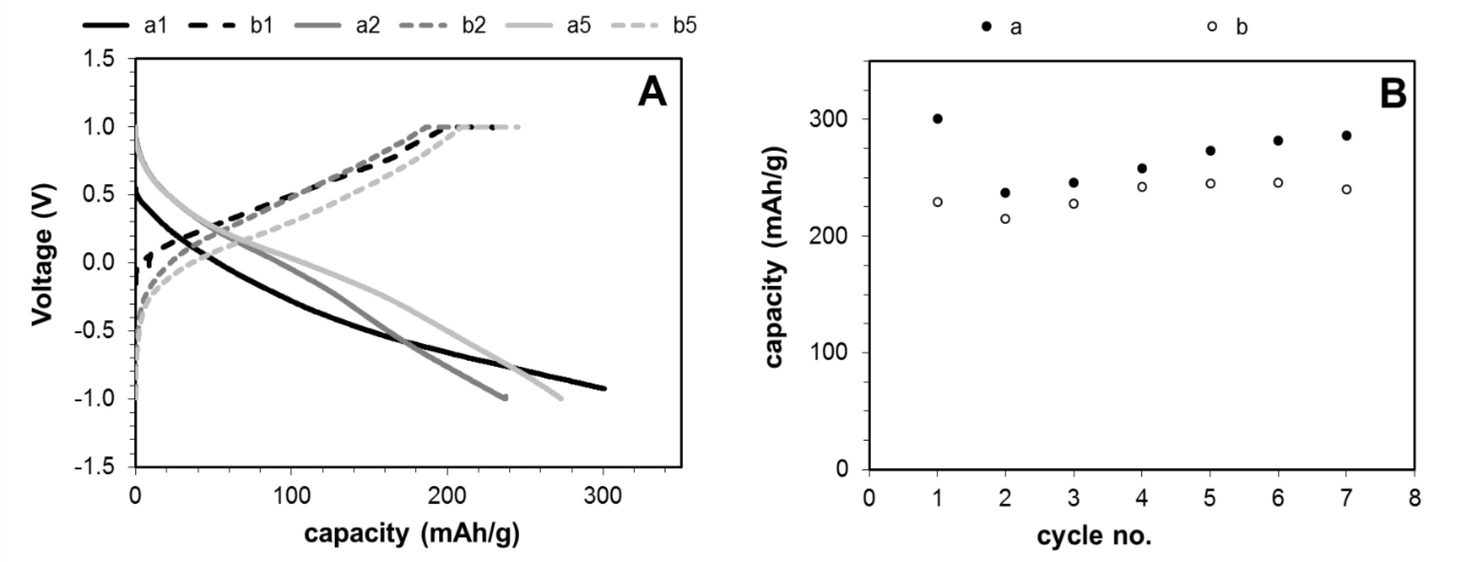
M. Okoshi, Y. Yamada, A. Yamada and H. Nakai, *J. Electrochem. Soc.*, **2013**, *160,* A2160

# Cathode: $Mg_xV_2O_y \bullet 1.8H_2O$

## Galvanostatic cycling




Galvanostatic cycle test at C/10 of $Mg_{0.1}V_2O_5$ in 0.5 M $Mg(ClO_4)_2$ $CH_3CN$ electrolyte versus $Ag/Ag^+$.

Capacity >200 mAh/g is maintained.

> 3.0 V versus Mg

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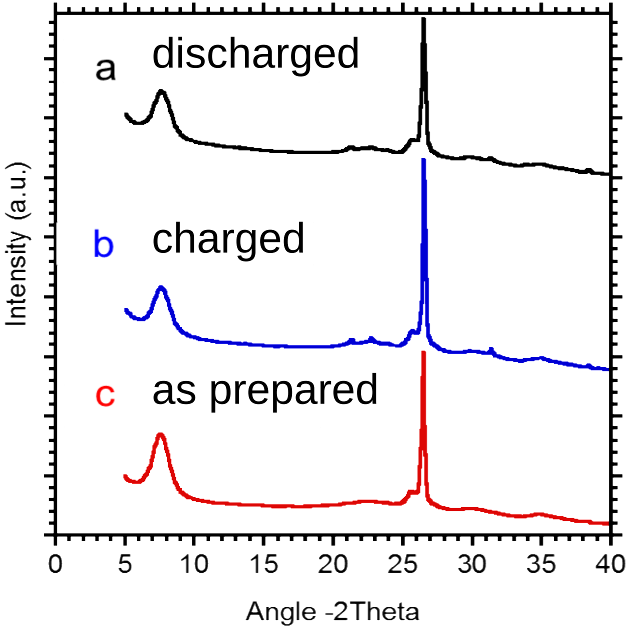
# Cathode: $Mg_{0.1}V_2O_y \bullet 1.8H_2O$

## Characterization after cycling




peak at 26º 2 theta due to graphite.

No change in the 2-theta position of the (001) peak position at 7º 2theta.

No change in the interlayer spacing of the vanadium oxygen layers.

Consistent with no change in interlayer water content.

Consistent d-spacing upon $Mg^{2+}$ insertion and removal bodes well for capacity retention.

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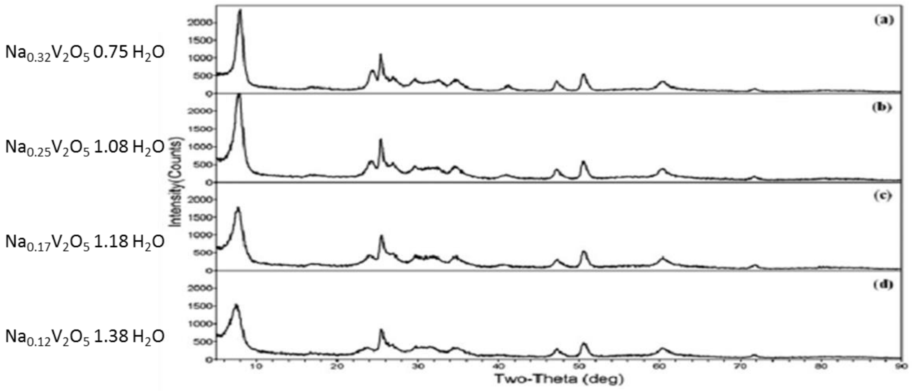
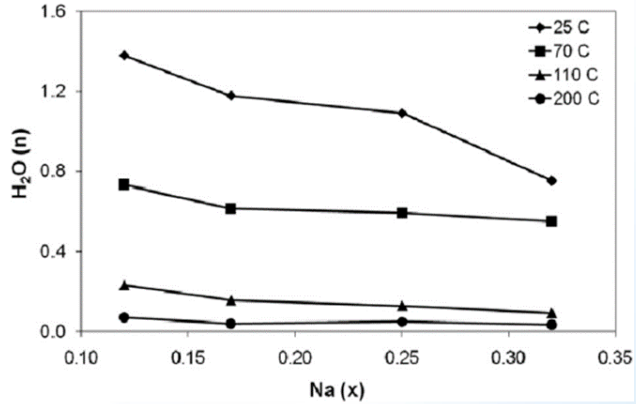
# Cathode: $Na_xV_2O_y \cdot ZH_2O$

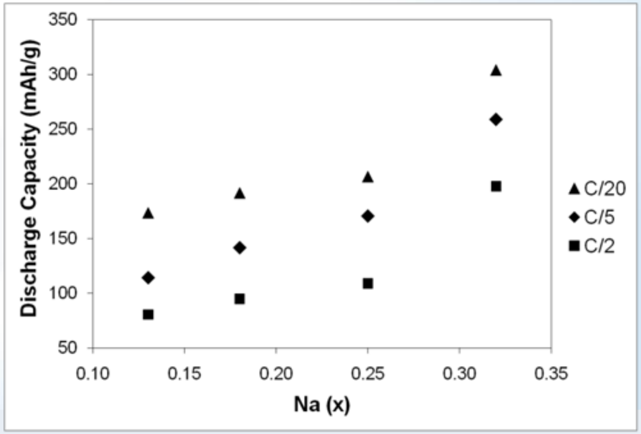
## Influence of $Na^+/V$ ratio and water content




Capacity relates to Na and water content

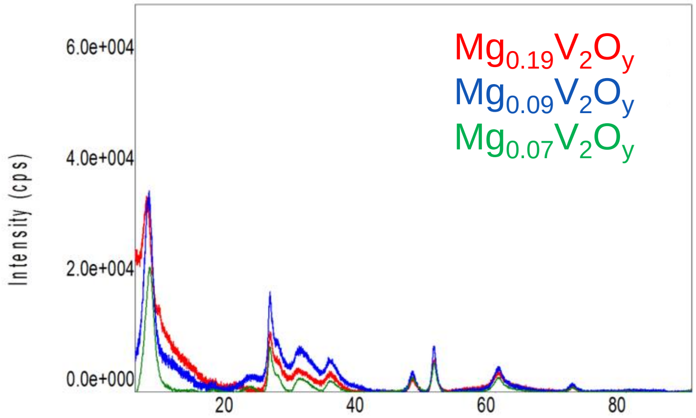
~200% capacity (C/20, C/5, C/2) increase with increasing Na content for $Na_{0.12}V_2O_5 \cdot 0.23H_2O$ to $Na_{0.32}V_2O_5 \cdot 0.01H_2O$

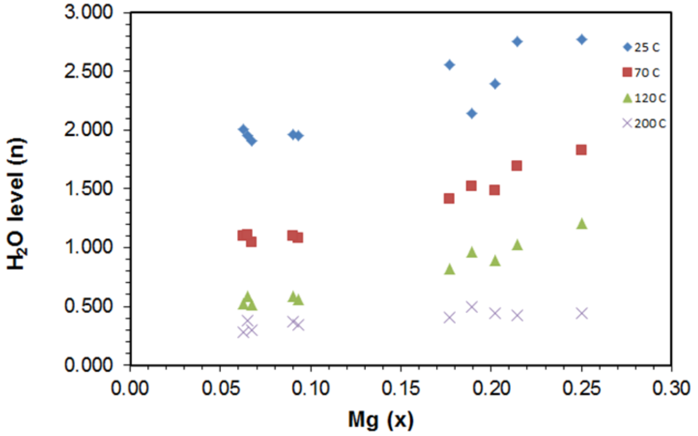



C. Lee, A. Marschilok, A. Subramanian, K. Takeuchi, E. Takeuchi, *Phys. Chem. Chem. Phys.*, **2011,** *13(40),*18047-18054.

# Cathode: $Mg_xV_2O_y \cdot ZH_2O$

## Influence of $Mg^{2+}$/V ratio and water content




- $Mg_xV_2O_y \cdot ZH_2O$ samples (0.1 ≤ x ≤ 0.25) were prepared
- $H_2O$ content relates to Mg/V ratio, reflected in d-spacing
- Electrochemistry in progress

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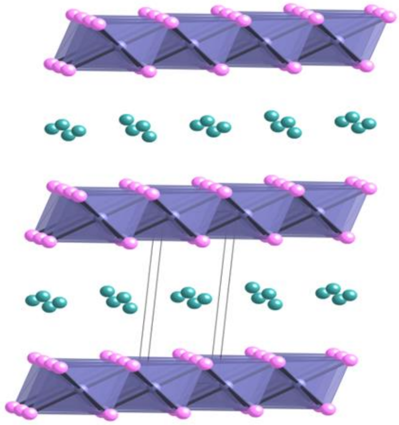
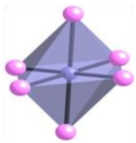
# Cathode: $Mg_{0.1}MnO_2 \cdot ZH_2O$

## Material structure





Magnesium manganese oxide, birnessite, $Mg_xMnO_2$ has a layered structure of edge sharing $MnO_6$ octahedra, where $Mg^{2+}$ cations are between the layers

Recent report indicated reversible (70 mAh/g) electrochemical performance with magnesium

Some capacity fade was noted and attributed to possible cathode solubility

S. Rasul, S. Suzuki, S. Yamaguchi, and M. Miyayama, *Electrochim. Acta,* **2012,** *82,* 243-249.

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# Cathode: $Mg_{0.1}MnO_2 \cdot ZH_2O$

## Material synthesis and characterization

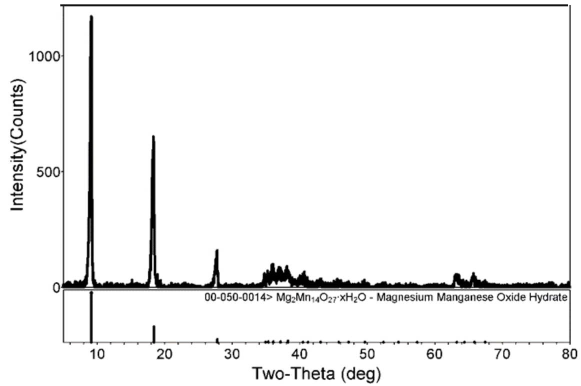
Two-Step Synthesis

Precipitation

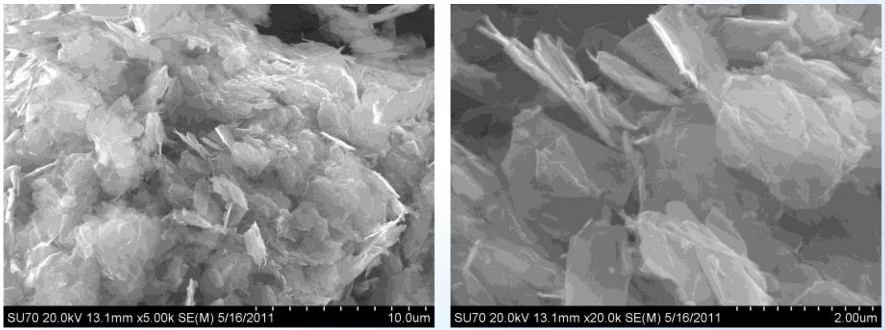
↓

Ion exchange

$Mg_{0.1}MnO_2$ was prepared by a two-step scalable process where the first step was a precipitation to form $Na_yMnO_2$ followed by ion exchange.




XRD agrees with reference pattern[1]




platelet morphology via SEM

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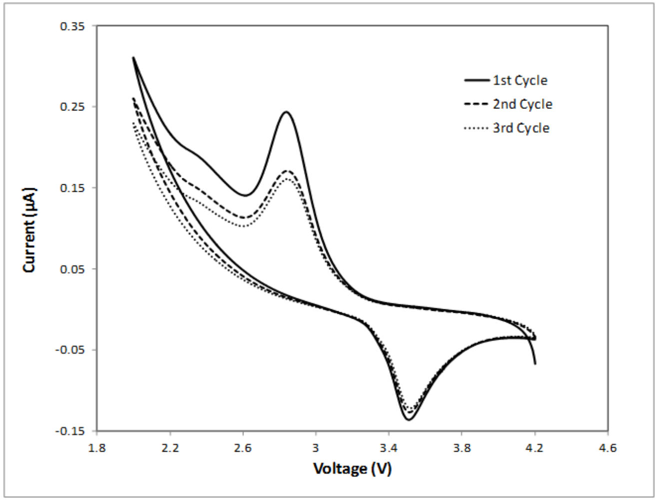
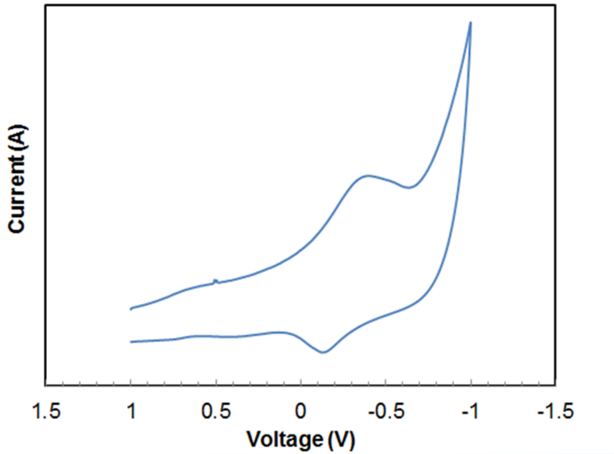
1. K. Kumar, A. Usui, W. Paplawsky B. Gedullin, and G. Arrhenius, *Miner. Mag.*, **1994**, *58,* 425

# Cathode: $Mg_{0.1}MnO_2 \bullet ZH_2O$

## Cyclic voltammetry in $Li^+$ and $Mg^{2+}$ systems




$Mg_xMnO_2$ showed quasi-reversible electrochemical behavior between 2.5 V and 3.5 V (vs. $Li/Li^+$)

Electrochemical quasi-reversibility in $Mg^{2+}$ based electrolyte vs. $Ag/Ag^+$ was demonstrated

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# Anode: Alternatives to Mg: Bi metal

## Electrodeposition of Bi metal

$$2Bi + 3Mg^{2+} + 6e^- \rightleftharpoons Bi_2Mg_3$$

Theoretical capacity: 385 mAh/g

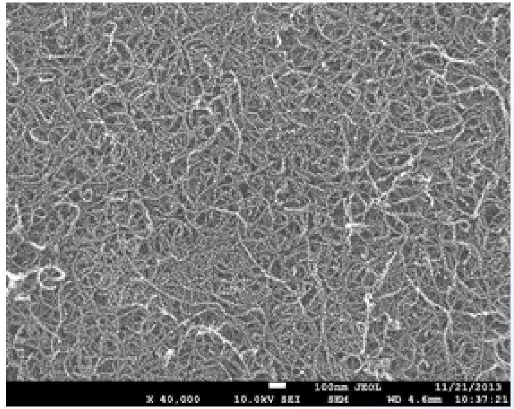
Electrochemistry demonstrating quasi-reversibility in electrolyte using non-corrosive salts has been recently demonstrated.

T. Arthur, N. Singh and M. Matsui, *Electrochem. Comm.*, **2012,** *16,* 103.

Y. Shao, M. Gu, X. Li, Z. Nie, P. Zuo, G. Li, T. Liu, J. Xiao, Y. Cheng, C. Wang, J.-G. Zhang and J. Liu, *Nano Lett.*, **2014**, *255,* 14.

# Anode: Alternatives to Mg: Bi/CNT

## Advantages of carbon nanotube substrate




Eliminates use of metal foil support

Support acts as the conductive matrix

Lighter weight than metal foils

Eliminate possibility of foil corrosion

Eliminate mass and volume of binder and additional carbon

3-D nature of substrate allows electrolyte ion access

A. Marschilok, C. Lee, A. Subramanian, K. Takeuchi, and E. Takeuchi, *Energy Environ. Sci.*, **2011,** *4(8),* 2943-2951.

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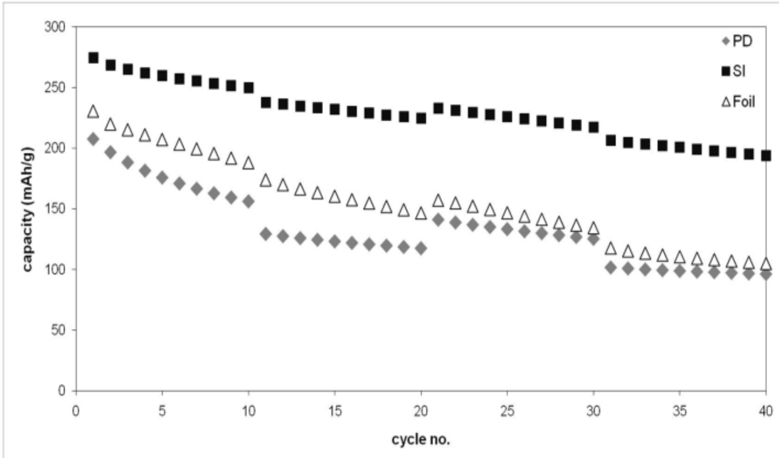
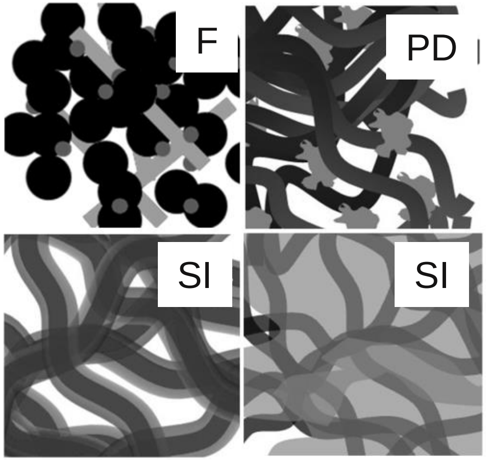
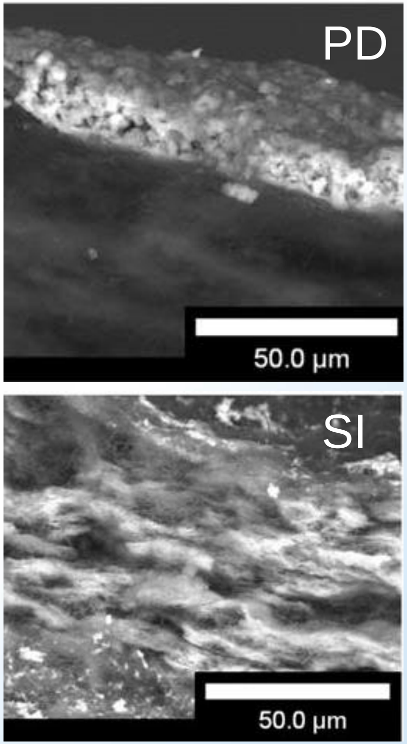
# Lightweight composite electrodes

## Carbon nanotube substrates as electrode supports




Demonstrate CNT substrates as electrode supports

Save up to 76% mass at cell level

Improved capacity, rate capability, capacity retention


E. Takeuchi, A. Marschilok, K. Takeuchi. *Electrochemistry,* **2012,** *80(10),* 700-705, *invited highlight.*

A. Marschilok, C. Lee, A. Subramanian, K. Takeuchi, E. Takeuchi, *Energy Environ. Sci.*, **2011,** *4,* 2943-51.

A. Marschilok, C. Schaffer, K. Takeuchi, E. Takeuchi, *J. Composite Mater.*, **2013,** *47(1),* 41-9.

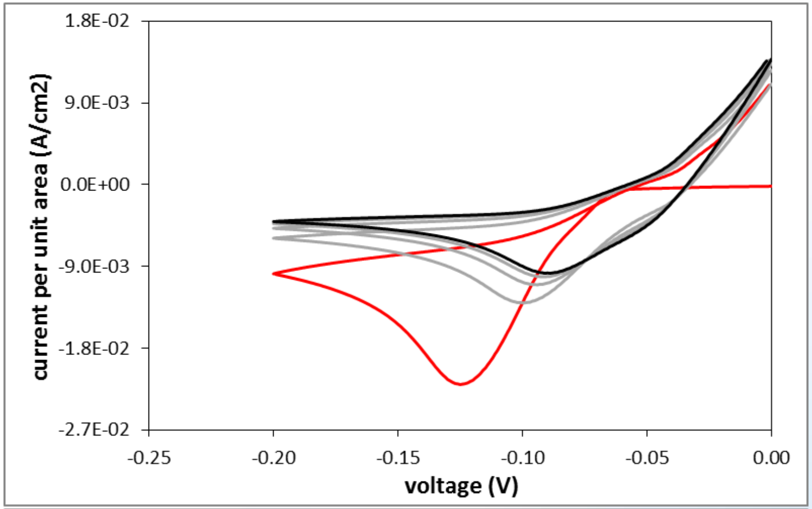
# Anode: electrodeposited Bi, EQCM

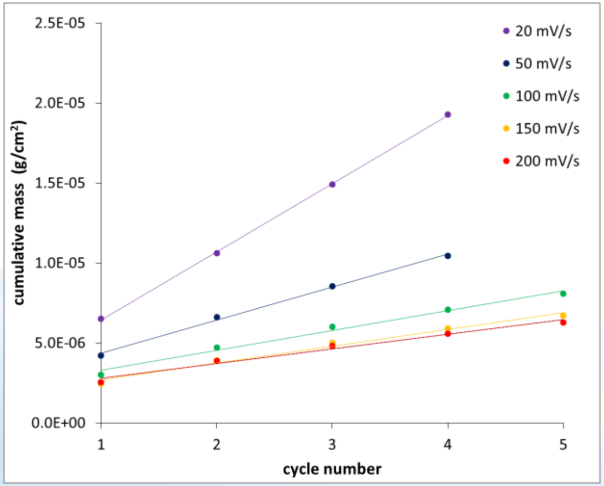
## Electrochemical Quartz Crystal Microbalance on Au

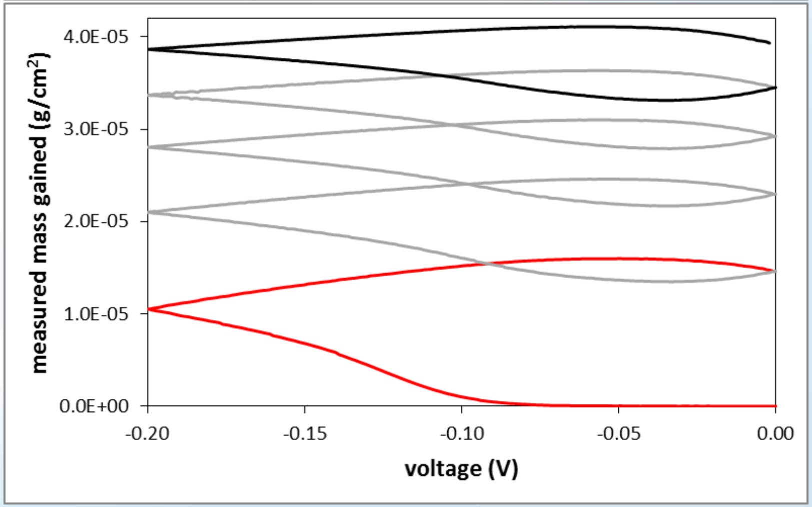
Deposition was quantified using EQCM on a gold electrode.

Linear relationship of mass deposited versus cycle number was obtained.

Can control deposition amount by cycle number and scan rate.

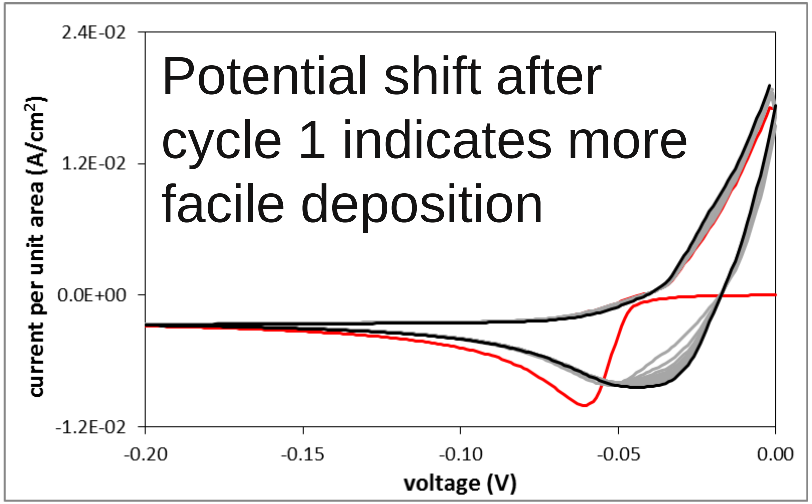


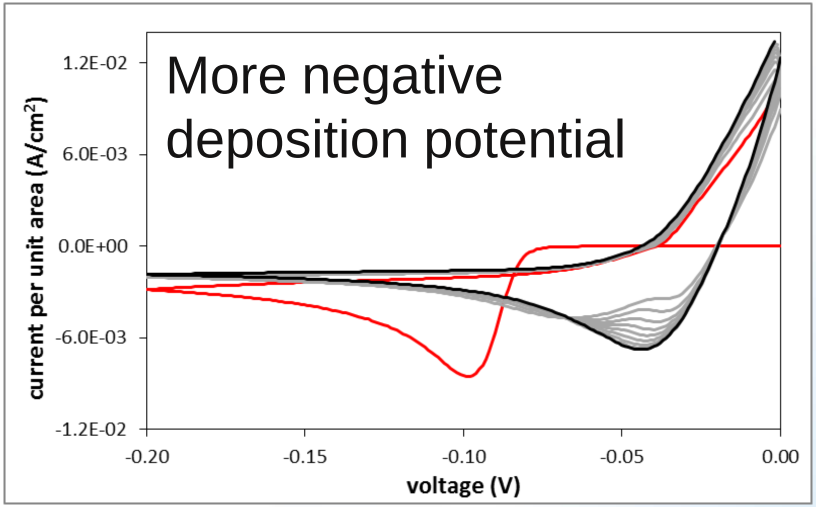



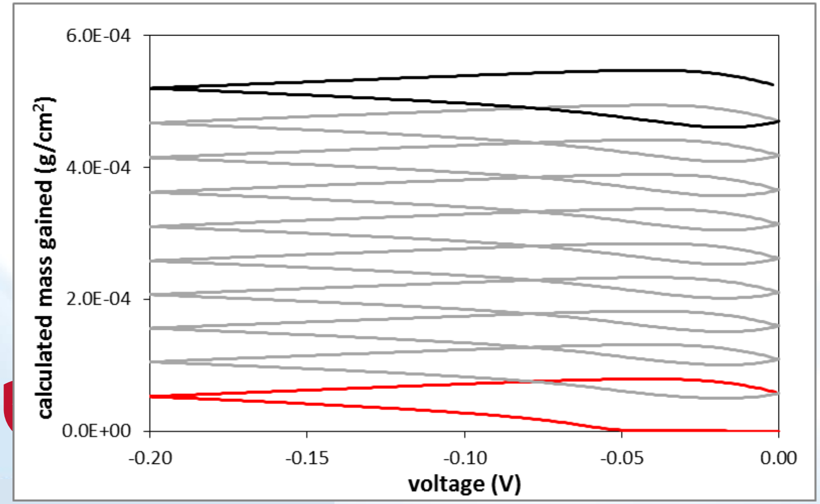



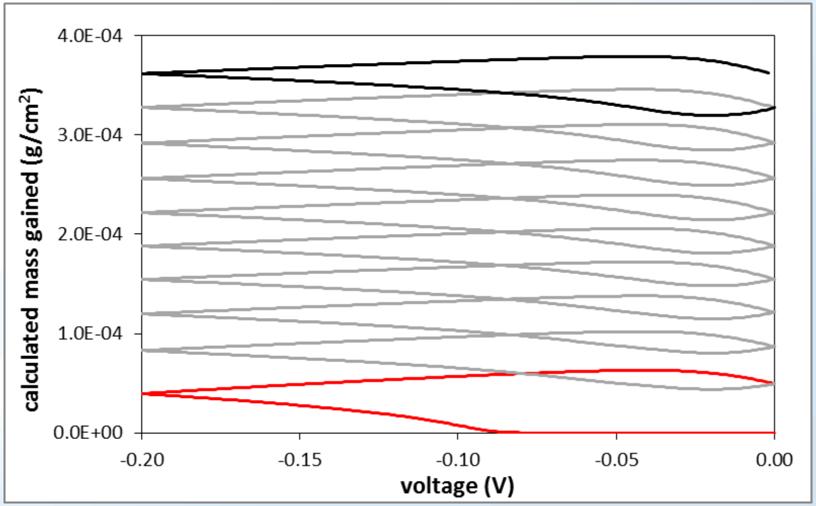
# Anode: electrodeposited Bi

Left = Au disk Right = flat glassy carbon



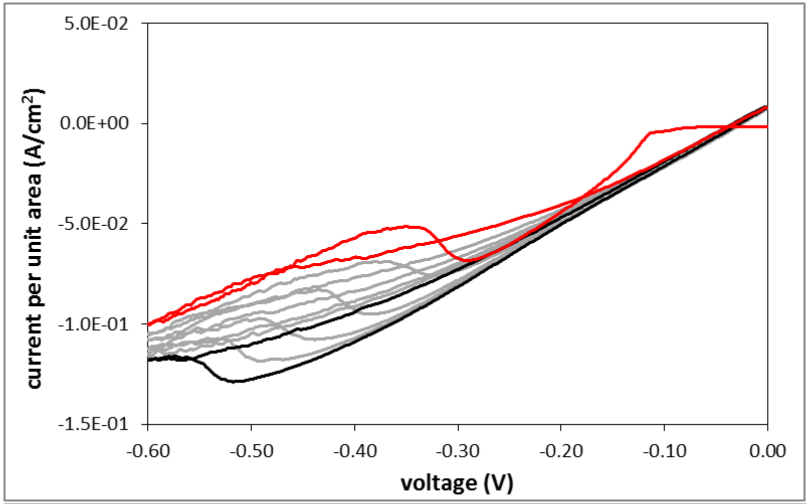



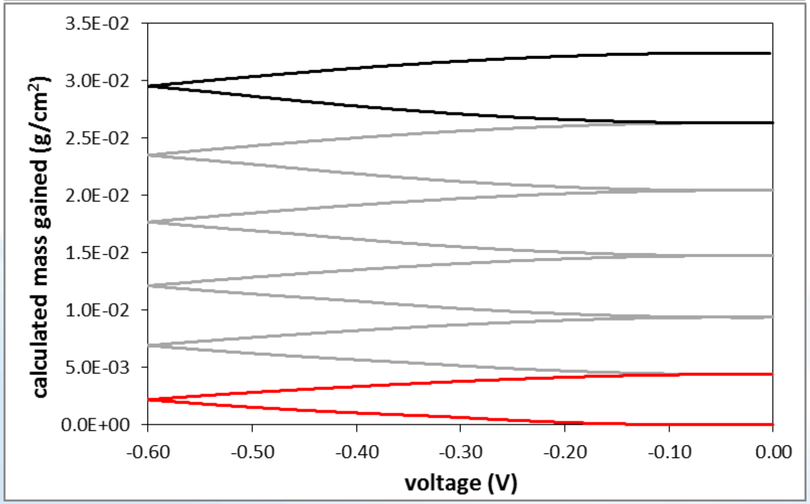



# Anode: electrodeposited Bi

## Bi on CNT substrate

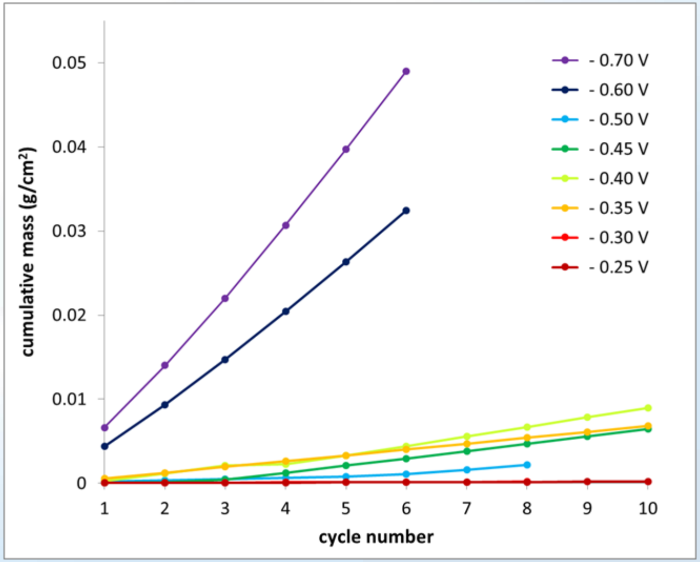



Even more negative deposition potential on CNT substrate.

On cycle 1 for Au and glassy carbon flat disk, Bi can fully cover electrode with multiple monolayers.

Deposition on 3D CNT substrate does not fully cover all surfaces on cycle 1.



# Anode: electrodeposited Bi

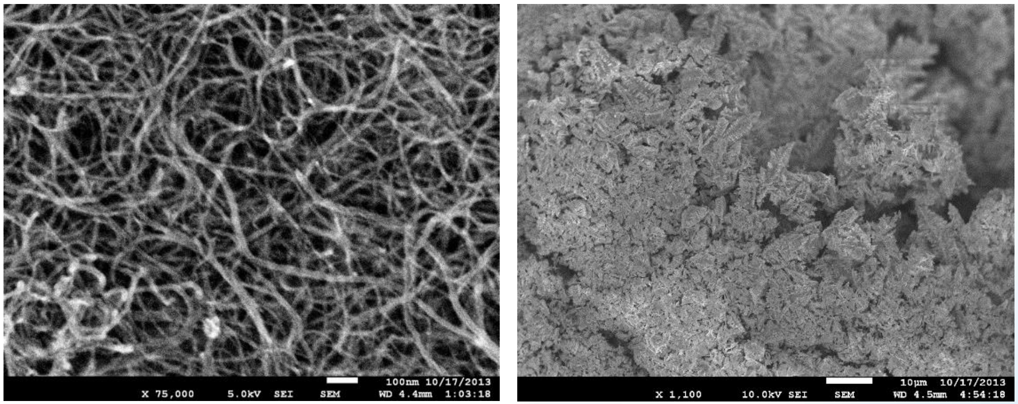
## Bi on CNT substrate

CNT substrate

↓

Bi Deposition

Bi-CNT was prepared by electrodepostion of Bi on CNTs.




Scanning Electron Microscopy (SEM) of
Carbon nanotubes (L) & Bismuth-coated CNTs (R).

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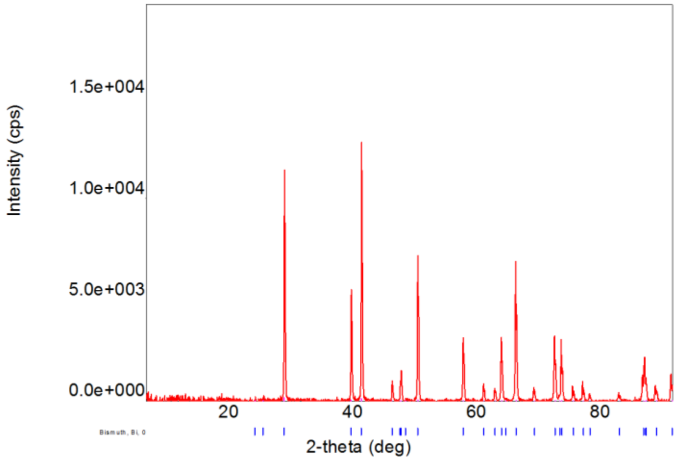
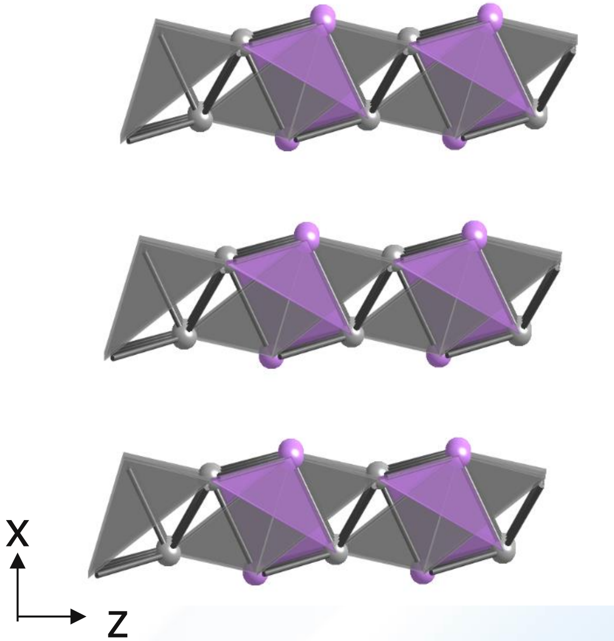
R. DiLeo, Q. Zhang, A. Marschilok, K. Takeuchi, and E. Takeuchi, *Submitted for publication*.

# Anode: electrodeposited Bi

## Bi on CNT substrate




X-ray powder diffraction of Bi deposited on CNT substrate matches Bi metal reference pattern




Crystallographic structure of Bi metal

R. DiLeo, Q. Zhang, A. Marschilok, K. Takeuchi, and E. Takeuchi, *Submitted for publication*.

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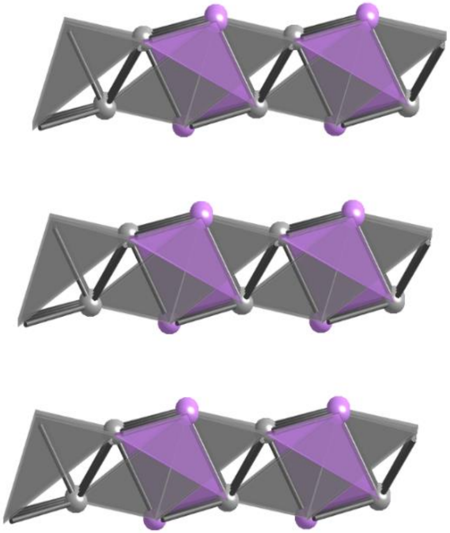
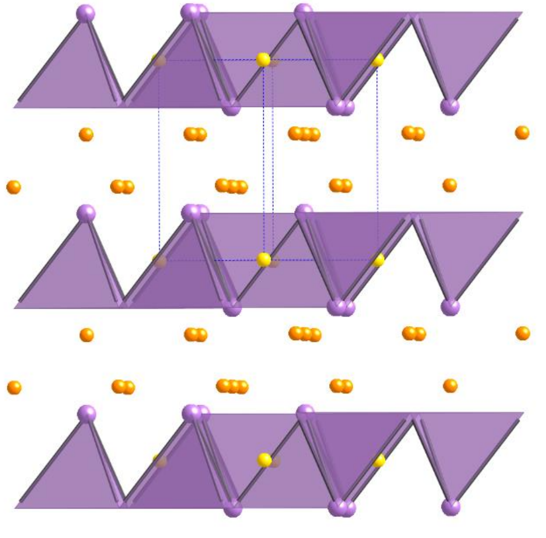
# Mg electrochemistry

## Anode: formation of $Mg_3Bi_2$

C (theoretical) = 385 mAh/g Bi

$3Mg^{2+} + 2Bi + 6e^- \rightleftarrows Mg_3Bi_2$





Bi metal $\qquad$ $Mg_3Bi_2$

Bi-Bi bond distance increases 25-40%

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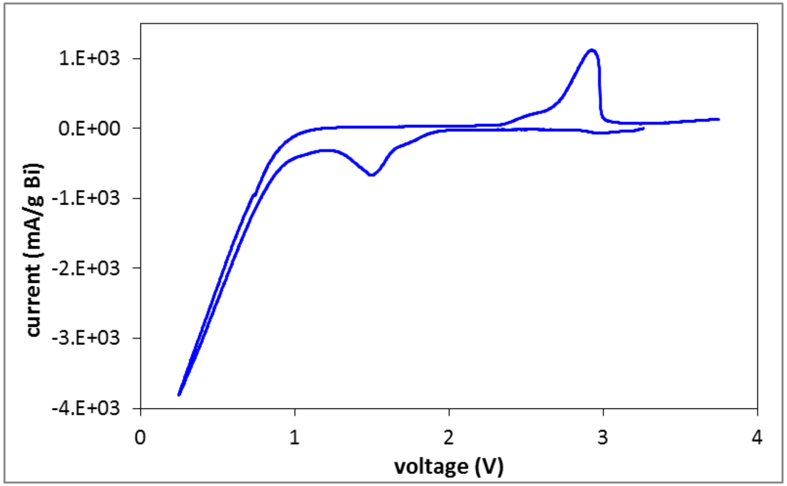
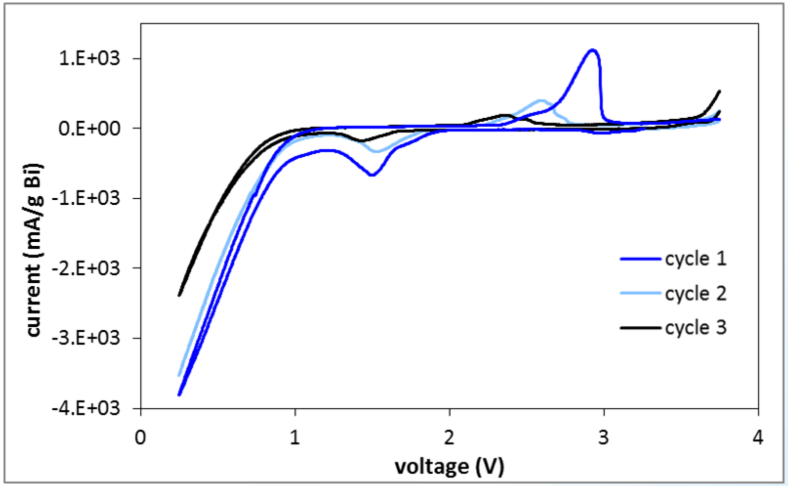
R. DiLeo, Q. Zhang, A. Marschilok, K. Takeuchi, and E. Takeuchi, *Submitted for publication*.

# Mg electrochemistry

## Anode: electrodeposited Bi on CNT




Quasireversible electrochemistry demonstrated in $Mg^{2+}$ electrolyte

| | | |
|---|---|---|
| Cycle 1 | C/2 124 mAh/g | C/10 180 mAh/g |
| Cycle 2 | C/2 50% retention | C/10 60% retention |
| Cycle 3 | C/2 98% retention | |

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R. DiLeo, Q. Zhang, A. Marschilok, K. Takeuchi, and E. Takeuchi, *Submitted for publication*.

# Electrolyte

Necessary properties

- high mobility of conductive ions
- functional voltage window
- low viscosity
- high conductivity
- adequate [$Mg^{2+}$] to support battery performance

Desirable properties

- non-corrosive electrolyte salts
- low volatility
- non-flammable

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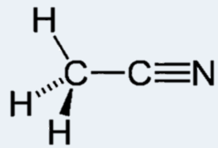
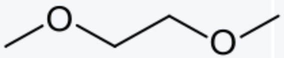
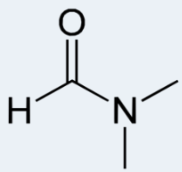
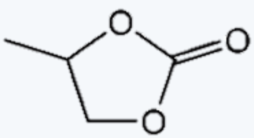
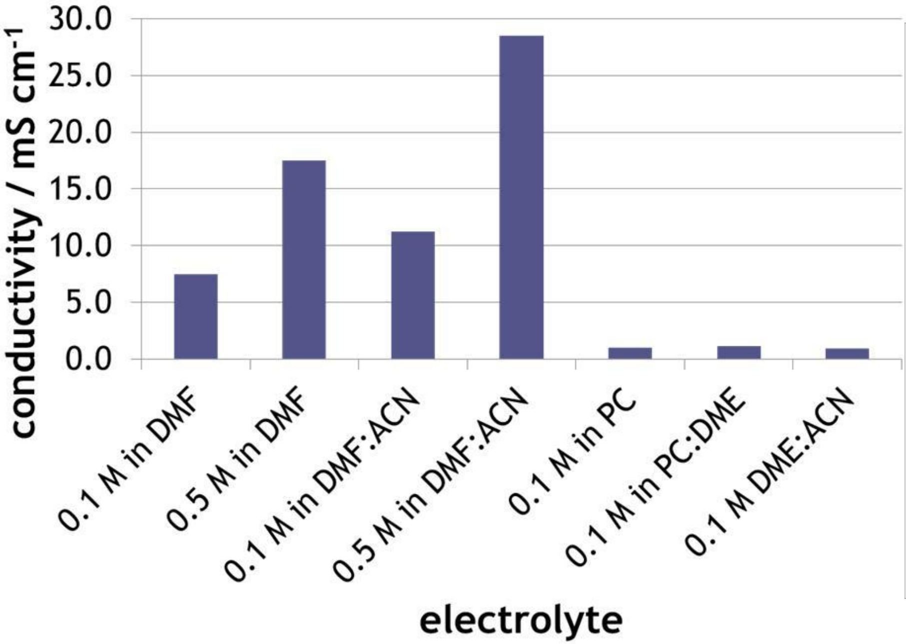
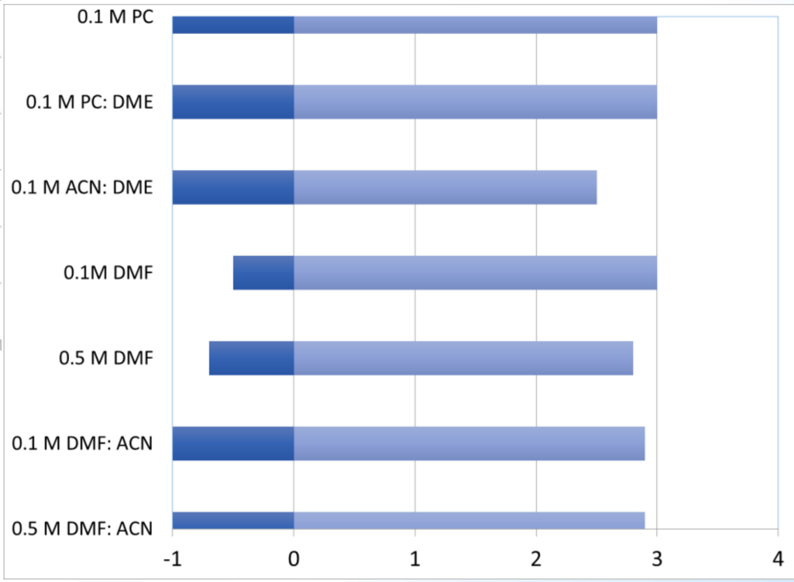
# Electrolyte Solvent

| Solvent | Formula | Structure | Type | Dielectric constant | Viscosity cP, 25°C |
|---|---|---|---|---|---|
| acetonitrile | $CH_3CN$ |  | nitrile | 38 | 0.34 |
| dimethoxy ethane | $C_4H_{10}O_2$ |  | ether | 7 | 0.41 |
| N,N-dimethyl formamide | $(CH_3)_2NC(O)H$ |  | amide | 38 | 0.92 |
| propylene carbonate | $C_4H_6O_3$ |  | carbonate | 64 | 2.40 |

# Electrolyte




Voltage limits versus $Mg/Mg^{2+}$




Salt solubility can be a limitation for conductivity

Several combinations with adequate voltage window were identified

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# Electrolyte

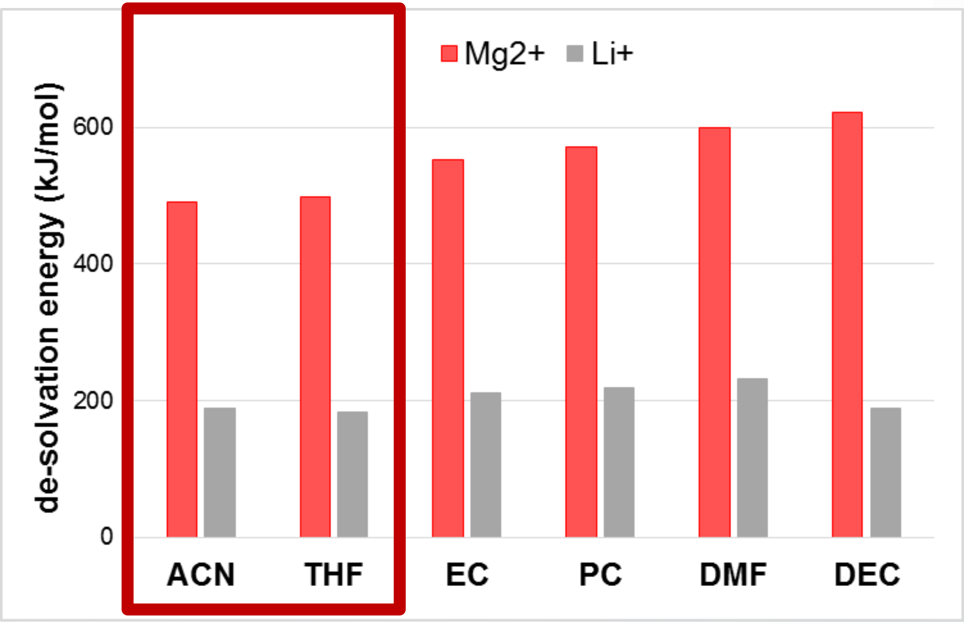
## Profound influence of electrolyte solvent

De-solvation energy of $Mg^{2+}$ is larger than $Li^+$ by 340-560 kJ/mol

Significant difference amount solvents is predicted

Electrochemical results reflect difference in de-solvation energy

volatile and flammable




M. Okoshi, Y. Yamada, A. Yamada and H. Nakai, *J. Electrochem. Soc.*, **2013,** *160,* A2160.

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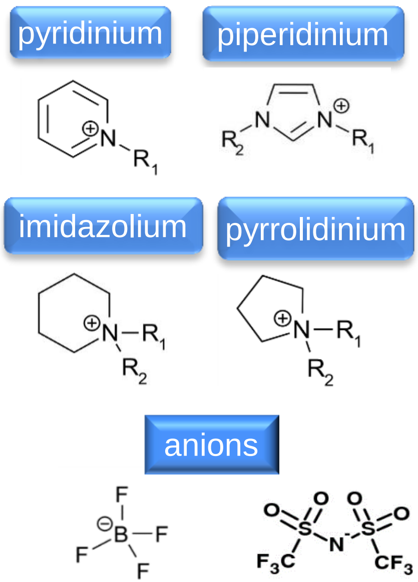
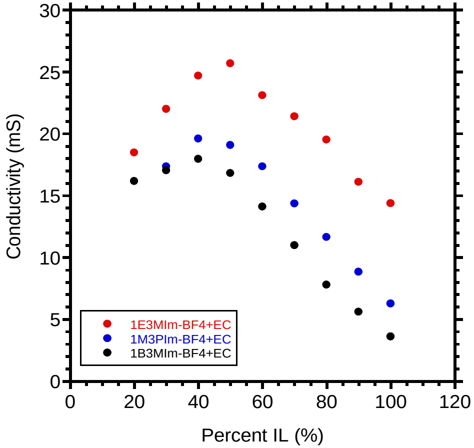
# Electrolyte

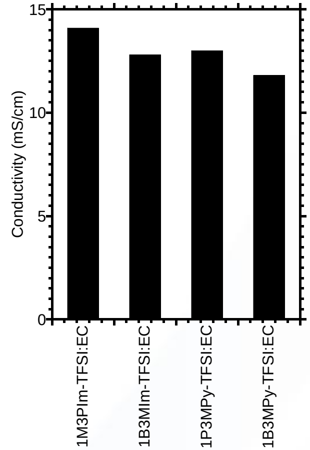
## Ionic Liquid (IL) based hybrid non-flammable electrolytes

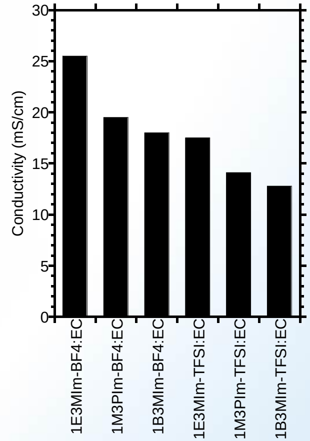
Systematic study of hybrid IL-carbonate electrolytes.

Promote development of future safe, high voltage battery systems.



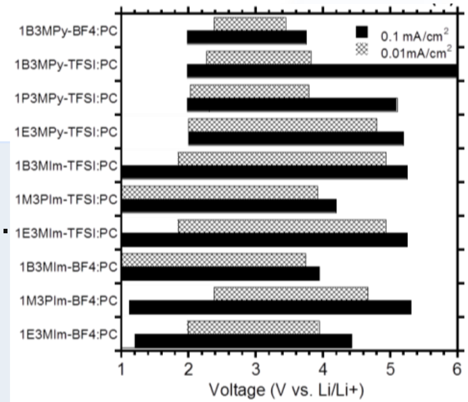



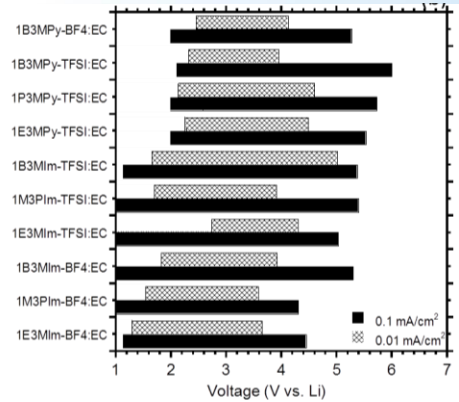




R. DiLeo, A. Marschilok, K. Takeuchi, E. Takeuchi, *Electrochim. Acta*, **2013,** *109,* 27-32.

R. DiLeo, A. Marschilok, K. Takeuchi, E. Takeuchi, *J. Electrochem. Soc.*, **2013,** *160(9),* A1399-405.

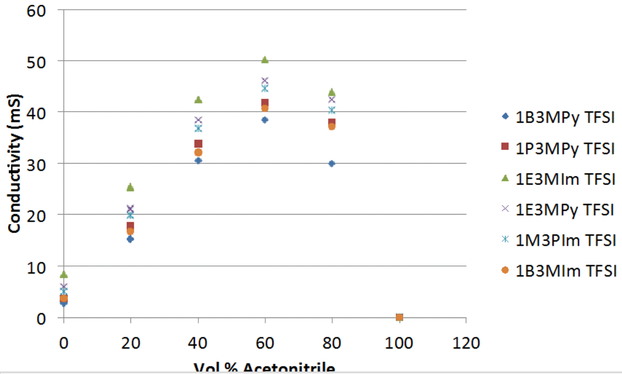


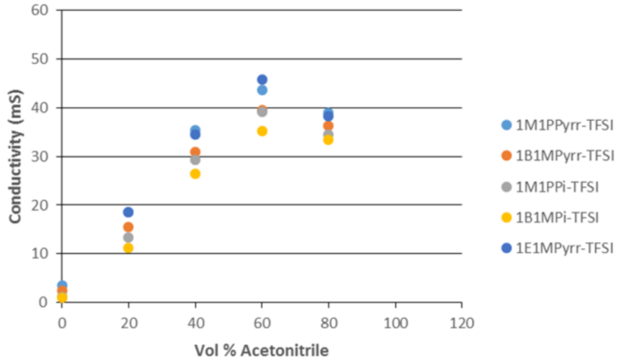



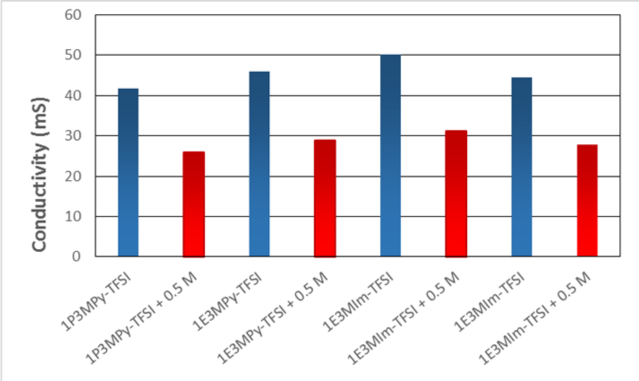
# Electrolyte

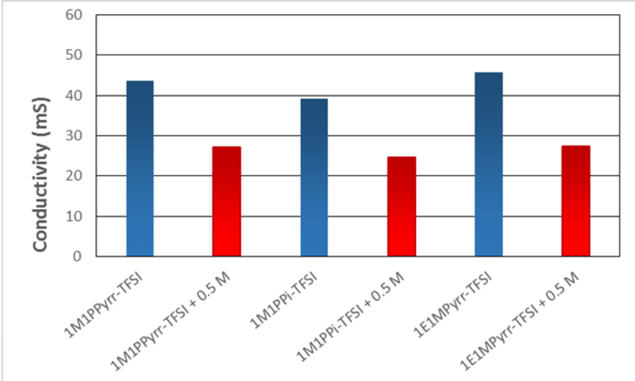
## Ionic Liquid (IL) based hybrid non-flammable electrolytes

Systematic study of hybrid IL-acetonitrile electrolytes




Conductivity of ~20 – 30 mS/cm demonstrated with Mg salt

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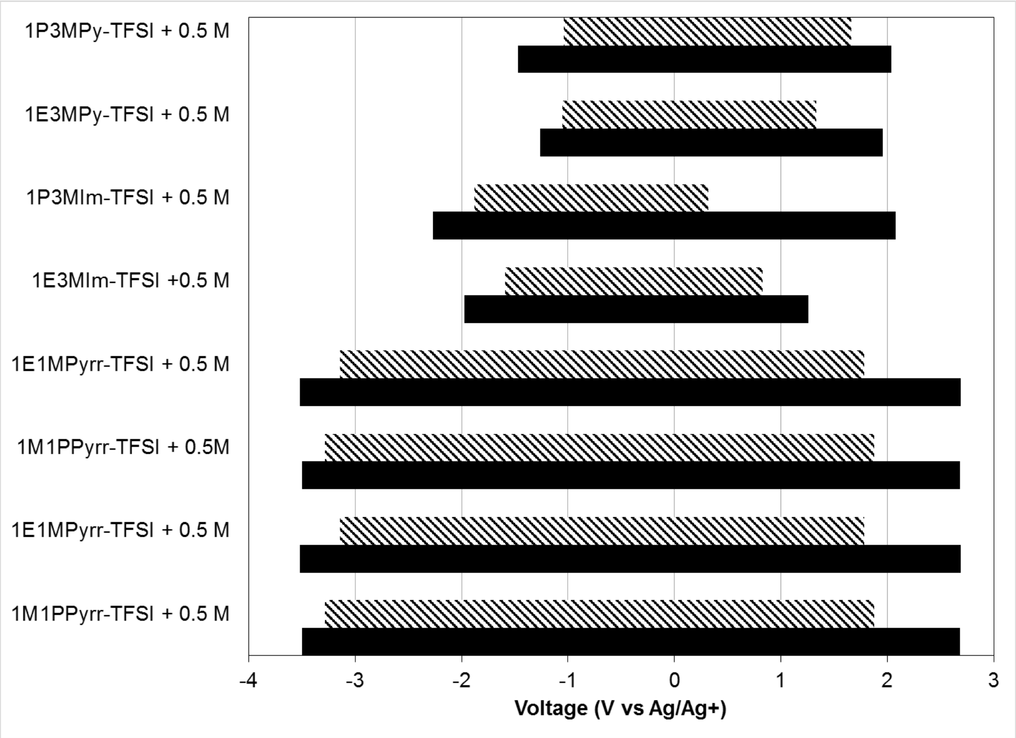
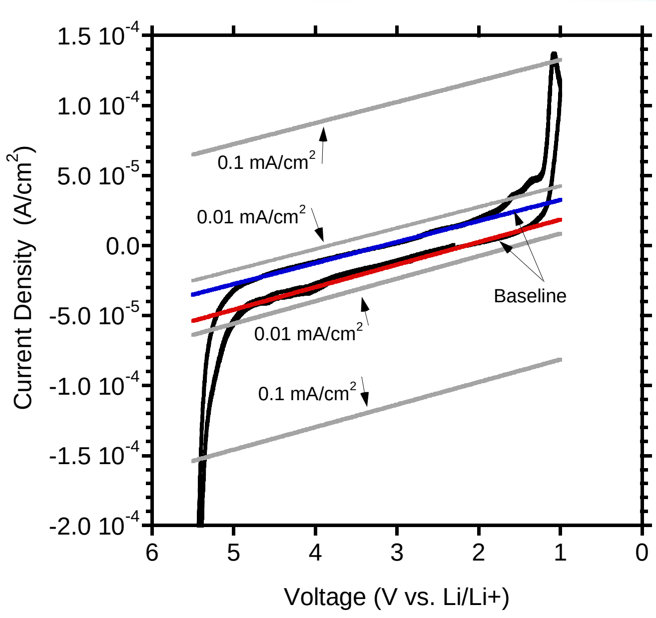
C. Cama, M. Huie, A. Marschilok, K. Takeuchi, and E. Takeuchi, *In preparation*.

# Electrolyte

## Ionic Liquid (IL) based hybrid non-flammable electrolytes

Systematic study of hybrid IL-acetonitrile electrolytes



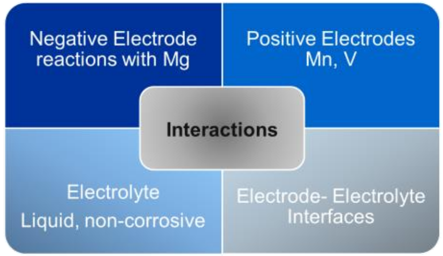




Voltage stability > 5 V range demonstrated hybrid IL electrolytes

Stony Brook University

C. Cama, M. Huie, A. Marschilok, K. Takeuchi, and E. Takeuchi, *In preparation*.

# Summary




## Cathode

**$Mg_xV_2O_y$** scalable process, systematic control of Mg(x) content

**$Mg_{0.1}V_2O_y$** >200 mAh/g in non-corrosive $Mg^{2+}$ electrolyte
crystallographic stability upon $Mg^{2+}$ insertion / removal

Cycling of metal oxides - high voltage and capacity

## Anode

**Bi** tunable electrodeposition based preparation on CNT substrate
>180 mAh/g in non-corrosive $Mg^{2+}$ electrolyte
3D electrode reversible electrochemistry, conventional electrolytes

## Electrolyte

**H-IL** non-flammable hybrid ionic liquid-Mg salt electrolytes with appropriate conductivity, and voltage window for implementation

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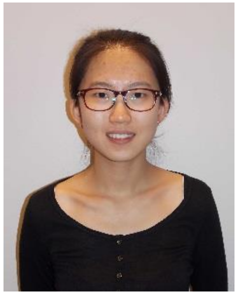
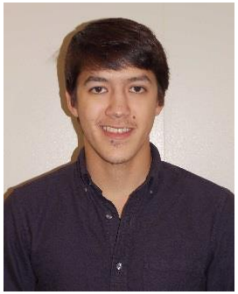
# Collaborators and Participants

Kenneth J. Takeuchi, Ph.D.
SUNY Distinguished Teaching Professor

Amy C. Marschilok, Ph.D.
Research Associate Professor

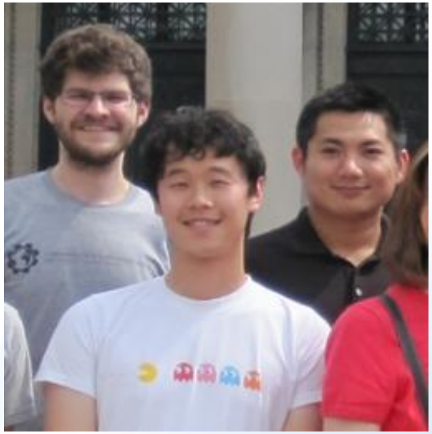


Qing Zhang



Matt Huie

Christina Cama



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Roberta DiLeo, Ph.D.

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Dr. Paul Clem
Manager, Electronic, Optical and Nano Materials
Sandia National Laboratories

Sandia National Laboratories

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