Next Generation Battery Alternative to Lithium Ion: Magnesium Ion Based Batteries

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Stony Brook University
Brookhaven Science Associates

EESAT 2015 Technical Conference
Portland, OR. 24Sep2015, 10:15 -12:00

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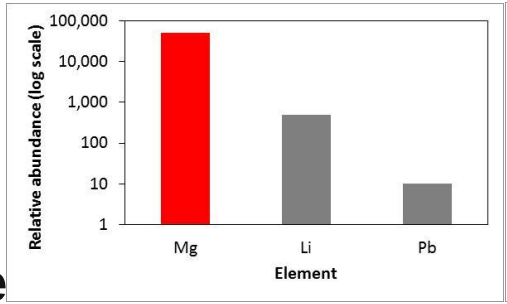
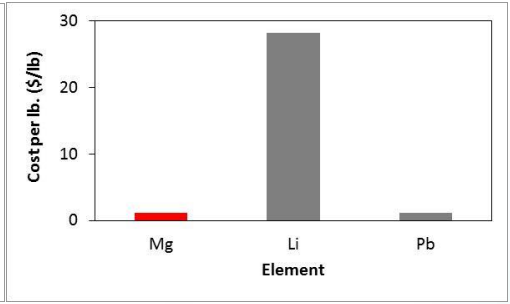
Motivation





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

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

	Mg	Li	Pb
ionic radius, Å	**0.72**	0.76	1.19
melt. pt.,^{o}C	**650**	181	328
mAh/g	2205	**3862**	259
mAh/cc	**3837**	2047	2926
$/lb	**$1.12**	$28	$1.68
$/kWh	**$2.5**	$58	$31

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.

Approach to Mg Battery System

The necessity of systems level understanding

Negative Electrode | Positive Electrodes

Coordination Chemistry Reviews 287 (2015) 15–27

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journal homepage: www.elsevier.com/locate/ccr

Review

Cathode materials for magnesium and magnesium-ion based batteries

Matthew M. Huie[a], David C. Bock[b], Esther S. Takeuchi[a,b,c], Amy C. Marschilok[a,b], Kenneth J. Takeuchi[a,b,*]

M. Huie, D. Bock, E. Takeuchi, A. Marschilok, K. Takeuchi
Coord. Chem. Rev. 287 (2015) 15-27. Invited.

Cathode: $Mg_{0.1}V_2O_y \cdot 1.8H_2O$

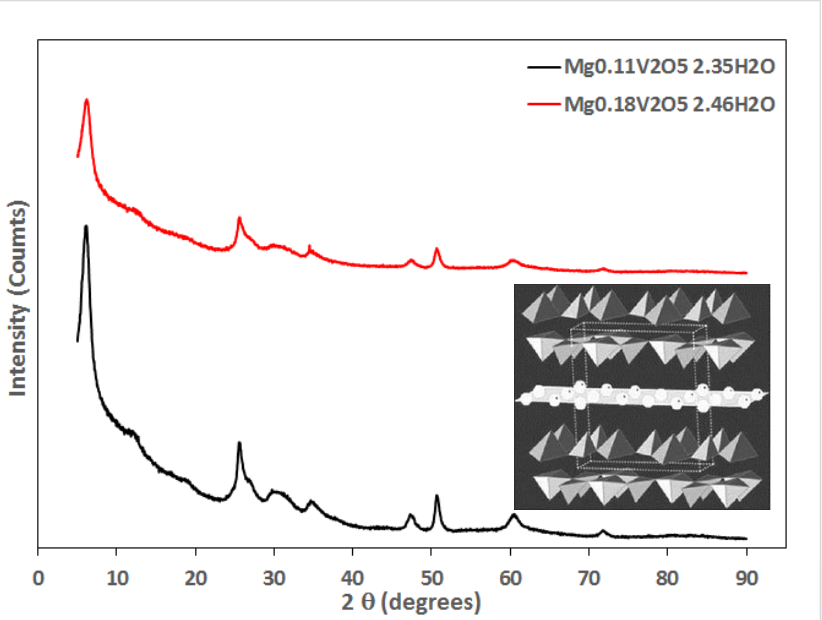
Material synthesis

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 $Mg_xV_2O_5$ (x = 0.11, 0.18) 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.

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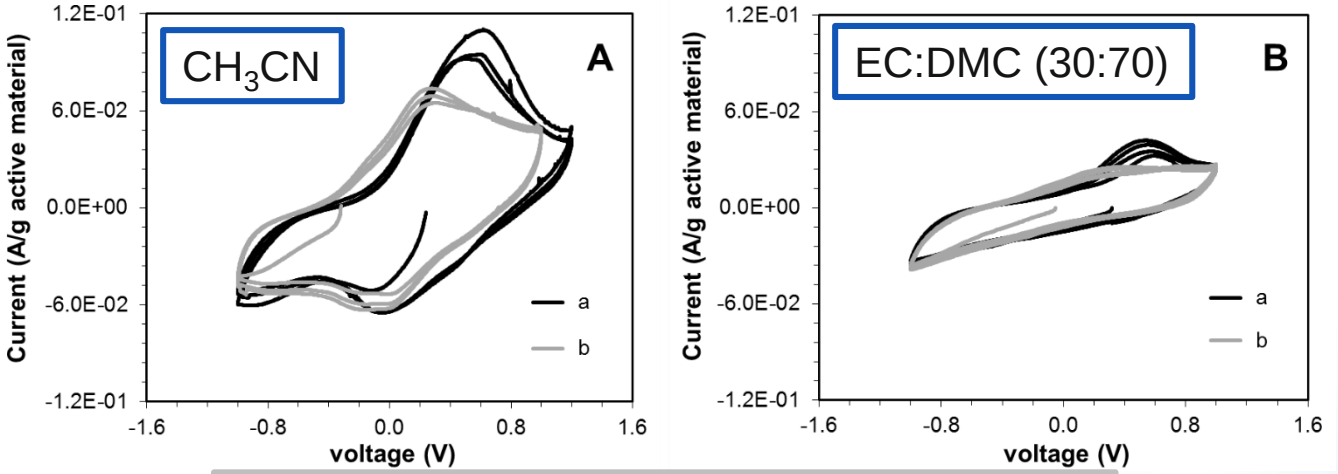
Cathode: $Mg_{0.1}V_2O_y \cdot 1.8H_2O$

Results of voltammetry: significant solvent effect



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

De-solvation energy of Mg^{2+} in EC, DEC, PC > CH_3CN

Slow scan voltammetry at 1E-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.

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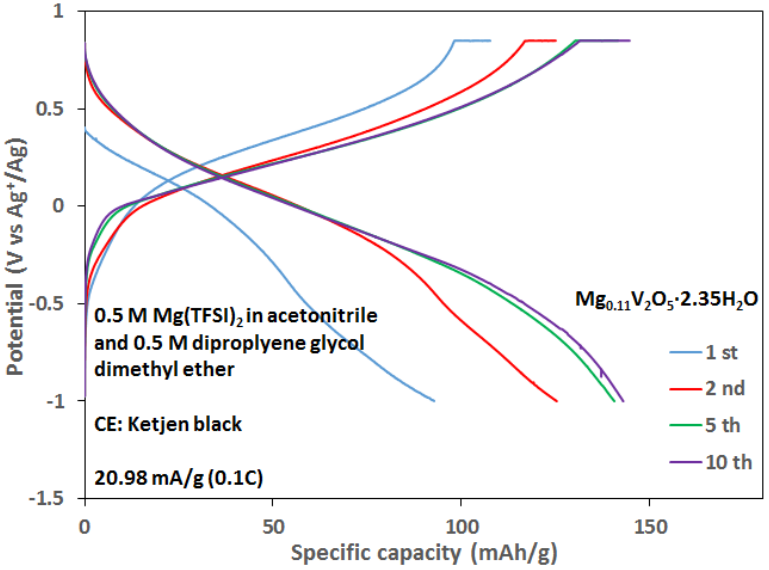
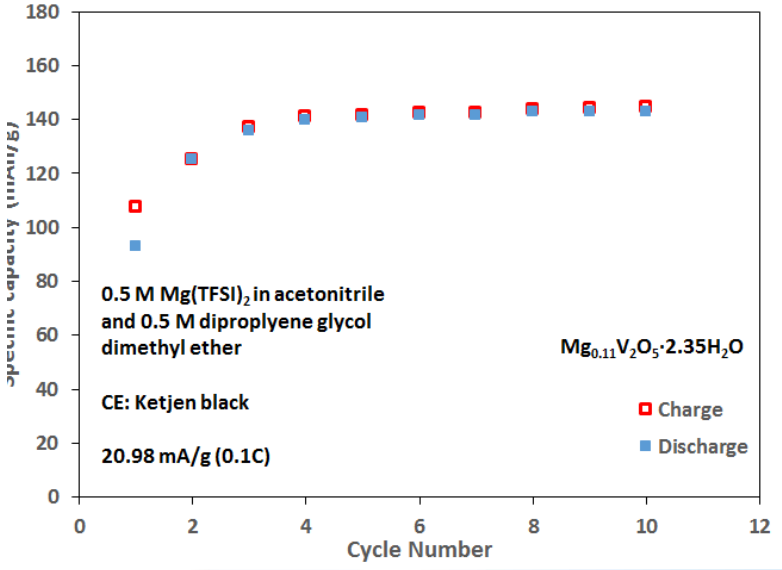
Cathode: $Mg_xV_2O_5 \cdot nH_2O$

Galvanostatic cycling in Mg electrolyte





$Mg_{0.11}V_2O_5 \cdot 2.35H_2O$ can deliver ~140 mAh/g in 0.5 M $Mg(TFSI)_2$. Capacity increased in the first cycles, then stable at ~140 mAh/g.

$Mg_{0.11}V_2O_5 \cdot 2.35H_2O$ capacity > $Mg_{0.18}V_2O_5 \cdot 2.35H_2O$

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J. Yin, A. Marschilok, K. Takeuchi, E. Takeuchi
In preparation for publication

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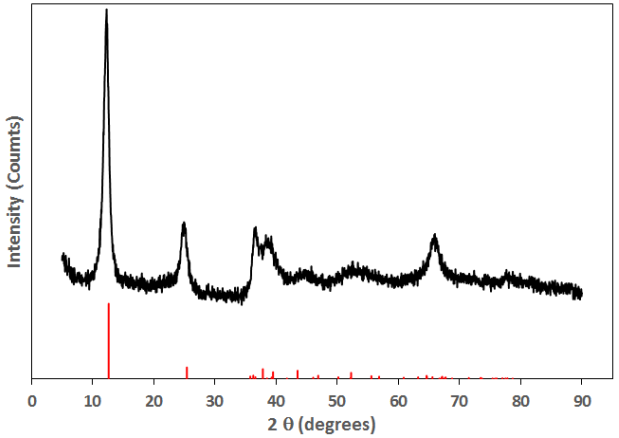
Cathode: Mg-birnessite

Low cost, low toxicity source materials

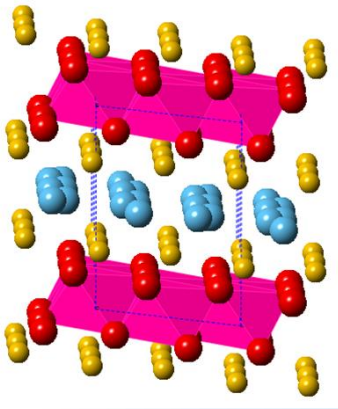
Two-Step Synthesis

Precipitation

Ion exchange



XRD pattern of Mg-birnessite with standard index



Mg-birnessite was prepared by a two-step scalable process

room temperature precipitation reaction for Na-birnessite

followed by ion exchange

monoclinic phase (space group C 2/m)

a=5.050 Å, b=2.846 Å, c=7.054 Å, b=96.63°

Pink, Mn; Red, O; Yellow, Mg; Blue, H_2O.

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J. Yin, A. Marschilok, K. Takeuchi, E. Takeuchi
Submitted for publication

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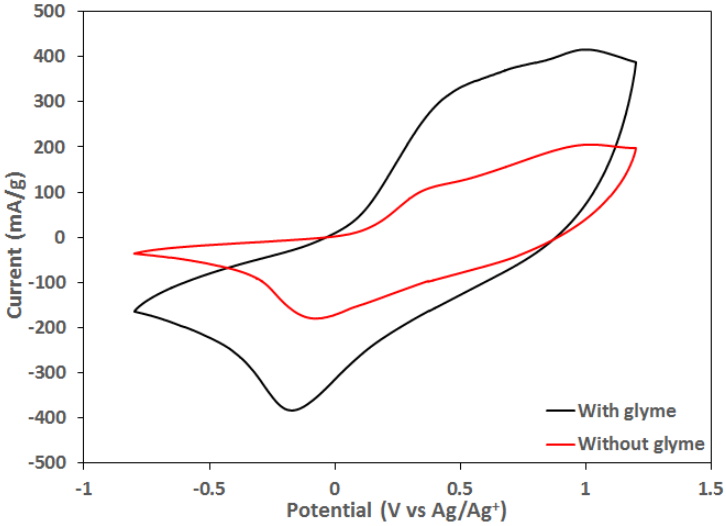
Cathode: Mg-birnessite

Cyclic voltammetry in Mg electrolyte, new electrolyte



Electrolyte:
0.4 M $Mg(TFSI)_2$ and 0.5M Dipropylene glycol dimethyl ether (Dipro glyme) in Acetonitrile

Glyme with higher boiling point and lower toxicity than many ethers
Provides improved Mg^{2+} coordination and improved performance

working = Mg-birnessite , reference=Ag/Ag^+,

Electrolyte: 0.4 M $Mg(TFSI)_2$ acetonitrile, water content: Mg/water=1/6

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Patent disclosure filed

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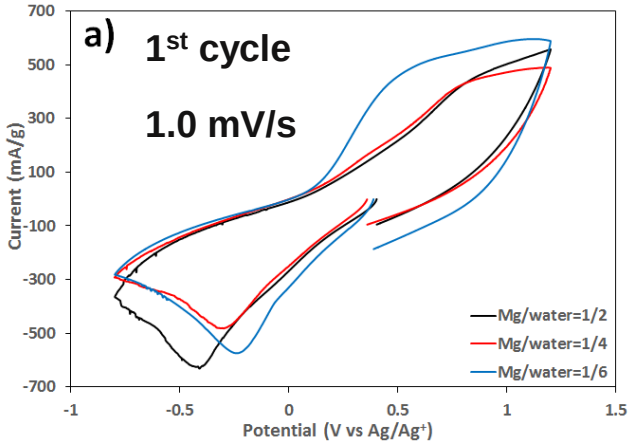
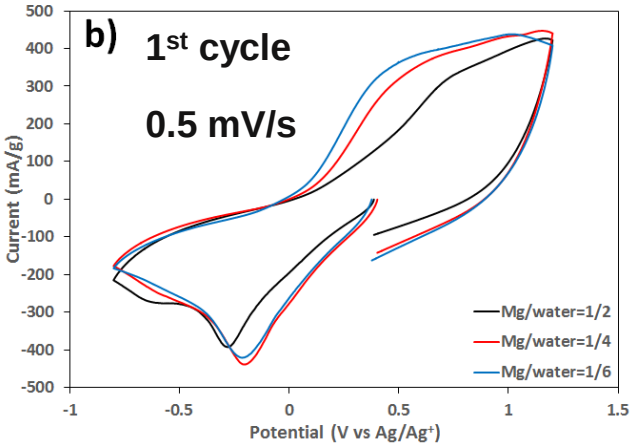
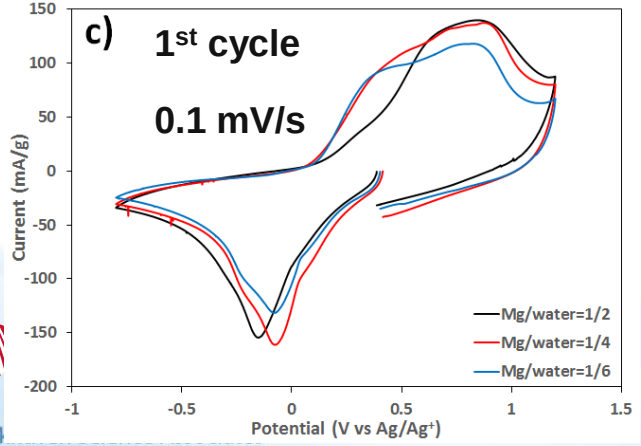
Cathode: Mg-birnessite

Cyclic voltammetry in Mg electrolyte: impact of water







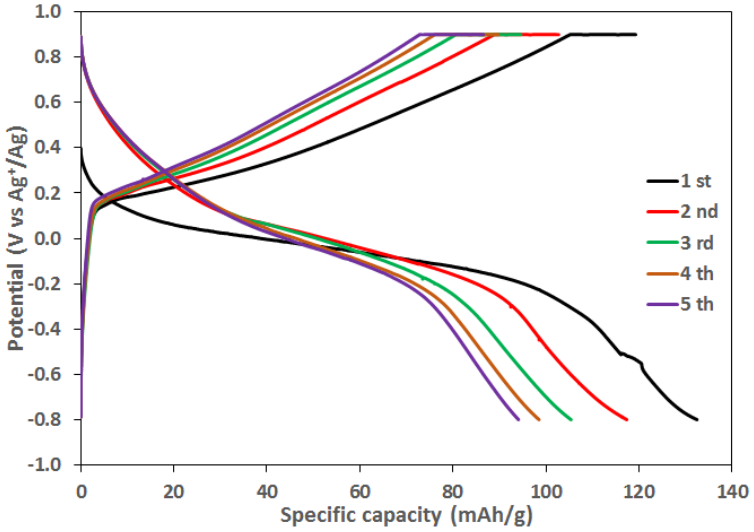
working = Mg-birnessite ,reference=Ag/Ag^+.

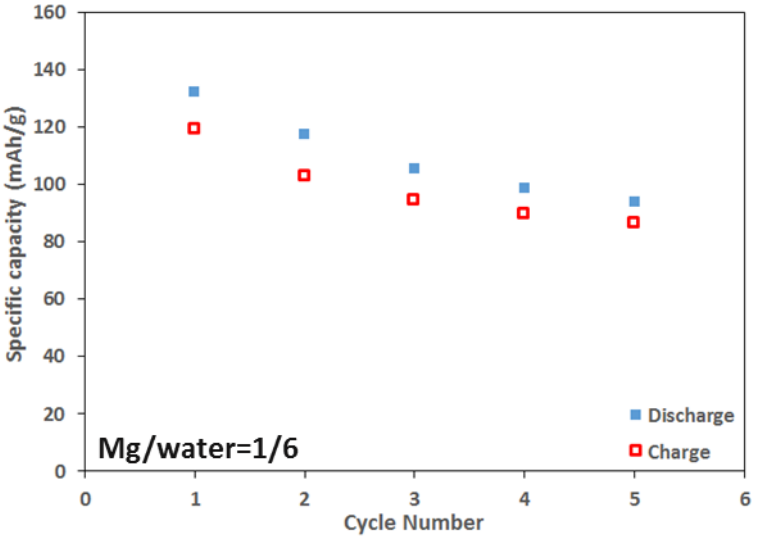
Electrolyte: 0.4 M $Mg(TFSI)_2$ and 0.5M Dipropylene glycol dimethyl ether in Acetonitrile with added water

Best Ratio : Mg^{2+}/H_2O = 1/6

Cathode: Mg-birnessite

Galvanostatic cycling in Mg electrolyte



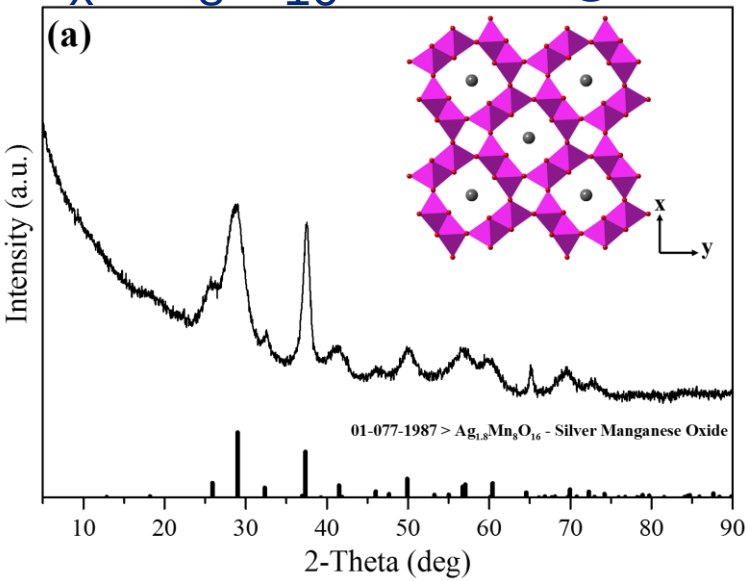


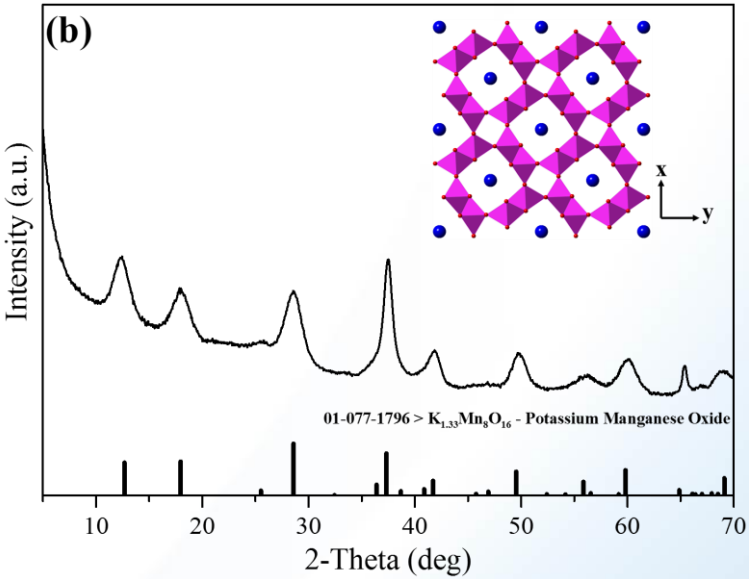
working = Mg-birnessite , reference=Ag/Ag^+, Electrolyte: 0.4 M $Mg(TFSI)_2$ and dipropylene glycol dimethyl ether, acetonitrile, water content: Mg/water=1/6 . Begins to stabilize at ~ 80 mAh/g.

Current: 0.2 C

Tunnel structured Manganese Oxide

$M_xMn_8O_{16}$ M = Ag, K





Ag-OMS-2:
$Ag_{1.22}Mn_8O_{16}{\cdot}2.90H_2O$

K-OMS-2:
$K_{0.68}Mn_8O_{16}{\cdot}0.88H_2O$

Low temperature, scalable, aqueous based syntheses

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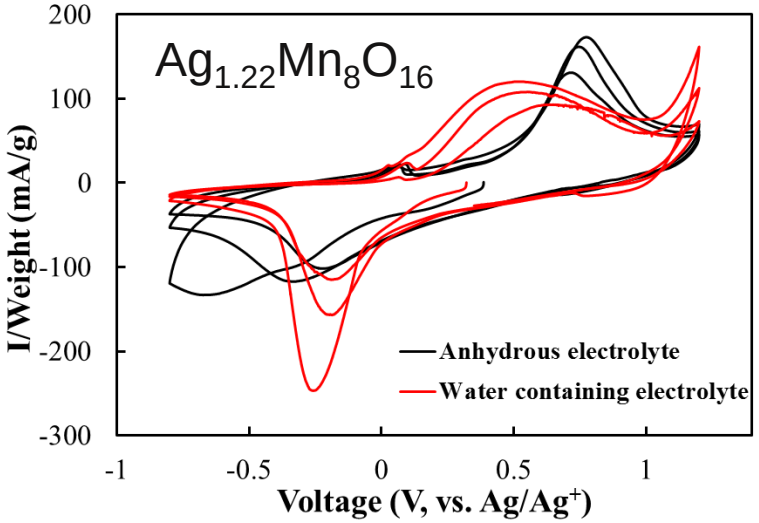
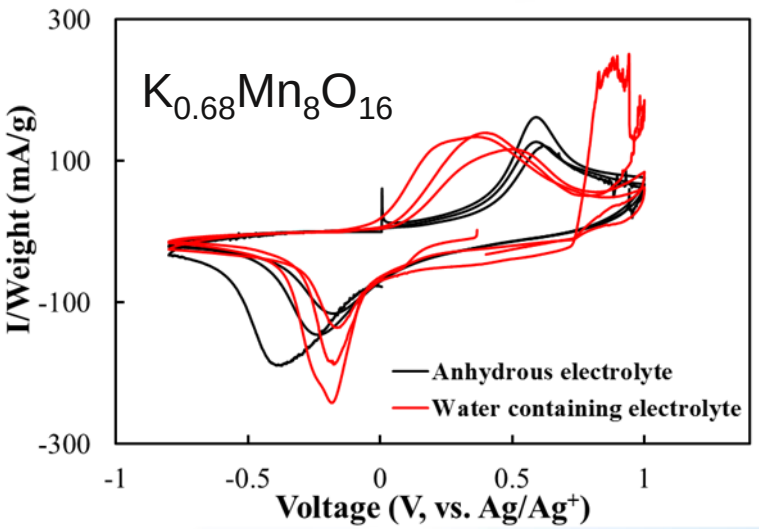
Cathode: $M_xMn_8O_{16}$ M = Ag, K

Cyclic voltammetry in Mg electrolyte





0.5 M $Mg(TFSI)_2$ and 0.5 M dipropylene glycol dimethyl ether in acetonitrile

Improved reversibility with water in electrolyte $Mg^{2+}/H_2O = 1/6$

Stony Brook University
Brookhaven Science Associates

J. Huang, A. Poyraz, A. Marschilok, K. Takeuchi, E. Takeuchi, Submitted for publication

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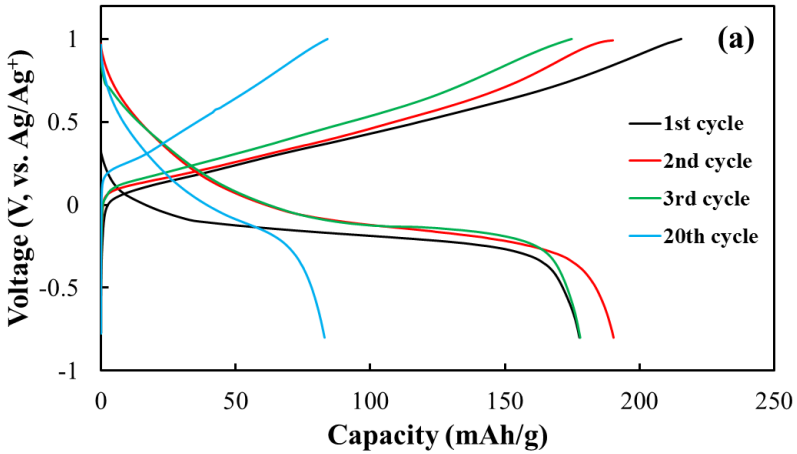
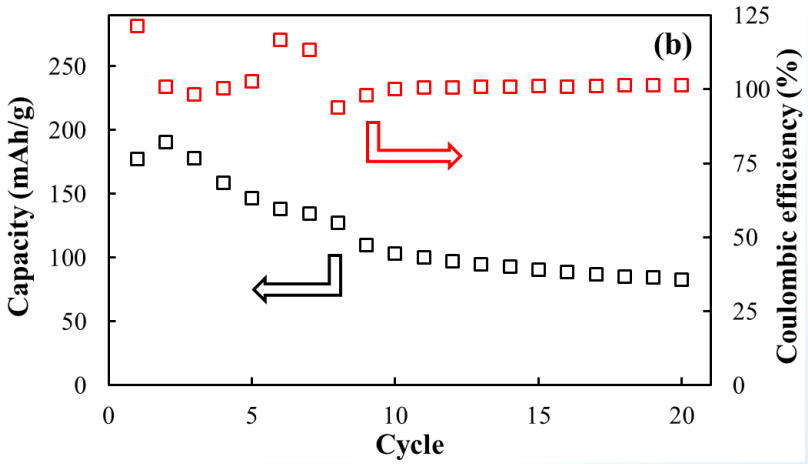
Cathode: Ag-OMS-2

Galvanostatic cycling in water containing electrolyte





The capacity of initial cycles is > 150 mAh/g
Stabilizes at ~ 80 mAh/g
Voltage versus Mg is 2.6 V

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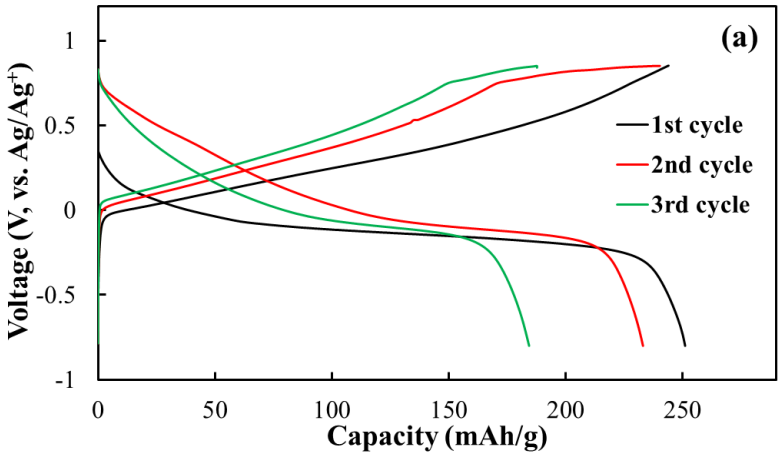
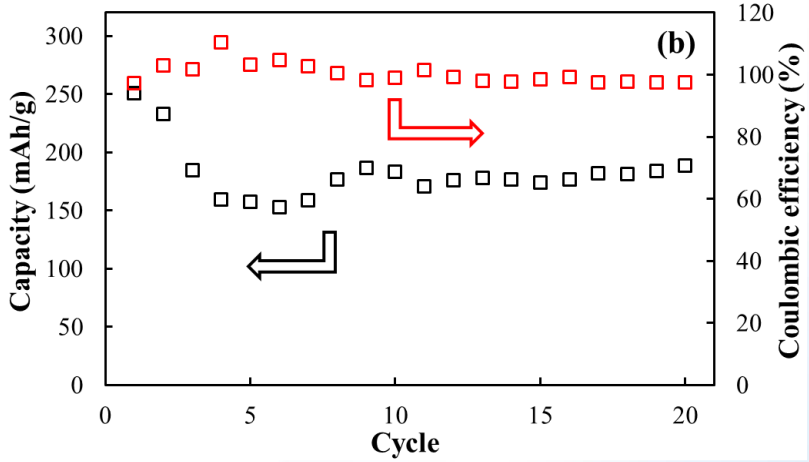
Cathode: K-OMS-2

Galvanostatic cycling in water containing electrolyte





Higher initial capacity (250 mAh/g)
Capacity stabilizes >150 mAh/g
High coulombic efficiency
Voltage versus Mg is 2.6 V
Low cost material

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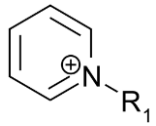
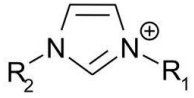
Mg-ion Hybrid Electrolytes: non-flammable

Ionic Liquid Name	Abbreviation
1-Methyl-1-Propyl-Piperidinium bis(trifluoromethylsulfonyl)imide	1M1PPi-TFSI
1-Butyl-1-Methyl-Piperidinium bis(trifluoromethylsulfonyl)imide	1B1MPi-TFSI
1-Ethyl-1-Methly-Pyrrolidinium bis(trifluoromethylsulfonyl)imide	1E1MPyrr-TFSI
1-Methyl-1-Propyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide	1M1PPyrr-TFSI
1-Butyl-1-Methyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide	1B1MPyrr-TFSI
1-Ethyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide	1E3MIm-TFSI
1-Methyl-3-Propyl-Imidazolium bis(trifluoromethylsulfonyl)imide	1M3PIm-TFSI
1-Butyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide	1B3MIm-TFSI
1-Ethyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide	1E3MPy-TFSI
1-Propyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide	1P3MPy-TFSI
1-Butyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide	1B3MPy-TFSI

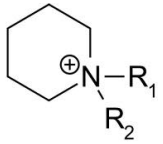
Pyridinium



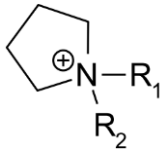
Imidazolium



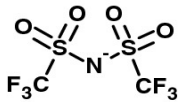
Piperidinium



Pyrrolidinium

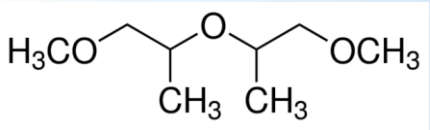


Bis(trifluoromethylsulfonyl)imide



Combine ionic liquids with co-solvents. IL provides safety, co-solvent improves conductivity.

- Acetonitrile (ACN)
- Di(propylene glycol) dimethyl ether



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M. Huie, C. Cama, A. Marschilok, K. Takeuchi, E. Takeuchi
In preparation for publication

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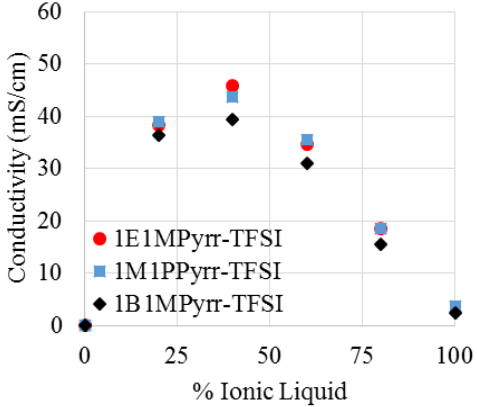
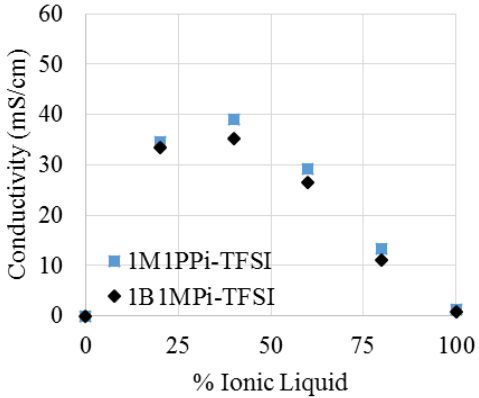
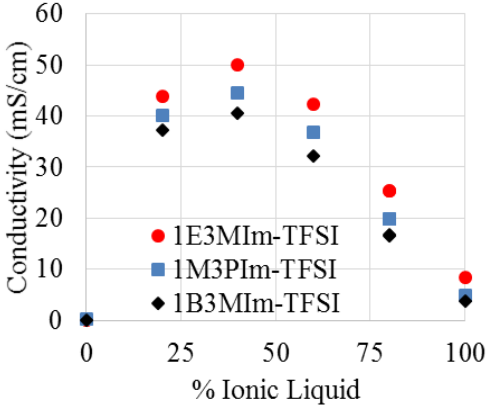
Hybrid IL-Acetonitrile Electrolytes

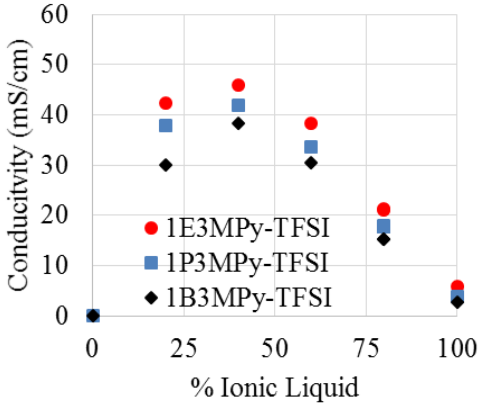
Conductivity





	Conductivity (mS/cm)		
IL	No Salt	0.5 M salt	% IL
1E1MPyrr-TFSI	46	27	40
1M1PPyrr-TFSI	44	27	40
1M1PPi-TFSI	39	25	40
1E3MPy-TFSI	46	29	40
1P3MPy-TFSI	42	26	40
1E3MIm-TFSI	50	26	40
1M3PIm-TFSI	45	25	40





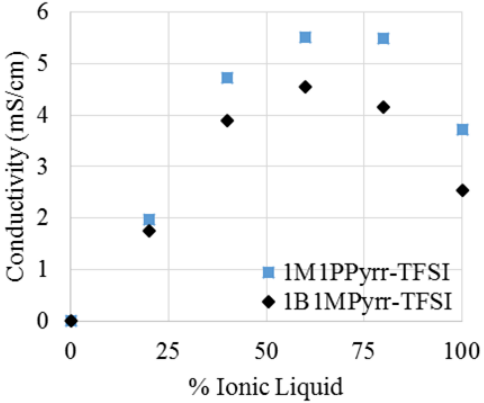
Max conductivity at 40% IL

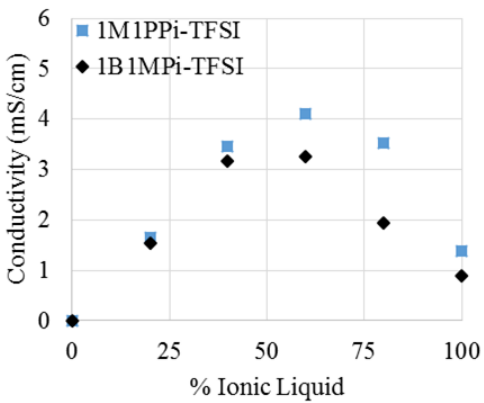
Unsaturated cations and smaller ring size → Better conductivity

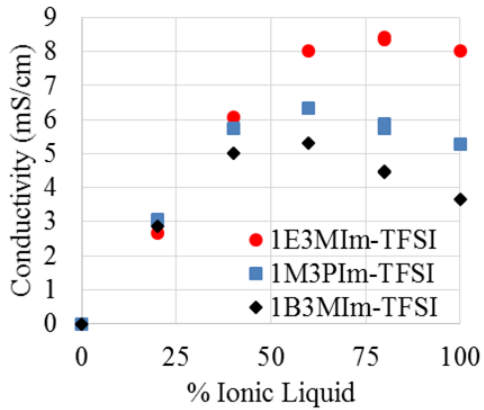
0.5 M $Mg(TFSI)_2$ decreases conductivity ~50%

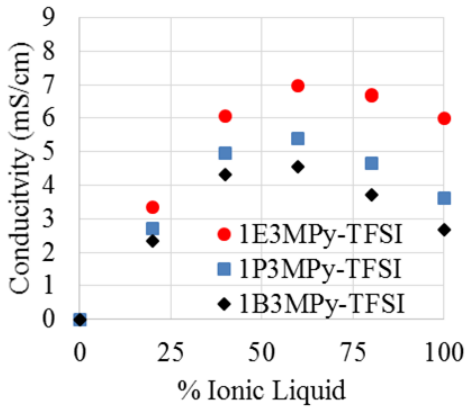
Hybrid IL-DPGME Electrolytes

Conductivity









	Conductivity (mS/cm)		
IL	No Salt	0.5 M salt	% IL
1M1PPyrr-TFSI	5.5	2.5	60
1M1PPi-TFSI	4.1	1.9	60
1P3MPy-TFSI	5.4	2.5	60

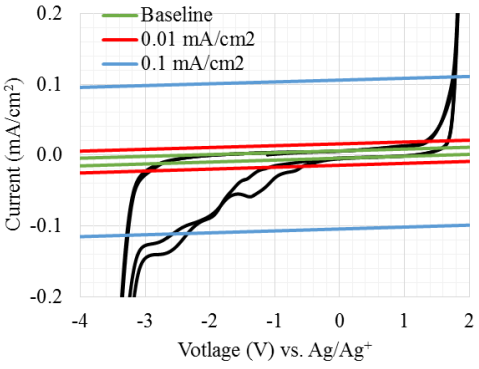
About less conductive than ACN solutions

Unsaturated cations and smaller ring size → Better conductivity

0.5 M $Mg(TFSI)_2$ decreases conductivity

Hybrid IL Electrolytes

Voltage Window of Stability

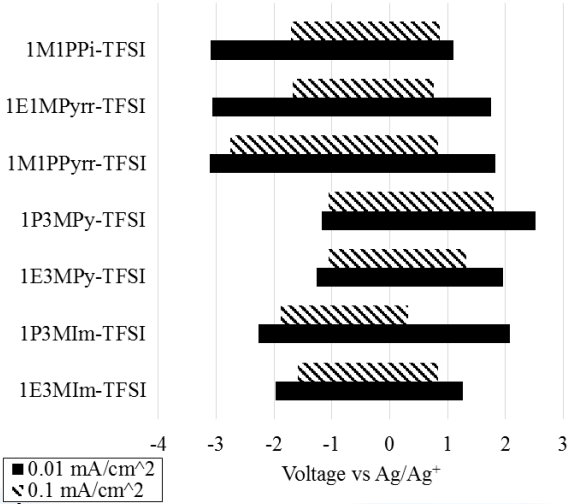


0.5 M $Mg(TFSI)_2$

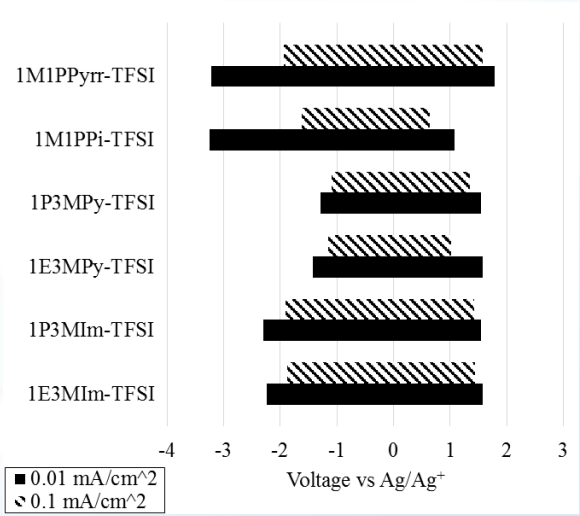
All electrolytes >3.0 V window of stability for 0.1 mA/cm^2 limit

Saturated cation ring → larger window

IL/Acetonitrile



IL/DPGME



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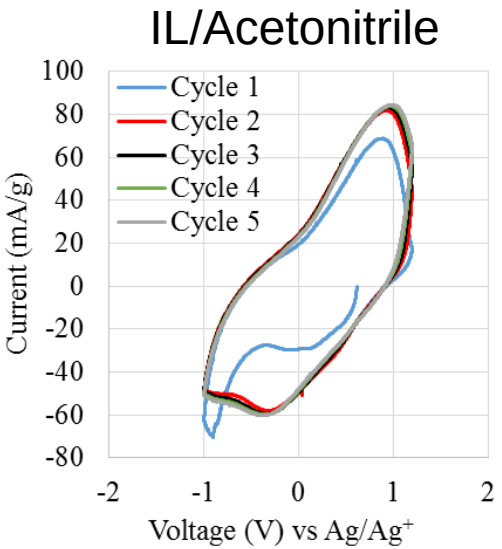
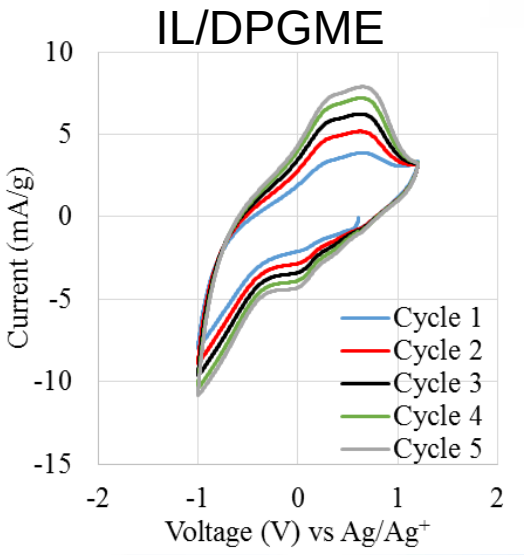
Hybrid IL Electrolytes

Cathode: $Mg_{0.07}V_2O_5$

Electrolyte	E_{ox} (V)	E_{red} (V)	$\Delta(E_{ox}-E_{red})$	I_{ox} (mA/g)	I_{red} (mA/g)
1M1PPi-TFSI/Acetonitrile	1.00	-0.38	1.38	83.9	-60.3
1M1PPi-TFSI/DPGME	0.20; 0.74	0	0.20; 0.74	7.5; 7.8	-4.3
Acetonitrile	0.80	-0.05	0.85	43.5	-32.8



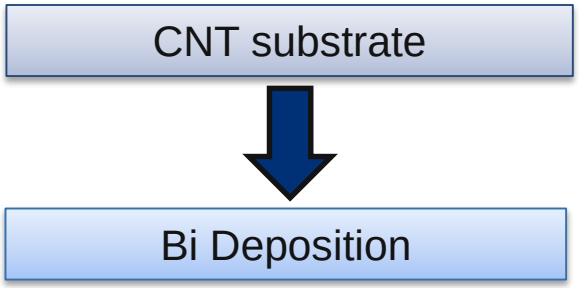


DPGME → Lower current, less polarization

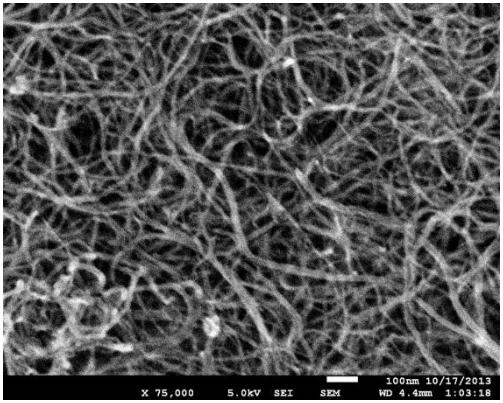
IL/acetontrile → Higher peak current

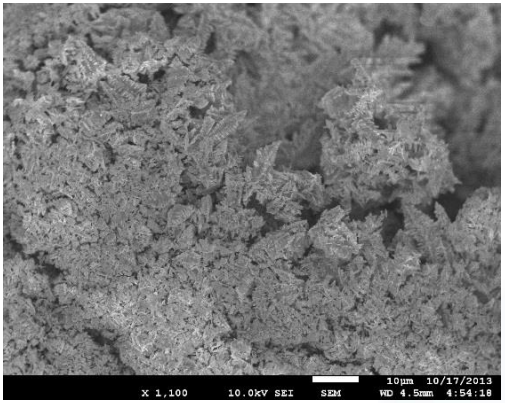
Anode: electrodeposited Bi

Bi on CNT substrate

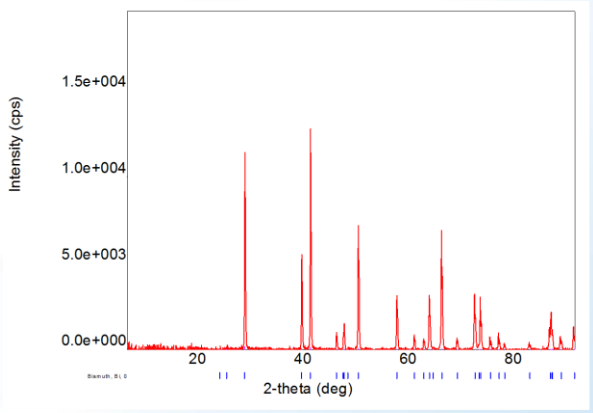


Bi-CNT was prepared by electrodepostion of Bi on CNTs
Enables use of new electrolytes
Capacity ~ 180 mAh/g.





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



X-ray powder diffraction of Bi on CNT

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R. DiLeo, Q. Zhang, A. Marschilok, K. Takeuchi, and E. Takeuchi, *Electrochem Lett. 4 (1) A10-A14 (2015).*

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Summary

Cathode

High voltage cathode systems that function in non-corrosive Mg^{2+} electrolyte demonstrated. Scalable, low temperature syntheses.

$Mg_{0.1}V_2O_y$ >140 mAh/g

Mg_xMnO_y ~ 80 mAh/g

$M_xMn_8O_{16}$ M = Ag, K ~150 mAh/g

Anode

Bi tunable electrodeposition based preparation on CNT substrate >180 mAh/g in non-corrosive Mg^{2+} electrolyte

Electrolyte

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

Intellectual Property

2011: Composite electrodes, methods of making, and uses thereof

2013: Electrode materials for Group II cation based batteries

2014: Hybrid electrolytes for group II cation based batteries

2015: High voltage cathode materials for group II cation based batteries

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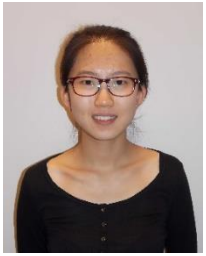

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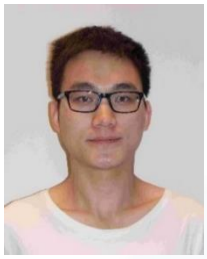

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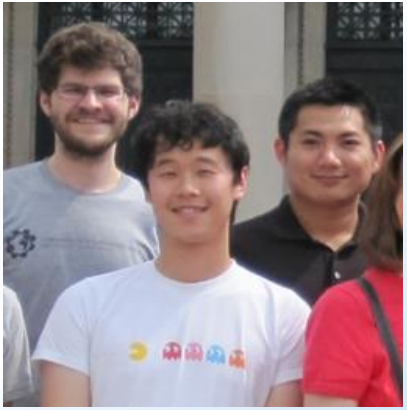

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