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

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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

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.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Li</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic radius, Å</td>
<td>0.72</td>
<td>0.76</td>
<td>1.19</td>
</tr>
<tr>
<td>melt. pt., °C</td>
<td>650</td>
<td>181</td>
<td>328</td>
</tr>
<tr>
<td>mAh/g</td>
<td>2205</td>
<td><strong>3862</strong></td>
<td>259</td>
</tr>
<tr>
<td>mAh/cc</td>
<td><strong>3837</strong></td>
<td>2047</td>
<td>2926</td>
</tr>
<tr>
<td>$/lb</td>
<td><strong>$1.12</strong></td>
<td>$28</td>
<td>$1.68</td>
</tr>
<tr>
<td>$/kWh</td>
<td><strong>$2.5</strong></td>
<td>$58</td>
<td>$31</td>
</tr>
</tbody>
</table>
Approach to Mg Battery System
The necessity of systems level understanding

M. Huie, D. Bock, E. Takeuchi, A. Marschilok, K. Takeuchi
Cathode: Mg$_{0.1}$V$_2$O$_y$•1.8H$_2$O

Material synthesis

Two-Step Synthesis

Ion exchange

Sol gel reaction

Mg$_x$V$_2$O$_y$ was prepared by a two-step **scalable process** where the first step was an ion exchange reaction of MgV$_2$O$_6$ followed by a sol gel reaction.

X-ray powder diffraction pattern of Mg$_x$V$_2$O$_5$ (x = 0.11, 0.18)

Schematic of Mg$_x$V$_2$O$_5$ structure

Cathode: Mg$_{0.1}$V$_2$O$_y$•1.8H$_2$O
Results of voltammetry: significant solvent effect

De-solvation energy of Mg$^{2+}$ in EC, DEC, PC > CH$_3$CN
Slow scan voltammetry at 1E-4 V/s.
working = Mg$_{0.1}$V$_2$O$_5$, reference = Ag/Ag$^+$, auxiliary = Pt.

Cathode: $\text{Mg}_x \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$

Galvanostatic cycling in Mg electrolyte

$\text{Mg}_{0.11} \text{V}_2\text{O}_5 \cdot 2.35\text{H}_2\text{O}$ can deliver $\sim 140$ mAh/g in 0.5 M Mg(TFSI)$_2$. Capacity increased in the first cycles, then stable at $\sim 140$ mAh/g.

$\text{Mg}_{0.11} \text{V}_2\text{O}_5 \cdot 2.35\text{H}_2\text{O}$ capacity $> \text{Mg}_{0.18} \text{V}_2\text{O}_5 \cdot 2.35\text{H}_2\text{O}$

J. Yin, A. Marschilok, K. Takeuchi, E. Takeuchi

In preparation for publication
Mg-birnessite was prepared by a two-step scalable process:

1. Room temperature precipitation reaction for Na-birnessite
2. Followed by ion exchange

XRD pattern of Mg-birnessite with standard index

- Monoclinic phase (space group C 2/m)
- \( a = 5.050 \, \text{Å}, \ b = 2.846 \, \text{Å}, \ c = 7.054 \, \text{Å}, \ b = 96.63^\circ \)
- Pink, Mn; Red, O; Yellow, Mg; Blue, \( H_2O \).

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

Patent disclosure filed
Cathode: Mg-birnessite
Cyclic voltammetry in Mg electrolyte: impact of water

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

Cyclic voltammetry in Mg electrolyte

$0.5 \text{ M Mg(TFSI)}_2$ and $0.5 \text{ M dipropylene glycol dimethyl ether in acetonitrile}$

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

J. Huang, A. Poyraz, A. Marschilok, K. Takeuchi, E. Takeuchi, Submitted for publication
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
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
### Mg-ion Hybrid Electrolytes: non-flammable

<table>
<thead>
<tr>
<th>Ionic Liquid Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methyl-1-Propyl-Piperidinium bis(trifluoromethylsulfonyl)imide</td>
<td>1M1PPi-TFSI</td>
</tr>
<tr>
<td>1-Butyl-1-Methyl-Piperidinium bis(trifluoromethylsulfonyl)imide</td>
<td>1B1MPPi-TFSI</td>
</tr>
<tr>
<td>1-Ethyl-1-Methyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide</td>
<td>1E1MPyrr-TFSI</td>
</tr>
<tr>
<td>1-Methyl-1-Propyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide</td>
<td>1M1PPyrr-TFSI</td>
</tr>
<tr>
<td>1-Butyl-1-Methyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide</td>
<td>1B1MPyrr-TFSI</td>
</tr>
<tr>
<td>1-Ethyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>1E3MIm-TFSI</td>
</tr>
<tr>
<td>1-Methyl-3-Propyl-Imidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>1M3PIm-TFSI</td>
</tr>
<tr>
<td>1-Butyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>1B3MIm-TFSI</td>
</tr>
<tr>
<td>1-Ethyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>1E3MPy-TFSI</td>
</tr>
<tr>
<td>1-Propyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>1P3MPy-TFSI</td>
</tr>
<tr>
<td>1-Butyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>1B3MPy-TFSI</td>
</tr>
</tbody>
</table>

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

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

[Stony Brook University logo]

M. Huie, C. Cama, A. Marschilok, K. Takeuchi, E. Takeuchi
In preparation for publication
Hybrid IL-Acetonitrile Electrolytes

Conductivity

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

<table>
<thead>
<tr>
<th>IL</th>
<th>Conductivity (mS/cm)</th>
<th>0.5 M salt</th>
<th>% IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M1PPyrr-TFSI</td>
<td>5.5</td>
<td>2.5</td>
<td>60</td>
</tr>
<tr>
<td>1M1PPi-TFSI</td>
<td>4.1</td>
<td>1.9</td>
<td>60</td>
</tr>
<tr>
<td>1P3MPy-TFSI</td>
<td>5.4</td>
<td>2.5</td>
<td>60</td>
</tr>
</tbody>
</table>

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

![Graph showing voltage window of stability for different electrolytes and current limits.](image)
Hybrid IL Electrolytes
Cathode: Mg\textsubscript{0.07}V\textsubscript{2}O\textsubscript{5}

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

DPGME → Lower current, less polarization
IL/acetonitrile → Higher peak current
Anode: electrodeposited Bi
Bi on CNT substrate

CNT substrate

Bi Deposition

Bi-CNT was prepared by electrodeposion 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

R. DiLeo, Q. Zhang, A. Marschilok, K. Takeuchi, and E. Takeuchi,
Summary

Cathode

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

$\text{Mg}_{0.1}V_2O_y > 140 \text{ mAh/g}$

$\text{Mg}_x\text{MnO}_y \sim 80 \text{ mAh/g}$

$\text{M}_x\text{Mn}_8\text{O}_{16} \quad M = \text{Ag, K} \sim 150 \text{ mAh/g}$

Anode

Bi tunable electrodeposition based preparation on CNT substrate $> 180 \text{ mAh/g}$ 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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