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JOINT CENTER FOR ENERGY STORAGE RESEARCH

Performance of a MgS battery using Grignard Based Electrolytes

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Sandia National Laboratories

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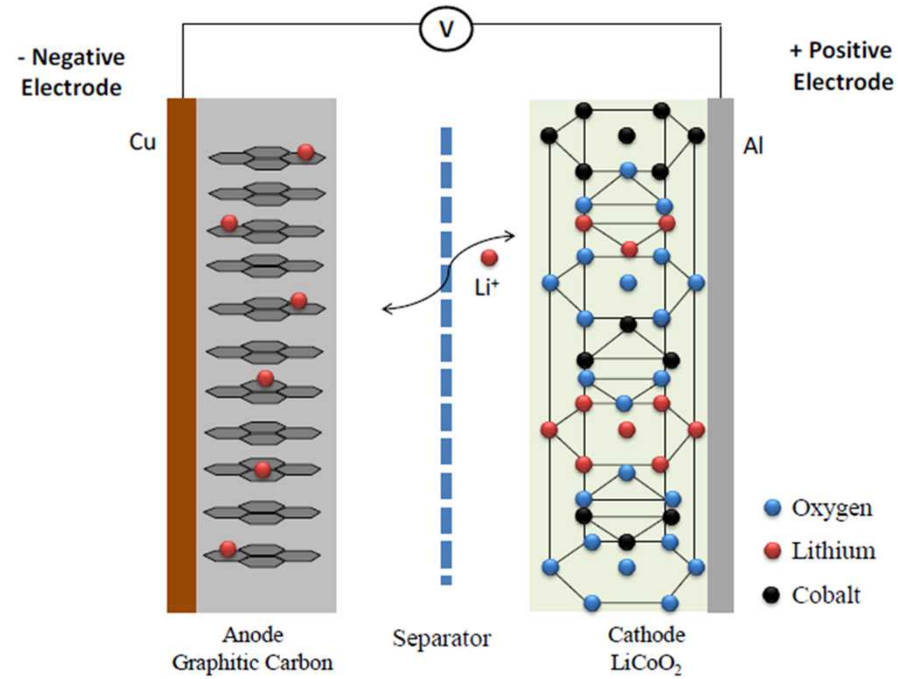
Current State of the Art in Energy Storage The Lithium Ion Battery



- One of the greatest success in electrochemical energy storage
- It has been adapted to many different platforms and form factors
- As transformative as this technology is it can be argued that it is reaching its theoretical limit

http://www.bombayharbor.com/Product/13263/Battery_Ion_Battery_Pack_Lithium_Battery_Lim_Ion.html
Image provided by Chelsea Snyder

The Next Generation of Energy: Beyond Lithium Ion…

- To move beyond Li ion different strategies are needed…

  Use of a metallic anode

  Multivalent ions

  Chemical conversion vs intercalation

- A daunting task to overcome the past 20 years of R+D put into current Li ion tech

Element	Mass	mA/hour	mA/hour/g
LiC6	79	26801	339
H	1	26801	26801
Be	9.01	53603	5949
Li	6.94	26801	3862
Al	26.982	80404	2980
Mg	24.03	53603	2231
Ca	40	53603	1340
Na	23	26801	1165
K	39.098	26801	685
NiMnCoO2	66.018	53603	160
N	14	80404	5743
O	16	53603	3350
P	30.97	80404	2596
S	32	53603	1675
Mg2CoSiO4	201	107206	533
Mg aMnO2	110.9	53603	483
MgMoO3	167.94	53603	319
Mg V2O5	205.88	53603	260
Mg2Mo6S8	882.24	107206	122

Beyond Lithium Ion: Lithium Sulfur Battery (chemical conversion)

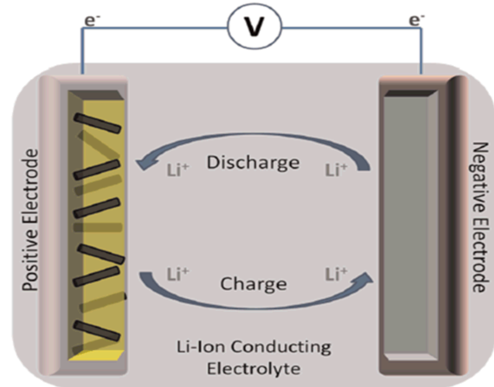
- Lithium sulfur batteries have been extensively studied

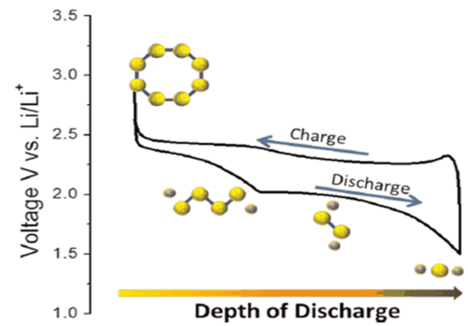
- They suffer from two major drawbacks…

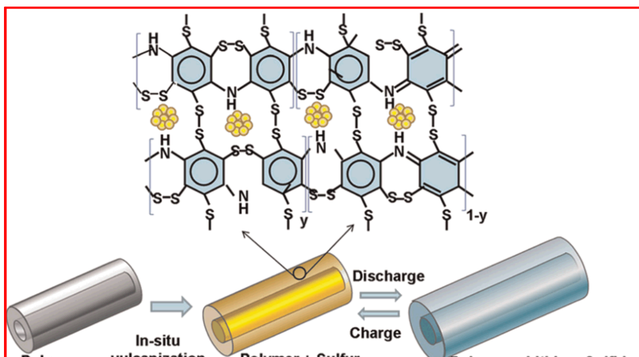
  Sulfur is ionically and electrically insulating

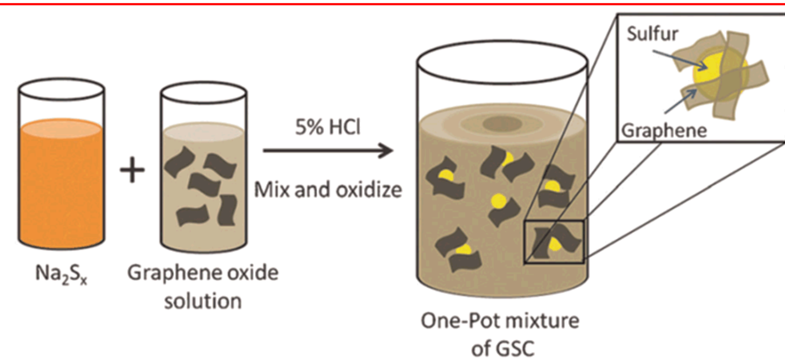
  Sulfur shuttle mechanism

- Much of the work done in this field is done to mitigate these problems…





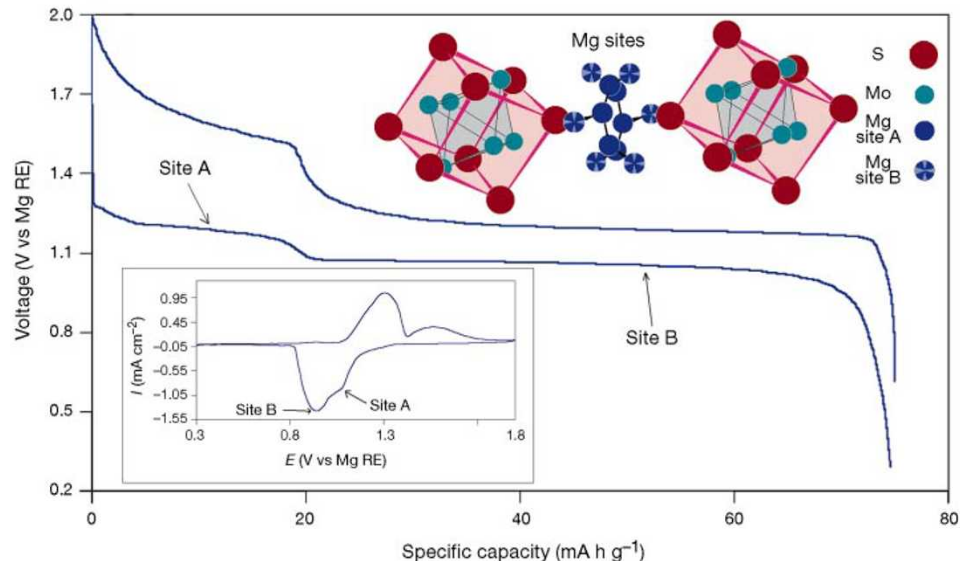




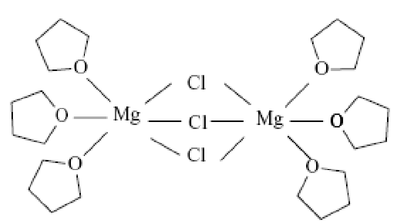
Evers, S.; Nazar, L. F., New Approaches for High Energy Density Lithium-Sulfur Battery Cathodes. Accounts Chem. Res. 2013, 46 (5), 1135-1143.

Beyond Lithium Ion: Prototype Mg Battery (multivalent ion)

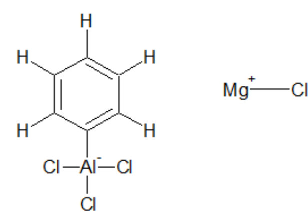
- Proof of concept work proposed by Gregory showing intercalation of Mg into metal oxides and sulfides with a Grignard reagent
- Aurbach improved on Gregory's work by introducing a new electrolyte and cathode that was able to reversibly intercalate Mg ions
- Aurbach's electrolytes the dichlorocomplex (DCC) and the all phenyl complex (APC) improved many aspects of performance



DCC



+ Al-Cl$_3$-Et -



APC

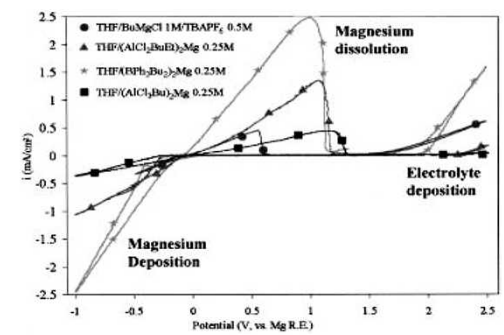


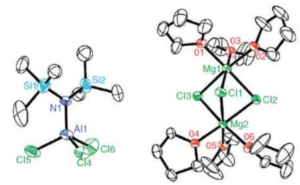
Fig. 3. Typical voltammetric behavior of Pt electrodes in different electrolyte solutions, as indicated, in which reversible magnesium deposition was obtained: BuMgCl/THF 0.25M; $Mg(BPh_2Bu_2)_2$/THF 0.25M; $Mg(AlCl_2BuEt)_2$/THF; $Mg(AlCl_3Bu)_2$/THF 0.25 M (Ref. 20).

Aurbach, D.; Lu, Z.; Schechter, A.; Gofer, Y.; Gizbar, H.; Turgeman, R.; Cohen, Y.; Moshkovich, M.; Levi, E., Prototype systems for rechargeable magnesium batteries. Nature 2000, 407 (6805), 724-727.

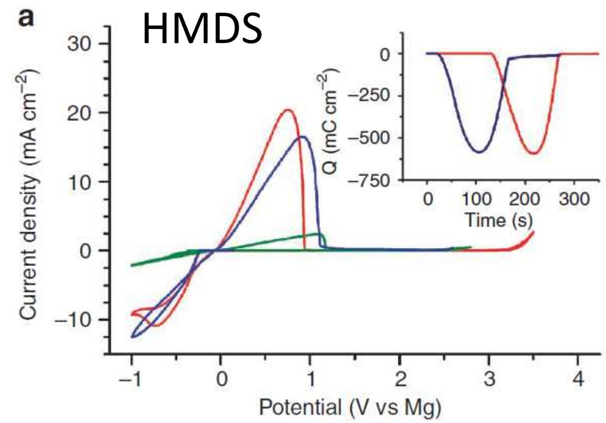
Aurbach, D.; Weissman, I.; Gofer, Y.; Levi, E., Nonaqueous magnesium electrochemistry and its application in secondary batteries. Chemical Record 2003, 3 (1), 61-73.

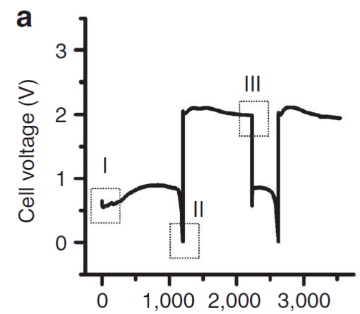
Magnesium Sulfur Utilizing all the Strategies

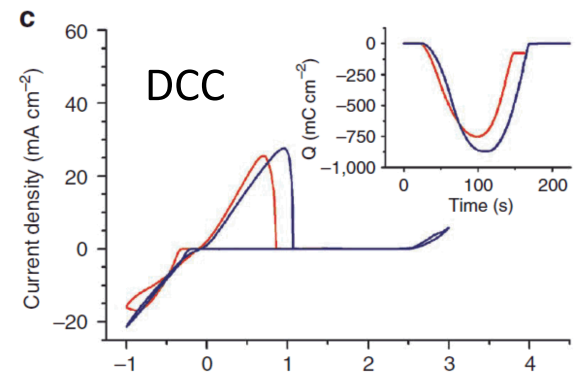
- Utilizing a multivalent ion may solve some of the experienced by LiS system
- Pairing two earth abundant elements allows for a low cost battery
- Muldoon showed proof of concept work using a new electrolyte. Explains that the reactivity of the Grignard based electrolytes may cause problems.
- Is a Mg sulfur battery utilizing the well characterized Grignard based electrolyte possible?



Mg HMDS electrolyte





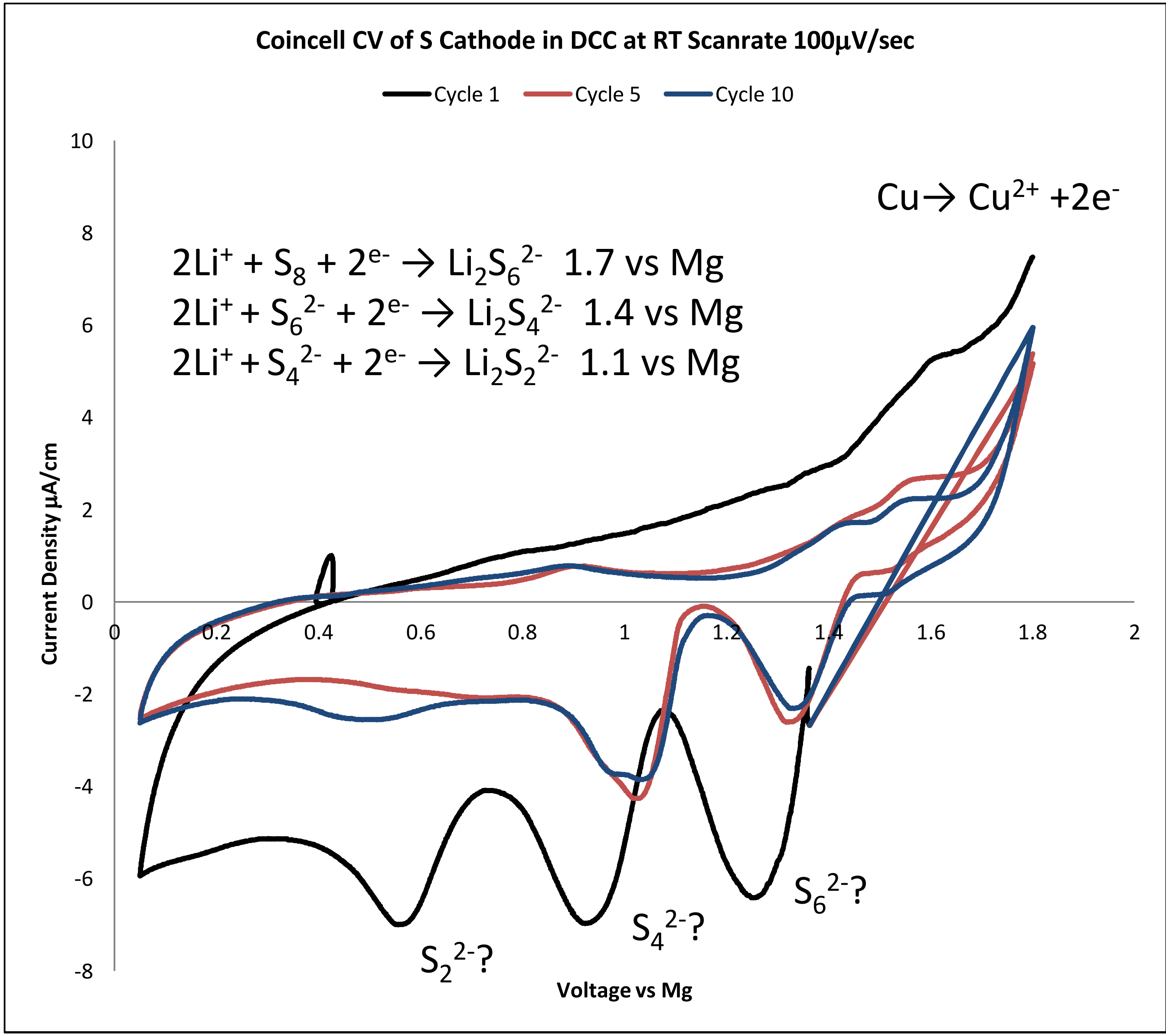


Hee Soo, K.; Arthur, T. S.; Allred, G. D.; Zajicek, J.; Newman, J. G.; Rodnyansky, A. E.; Oliver, A. G.; Boggess, W. C.; Muldoon, J., Structure and compatibility of a magnesium electrolyte with a sulphur cathode. Nature Communications 2011, 2, 427

Muldoon, J.; Bucur, C. B.; Oliver, A. G.; Sugimoto, T.; Matsui, M.; Kim, H. S.; Allred, G. D.; Zajicek, J.; Kotani, Y., Electrolyte roadblocks to a magnesium rechargeable battery. Energy & Environmental Science 2012, 5 (3), 5941-5950.

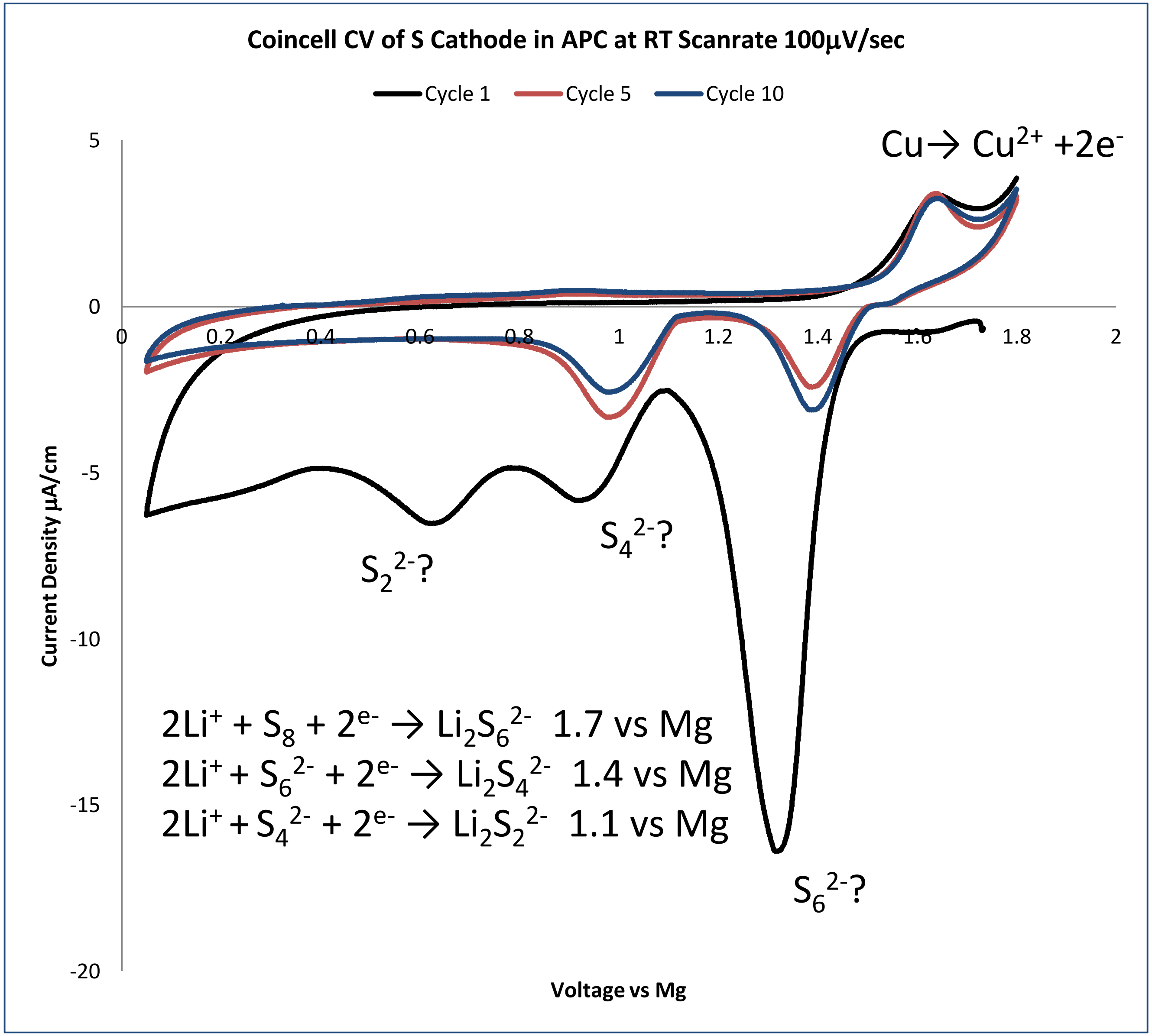
Slow Scanning Cyclic Voltammetry Results

- Electrochemical activity
- Three reduction peaks possible short chain poly sulfide formation?
- Asymmetry between charge and discharge consistent with LiS system



Slow Scanning Cyclic Voltammetry Differences in Electrolyte

- DCC reaches steady state faster than APC
- APC shows much larger S_6 reduction
- DCC higher coloumbic efficiency
- Conclusion: In a full cell SSCV suggests that DCC would preform better



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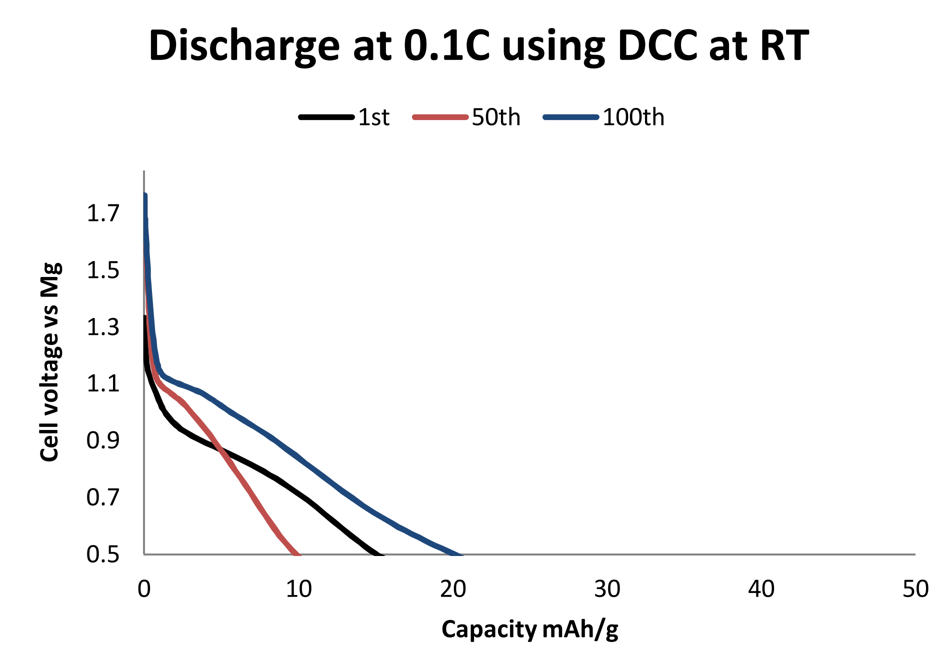
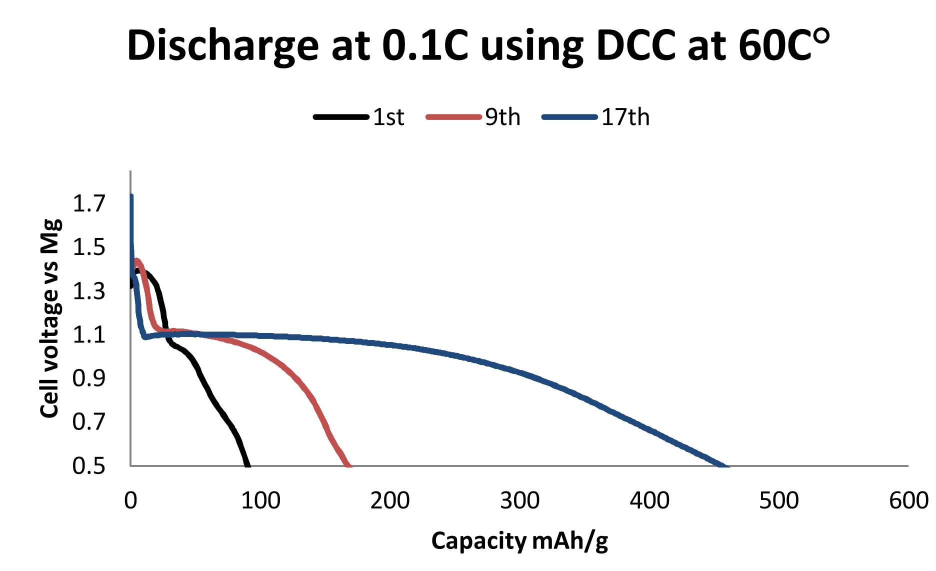
Full Cell Test Results

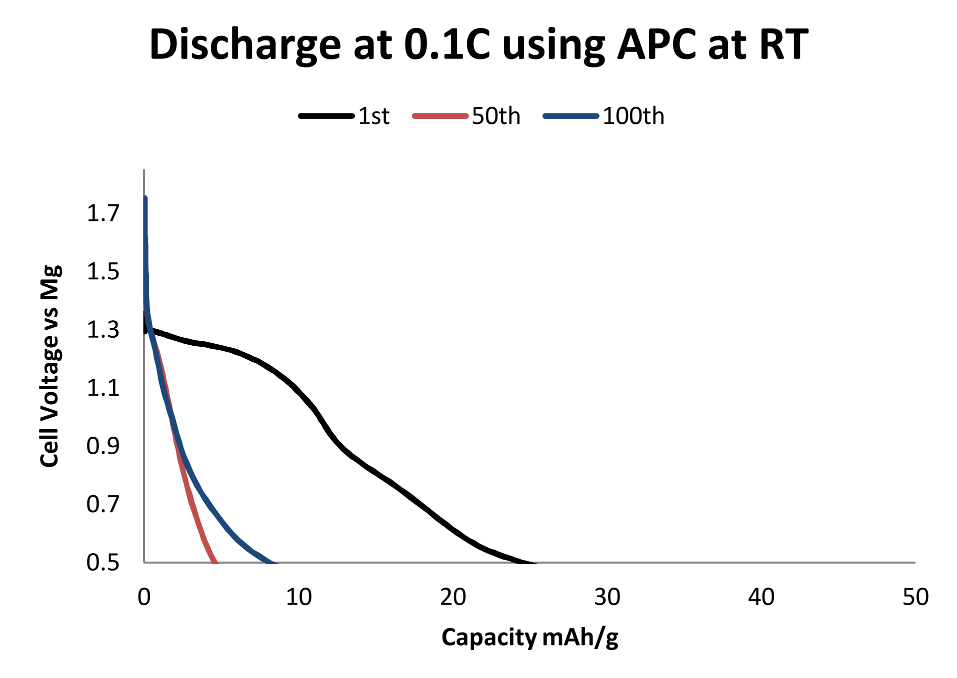
- Full cells were fabricated for both electrolytes and put on test
- Results show kinetic limitations
- 60C° discharge data shows behavior similar to lithium systems
- The capacity increases with cycle unlike Li systems

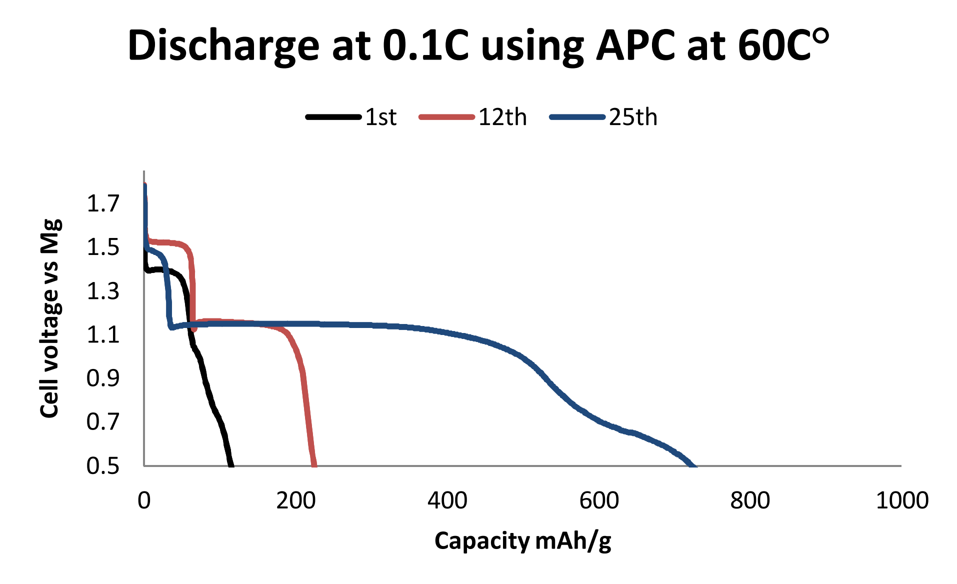




Full Cell Test Results

- APC behaves very similar to DCC
- Consistent with SSCV results DCC increases in capacity more rapidly than APC
- The voltammetry of APC is more defined than DCC this because APC has higher conductivity
- In both cases a stable discharge voltage of ~1.1V vs Mg and increasing capacity persist.





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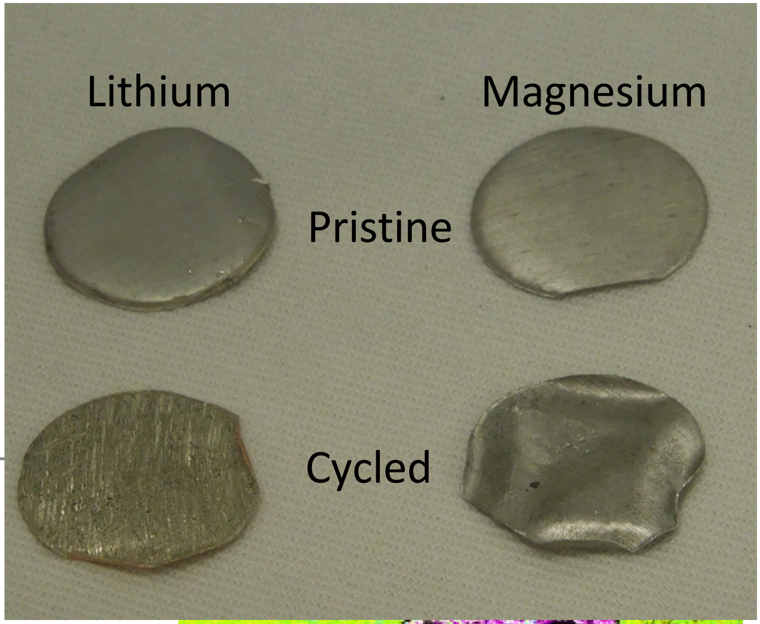
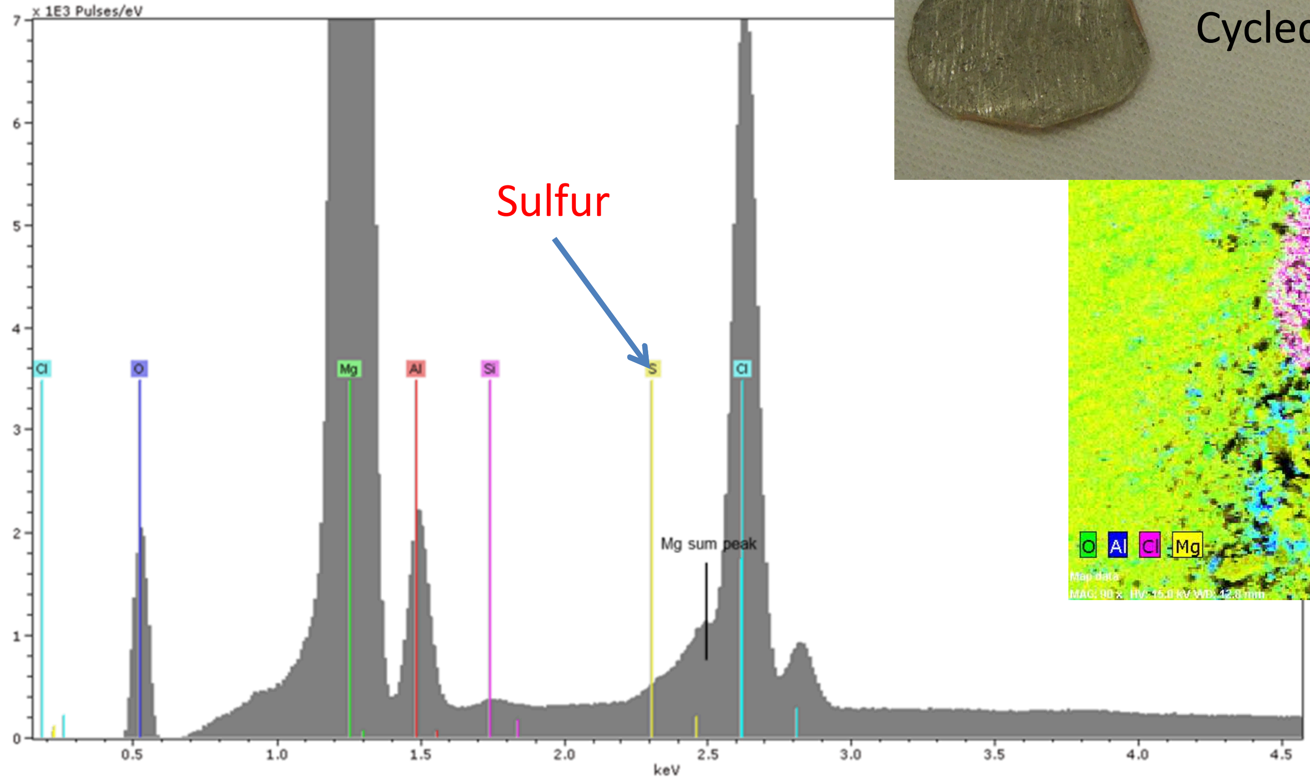
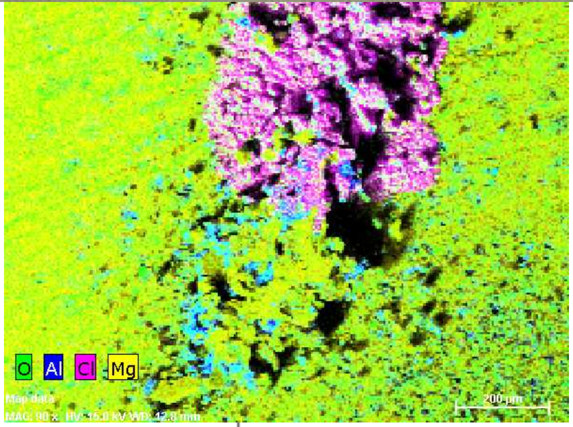
Postmortem Analysis of Anode

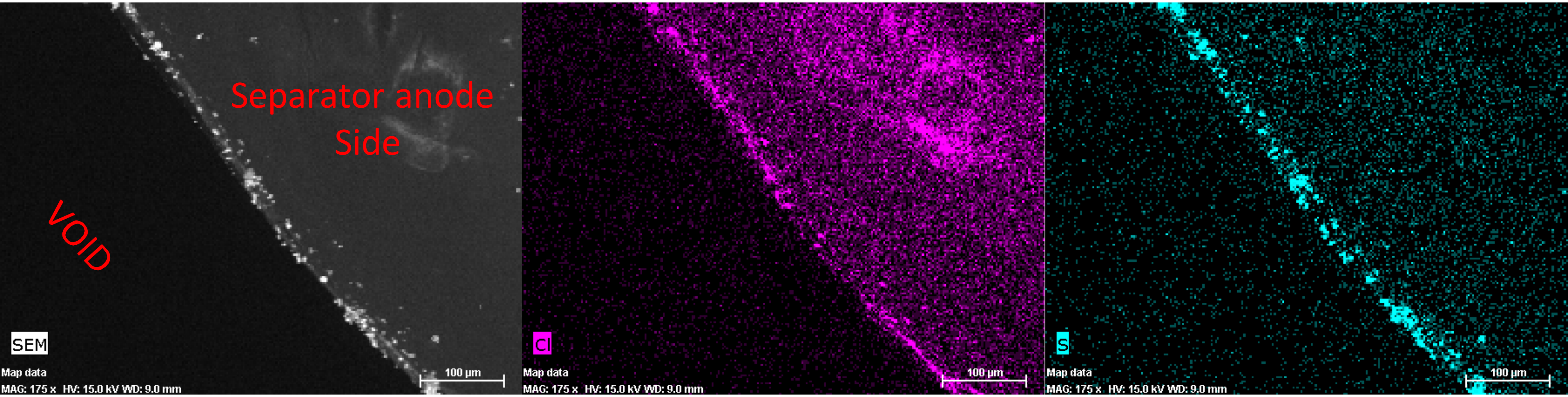
- SEM elemental map and spectra of the Mg Metal anode
- We do not see evidence of sulfur
- Metal anodes removed after 10 cycles of SSCV at 100μV/s at RT



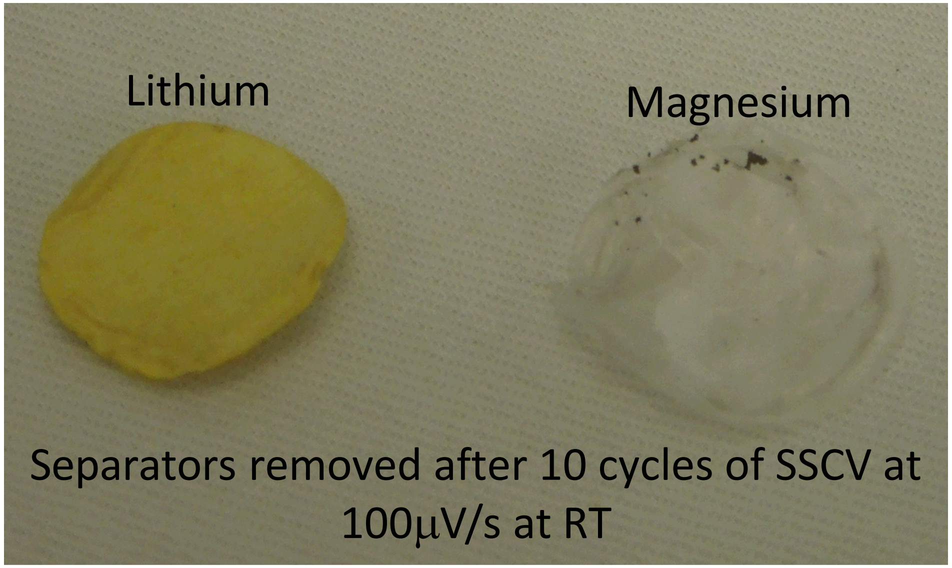




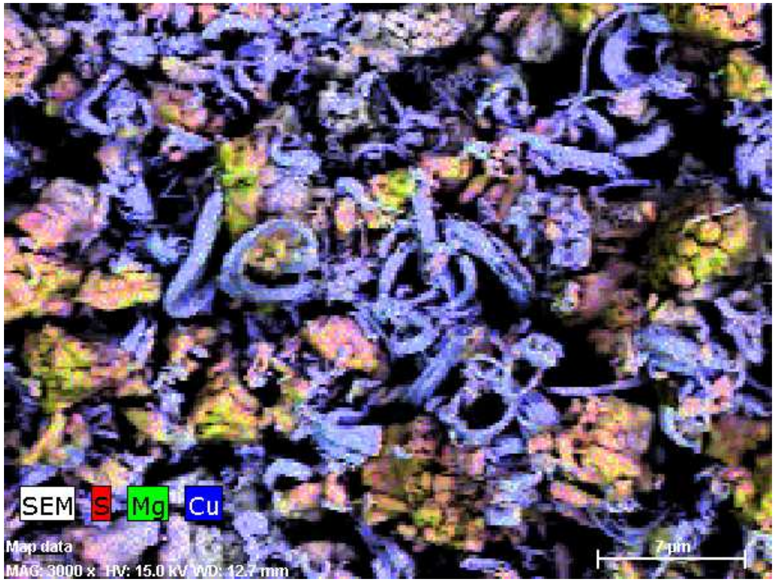
Post Mortem SEM of Separator (Anode Side)



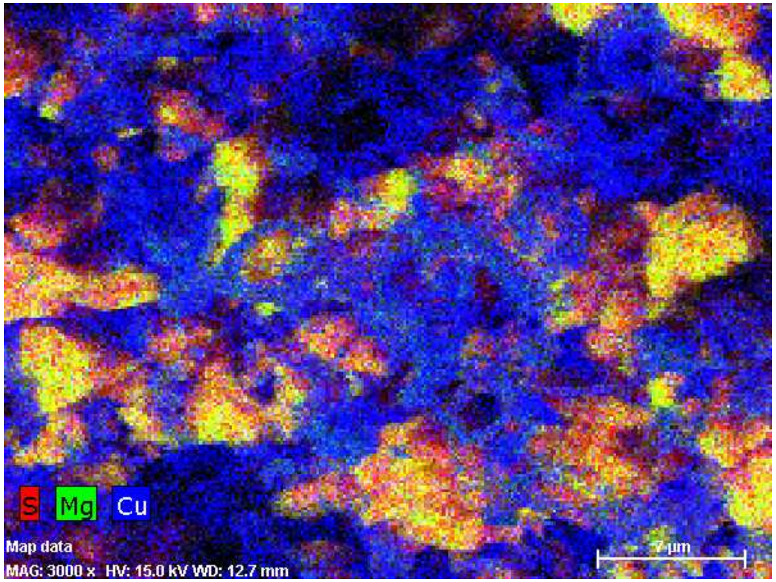
- If sulfur is not present on the anode will it be present in the cathode?
- It can be argued that that the trace signal in the sulfur map is material ripped off the cathode
- This indicates that very little polysulfides are made



Post Mortem SEM of Cathode



- EDX shows a precipitated Mg_xS_y compound onto the cathode
- Is this compound a result of insoluble polysulfides?
- It is believed that copper may be playing a role in this chemistry but more studies are required



Impact and Future Directions

- **Grignard based electrolytes do work in a sulfur system**
- **No evidence of accumulated sulfur on anode or in separator suggesting the suppression of polysulfides**
- **Will utilization of a nanostructured electrode improve the performance of this chemistry?**
- **What we learn from a Mg system could be applied to a Ca system increasing the energy density…**

Key Take-Away

- **A new sulfur chemistry was developed which suppresses the formation of polysulfides**

Acknowledgements

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