Fluorination of α-MnO_2 for Energy Storage Devices

MATE 491 - Fall 2017

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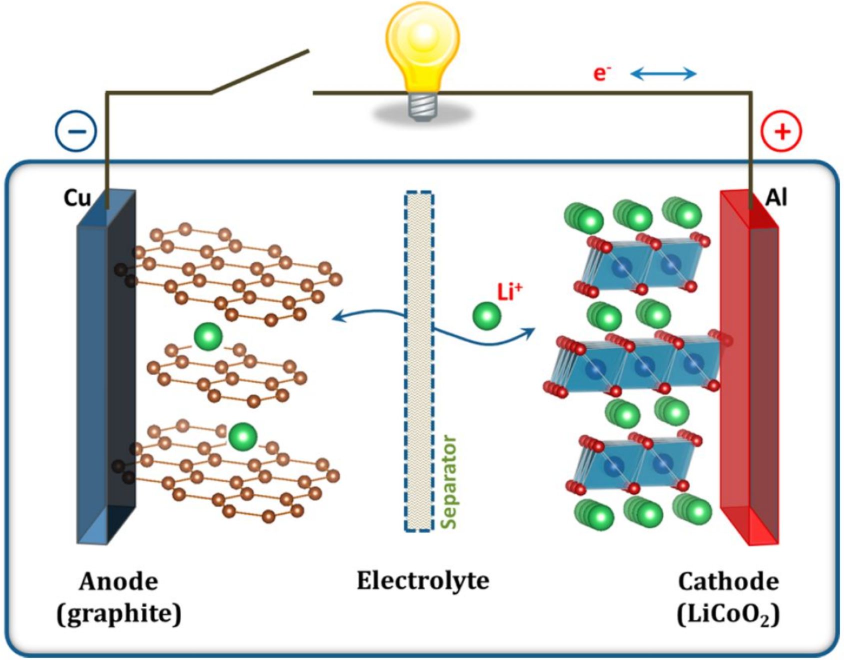
Mentors: Bryan Byles & Jiayi Wang

Li-Ion Battery

- Secondary battery
- Anode
  - Carbon material, tin, etc.
- Cathode
  - Oxide material containing Li
- Electrolyte
  - Solid or liquid
- Volumetric energy density has been greatly increased - controlling size and morphology of active materials, architecture of current collectors - reaching its limits
- Challenge - increase energy density while maintaining or increasing cyclability



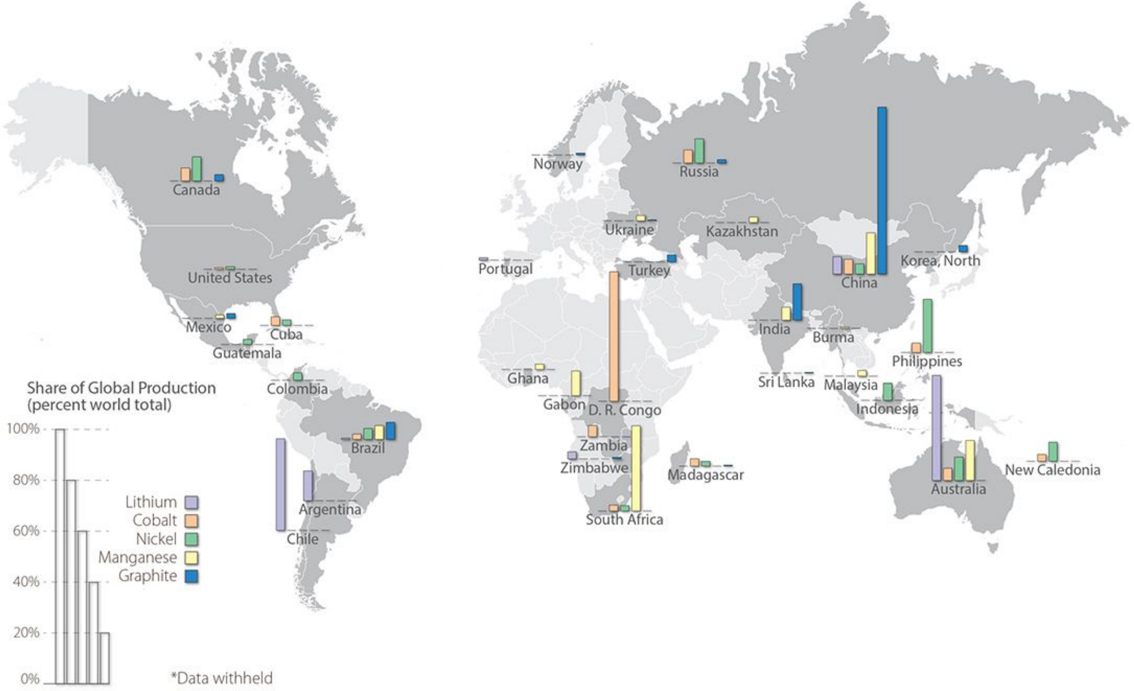
JB Goodenough, *Journal of the American Chemical Society* **2013** *135* (4), 1167-1176

Problem Statement

- The demand for energy storage is increasing exponentially

- The supply of lithium and other common materials (such as cobalt for $LiCoO_2$) is limited and volatile

- Many of these materials are costly



http://www.manufacturingcleanenergy.org/images/blog-20160413-global_mining_map.jpg

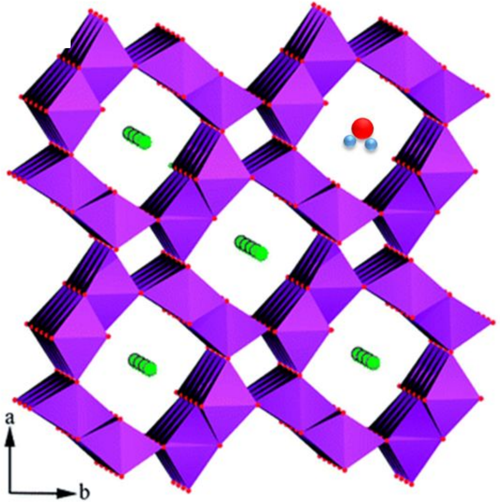
Problem Statement

- Mn is more abundant and supply chain is more diverse
  - At least 100x more abundant than cobalt [Gaines]

- Interest in 1-dimensional tunnel structure of $K_{0.13}MnO_2$
- α-MnO_2 has shown excellent electrochemical properties
  - **High theoretical discharge capacity**: 308 mAh/g
  - $LiCoO_2$: 273 mAh/g (theoretical)
  - $LiFePO_4$: 170 mAh/g (theoretical)

  - **Possible candidate in beyond lithium-ion batteries**
    - Mg-ion: " α-MnO2 is a promising candidate as cathode material for rechargeable Mg batteries if the capacity retention can be significantly improved."

Red Oxygen
Green Cations
Purple Manganese
Blue Hydrogen



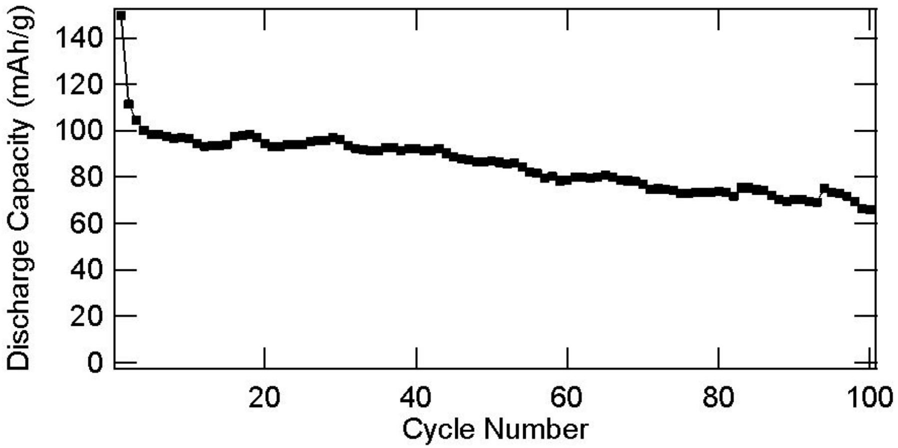
Yuming Dong et al. *RSC Adv.*, 2014, 4, 39167-39173

Gaines, L., & Nelson, P. (2009, March). Lithium-ion batteries: possible materials issues. In *13th international battery materials recycling seminar and exhibit.*

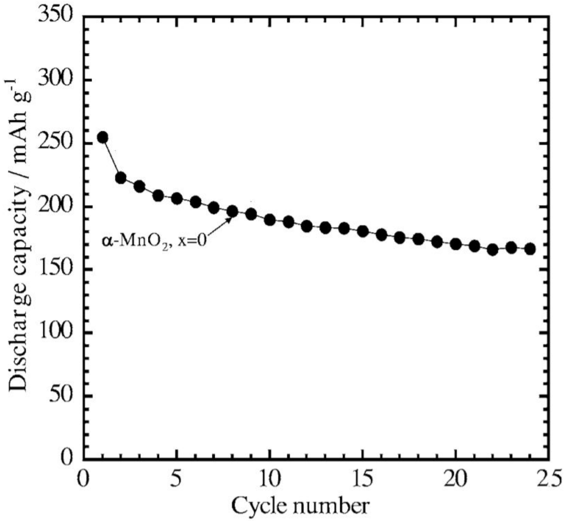
Zhang, Ruigang, et al. "α-MnO 2 as a cathode material for rechargeable Mg batteries." *Electrochemistry Communications*23 (2012): 110-113.

Low Cyclability of α-MnO_2

- Mn dissolution (Mn^{2+}) leads to Mn coating on anodes and structural instability
- Mn oxidation changes (Mn^{3+}) leading to Jahn Teller distortions and structural instabilities



Bryan Byles. Unpublished data. Cycling test of α-MnO_2.



Teruhito Sasaki et al., *Electrochemical and Solid-State Letters,* **8** 9 A471-A475 2005

What is our goal?

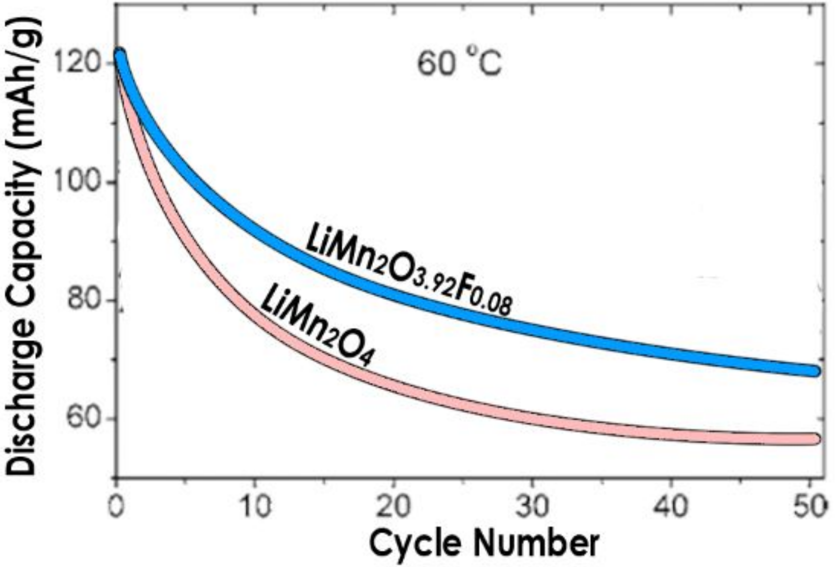
- Achieve better electrochemical performance with α-MnO_2, specifically improving capacity retention while maintaining high discharge capacity

How do we plan to achieve this?

- Fluorination of α-MnO_2 nanostructures

Fluorination Motivation

- $MnO_2 \rightarrow MnO_{2-x}F_x$
  - $x = 0 - 0.2$
- Fluorination has increased electrochemical performance in similar materials:
  - $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: 86% → 97% retention [Kim, G]
    - 50 cycles, x = 0.1
  - $LiMn_2O_4$: 50% → 67% retention [Choi]
    - 50 cycles, x = 0.08
  - $LiNi_{0.5}Mn_{1.5}O_4$: 82% → 95% retention [Kim, D]
    - 100 cycles, x = 0.1
- Not as much work on anion vs cation doping



Kim, Dae-wook, et al. *NPG Asia Materials* 9.7 (2017): e398.

Choi, W., & Manthiram, A. (2006). *Electrochemical and solid-state letters*, *9*(5), A245-A248.

Kim, G-H., et al. *Journal of the Electrochemical Society* 152.9 (2005): A1707-A1713.

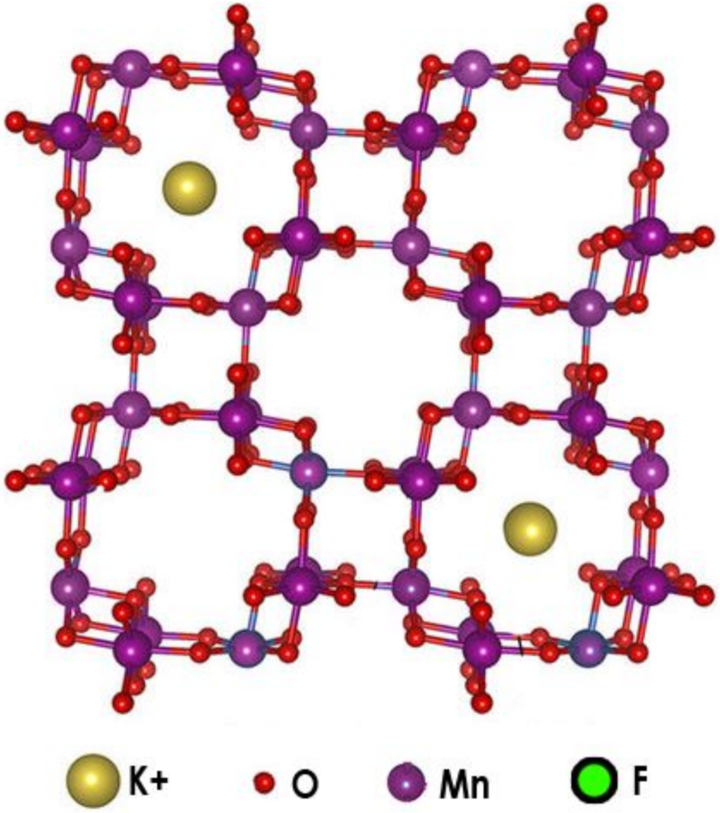
Fluorination Mechanism

Three possible mechanisms:

- Fluoride incorporates into lattice at oxygen sites
    - *F%* dependency on oxygen vacancies in thin films
- Fluorine adsorbs onto surface
- Fluorine occupies interstitial site

Effects:

- Stronger bonding (Mn-F vs Mn-O)
- Change in lattice parameter
- Crystal structure preservation



Tseng, Li-Ting, et al., *Scientific reports* 5 (2015).

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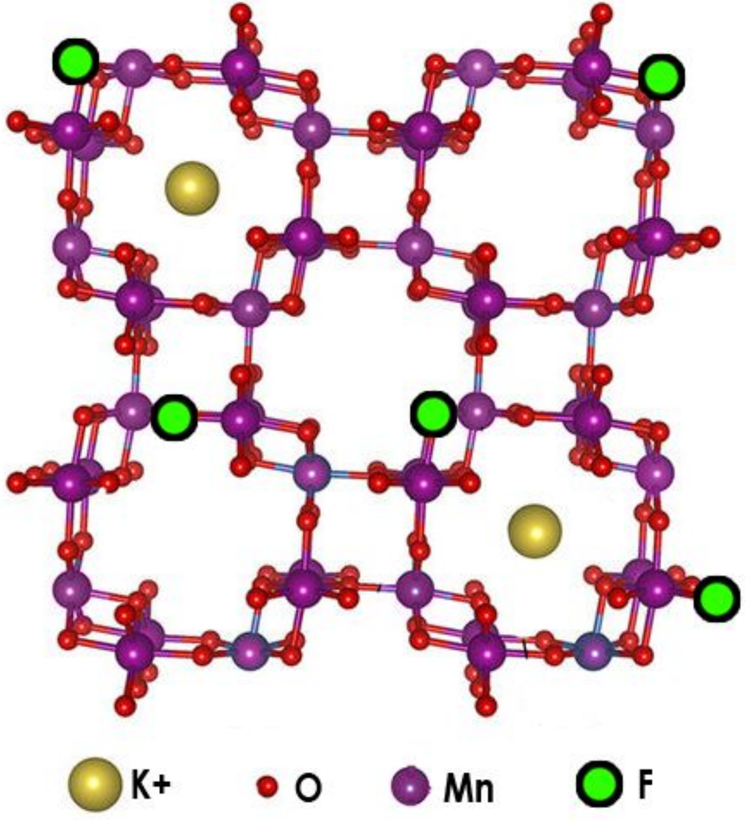
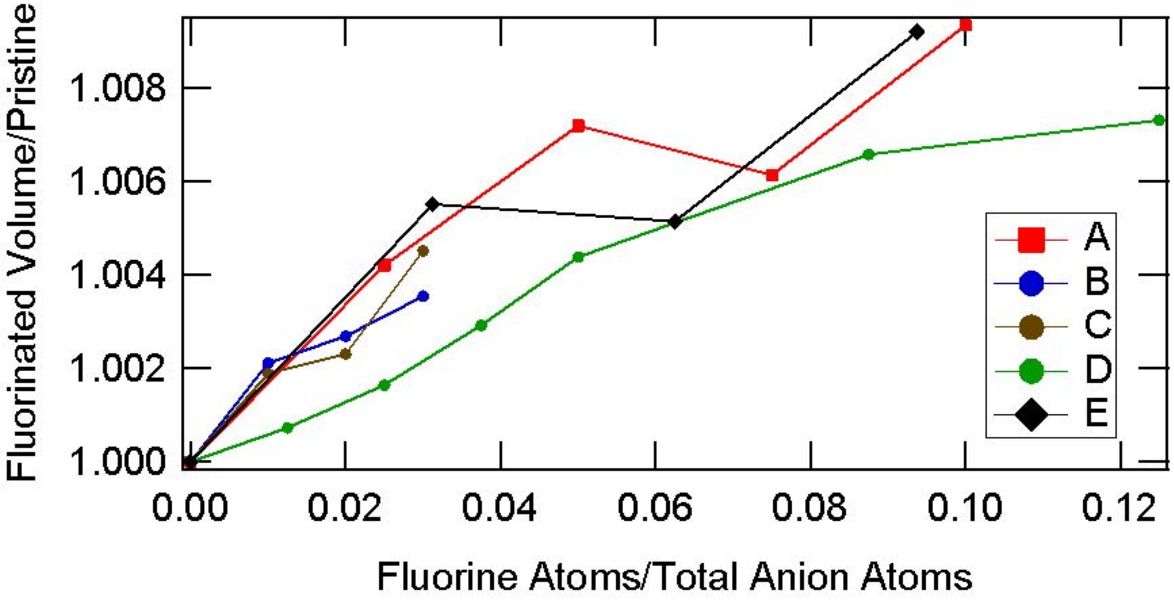


Tseng, Li-Ting, et al., *Scientific reports* 5 (2015).

How does fluorine get incorporated in lattice?

- Fluorine substitutional
- F^- = 1.29 Å[Hirai]
- O^{2-} = 1.35 Å[Hirai]
- Transition metal reduction increases unit cell size

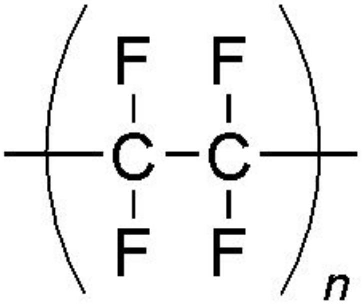


D. Hirai, E. Climent-Pascual, and R. J. Cava, *Phys. Rev. B*, vol. 84, no. 17, p. 174519, Nov. 2011.

[A] P. Yue, Z. Wang, H. Guo, X. Xiong, and X. Li, *Electrochim. Acta*, vol. 92, no. Supplement C, pp. 1–8, 2013.
[B] D. Kim et al., *Npg Asia Mater.*, vol. 9, p. e398, Jul. 2017.
[C] G.-H. Kim, J.-H. Kim, S.-T. Myung, C. S. Yoon, and Y.-K. Sun, *J. Electrochem. Soc.* , vol. 152, no. 9, pp. A1707–A1713, Sep. 2005.
[D] P. Yue et al., *Electrochim. Acta*, vol. 95, no. Supplement C, pp. 112–118, 2013.

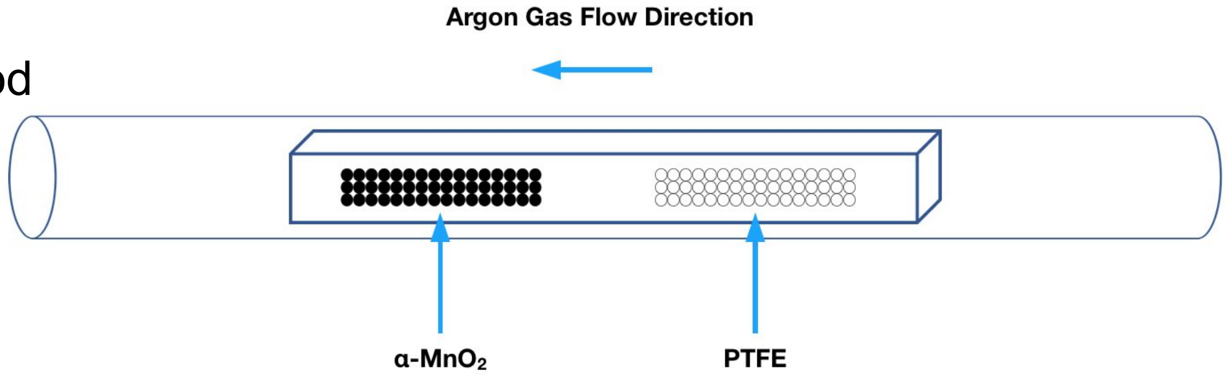
Synthesis and Fluorination

- Hydrothermal Synthesis
  - $KMnO_4$ + NH_4Cl in H_2O, 150°C for 48 hours
  - $K_{0.13}MnO_2$



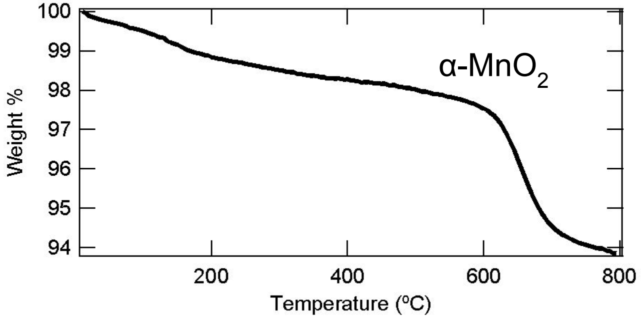
https://upload.wikimedia.org/wikipedia/commons/5/55/PTFE_structure.png

- Vapor Transport Method
  - Time
  - Temperature
  - Carrier Gas
  - Polymer Reagent



Experimental Parameters

Fluorination Parameters					
Run	Time (Hours)	Temperature (°C)	Fluorine Source	Gas Flow (Ar, sccm)	Complete?
1	4	380	PTFE	1/4	Yes
2	4	280	PTFE	1/4	Yes
3	4	180	PTFE	1/4	Yes
4	12	380	PTFE	1/4	Yes
5	12	280	PTFE	1/4	Yes
6	12	180	PTFE	1/4	Yes
7	24	380	PTFE	1/4	Yes
8	24	280	PTFE	1/4	Yes
9	24	180	PTFE	1/4	No
10	4	180	Pristine Sample	1/4	Yes
11	4	180	Non-fluoro Polymer	1/4	No



Bryan Byles. Unpublished data.

Characterization

- Materials characterization
  - Powder XRD
  - SEM/EDX
  - XPS

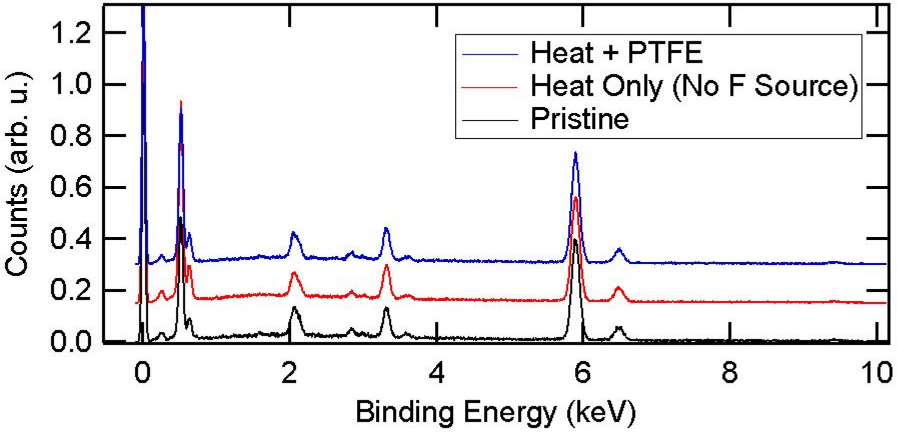
- Electrochemical Performance
  - **Discharge capacity (Energy Density)**
  - **Capacity retention**
  - Rate capability
  - Cyclic Voltammetry

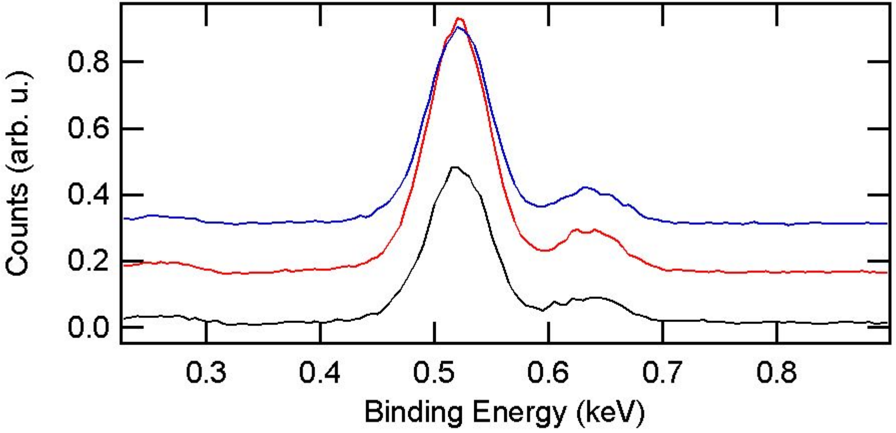
Rigaku Benchtop Miniflex XRD.

http://media.labcompare.com/m/1/product/57229-400x300.jpg

Results and Discussion

- Mn Lα peak (0.637 keV)[Newbury]
- F Kα peak (0.677 keV)[Newbury]

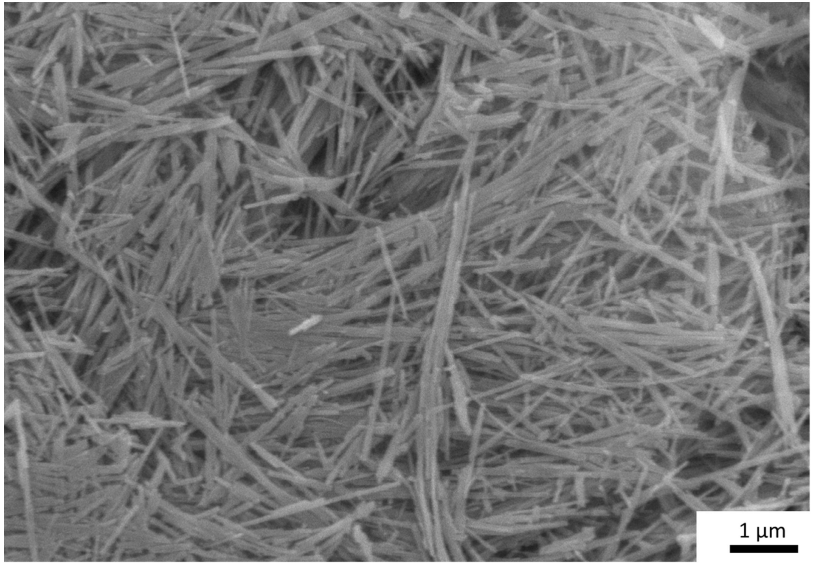


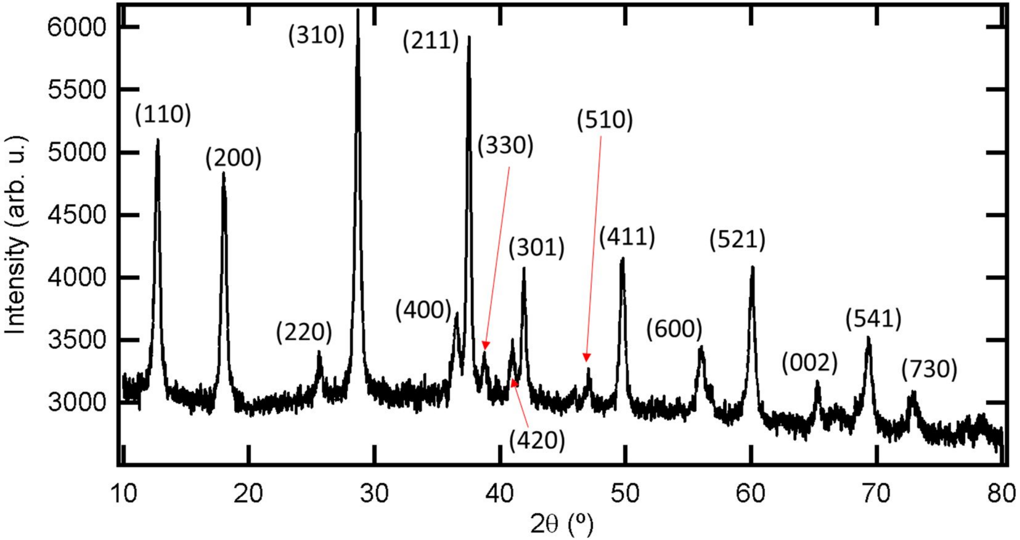


D. E. Newbury, Microsc. Microanal., vol. 11, no. 6, pp. 545–561, 2005.

Results and Discussion

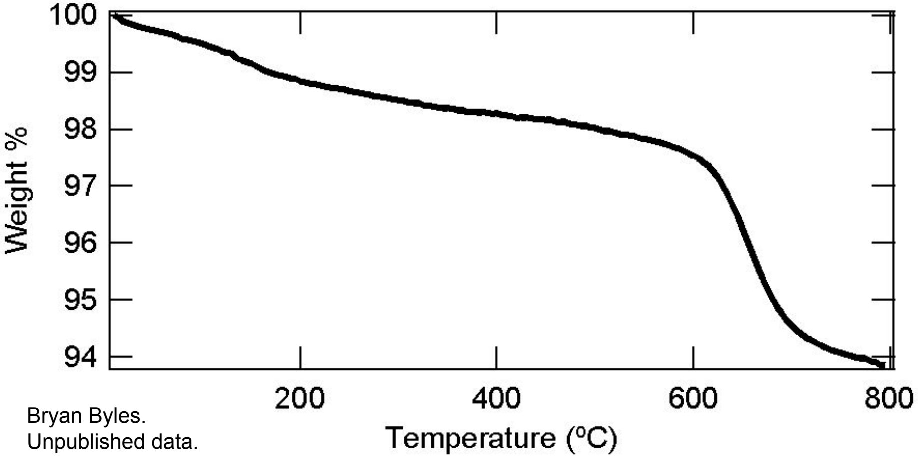
- Nanowires!
- I4/m crystal (PDF#01-077-1796)!



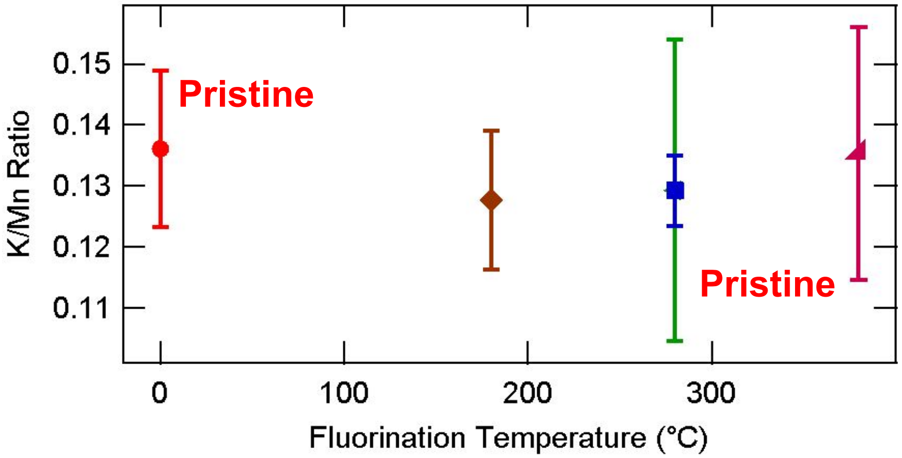


Results and Discussion

- K/Mn Stability

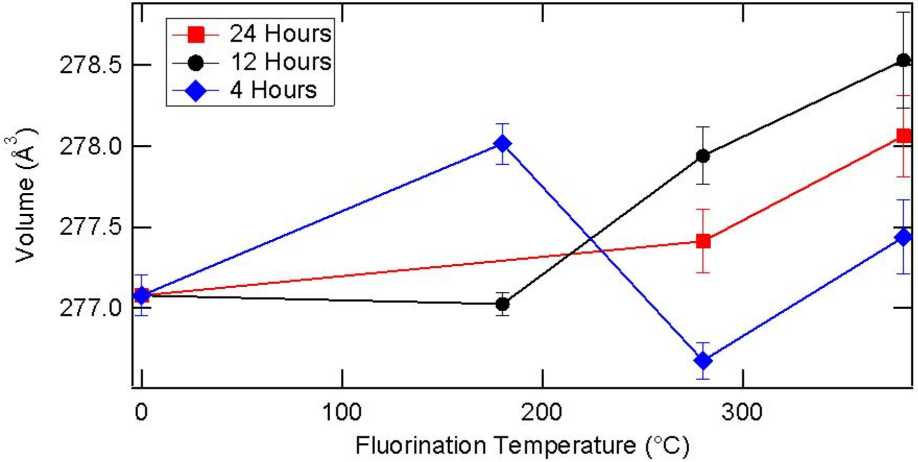


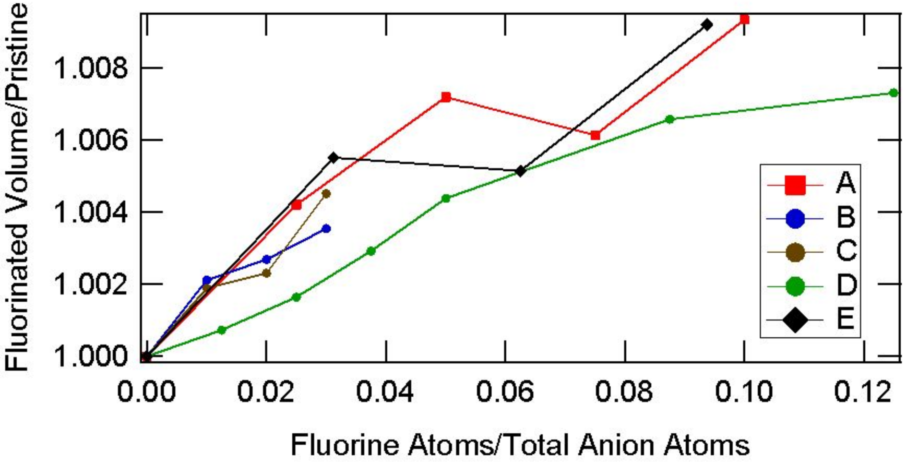
Bryan Byles.
Unpublished data.



Results and Discussion

- Volume increase agrees with literature
- Temperature ∝ F%[Moon]
- Kinetically activated?



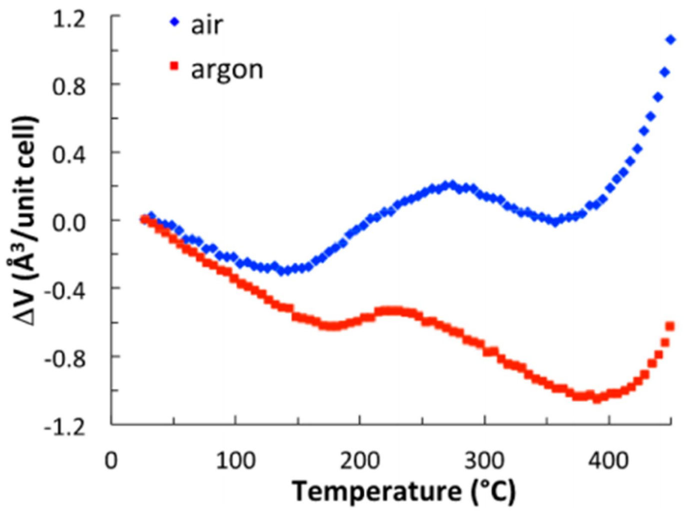


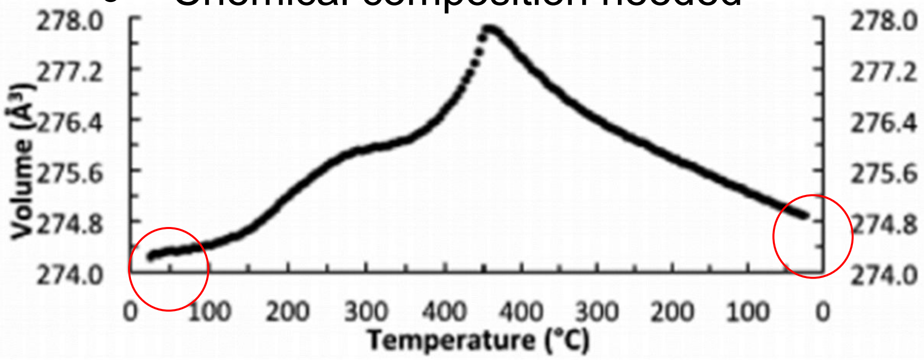
E. J. Moon, A. K. Choquette, A. Huon, S. Z. Kulesa, D. Barbash, and S. J. May, *APL Mater.*, vol. 3, no. 6, p. 62511, May 2015.

[A] P. Yue, Z. Wang, H. Guo, X. Xiong, and X. Li, *Electrochim. Acta*, vol. 92, no. Supplement C, pp. 1–8, 2013.
[B] D. Kim et al., *Npg Asia Mater.*, vol. 9, p. e398, Jul. 2017.
[C] G.-H. Kim, J.-H. Kim, S.-T. Myung, C. S. Yoon, and Y.-K. Sun, *J. Electrochem. Soc.* , vol. 152, no. 9, pp. A1707–A1713, Sep. 2005.
[D] P. Yue et al., *Electrochim. Acta*, vol. 95, no. Supplement C, pp. 112–118, 2013.

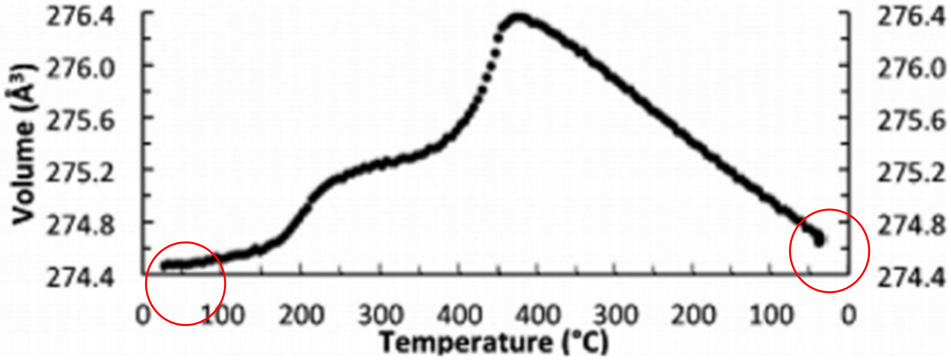
Results and Discussion

- Difficult to determine effects from volume changes alone
  - Heat → water loss → volume decrease
  - But… increase in volume when cooling to RT
- Chemical composition needed





Hydrated α-MnO_2 annealed in Air

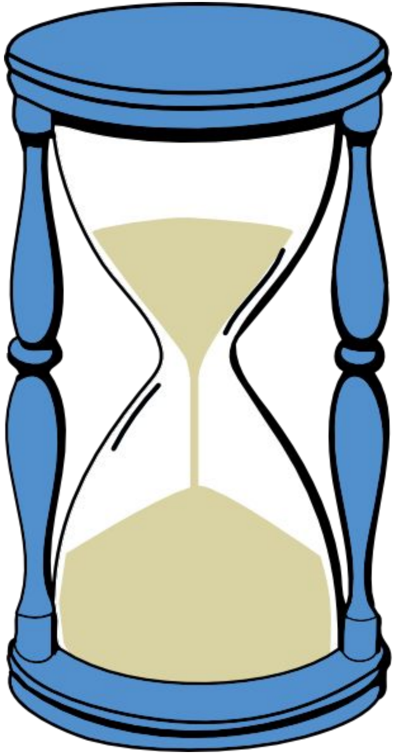


Hydrated α-MnO_2 annealed in Ar

Z. Yang et al., Chem. Mater., vol. 29, no. 4, pp. 1507–1517, 2017.

Next few months...

- Continue with experimental matrix
- Explore magnetic properties
  - VSM (magnetometry)
- Structural characterization
  - See changes in XRD with battery cycling
  - Rietveld analysis
- Electrochemical testing
  - Cycling tests
  - Cyclic voltammetry



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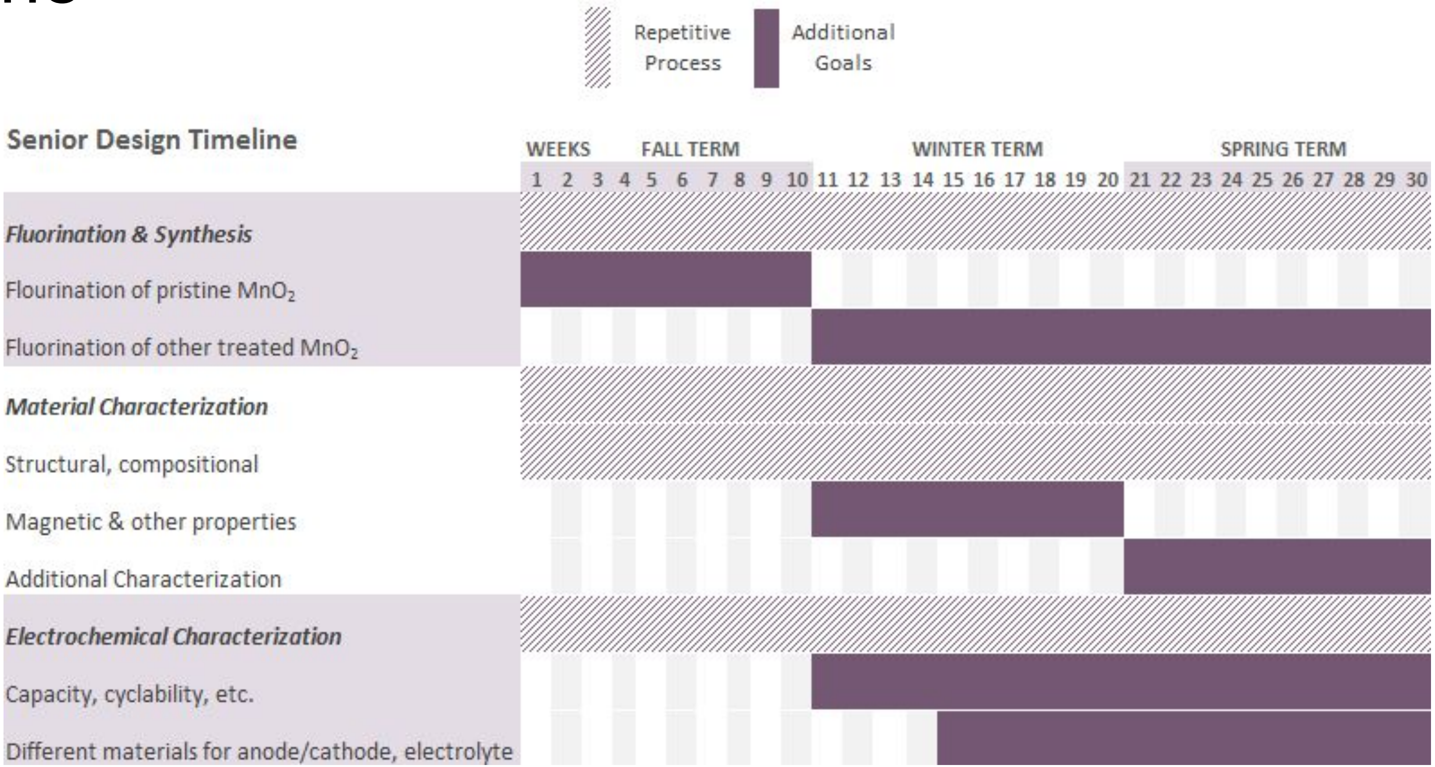
Timeline


Repetitive Process
Additional Goals
Senior Design Timeline
WEEKS
FALL TERM
WINTER TERM
SPRING TERM
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Fluorination & Synthesis
Flourination of pristine MnO_2
Fluorination of other treated MnO_2
Material Characterization
Structural, compositional
Magnetic & other properties
Additional Characterization
Electrochemical Characterization
Capacity, cyclability, etc.
Different materials for anode/cathode, electrolyte

Budget (MEG = Materials Electrochemistry Group, OFI = Oxide Films & Interfaces Group)

	Item	Cost($)	Real Cost ($)	Provider
Lab Supplies	Sample capsules	20	0	OFI
	Quartz tube	50	0	OFI
	Aluminum Foil	10	0	OFI
	Acetone	30	0	OFI
	IPA	30	0	OFI
	Argon Gas	300	55	OFI
	Miscellaneous	20	0	OFI
	PTFE	50	50	OFI
	Subtotal:	***510***	***105***	
Lab Equipment	Tube Furnace	2000	0	OFI
	Autoclave	3000	0	MEG
	Subtotal:	***5000***	***0***	
Equipment Subscription	XRD (Rigaku SmartLab) (9 months)	1000	1000	OFI
	XPS (PHI VersaProbe 5000) (9 months)	3000	0	OFI
	SEM/EDS (Zeiss Supra 50VP, EDAX) (9 months)	2500	0	OFI
	Subtotal:	***6500***	***1000***	
Raw Materials	$KMnO_4$	50	0	MEG
	NH_4Cl	20	0	MEG
	De-ionized Water	30	0	MEG
	Miscellaneous	20	0	MEG
	Subtotal:	120	***0***	
	Total:	***$ 12,130.00***	***$ 1,105.00***	

The "Cost" column is of outright costs for the project, the "Real Cost" considers that many project components are already in use or contained in the supporting lab groups.

Constraints

http://d2ankhno1rduyf.cloudfront.net/wp-content/uploads/2017/02/Product-Constraints.jpg

- Experimental design constraints
  - Fluorination temperature
- α-MnO_2 is not available commercially—limited material
- Limited lab resources
  - Furnace, XRD, XPS, etc
  - Fluorinations take up to 24 hour
- No expected environmental, societal, or ethical impacts/conflicts
- University safety procedures will be adhered to throughout the project
  - Standards will be used when available, such as:
    - J3021-201410 (*SAE International*) - *Recommended Practice for Determining Material Properties of Li-Battery Cathode Active Materials*
    - Industry-established best practices when no standards available (e.g synthesis)

Safety

- Synthesis
  - High pressure autoclaves
  - High temperature synthesis
  - 16 M HNO_3
- Characterization
  - Alkali metals
  - X-ray radiation danger

https://us.quanta.com/wp-content/uploads/2017/03/safetyman.jpg

Safeguards

- BioRAFT safety training
- “Buddy” System
- Personal protective equipment
- Fume hoods and glove box synthesis
- Vigilance and Caution

Acknowledgements

- **Advisors:** Dr. Ekaterina Pomerantseva and Dr. Steven May
- **Graduate Mentors**: Bryan Byles and Jiayi Wang
- Materials Electrochemistry Group (MEG)
    - Mallory Clites for SEM, Patrick West for acid-leaching help
- Oxide Films and Interfaces Group (OFI)
- Drexel CRF Staff

Thank You

DREXEL UNIVERSITY
Materials Science and Engineering
College of Engineering

MEG

Materials Electrochemistry Group

Oxide Films & Interfaces Group

Budget (MEG = Materials Electrochemistry Group, OFI = Oxide Films & Interfaces Group)

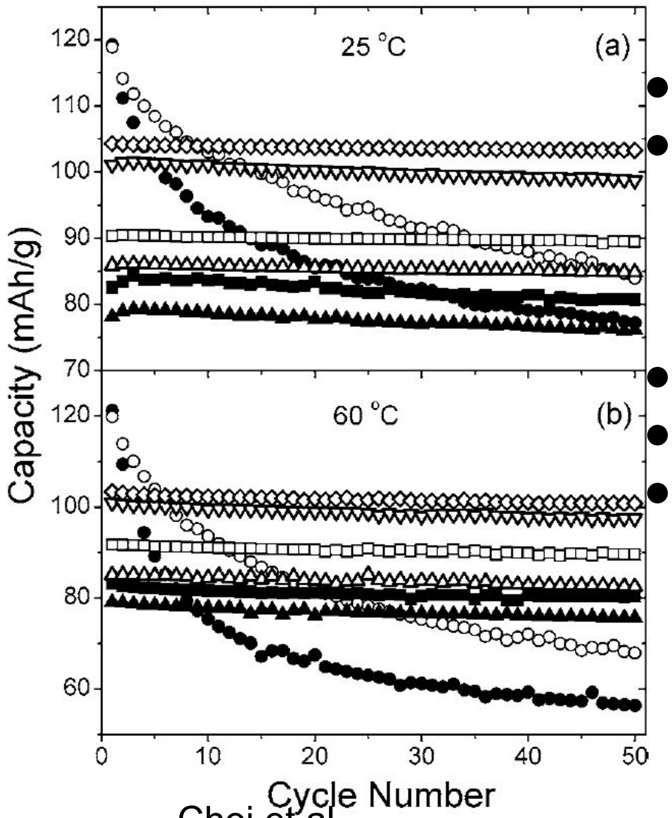
CRF equipment usage:

- Miniflex XRD (OFI)
- SEM/EDX (MEG)
- XPS (OFI + MEG)

Other equipment:

- Tube furnace (OFI)
- Electrochemical testing (MEG)
- PPMS/Magnetometer (OFI)

Materials: α-MnO_2 (MEG), PTFE (OFI), Miscellaneous (OFI + MEG)



Choi et al.

Figure 2. Comparison of the electrochemical cycling performances at (a) 25 and (b) 60°C of $LiMn_{2-y-z}Li_yM_zO_{4-\eta}F_\eta$: (●) $LiMn_2O_4$, (○) $LiMn_2O_{3.92}F_{0.08}$, (▲) $LiMn_{1.8}Li_{0.2}O_4$, (△) $LiMn_{1.8}Li_{0.2}O_{3.88}F_{0.12}$, (▽) $LiMn_{1.8}Li_{0.2}O_{3.79}F_{0.21}$, (■) $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_4$, (□) $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.9}F_{0.1}$ and (◇) $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$.

- $LiMn_2O_4$ fluorinated into $LiMn_{2-x}O_{4-n}F_n$
- Capacity retention was increased by fluorine substitution - lattice parameters changed but structure remained the same
- $LiMn_2O_4$ - about 50% capacity fade
- Various $LiMn_{2-x}O_{4-n}F_n$ samples = 0.9 -
- 2.6% capacity fade