Synthesis and Characterization of Alkali Metal Ion Battery Cathode Materials from Novel Single-source Metal Alkoxides

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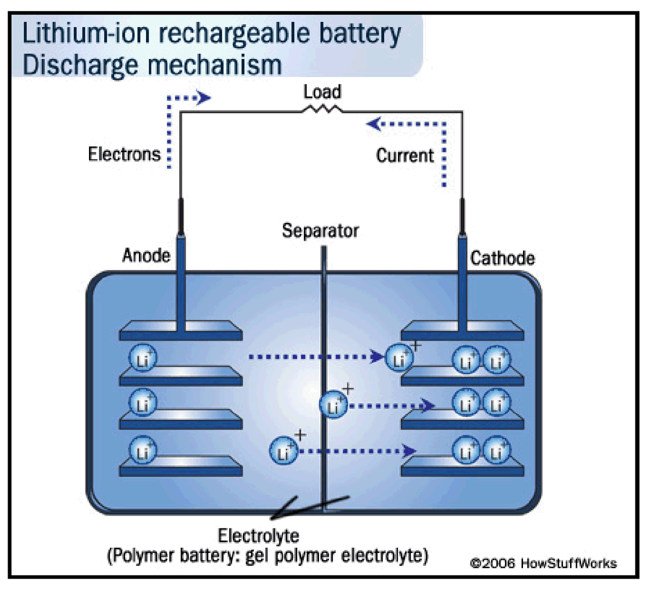
AIB's have wide spread use due to their high power and recyclability

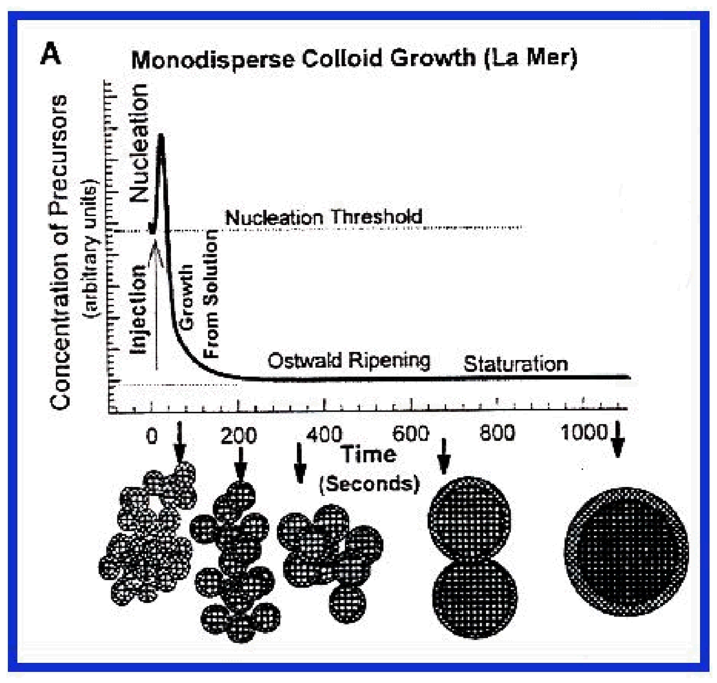
The 'green' properties of LIB's and their light weight nature make them perfect for vast majority of small portable consumer devices with high energy drain demands. They are also ideal for larger products such as electric-based cars and even Segways.



Unfortunately, LIB's also have drawbacks The battery is repeatedly cycled throughout it's life. This leads to the collapse, or pulverization, of the structure. LIBs have three basic components : an anode, a cathode, and something to separate the two (electrolyte). For a LIB, lithium ions are transferred back and forth from the anode and cathode during discharge/recharge cycles. Thus, the term 'rocking chair' batteries. During this cycling only a fraction of the Li ions can be removed otherwise, the matrix materials collapse. This limits the amount of energy that can be used.

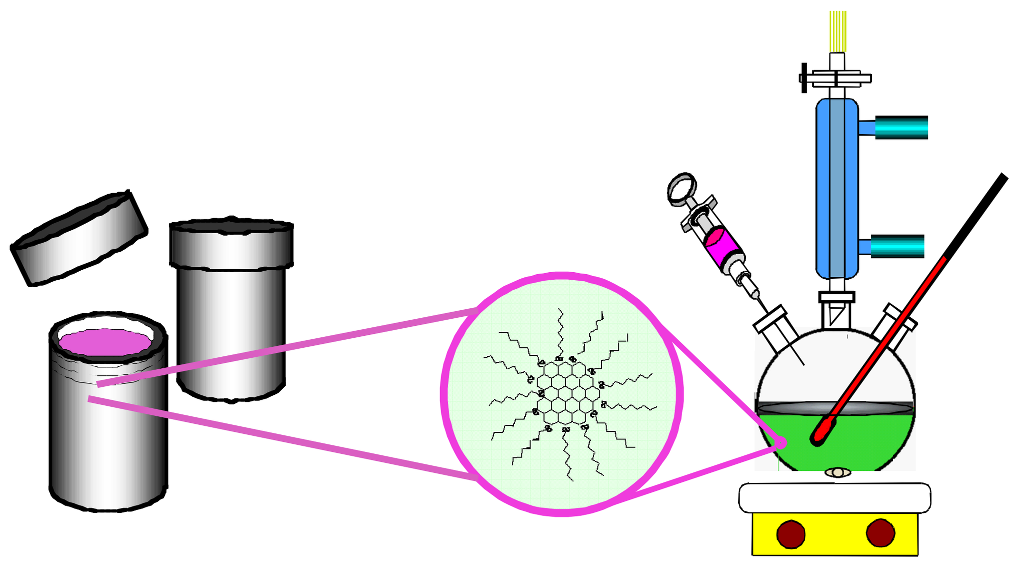
Could AIB's be improved using nanomaterials?

When working on the nanoscale one encounters an array of new physical phenomena. Properties such as Van der Waal and London Dispersion force largely dictate what happens at this scale. These new important and intriguing properties lead to very different material properties.



La Mer growth diagram and Ostwald ripening

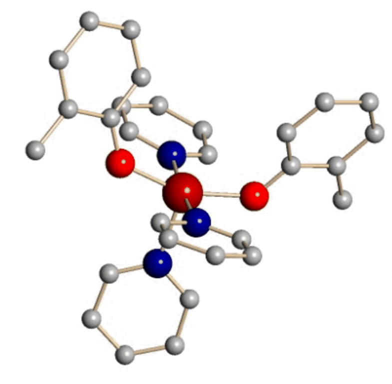
Several routes for generating nanoparticles are employed by our group. Two of the common synthesis routes are solution precipitation (SPPT) and solvothermal (SOLVO). In these routes, nanoparticles are generated by the La Mer growth process and grow by Ostwald ripening. As supersaturated solution exceeds the nucleation threshold and reaches the critical limiting super saturation point, a homogeneous 'nucleation shower' occurs resulting in the formation of growth nuclei. After the nucleation shower occurs, the precursor concentration drops below the nucleation threshold, resulting in no new particle formation With progression of time, particles grow based on Ostwald ripening.



Variables
- temp
- time
- solvent
- surfactant
- precursor

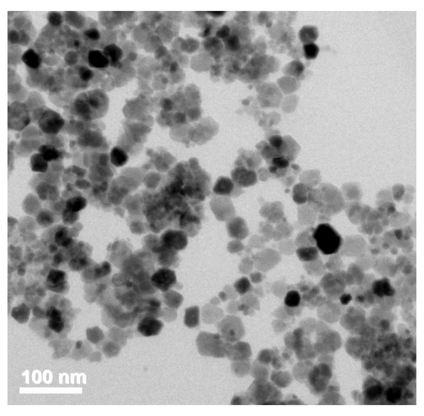
Standard Parr-acid Digestion Bomb setup *General Solution Precipitation (SPPT) Setup*

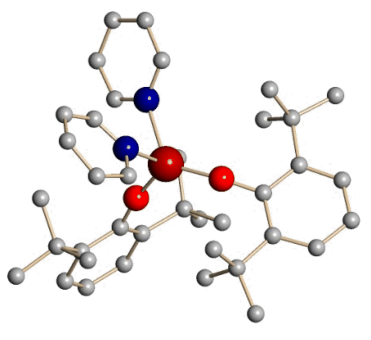
Novel iron and lithium iron double aryloxides were investigated for nanomaterial production



$Fe(oMP)_2(py)_3$

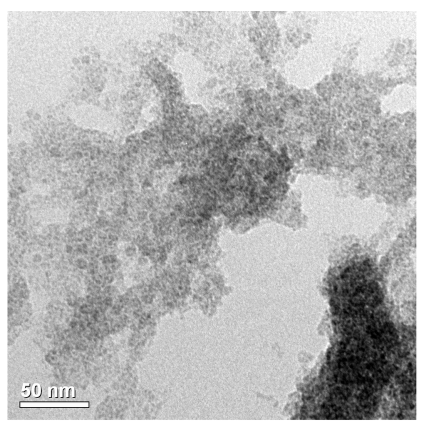
solvo
py

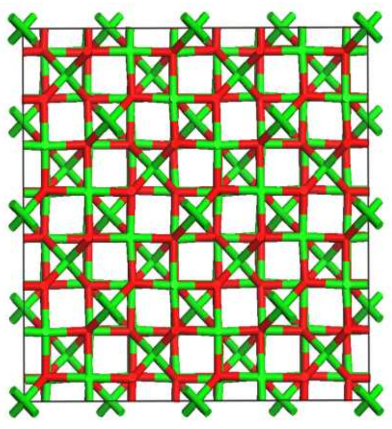




$Fe(DBP)_2(py)_2$

solvo
py

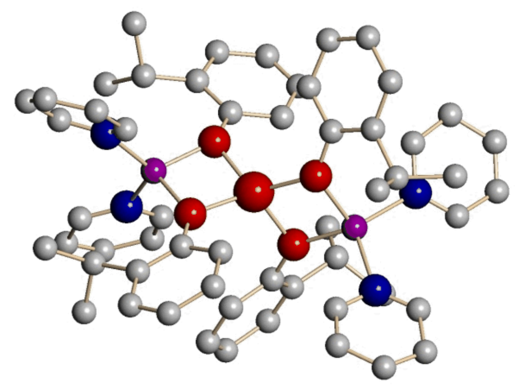




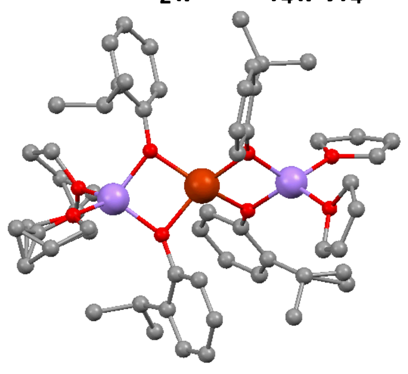
Maghemite Phase

The Boyle Group previously investigated the synthesis and characterization of a series of iron aryloxides and the resultant iron oxide nanomaterials. When materials were synthesized, each sample produced the iron deficient maghemite-C phase of Fe_2O_3. Unfortunately these materials didn't cycle well with lithium. It appears the phase coordination may have been too constricted to allow lithium to enter the structure.

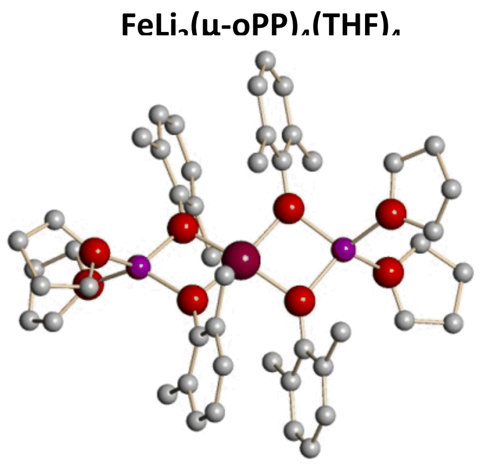
Boyle, et al. Inorganic Chem. 2011.



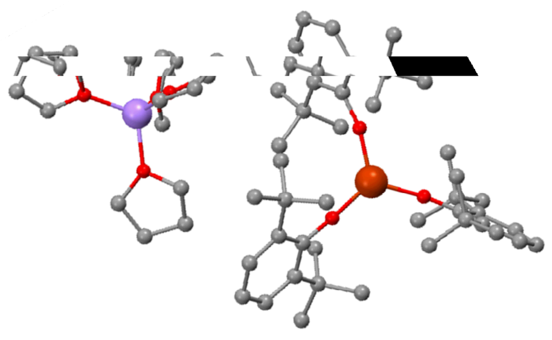
$FeLi_2(\mu\text{-}oPP)_4(py)_4$



$FeLi_2(\mu\text{-}oPP)_4(THF)_4$

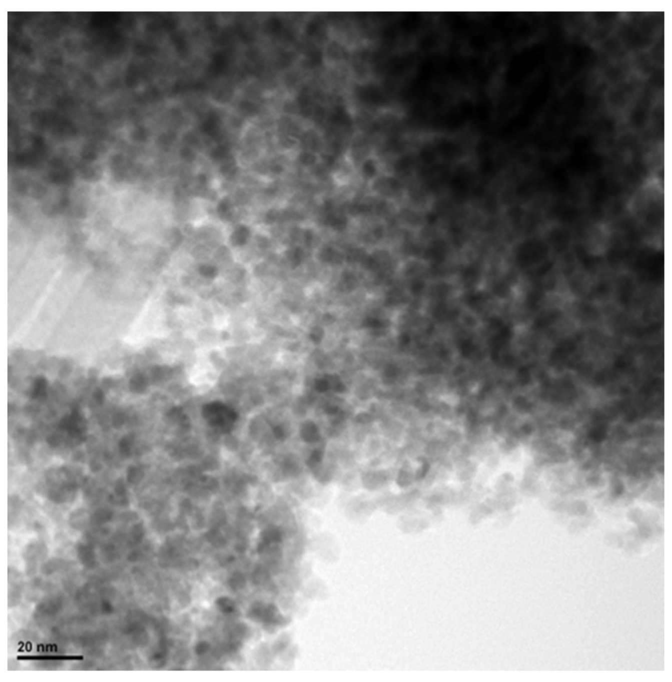


$FeLi_2(\mu\text{-}DMP)_4(THF)_4$



$Fe(DBP)_3Li(THF)_4$

solvo
py/Diox



Characteristic TEM of $FeLiO_2$

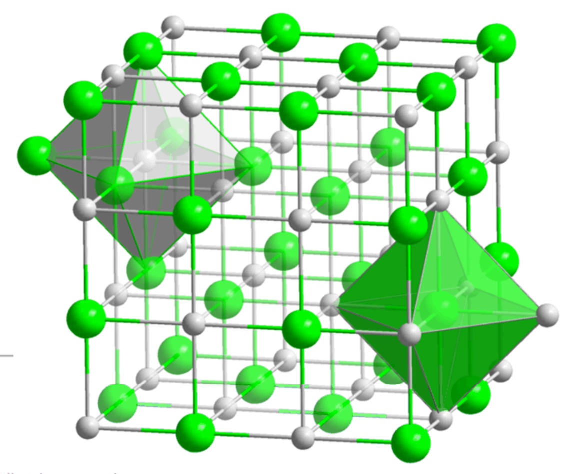
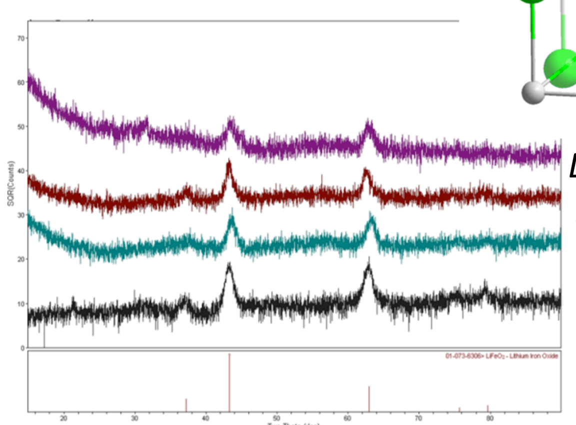


Diagram showing cubic structure of the $FeLIO_2$



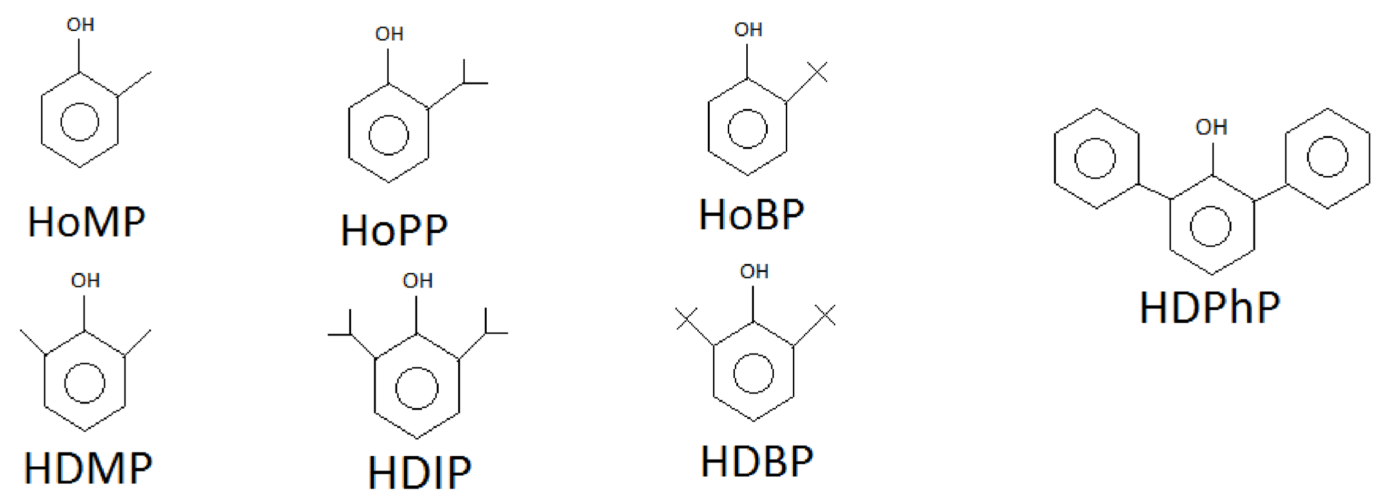
PXRD of generated nanoparticles with PDF of $LiFeO_2$

Following the iron aryloxide research, it was reasoned that by adding lithium to the original structure it maybe easier to move the Li ion. A novel set of iron lithium aryloxides were synthesized $[FeLi_2(OAr)_4]$, characterized, and subjected to SOLVO conditions using pyridine (or dioxane for THF adducts) as the solvent system. The nanomaterials formed were irregular in shape and generally well under 10nm in size. The phase identified as the $FeLiO_2$ derived is of a wüstite (FeO) like phase. While electrochemical evaluation of these materials indicated that some Li could be extracted, it was substantially below any useable voltage levels. The low extraction for the $LiFeO_2$ was again attributed to the closed structure of this phase of material.

Boyle, Neville et al. Polyhedron 2013.

Will Mn based AIB's precursors have better phase material conversion in comparison to Fe?

$$M(Mes)_2 + 4\ H(OAr) + n\ AN(TMS)_2 \longrightarrow A_nM(OAr)_{2+n} + 2\ H\text{-}Mes + 2\ HN(TMS)_2$$



MnLi(OAr) Results

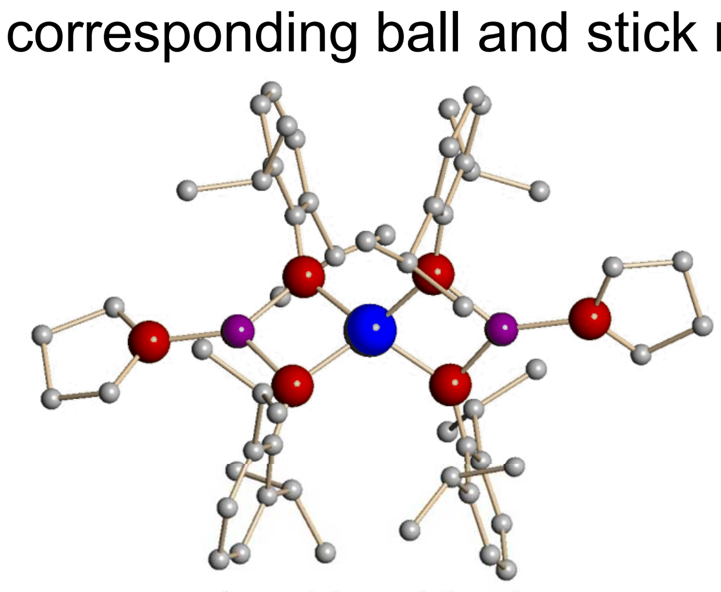
H-OAr	THF	py
H-oMP	A	
H-oPP		B
H-oBP		
H-DMP	C	D
H-DIP	E	
H-DBP		
H-DPhP		

MnNa(OAr) Results

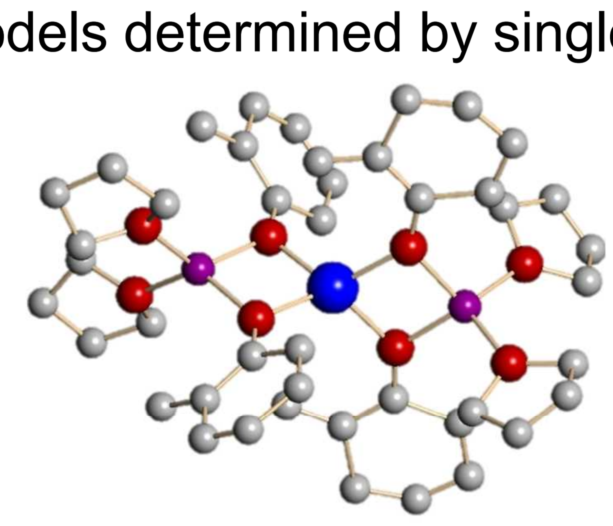
H-OAr	THF	py
H-oMP		
H-oPP		
H-oBP		
H-DMP	F (1:2) G (1:1)	H
H-DIP		I
H-DBP	J	
H-DPhP		

Table's: Products isolated form GREEN: single-source; YELLOW (salt); ORANGE: M only; PURPLE: Li only; WHITE: only oils or powders isolated.

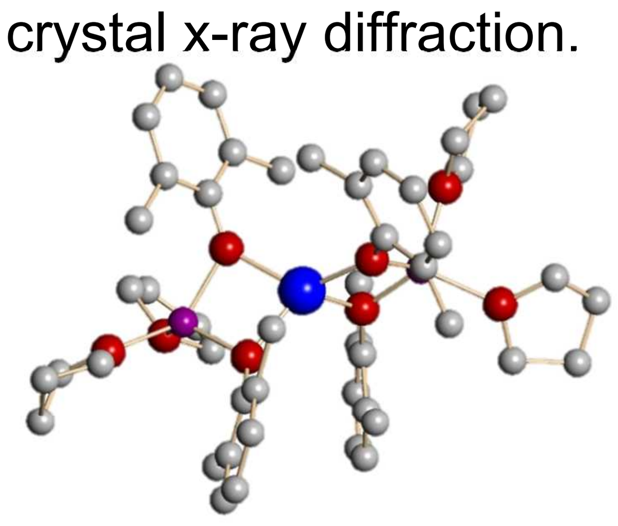
The synthesis of the $A_2M(OAr)_{2+n}$ compounds followed the reaction of $M(Mes)_2$ (M = Mn, Co) in the toluene with four equivalents of the appropriate H-OAr. After 10 min, the ANR_2 was added to the reaction, usually resulting in a color change. The mixture was stirred for a minimum of 12 hrs. and then set aside with the cap loose until crystals formed. To the right are tables describing the results of the reactions with corresponding ball and stick models determined by single crystal x-ray diffraction.



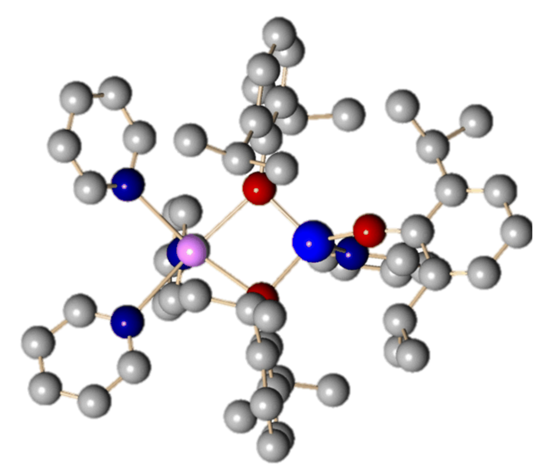
E) $MnLi_2(\mu\text{-}DIP)_4(THF)_4$



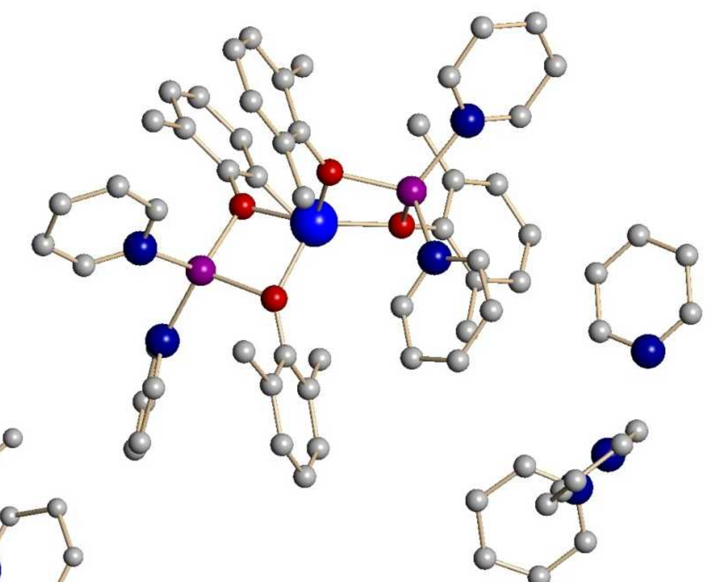
A) $MnLi_2(\mu\text{-}oMP)_4(THF)_4$



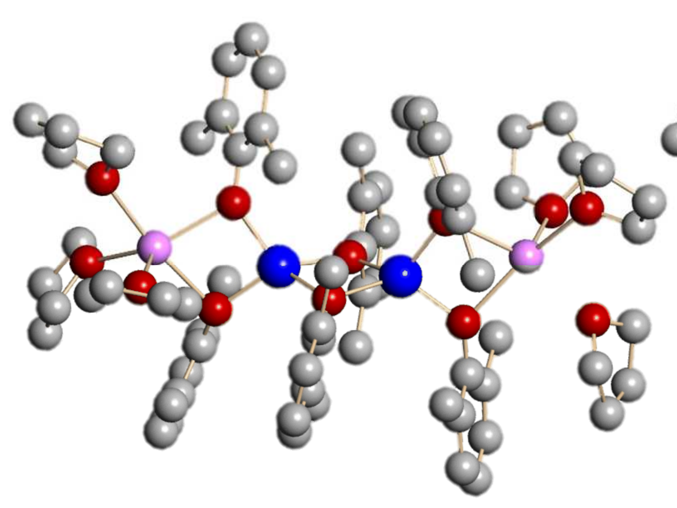
C) $MnLi_2(\mu\text{-}DMP)_4(THF)_4$



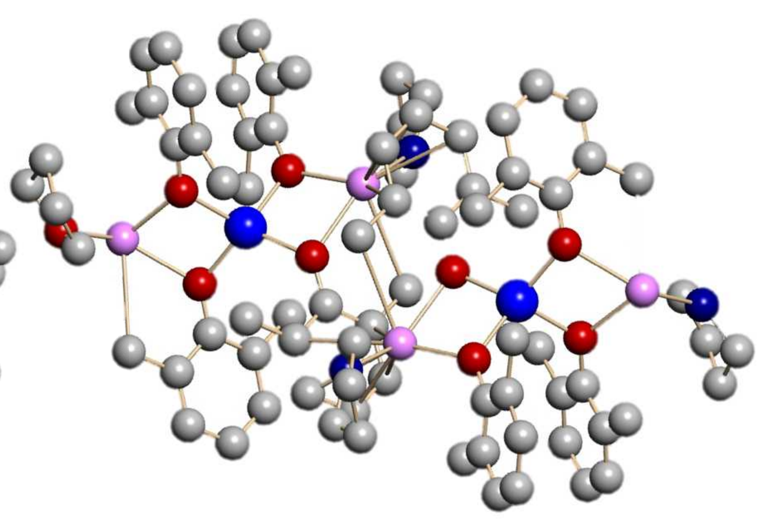
I) $MnNa((DIP)\mu\text{-}DIP)_2(py)_3$



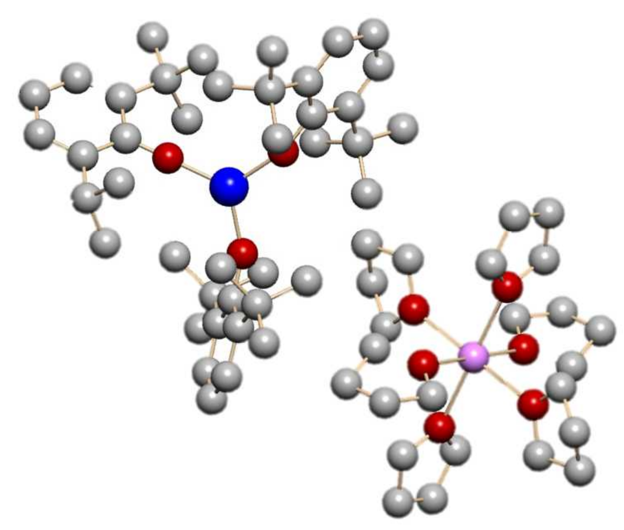
D) $MnLi_2(\mu\text{-}DMP)_4(py)_4\ (py)_3$



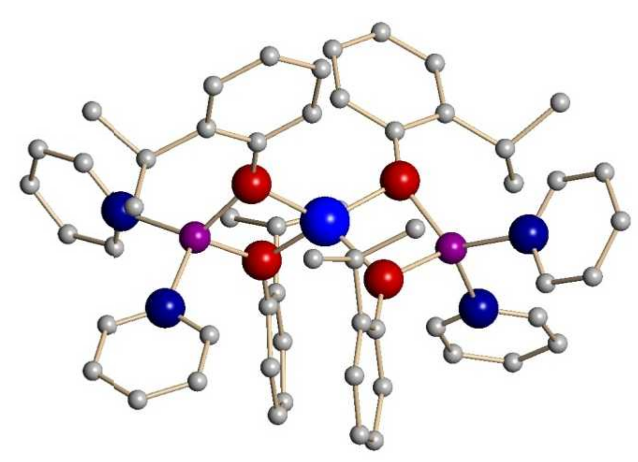
G) $MnNa_2(\mu\text{-}DMP)_4(THF)_4$



F) $MnnA_2(\mu\text{-}DMP)_4(THF)_2$



J) $Mn(DBP)_3Na(THF)_4$

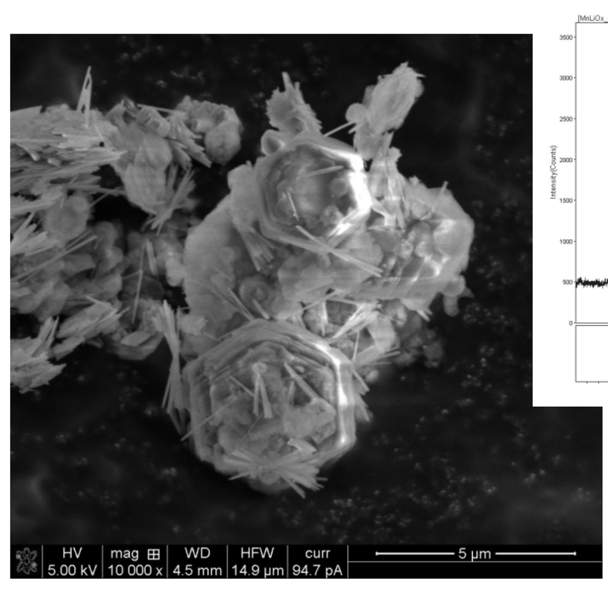


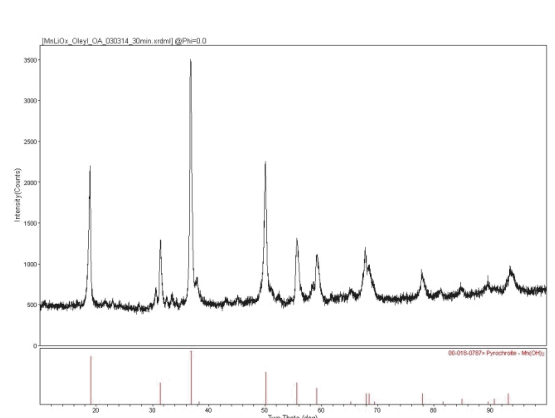
B) $MnLi_2(\mu\text{-}oPP)_4(py)_4$

Aryloxide single source precursors were processed to form materials and thin films

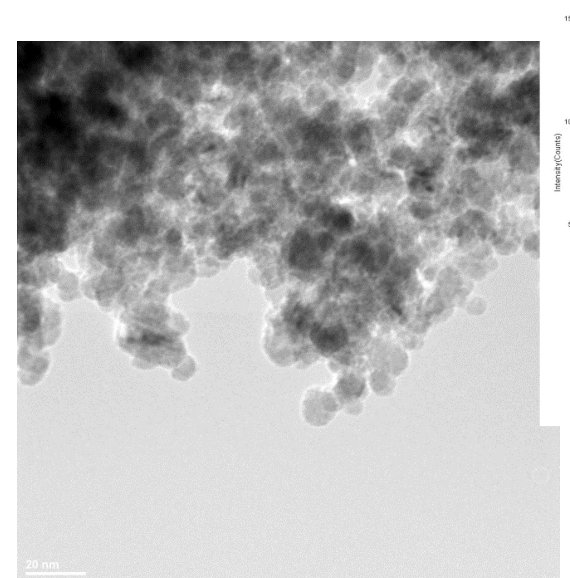
$$MnLi_2(DMP)_4py_4 \xrightarrow[\text{i - pyridine; ii - Oleylamine/OA}]{\text{SOLVO}} Mn_xLi_yO_z$$

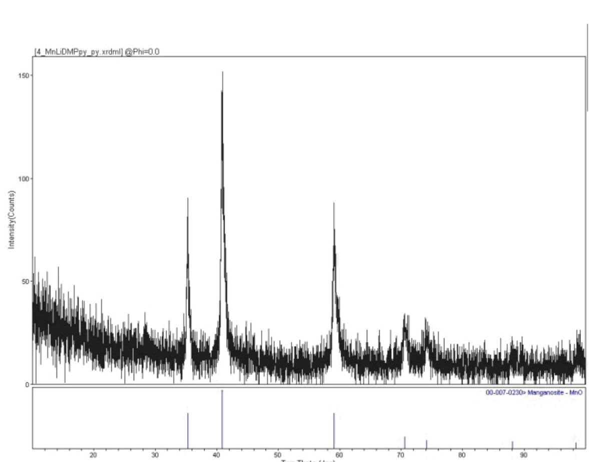
SOLVO conditions used (80 mL of solvent, 185°C, 24 hrs). The product was isolated by centrifugation and for pyridine washed in hexanes to remove excess organics; for oleylamine\OA samples, toluene and MeOH were used to wash the product. Due to the Li ion's mobility in polar solvents neither material retained Li. The end phases were determined to be crystalline Mn(OH)2 from the Oleyl/OA and irregular nanoparticles of MnO from the pyridine synthesis.





SEM & PXRD of $MN(OH)_2$ ofrom Oleylamine/Oleyic Acid synthesis



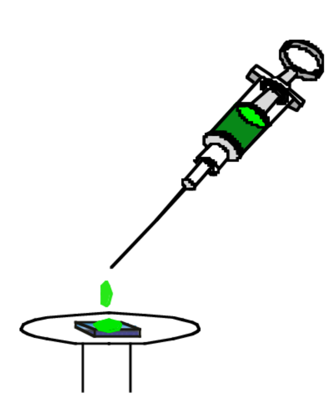


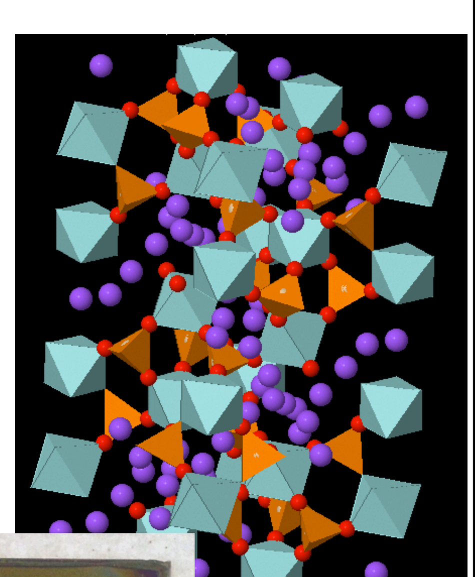
TEM &PXRD of nanomaterials from py

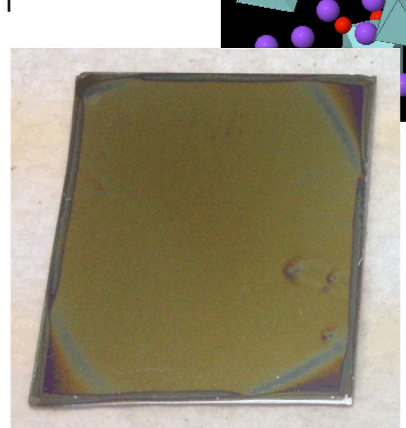
NaSICON (Sodium Super Ionic Conductor)

$$Na_{1+x}Zr_2P_{3-x}Si_xO_{12} \xrightarrow{X=2} Na_3Zr_2PSi_2O_{12}$$

NaSICON is a high conductivity solid state electrolyte that is stable gains molten sodium. A number of Sandia National Lab scientists are working to develop a variety of Na based battery applications. Preparation of the $MnNa_yO_x$ films were prepared by first making an 0.2M $MnNa_2(DMP)_4THF_4$ solution and pulling that into a syringe. The solution was then spin coated onto a substrate and dried at 300ºC on a heat plate. Additional layers were applied to subsequent samples.





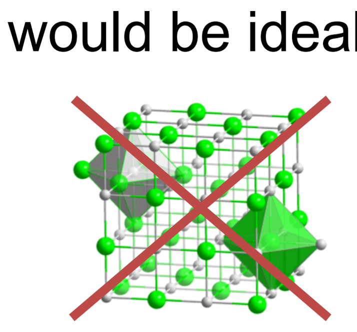


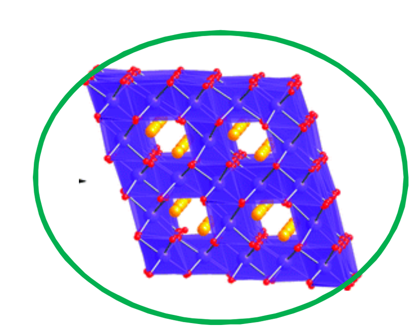
Summary and Conclusion

- A new family of $MnLiA_2(OAr)_4$ compounds have been synthesized and characterized.
- A new family of $MnNa_2(OAr)_4$ compounds have been synthesized and characterized.
- Nanomaterials and thin films of MnAOx were developed using the aforementioned compounds and characterized by PXRD.
- The average size of the py adduct based materials has been determined to be <10 nm, as characterized by TEM.

Future Work

- Revise syntheses conditions (ligand, solvent, etc) to prevent Li ions from transferring into the solvent. Spinel phase Mn_2LiO_2 would be ideal.





- Electrochemical characterization of the nanomaterials.
- Revisit the $LiCo_2(OAr)_4$ family and change the solvent system for nanomaterial generation possibly yielding $LiCoO_x$ nanomaterials.

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