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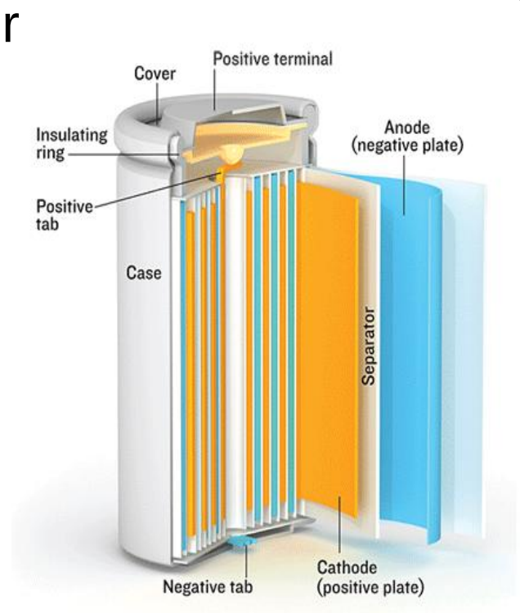
Vanadium alkoxides for production of nanomaterials for lithium ion battery applications

Sarah M. Hoppe, Leigh Anna M. Ottley, Timothy J. Boyle, Michael Neville
Sandia National Laboratories, Advanced Materials Laboratory 1001 University Blvd. Albuquerque New Mexico 87106

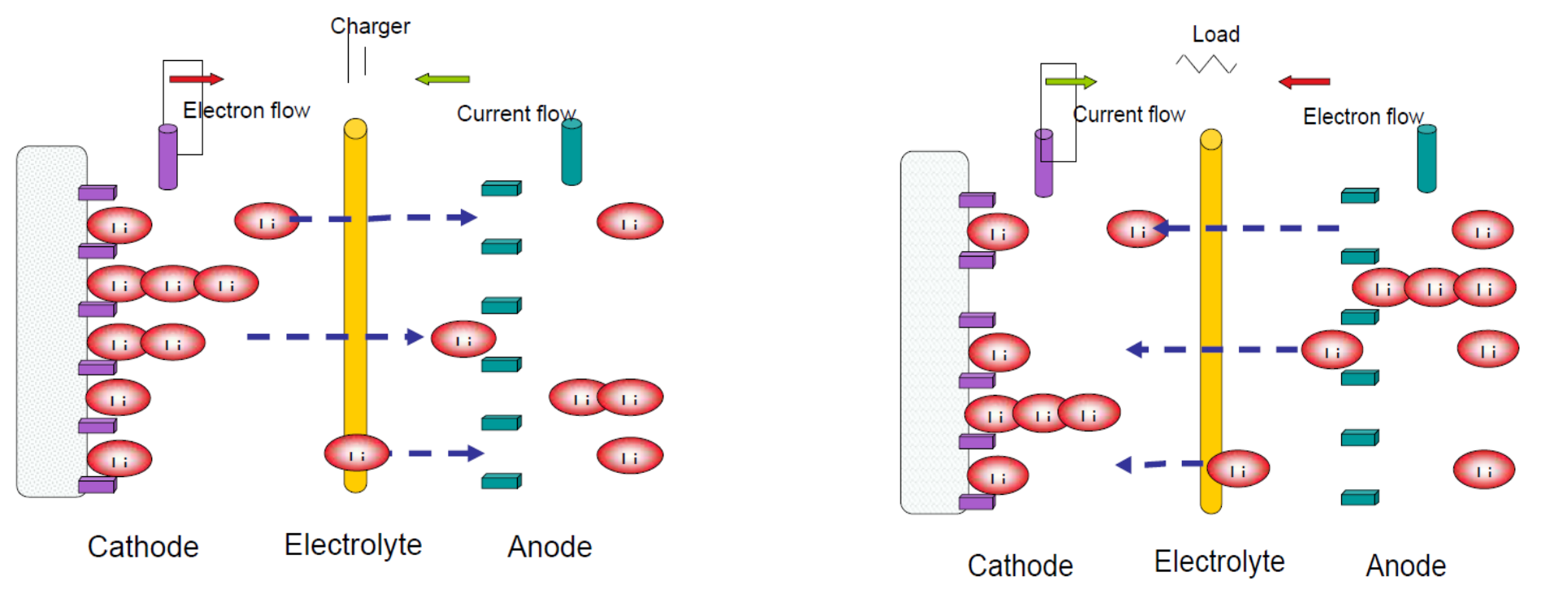
Lithium Ion Batteries

Lithium ion batteries are commonly used to power portable electronic devices because they have a number of advantages:



- Rechargable
- Low environmental impact upon disposal
- High energy density
- High currents for large demand devices
- Low maintenance

The batteries are made of three main components: a cathode, an anode, and a separator. Li^+ ions are shuttled from the cathode to the anode and back during charging and discharging, respectively. Over many cycles of this shuttling, the cathode and anode materials begin to degrade as the Li^+ is incorporated and then pulled away and the battery no longer functions properly.



Recently, it has been shown that nanomaterials can better withstand continued Li^+ shuttling and have the potential to produce more efficient, longer lasting batteries. Currently, anode materials can achieve a capacity of 370 mAh/g while common cathode materials, like $LiCoO_2$, can achieve only 140 mAh/g. It has been shown that nanoparticles of vanadium pentoxide, V_2O_5, are capable of achieving capacities as high as 300 mAh/g. However, there are few simple, robust procedures for generating high yield V_2O_5 nanomaterials from simple alkoxides. This project aims to synthesize novel vanadium alkoxides and then employ them in nanoparticle systems to find an easy, reproducible route to V_2O_5 and Li_yVO_x nanomaterials for use in Li-ion battery cathodes.

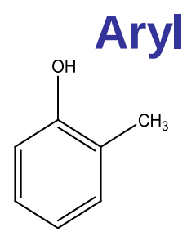
S.H. Ng, et. al., J. Power Sources. 174 (2007) 1032 G. Li, et. al., J. Phys. Chem. B. 110 (2006) 9383

Metal Alkoxides

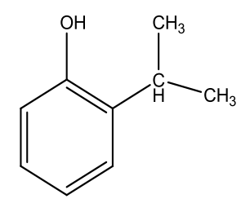
Metal alkoxides ($M(OR)_x$) are widely used precursors for the production of ceramic materials. In addition to often being commercially available, the physical and chemical properties (i.e., hydrolysis susceptibility, solubility, volatility, etc) of these precursors are easily tailored through manipulations of the pendant ligand sets. The structural arrangement of $M(OR)_x$ has been found to play a critical role in determining the final ceramic material properties generated from them. Therefore, control over the final materials properties are more easily realized when the structural properties of the $M(OR)_x$ precursors have been elucidated.

A number of ligands have been explored for metal alkoxides. We have found that varying the steric bulk in the *ortho* position of the aryloxide derivatives has the greatest impact on the final structure. The commercially available mono and di-substituted ligands of interest are shown below.

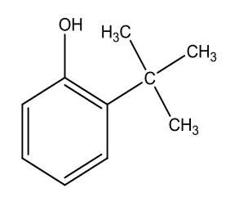
Aryl alcohols



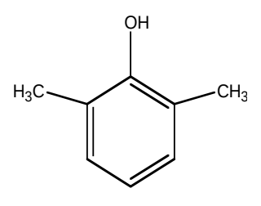
H-*o*MP
(2- methylphenol)



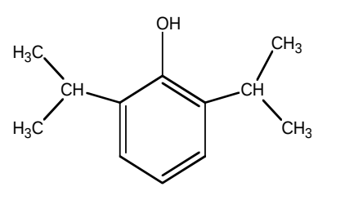
H-*o*PP
(2- isopropylphenol)



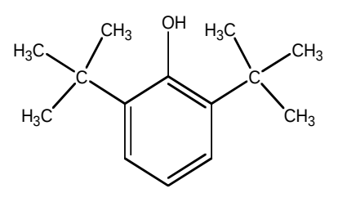
H-oBP
(2- *tert*butylphenol)



H-DMP
(2,6- dimethylphenol)



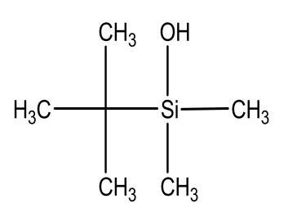
H-DIP
(2,6- diisopropylphenol)



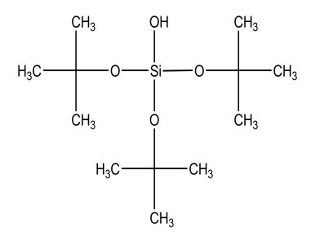
H-DBP
(2,6- di-tert-butylphenol)

The variations in steric hindrance coupled with the small changes in electronics make the siloxide ligands of interest as well. Some of these are shown below.

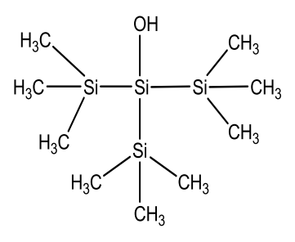
Silanols



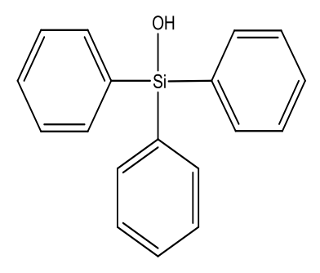
H-DMBS
(dimethyl-tert-butylsilanol)



H-TOBS
(tris(tert-butoxy)silanol)



H-SST
(tris(trimethylsilyl)silanol)



H-TPS
(triphenylsilanol)

Nanomaterials Synthesis

Of the many routes used to generate nanomaterials, our laboratory employs two: (i) solution precipitation (SPPT) which involves heating the sample in the selected solvent and surfactant until precipitation occurs and (ii) solvothermal (SOLVO) which involves adding the sample to a Parr^{TM} acid digestion bomb, adding the desired solvent, and "pressure cooking" at a set temperature for a predetermined length of time.

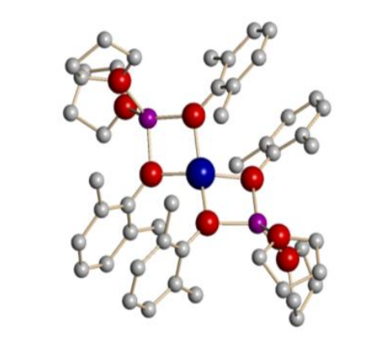
Solution Precipitation route (SPPT)

Parr Digestion Bomb (SOLVO)

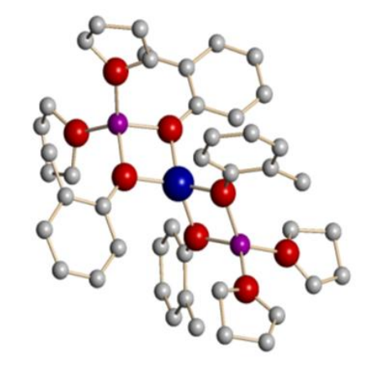
A variety of solvent systems are available for the production of nanomaterials. The SPPT route generally produces nanodots; whereas the SOLVO route tends to produce more complex shapes.

Single Source $LiCoO_2$ Precursors for Nanomaterials

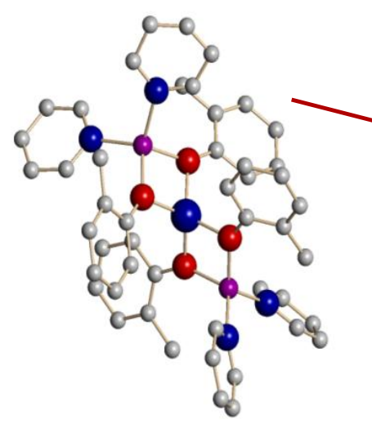
Previously, our group has synthesized a series of mixed metal aryloxides as single source precursors to $LiCoO_2$. All were trinuclear with tetrahydrofuran or pyridine bound as a solvent.



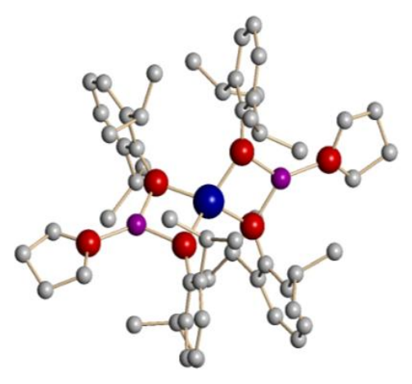
$Li_2Co(DMP)_4(THF)_4$



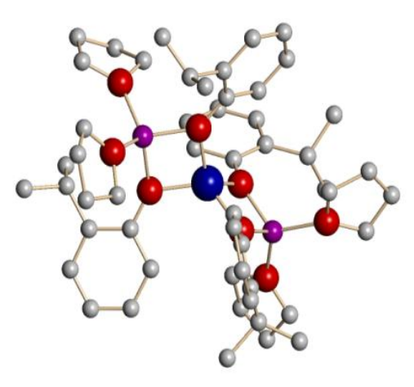
$Li_2Co(oMP)_4(THF)_4$



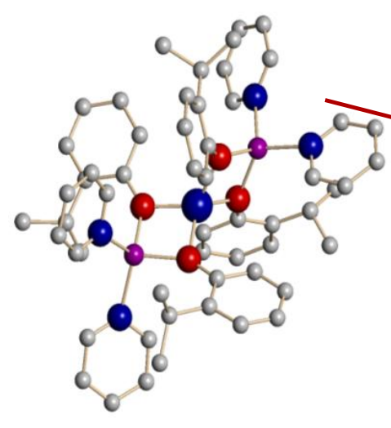
$Li_2Co(oMP)_4(py)_4$



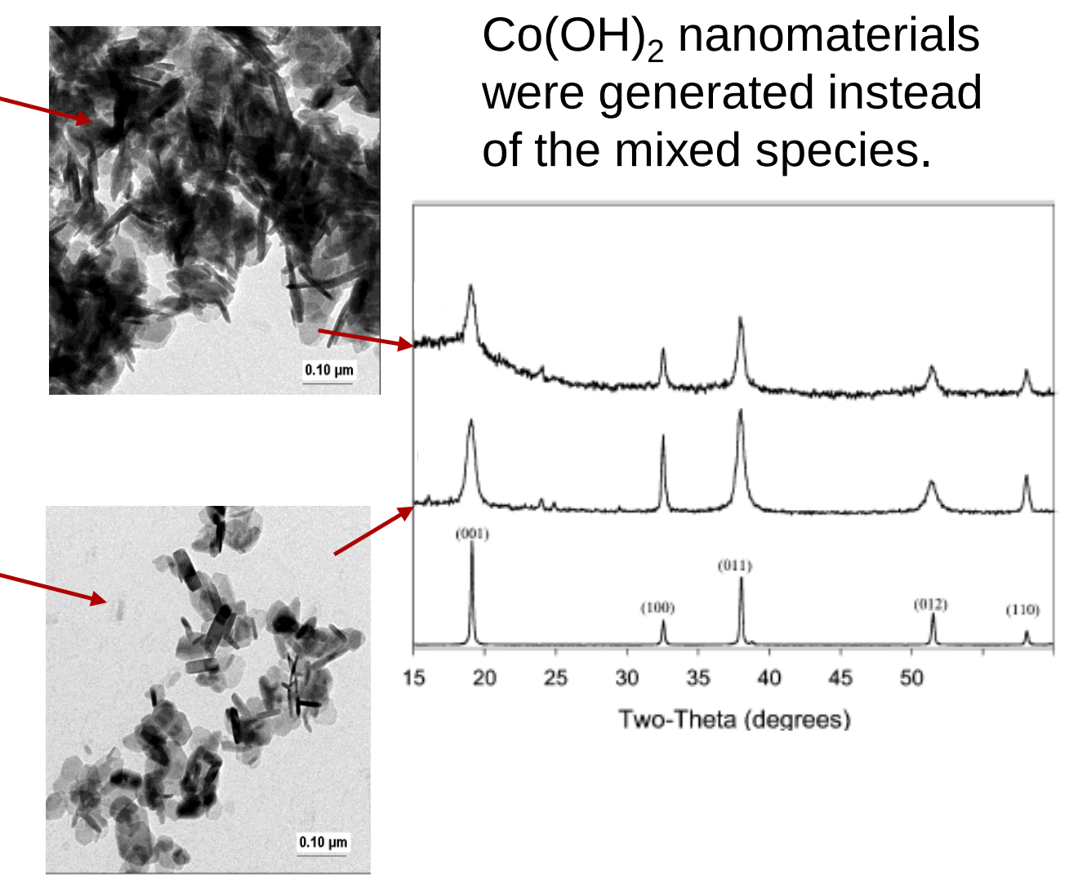
$Li_2Co(DIP)_4(THF)_2$



$Li_2Co(oPP)_4(THF)_4$



$Li_2Co(oPP)_4(py)_4$

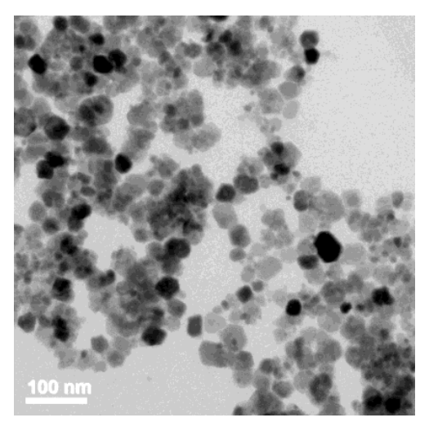


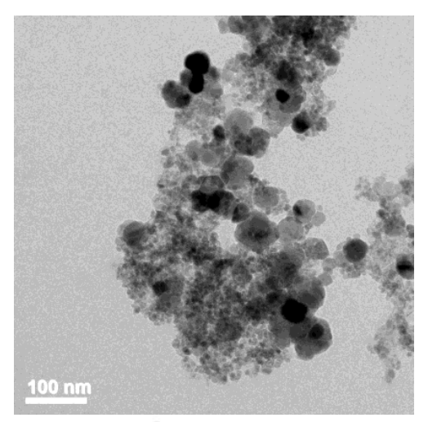
$Co(OH)_2$ nanomaterials were generated instead of the mixed species.

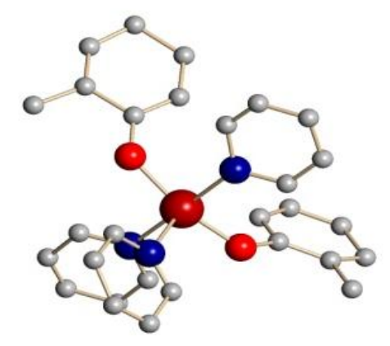
T.J. Boyle, et. al., Chem. Mater. 15 (2003) 3903.

Single Source $LiFeO_2$ Precursors for Nanomaterials

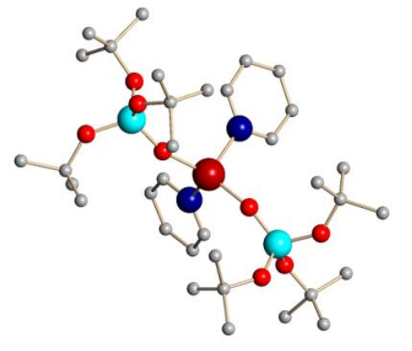
Recent efforts have focused on $Fe(OR)_2$ precursors. In order to generate crystals, it was necessary to use pyridine as the solvent, which led to mononuclear species. These precursors have (under SOLVO conditions) yielded maghemite nanomaterials.





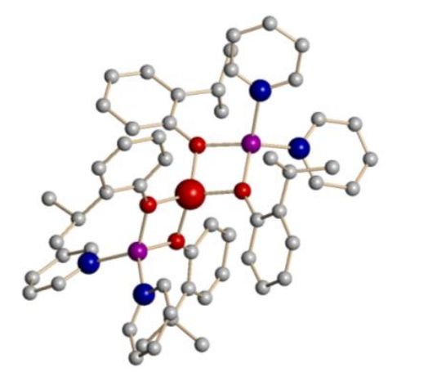


$Fe(oMP)_2(py)_3$

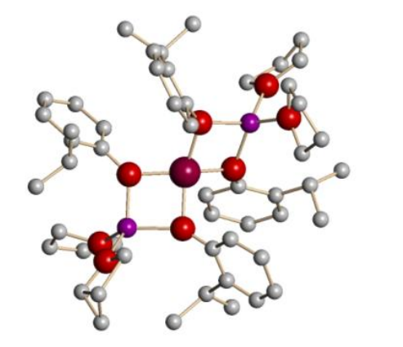


$Fe(TOBS)_2(py)_2$

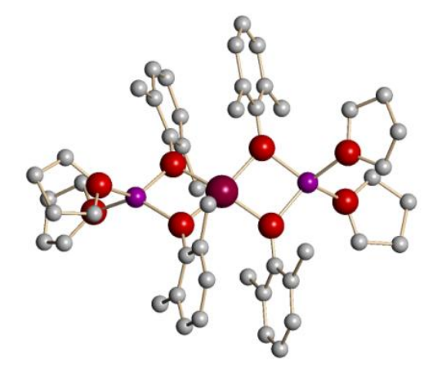
Attempts to generate single source precursors for the Fe and Mn have been successful.



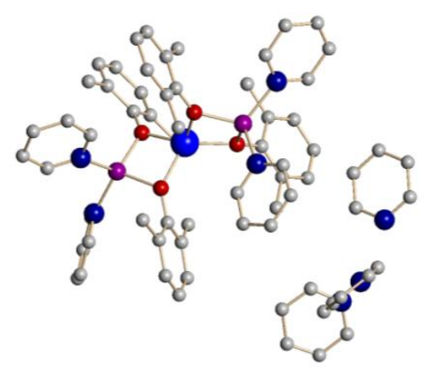
$Li_2Fe(py)_4(\mu\text{-}oPP)_4$



$Li_2Fe(THF)_4(\mu\text{-}oPP)_4$



$Li_2Fe(THF)_4(\mu\text{-}DMP)_4$

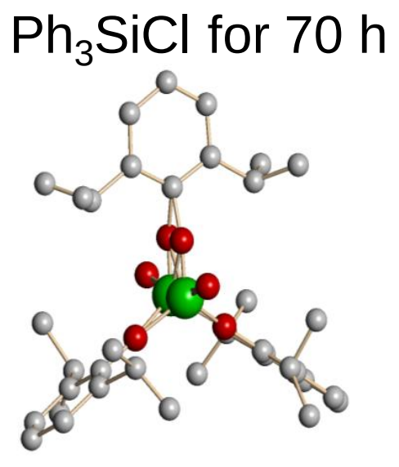


$Li_2Mn(\mu\text{-}DMP)_4(py)_4\bullet 3py$

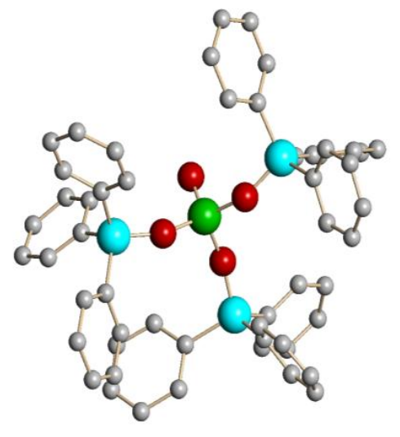
Similar structures as noted for the Co have been produced for the majority of compounds. Upon introduction of sterically hindered ligands, salt formation is observed.

Vanadium Alkoxides

The number of available literature $V(OR)_x$ compounds is limited to two precursors. Both are monomeric with an oxo ligand present. The synthesis of $V(O)(DIP)_3$ was achieved using $VCl(DIP)_2(THF)_2$ and $Li(SC_6H_2Me_3\text{-}2,4,6)$. The synthesis of $V(O)(TPS)_3$ was achieved by refluxing $AgVO_3$ and Ph_3SiCl for 70 h in 1,2-dichloroethane and filtering.

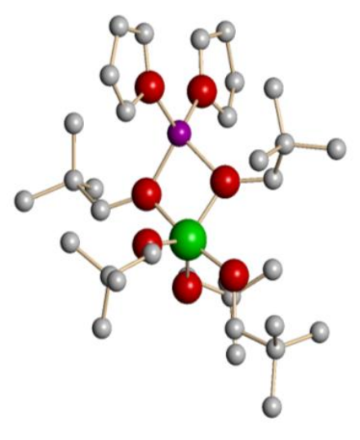


[1]$V(O)(DIP)_3$

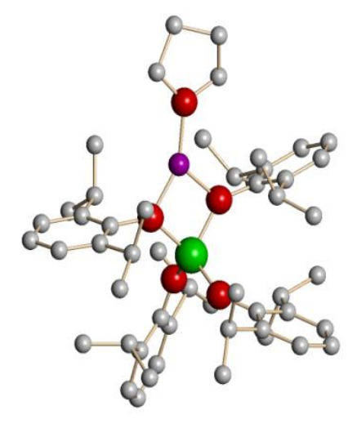


[2]$V(O)(TPS)_3$

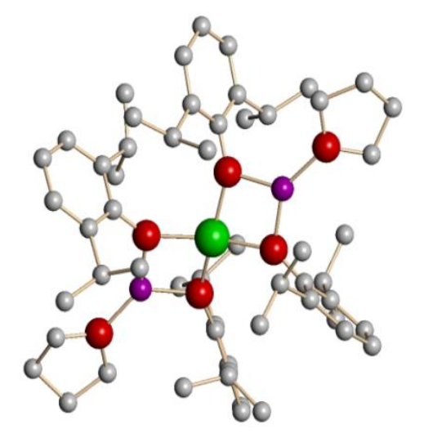
The list of mixed Li/V compounds is somewhat larger with a variety of 1:1 and 2:1species available. The synthesis of these compounds was undertaken using $VCl_3{\cdot}3THF$, $[V_2Cl_{3(}THF)_6](PF_6)$, or $V_2(\mu\text{-}ONep)_2(ONep)_6$ and the appropriate LiOR.



[3]$Li(THF)_2V(ONep)_5$



[4]$Li(THF)V(DIP)_4$



[5]$Li_2(THF)_2V(DIP)_4$

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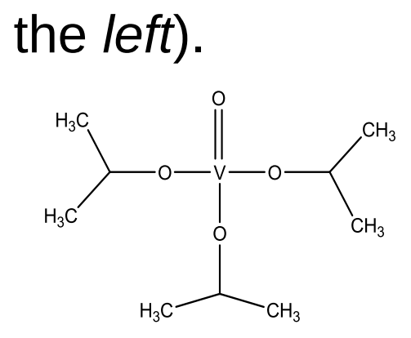
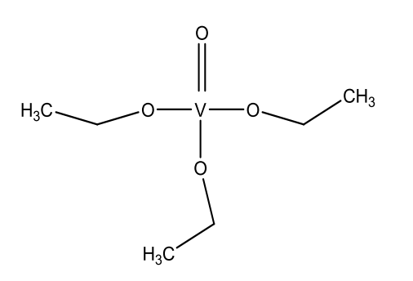
[1]R.A. Henderson, et. al., J. Organomet. Chem. 554 (1998) 195.
[2]M. Huang, et. al., Inorg. Chem. 32 (1993) 2287. [3]D.M. Reis, et. al., J. Braz. Chem. Soc. 20 (2009) 613.
[4]W.C.A. Wilisch, et. al., Inorg. Chem. 27 (1988) 4333. [5]M.J. Scott, et. al., J. Am. Chem. Soc. 112 (1990) 2429.

A study of the synthesis of a series of vanadium aryloxides was undertaken from the reaction of commercially available $V(O)(OR)_3$ precursors (below) and a series of aryl alcohols (see ligands to the *left*).



$V(O)(OPr^i)_3$
(vanadium oxytriisopropoxide)



$V(O)(OEt)_3$
(vanadium oxytriethoxide)

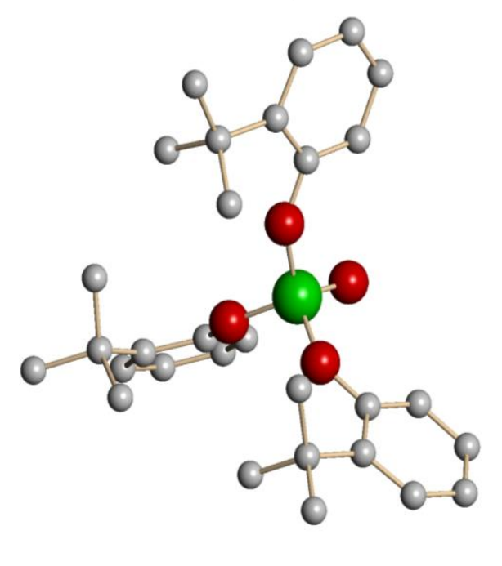
Commercially available $V(O)(OR)_3$ precursors

● Vanadium ● Oxygen ● Nitrogen
● Silicon ● Carbon

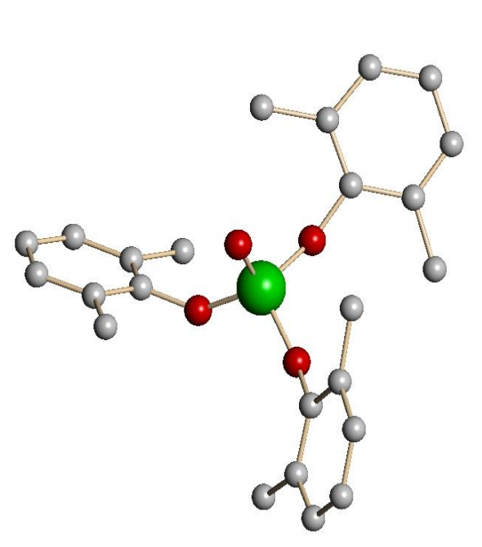
These color schemes are used in all structures shown

When difficulties in crystallizing the remaining aryloxides arose, a study of silanols ($HOSiR_3$) was started. Four $HOSiR_3$ were selected for study due to the structural variations noted for these ligands. The reactions were conducted under identical conditions as noted for the aryloxide system. Three novel siloxides have been synthesized (shown at right).

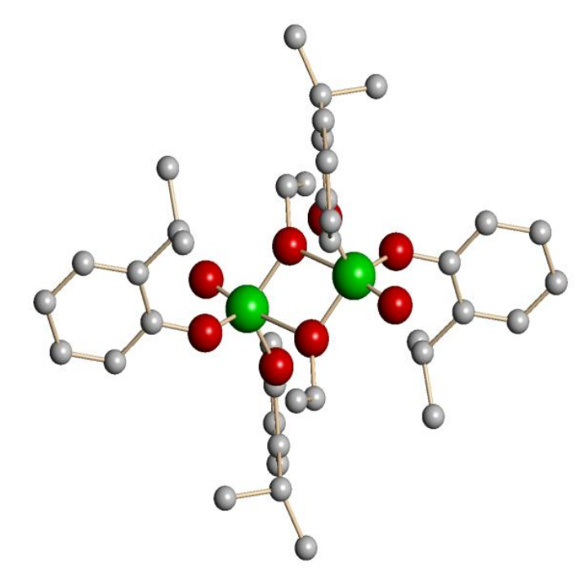
$$V(O)(OR)_3 + 3\ H\text{-}OAr \longrightarrow V(O)(OAr)_3 + 3HOAr$$



$V(O)(oBP)_3$



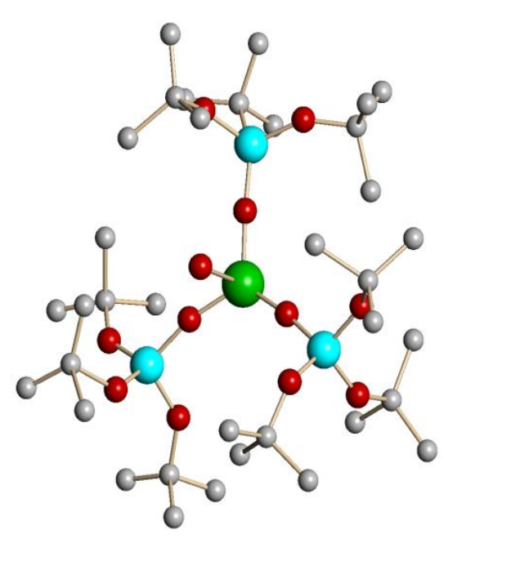
$V(O)(DMP)_3$



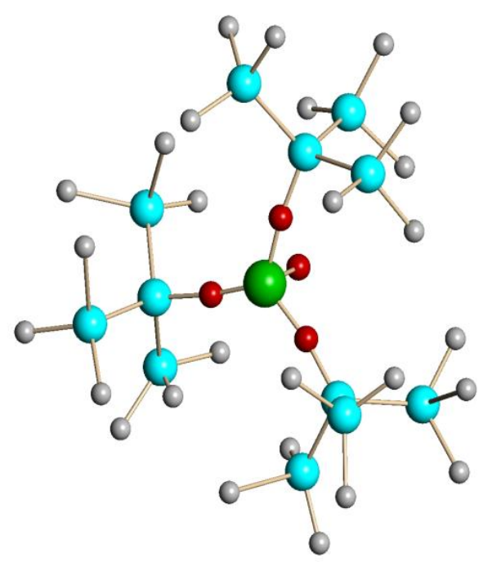
$[V(O)(OEt)(oPP)_2]_2$

The products isolated were monomers for the larger OPr^i derivatives; however, the reduction in the sterics of the OEt ligand led to a dinuclear species.

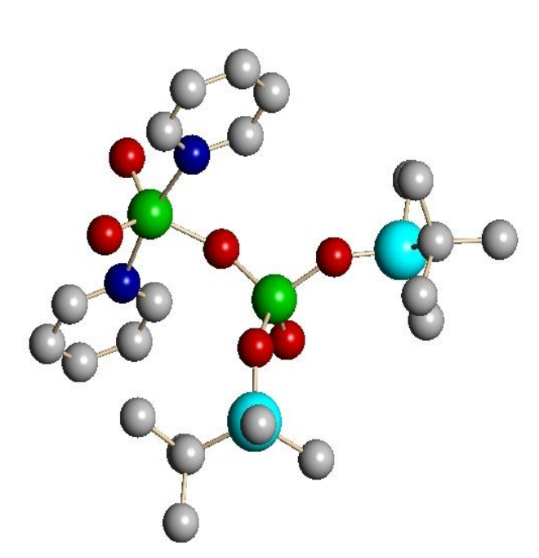
$$V(O)(OPr^i)_3 + 3\ H\text{-}OSiR_3 \longrightarrow V(O)(OSiR_3)_3 + 3\ H\text{-}OPr^i$$



$V(O)(TOBS)_3$



$V(O)(SST)_3$

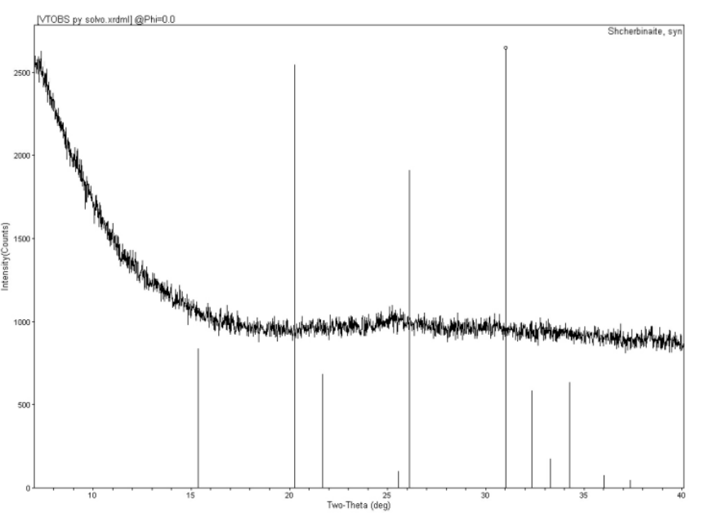


$V(O)_2(py)_2(\mu\text{-}O)V(O)(DMBS)_2$

The $OSiR_3$ ligands also generated monomers for the more sterically demanding ligands with a bridging oxide for the smaller DMBS ligand.

Nanoparticles of Vanadium Compounds

The synthesis of nanomaterials using the previously identified $V(O)(OR)_3$ precursors employed two routes. The precursors were dissolved in the appropriate solvent system (see right) under an argon atmosphere and either sealed in the bomb or transferred to a syringe which was injected into a heated solution. The resulting precipitate was collected by centrifugation , washed three times with appropriate solvent and air dried. PXRD analyses indicate that all materials are amorphous (select pattern shown below)



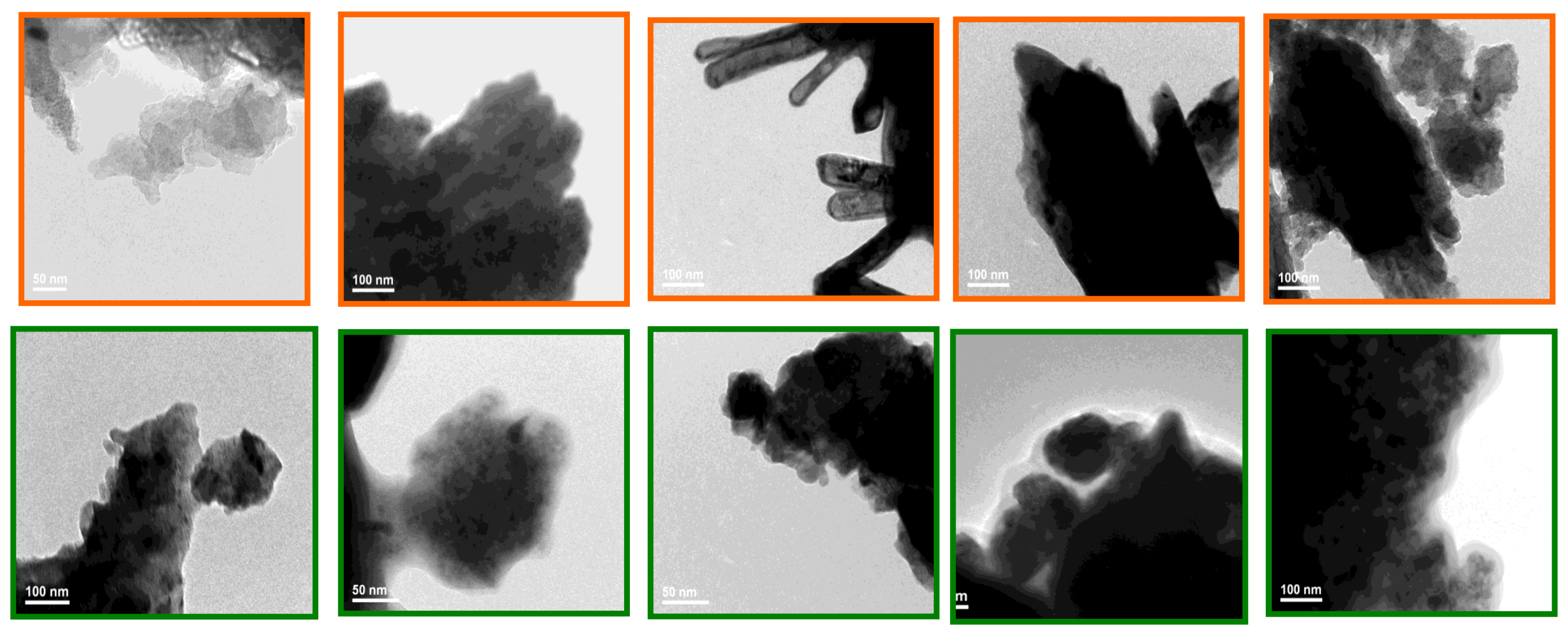
The isolated powder was reslurried in hexanes and a drop was placed on the TEM grid. The resulting TEM images are shown below.

SOLVO

- 25 mL pyridine (py)
- heated at 180°C for 24 hrs
- washed with hex

SPPT

- 20 mL trioctylamine (TOA)
- 2 mL oleic acid (OA)
- heated to 360°C for 30 mins
- washed with EtOH



$V(O)(oBP)_3$ $V(O)(DMP)_3$ $V(O)_2(py)_2(\mu\text{-}O)V(O)(DMBS)_2$ $V(O)(TOBS)_3$ $V(O)(SST)_3$

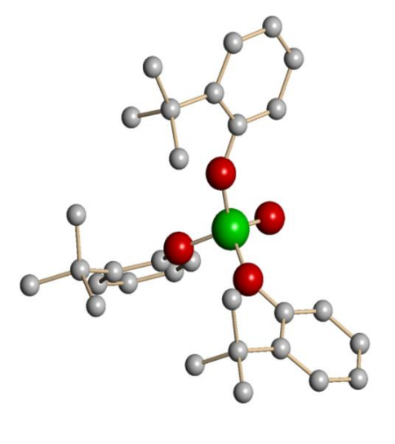
The TEM instrument used was a Philips CM 30 operating at 300 keV accelerating voltage with a LaB_6 source and a line-to-line resoution of 0.18 nm. The instrument is equipped with a Noran System Six energy dispersive X-ray spectrometer for element characterization.

The nanoparticles observed for the SOLVO reactions showed rods varying in width from 10 nm to 50 nm for all pendant ligand moieties used. Nanorods and wires are of interest for battery applications, so this system will be further investigated in a effort to yield readily reproducible rods.

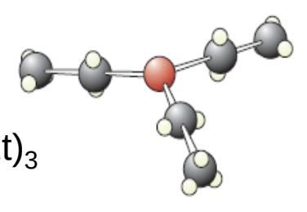
Those observed for the SPPT route favor the formation of nanodots. For the solvent/surfactant system used, most particles did not readily precipitate. Other solvent systems will be investigated in an attempt to generate better particles that will be of use for battery applications.

Alterantive Vanadium Nanoparticles

Vanadium Boride



$V(O)(oBP)_3$

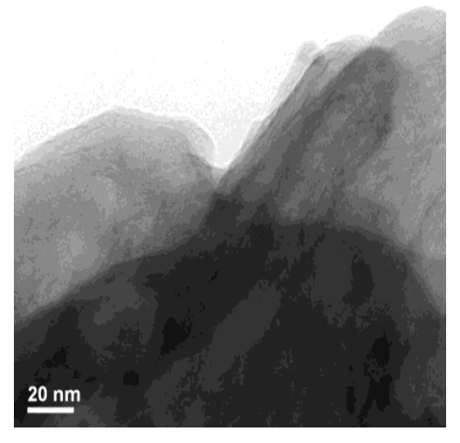


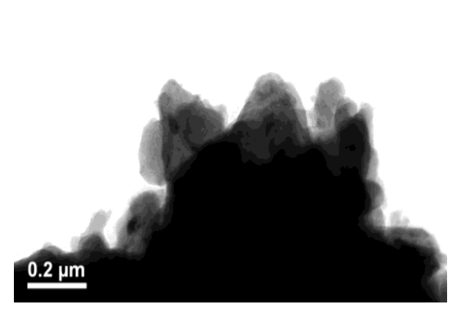
$B(Et)_3$

SOLVO in py

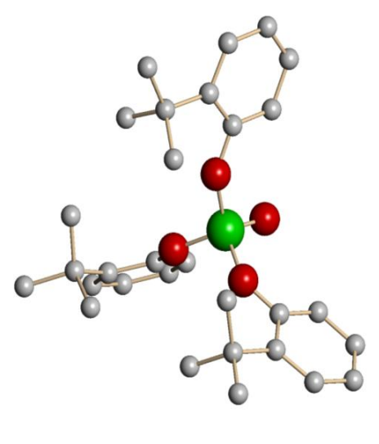
180°C, 24 hrs

Vanadium boride synthesis was attempted to see if it could be made by a simple SOLVO route. These materials are of interest because of their proposed high energy density for use in batteries for small electronic devices.





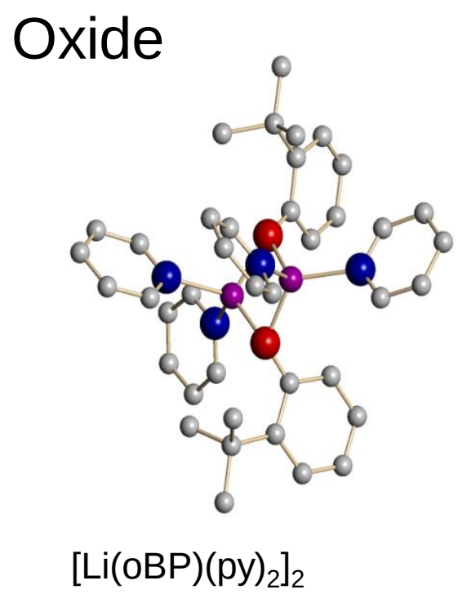
Lithium Vanadium Oxide



$V(O)(oBP)_3$

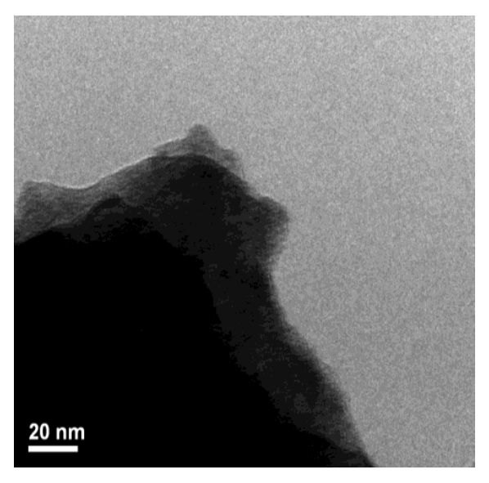
SOLVO in py

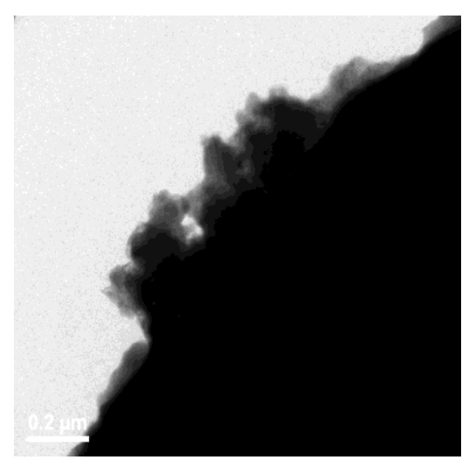
180°C, 24 hrs



$[Li(oBP)(py)_2]_2$

Lithium vanadium oxide synthesis was begun because it is a well known cathode material for Li-ion batteries. The goal was to see if a simple SOLVO route would be successful, and if the resulting nanomaterials had improved electronic properties compared to the bulk powders commonly used.





Summary and Future Work

- Synthesized a novel family of vanadium oxo, alkoxide compounds.
- Nanoparticles were synthesized from these compounds using a variety of processing routes:
  - (i) SOLVO generated nanorods;
  - (ii) SPPT formed nanodots.
- Other nanoparticle systems, such as MeIm/H2O for SPPT, will be investigated.
- Work has begun on trying to synthesize single source $Li_y\mathit{V(OR)}_x$ precursors.
- These single source precursors could lead to a simple route for the production of Li_yVO_x nanomaterials for Li-ion batteries.

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