



Chemical solution based methods for nanoparticle and core-shell synthesis

Inorganic and Physical Chemistry

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IMO-IMOMEC



The IMO-IPC lab

Hasselt University and IMO-IMOMECE

IMEC

1900 people (500 guests)



IMO-IMOMECE

110 people (50 PhD students)



IMO-IPC lab

19 people (13 PhD students)

Development and characterization of new material systems for (bio-)electronics and nanotechnology in the areas of **energy** and **health**

Expert groups in

- Plastic electronics
- Molecular electronics and Biosensors
- Wide band gap materials
- **Chemical synthesis of inorganic nanomaterials**
- Reliability aspects of material systems
- Nanophysics
- Chemical and physical characterization

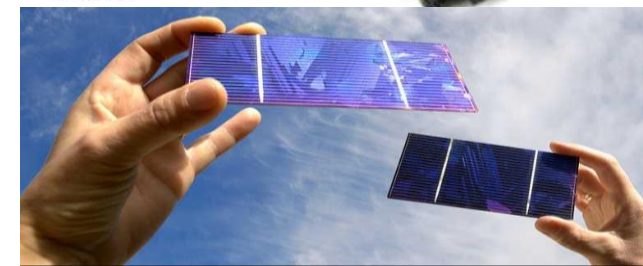
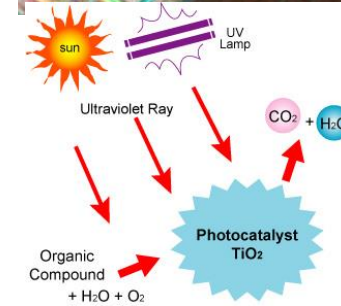
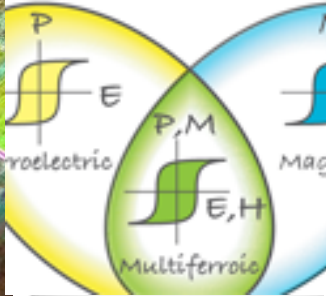
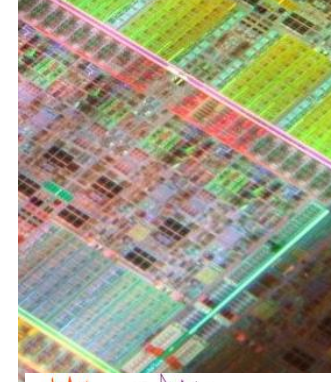
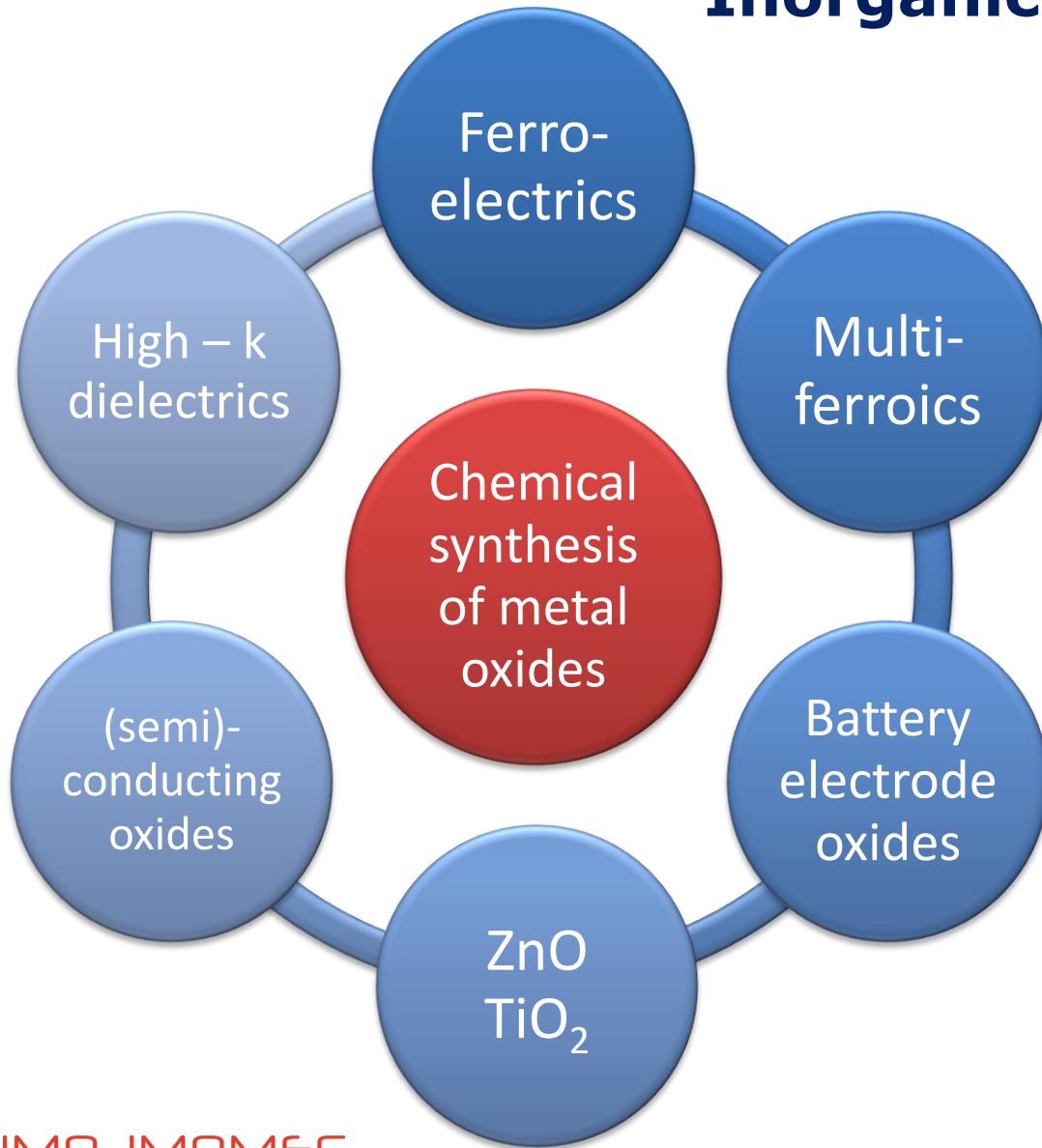


IMO-IMOMECE

▶▶ UHASSELT imec

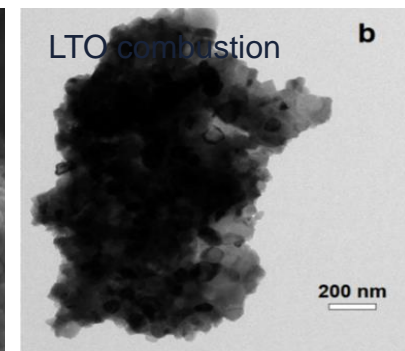
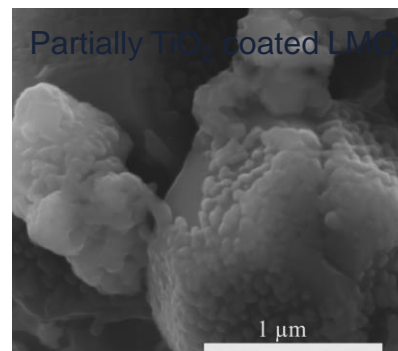
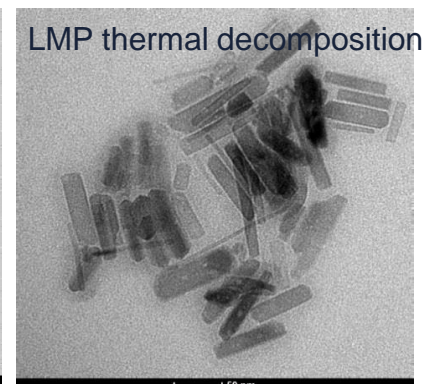
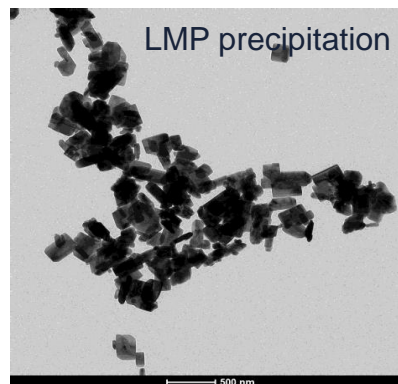


The IMO-IPC lab Inorganic & Physical Chemistry



Examples of LIB electrode materials

- **LiFePO_4 , LiMnPO_4 , $\text{LiFe}_{0.3}\text{Mn}_{0.7}\text{PO}_4$**
 - Aqueous solution-gel (+ ball milling), precipitation and thermal decomposition synthesis methods
- **LiMn_2O_4**
 - Solution-gel synthesis
- **TiO_2 coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$**
 - Heterogeneous nucleation on LNMO
- **(Doped) $\text{Li}_4\text{Ti}_5\text{O}_{12}$**
 - Combustion synthesis
- **$\text{LiNi}_{0.5}\text{Mn}_{0.3-y}\text{X}_y\text{Co}_{0.2}\text{O}_2$**
 - Aqueous solution-gel synthesis



And of course
Solid inorganic
electrolytes

Goal of the lecture

To provide a catalog of sol(ution) based synthesis methods

To illustrate some of the basic chemistry behind

By showing a few examples for battery materials

To see the common points and the differences

To question what further research is needed still

Synthesis

Metaloxides / polyanion compounds



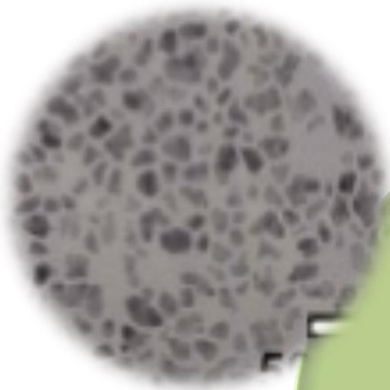
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KNOWLEDGE IN ACTION

Synthesis

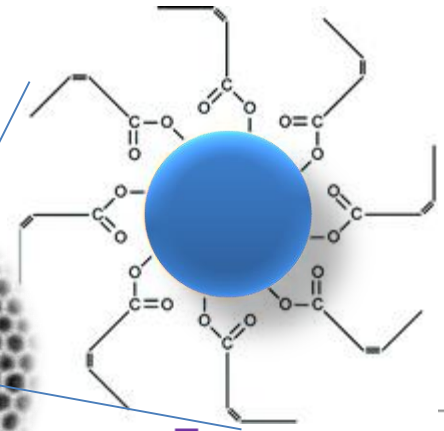
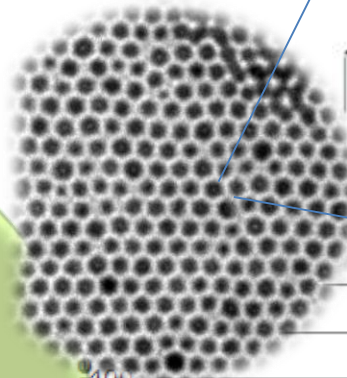
Top down approach

Solid state reaction
Milling

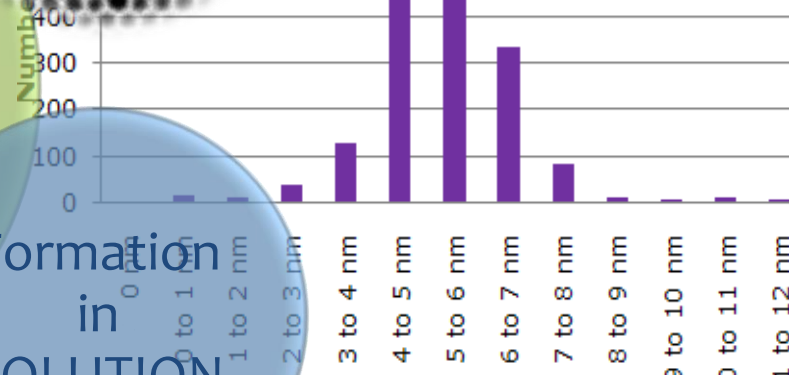


Synthesis

Pyrolysis of vaporized liquid or gas



Formation in SOLUTION



Bottom up approach

Synthesis

Top down approach

Simple
High yield
High throughput
Low control over size, shape and surface
'dry' powder needs to be dispersed
'dry' powder safety issues

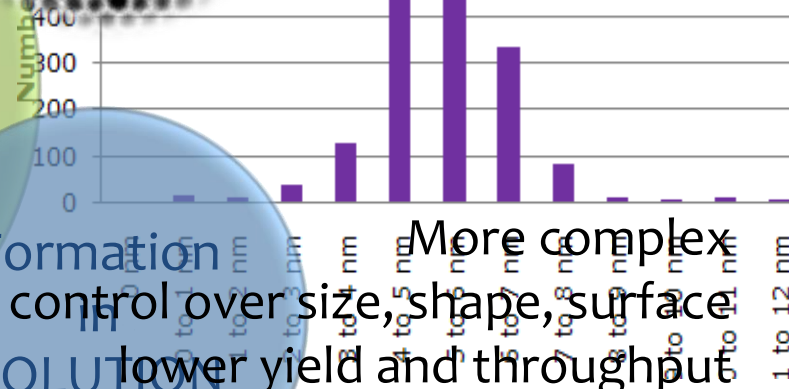
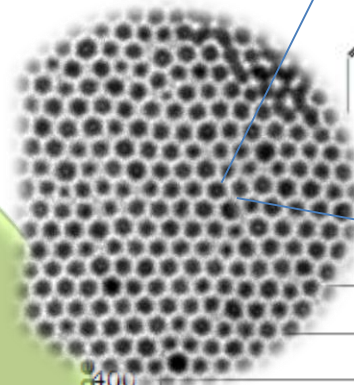
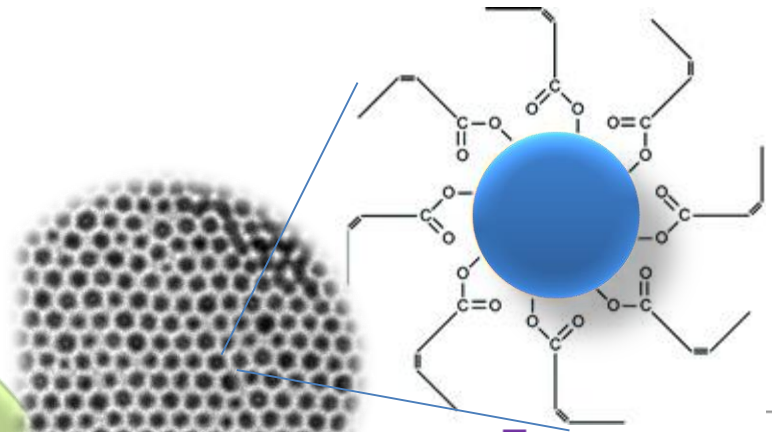
Solid state
Milling

Synthesis

Pyrolysis
of
vaporized
liquid or gas

Formation in SOLUTION
High control over size, shape, surface
lower yield and throughput
dispersion often included
One might need to change solvent or surface
depending on application

Bottom up approach

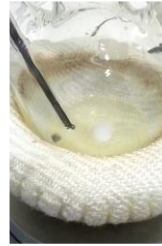


Chemical solution based synthesis



(Aqueous) sol(ution)-gel

- Solution with complexated metal ions
- Thermal treatment: decomposition of complexing agents and crystallization



Thermal decomposition

- Precursor decomposes in high boiling apolar solvent
- In presence of surfactants



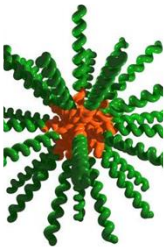
Hydro/solvothermal

- Hydrolysis and condensation
- Elevated T and p



Controlled precipitation

- Precipitation induced by e.g. change of pH
- Low T



Micelle nanoreactors

- Micelles of surfactants or blockcopolymers
- Loaded with precursors



Combustion

- Dried solution of high energetic starting products + complexing agents
- Autocombustion at low T

Wet chemical synthesis

(Aqueous) sol(ution)-gel routes



What is sol-gel ?

Classic alkoxide sol-gel: Chemical reactions

The Three Primary Reactions in Silica Gel Formation via the Alkoxide Technique

Hydrolysis

Water
Condensation

Alcohol
Condensation

Other metal ions?
- More electropositive (stronger lewis acid) than Si => more susceptible to nucleophilic attack
- TM has preferred CN higher than valence
=> Less degrees of freedom for long range arrangement of polyhedra => often semi/microcrystalline materials

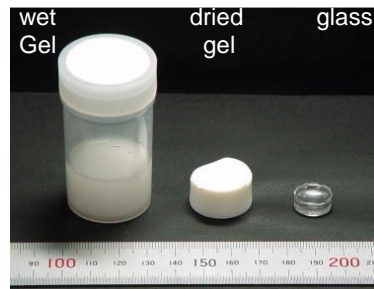
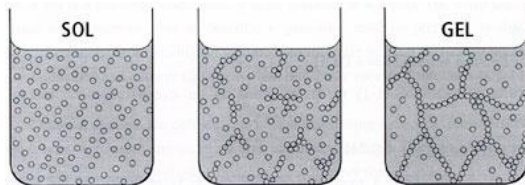
Once silanol groups form, they can condense through two different reactions to form connective silicon-oxygen-silicon bridges

Sol:

stable suspension of colloidal particles in a liquid

Gel:

porous 3D continuous solid network surrounding and supporting a continuous liquid phase; often formed by covalent bonds between sol particles. In case hydrogen bonds or VdW forces: gel formation is reversible



Silica aerogel



What is sol-gel ? Thermodynamics & kinetics

For example: first step = hydrolysis TEOS $Q_0^j + H_2O \xrightleftharpoons[\kappa_{h0}^-]{\kappa_{h0}^+} Q_0^{j+1} + EtOH$

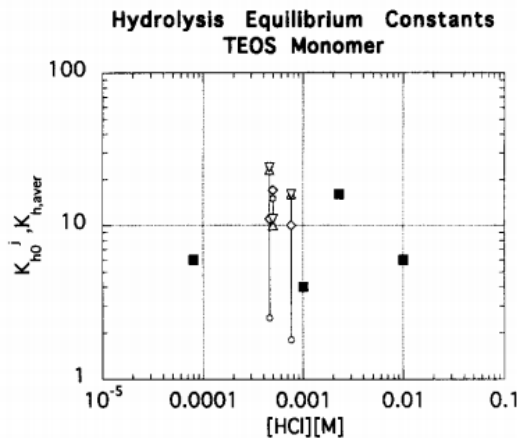
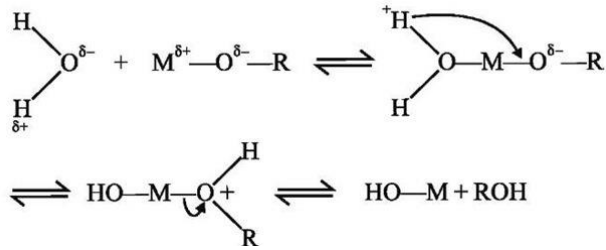


Fig. 4. Hydrolysis equilibrium constants for TEOS-derived monomers. Filled symbols: averaged equilibrium constants $K_{h,aver}$ (data from [26,39]). Open symbols: detailed equilibrium constants K_{h0}^j (data from [24,38]). O: $j = 1$, \diamond : $j = 2$, Δ : $j = 3$, ∇ : $j = 4$.

Almost no influence of pH
(acid addition)

Hydrolysis more favoured in basic conditions

Kinetics control & complexation

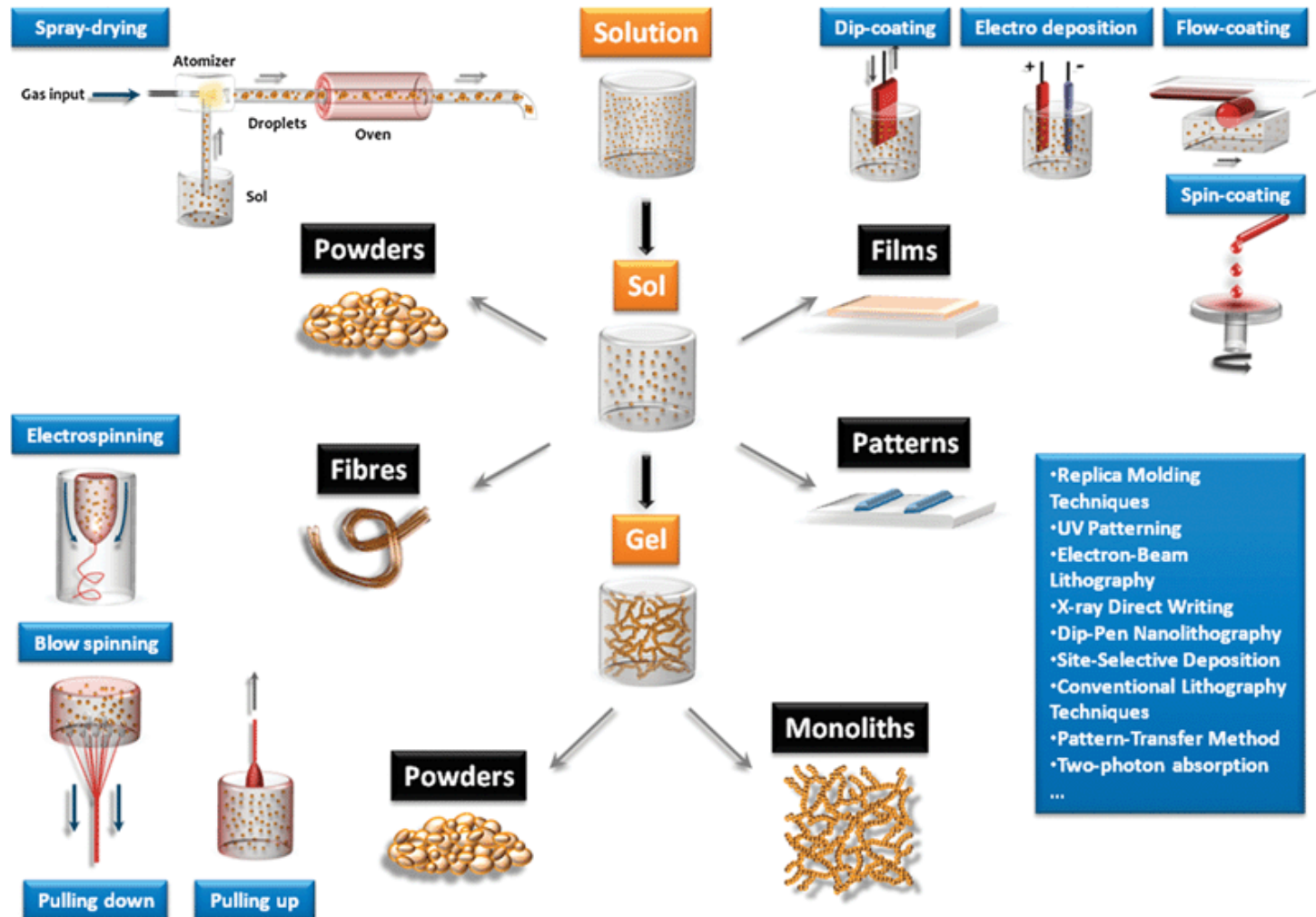
- Silica: needs catalysis of hydrolysis (and condensation)
- Other metal oxides:
 - Very high reactivity
 - precipitate immediately upon addition of water
 - reactivity must be reduced e.g. by complexation with carboxylates
 - terminology: hybrid sol-gel

Ligands also enhance gel formation / prevent precipitation

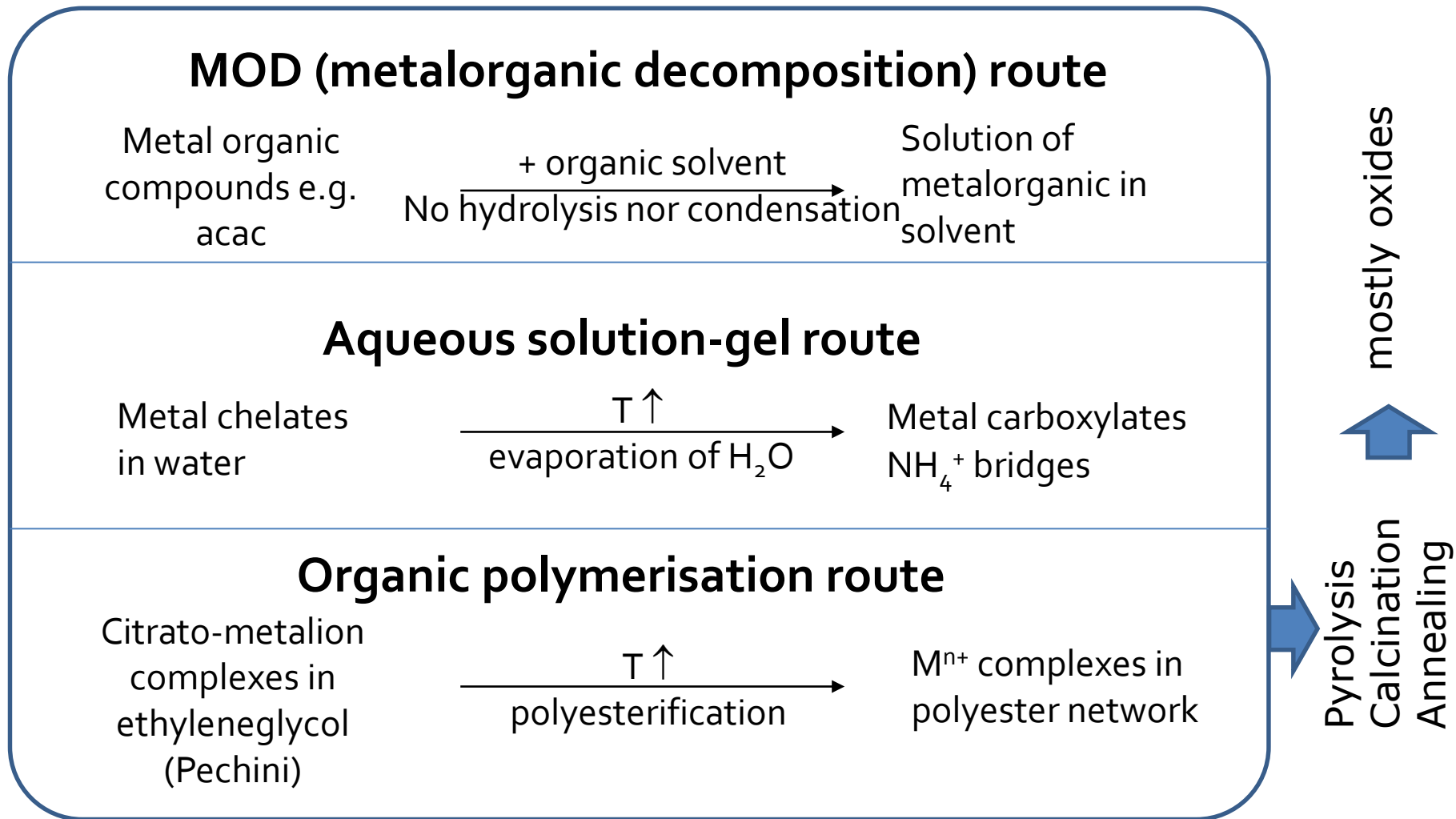
Ligands affect microstructure and texture of the gels

What can be done with sol-gel?

Possibilities of further evolvement



What is strictly not sol-gel? Related routes



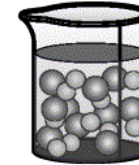
What is strictly not sol-gel? Related routes

Starting materials (alkoxides, salts, ligands, solvents...)

Dissolution / hydrolysis & condensation



Sol or solution
= liquid precursor

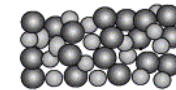


← Ti-precursor
← M-carboxylate

Solvent evaporation / chemical reaction



Gel
(covalent, hydrogen,
VdW bonds)

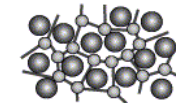


← M-carboxylate
← Ti-precursor

Heat treat → decompose organics



Amorphous oxide
(with impurities)

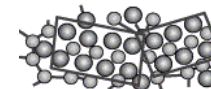


← M-carboxylate
← TiO₂

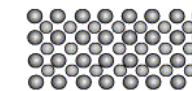
Heat treat → crystallize / tune vacancies



Crystalline
oxide



Nanocrystals



Perovskite crystal

**What comes after
the precursor?**

**Thermal
treatment**

Pyrolysis
Calcination
Annealing



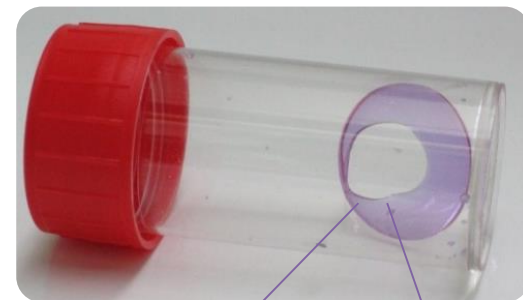
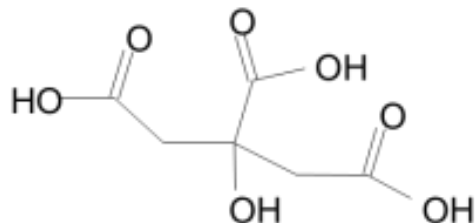
mostly oxides

Focus:

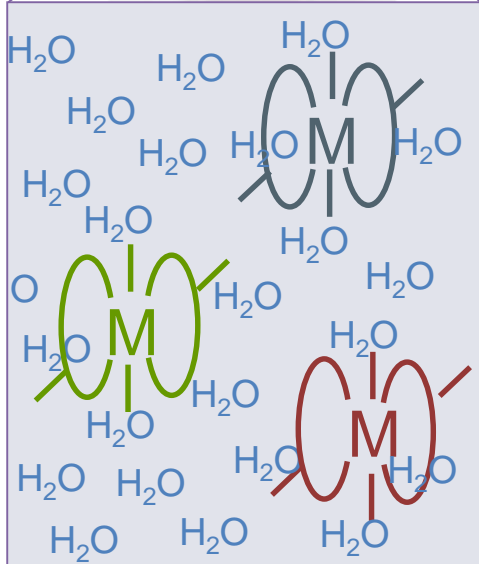
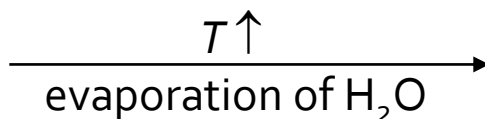
Aqueous citrate based solution and gel chemistry



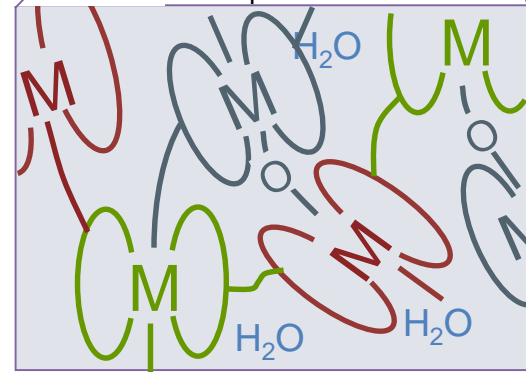
Metal chelates in water



Aqueous solution-gel route



Metal carboxylates
NH₄⁺ bridges



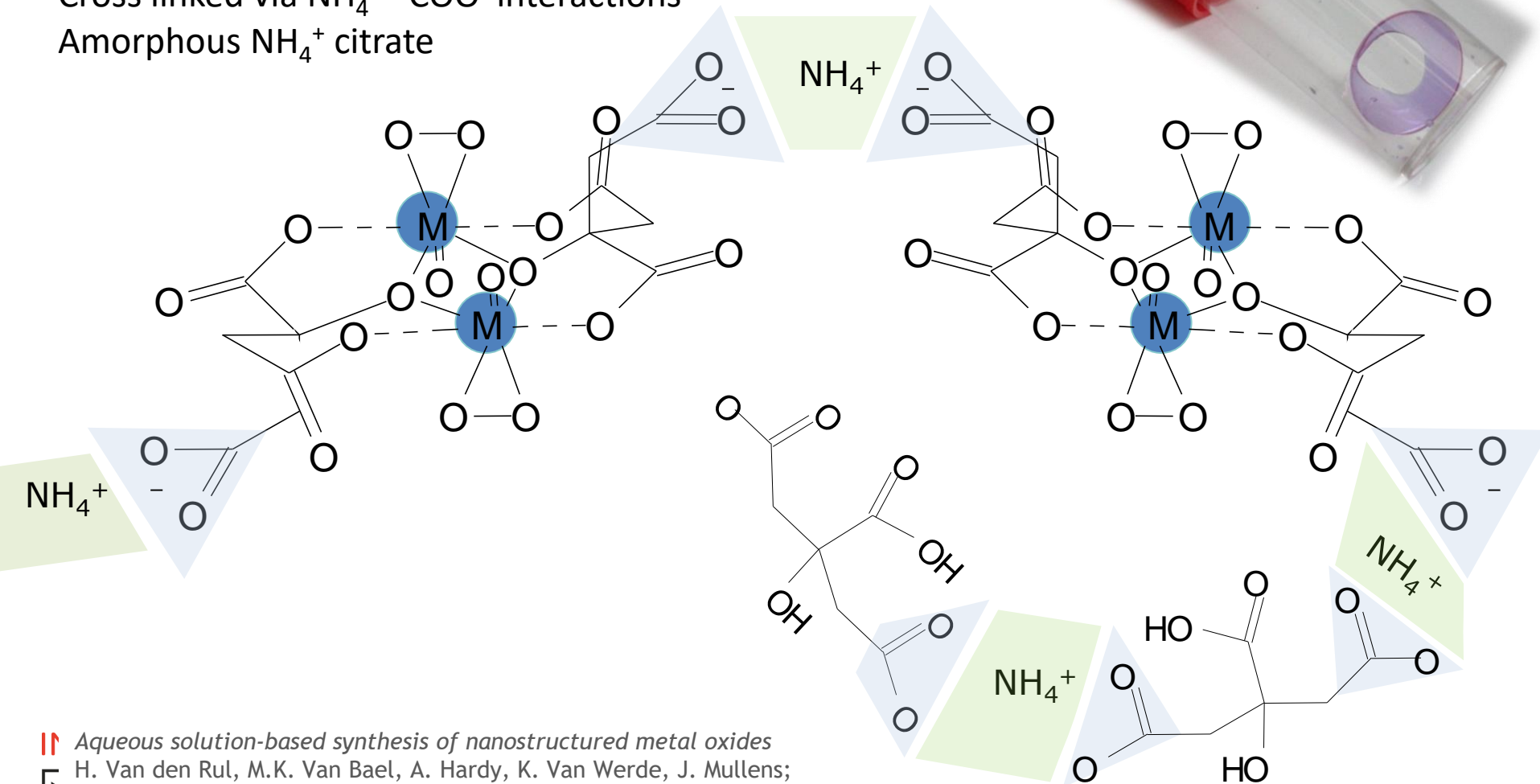
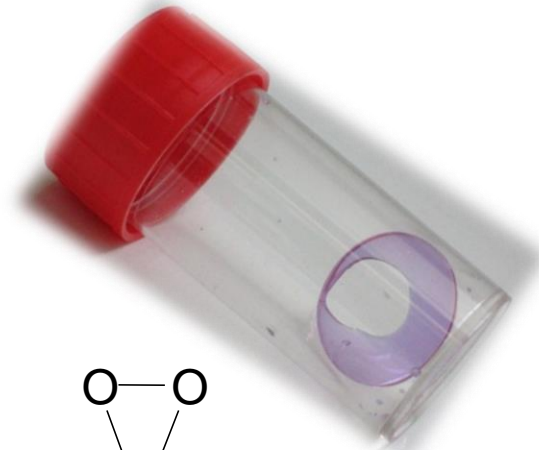
Focus: Water based solution-gel chemistry

Gel

Metal citrate complexes

Cross linked via NH_4^+ - COO^- interactions

Amorphous NH_4^+ citrate



↑ *Aqueous solution-based synthesis of nanostructured metal oxides*

▶ H. Van den Rul, M.K. Van Bael, A. Hardy, K. Van Werde, J. Mullens;

in 'Handbook of nanoceramics and their based nanodevices', Eds. T.Y. Tseng en H.S. Nalwa, American Scientific Publishers, (2009)

Focus: Water based solution-gel chemistry

Water based M-precursors
Can be 'easily' mixed

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|--|
| H | | | | | | | | | | | | | | | | | He | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | | |
| | | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | |
| | | | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | |

Aqueous Solution-Based Synthesis of Nanostructured Metal Oxides, H. Van den Rul, M.K. Van Bael et al Chapter in Handbook of Nanoceramics and Their Based Nanodevices, Ed. T-Y Tseng and H. S. Nalwa (2009)

Advantages and disadvantages of sol(ution)-gel

Advantages

- Molecular scale mixing
- High homogeneity
- Relatively low T (200-600°C and up), short time
- High crystallinity
- Nanopowders possible
- Versatility in metal ion composition
- Wide range of routes available from literature
- Mainly oxides (phosphates)

Aqueous routes

- Limited risks (environment and safety)
- Inexpensive solvent (water) and starting products
- Synthesis and storage in ambient conditions

Challenges

- Alkoxides can be expensive
- Large volume changes during gelation and drying / calcination
- Porosity control
- Particle size distribution can be broad
- Agglomeration
- Mainly aimed at oxides

Sol-gel synthesis of LIB materials in literature

- Numerous examples
- Better electrochemical performance compared to powders from traditional solid state reactions
 - reversible capacity,
 - cycling behavior and
 - rate capability
- Precursors
 - Li sources: LiNO_3 , LiOAc , Li_2CO_3 , LiOH
 - Sources for metals: oxides, salts (nitrate, acetate, ...)
 - Ligands:
 - succinic acid,
 - oxalic acid,
 - malic acid,
 - tartaric acid,
 - acrylic acid,
 - citric acid,
 - humic acid and
 - polymers like poly(acrylic acid) (PAA) and poly(vinylpyrrolidone) (PVP)

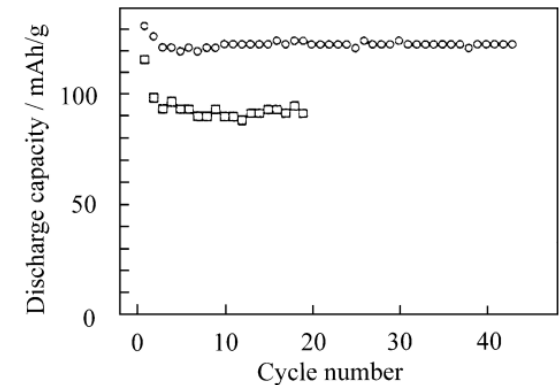
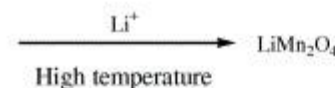
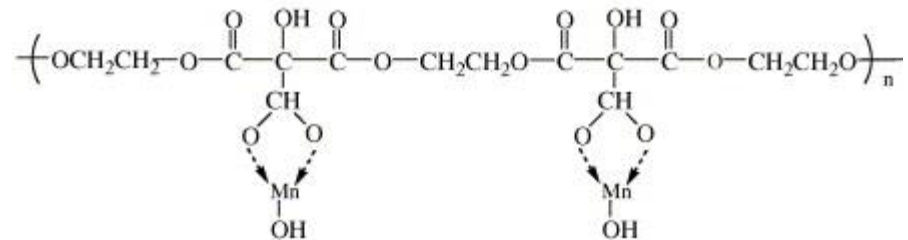
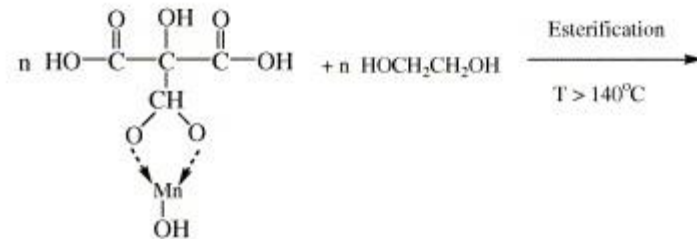
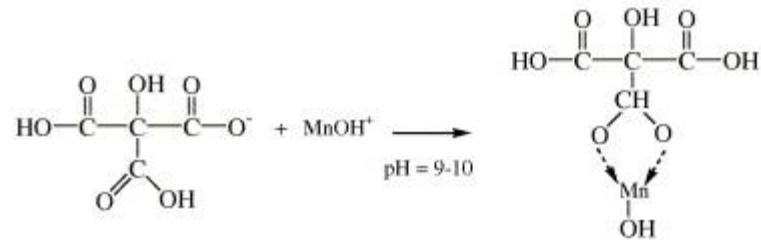


Fig. 1 Comparison of the cycling behavior of LiCoO_2 prepared by sol-gel methods (*open circles*) and traditional solid-phase methods (*open squares*) (from [9])

Sol-gel synthesis of LIB materials in literature

- Shake / bake / measure versus understanding the synthesis
 - Everybody can carry out a "sol-gel" recipe,
 - Understanding the mechanisms can be hard
 - Yet sometimes imperative to fully control the final properties



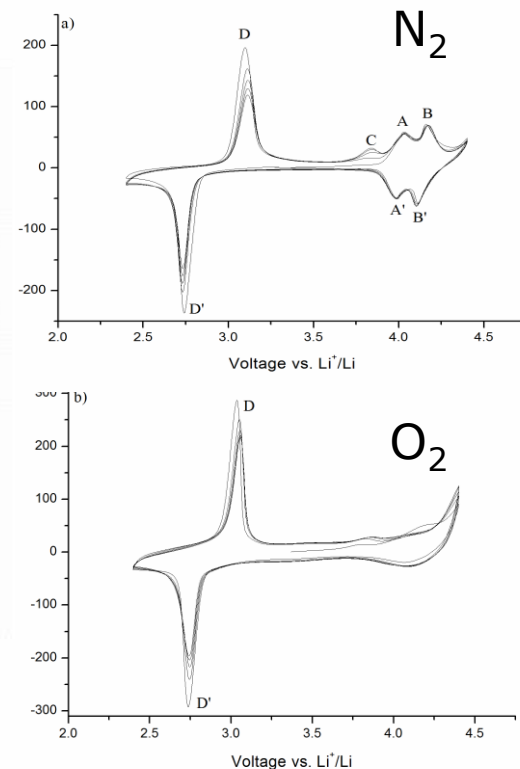
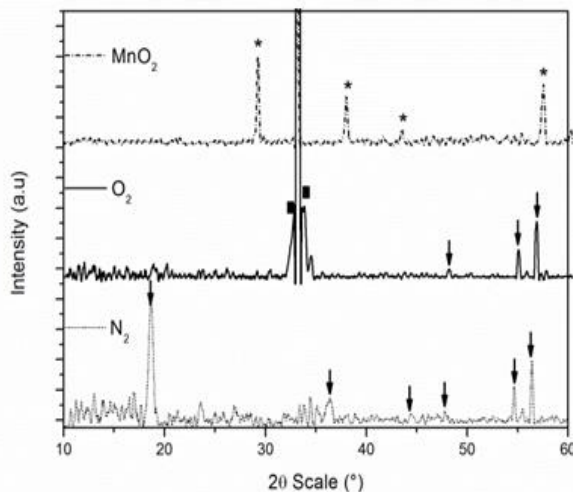
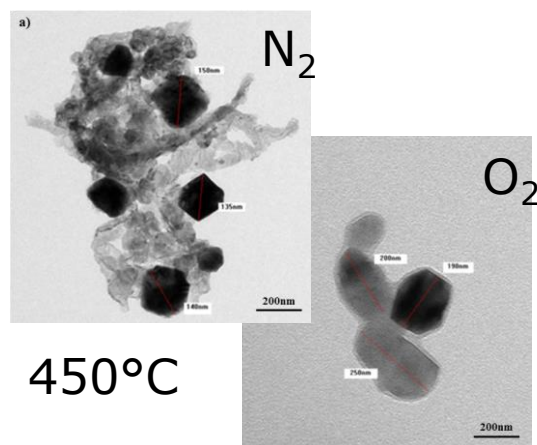
L.J. Fu, Progress in Materials, 2005, 50 (7) 881

Not sol-gel → Pechini

*What is going on here?
Lots of questions
unanswered*

Example: precursor chemistry – phase formation LMO from aq CSD

- Mn^{3+} precursor \rightarrow $\text{Mn}^{3,5+}$ in LMO
 - Citrate in precursor \rightarrow partial Mn oxidation
 - O_2 ambient \rightarrow full Mn oxidation + disproportionation \rightarrow phase segregation
- Electrochemical properties!



What tools can we use to learn more?

ICP-AES, ICP-MS,
NMR, Raman, UV/Vis,
Chromatography,
XANES, rheology,
voltammetry...

NMR, Raman, FTIR,
UV/Vis, XANES, SAXS,
EXAFS,...

In-situ XRD, TGA-
MS/FTIR, DSC, FTIR,
NMR, Raman, quick
XANES, XPS,
electrochemical,...

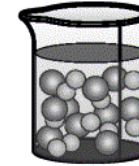
XRD, neutron
scattering, TEM,
electrochemical, zeta
potential, DLS,...

Starting materials (alkoxides,
salts, ligands, solvents...)

Dissolution / hydrolysis & condensation



Sol or solution
= liquid precursor

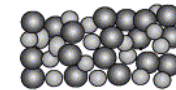


← Ti-precursor
← M-carboxylate

Solvent evaporation / chemical reaction



Amorphous,
homogeneous gel
(covalent, hydrogen,
VdW bonds)

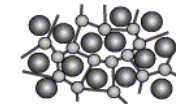


← M-carboxylate
← Ti-precursor

Heat treat → decompose organics



Amorphous oxide
(with impurities)

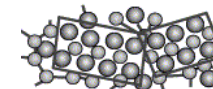


← M-carboxylate
← TiO₂

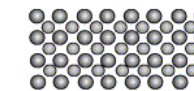
Heat treat → crystallize / tune vacancies



Crystalline
oxide



Nanocrystals



Perovskite crystal

Index of interesting reviews / books

- The sol-gel handbook, D. Levy & M. Zayat ed., 2015, Wiley VCH
- Sol-gel Science: The Physics and Chemistry of Sol-gel Processing, G.W. Scherer, C.J. Brinker ed., 1990, Academic press
- The Chemistry of Aqua Ions: Synthesis, Structure and Reactivity: A Tour Through the Periodic Table of the Elements, D.T. Richens, 1997, Wiley
- Cathode materials for lithium ion batteries prepared by sol-gel methods, H. Liu et al, J Solid State Electrochem (2004) 8: 450. doi:10.1007/s10008-004-0521-1
- Electrode materials for lithium secondary batteries prepared by sol-gel methods, L.J. Fu et al., Progr. in mater. sci. (2005) 50: 881 (repeats some)

- Useful search terms: sol-gel, Pechini, polymerizable complex, solution-gel, metalorganic decomposition

Wet chemical synthesis

Controlled precipitation



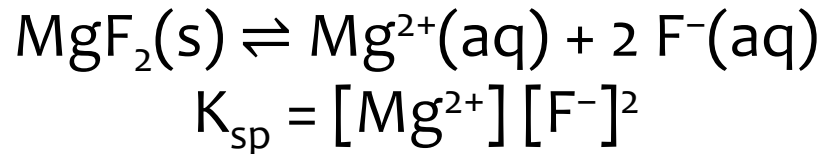
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KNOWLEDGE IN ACTION

What is a (co)precipitation reaction?

■ Precipitation

- Reverse of a dissolution reaction
- Exceedance of the solubility (K_{sp})
= supersaturation (thermodynamics)

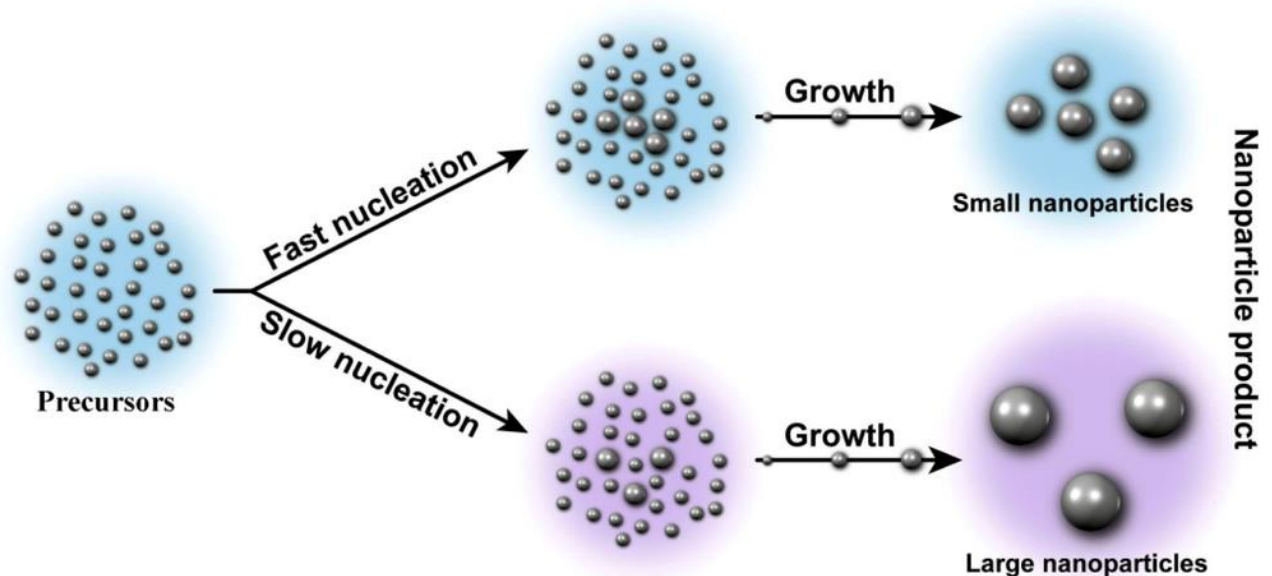


■ Coprecipitation

- Carrying down a substance, during formation of a precipitate, of a substance which is normally soluble under these conditions
 - Inclusion: Impurity occupies a lattice site
 - Adsorption: Impurity weakly adsorbed to the precipitate surface
 - Occlusion: Impurity physically trapped in the growing precipitate

Stages of (co)precipitation

- Two main stages
 - Nucleation (kinetics)
 - Heterogeneous: at nucleation sites on surfaces
 - Homogeneous: away from a surface, in solution
 - Growth
 - Growth of the crystallites

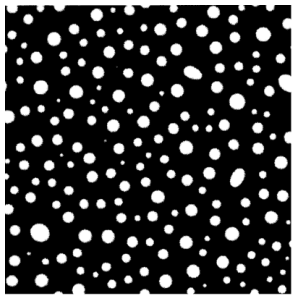


Afterwards: aging of the precipitate

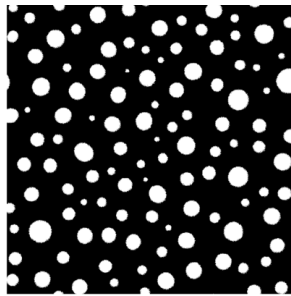
- Ostwald ripening
 - Dissolution of small crystals or sol particles and the redeposition of the dissolved species on the surfaces of larger crystals or sol particles
 - Larger particles energetically favoured in comparison to small particles (lowering specific surface area)

- Digestive ripening
 - Small particles grow at the expense of larger particles → monodisperse
 - Not well understood

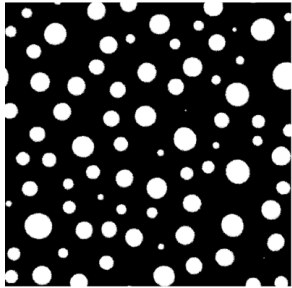
Controlling growth of particles



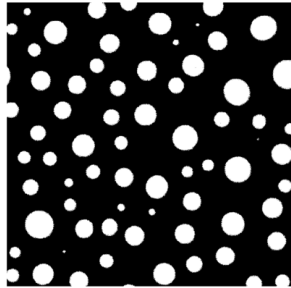
t=10000



t=40000



t=80000



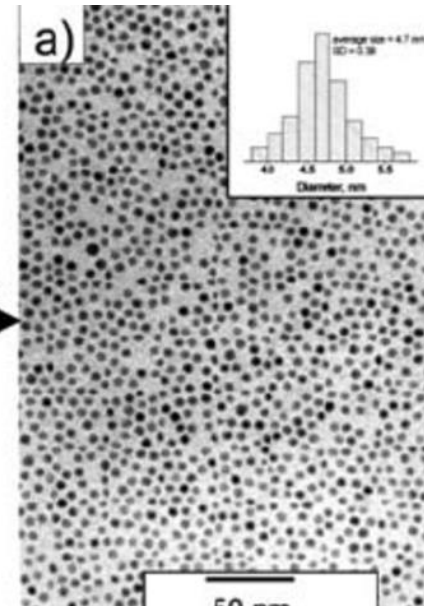
t=100000

D. Fan, S.P. Chen, L.Q. Chen, P.W. Voorhees, Phase-field simulation of 2-D Ostwald ripening in the high volume fraction regime, *Acta Mater.* 50 (2002) 1895–1907. doi:10.1016/S1359-6454(01)00393-7.

Q. Zhang, J. Xie, Y. Yu, J.Y. Lee, Monodispersity control in the synthesis of monometallic and bimetallic quasi-spherical gold and silver nanoparticles., *Nanoscale.* 2 (2010) 1962–1975. doi:10.1039/c0nr00155d.



Digestive ripening



Advantages and disadvantages of precipitation

Advantages

- Low temperatures
 - Metastable products
 - Reduced particle growth → NPs
- Reactive and/or high surface area materials
- Oxides, phosphates, carbonates,...

Disadvantages

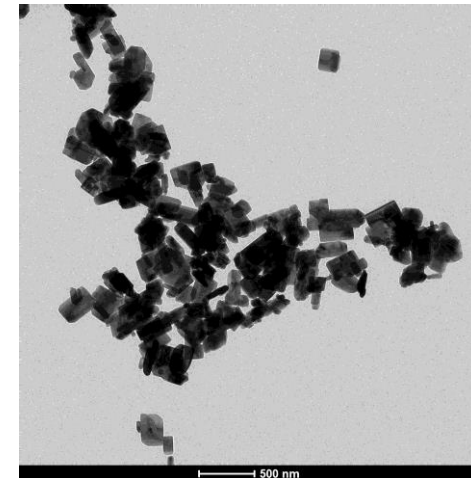
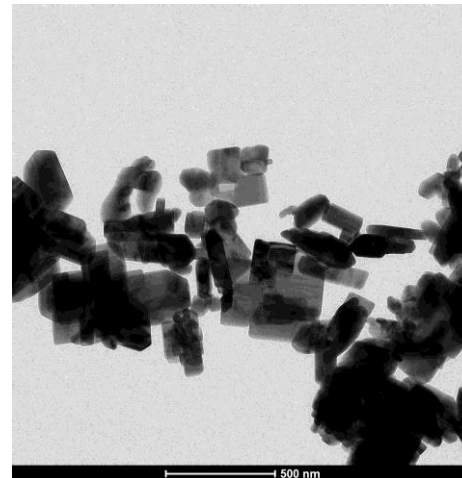
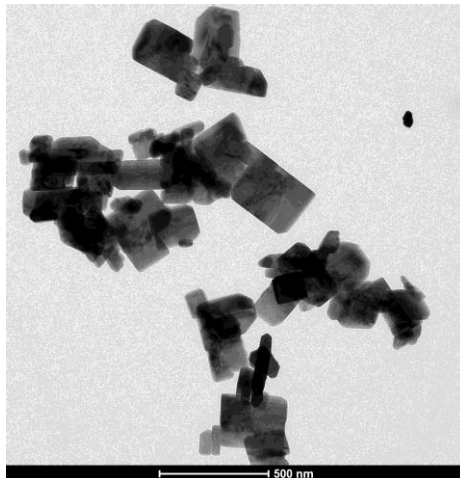
- appropriate precursor needed
- Inadequate co-precipitation of different ions leads to inhomogeneity
- Metastable products are often unstable in applications where high temperatures are used or single crystals are needed

PCS particle sizes

d_{10} : 77 nm

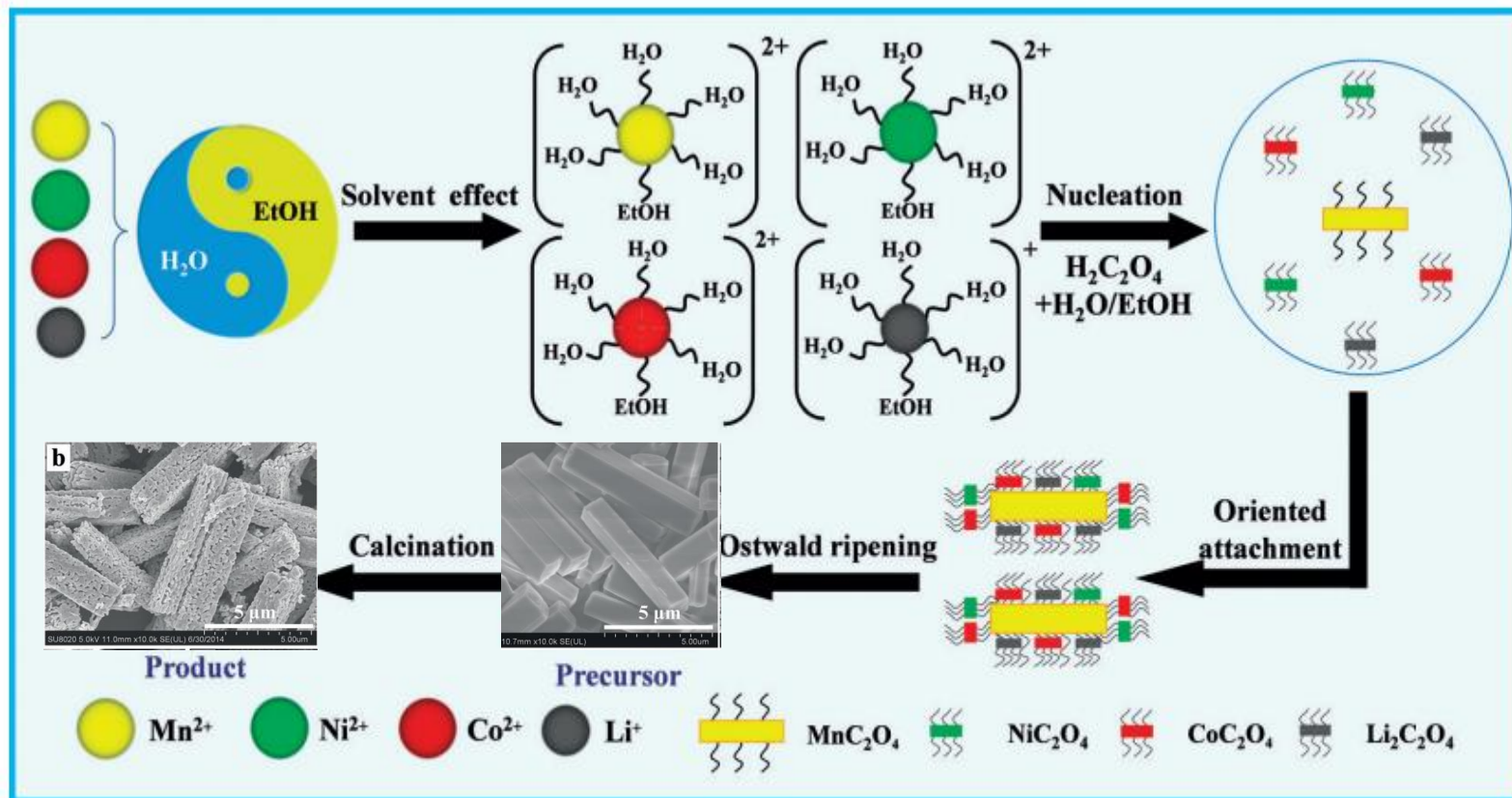
d_{50} : 145 nm

d_{90} : 270 nm



Precipitation synthesis of LIB materials in literature

Oxalate coprecipitation and
topotactic conversion to the oxide



Scheme 1. Illustration of ethanol mediated co-precipitation coupled with subsequent calcination for the formation of $0.5 \text{Li}_2\text{MnO}_3 \cdot 0.5 \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ 1D porous micro- and nanostructured bars.

Precipitation synthesis of LIB materials in literature

- One-Step Low-Temperature Route for the Preparation of Electrochemically Active LiMnPO_4 Powders

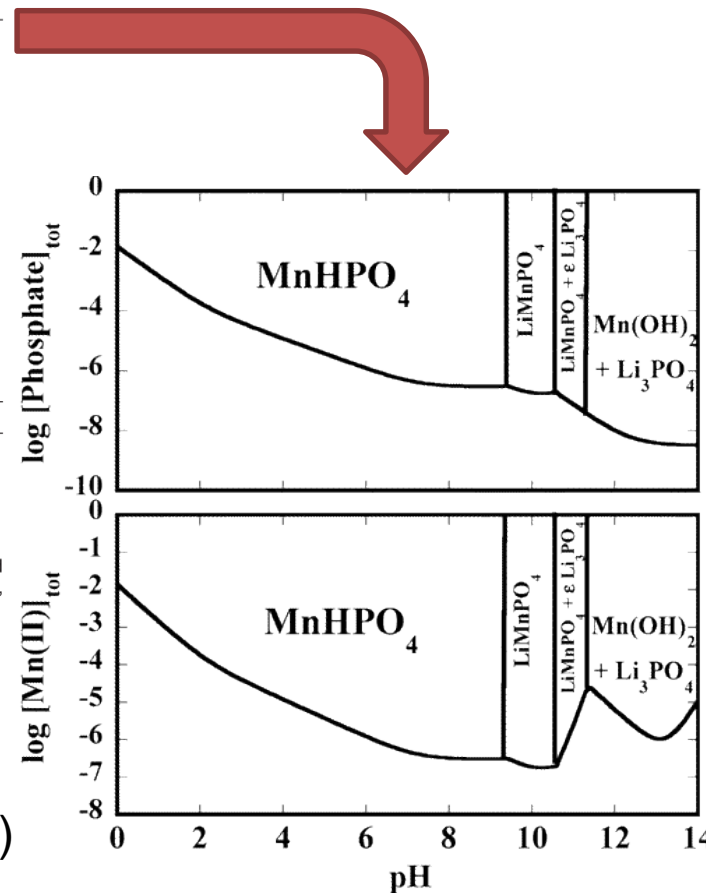
Mass Action Law Equations

| eq no. | equilibrium reactions | symbol for constant | equation |
|--------|---|-----------------------------------|---|
| 1 | $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ | K_w | $K_w = [\text{H}^+] \cdot [\text{OH}^-]$ |
| 2 | $\text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-} + \text{H}^+$ | K_{h1} | $K_{h1} = [\text{PO}_4^{3-}] \cdot [\text{H}^+] / [\text{HPO}_4^{2-}]$ |
| 3 | $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$ | K_{h2} | $K_{h2} = [\text{HPO}_4^{2-}] \cdot [\text{H}^+] / [\text{H}_2\text{PO}_4^-]$ |
| 4 | $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$ | K_{h3} | $K_{h3} = [\text{H}_2\text{PO}_4^-] \cdot [\text{H}^+] / [\text{H}_3\text{PO}_4]$ |
| 5 | $\text{Mn}^{2+} + \text{OH}^- \rightleftharpoons \text{Mn}(\text{OH})^+$ | β_1 | $\beta_1 = [\text{Mn}(\text{OH})^+] / ([\text{Mn}^{2+}] \cdot [\text{OH}^-])$ |
| 6 | $\text{Mn}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Mn}(\text{OH})_2$ | β_2 | $\beta_2 = [\text{Mn}(\text{OH})_2] / ([\text{Mn}^{2+}] \cdot [\text{OH}^-]^2)$ |
| 7 | $\text{Mn}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Mn}(\text{OH})_3^-$ | β_3 | $\beta_3 = [\text{Mn}(\text{OH})_3^-] / ([\text{Mn}^{2+}] \cdot [\text{OH}^-]^3)$ |
| 8 | $\text{Mn}^{2+} + 4 \text{OH}^- \rightleftharpoons \text{Mn}(\text{OH})_4^{2-}$ | β_4 | $\beta_4 = [\text{Mn}(\text{OH})_4^{2-}] / ([\text{Mn}^{2+}] \cdot [\text{OH}^-]^4)$ |
| 9 | $2 \text{Mn}^{2+} + \text{OH}^- \rightleftharpoons \text{Mn}_2(\text{OH})_3^{3+}$ | β_{12} | $\beta_{12} = [\text{Mn}_2(\text{OH})_3^{3+}] / ([\text{Mn}^{2+}]^2 \cdot [\text{OH}^-])$ |
| 10 | $2 \text{Mn}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Mn}_2(\text{OH})_3^{3+}$ | β_{32} | $\beta_{32} = [\text{Mn}_2(\text{OH})_3^{3+}] / ([\text{Mn}^{2+}]^2 \cdot [\text{OH}^-]^3)$ |
| 11 | $\text{Mn}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{MnHPO}_4$ | $K(\text{MnHPO}_4)$ | $K(\text{MnHPO}_4) = [\text{MnHPO}_4] / ([\text{Mn}^{2+}] \cdot [\text{HPO}_4^{2-}])$ |
| 12 | $\text{Mn}(\text{OH})_2 \rightleftharpoons \text{Mn}^{2+} + 2 \text{OH}^-$ | $K_s(\text{Mn}(\text{OH})_2)$ | $K_s(\text{Mn}(\text{OH})_2) = [\text{Mn}^{2+}] \cdot [\text{OH}^-]^2$ |
| 13 | $\text{MnHPO}_4 \rightleftharpoons \text{Mn}^{2+} + \text{HPO}_4^{2-}$ | $K_s(\text{MnHPO}_4)$ | $K_s(\text{MnHPO}_4) = [\text{Mn}^{2+}] \cdot [\text{HPO}_4^{2-}]$ |
| 14 | $\text{Mn}_3(\text{PO}_4)_2 \rightleftharpoons 3 \text{Mn}^{2+} + 2 \text{PO}_4^{3-}$ | $K_s(\text{Mn}_3(\text{PO}_4)_2)$ | $K_s(\text{Mn}_3(\text{PO}_4)_2) = [\text{Mn}^{2+}]^3 \cdot [\text{PO}_4^{3-}]^2$ |
| 15 | $\text{Li}_3\text{PO}_4 \rightleftharpoons 3 \text{Li}^+ + \text{PO}_4^{3-}$ | $K_s(\text{Li}_3\text{PO}_4)$ | $K_s(\text{Li}_3\text{PO}_4) = [\text{Li}^+]^3 \cdot [\text{PO}_4^{3-}]$ |
| 16 | $\text{LiMnPO}_4 \rightleftharpoons \text{Li}^+ + \text{Mn}^{2+} + \text{PO}_4^{3-}$ | $K_s(\text{LiMnPO}_4)$ | $K_s(\text{LiMnPO}_4) = [\text{Li}^+] \cdot [\text{Mn}^{2+}] \cdot [\text{PO}_4^{3-}]$ |

Mass Balance Equations

| eq no. | equation |
|--------|--|
| 17 | $[\text{Mn}(\text{II})]_{\text{tot}}^i = [\text{Mn}^{2+}] + [\text{Mn}(\text{OH})^+] + [\text{Mn}(\text{OH})_2] + [\text{Mn}(\text{OH})_3^-] + [\text{Mn}(\text{OH})_4^{2-}] + 2[\text{Mn}_2(\text{OH})_3^{3+}] + 2[\text{Mn}_2(\text{OH})_3^{3+}] + [\text{MnHPO}_4]$ |
| 18 | $[\text{Phosphate}]_{\text{tot}}^i = [\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4] + [\text{MnHPO}_4]$ |
| 19 | $[\text{Mn}(\text{II})]_{\text{tot}} - [\text{Mn}(\text{II})]_{\text{tot}} = [\text{Phosphate}]_{\text{tot}}^i - [\text{Phosphate}]_{\text{tot}}$ |
| 20 | $[\text{Mn}(\text{II})]_{\text{tot}}^i - [\text{Mn}(\text{II})]_{\text{tot}} = 3/2 \cdot ([\text{Phosphate}]_{\text{tot}}^i - [\text{Phosphate}]_{\text{tot}})$ |

^a $[\text{Mn}(\text{II})]_{\text{tot}}^i$ and $[\text{Phosphate}]_{\text{tot}}^i$ designate the initial total concentrations of Mn(II) and phosphate before the precipitation of solid phases, respectively. $[\text{Mn}(\text{II})]_{\text{tot}}$ and $[\text{Phosphate}]_{\text{tot}}$ designate the total concentrations of Mn(II) and phosphate in equilibrium conditions, respectively.



Thermodynamic study of all species and equilibria

Inducing precipitation by changing pH (addition of LiOH)

Index of interesting reviews / books

- Useful search terms:
 - chimie douce, soft chemistry (included electrochemical reaction synthesis),
 - co-precipitation,
 - chemical bath deposition
- For example
 - 10.1039/JM9960601149 Preparation by a 'chimie douce' route and characterization of $(\text{LiNi}_z\text{Mn}_{1-z}\text{O}_2)$ ($0.5 \leq z \leq 1$) cathode materials; Daniel Caurant, Noël Baffler, Valérie Bianchi, Gilles Grégoire and Stéphane Bach, J. Mater. Chem. 1996 6 1149
 - 10.1021/cm030347b Delacourt et al.

Wet chemical synthesis

Hydro/solvo/ionothermal synthesis



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What is hydro/solvo/ionothermal synthesis?

- Precipitation reactions (following hydrolysis and condensation of metal ions), under elevated pressure and temperature in a pressure vessel
 - Dissolving \rightarrow reactants more soluble under hydrothermal conditions ($>RT$, >1 atm)
 - Recrystallization (recovery) \rightarrow direct crystallization from solutions when supersaturation reached
- Several variants
 - hydrothermal \rightarrow water as the solvent
 - solvothermal \rightarrow organic solvent
 - Ionothermal \rightarrow ionic liquid solvent
- Several keywords
 - Mineralizers / solvents
 - Surfactants



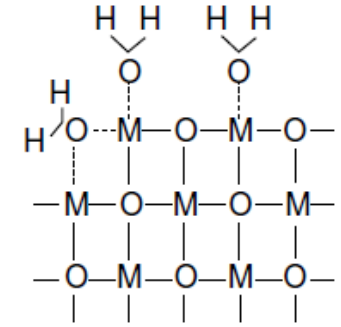
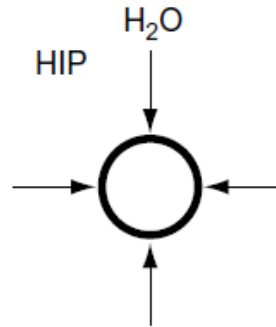
Mineralizers / solvents

- “inorganic or organic additives with high concentrations (e.g., 10 M) to control the pH of solution.” [1] e.g. HNO_3 , NaOH , KOH , HCOOH , etc.
- Aqueous or non-aqueous solvents can act as mineralizers as well
- Water can also act as:
 - P, T transfer medium
 - Adsorbate/adsorbent
 - Solvent
 - Reagent/reactant

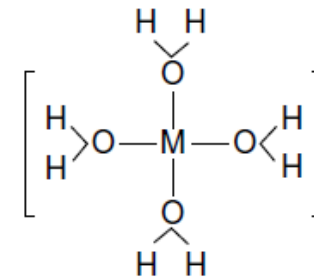
High-temperature–high-pressure solution/vapor

1. P, T medium
(mechanical energy transfer medium)

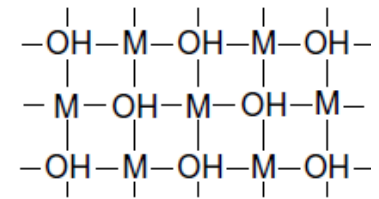
2. Adsorbate/Adsorbent
(reaction accelerator, catalyzer)



3. Solvent
(dissolution, precipitation)



4. Reagent/Reactant
(hydration, hydrolysis, etc.)



[2]

Surfactants

- Organics or inorganics in relatively low concentrations
- Alters hydrophobic/hydrophilic behavior of surfaces
- Controls the nucleation → size, shape, phase homogeneity and dispersibility of formed particles

3. Thermodynamics

- Determining the exact reaction equilibria in real systems is difficult due to presence of many different species
- Several thermodynamic models proposed to calculate solubility of species
- Revised Helgeson-Kirkham-Flowers (HKF) model provides equilibrium constant (K) calculations for:
 - Aqueous hydrothermal systems
 - Hundreds of inorganic compounds
 - Wide ranges of conditions (25-1000°C, 0.1-500 MPa)

Revised Helgeson-Kirkham-Flowers (HKF) model

$$\ln K_{T,\rho} = \ln K_{T_r,\rho_r} - \frac{\Delta H_{T_r,\rho_r}^0 + \beta(1 - \rho^*)^{\frac{2}{3}} + \alpha \Delta \omega_{T_r,\rho_r} T_r}{R} \times \left(\frac{1}{T} - \frac{1}{T_r} \right) - \frac{\Delta \omega_{T,\rho}}{RT} \left(\frac{1}{\varepsilon} - 1 \right) + \frac{\Delta \omega_{T_r,\rho_r}}{RT} \left(\frac{1}{\varepsilon_{T_r,\rho_r}} - 1 \right)$$

$$\beta = \lambda_1 \left(\Delta C_{P,T_r,\rho_r}^0 + \lambda_2 \Delta \omega_{T_r,\rho_r} \right) + \lambda_3$$

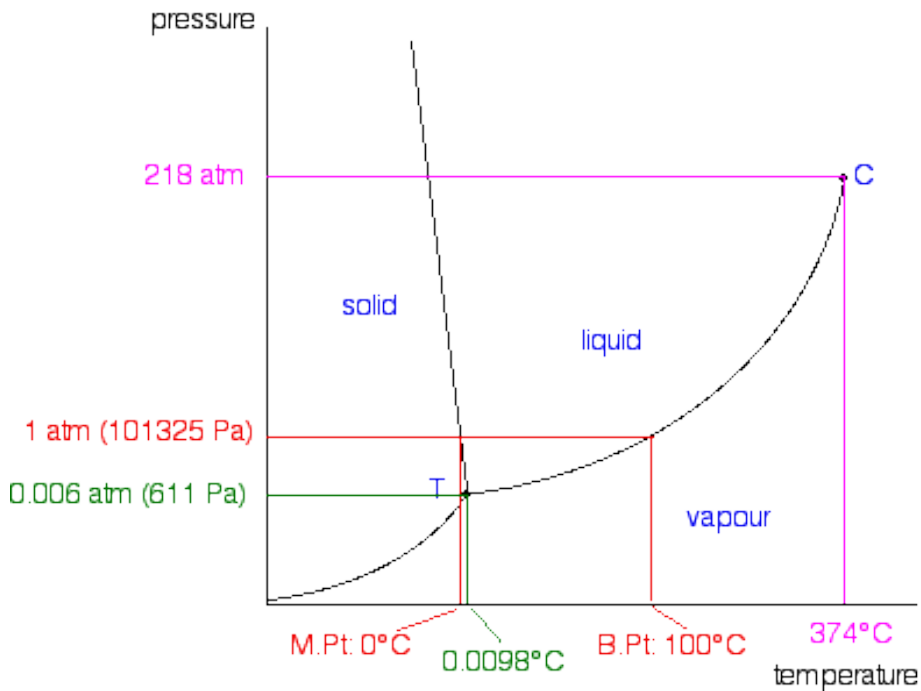
- K: equilibrium constant
- 'r' refers to the reference state (25°C, 0.5 MPa)
- α : $6.385 \times 10^{-5} \text{ K}^{-1}$
- ε : dielectric constant of water
- ω : parameter defined by reaction system
- β : reaction-dependent constant
- $\Delta C_{P,T_r,\rho_r}^0$: heat capacity
- $\lambda_1 = 97.66 \text{ K}$
- $\lambda_2 = 2 \times 10^{-4} \text{ K}^{-1}$
- $\lambda_3 = -3.317 \times 10^2 \text{ J/mol}$

$$\rho^* = \frac{\text{density of water in actual cond.}}{\text{density of water in reference cond.}}$$

Solubility of species and growth depend on solvent properties such as:

- Viscosity
- Density
- Dielectric constant

Supercritical conditions



<http://www.chemguide.co.uk/physical/phaseseqia/phasediags.html>

- Critical condition for water: 218 atm, 374°C
- Critical condition for ethanol: 60 atm, 241°C

- Dielectric constant of water is 78 at RT, 1 atm
- Dielectric constant of water reduces to 2-10 in the critical region
- Reduced dielectric constant of water reduces the solubility of polar solute species in the supercritical water → high supersaturation → easy nucleation and growth
- Reduced dielectric constant and reduced polarity of water allows solubility of organic solute species in the supercritical water → additives controlling the crystal nucleation and growth

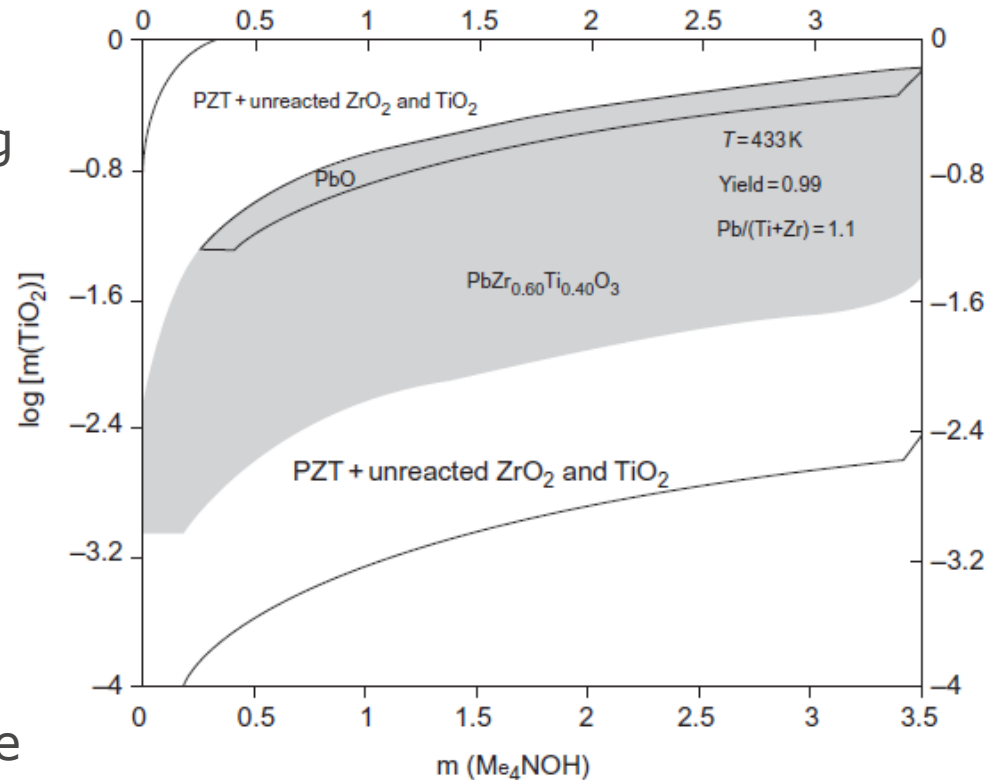
4. Kinetics

- Hydro/solvothermal synthesis is a crystallization process involving:
 - Reaching supersaturation $\left(\frac{\text{actual concentration}}{\text{saturation concentration}}\right)$ of species in the solution and crystal nucleation
 - Precipitation
 - Subsequent growth
- Particle size/morphology is controlled by
 - Supersaturation and
 - nucleation and growth rate; which can be controlled by:
 - Precursors
 - Reactant concentration
 - Additives
 - Filling of the vessel
 - Temperature
 - Time
 - pH
 - etc.

[1]

5. Intelligent engineering of materials

- Researchers giving up the Edisonian trial and errors approach for designing hydrothermal experiments, which is highly time consuming and very expensive
- Thermodynamic models are constructed instead
 - e.g. HKF model
- The main objective of the models is to calculate the optimum synthesis conditions for the formation of phase-pure materials with controlled size and shape to some extent
 - Stability and yield diagrams are used



Advantages and disadvantages of hydro/solvo/ionothermal synthesis

Advantages

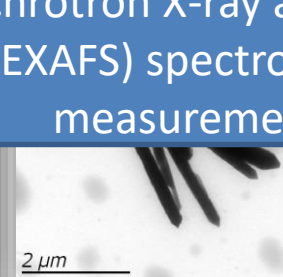
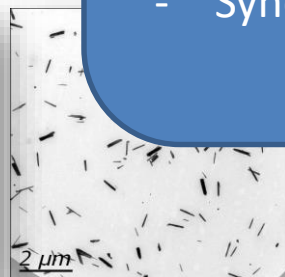
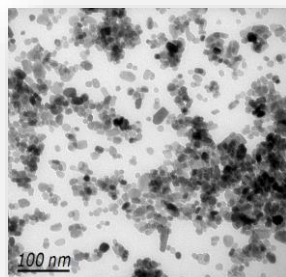
- Highly dispersed nanopowders
- Variety of particle morphologies (nanosheets, - rods, etc.)
- Strong control over particle size distribution,
- Simultaneous synthesis and crystallization at low temperatures (few 100°C)
- Many different chemistries (oxides, phosphates, polyanions, carbonates,...)
- Epitaxial shell growth possible

Challenges

- Upscaling
- Complex compositions as in multimetal oxides difficult to control → wrong phase formation
- Often still a black box

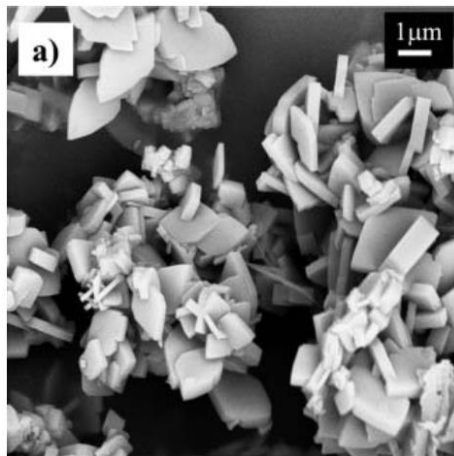
Tools/ characterization techniques that allow deeper insight into hydro/solvo/ionothermal mechanisms:

- in-situ UV/Vis
- in-situ FTIR/Raman
- HR-SEM/TEM
- Synchrotron X-ray absorption (EXAFS) spectroscopic measurements

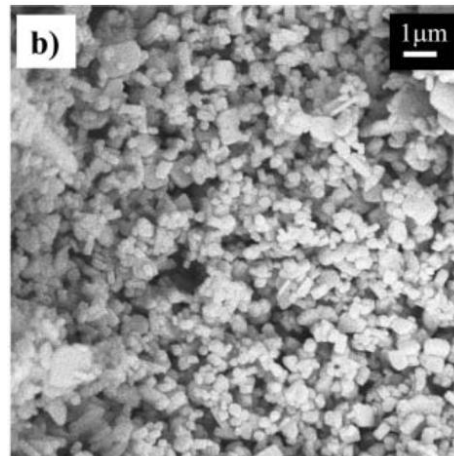


Hydrothermal synthesis of LIB materials in literature

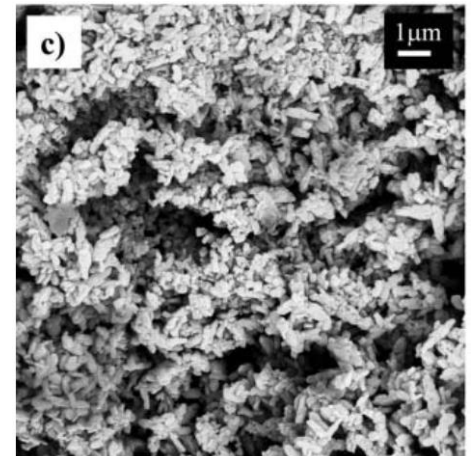
- Hydrothermal synthesis of single phase, nanocrystalline LiFePO_4 :
 - $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, H_3PO_4 , $\text{LiOH} \cdot \text{H}_2\text{O}$
 - 140-220°C, 0.5-24 h, 600-800°C subsequent sintering
- Crystallite size is controlled by controlling:
 - Precursor concentration
 - Lower $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ conc.: 1-5 micron sized platelets (figure a)
 - Higher $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ conc.: more nucleation sites, smaller particles (250 nm) (figure c)
 - Reaction temperature
 - Lower temperatures produces smaller particles (figure b)
 - Fe disorder at lower temperatures → detrimental for electrochemical perf.
 - A balance between temperature and concentration must be selected



0.25 M (Fe), 190°C



0.25 M (Fe), 140°C

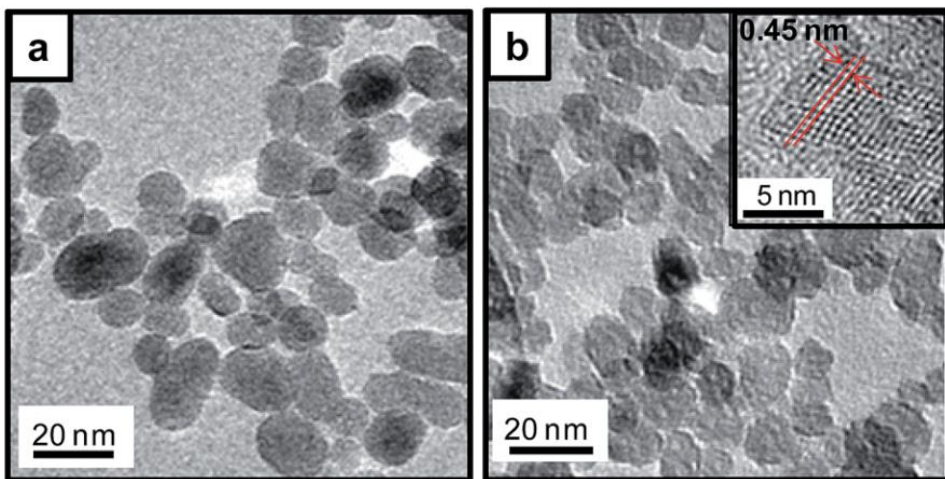
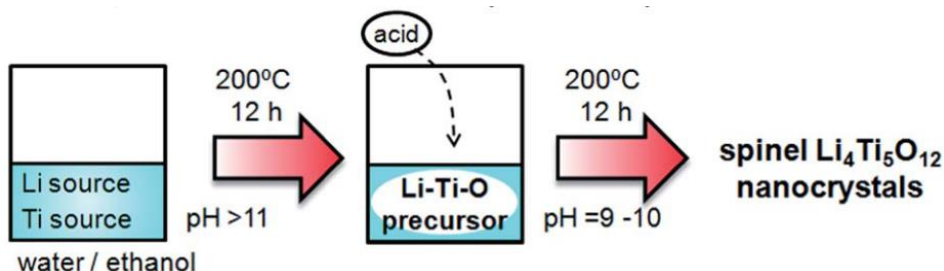
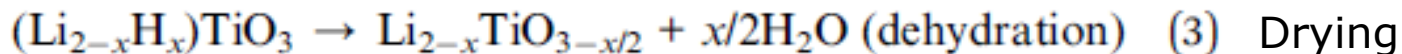
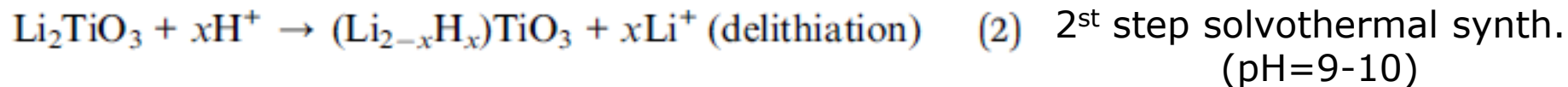
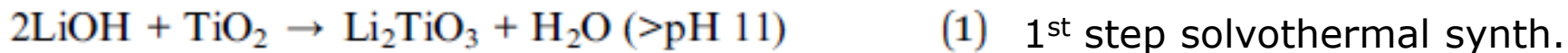


0.75 M (Fe), 190°C

Ellis, B., et al. *J. Mater. Chem.*,
2007. **17**(30): p. 3248.
Verónica Palomares and Teófilo
Rojo (2012), *Lithium Ion
Batteries - New
Developments*, Dr. Ilias
Belharouak (Ed.)

Solvothermal synthesis of LIB materials in literature

- Solvothermal, 2-step, pH controlled spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) nanocrystal synthesis in water-ethanol mixture, at 200°C
- Li_2TiO_3 impurity phase avoided by pH control
- LTO formation through delithiation and dehydration from the precursor:



After 1st step

After 2nd step

Ionothermal synthesis of LIB materials in literature

- Metal fluorosulfate systems, i.e. LiMSO_4F (M=Fe, Co, Ni, Mn)
 - e.g. LiFeSO_4F → good conductivity and low cost without nanosizing and carbon coating, while necessary for LiFePO_4 with lower conductivity
- Synthesis can be difficult due to high temperature decomposition and hygroscopic nature of sulfates → high T solid state synthesis and aq. hydro/solvothermal synthesis ruled out
- LiFeSO_4F by ionothermal synthesis:
 - 1. Dehydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ at 200°C , under vacuum
 - 2. Reaction of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and LiF in EMI-TFSI (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl imide) ionic liquid, in a PTFE liner bomb, at 300°C , for 5 h
 - EMI-TFSI provides high chemical/thermal stability, adequate solvating properties and negligible volatility

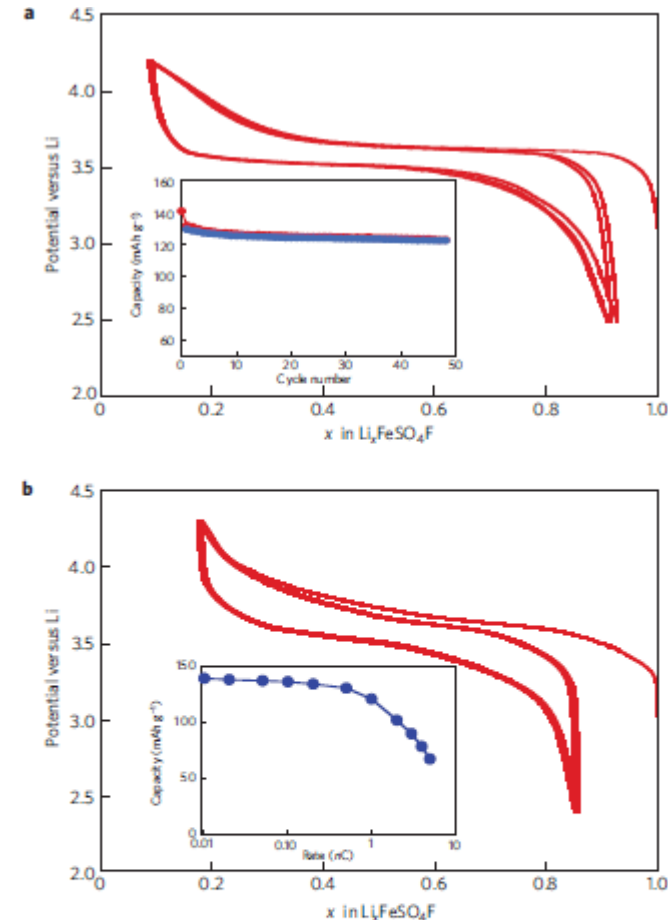


Figure 4 | Electrochemical characterizations of LiFeSO_4F powders. **a, b,** Charge/discharge galvanostatic curves for $\text{Li}/\text{LiFeSO}_4\text{F}$ cells cycled between 2.5 and 4.2 V at C/10 (1 Li in 10 h) (**a**) and C/2 (1 Li in 2 h) (**b**), highlighting the sustained reversible capacity of the electrode and the near 100% cycling capacity efficiency. Electrodes were made by ball-milling for 15 min and 30 min LiFeSO_4F (85%)/carbon (15%) mixtures for the cells in **a** and **b**, respectively. The capacity retention of such cells (red for charge and blue for discharge) together with their power rate (discharge capacity is plotted as a function of the rate nC) are shown as insets in **a** and **b**, respectively. The power rate was defined through the collection of signature curves²⁸ using a discharge cutoff potential of 2.5 V. Within such measurements, currents of 1.2 mA cm^{-2} were used for the 1 C rate.

Index of interesting reviews / books

- K. Byrappa and M. Yoshimura, Handbook of hydrothermal technology. 2013.
- Jianlin Li and Ji Wu. Synthesis of Nanoparticles via Solvothermal and Hydrothermal Methods, in Handbook of Nanoparticles. 2015
- Verónica Palomares and Teófilo Rojo (2012), Synthesis Processes for Li-Ion Battery Electrodes – From Solid State Reaction to Solvothermal Self-Assembly Methods, Lithium Ion Batteries - New Developments, Dr. Ilias Belharouak (Ed.)
- Hiromichi Hayashi and Yukiya Hakuta. Hydrothermal Synthesis of Metal Oxide Nanoparticles in Supercritical Water. Materials, 2010. 3(7): p. 3794-3817.
- Byrappa, K. and T. Adschiri, *Hydrothermal technology for nanotechnology*. Progress in Crystal Growth and Characterization of Materials, 2007. **53**(2): p. 117-166.
- Keywords: mineralizer, solvent, solubility, crystallization, supercritical, autoclave, liner, viscosity, dielectric constant, density, high temperature-pressure, ...

Wet chemical synthesis

Thermal decomposition



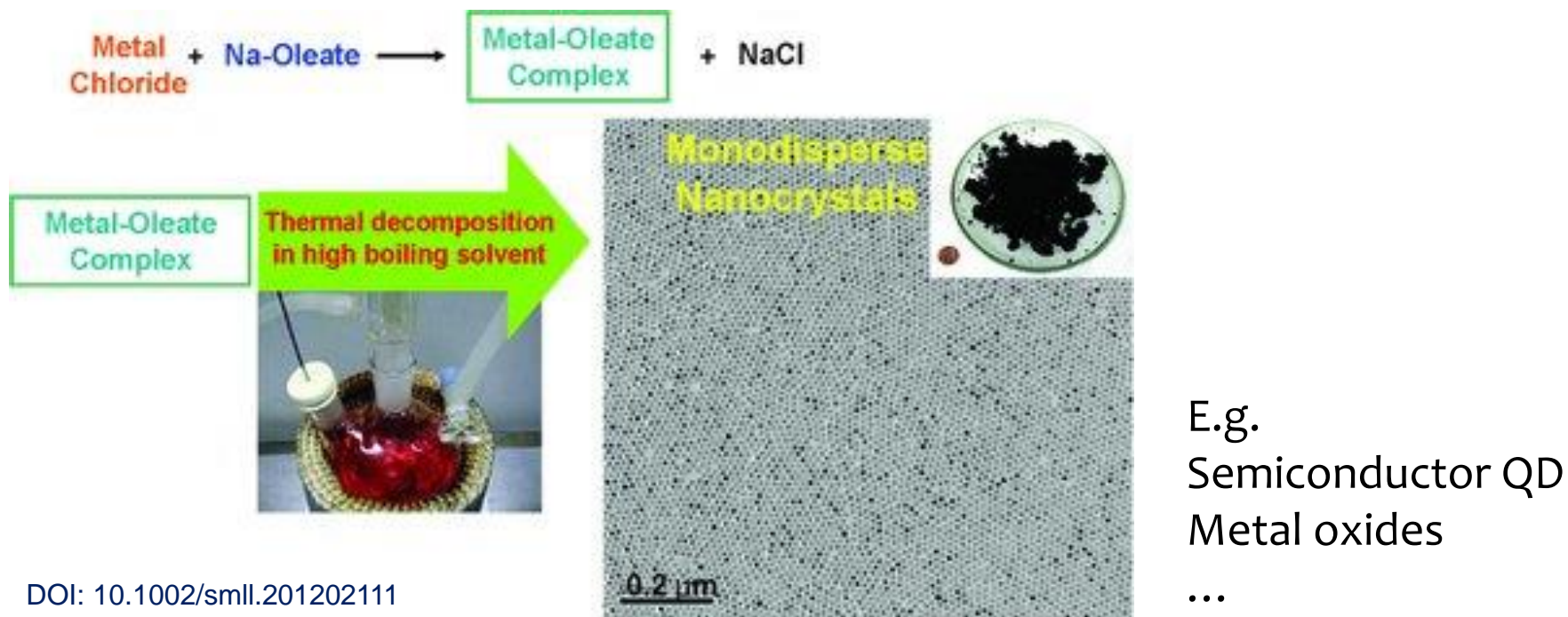
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KNOWLEDGE IN ACTION

Thermal decomposition synthesis – often QDs

Thermal decomposition

of precursor in high boiling apolar solvent and in the presence of surfactant molecules



DOI: 10.1002/smll.201202111

Thermal Decomposition

- Non-aqueous sol gel chemistry
- Chemical transformation
 - Of precursors dissolved in organic solvent
 - Into metal oxide network
 - Under exclusion of water
 - Surfactant assisted
- Advantage over conventional sol-gel chemistries
 - Greater control over physical dimensions of produced product

Thermal Decomposition

- Creation of hydrophilic MO_x particles in hydrophobic environment
 - Use of precursors soluble in organic solvents
 - Yet yielding MO_x particles are not organic compatible
 - Addition of surfactants
 - Surfactants cap growing particles resulting in control of particle dimensions
 - Allowing low incidence of agglomeration

Thermal Decomposition

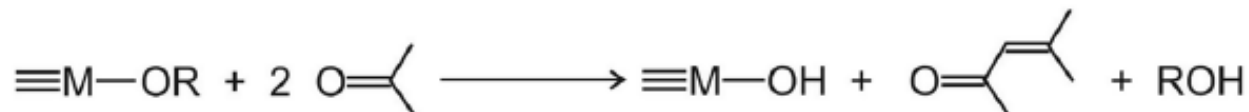
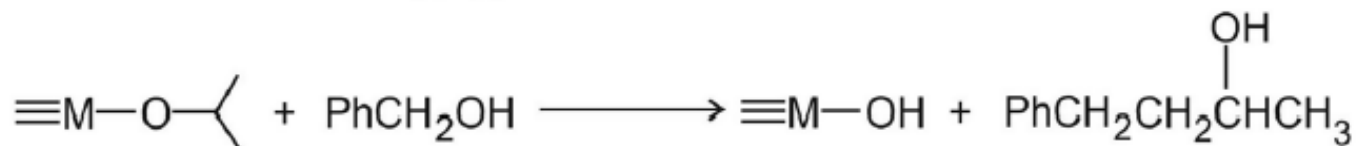
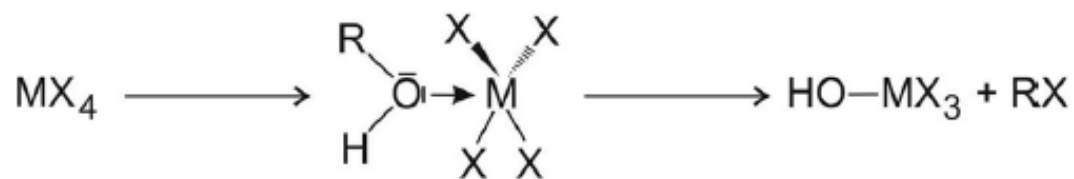
- Requires high boiling solvent to create crystalline MO_x
- Oxygen moiety
- Reaction to release O and form MO_x

- Examples
 - Benzyl alcohol
 - Tert-butyl alcohol
 - Propyl Ethers
 - Acetophenone
 - Carboxylic acids
 - Benzylamine

Chemical reactions

Initiation: 3 types of reaction

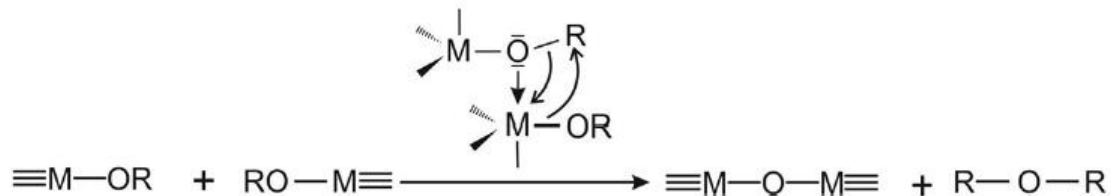
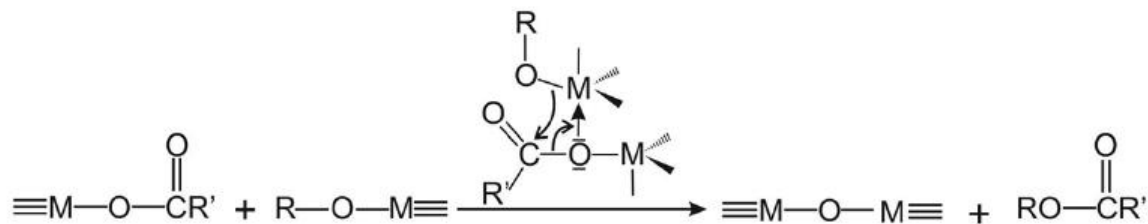
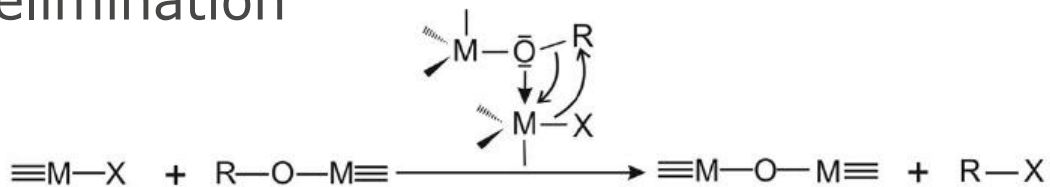
1. metal halides and alcohols
2. alkoxide + alcohol
3. aldol condensation



Chemical reactions

After initial reaction

- Oxo bridges under aprotic conditions
 1. alkyl halide elimination
 2. ester elimination
 3. ether elimination



Thermal decomposition synthesis – overall mechanism

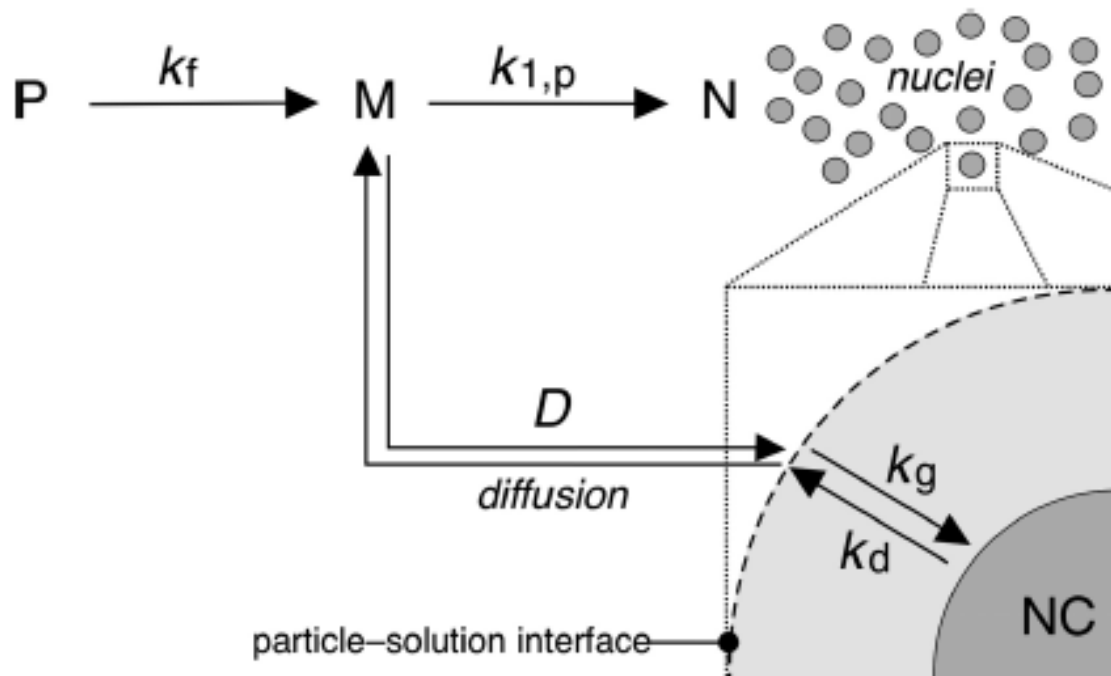


Figure 3. Schematic outlining the mechanism of NC nucleation and growth. First, precursors (P) disassociate into monomers (M), followed by the formation of nuclei (N). The nascent nuclei grow as monomer diffuses to the particle-solution interface and then reacts, becoming incorporated into the crystal lattice.

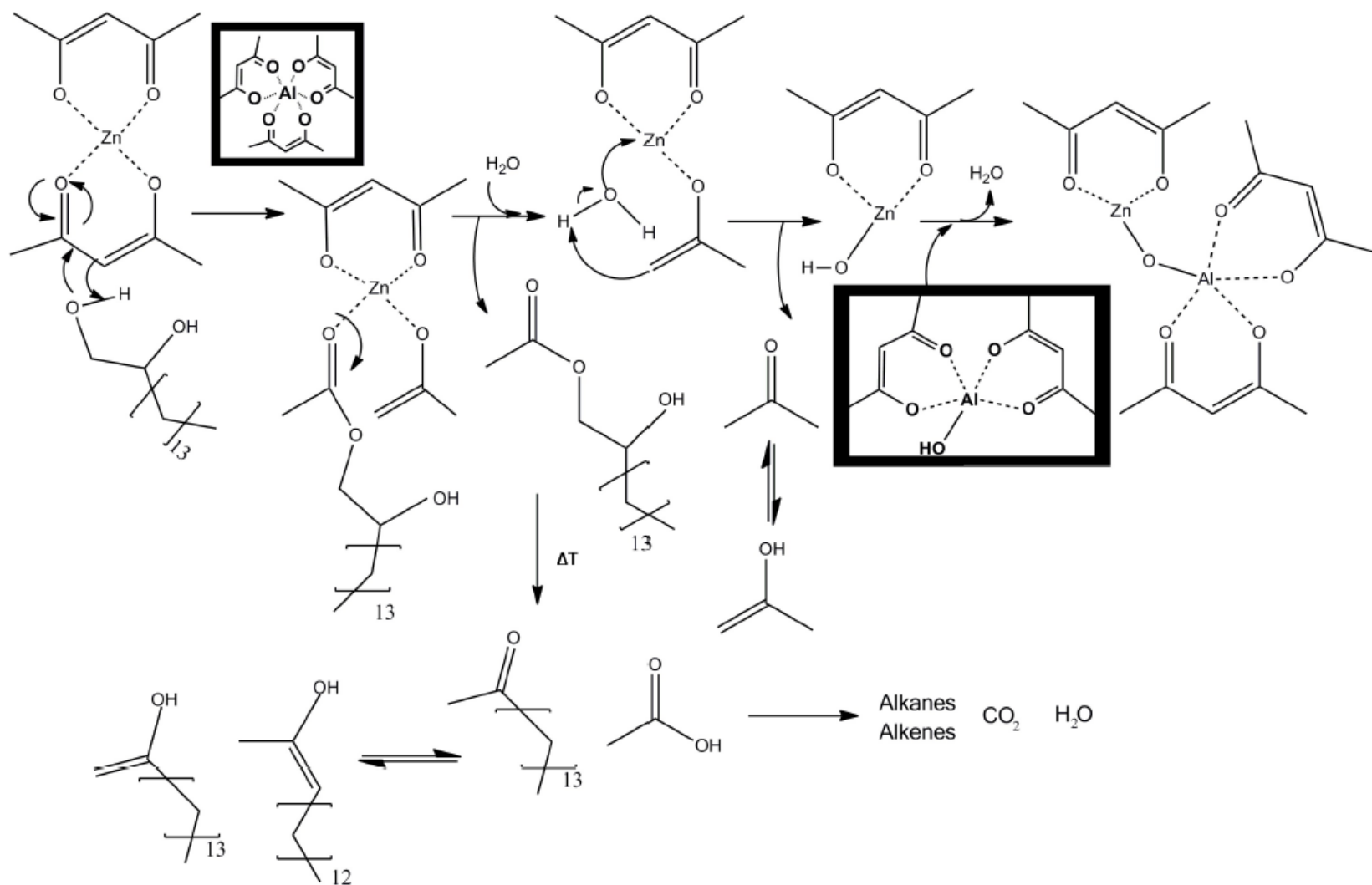


Figure 4.3: Synthesis mechanism of the heating-up thermal decomposition mechanism of ZnO:Al nanoparticles.

Advantages and disadvantages of thermal decomposition synthesis

Advantages

- Excellent control over particle dimensions
- Allows for building of complex structures
- Possible due to prevention of agglomeration
- Low temperature

Disadvantages

- Excessive use of solvent
- Large quantity of initiator reagents
- Limited yield per batch
- Toxicity of reactions compared to aqueous routes

Examples of LIB materials thermal decomposition synthesis from literature

- [1] S. Jiang et al. / Electrochimica Acta 191 (2016) 364–374
- [2] D. Wei et al. / Journal of Alloys and Compounds 714 (2017) 13-19
- [3] J. Zhang et al. Colloids and Surfaces A 529 (2017) 677–685
- [4] Y. Zhang et al. / Journal of Power Sources 292 (2015) 58-65
- [5] Y. Xuanye et al. / Solid State Ionics 289 (2016) 159–167

Review on heating up synthesis

J. van Embden, Chem. Mater., 2015, 27, 2246

Wet chemical synthesis

(auto)combustion synthesis



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Comparison to sol-gel and related routes

Precursor

Chemical reaction

oxide / metal / phosphate

Why high temperature (600° C)?

Kinetics

Free energy
change

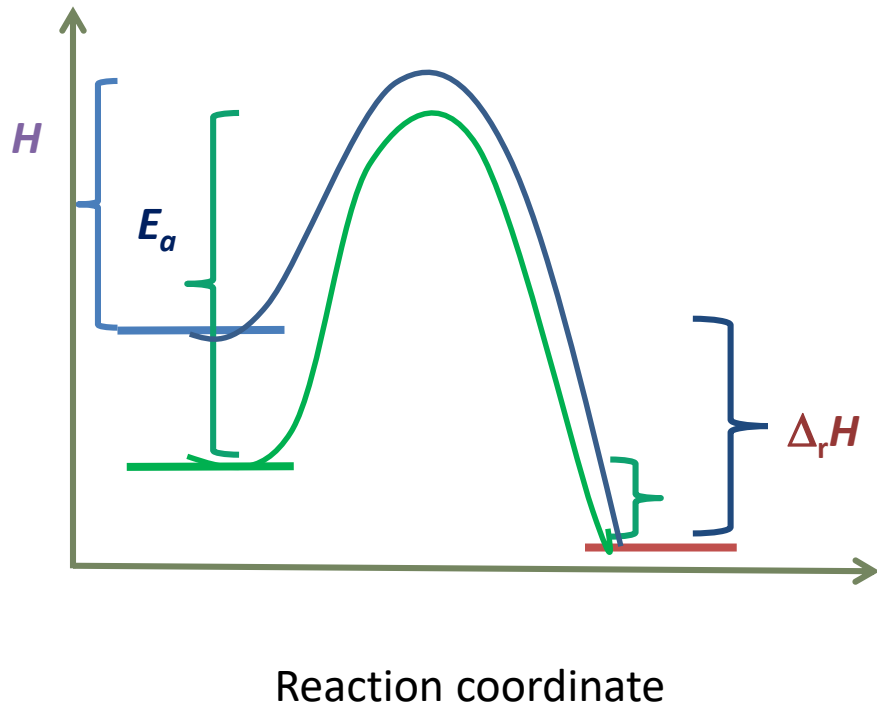
Activation
controlled

Diffusion
controlled

Reaction
enthalpy

Reaction
entropy

(Auto)combustion synthesis



High activation energy

→ Need $E_a \downarrow$ & $\Delta_r H \uparrow$

→ Use starting products with higher H

Autocombustion reactions:

- Self generation of heat, available for crystallization of the oxide
- Lower external temperature required

(Auto)combustion synthesis: in practice

Self-sustainable reaction leading to internal heating
→ oxide formation

Requirements:

- Heat to initiate the reaction
- Fuel with high ΔH_c
- Oxidizer: O_2 or added NO_3^-
- Optimal oxidizer/fuel ratio !

Possible fuels:

- Glycine
- Citric acid
- ...

i.e. Often ligands available for solubilizing metal ions in the first stage of the synthesis

$$\phi_e = \frac{\sum(\text{Coefficient of oxidizing elements in specific formula})(\text{Valency})}{(-1)\sum(\text{Coefficient of reducing elements in specific formula})(\text{Valency})}$$

Advantages and disadvantages of (auto)combustion synthesis

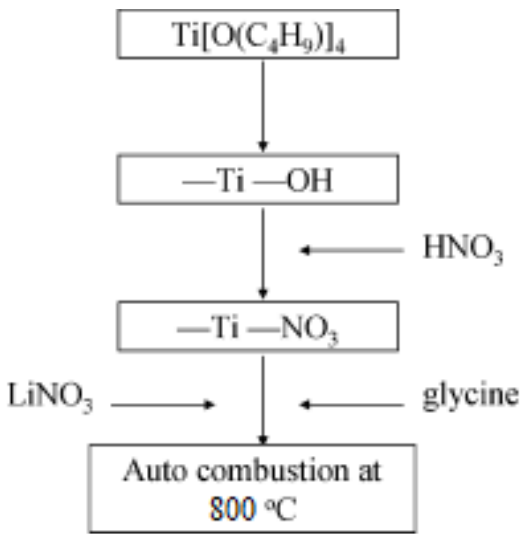
Advantages

- Low external temperature supplied, self ignition forms oxides
- Very short reaction times
- Cost effective
- Homogeneous products

Challenges

- Empirical optimization of optimal fuel/oxidizer ratio
- Explosive mixture
- Complex mechanism
- Product properties depend on processing conditions
 - Gas flow rate
 - Atmosphere

Combustion synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$: ex. 2



NO_3^- as oxidizer
Glycine as fuel

Combustion temperature of **800 °C**, seconds

High cycling stability:
>95% capacity retention after 100 cycles

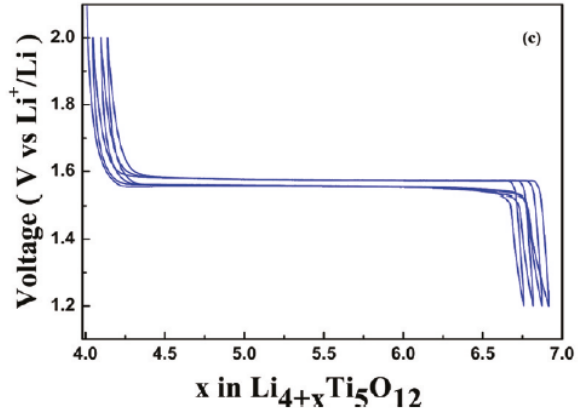


Figure 5. Structure of (a) spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (b) ordered rocksalt-phase $\text{Li}_7\text{Ti}_5\text{O}_{12}$; (c) voltage-composition curves showing the electrochemical transformation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – $\text{Li}_7\text{Ti}_5\text{O}_{12}$ during galvanostatic charge–discharge cycles at C/2 rate at 30 °C.

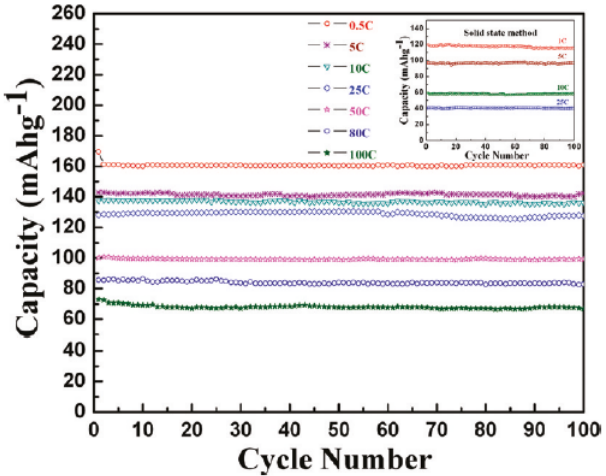
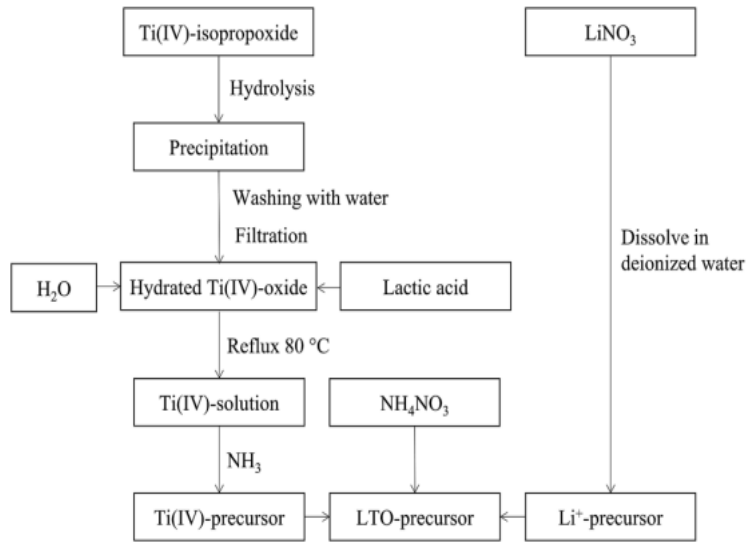


Figure 7. Capacity versus cycle number plot for nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized by the combustion method at different discharge rates. Inset shows capacity versus cycle number for bulk $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

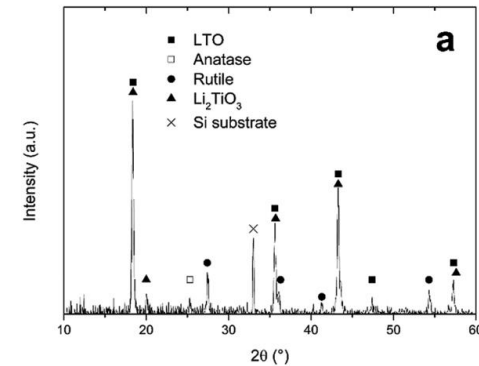
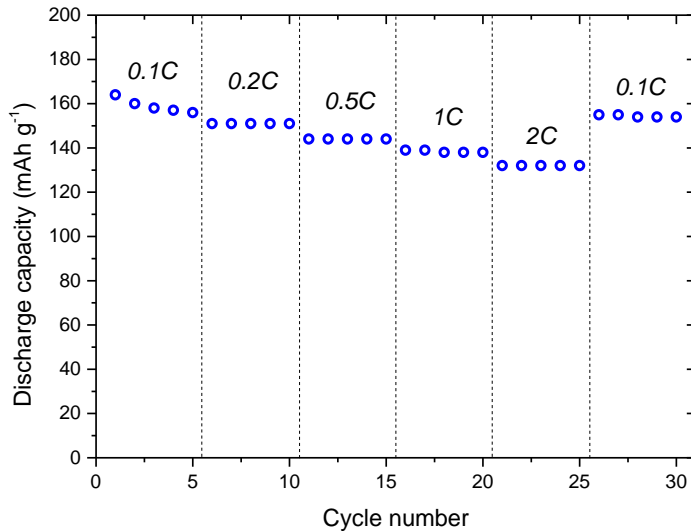
Combustion synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$: ex. 3



NO_3^- as oxidizer
Lactic acid as fuel

Combustion temperature of
300 °C, no higher

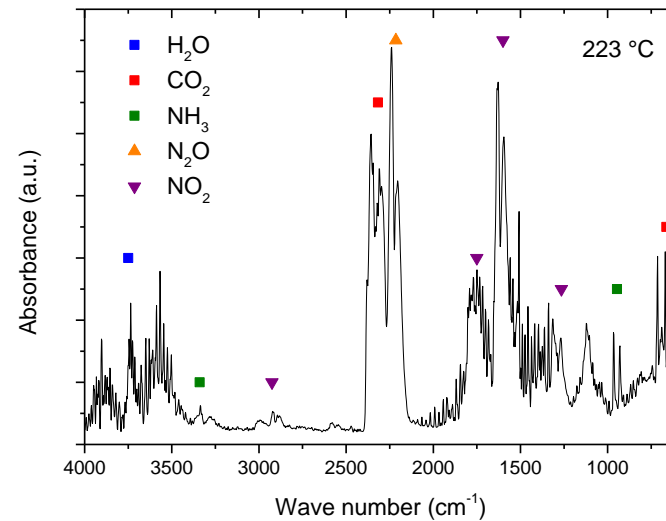
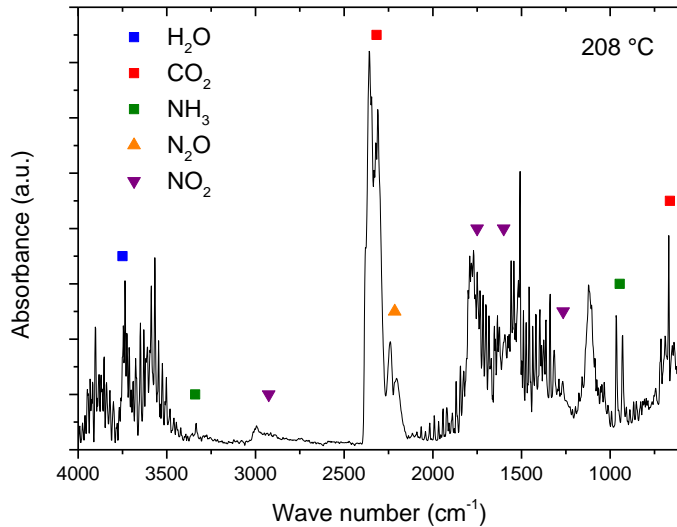
Lithium rich and poor
impurities



Capacity of 164 mAh/g
(175 mAh/g theoretically) and
retention of 94.9% after 100 cycles

Combustion synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$: ex. 3

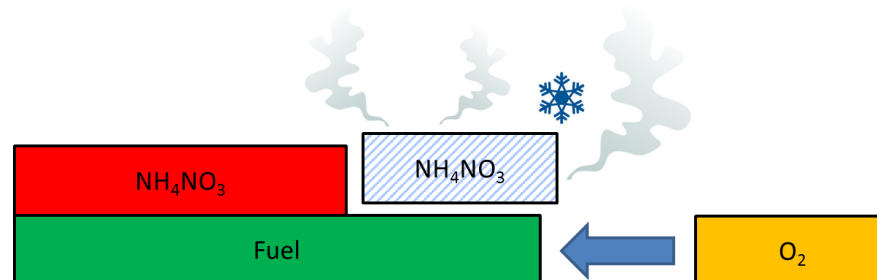
Dual role of NH_4NO_3



Evolved
gas
analysis by
TGA-FTIR

Proposed mechanism

- Melting/evaporating/endothermic degradation of NH_4NO_3 absorbs heat
Prevents heat build up
→ prevents auto combustion until excess NH_4NO_3 is degraded
- O_2 from atmosphere around the sample, takes part in the reaction



Core-shell nanoparticles

Using chemical solution based routes



Why use core-shell materials in LIBs?

- To prevent electrode reactions with the electrolyte and dissolution of active substances. e.g. Mn in L(N)MO
- To act as HF scavenger and react with the released HF from the electrolyte prior to the active core. e.g. Al_2O_3 , ZrO_2 , etc.
- To bring new physical/chemical properties. e.g. increased electronic/ionic conductivity
- Increased rate performance, reversible capacity & cycling stability



Solution-based core-shell synthesis methods

1. Heterogeneous nucleation of the solid shell phase
2. Hydro/solvothermal synthesis
3. Assembly by electrostatic interactions (heterocoagulation)
4. Thermal decomposition synthesis
5. Spraycoating

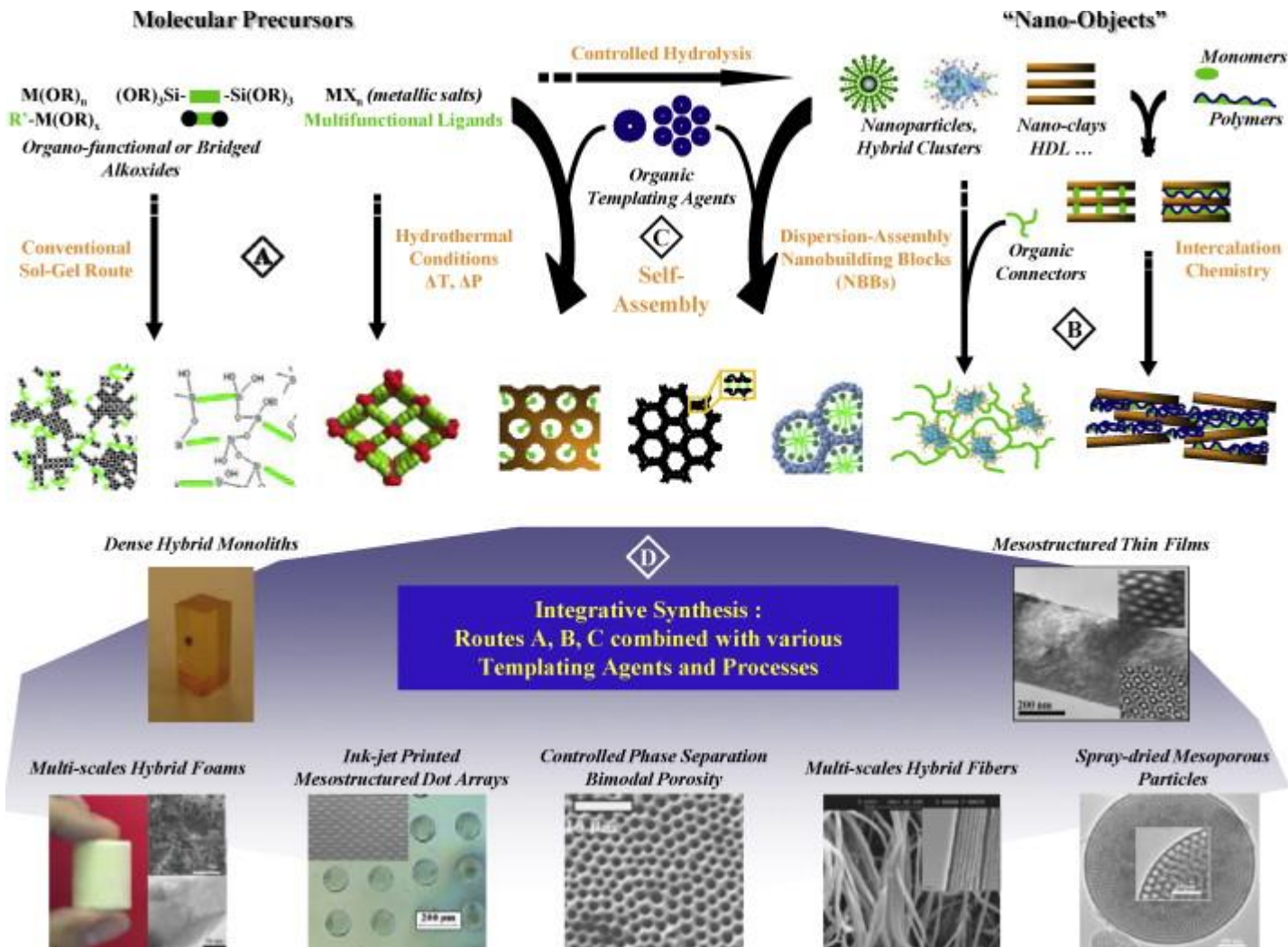
Hierarchically structured nanoparticles

Using chemical solution based routes



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Summary

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Chemical solution based synthesis

basic principles

- **Aqueous solution-gel and (auto)combustion synthesis:**
 - Intimate mixing of metal ions in a precursor phase (solution)
 - Burning the precursor components
 - Reaction of metal ions with oxygen (/phosphate) to form oxide
 - **(co-)precipitation, hydro/solvo/ionothermal, micellar reactions**
 - Based on precipitation reactions
 - Hydroxide – oxide / phosphates are formed from ions in solution
 - Solubility = key
 - **(non-)aqueous sol-gel, thermal decomposition, solvolysis reaction**
 - Reaction involving solvent leads to formation of oxide
 - In theory, no external oxygen supply required
- ! Generalization => exceptions

Future

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Do we still need research on **synthesis**?

- Inorganic materials link structure with a specific function (metal oxides for batteries, perovskites for solar cells, metal clusters for catalysis,...)
- Correlation of materials properties with composition, atomic structure, crystallinity and defects → databases
- Recently:
 - particle size and morphology are taken into account as well
 - E.g hierarchical materials
 - Also: in silico strategies for materials design take over from quests of materials discovery

Pinchpoint: when attempting to synthesize these rapidly designed targets

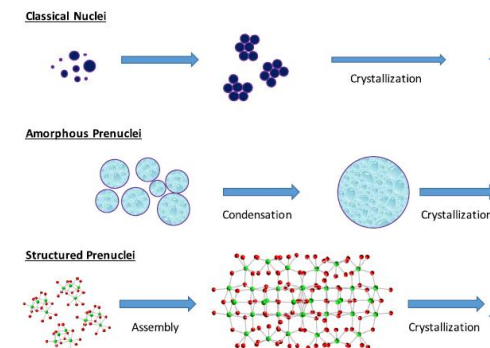
- Understanding how and when ion correlations develop is missing

→ mechanistic framework is needed for synthesis of inorganic extended solids

→ requires to codify synthesis of inorganic extended solids

- Understanding
 - Cataloging
 - Covering pre-nucleation – nucleation – mesoscale assembly
- } Of principal reaction types

→ synthesis-by-design



Thank you for this invitation

Thank you for your attention

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