Chemical solution based methods for nanoparticle and core-shell synthesis
Inorganic and Physical Chemistry
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The IMO-IPC lab
Hasselt University and IMO-IMOMEC

IMEC
1900 people (500 guests)

IMO-IMOMEC
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
The IMO-IPC lab
Inorganic & Physical Chemistry

Chemical synthesis of metal oxides

Ferro-electrics

High – k dielectrics

Multi-ferroics

Battery electrode oxides

(semi)-conducting oxides

ZnO, TiO₂ (semi-conducting oxides)

High-k dielectrics

Multi-ferroics

Battery electrode oxides

ZnO, TiO₂ (semi-conducting oxides)
Examples of LIB electrode materials

- **LiFePO$_4$, LiMnPO$_4$, LiFe$_{0.3}$Mn$_{0.7}$PO$_4$**
  - Aqueous solution-gel (+ ball milling), precipitation and thermal decomposition synthesis methods

- **LiMn$_2$O$_4$**
  - Solution-gel synthesis

- **TiO$_2$ coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$**
  - Heterogeneous nucleation on LNMO

- **(Doped) Li$_4$Ti$_5$O$_{12}$**
  - Combustion synthesis

- **LiNi$_{0.5}$Mn$_{0.3-y}$X$_y$Co$_{0.2}$O$_2$**
  - Aqueous solution-gel synthesis

And of course
Solid inorganic electrolytes
Goal of the lecture

To provide a catalog of solution-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
Synthesis

Top down approach

- Solid state reaction
- Milling

Pyrolysis of vaporized liquid or gas

Formation in SOLUTION

Bottom up approach
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

More complex
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

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

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
What is sol-gel? Thermodynamics & kinetics

For example: first step = hydrolysis TEOS

\[
Q_0^i + H_2O \xrightleftharpoons[k_h^{i-1}]{k_h^i} Q_0^{i+1} + EtOH
\]

- 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

Almost no influence of pH (acid addition)
What can be done with sol-gel?

Possibilities of further evolvement

Michel Prassas google + sol-gel science and technology community
What is strictly not sol-gel? Related routes

**MOD (metalorganic decomposition) route**
- Metal organic compounds e.g. acac
- + organic solvent
- No hydrolysis nor condensation
- Solution of metalorganic in solvent

**Aqueous solution-gel route**
- Metal chelates in water
- \( T \uparrow \) evaporation of \( \text{H}_2\text{O} \)
- Metal carboxylates \( \text{NH}_4^+ \) bridges

**Organic polymerisation route**
- Citrato-metalion complexes in ethyleneglycol (Pechini)
- \( T \uparrow \) polyesterification
- \( \text{M}^{n+} \) complexes in polyester network

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 Mostly oxides

 Pyrolysis

 Calcination

 Annealing
What is strictly not sol-gel? Related routes

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

Dissolution / hydrolysis & condensation

Sol or solution = liquid precursor

Solvent evaporation / chemical reaction

Gel (covalent, hydrogen, VdW bonds)

Heat treat → decompose organics

Amorphous oxide (with impurities)

Heat treat → crystallize / tune vacancies

Crystalline oxide

What comes after the precursor?

Thermal treatment

Pyrolysis
Calcination
Annealing
mostly oxides

Focus:
Aqueous citrate based solution and gel chemistry

Aqueous solution-gel route

$\text{Metal chelates in water}$

$\xrightarrow{T \uparrow}$ evaporation of $\text{H}_2\text{O}$

$\text{Metal carboxylates } \text{NH}_4^+ \text{ bridges}$
Focus: Water based solution-gel chemistry

Gel
Metal citrate complexes
Cross linked via $\text{NH}_4^+$- COO$^-$ interactions
Amorphous $\text{NH}_4^+$ citrate

Gel Structure:

$\text{NH}_4^+$
$\text{M}$
$\text{NH}_4^+$

Aqueous solution-based synthesis of nanostructured metal oxides
Focus: Water based solution-gel chemistry

Water based M-precursors
Can be ‘easily’ mixed

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)

#### 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

#### Aqueous routes

- Limited risks (environment and safety)
- Inexpensive solvent (water) and starting products
- Synthesis and storage in ambient conditions
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$_2$CO$_3$, 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])

H. Liu doi:10.1007/s10008-004-0521-1
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

What is going on here?
Lots of questions unanswered

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

Not sol-gel → Pechini
Example: precursor chemistry – phase formation
LMO from aq CSD

- Mn$^{3+}$ precursor $\rightarrow$ 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

Solvent evaporation / chemical reaction

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

Heat treat \( \Rightarrow \) decompose organics

Amorphous oxide (with impurities)

Heat treat \( \Rightarrow \) crystallize / tune vacancies

Crystalline oxide

R.W. Schwartz, [https://doi.org/10.1016/j.crci.2004.01.007](https://doi.org/10.1016/j.crci.2004.01.007)
Index of interesting reviews / books

- 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
What is a (co)precipitation reaction?

- **Precipitation**
  - Reverse of a dissolution reaction
  - Exceedance of the solubility ($K_{sp}$) = supersaturation (thermodynamics)
    \[
    MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2 \text{F}^-(aq)
    \]
    \[
    K_{sp} = [Mg^{2+}][F^-]^2
    \]

- **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


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
- $d_{10}: 77 \text{ nm}$
- $d_{50}: 145 \text{ nm}$
- $d_{90}: 270 \text{ nm}$
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 0.5Li$_2$MnO$_3$·0.5LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ 1D porous micro- and nanostructured bars.

One-Step Low-Temperature Route for the Preparation of Electrochemically Active LiMnPO\textsubscript{4} Powders

Mass Action Law Equations

<table>
<thead>
<tr>
<th>eq no.</th>
<th>equilibrium reactions</th>
<th>symbol for constant</th>
<th>equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H\textsubscript{2}O $\rightleftharpoons$ H\textsuperscript{+} + OH\textsuperscript{-}</td>
<td>$K_w$</td>
<td>$K_w = [H^+][OH^-]$</td>
</tr>
<tr>
<td>2</td>
<td>HPO\textsubscript{4}\textsuperscript{2-} $\rightleftharpoons$ PO\textsubscript{4}\textsuperscript{3-} + H\textsuperscript{+}</td>
<td>$K_{h1}$</td>
<td>$K_{h1} = [PO_4^{3-}][H^+]/[HPO_4^{2-}]$</td>
</tr>
<tr>
<td>3</td>
<td>H\textsubscript{2}PO\textsubscript{4} $\rightleftharpoons$ HPO\textsubscript{4}\textsuperscript{2-} + H\textsuperscript{+}</td>
<td>$K_{h2}$</td>
<td>$K_{h2} = [HPO_4^{2-}][H^+]/[H_2PO_4]$</td>
</tr>
<tr>
<td>4</td>
<td>H\textsubscript{2}PO\textsubscript{4} $\rightleftharpoons$ HPO\textsubscript{4}\textsuperscript{2-} + H\textsuperscript{+}</td>
<td>$K_{h3}$</td>
<td>$K_{h3} = [HPO_4^{2-}][H^+]/[H_2PO_4]$</td>
</tr>
<tr>
<td>5</td>
<td>Mn\textsuperscript{2+} + OH\textsuperscript{-} $\rightleftharpoons$ Mn(OH)\textsuperscript{+}</td>
<td>$\beta_1$</td>
<td>$\beta_1 = [Mn(OH)]/[Mn^{2+}][OH^-]$</td>
</tr>
<tr>
<td>6</td>
<td>Mn\textsuperscript{2+} + 2 OH\textsuperscript{-} $\rightleftharpoons$ Mn(OH)\textsubscript{2}</td>
<td>$\beta_2$</td>
<td>$\beta_2 = [Mn(OH)\textsubscript{2}]/[Mn^{2+}][2OH^-]$</td>
</tr>
<tr>
<td>7</td>
<td>Mn\textsuperscript{2+} + 3 OH\textsuperscript{-} $\rightleftharpoons$ Mn(OH)\textsubscript{3}</td>
<td>$\beta_3$</td>
<td>$\beta_3 = [Mn(OH)\textsubscript{3}]/[Mn^{2+}][3OH^-]$</td>
</tr>
<tr>
<td>8</td>
<td>Mn\textsuperscript{2+} + 4 OH\textsuperscript{-} $\rightleftharpoons$ Mn(OH)\textsubscript{4}</td>
<td>$\beta_4$</td>
<td>$\beta_4 = [Mn(OH)\textsubscript{4}]/[Mn^{2+}][4OH^-]$</td>
</tr>
<tr>
<td>9</td>
<td>2 Mn\textsuperscript{2+} + OH\textsuperscript{-} $\rightleftharpoons$ Mn\textsubscript{2}O\textsubscript{3}\textsuperscript{+}</td>
<td>$\beta_{12}$</td>
<td>$\beta_{12} = [Mn_2O_3^+]/[2Mn^{2+}][OH^-]$</td>
</tr>
<tr>
<td>10</td>
<td>2 Mn\textsuperscript{2+} + 3 OH\textsuperscript{-} $\rightleftharpoons$ Mn\textsubscript{2}O\textsubscript{4}</td>
<td>$\beta_{32}$</td>
<td>$\beta_{32} = [Mn_2O_4]/[2Mn^{2+}][3OH^-]$</td>
</tr>
<tr>
<td>11</td>
<td>Mn\textsuperscript{2+} + HPO\textsubscript{4}\textsuperscript{2-} $\rightleftharpoons$ MnHPO\textsubscript{4}</td>
<td>$K_{MN(HPO_4)}$</td>
<td>$K_{MN(HPO_4)} = [MnHPO_4]/[Mn^{2+}][HPO_4^{2-}]$</td>
</tr>
<tr>
<td>12</td>
<td>Mn(OH)\textsubscript{2} $\rightleftharpoons$ Mn\textsuperscript{2+} + 2 OH\textsuperscript{-}</td>
<td>$K_{(Mn(OH)\textsubscript{2})}$</td>
<td>$K_{(Mn(OH)\textsubscript{2})} = [Mn^{2+}][2OH^-]/[Mn(OH)\textsubscript{2}]$</td>
</tr>
<tr>
<td>13</td>
<td>MnHPO\textsubscript{4} $\rightleftharpoons$ Mn\textsuperscript{2+} + HPO\textsubscript{4}\textsuperscript{2-}</td>
<td>$K_{(MnHPO_4)}$</td>
<td>$K_{(MnHPO_4)} = [Mn^{2+}][HPO_4^{2-}]/[MnHPO_4]$</td>
</tr>
<tr>
<td>14</td>
<td>Mn\textsubscript{2}O\textsubscript{4} $\rightleftharpoons$ 3 Mn\textsuperscript{2+} + 2 PO\textsubscript{4}\textsuperscript{3-}</td>
<td>$K_{(Mn_2O_4)}$</td>
<td>$K_{(Mn_2O_4)} = [Mn_2O_4]/[3Mn^{2+}][2PO_4^{3-}]$</td>
</tr>
<tr>
<td>15</td>
<td>Li\textsuperscript{+} + PO\textsubscript{4}\textsuperscript{3-} $\rightleftharpoons$ Li\textsuperscript{+} + PO\textsubscript{4}\textsuperscript{3-}</td>
<td>$K_{(LiPO_4)}$</td>
<td>$K_{(LiPO_4)} = [Li^{+}][PO_4^{3-}]/[Li^{+}][PO_4^{3-}]$</td>
</tr>
<tr>
<td>16</td>
<td>Li$_2$MnPO\textsubscript{4} $\rightleftharpoons$ Li\textsuperscript{+} + Mn\textsuperscript{2+} + PO\textsubscript{4}\textsuperscript{3-}</td>
<td>$K_{(Li_2MnPO_4)}$</td>
<td>$K_{(Li_2MnPO_4)} = [Li^{+}][Mn^{2+}][PO_4^{3-}]/[Li_2MnPO_4]$</td>
</tr>
</tbody>
</table>

Mass Balance Equations

<table>
<thead>
<tr>
<th>eq no.</th>
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</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>[Mn(II)]\textsubscript{tot} = [Mn\textsuperscript{2+}] + [Mn(OH)\textsuperscript{+}] + [Mn(OH)\textsubscript{2}] + [Mn(OH)\textsubscript{3}] + [Mn(OH)\textsubscript{4}] + 2 [Mn\textsubscript{2}O\textsubscript{3}\textsuperscript{+}] + 2 [Mn\textsubscript{2}O\textsubscript{4}] + [MnHPO\textsubscript{4}]</td>
</tr>
<tr>
<td>18</td>
<td>[Phosphate]\textsubscript{tot} = [PO\textsubscript{4}\textsuperscript{3-}] + [HPO\textsubscript{4}\textsuperscript{2-}] + [H_2PO\textsubscript{4}] + [HPO\textsubscript{4}] + [H_3PO\textsubscript{4}] + [MnHPO\textsubscript{4}]</td>
</tr>
<tr>
<td>19</td>
<td>[Mn(II)]\textsubscript{tot} - [Mn(II)]\textsubscript{init} = [Phosphate]\textsubscript{tot} - [Phosphate]\textsubscript{init}</td>
</tr>
<tr>
<td>20</td>
<td>[Mn(II)]\textsubscript{tot} - [Mn(II)]\textsubscript{init} = 3/2 ([Phosphate]\textsubscript{tot} - [Phosphate]\textsubscript{init})</td>
</tr>
</tbody>
</table>

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 (LiNizMn1–zO2) (0.5≤z≤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
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

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

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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

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

\[
\beta = \lambda_1 \left( \Delta C_{P, T, \rho_R}^0 + \lambda_2 \Delta \omega_{T, \rho_R} \right) + \lambda_3
\]

- \( K \): equilibrium constant
- \( 'r' \) refers to the reference state (25°C, 0.5 MPa)
- \( \alpha \): 6.385 \( \times \) 10\( ^{-5} \) K\(^{-1} \)
- \( \varepsilon \): dielectric constant of water
- \( \omega \): parameter defined by reaction system
- \( \beta \): reaction-dependent constant
- \( \Delta C_{P, T, \rho_R}^0 \): heat capacity
- \( \lambda_1 = 97.66 \) K
- \( \lambda_2 = 2 \times 10^{-4} \) K\(^{-1} \)
- \( \lambda_3 = -3.317 \times 10^2 \) J/mol

Solubility of species and growth depend on solvent properties such as:
- Viscosity
- Density
- Dielectric constant

\[
\rho^* = \frac{\text{density of water in actual cond.}}{\text{density of water in reference cond.}}
\]
Supercritical conditions

- 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

Critical condition for water: 218 atm, 374°C
Critical condition for ethanol: 60 atm, 241°C
4. Kinetics

- Hydro/solvothermal synthesis is a crystallization process involving:
  - Reaching supersaturation \( \frac{\text{actual concentration}}{\text{saturation concentration}} \) 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.

5. Intelligent engineering of materials

- Researchers giving up the Edisonian trial and error 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

Calculated yield diagram of PbZr$_{0.6}$Ti$_{0.4}$O$_3$ at 433 K. PbAc$_2$, TiO$_2$, and ZrO$_2$ are used as starting materials for the calculations.

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$_4$:
  - $(\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}, \text{H}_3\text{PO}_4, \text{LiOH.H}_2\text{O}$
  - 140-220°C, 0.5-24 h, 600-800°C subsequent sintering

- Crystallite size is controlled by controlling:
  - Precursor concentration
    - Lower $(\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}$ conc.: 1-5 micron sized platelets (figure a)
    - Higher $(\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}$ 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

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 Li$_4$Ti$_5$O$_{12}$ (LTO) nanocrystal synthesis in water-ethanol mixture, at 200°C
- Li$_2$TiO$_3$ impurity phase avoided by pH control
- LTO formation through delithiation and dehydration from the precursor:

  $$2\text{LiOH} + \text{TiO}_2 \rightarrow \text{Li}_2\text{TiO}_3 + \text{H}_2\text{O} \ (>\text{pH 11}) \quad (1)$$

  $$\text{Li}_2\text{TiO}_3 + x\text{H}^+ \rightarrow (\text{Li}_{2-x}\text{H}_x)\text{TiO}_3 + x\text{Li}^+ \text{ (delithiation)} \quad (2)$$

  $$(\text{Li}_{2-x}\text{H}_x)\text{TiO}_3 \rightarrow \text{Li}_{2-x}\text{TiO}_{3-x/2} + x/2\text{H}_2\text{O} \text{ (dehydration)} \quad (3)$$

Ionothermal synthesis of LIB materials in literature

- Metal fluorosulfate systems, i.e. LiMSO$_4$F (M=Fe, Co, Ni, Mn)
  - e.g. LiFeSO$_4$F → 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$_4$F by ionothermal synthesis:
  1. Dehydration of FeSO$_4$·7H$_2$O to FeSO$_4$·H$_2$O at 200°C, under vacuum
  2. Reaction of FeSO$_4$·H$_2$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
Index of interesting reviews / books

- 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.)

- Keywords: mineralizer, solvent, solubility, crystallization, supercritical, autoclave, liner, viscosity, dielectric constant, density, high temperature-pressure, ...
Wet chemical synthesis

Thermal decomposition
Thermal decomposition synthesis – often QDs

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

E.g.
Semiconductor QD
Metal oxides

DOI: 10.1002/sml.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 \( \text{MO}_x \) particles in hydrophobic environment
  - Use of precursors soluble in organic solvents
  - Yet yielding \( \text{MO}_x \) 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

\[
\begin{align*}
\ce{\equiv M-X + RO-M &\rightarrow \equiv M-O-M &+ R-X} \\
\ce{\equiv M-O-CR' + RO-M &\rightarrow \equiv M-O-M &+ RO-CR'} \\
\ce{\equiv M-OR + RO-M &\rightarrow \equiv M-O-M &+ R-O-R}
\end{align*}
\]
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


Review on heating up synthesis
J. van Embden, Chem. Mater., 2015, 27, 2246
Wet chemical synthesis

(auto)combustion synthesis
Comparison to sol-gel and related routes

Precursor → Chemical reaction → oxide / metal / phosphate

Why high temperature (600°C)?

- Kinetics
  - Activation controlled
  - Diffusion controlled
- Free energy change
  - 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

Kim, Nature, 2011
Hennek JACS 2012
Kim JACS 2012
(Auto)combustion synthesis: in practice

Self-sustainable reaction leading to internal heating → oxide formation

Requirements:
- Heat to initiate the reaction
- Fuel with high $\Delta H_c$
- 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

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

*Patil, K.C. et al., Chemistry of nanocrystalline oxide materials, 2008, world scientific, Singapore*
### 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 Li$_4$Ti$_5$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 Li$_4$Ti$_5$O$_{12}$ and (b) ordered rocksalt-phase Li$_{4+x}$Ti$_5$O$_{12}$; (c) voltage-composition curves showing the electrochemical transformation of Li$_{4+x}$Ti$_5$O$_{12}$–Li$_4$Ti$_5$O$_{12}$ during galvanostatic charge-discharge cycles at C/2 rate at 30 °C.

Figure 7. Capacity versus cycle number plot for nanocrystalline Li$_4$Ti$_5$O$_{12}$ synthesized by the combustion method at different discharge rates. Inset shows capacity versus cycle number for bulk Li$_4$Ti$_5$O$_{12}$.
Combustion synthesis of Li$_4$Ti$_5$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 $\text{NH}_4\text{NO}_3$

**Proposed mechanism**

- Melting/evaporating/endothermic degradation of $\text{NH}_4\text{NO}_3$ absorbs heat
  - Prevents heat build up
  - $\Rightarrow$ prevents autocombustion until excess $\text{NH}_4\text{NO}_3$ is degraded
- $\text{O}_2$ 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. $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, 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
Clément Sanchez [10.1016/j.crci.2009.06.001]
Summary
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
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

→ synthesis-by-design

Soderholm and Mitchell APL MATERIALS 4, 053212 (2016)
Thank you for this invitation

Thank you for your attention

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