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Lithium Transition Metal Orthosilicates by Scalable and Inexpensive Synthesis Methods as Positive Electrode for Li-ion Batteries

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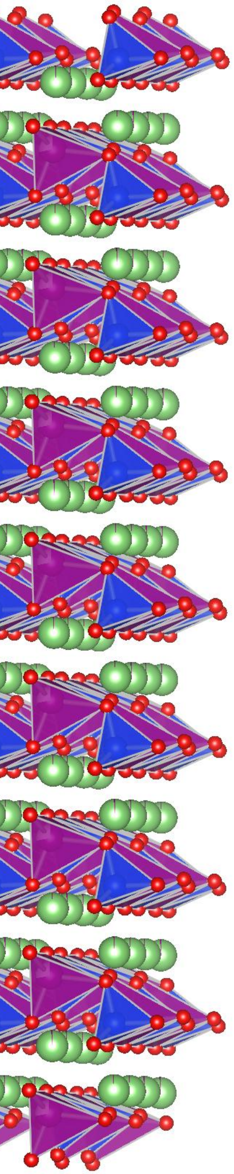
Wednesday the 2nd of December 2015

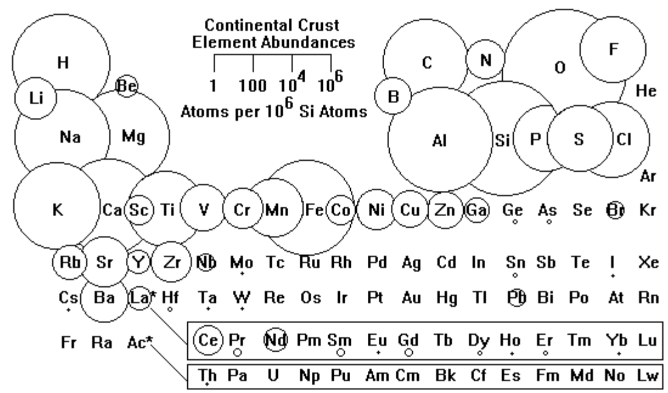
Motivation



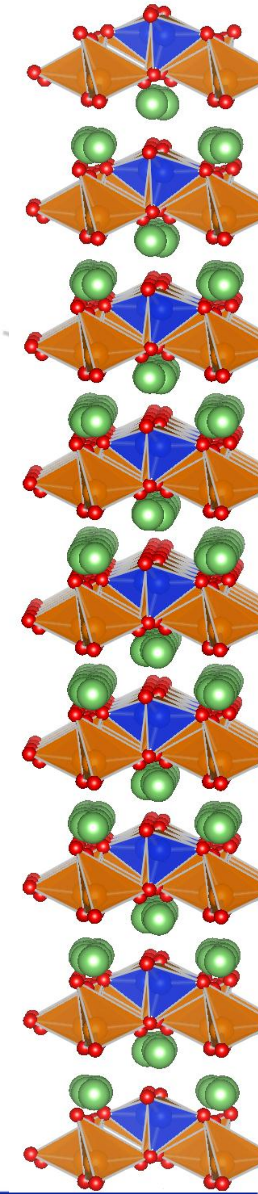
$LiCoO_2$ alone accounts for about 50% of the materials cost of a Li-ion battery

Li_2MSiO_4/C (M = Mn, Fe)

- Cheap and abundant precursors
- Theoretical capacity 166-333 mAh g^{-1} (reversible extraction beyond one Li per formula unit)
  - Accessible capacity of $LiCoO_2$ ~ 140 mAh g^{-1}
- Conductive coating and nano-sizing required



https://www.uwgb.edu/dutchs/PLANETS/Geochem.htm



Motivation

- Vast majority of reported Li_2MSiO_4/C syntheses are wet chemical methods
  - Sol-Gel
  - Solvothermal
  - …

➢ Time consuming, hardly scalable

If a new cathode material shall ever be commercialised, scalability and time efficiency are key factors

Mix and Fire

- Commercially available cheap precursors
  - Li_2CO_3 and Fe_2O_3 submicron powders (Rana Gruber AS)
  - Fumed silica (Wacker Chemie GmbH)
  - Sucrose (Dansukker)

➢ Inexpensive, quick and scalable

Assumption: Small reactants facilitate phase formation and the applied C source hinders particle growth

Mix and Fire

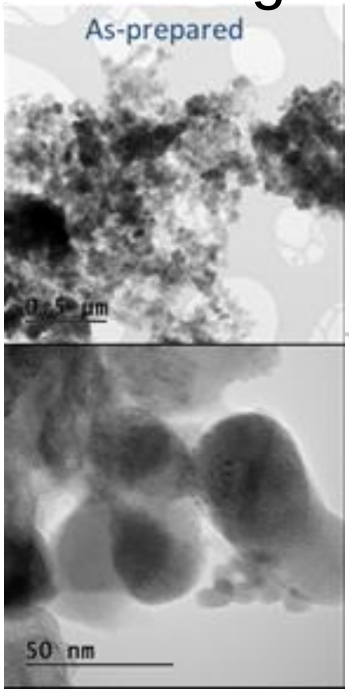
1. Mix

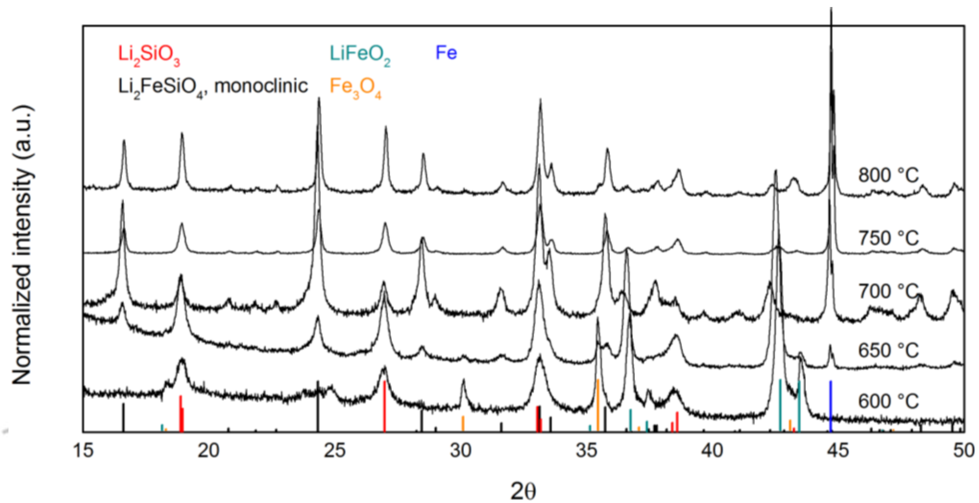
- 20 wt. % sucrose as carbon former
- Wet ball milling in EtOH (4h)
- Drying and pellet pressing

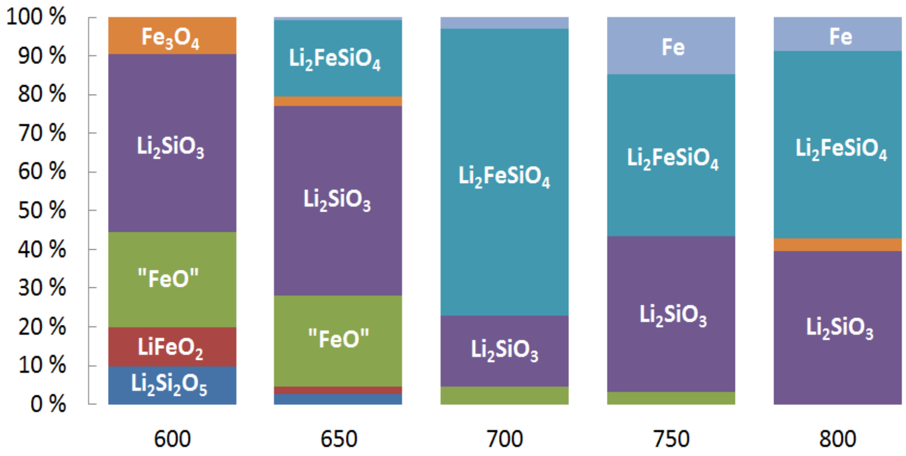
2. Fire

- 10 h in Ar at different temperatures ranging from 600 to 800 deg

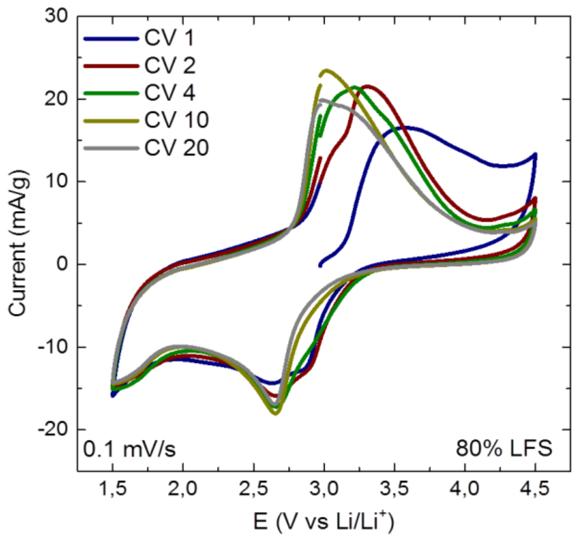
700 deg

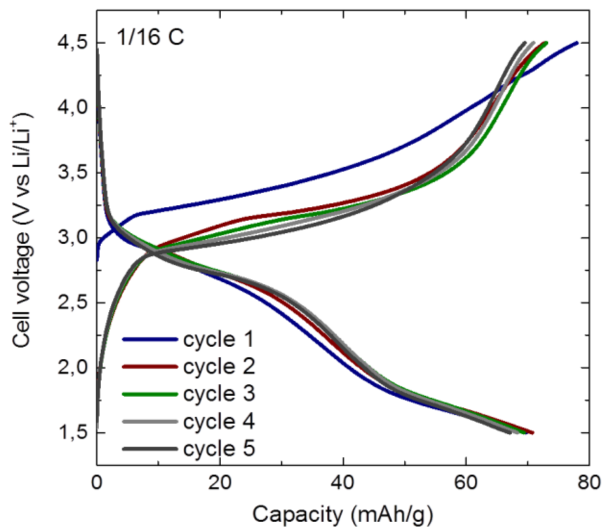


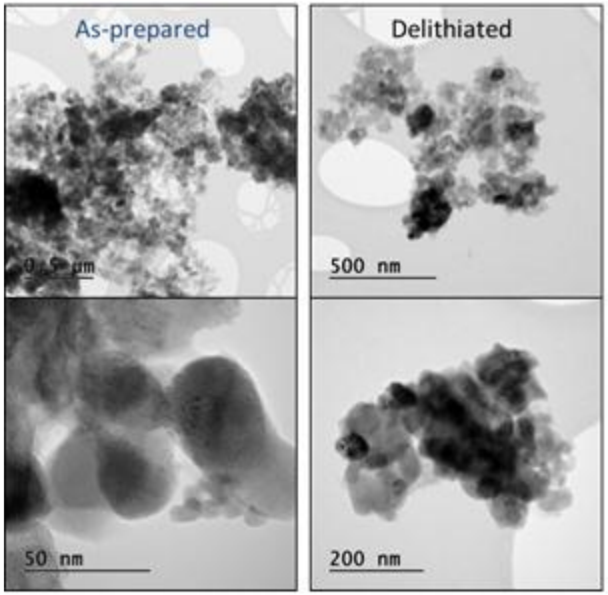


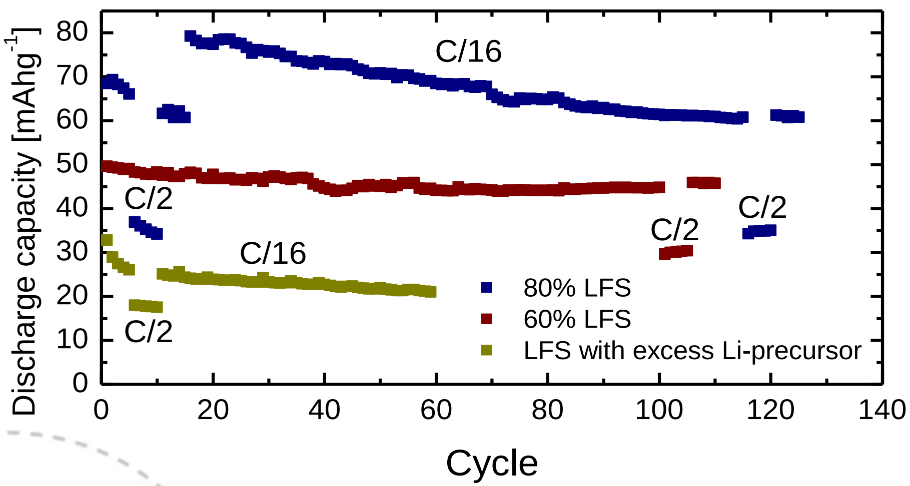


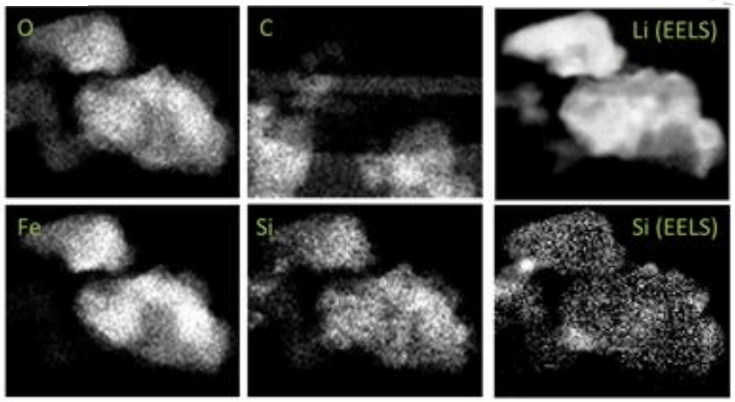
Mix and Fire









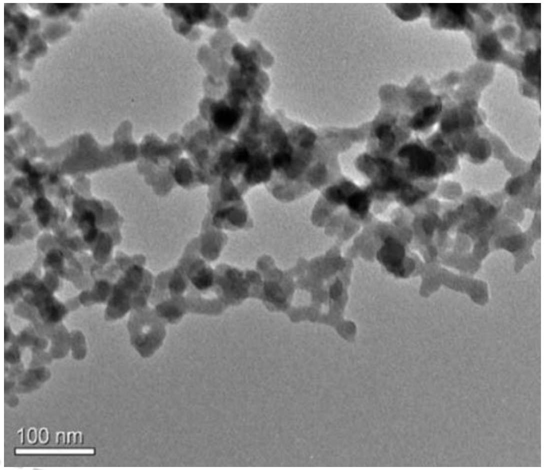


Delithiated sample	Li/Si ratio	Chemical comp.
Map 1	1.0	$LiFeSiO_4$
Map 2	1.5	$Li_{1.5}FeSiO_4$

A closer look at the Si precursor

Pyrogenic silica is commercially produced by Flame hydrolysis of $SiCl_4$

http://www.chem.hawaii.edu/Bil301/principles.html



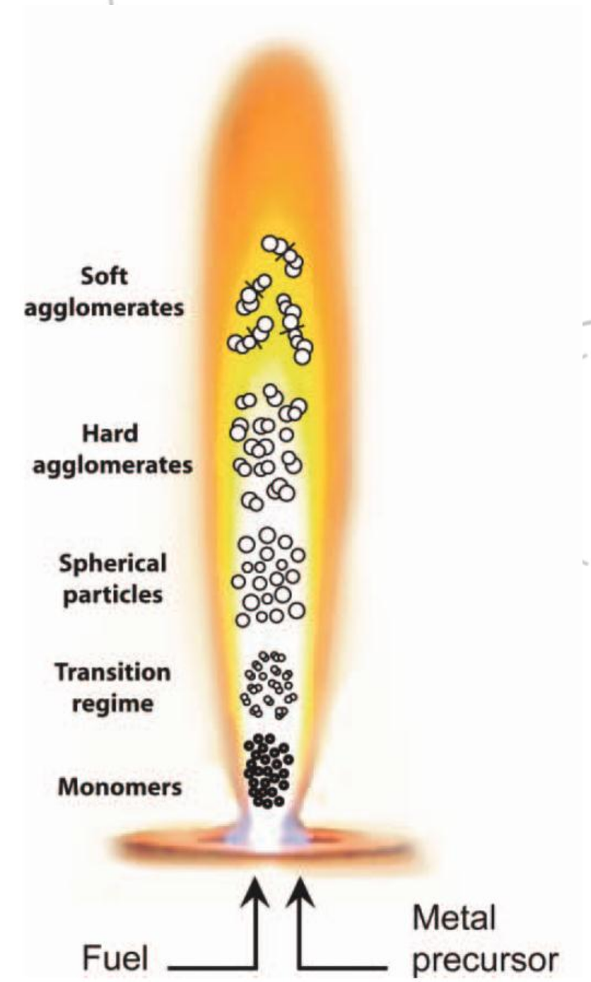
Wu *et al.* Soft Matter, 2012, 8, 10457–10463

http://www.aerosil.com/product/aerosil/en/services/packaging/Pages/default.aspx

Flame spray pyrolysis

Recent developments resulted in a process called Liquid-Feed Flame Spray Pyrolysis

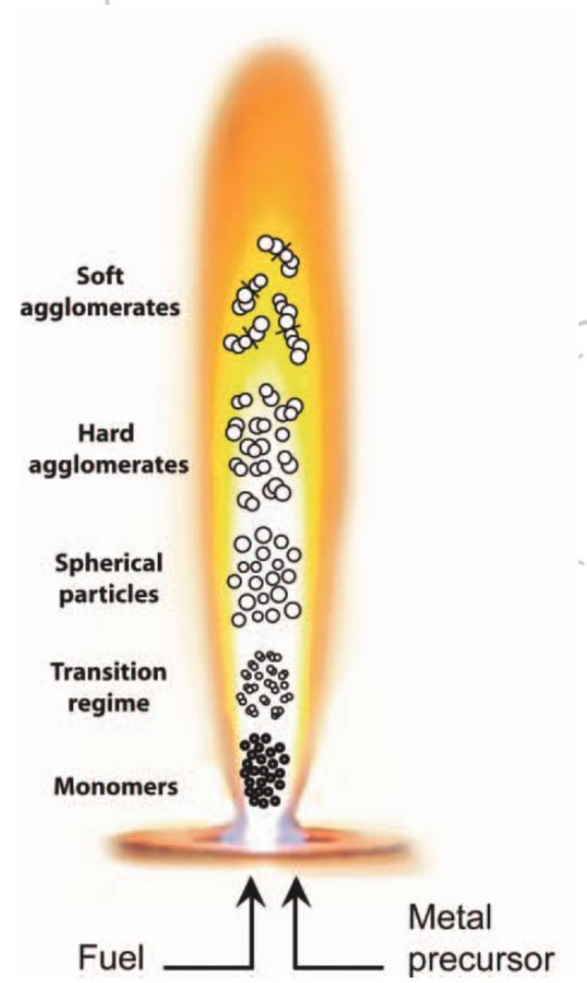
- Combination of flame hydrolysis and conventional spray pyrolysis
- Inherent advantages of both methods combined
  - Liquid precursor solution
  - Production of loosely agglomerated nano particles



Flame spray pyrolysis

Realistically, the oxidising nature and the extreme short residence time will make the phase formation of a quaterny oxide very unlikely

Commercial production limited to binary oxides



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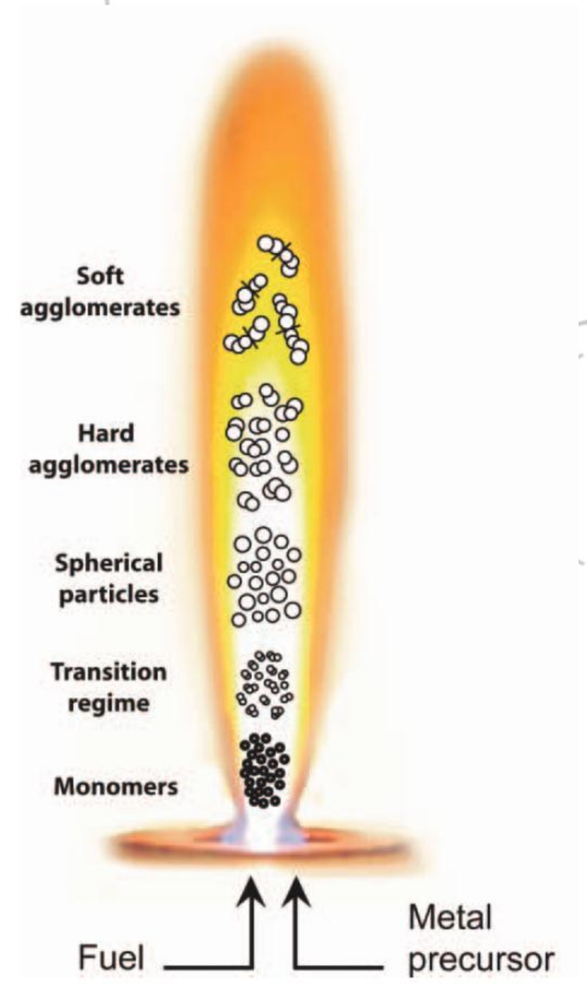


Hence, the combination of FSP with a reducing heat treatment and carbon coating in a single step

- Carbonising additives are of major importance to hinder particle growth

Flame spray pyrolysis

Flow chart

Solution preparation*

↓

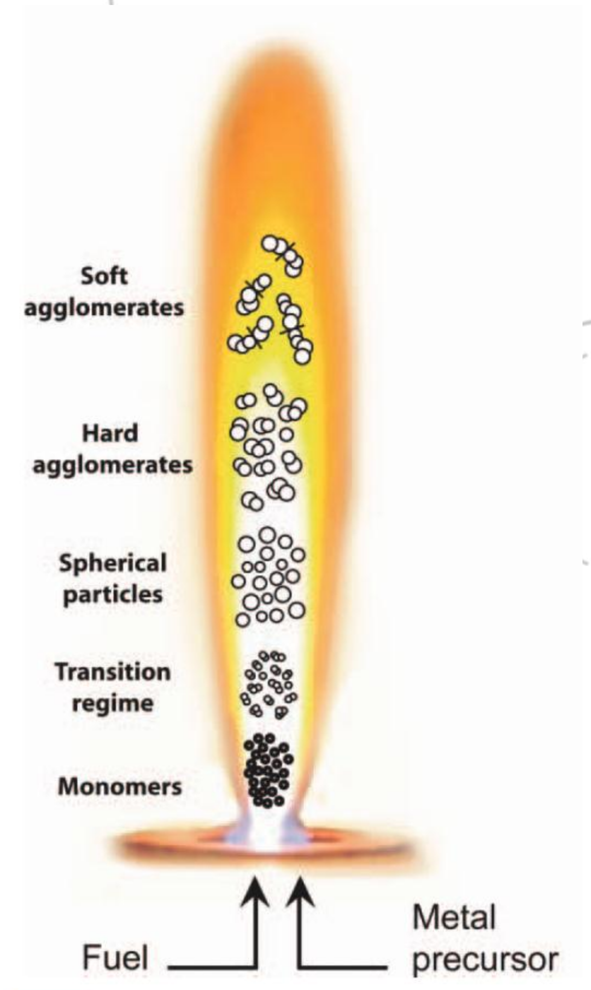
Flame Spray Pyrolysis

↓

Wet ball milling (addition corn starch as C source)

↓

Reducing heat treatment



* Metal nitrates and TEOS as precursors

Flame spray pyrolysis

Flow chart

Solution preparation*

↓

Flame Spray Pyrolysis

↓

Wet ball milling (addition corn starch as C source)

↓

Reducing heat treatment

Two important factors are highlighted to obtain highly active nano sized materials

1. **Solution combustibility**
   - **1:5 H_2O:EtOH compared to 1:5 p-Xylene:EtOH**
2. **Cation concentration**
   - **Highly concentrated $Fe(NO_3)_3$ solutions cause particle growth and aggregation (The behaviour was not observed for $Mn(NO_3)_2$**

* Metal nitrates and TEOS as precursors

Flame spray pyrolysis

Synthesised samples

LMS in two different precursor solutions*

LFS with two different precursor concentrations

LFMS 50/50 (Fe/Mn)

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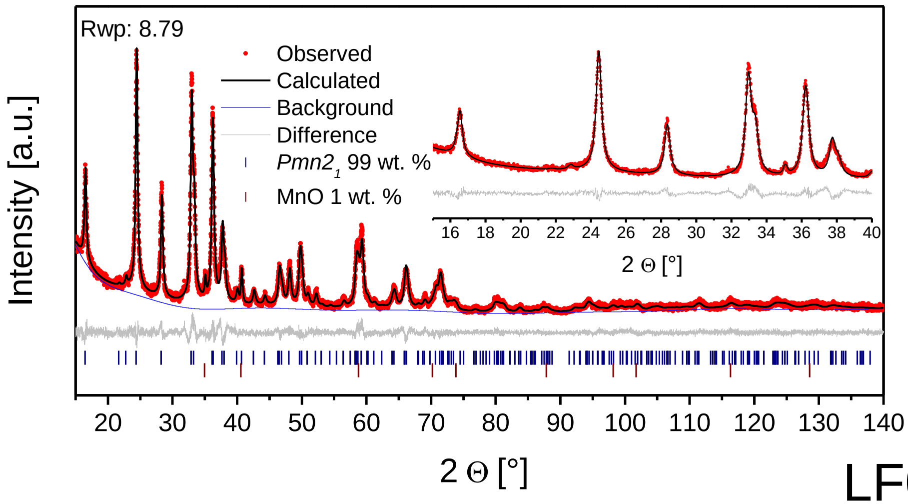
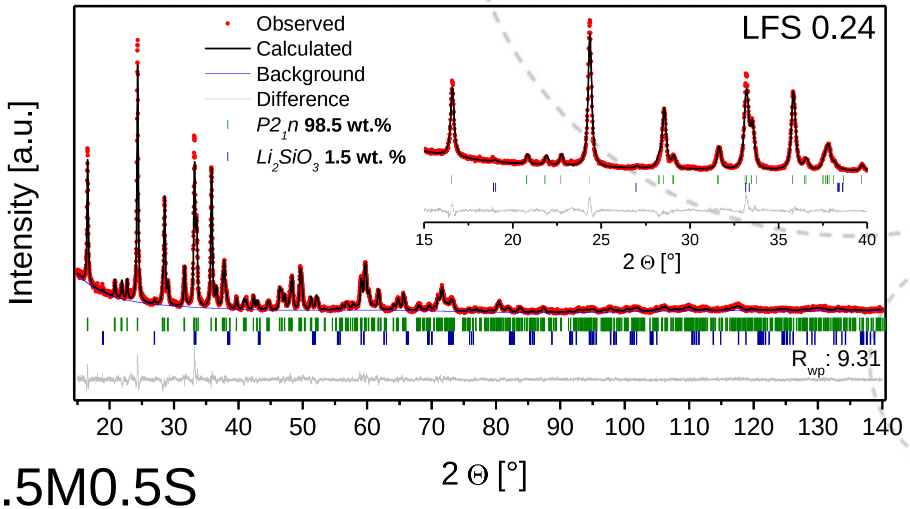
* Also Mn deficient samples were synthesised

Phase evolution

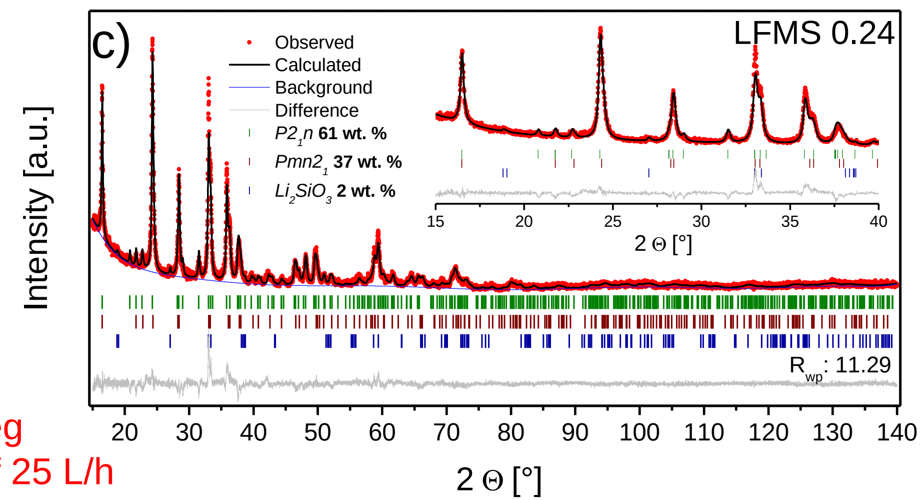
LM0.94S



LFS



LF0.5M0.5S



Heat treatments: 10 h 650 deg

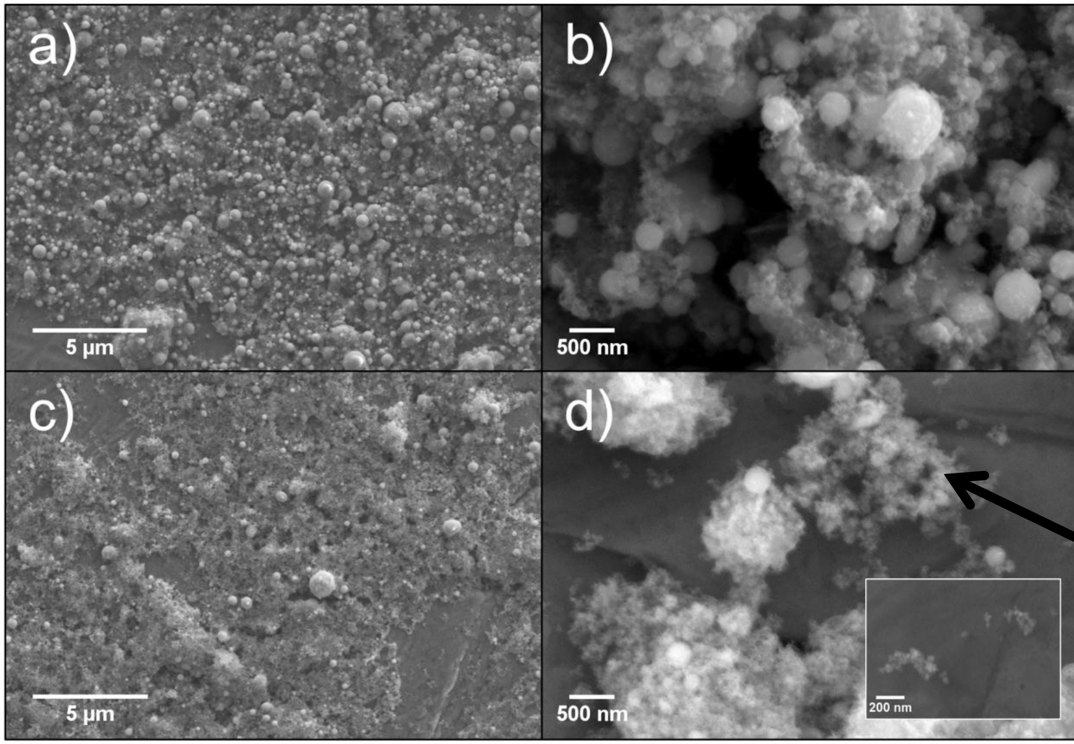
LMS: 5% H_2 in Ar flow rate of 25 L/h

LFS and LFMS: 2% H_2 in Ar flow rate of 10 L/h

Influence of the solution combustibility (LMS)

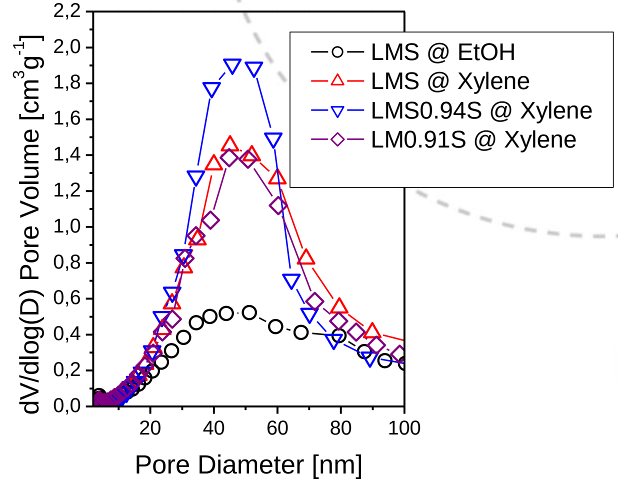
LMS @ EtOH

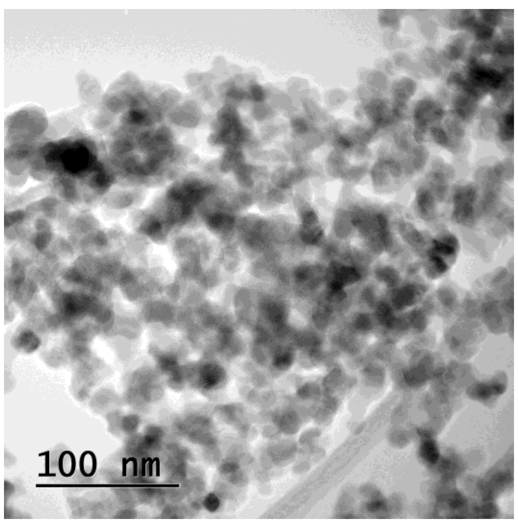
As-pyrolysed | Reduced



As-pyrolysed | Reduced

LMS @ Xylene



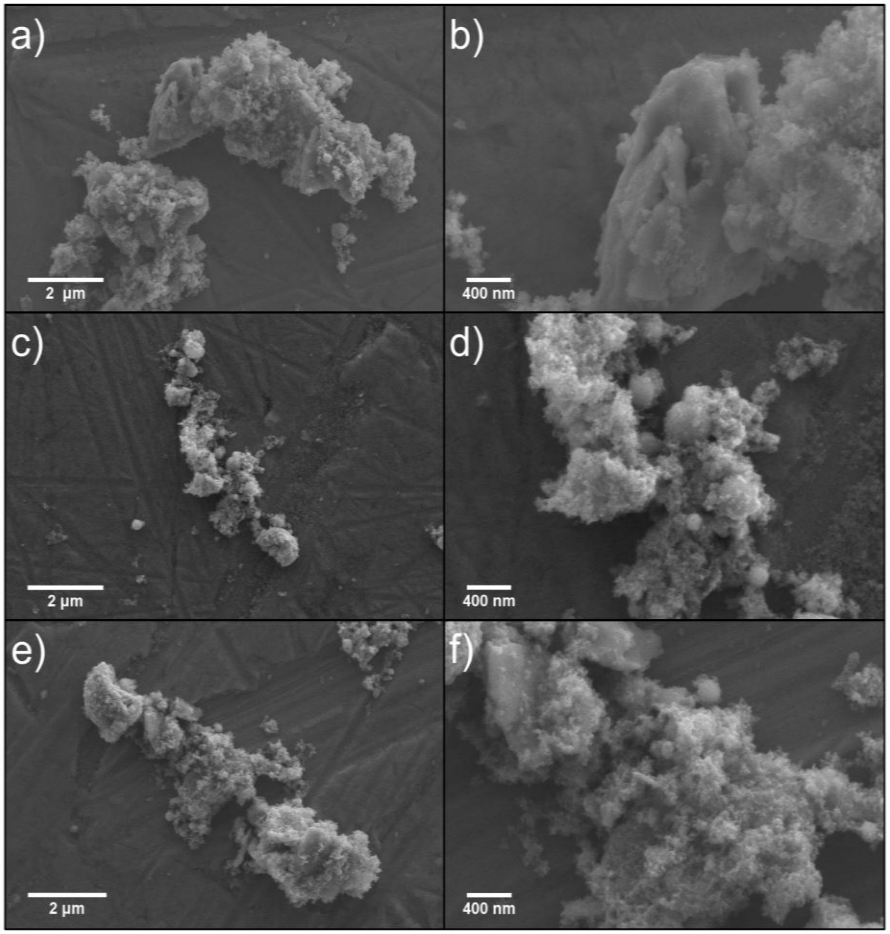


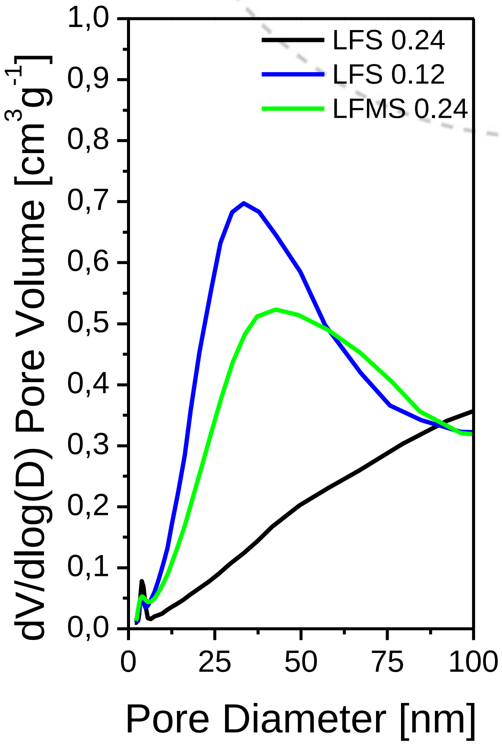
Influence of the precursor concentration (LFS)

LFS
high
conc.

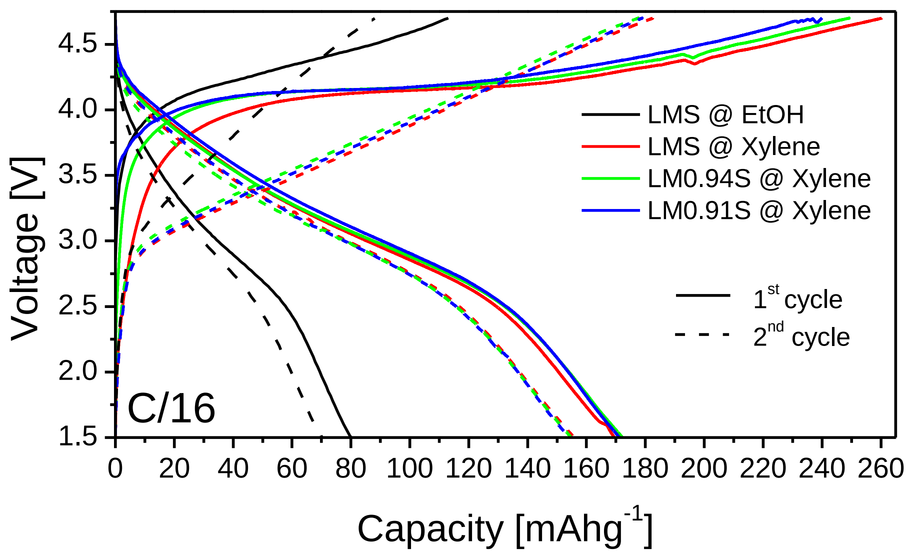
LFS
low
conc.

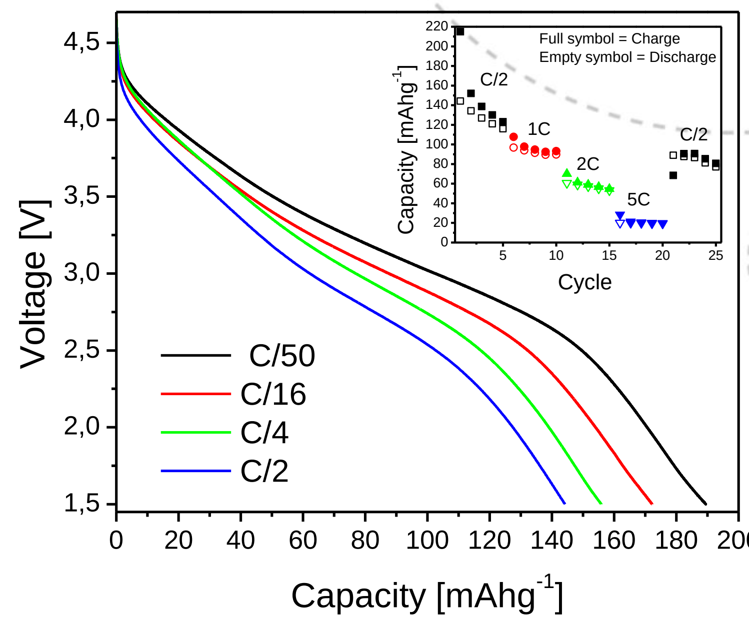
LFMS
high
conc.





Electrochemical response (LMS)





Charge rate C

1 C = 160 mA g^{-1}

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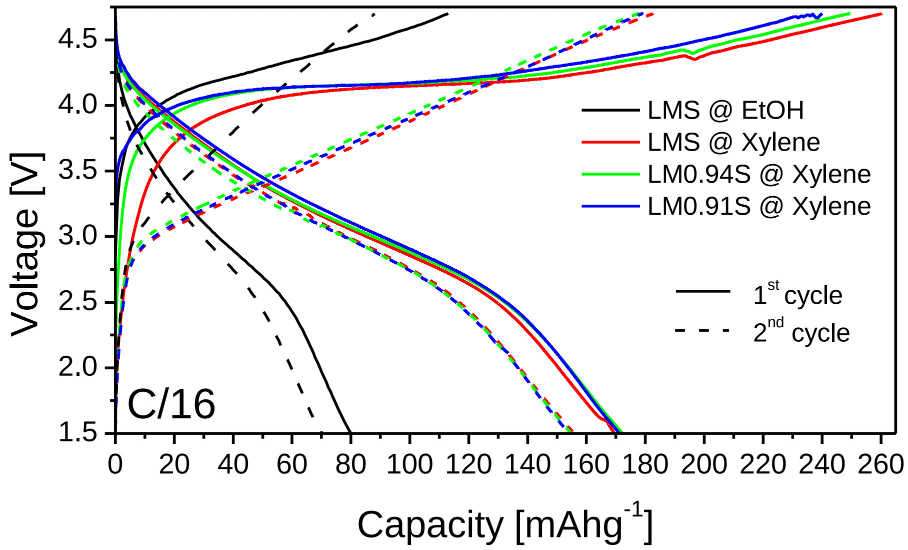
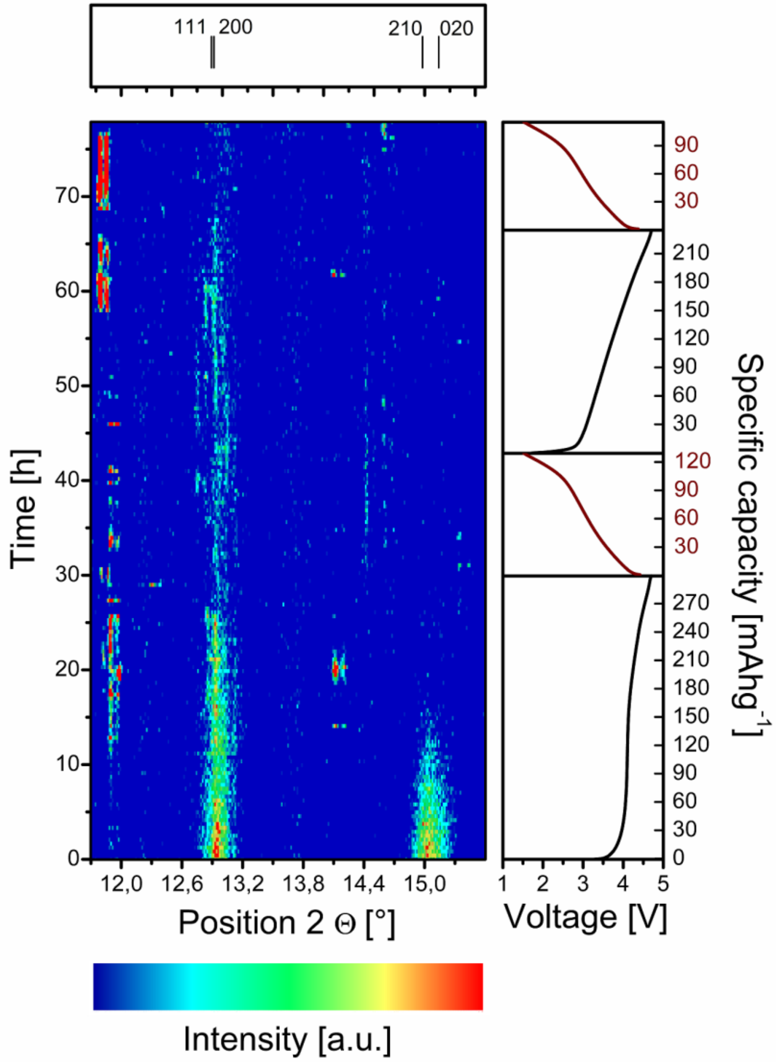
Electrochemical response (LMS)





Charge rate C

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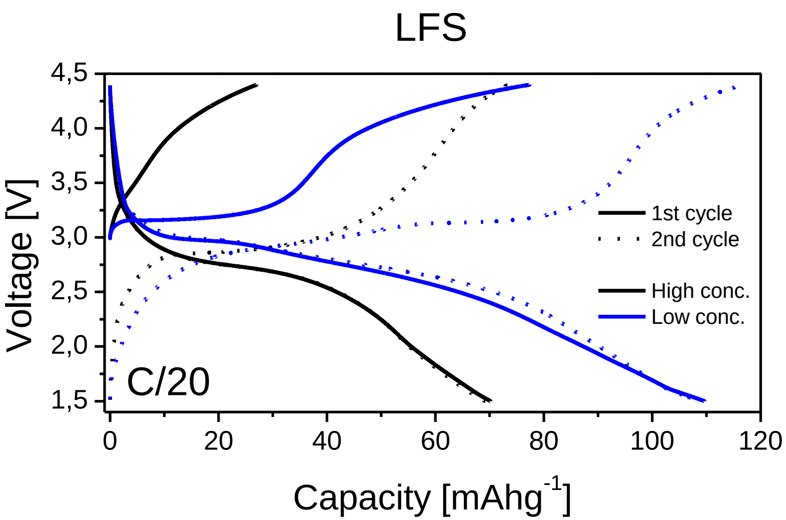
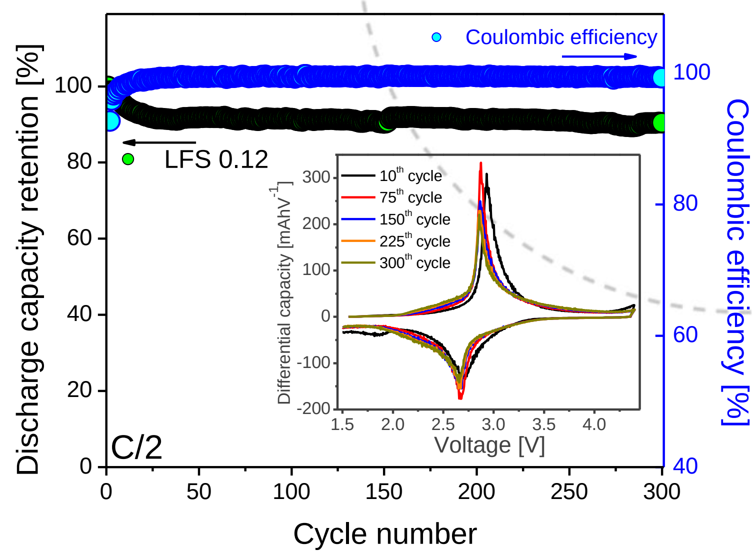
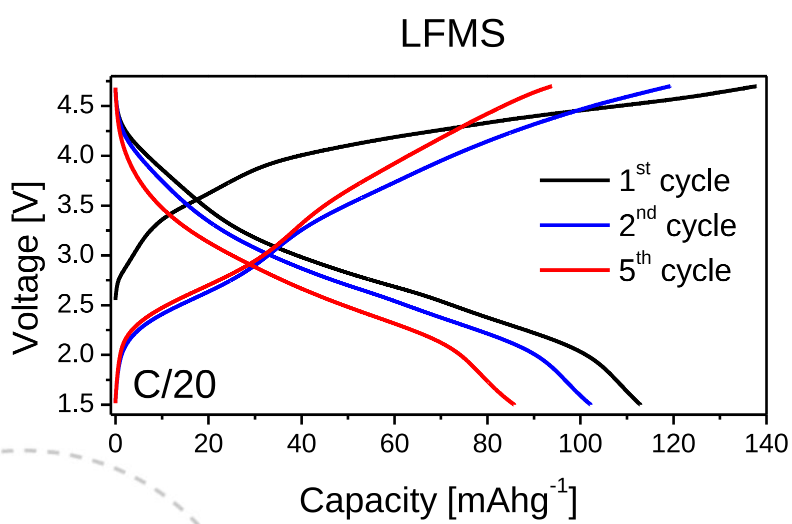
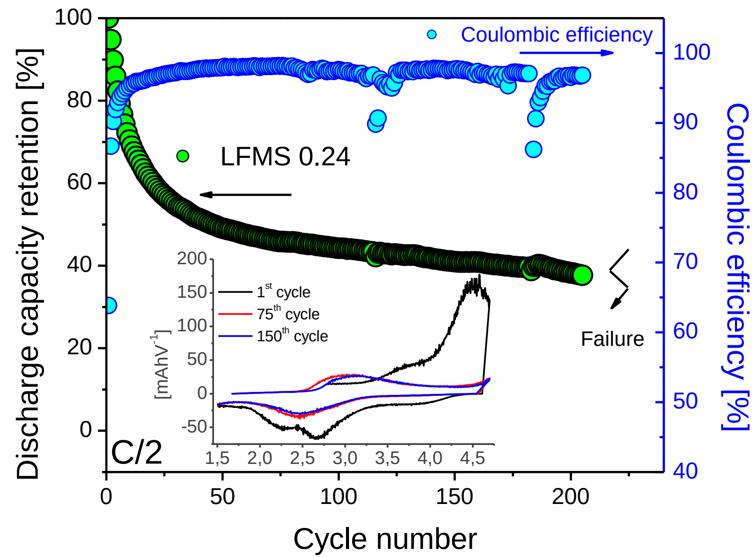
Electrochemical response (LFS and LFMS)

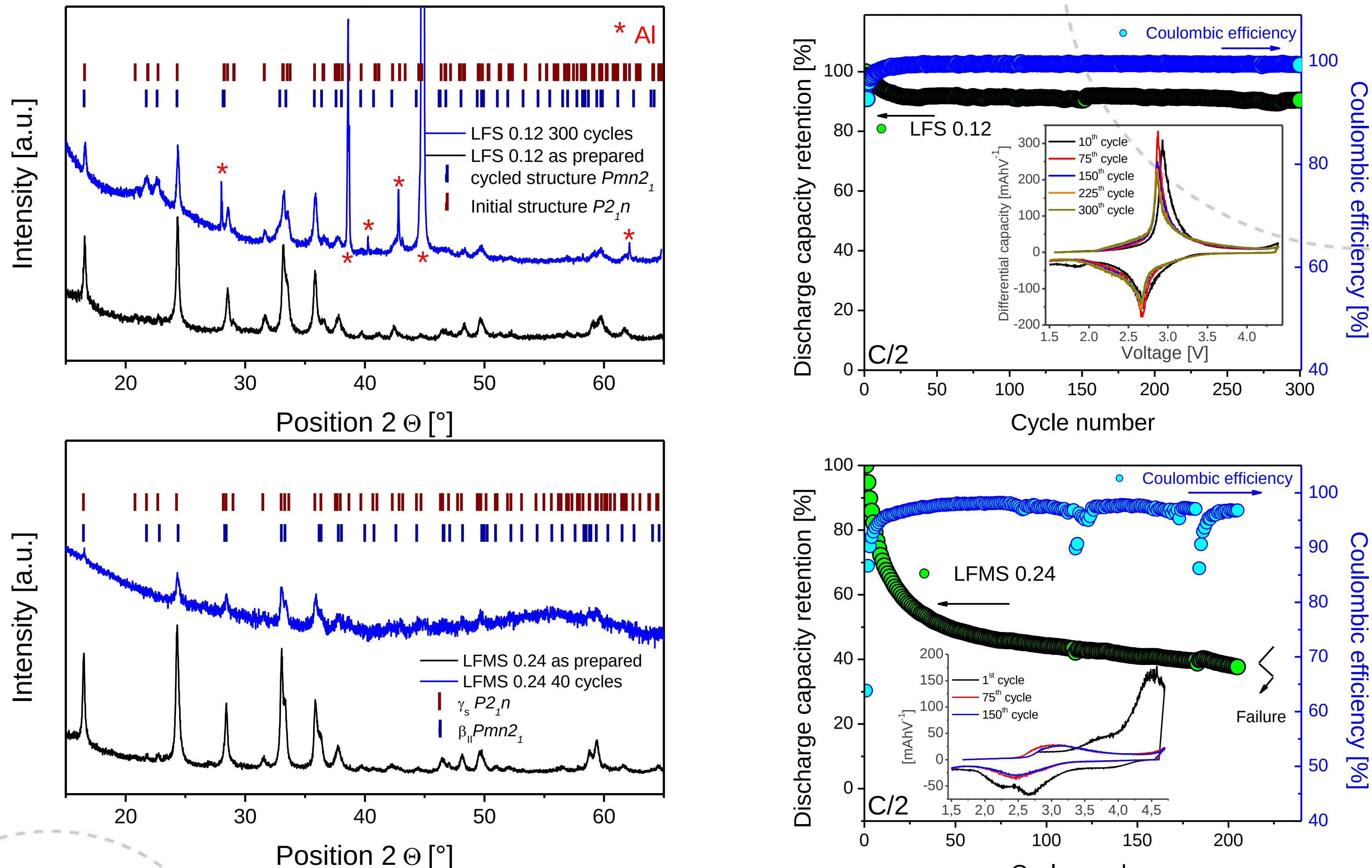




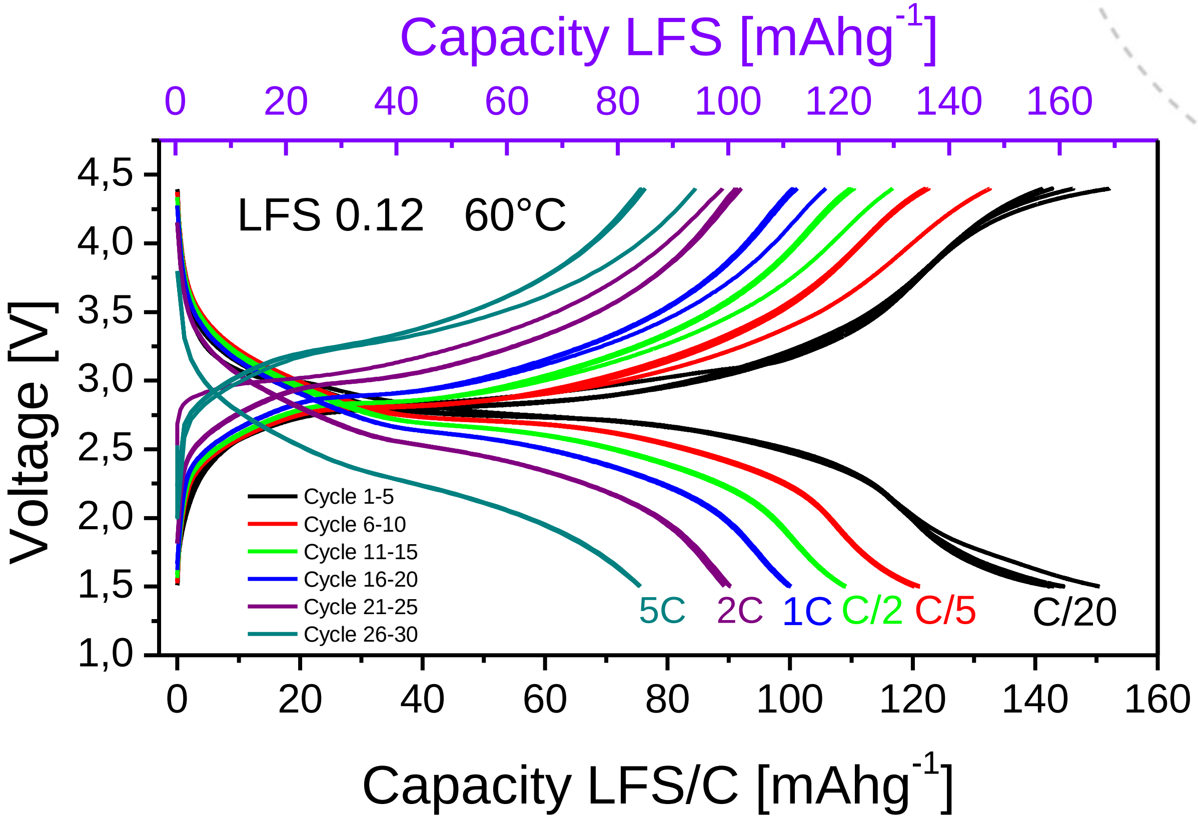




Electrochemical response (LFS and LFMS)



Electrochemical response (LFS at 60 deg)



Note, for the capacities of the top abscissa 10 wt. % carbon were deducted from the sample mass

Conclusions

Inexpensive solid state reaction yields in electrochemical active LFS:

– Challenging to achieve high phase purities and hence capacities

Flame spray pyrolysis of a EtOH/p-Xylene based solution was shown to be an adequate method to synthesise nano scale Li_2MSiO_4 compounds:

LMS:

– The reversible exchange of more than one Li per formula unit was shown
– Irreversible amorphisation of the structure during the first oxidation causes severe capacity decay

LFS:

– The precursor conc. showed a major influence on the morphology
– The reversible exchange of one Li per formula unit was possible at elevated temperature
– **Adjustment of the precursors could result in an easy and scalable method to produce highly active LFS as alternative low cost electrode**

Thank you for your kind attention!