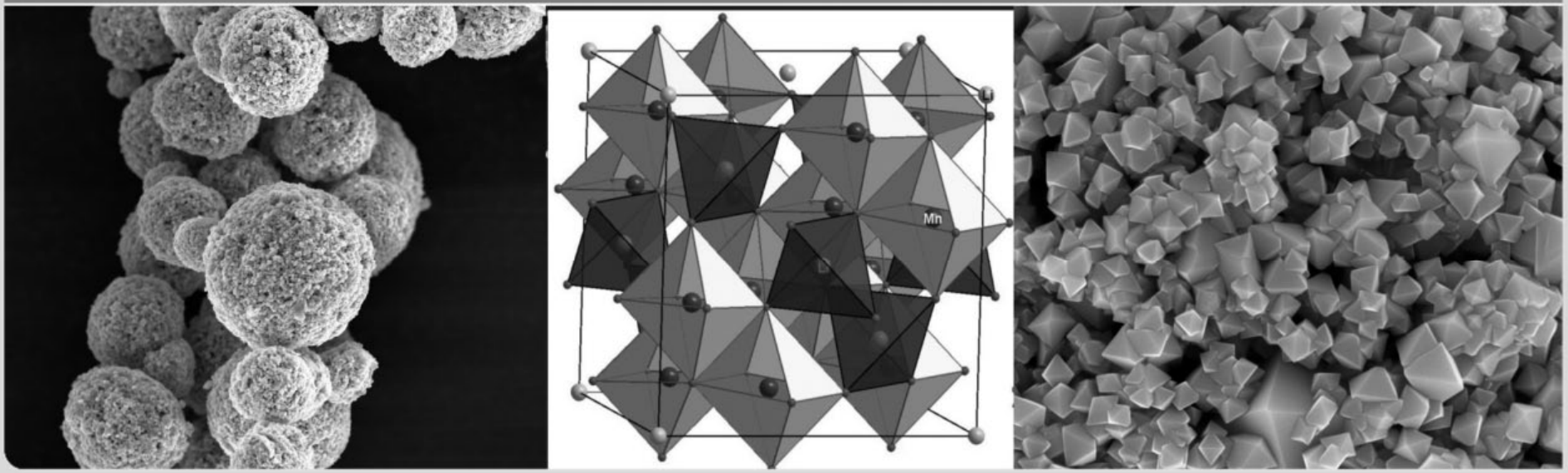
Karlsruher Institut für Technologie

Influence of synthesis conditions and processing on the cathode performance of 5V-spinel materials

Titanium doping of $LiNi_{0.5}Mn_{1.5}O_4$ spinel

M. Schroeder, D. Linder, M. Schön, S. Glatthaar, H. Geßwein and J. R. Binder

Institute for Applied Materials - Material Process Technology



Outline

- ***Introduction***
  Improvement of $LiNi_{0.5}Mn_{1.5}O_4$ (*LNMO*) cathode performance using Titanium doping and particle/powder processing (granulation)

- ***Motivation***
  Understanding doping (I) and particle processing (II) effects

- ***Processing I***
  Synthesis of $LiNi_{0.5}Mn_{1.5}O_4$ (*LNMO-I*) and $LiNi_{0.5}Mn_{1.5-x}\boldsymbol{Ti_x}O_4$ (*LNM**T**O-I*)

- ***Processing II***
  Granulation of $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5-x}\boldsymbol{Ti_x}O_4$ powders (*LNMO-II and LNM**T**O-II*)

- ***Processing III***
  „Post-doping“ of $LiNi_{0.5}Mn_{1.5}O_4$ materials: *LNM**T**O-III*

- ***Electrochemical performance***
  A comparison of *LNMO* and *LNM**T**O* materials

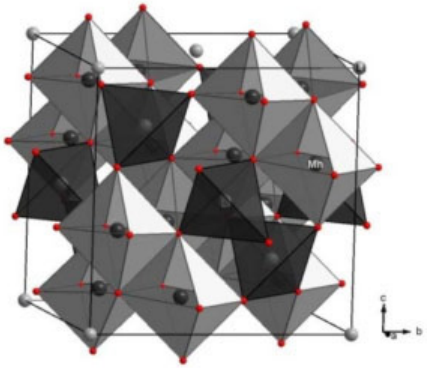
Introduction

- $LiNi_{0.5}Mn_{1.5}O_4$ (*LNMO*) 5V spinel material, capacities > 115 mAh/g

- Doping with cations (Co^{3+}, Fe^{3+}, Ti^{4+})

→ stabilization of spinel structure

→ modification of microstructure



Introduction

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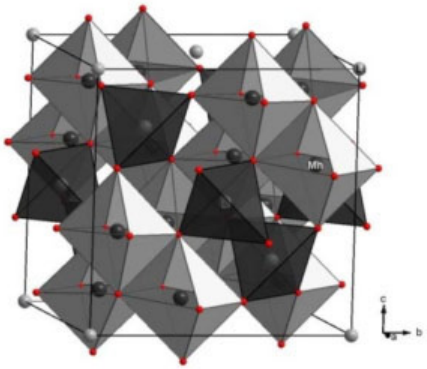
- Doping with cations (Co^{3+}, Fe^{3+}, **Ti^{4+}**)

→ stabilization of spinel structure

→ **modification of microstructure**

- $LiNi_{0.5}Mn_{1.5-x}\mathbf{\mathit{Ti}}_xO_4$ (*LNM**T**O*) with $x \leq 0.05$ capacities > 123 mAh/g



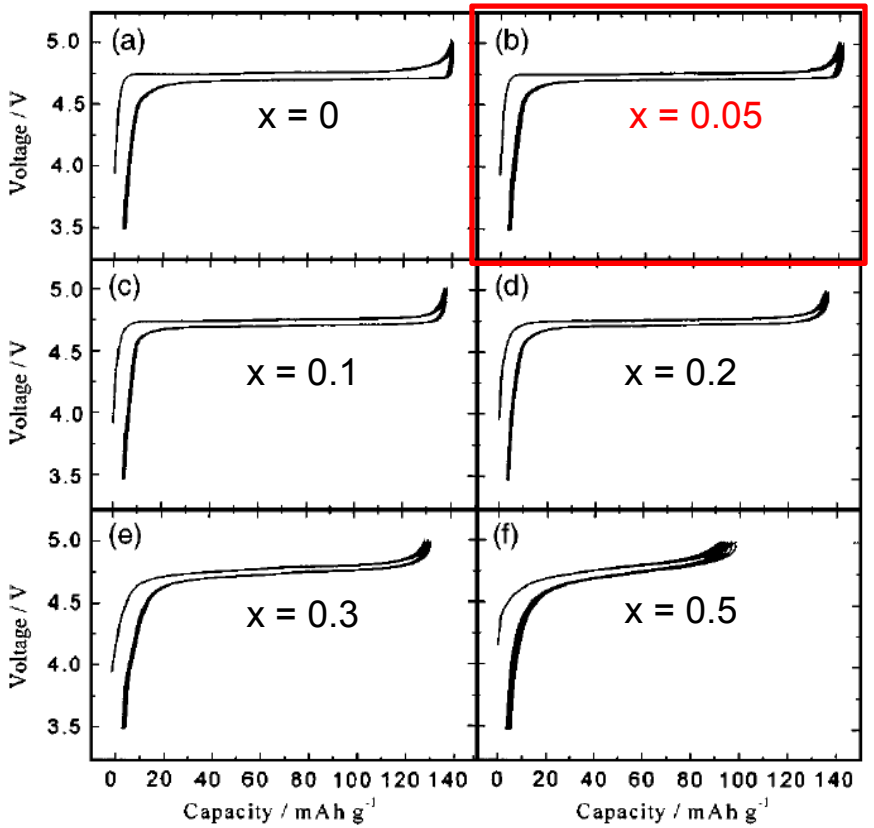


Figure 6. Voltage profiles of $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ with various Ti content, x (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.2$, (e) $x = 0.3$, and (f) $x = 0.5$.

J.-H. Kin, S.-T. Myung, C. S. Yoon, I.-H. Oh, Y.-K. Sun
J. Electrochem. Soc. **2004**, *151* (11), A1911-A1918

Introduction

- Preparation of $LiNi_{0.5}Mn_{1.5-x}\boldsymbol{Ti_x}O_4$ (*LNMTO*) material requires assisted sol-gel synthesis (chelating additives) + expensive post-treatment

- Spray drying process for preparation of $LiNi_{0.5}Mn_{1.5-x}\boldsymbol{Ti_x}O_4$ (*LNMTO*) precursor material and powder processing

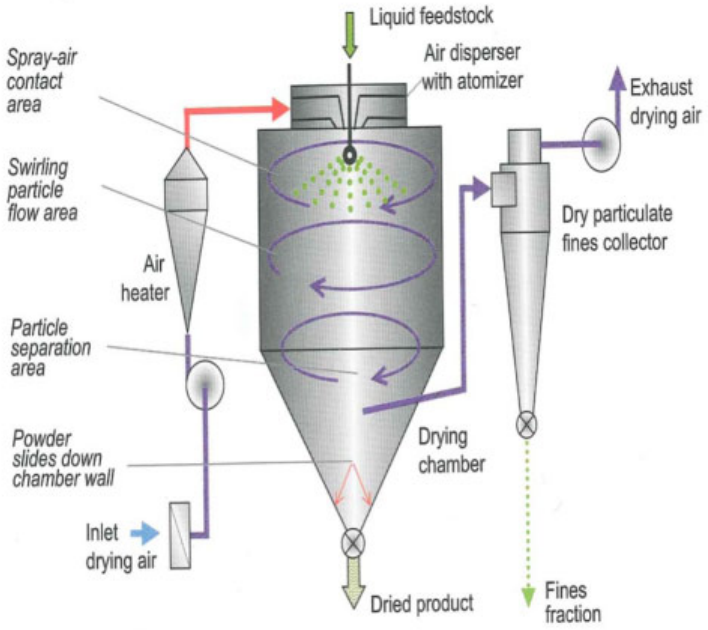
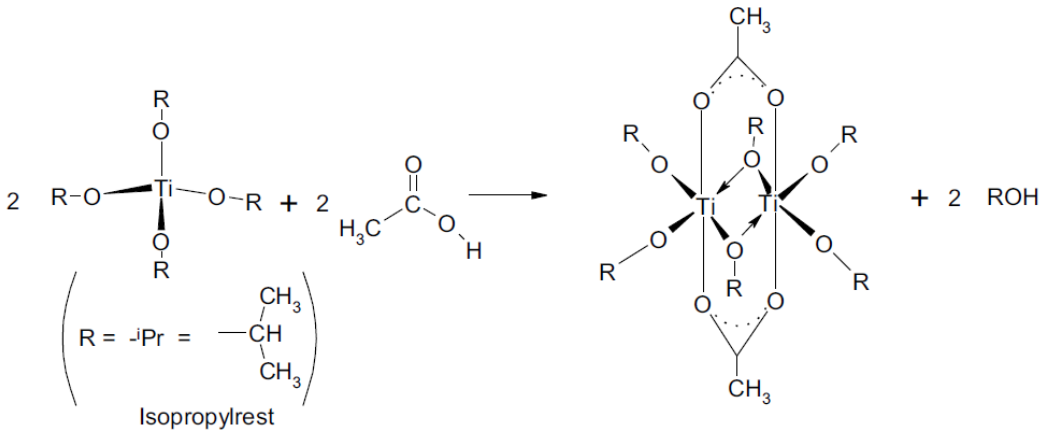


Figure 0.1 Basic Spray Dryer Flow Diagram

K. Masters, *Spray Drying in Practice,* Denmark: SprayDryConsult International ApS **2002**



J. Livage, C. Sanchez, F. Babonneau, *Chemistry of Advanced Materials,* New York, Weinheim: Wiley-VCH **1999**

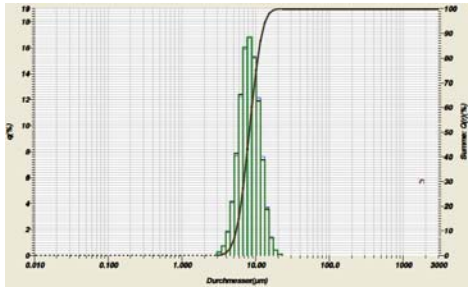
Motivation

- Preparation of Ti doped high performance 5V spinel materials applying process technology

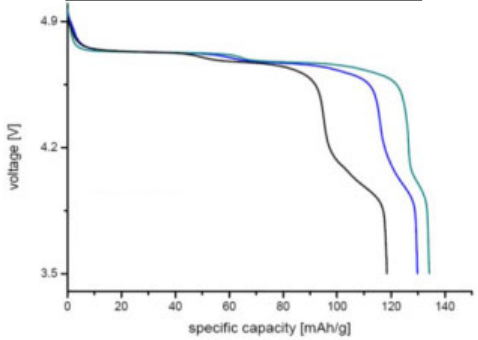
- Understanding the effect of doping on microstructure

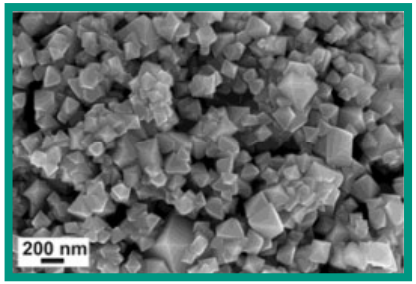
Synthesis/
Post-treatment
Processing

Microstructure
Chemical composition



Electrochemical performance





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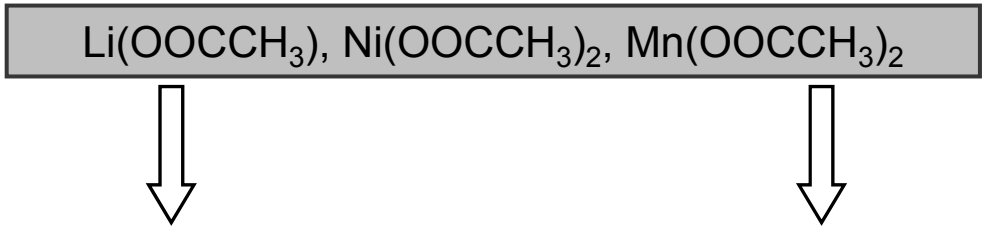
  A comparison of *LNMO* and *LNM**T**O* materials

Synthesis/Processing I: ***LNMO-I***

Solutions, no chelating additives



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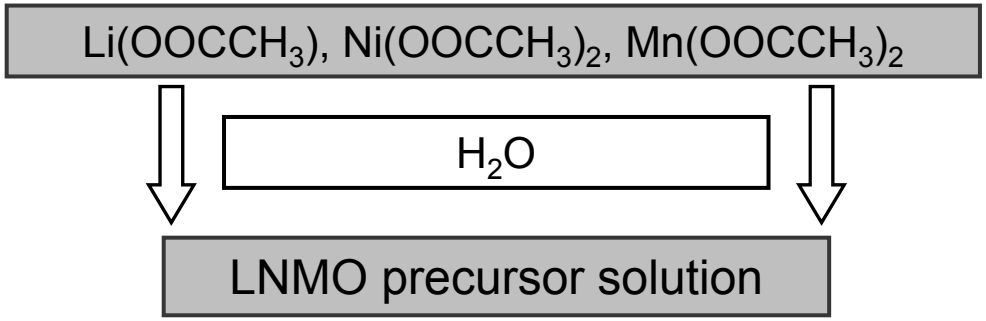

Synthesis/Processing I: *LNMO-I*

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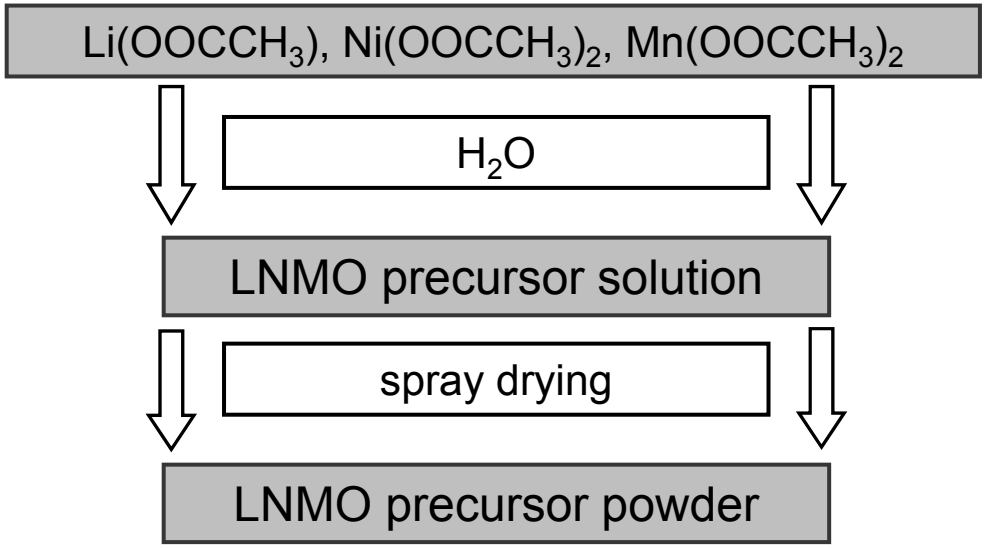

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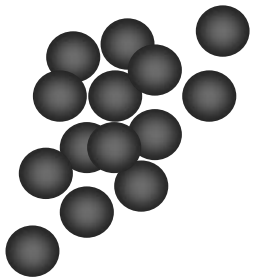
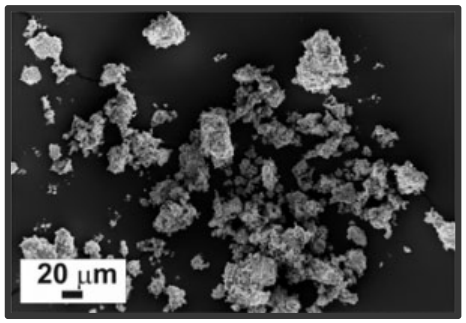


$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)



$Li(OOCCH_3)$, $Ni(OOCCH_3)_2$, $Mn(OOCCH_3)_2$

H_2O

LNMO precursor solution

spray drying

LNMO precursor powder

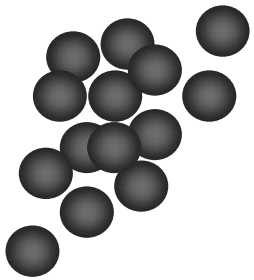
T_1 = 800°C

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)

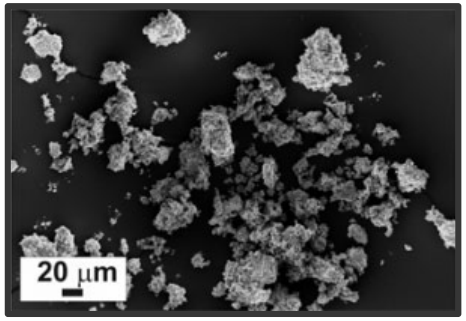
5V cathode material

Synthesis/Processing I: *LNMO-I*

Solutions, no chelating additives



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)



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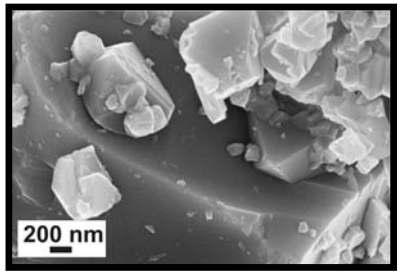
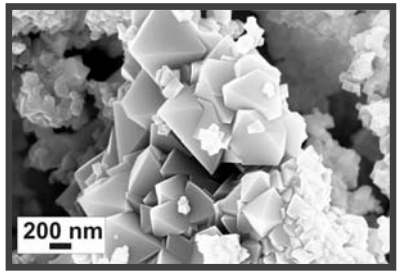


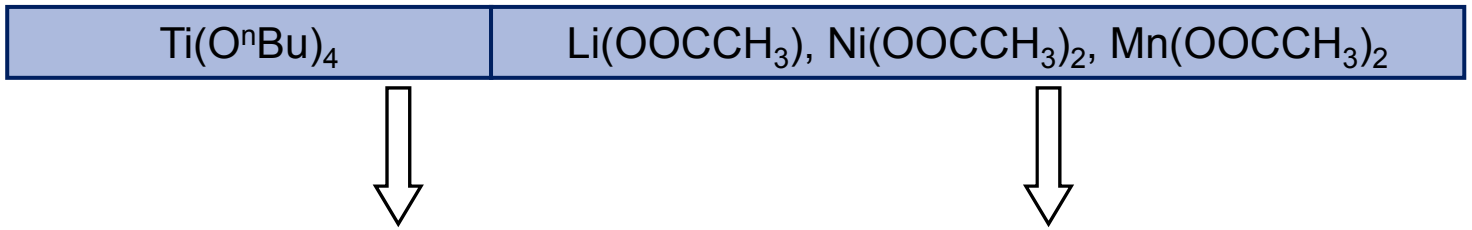
T_1 = 900°C



T_1 = 800°C

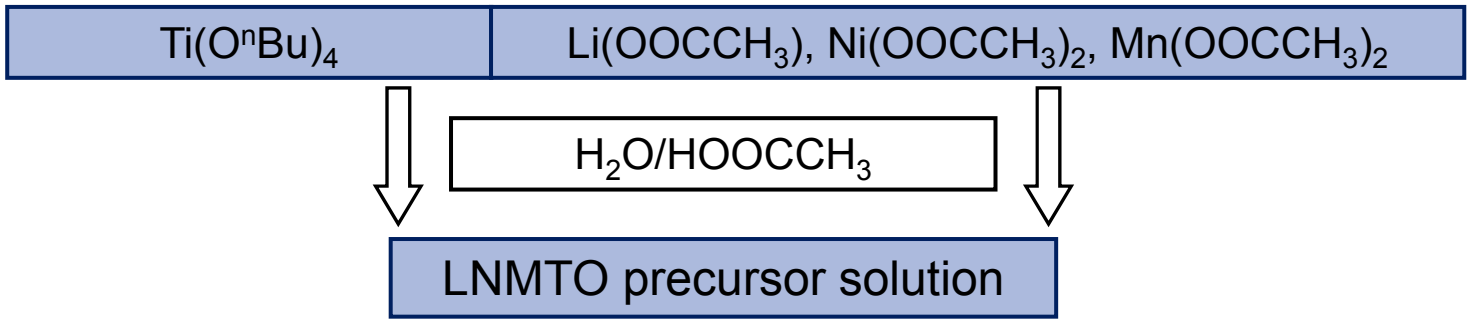
Synthesis/Processing I: *LNMTO-I*

Solutions, no chelating additives



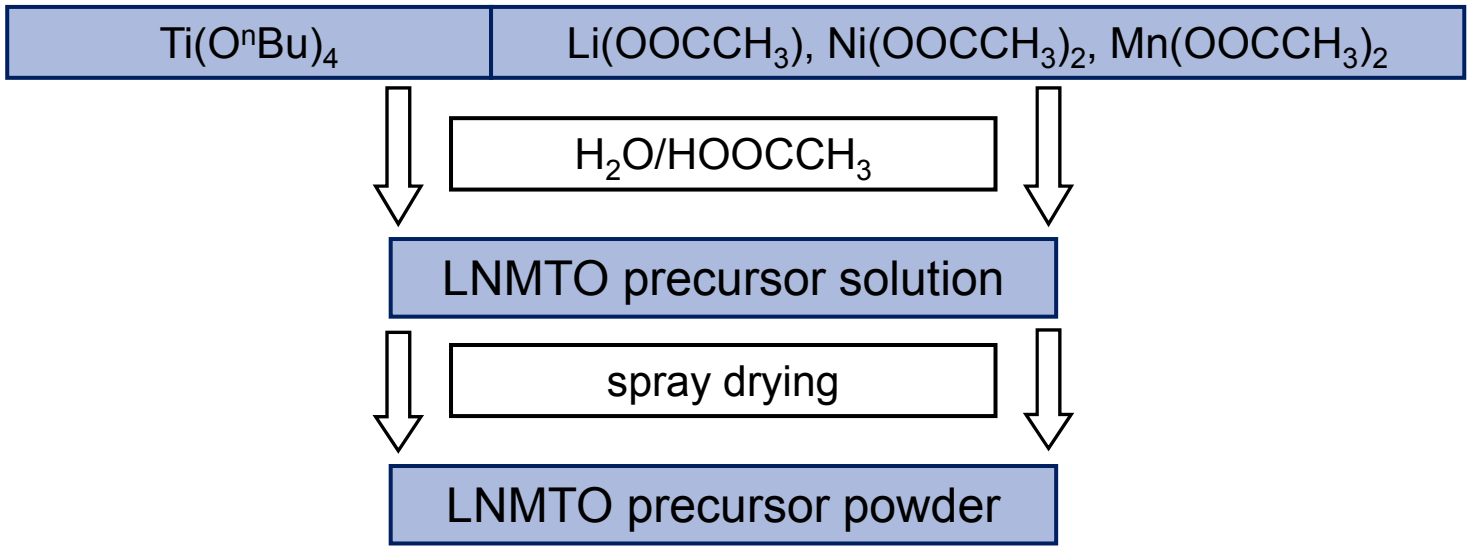
Synthesis/Processing I: *LNMTO-I*

Solutions, no chelating additives



Synthesis/Processing I: *LNMTO-I*

Solutions, no chelating additives



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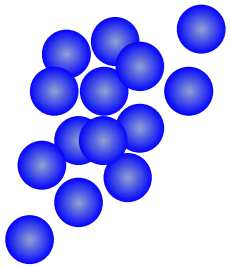
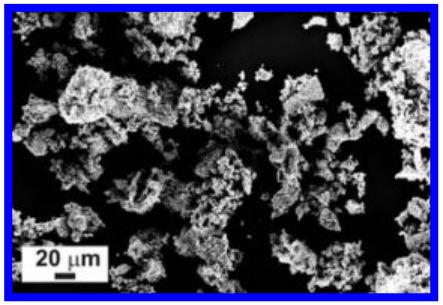
Solutions, no chelating additives



$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-I)



$Ti(O^nBu)_4$ | $Li(OOCCH_3)$, $Ni(OOCCH_3)_2$, $Mn(OOCCH_3)_2$

↓ $H_2O/HOOCCH_3$ ↓

LNMTO precursor solution

↓ spray drying ↓

LNMTO precursor powder

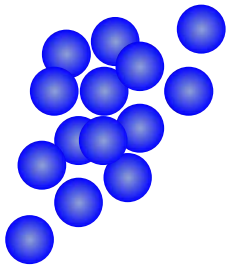
↓ **T_1 = 800°C**

$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-I)

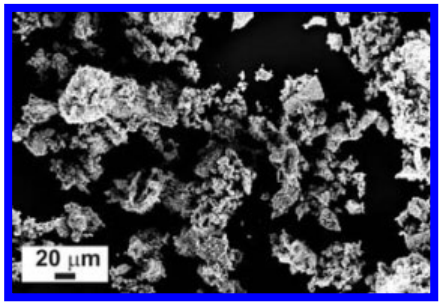
5V doped cathode material

Synthesis/Processing I: *LNMTO-I*

Solutions, no chelating additives



$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-I)



$Ti(O^nBu)_4$ | $Li(OOCCH_3)$, $Ni(OOCCH_3)_2$, $Mn(OOCCH_3)_2$

$H_2O/HOOCCH_3$

LNMTO precursor solution

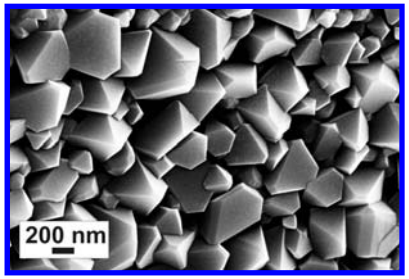
spray drying

LNMTO precursor powder

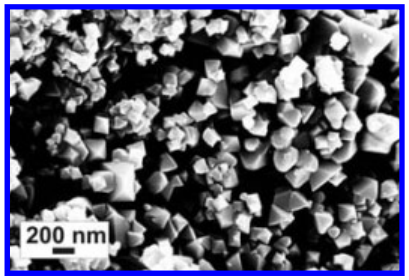
T_1 = 800°C

$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-I)

5V doped cathode material

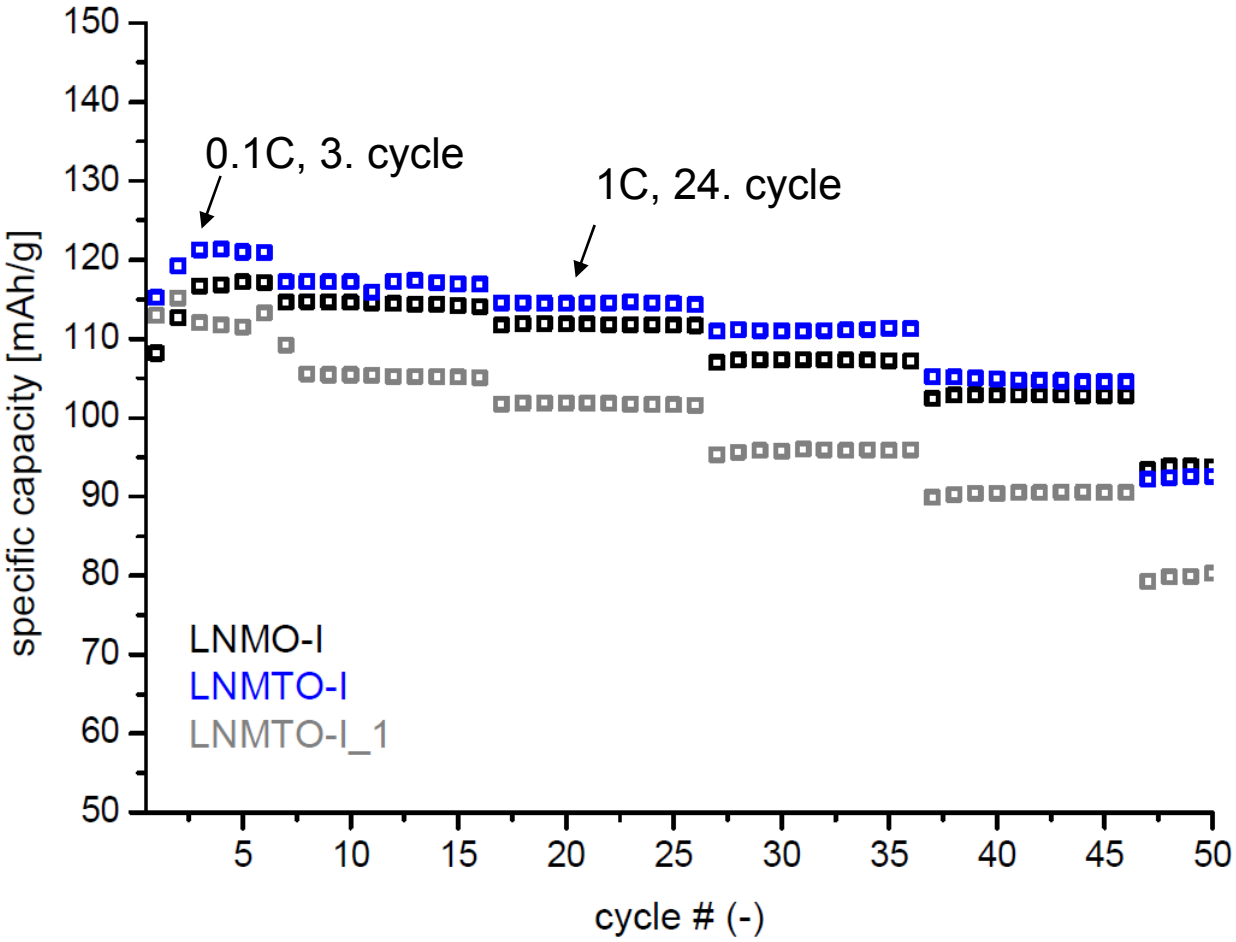


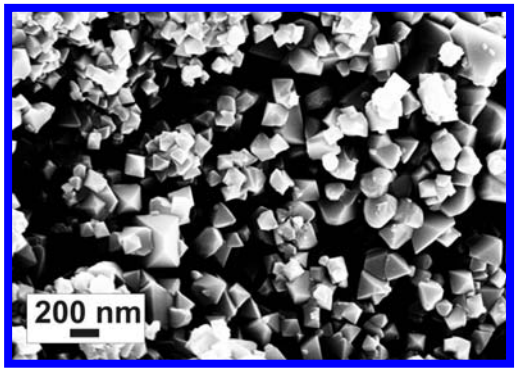
x = 0.3



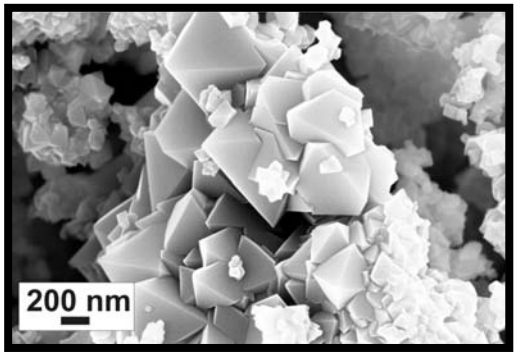
x = 0.04

LNMO-I ($LiNi_{0.5}Mn_{1.5}O_4$) **vs.** ***LNMTO-I*** ($LiNi_{0.5}Mn_{1.46}Ti_{0.04}O_4$)



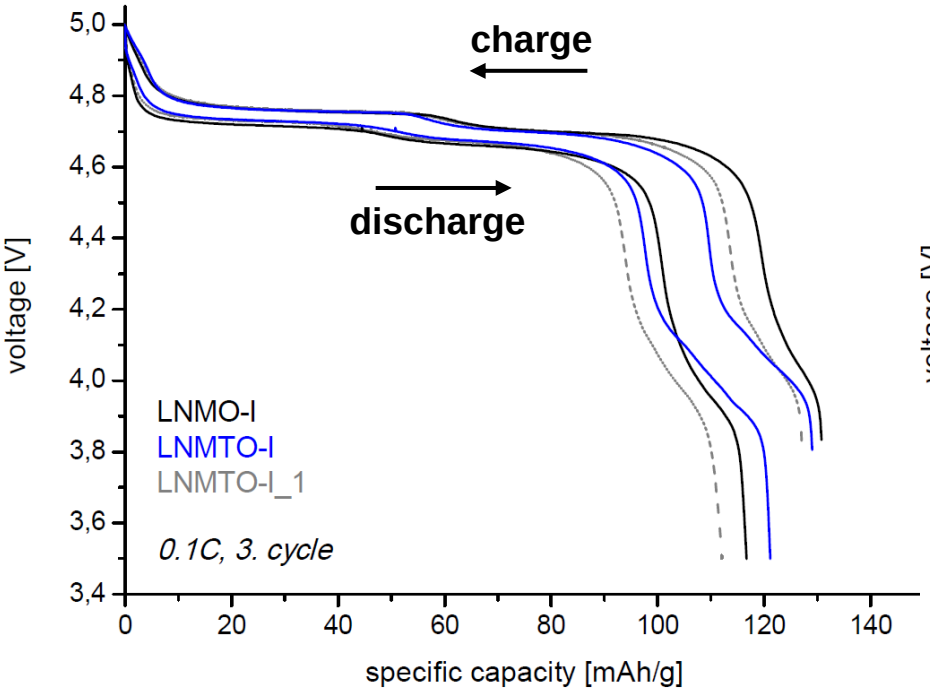


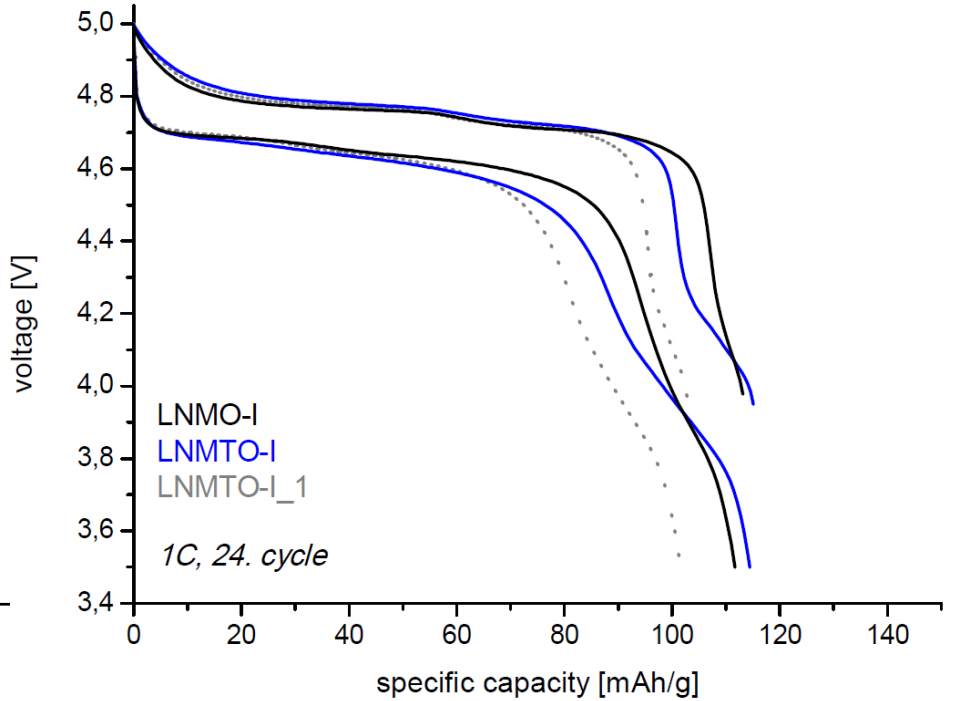
$LiNi_{0.5}Mn_{1.46}Ti_{0.04}O_4$



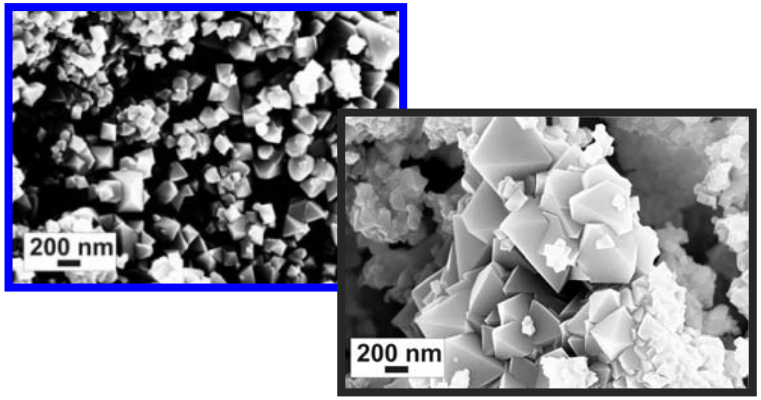
$LiNi_{0.5}Mn_{1.5}O_4$

LNMO-I vs. *LNMTO-I*: Ti-Doping provides (sometimes) higher capacities

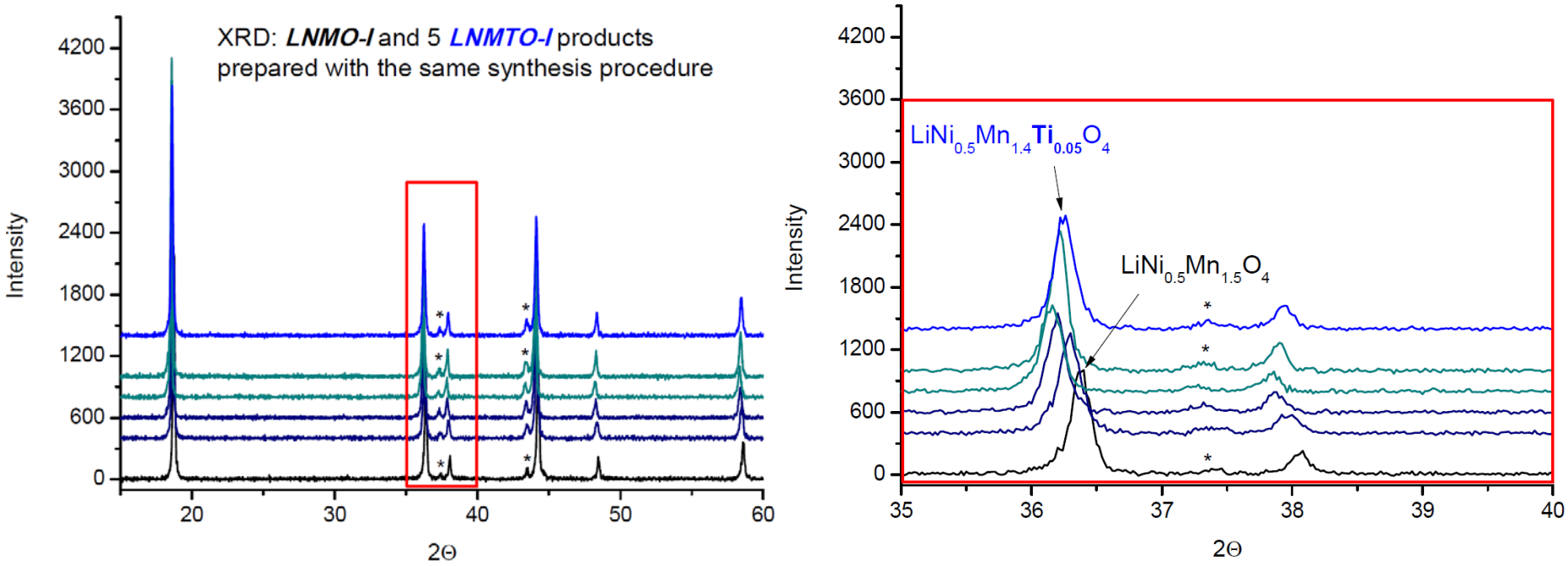




material	spec. surface (BET) [m^2/g]	d_{BET} [nm]	porosity [%]
LNMO-I	4.1-4.6	300-330	38
LNMTO-I	3.6-3.9	360-380	20-25



Simple synthesis: variable chemical composition!



- Substitution of Mn^{4+} with larger Ti^{4+} cations, more or less reflex shift to lower 2Θ values: ***variable degree of Titanium doping***
- Impurity phases

Summary I

- ***Synthesis/Processing I***

Ti-doping has a significant influence on particle morphology and cycling performance (in principle)

- ***Problem***

Slight variations of the chemical composition of Ti doped spinel materials, impurity phases

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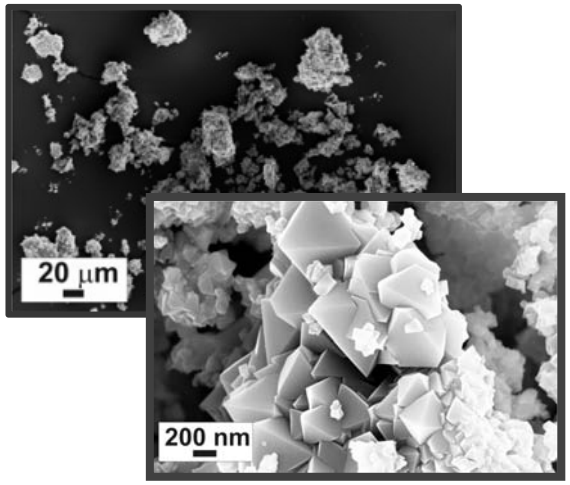
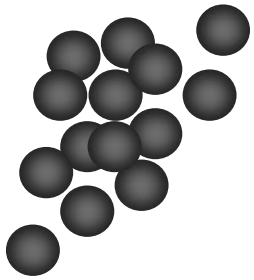
- ***Electrochemical performance***
  A comparison of *LNMO* and *LNM**T**O* materials

Synthesis/Processing II: *LNMO-II*

Particle processing



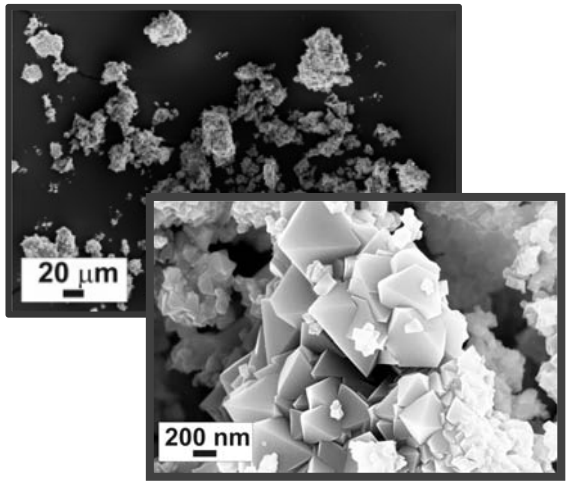
$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)

Synthesis/Processing II: *LNMO-II*

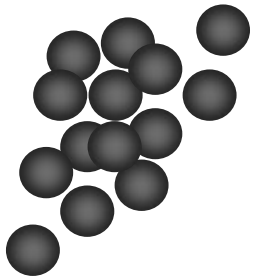
Particle processing



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material

ball milling/CH_3CH_2OH

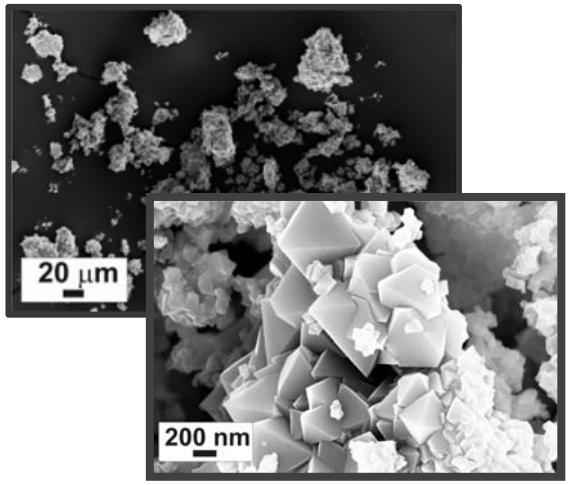
dispersion/feedstock
(cathode/CH_3CH_2OH)



$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-I)

Synthesis/Processing II: *LNMO-II*

Particle processing



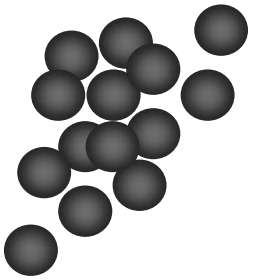
$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material

ball milling/CH_3CH_2OH

dispersion/feedstock
(cathode/CH_3CH_2OH)

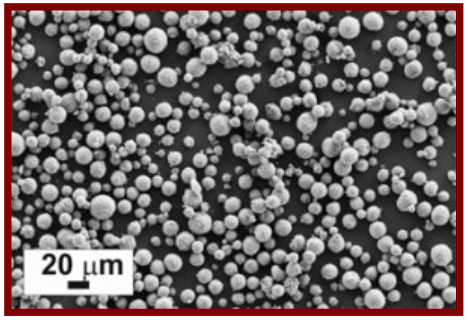
spray drying

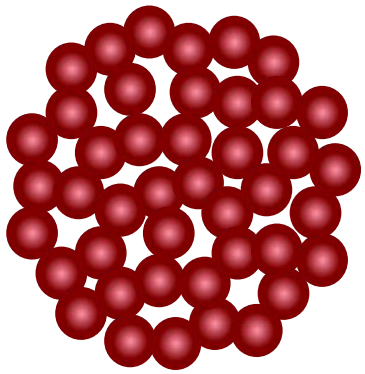
granules/agglomerates



$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-I)

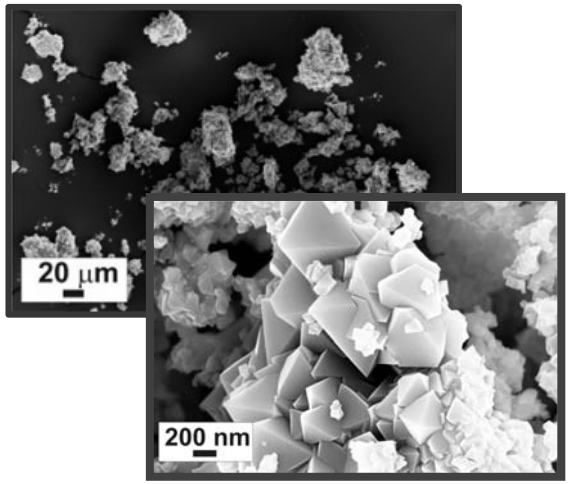
$LiNi_{0.5}Mn_{1.5}O_4$
LNMO-II



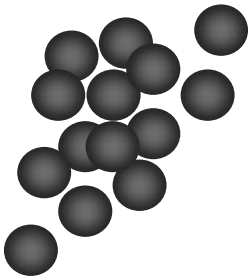


Synthesis/Processing II: *LNMO-II*

Particle processing



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material



$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-I)

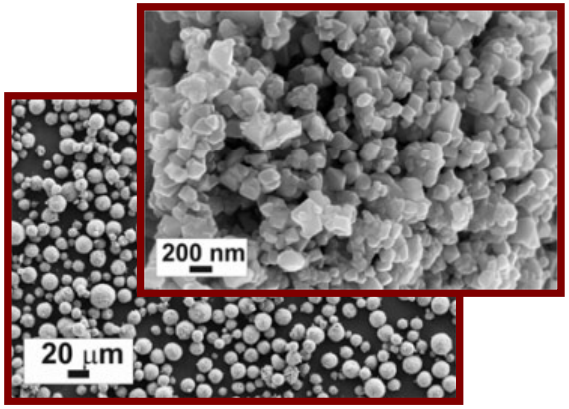
ball milling/CH_3CH_2OH

dispersion/feedstock
(cathode/CH_3CH_2OH)

spray drying

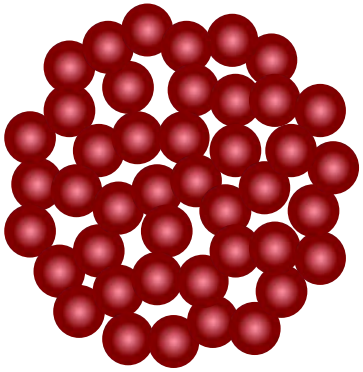
granules/agglomerates

T_2 = 780°C

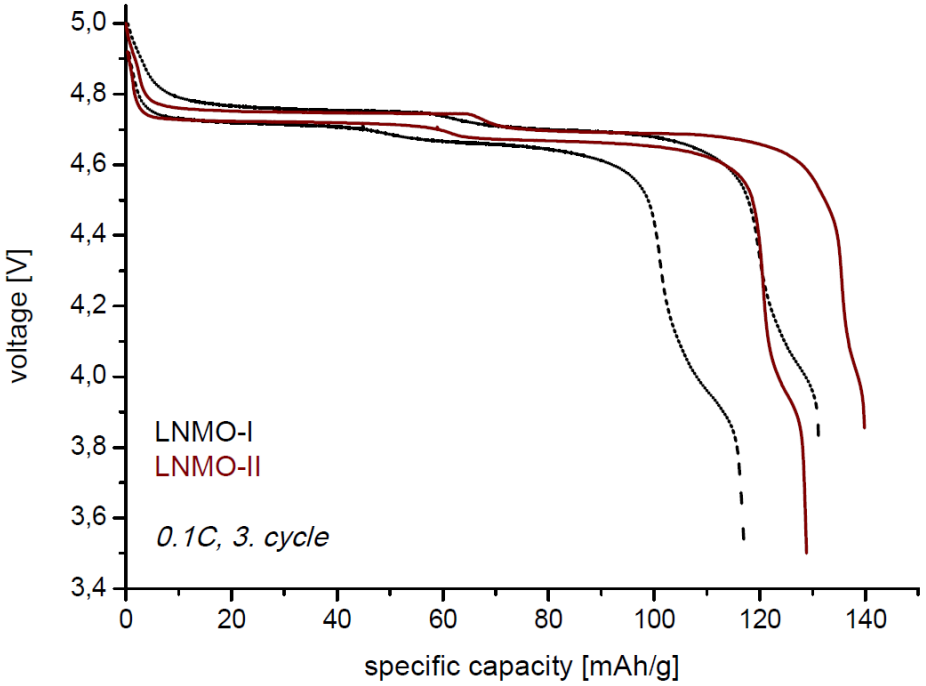


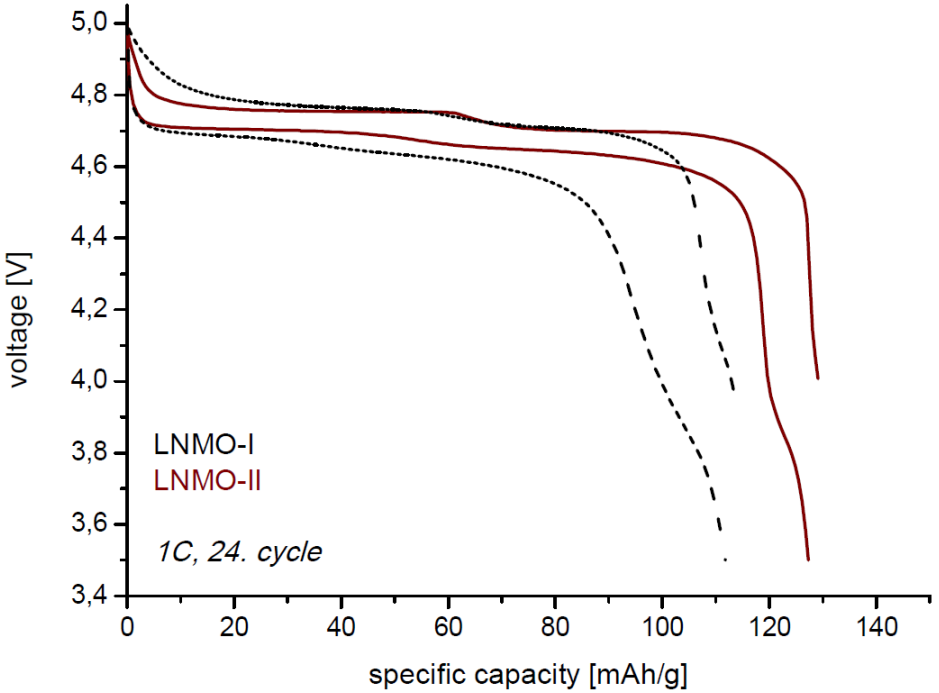
sintered granules
$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-II)
5V cathode material

$LiNi_{0.5}Mn_{1.5}O_4$
LNMO-II

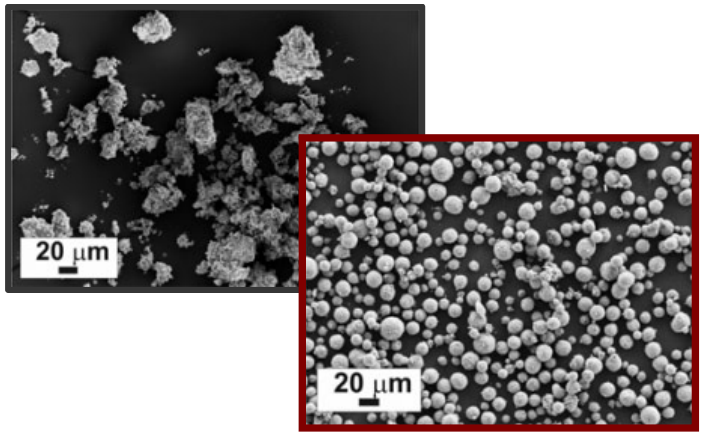


LNMO-I vs. *LNMO-II*: particle processing improves cathode performance



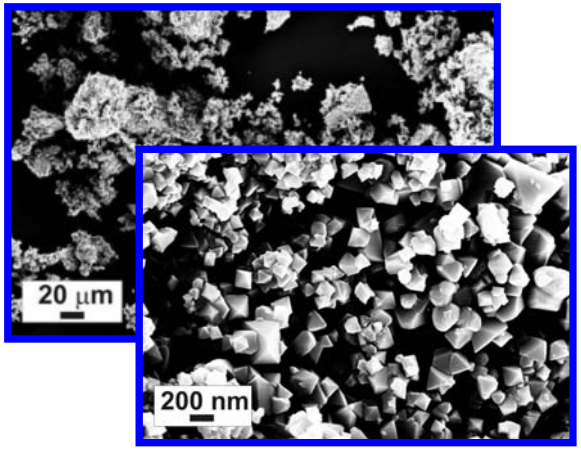


material	cap. [mAh/g] @ 0.1C	cap. [mAh/g] @ 1C	capacity retention [%]
LNMO-I	117	112	95
LNMO-II	129	127	98



Synthesis/Processing II: *LNMTO-II*

Particle processing



$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-I)
5V doped cathode material

ball milling/CH_3CH_2OH

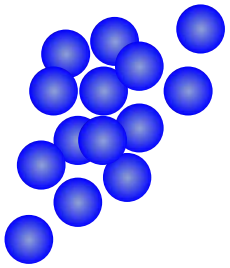
dispersion/feedstock
(cathode/CH_3CH_2OH)

spray drying

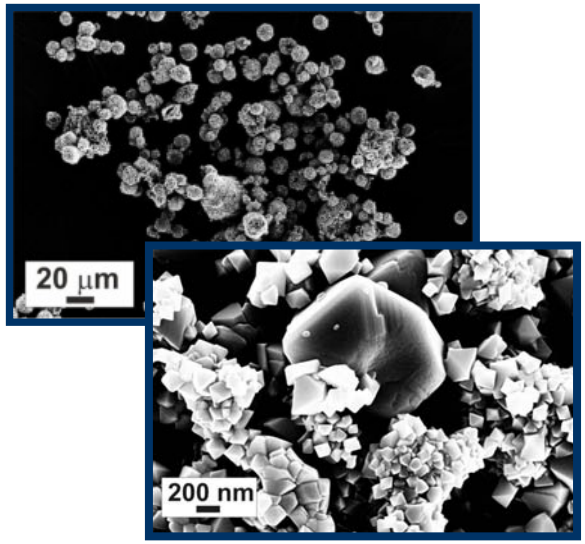
granules, agglomerates

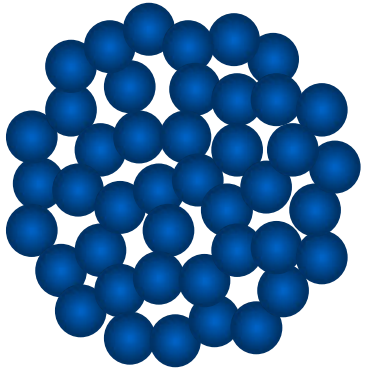
T_2 = 780°C

sintered granules
$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-II)
5V doped cathode material



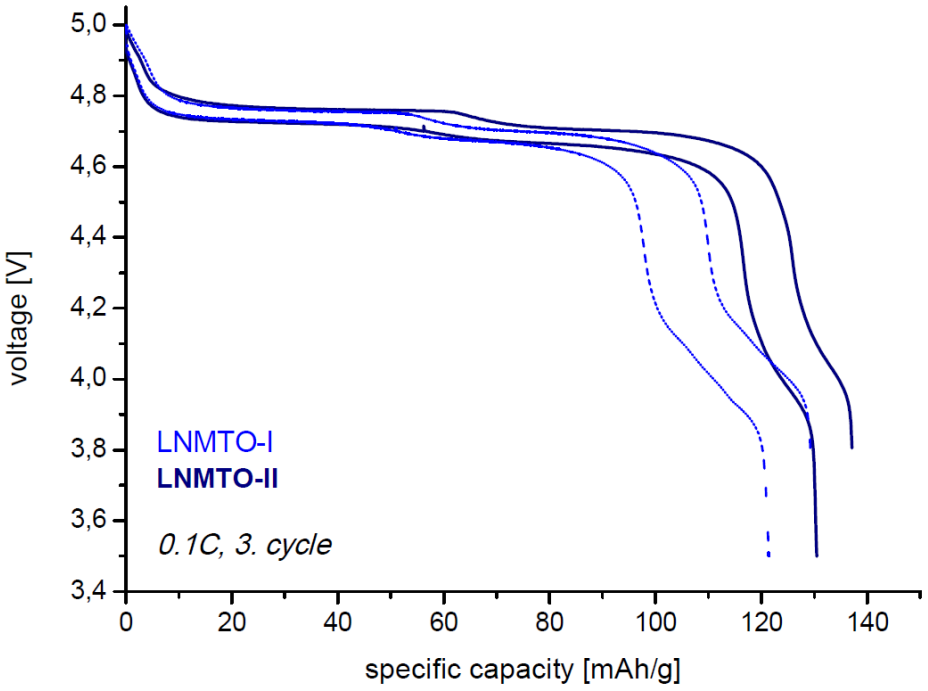
$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ (LNMTO-I)

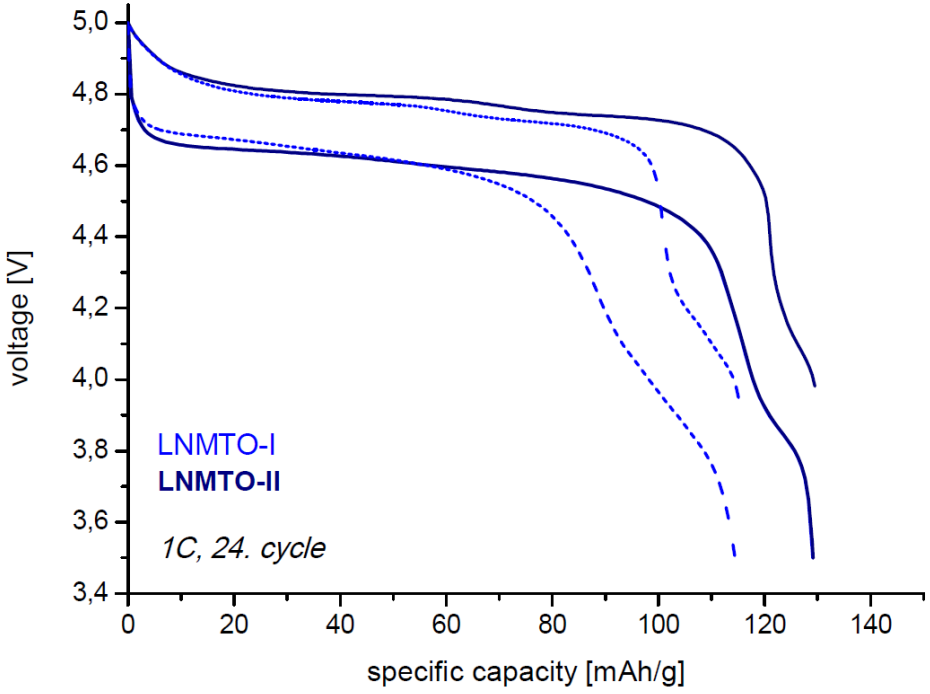




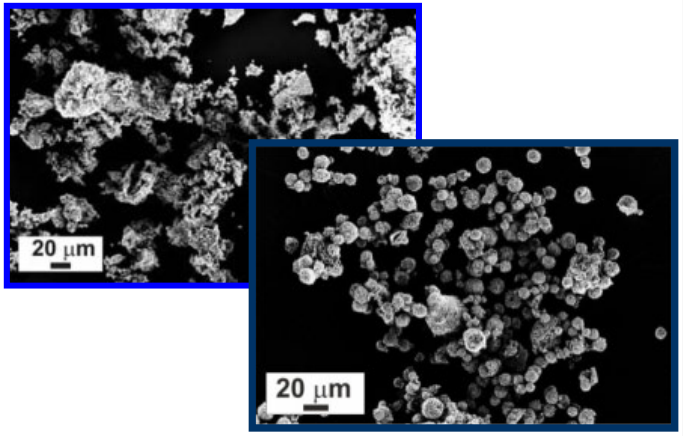
LNMTO-II

LNMTO-I vs. *LNMTO-II*: particle processing improves cathode performance

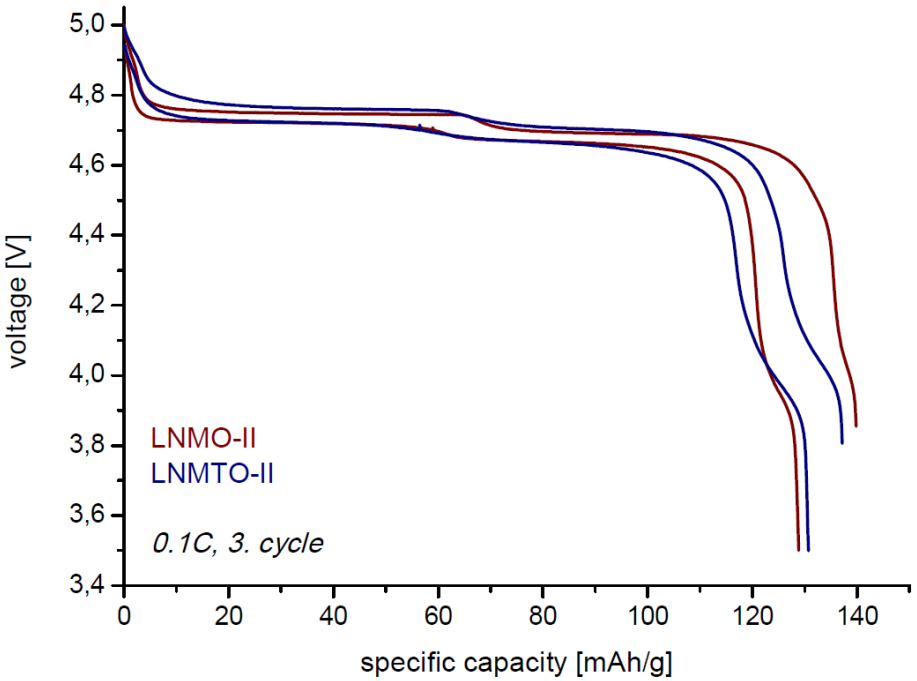


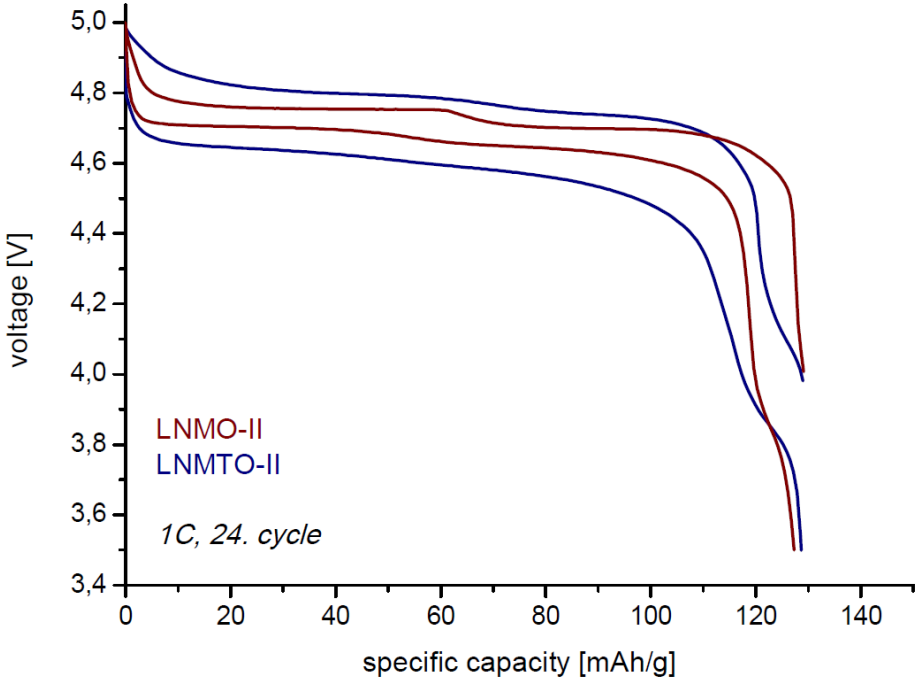


material	cap. [mAh/g] @ 0.1C	cap. [mAh/g] @ 1C	capacity retention [%]
LNMTO-I	121	114	94
LNMTO-II	130	129	99

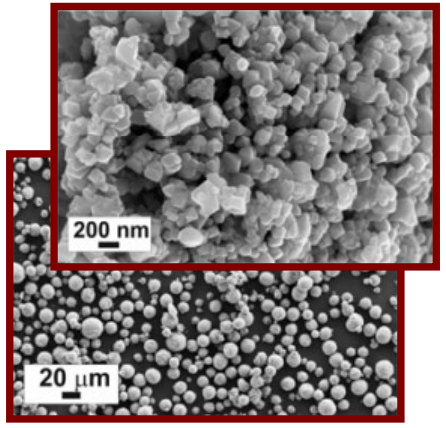


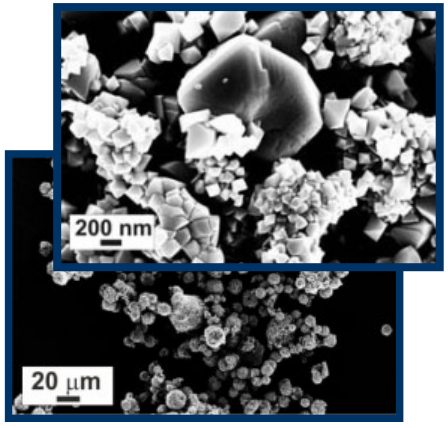
LNMO-II vs. *LNMTO-II*: particle processing is the dominant effect





material	spec. surface (BET) [m^2/g]	d_{BET} [nm]	porosity [%]
LNMO-II	5.7-6.1	230-240	35
LNMTO-II	4.3-5.9	230-325	22-30





Summary II: particle processing improves cathode performance

- ***Synthesis/Processing II***

Higher capacity (~ 12-15%, 15-20 mAh/g) and rate capability due to particle processing

- ***LNMTO-II***

Particle processing compensates variations in the chemical composition (impurity phases)

- Ti doping has a significant influence on the microstructure (interaction with electrolyte!)

How to utilize Titanium doping AND processing effect? (reproducible cathode performance!!)

How to utilize Titanium doping AND processing effect?
(reproducible cathode performance!!)

Remember LNMO-I material (117 mAh/g@0.1C)...

Outline

- ***Introduction***
  Improvement of $LiNi_{0.5}Mn_{1.5}O_4$ (*LNMO*) cathode performance using Titanium doping and particle/powder processing (granulation)

- ***Motivation***
  Understanding doping (I) and particle processing (II) effects

- ***Processing I***
  Synthesis of $LiNi_{0.5}Mn_{1.5}O_4$ (*LNMO-I*) and $LiNi_{0.5}Mn_{1.5-x}\mathbf{Ti_x}O_4$ (*LNM**T**O-I*)

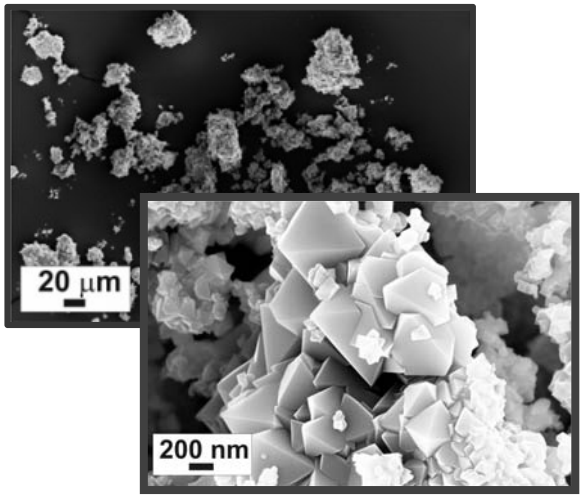
- ***Processing II***
  Granulation of $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{1.5-x}\mathbf{Ti_x}O_4$ powders (*LNMO-II and LNM**T**O-II*)

- ***Processing III***
  „Post-doping“ of $LiNi_{0.5}Mn_{1.5}O_4$ materials: *LNM**T**O-III*

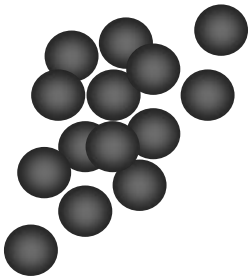
- ***Electrochemical performance***
  A comparison of *LNMO* and *LNM**T**O* materials

Synthesis/Processing III: *LNMTO-III*

Particle processing



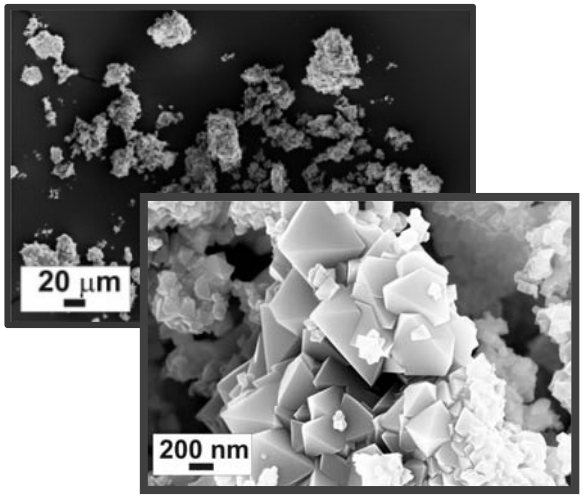
$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)

Synthesis/Processing III: *LNMTO-III*

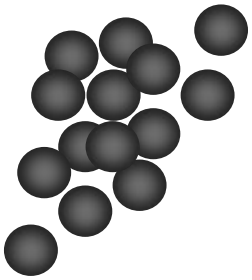
Particle processing



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material

ball milling/CH_3CH_2OH

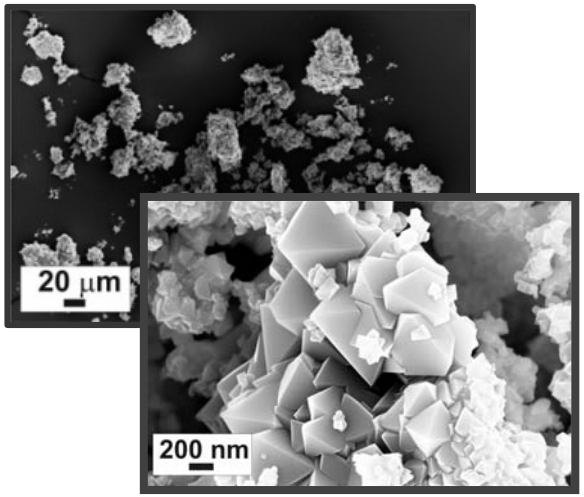
+Ti(^{n}OBu)$_4$
dispersion/feedstock
(cathode/CH_3CH_2OH)



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)

Synthesis/Processing III: *LNMTO-III*

Particle processing



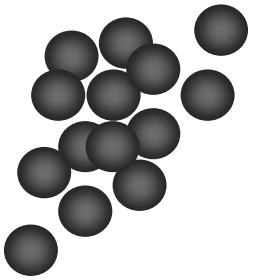
$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material

ball milling/CH_3CH_2OH

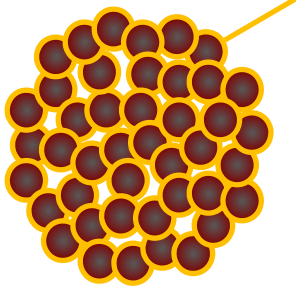
Ti-containing
dispersion/feedstock
(cathode/CH_3CH_2OH)

spray drying

coated granules/
agglomerates

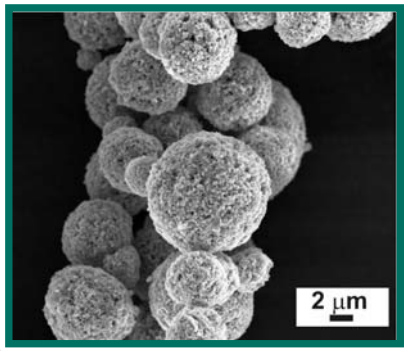


$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-I)



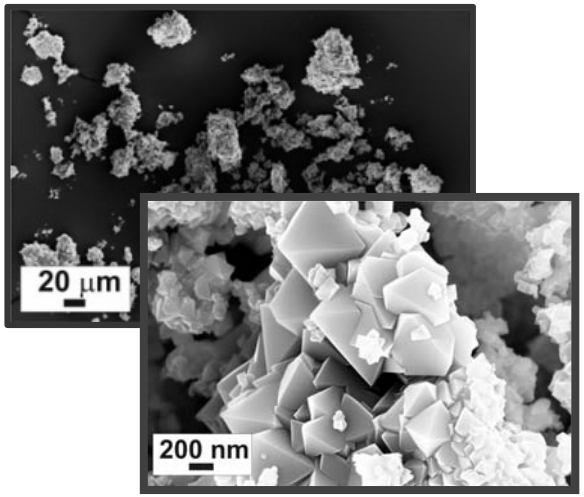
Ti-gel

$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-II)



Synthesis/Processing III: *LNMTO-III*

Particle processing



$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO-I)
5V cathode material

ball milling/CH_3CH_2OH

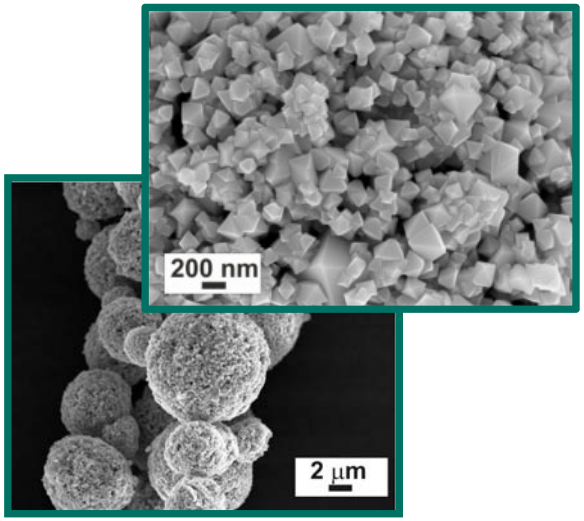
Ti-containing
dispersion/feedstock
(cathode/CH_3CH_2OH)

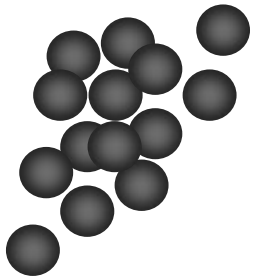
spray drying

coated granules/
agglomerates

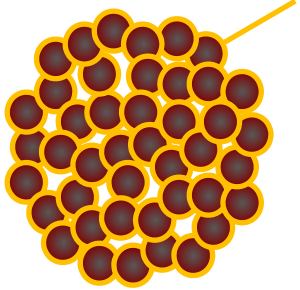
T_2 = 780°C

sintered granules
$LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ LNMTO-III
5V doped cathode material

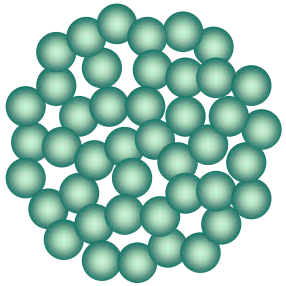




$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-I)

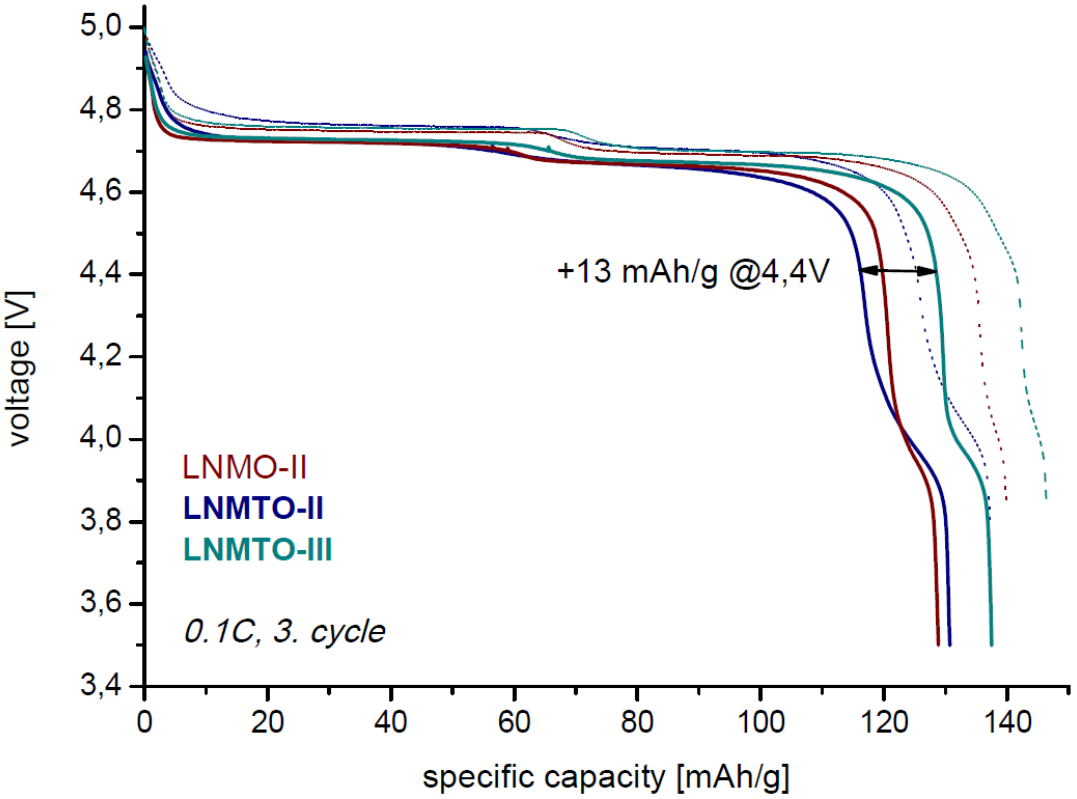


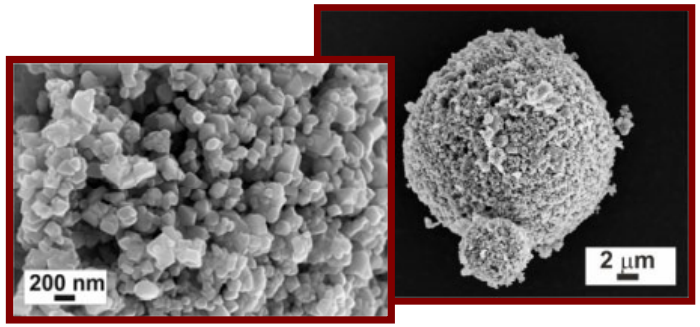
Ti-gel
$LiNi_{0.5}Mn_{1.5}O_4$
(LNMO-II)

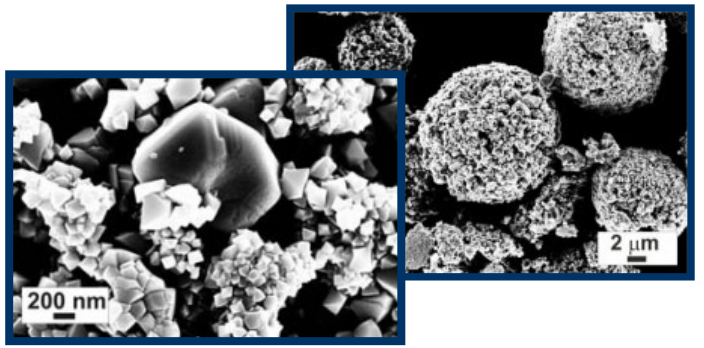


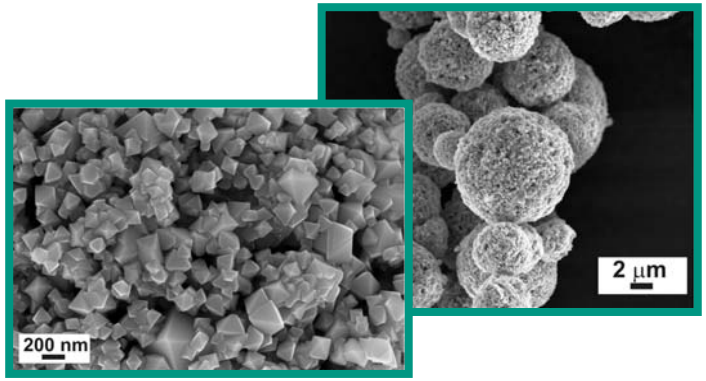
LNMTO-III

LNMO-II vs. *LNMTO-II* vs. *LNMTO-III*

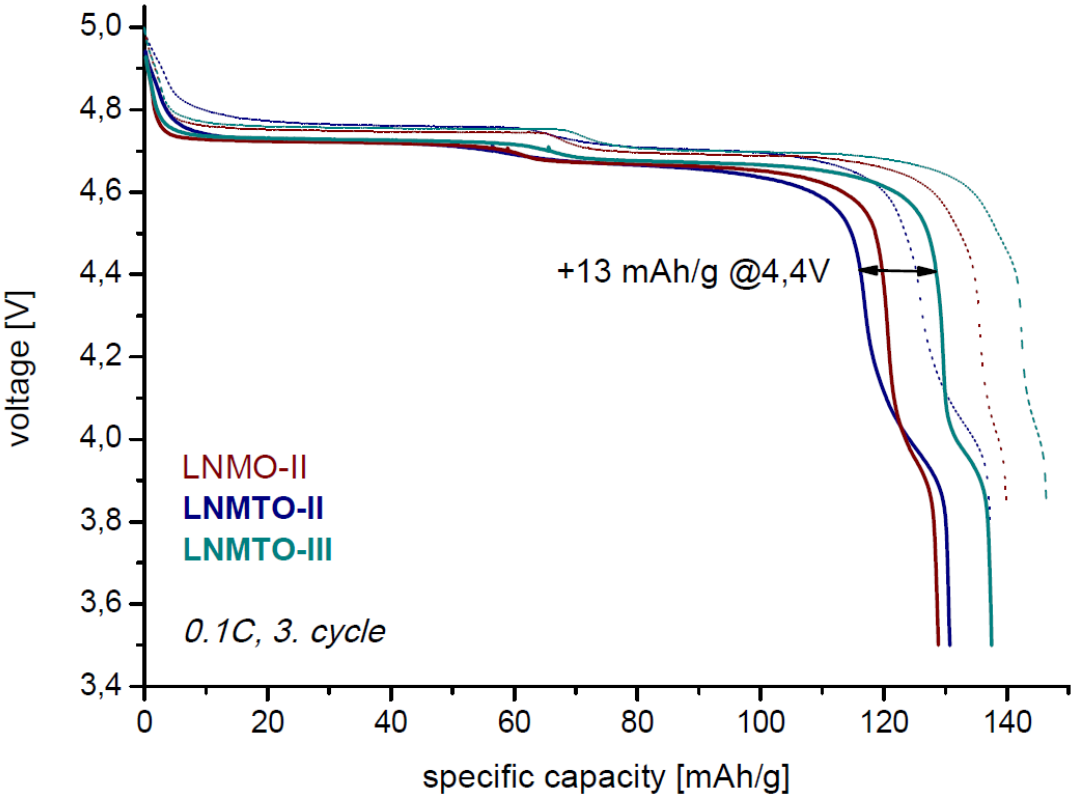


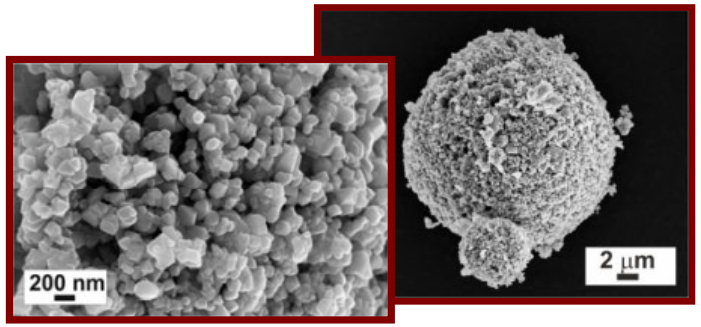


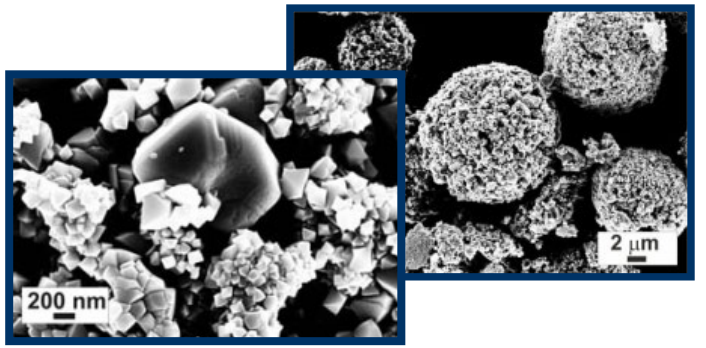


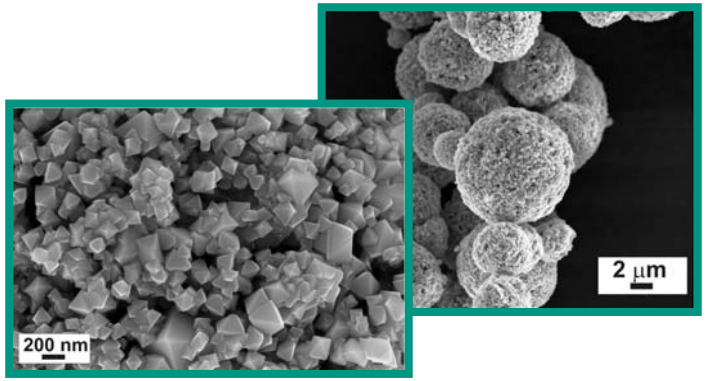


LNMO-II vs. *LNMTO-II* vs. *LNMTO-III*





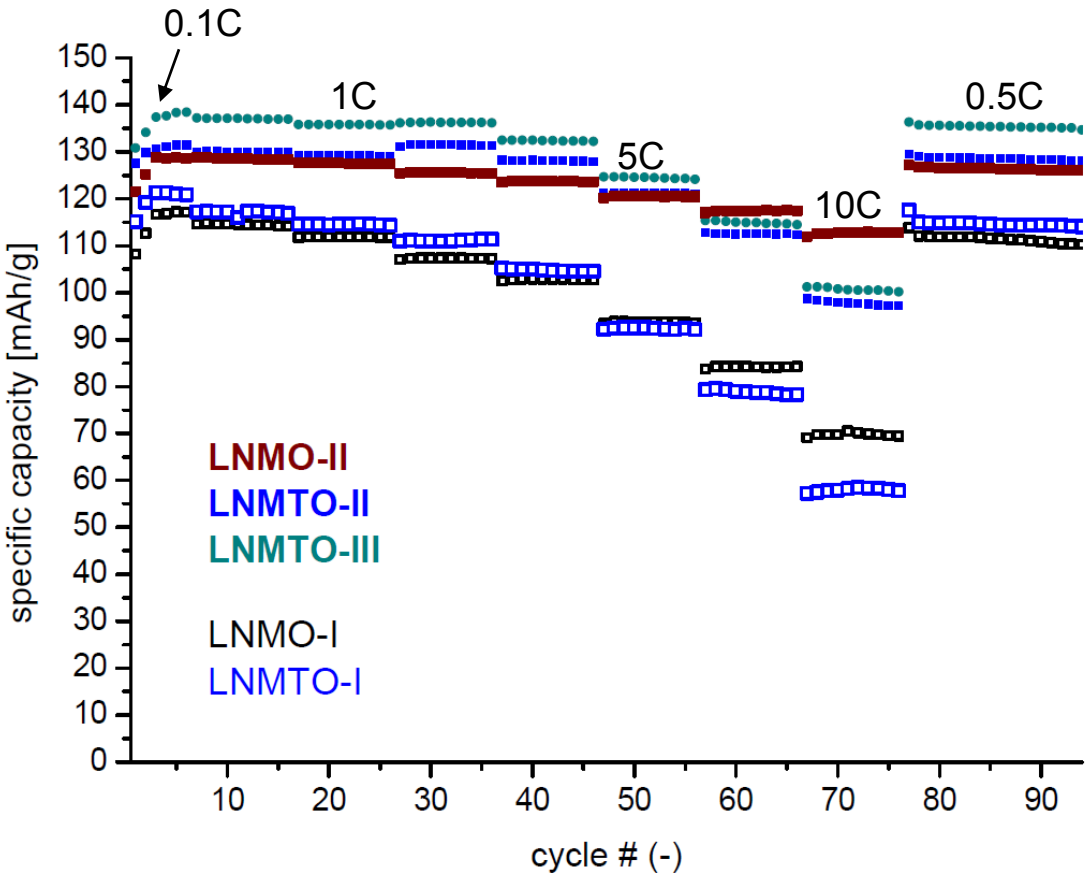




material	spec. surface (BET) [m^2/g]	d_{BET} [nm]	porosity [%]
LNMO-II	5.7-6.1	230-240	35
LNMTO-II	4.3	325	22-30
LNMTO-III	**5.1-5.7**	**240-270**	**42-48**

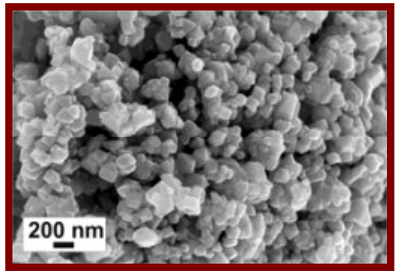
Best of Titanium doped 5V-spinels ($LiNi_{0.5}Mn_{1.46}Ti_{0.04}O_4$)

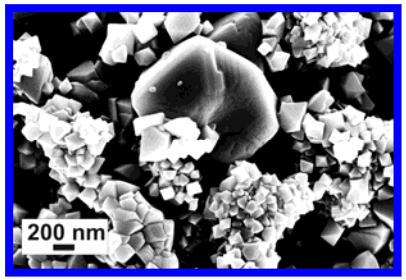
capacities @ 3,5-5,0 V	LNMO-I	LNMTO-I	LNMO-II	**LNMTO-II**	**LNMTO-III**
0.1C, 3. cycle	117 mAh/g	121 mAh/g	129 mAh/g	**130 mAh/g**	**138 mAh/g**
1C, 24. cycle	112 mAh/g	114 mAh/g	127 mAh/g	**129 mAh/g**	**137 mAh/g**

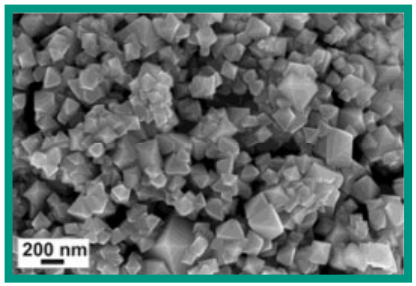


Summary III: *LNMO-II* vs. *LNMTO-II* vs. *LNMTO-III*

- Simple synthesis routes can be implemented using spray drying process and (additional) particle processing
- Particle processing (granulation) has the major influence on the electrochemical performance
- ***To provide materials with uniform morphology and chemical composition, powder processing and synthesis have to be merged: The sequence of synthesis and process steps determines the chemical composition and microstructure of materials and consequently electrode kinetics and power density.***







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