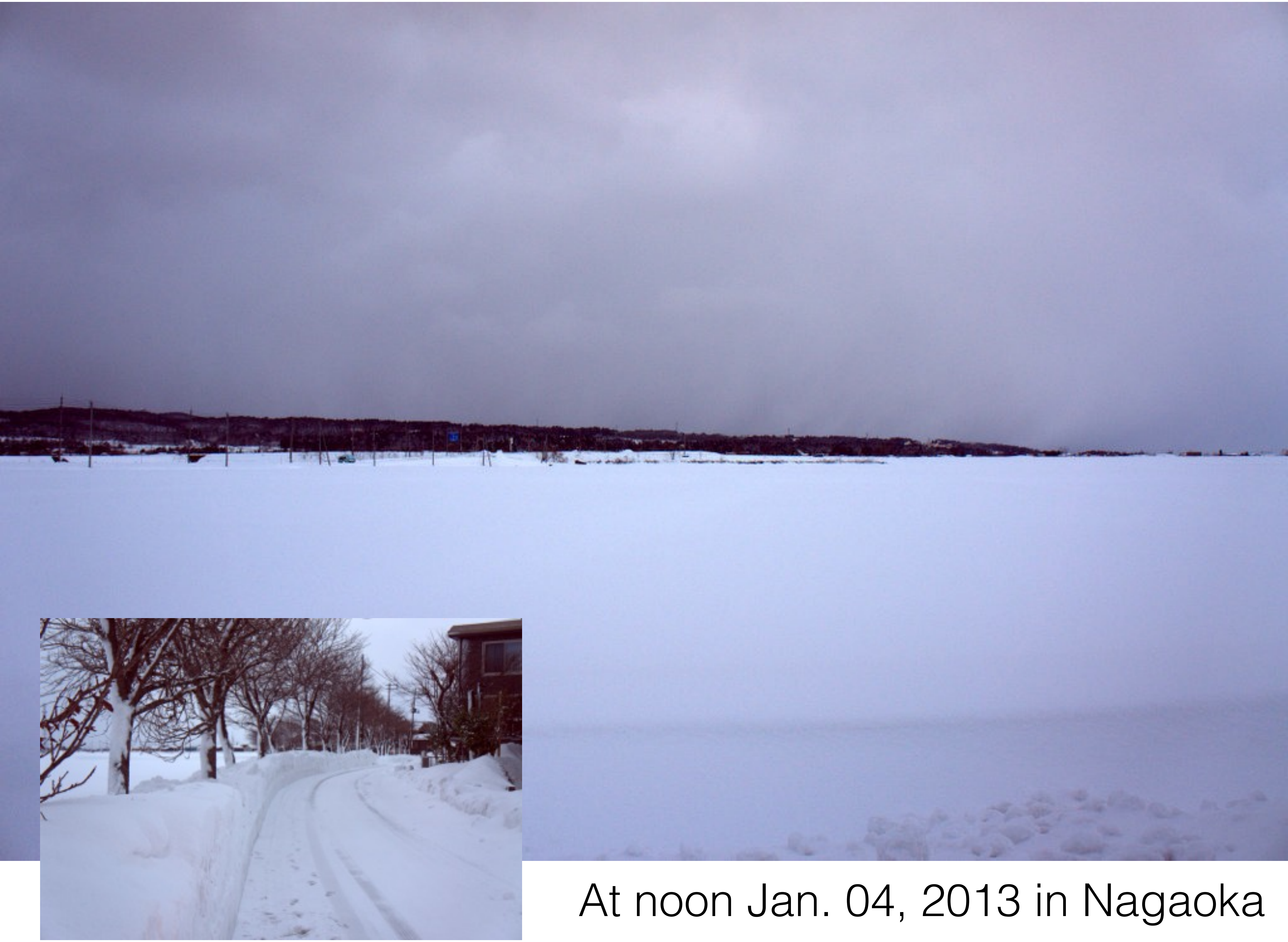


At noon Jan. 04, 2013 in Nagaoka

国立大学法人
長岡技術科学大学
Nagaoka University of Technology

Glass-ceramics for the Innovative Secondary Batteries

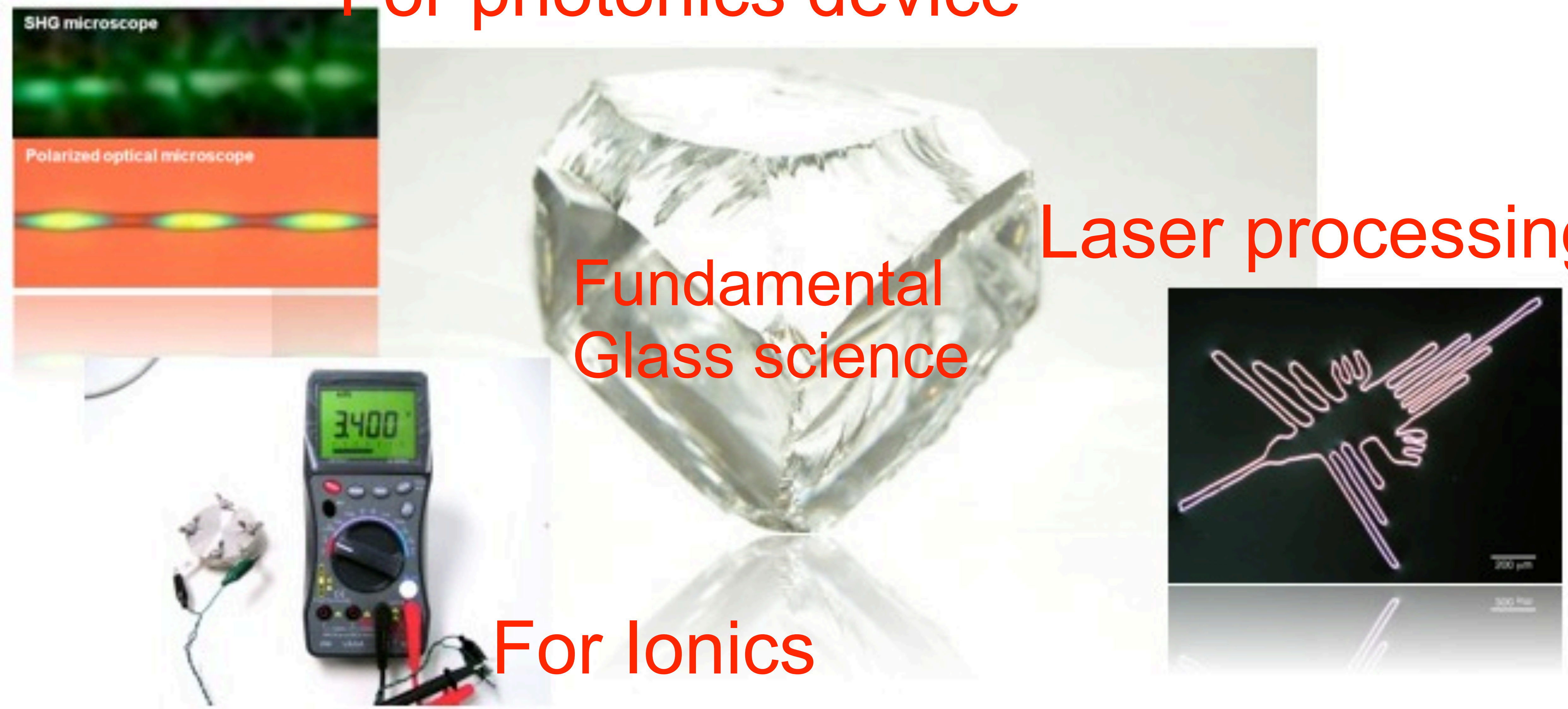
Tsuyoshi Honma

Nagaoka University of Technology

Nagaoka University of Technology
Functional Glass Engineering Laboratory

http://mst.nagaokaut.ac.jp/amorph/en

Focusing on the <u>crystallization</u> phenomena
to produce <u>functional glass</u> products
in <u>non-conventional oxide glass</u> system.

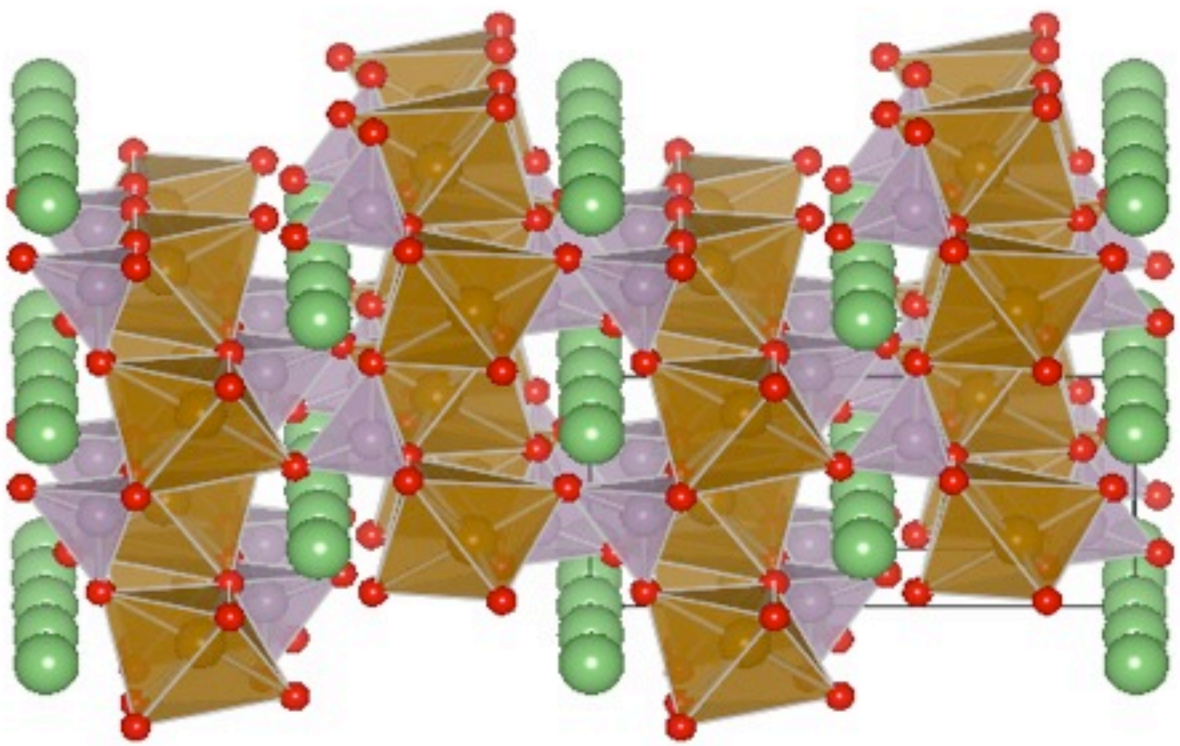


Nagaoka University of Technology
Functional Glass Engineering Laboratory

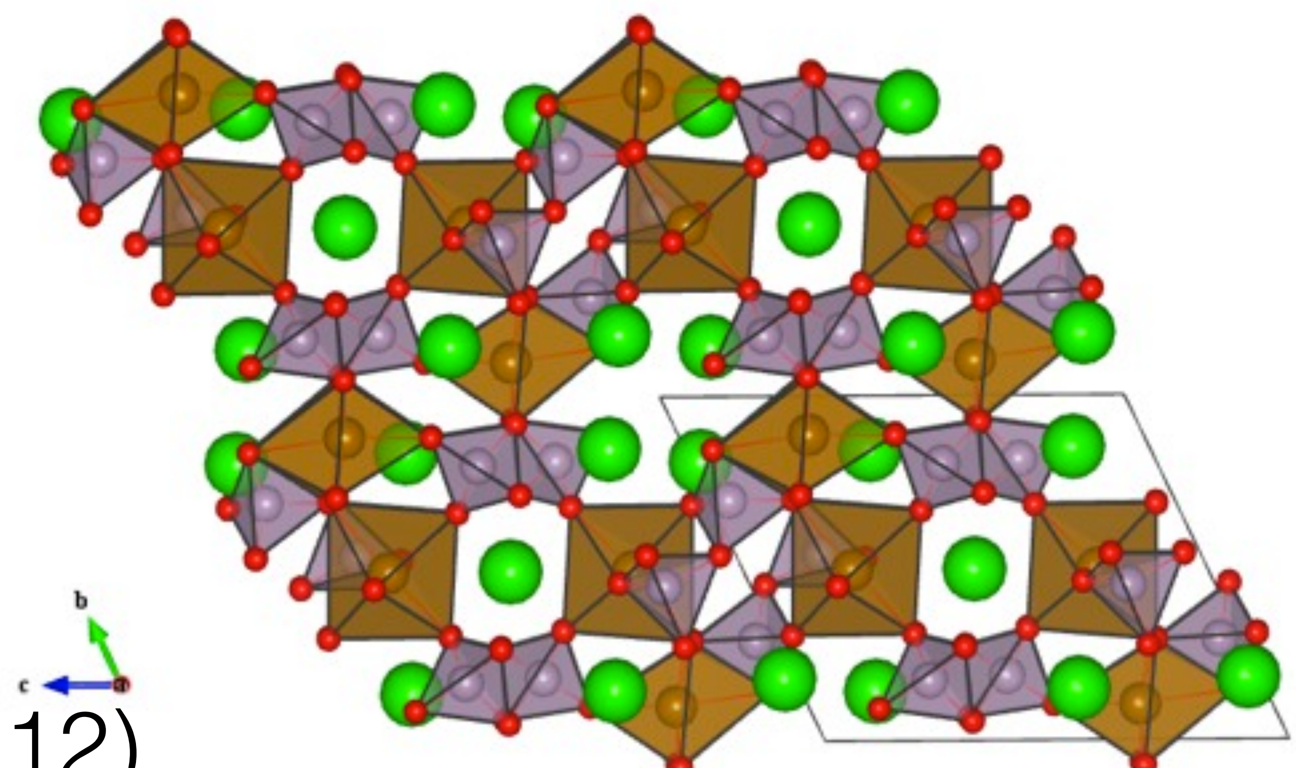
http://mst.nagaokaut.ac.jp/amorph/en

Focusing on the crystallization phenomena
to produce functional glass products
in non-conventional oxide glass system.

We are focusing about



$LiFePO_4$
for Li-ion batteries
by Jhon.B. Goodenough (1997)
J. E. Chem. Soc. 144, 1188(1997) cited 3563



$Na_2FeP_2O_7$
for Na-ion batteries
reported at first by us (2012)

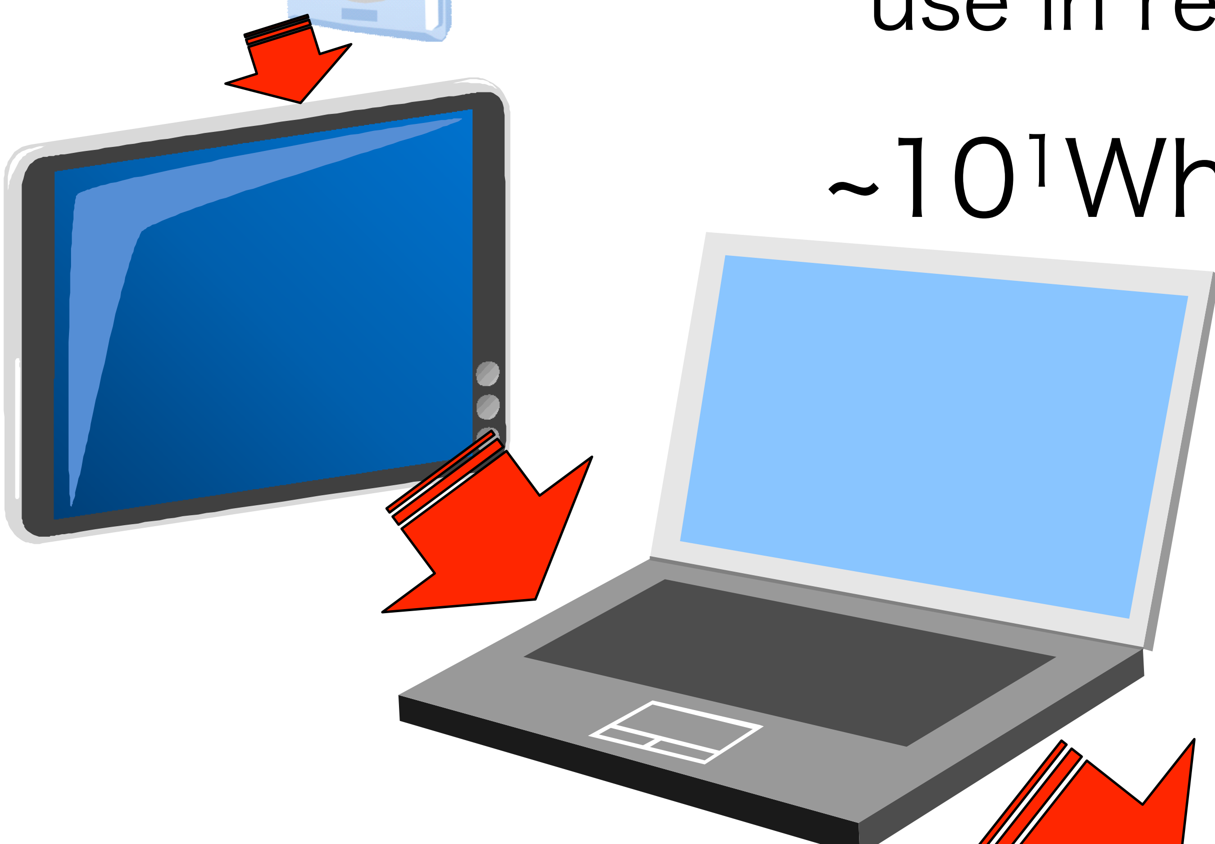
Outline

1. Introduction
   - About Li-ion batteries
     -advantages and the problems
   - Typical cathode active materials
   - Iron phosphate base $LiFePO_4$
2. Glass-ceramics for LiB
   - Sample preparation
   - Properties
3. Sodium ion batteries (NaB)
   - New cathode candidate $Na_2FeP_2O_7$ by glass-ceramics method
   - Battery performance
4. Conclusion

Lithium ion batteries

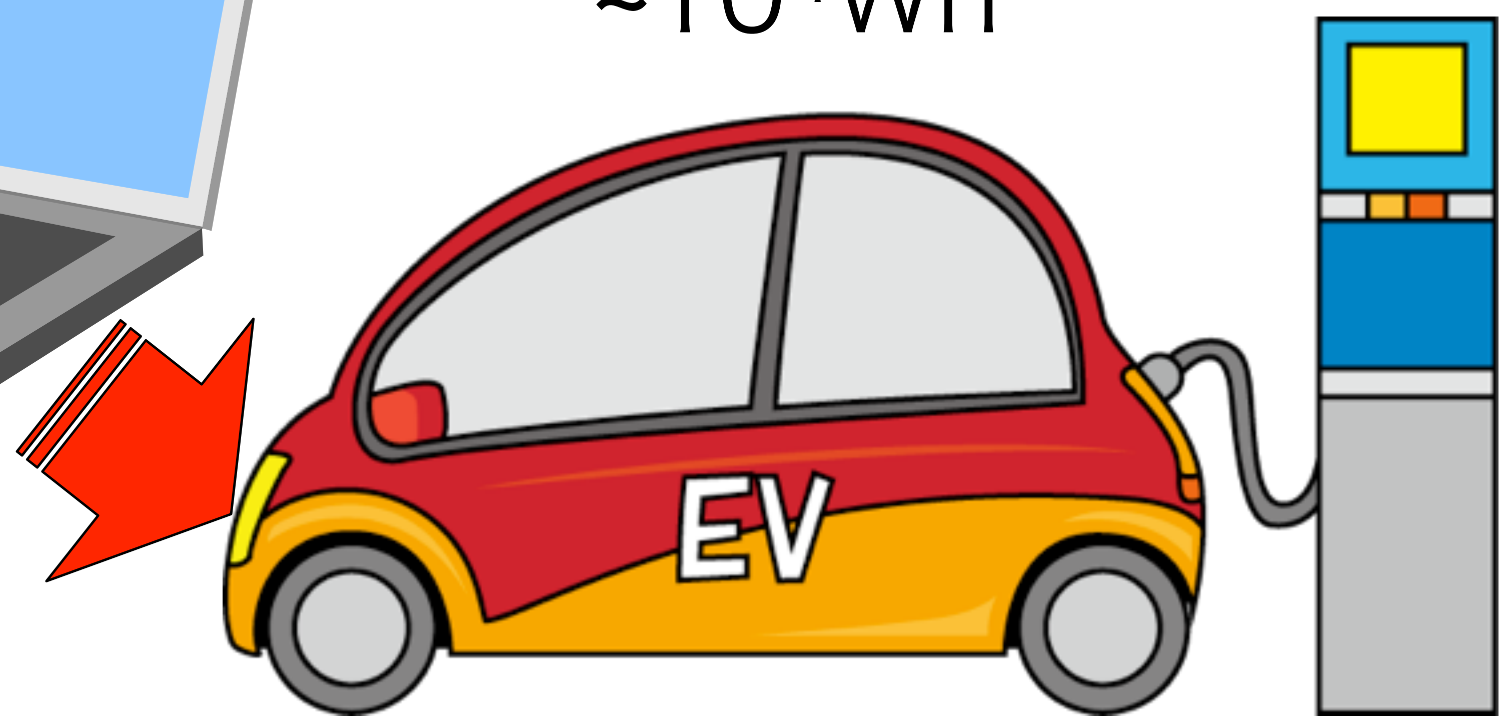
~Wh

Recently, high capacity batteries are required for EV, PHEV and stationary use in residential.



~10^1Wh

~10^4Wh



In residential

~12kWh/day

XEVs

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HV

TOYOTA prius, 1kWh

Plug-in HV(PHV)

TOYOTA priusPHV, 4.4kWh

Plug-in HEV(PHEV)

MITSUBISHI outlander, 12kWh

XEVs

Pure EV

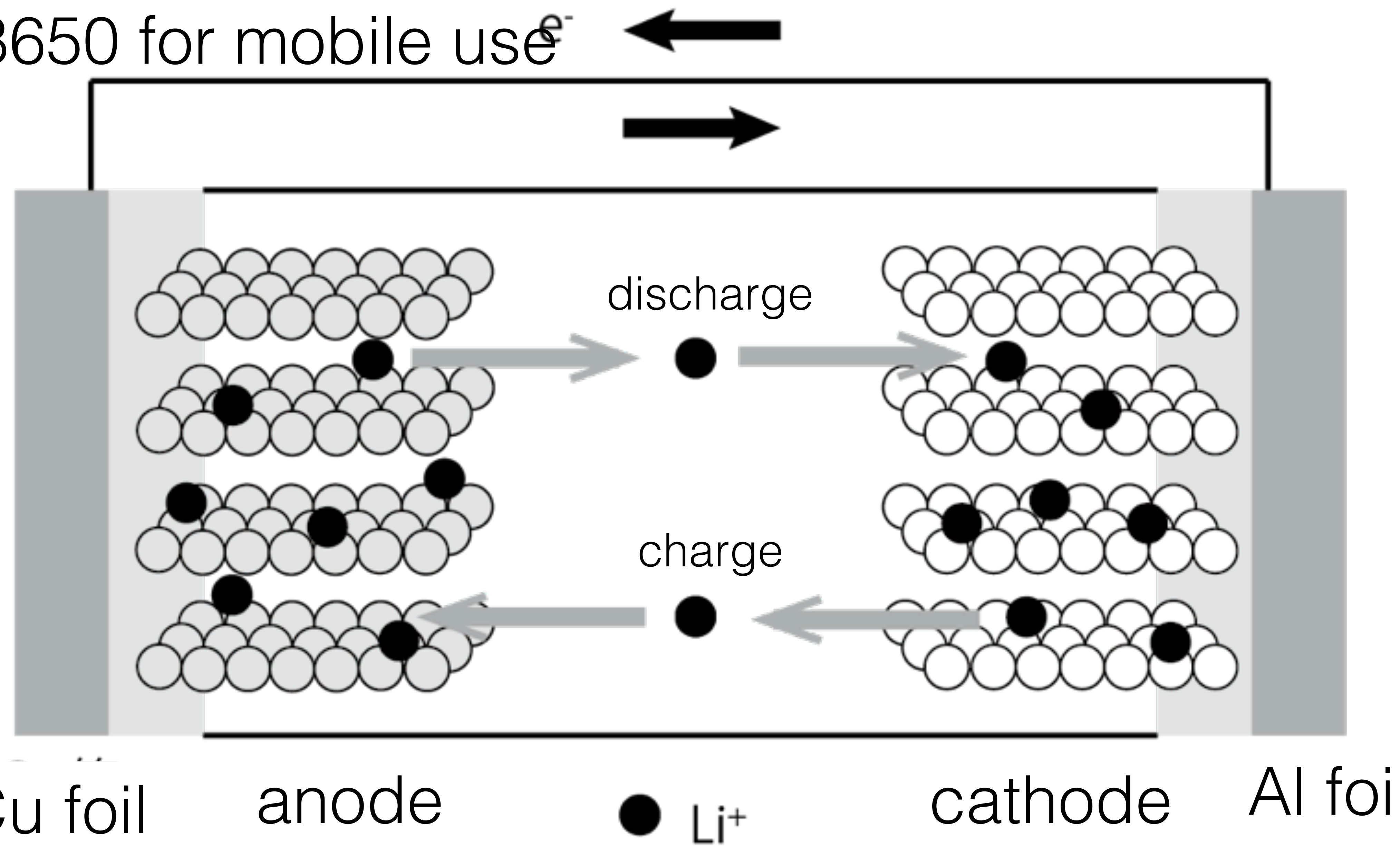
NISSAN LEAF, 24kWh

Tesla Model S, 85kWh

MITSUBISHI
iMIEV, 10.5-16kWh

Structure of Li ion battery

Type 18650 for mobile use



Cathode: $LiCoO_2$ transition metal oxides

Anode: Carbon black

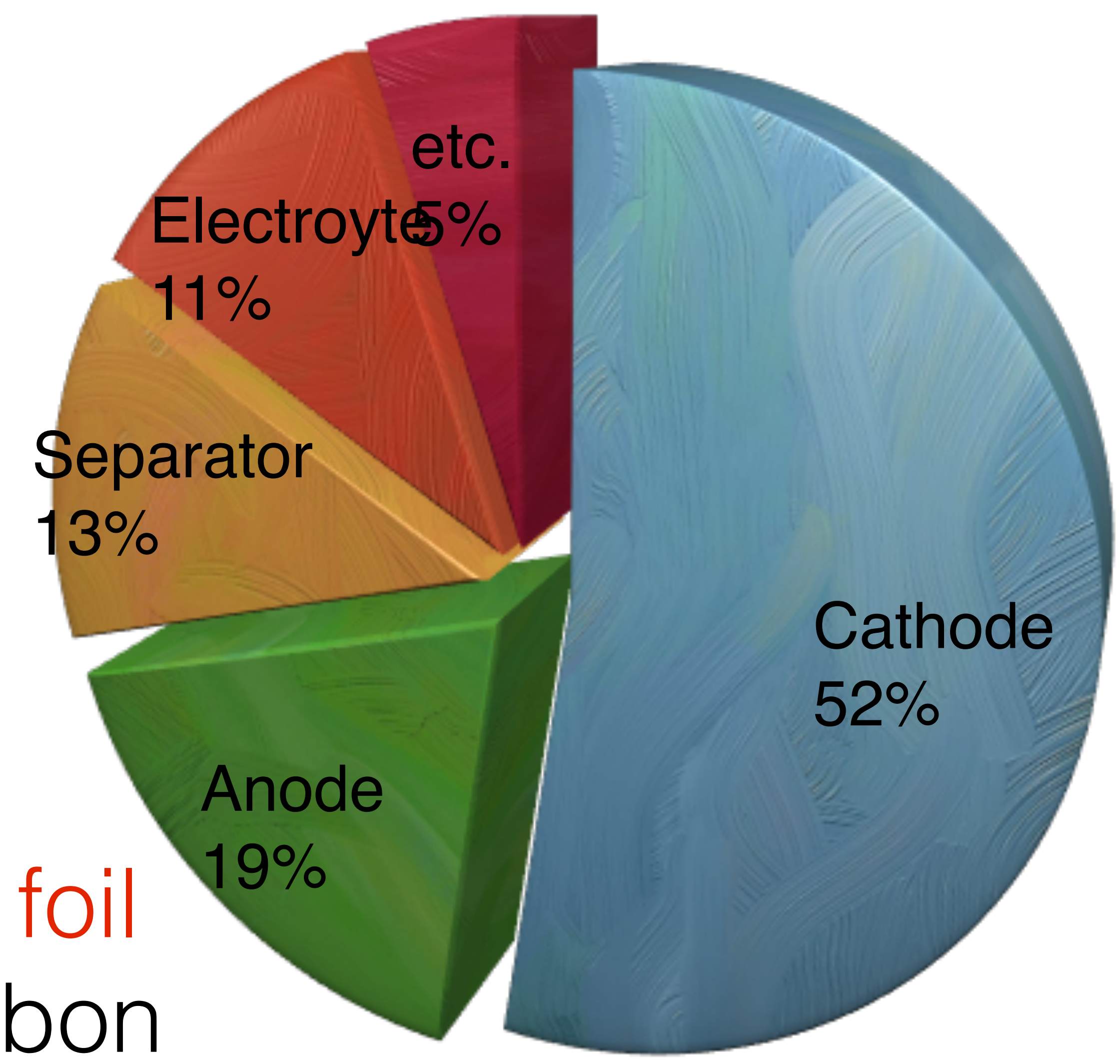
Collector: Al foil for cathode

Cu foil for anode

Breakdown of Materials cost

Materials cost is dominated by electrode

We needs valuable materials with cheap price



Cu foil
Carbon

Co_3O_4
$LiCO_3$
Al foil

http://www.jst-lcs.jp

Typical cathode structure

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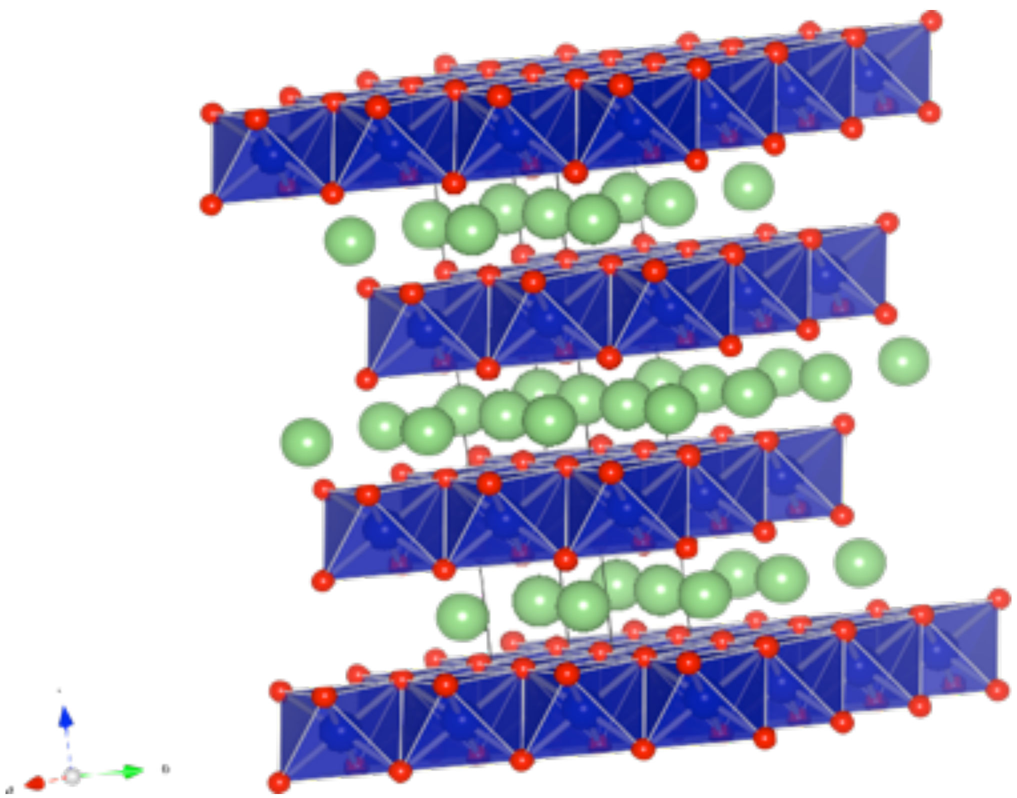
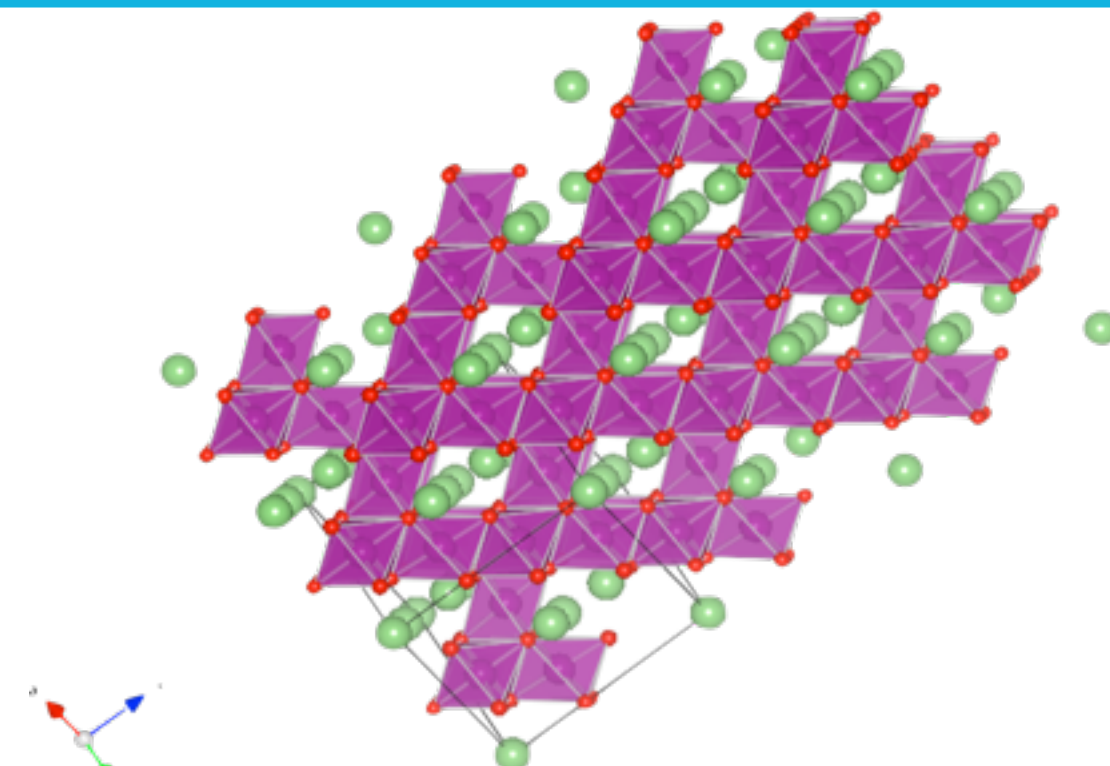
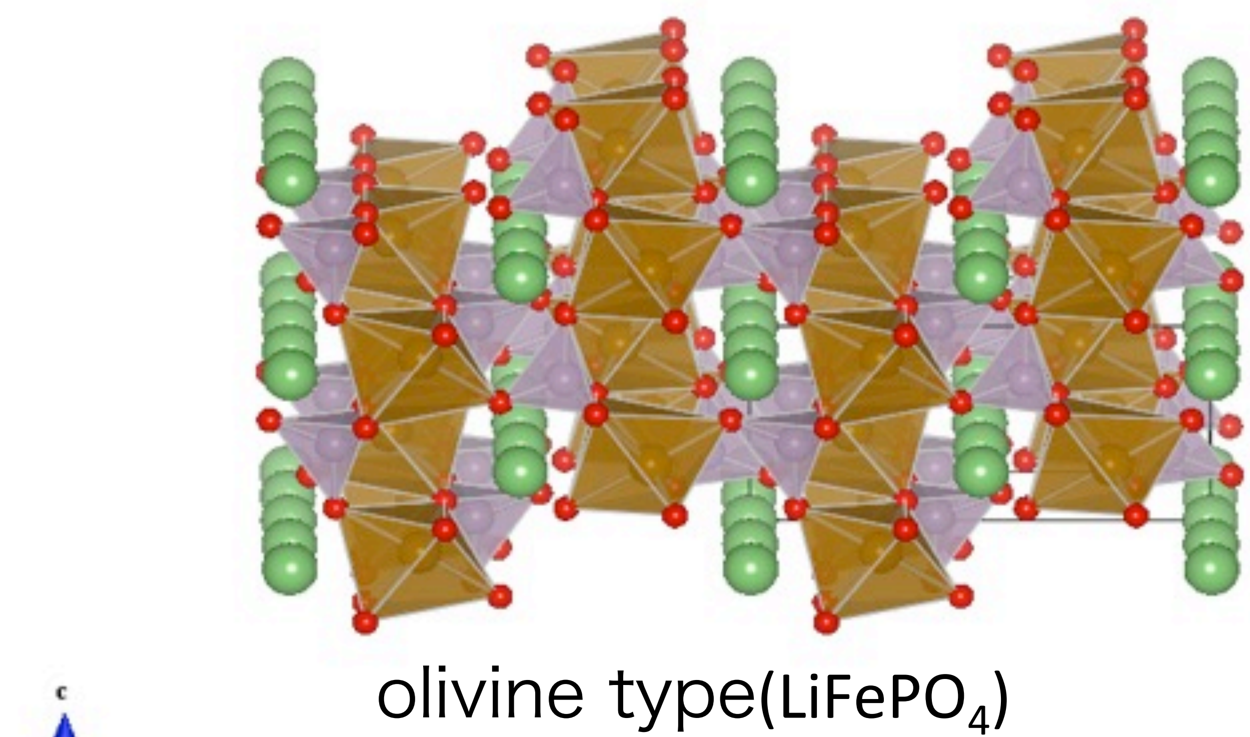


rock salt type

($LiCoO_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$)



spinel type($LiMn_2O_4$)



olivine type($LiFePO_4$)

olivine		spinel		rock salt
strong	←	stability	→	weak
insulator	←	electrical conductivity	→	good

Lithium ion secondary battery

Olivine type $LiFePO_4$ ← $LiCoO_2$ (in use)

A new cathode material without using cobalt oxide

Low cost

High theorical capacity

170mAh/g

Redox potential

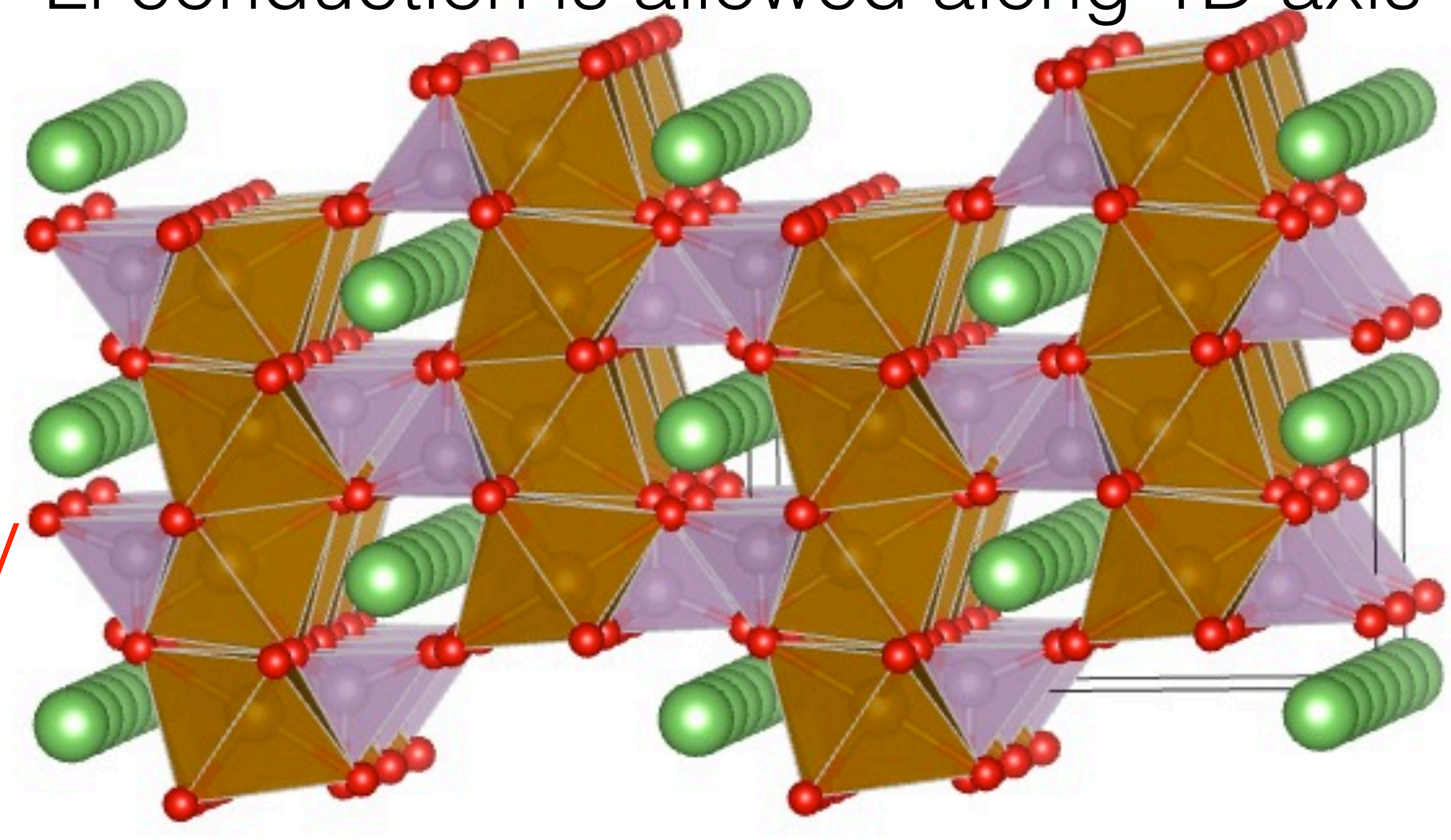
~3.5V

Poor electrical conductivity

σ_{elec}~$10^{-9}Scm^{-1}$

σ_{ion}~$10^{-11}Scm^{-1}$

Li conduction is allowed along 1D axis



Conventional : *Solid-state*, *sol-gel*, *hydrothermal* method etc.

Long processing time, *High-cost reagents*, *and Complicated process*

→ Our group has applied a ***Glass-Ceramics processing***

Simple process and cheap reagents

Lithium ion secondary battery

Olivine type $LiFePO_4$ ← ~~$LiCoO_2$ (in use)~~

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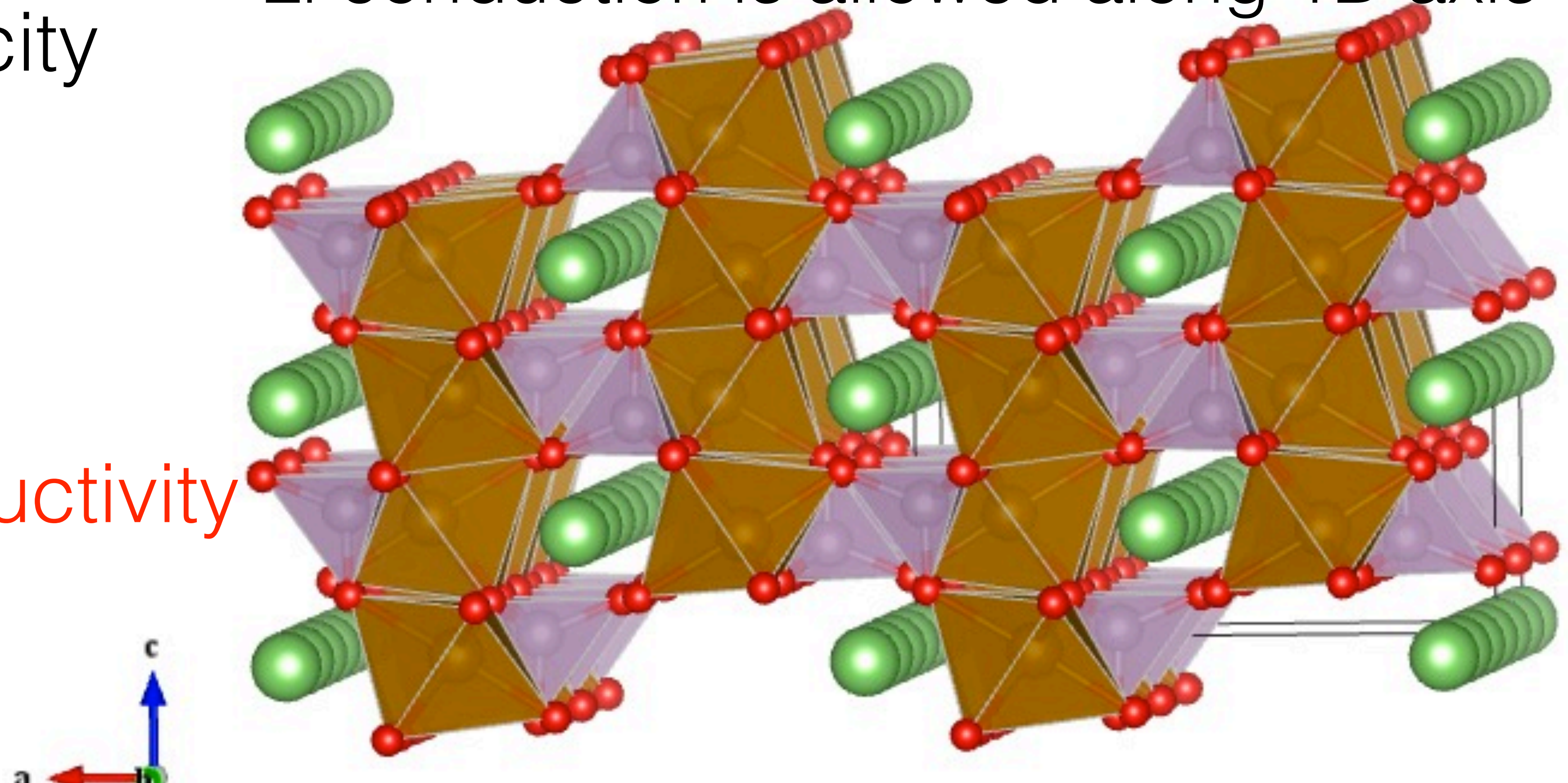

Conventional : *Solid-state*, *sol-gel*, *hydrothermal* method etc.

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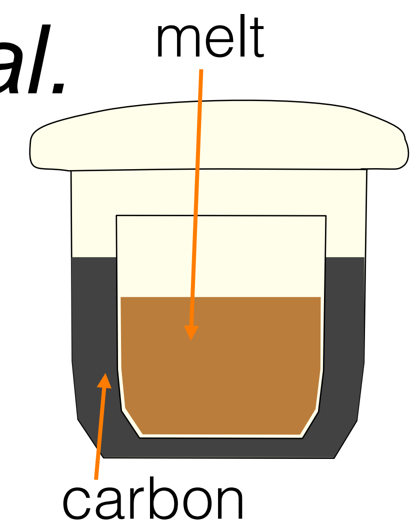
Simple process and cheap reagents

Glass-Ceramics (GC) processing

Li_2O-FeO-P_2O_5-Nb_2O_5 *K. Hirose et al.*

Addition of Niobium Oxide

Double Al_2O_3 crucible + carbon



Li_2O-Fe_2O_3-P_2O_5 *T. Honma et al.*

Melting in air is available

Cheap Fe_2O_3

Fe^{2+}/Fe^{3+} mixed valence

i.e. $Fe^{3+}/Fe=0.86$

Reduction during crystallization

Procedure

Melting

Plate glass

Pulverization

Crystallization

$LiFePO_4$

Cathode materials in the batteries are used as fine powders

Precursor glass prepared by melt quenching is bulk plate

Preparation of glass

In 1200°c air

$LiPO_3+Fe_2O_3$

quenching

Preparation of Glass-Ceramics

Preparation of Glass-Ceramics

1.Millling

Preparation of Glass-Ceramics

1.Millling

2.Screening

Preparation of Glass-Ceramics

1.Millling

2.Screening

3.Addition sugar(5-10%)

Preparation of Glass-Ceramics

1.Millling

2.Screening

3.Addition sugar(5-10%)

4. Baking(700˚C)

LFP Glass Powder

Preparation of Glass-Ceramics

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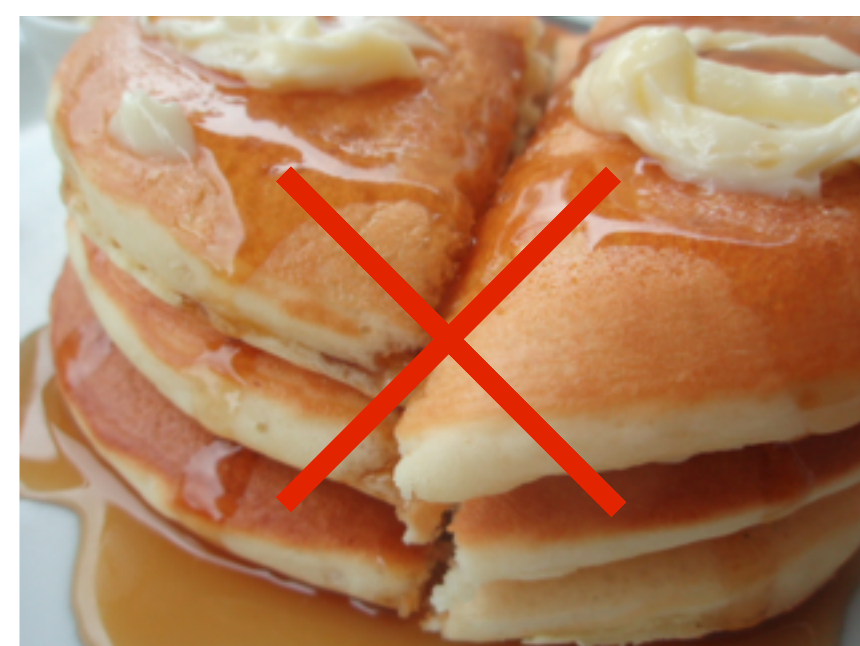
Nagaoka University of Technology

1.Millling

2.Screening

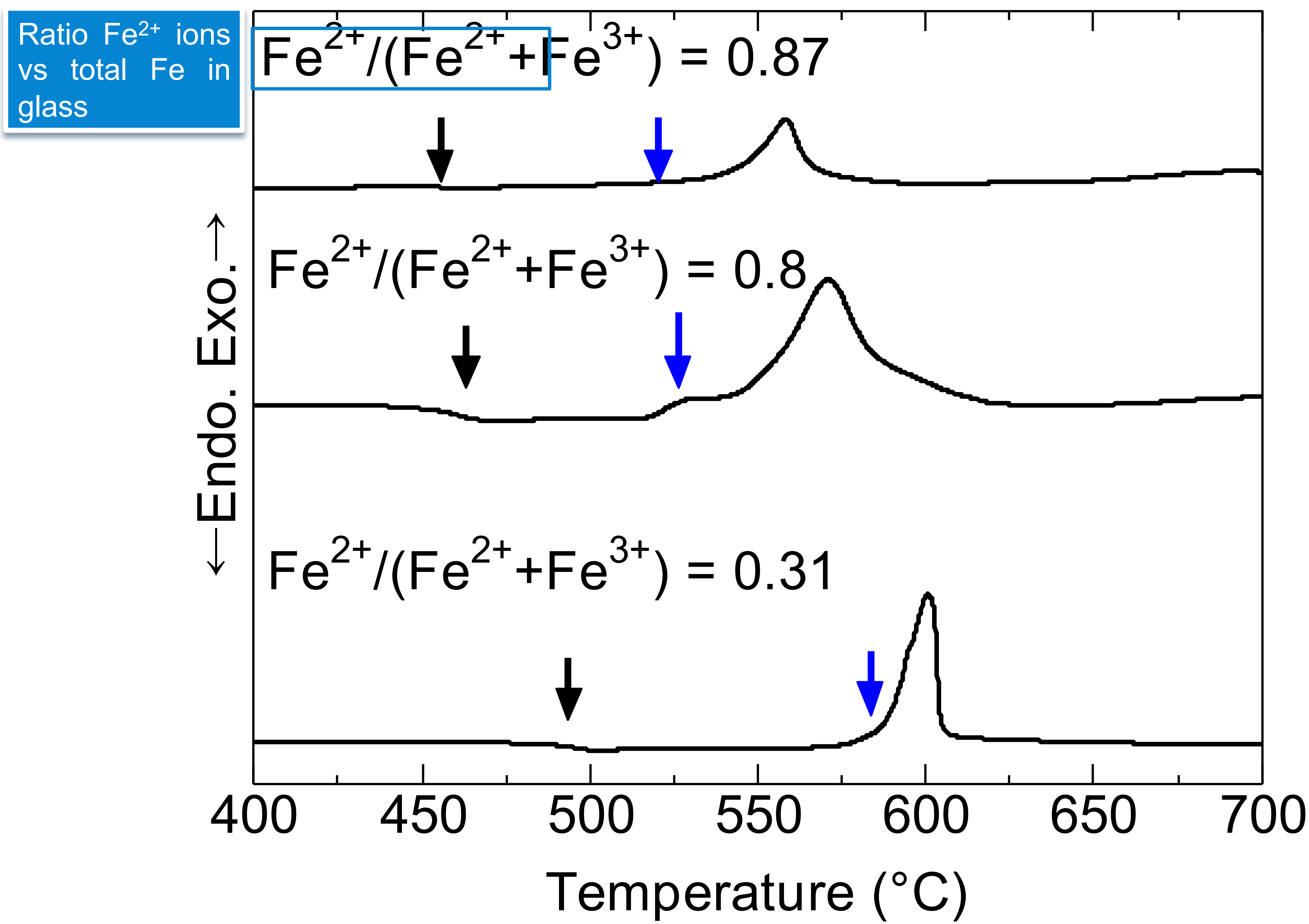
3.Addition sugar(5-10%)

4. Baking(700˚C)



Thermal property

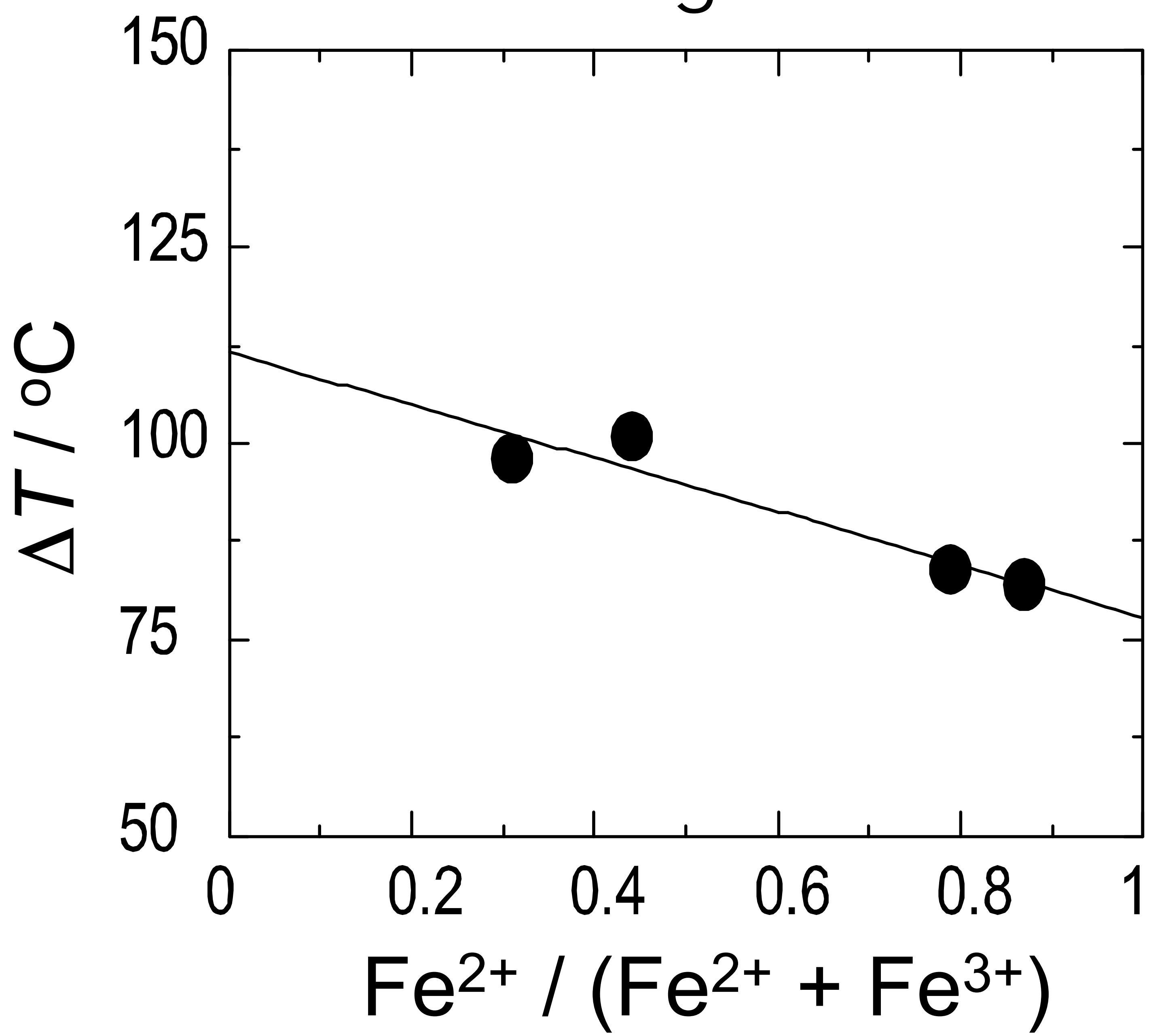
Thermal property depends on valence state



Glass formation tendency

Thermal stability(ΔT) of precursor glass

$\Delta T = Tc - Tg$



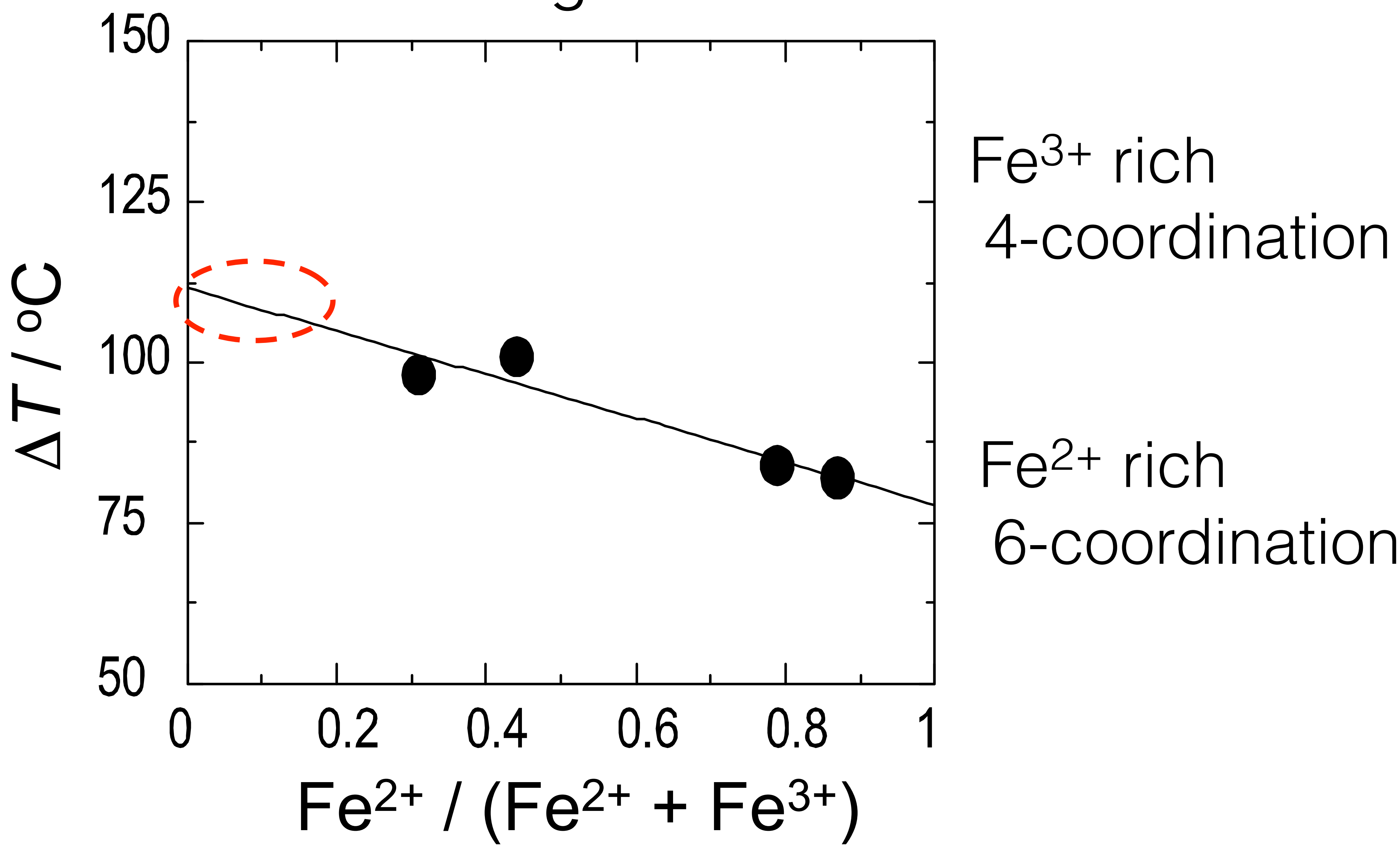
Fe^{3+} rich
4-coordination

Fe^{2+} rich
6-coordination

Glass formation tendency

Thermal stability(ΔT) of precursor glass

ΔT = Tc − Tg



effect of sugar addition

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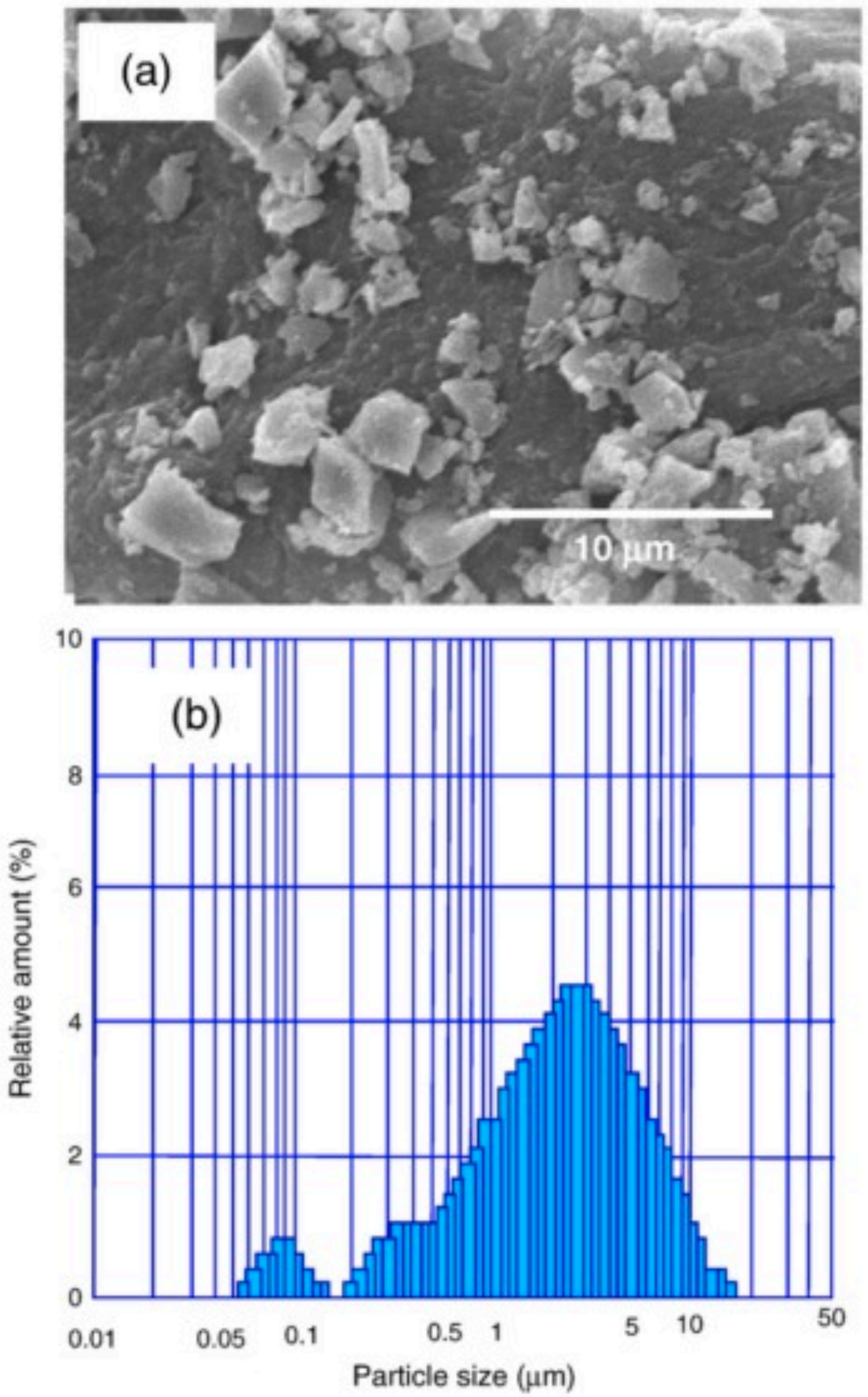
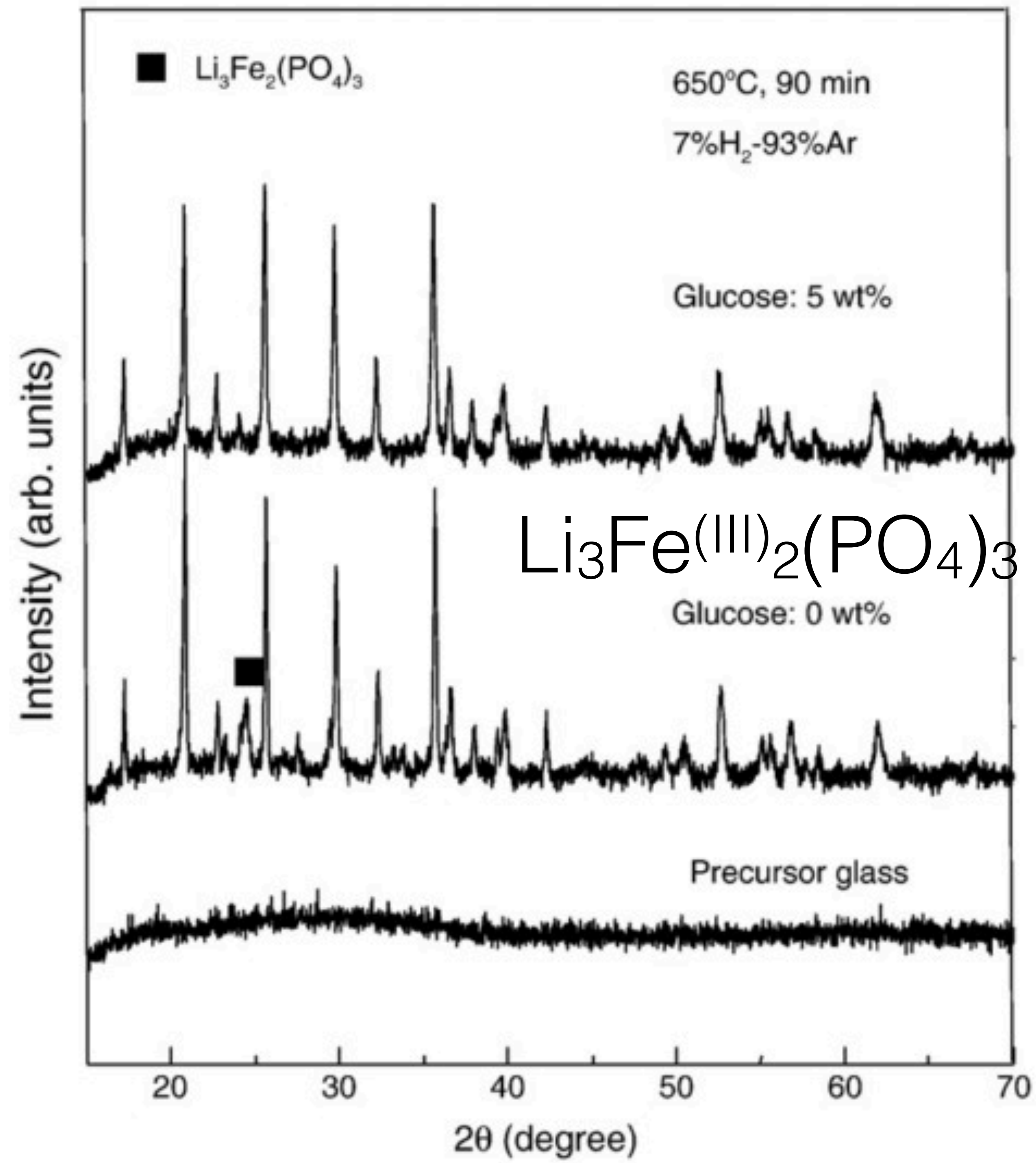
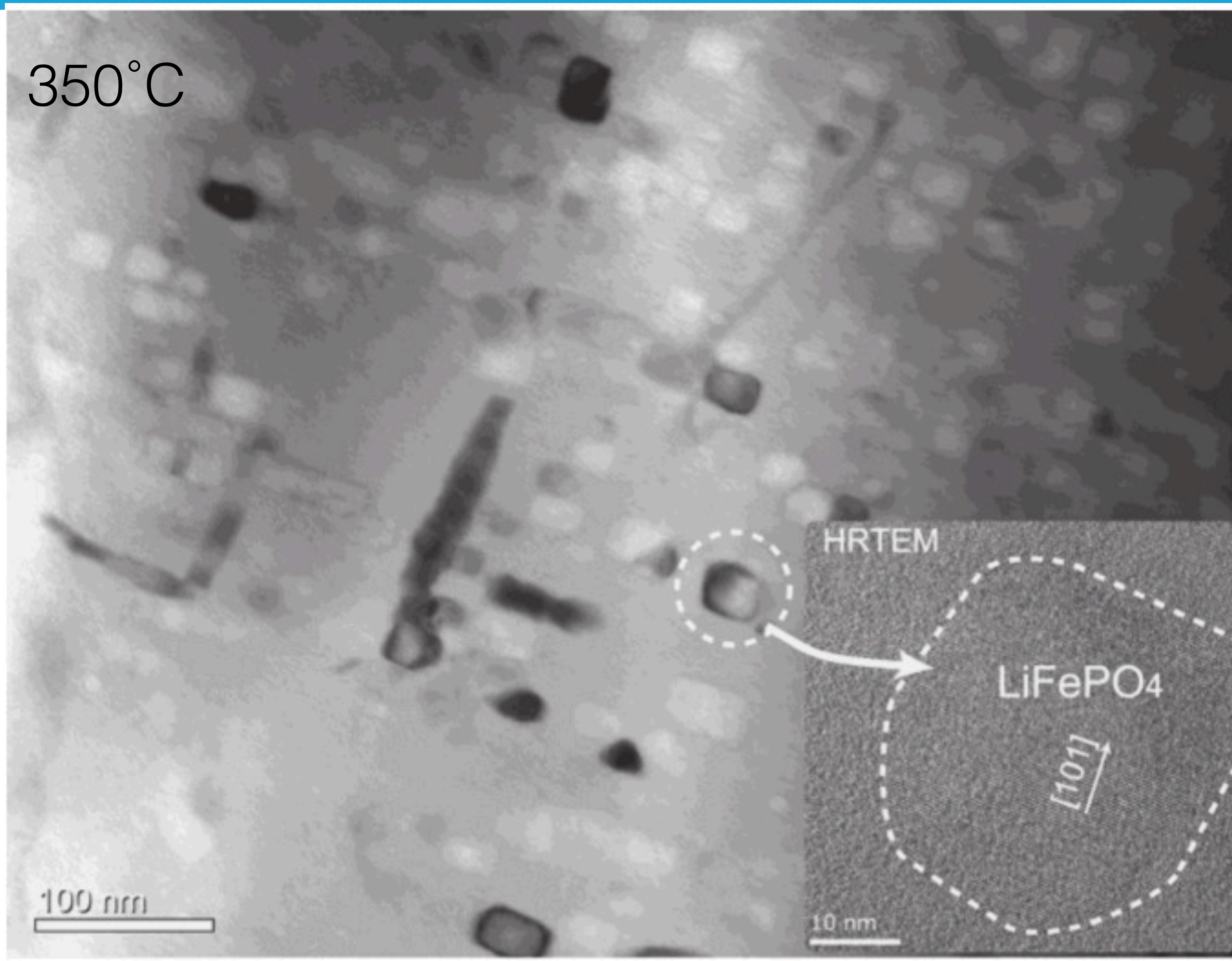




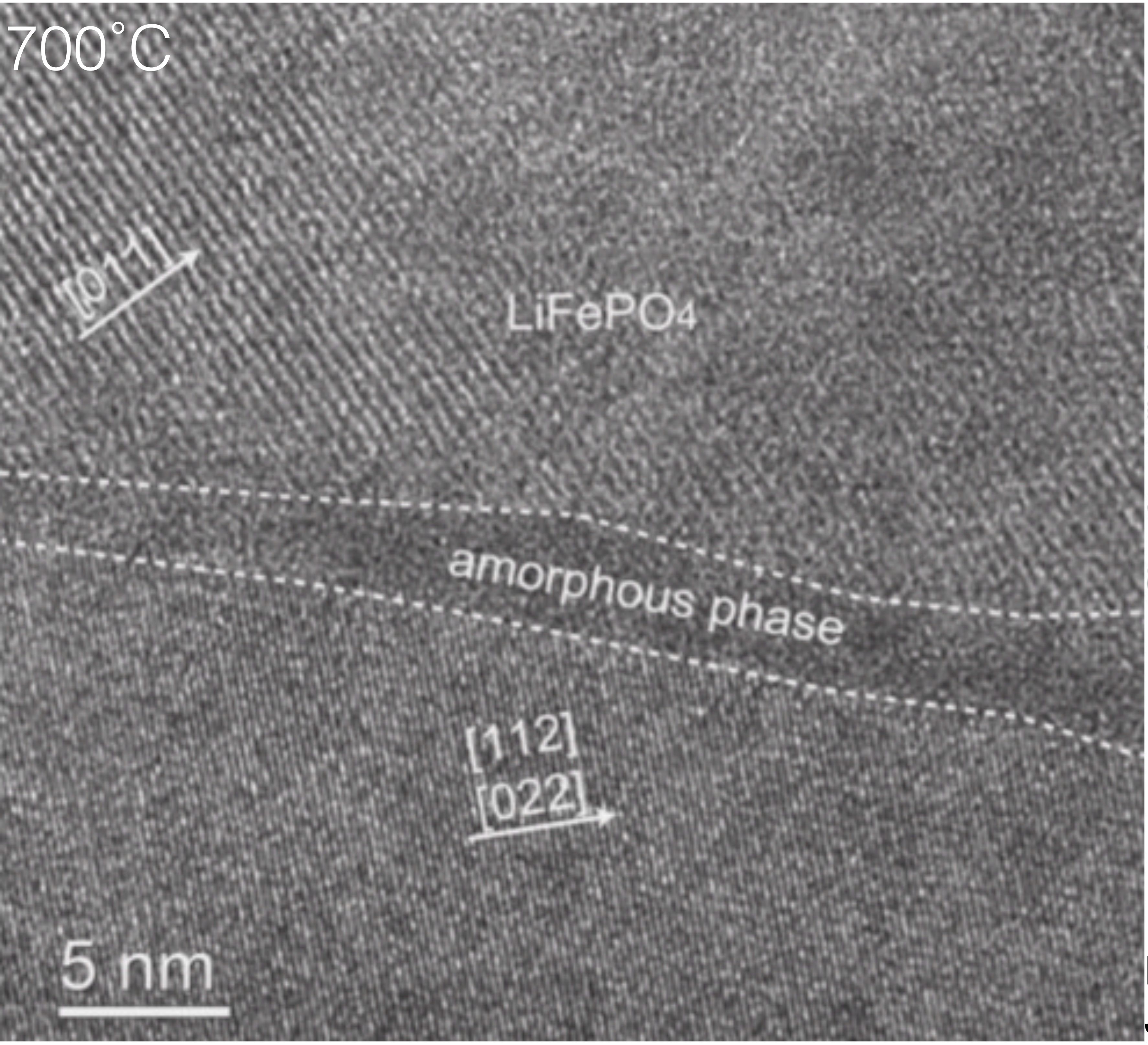
T.Honma et al., JNCS 356 3032 (2010)

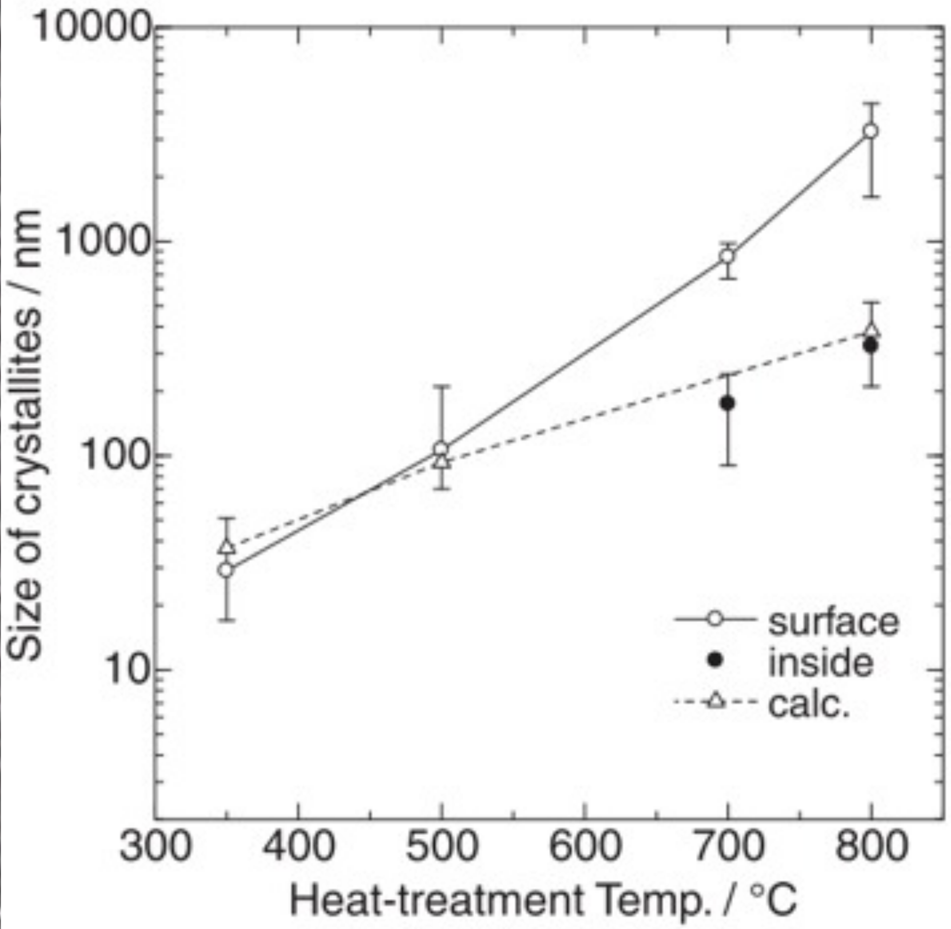
HR-TEM image



K. Nagamine et al., J. Ceram. Soc. Jpn,120, 193(2012)

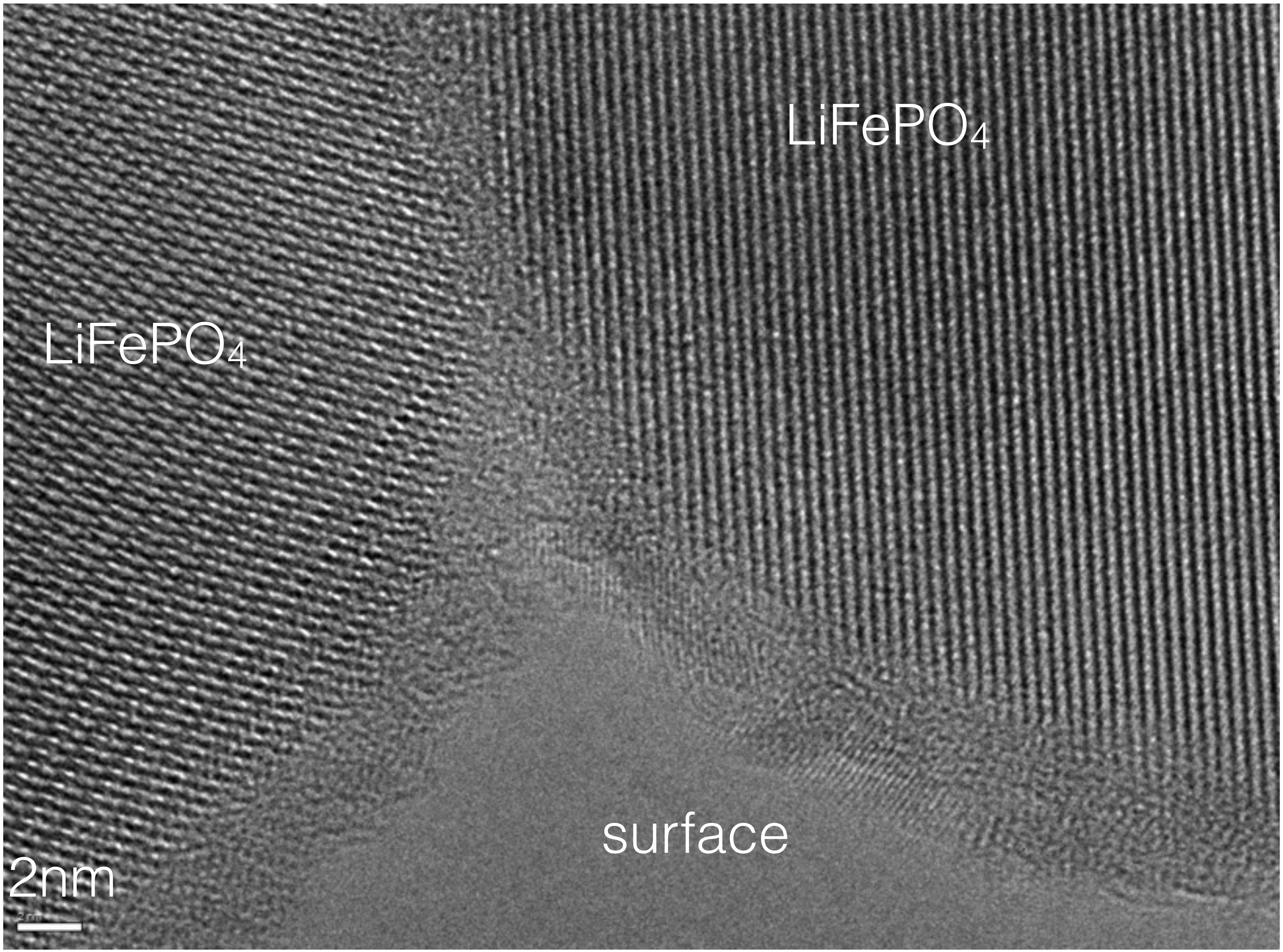
HR-TEM image





K. Nagamine et al., J. Ceram. Soc. Jpn,120, 193(2012)

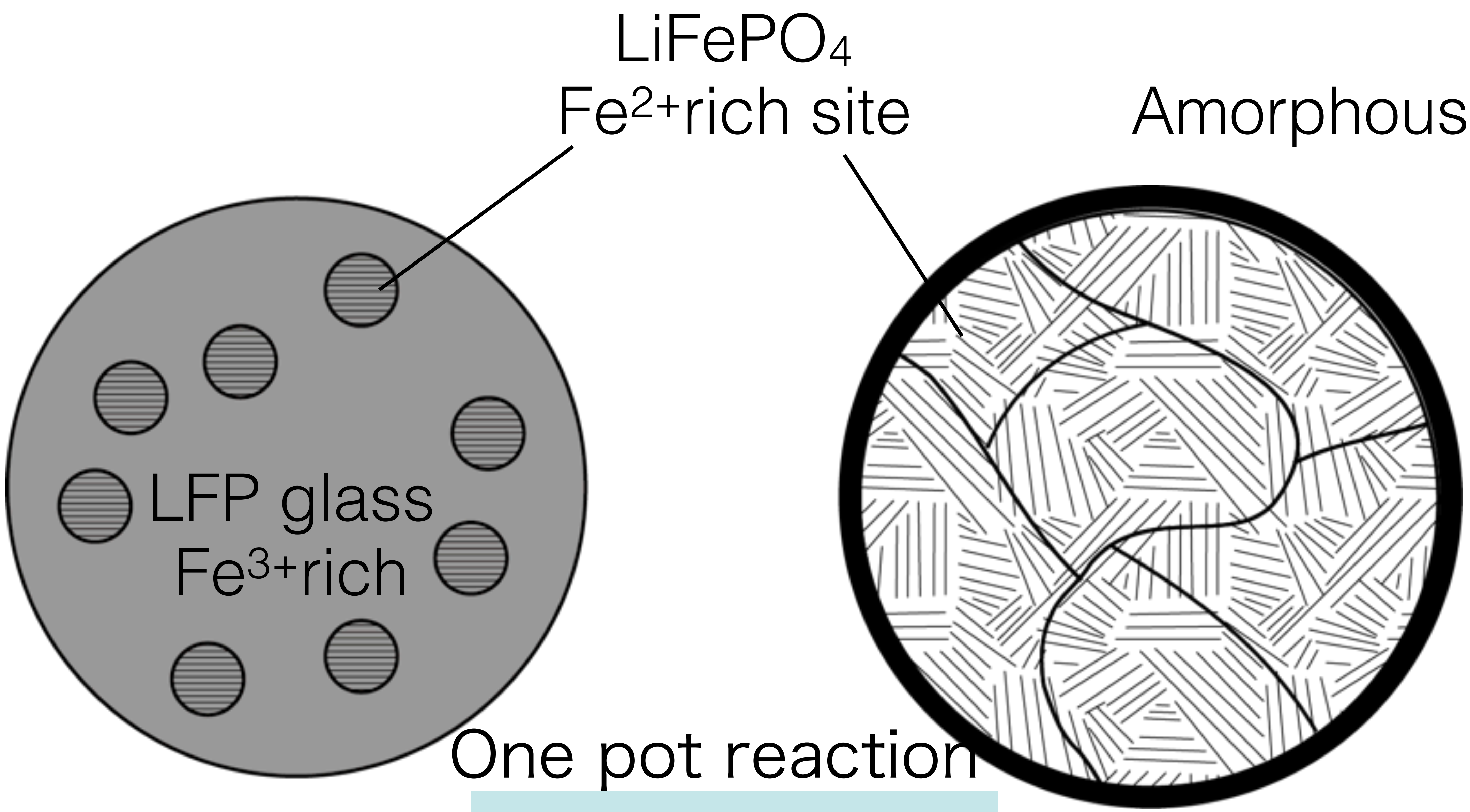
Carbon coating



By EDS
Amorphuos
phase

C, Fe,P,O

Crystallization mechanism



One pot reaction

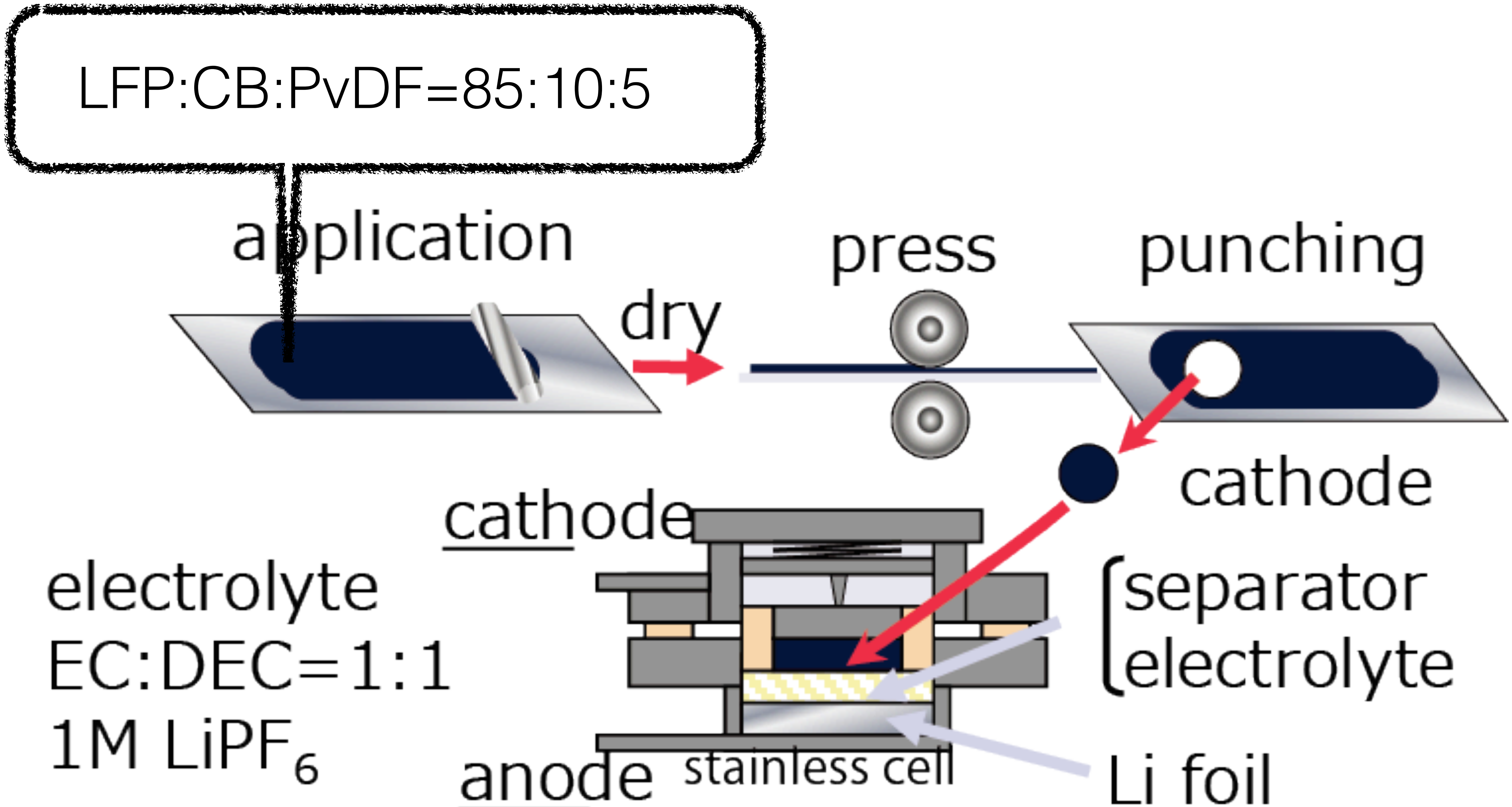
@350˚C

reduction of Fe^{3+}
crystallization
carbon coat

@700˚C

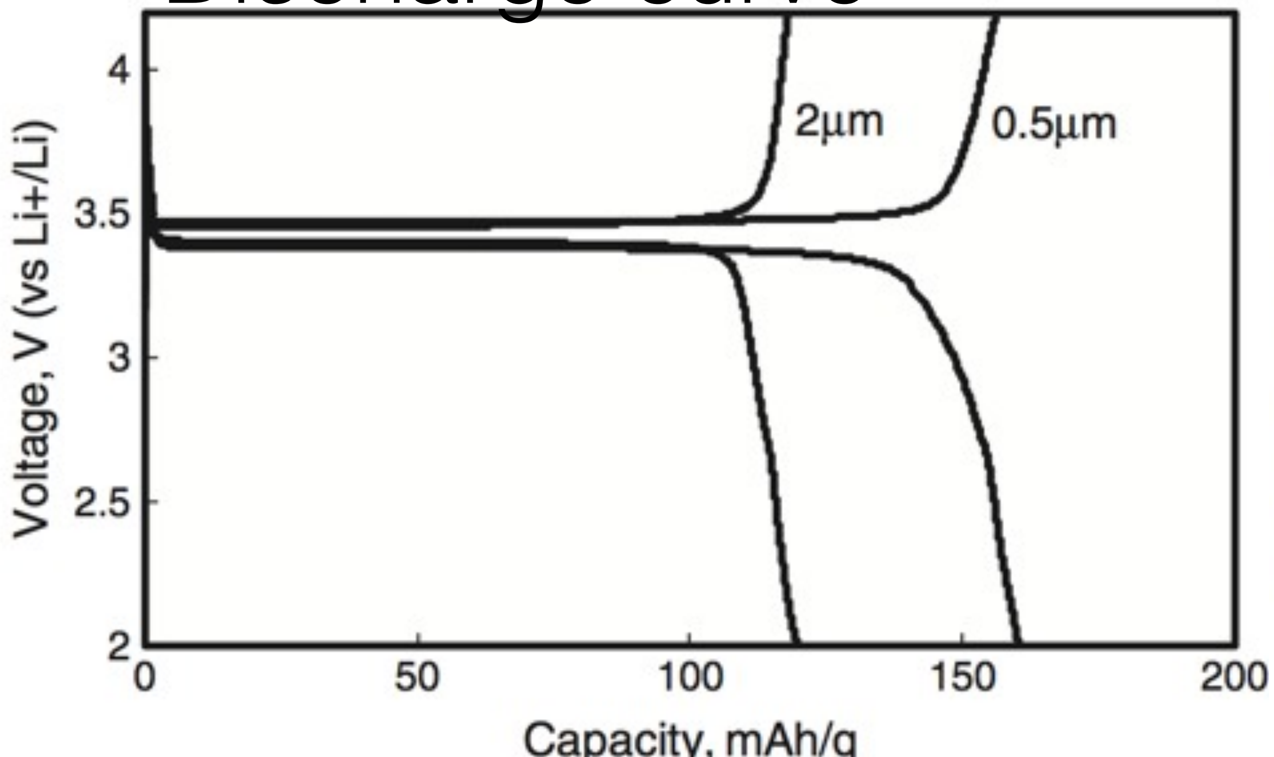
Hirose et al., Solid State Ionics, 178, 801(2007).
Honma et al.,J. Non-Cryst Solids, 356 3032 (2010).
Nagamine et al., J. Ceram Soc. Jpn., 120, 193(2012).

Preparation of LiB Cell

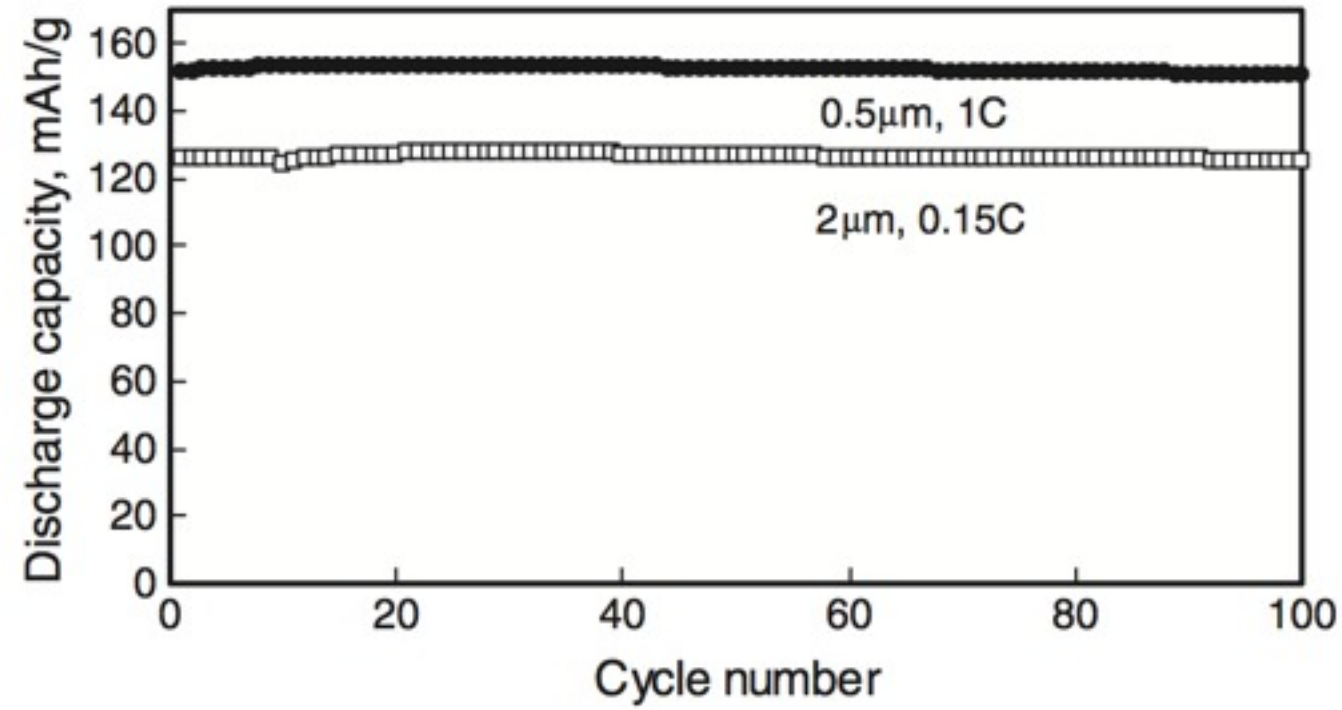


Battery performance of $LiFePO_4$ glass-ceramics

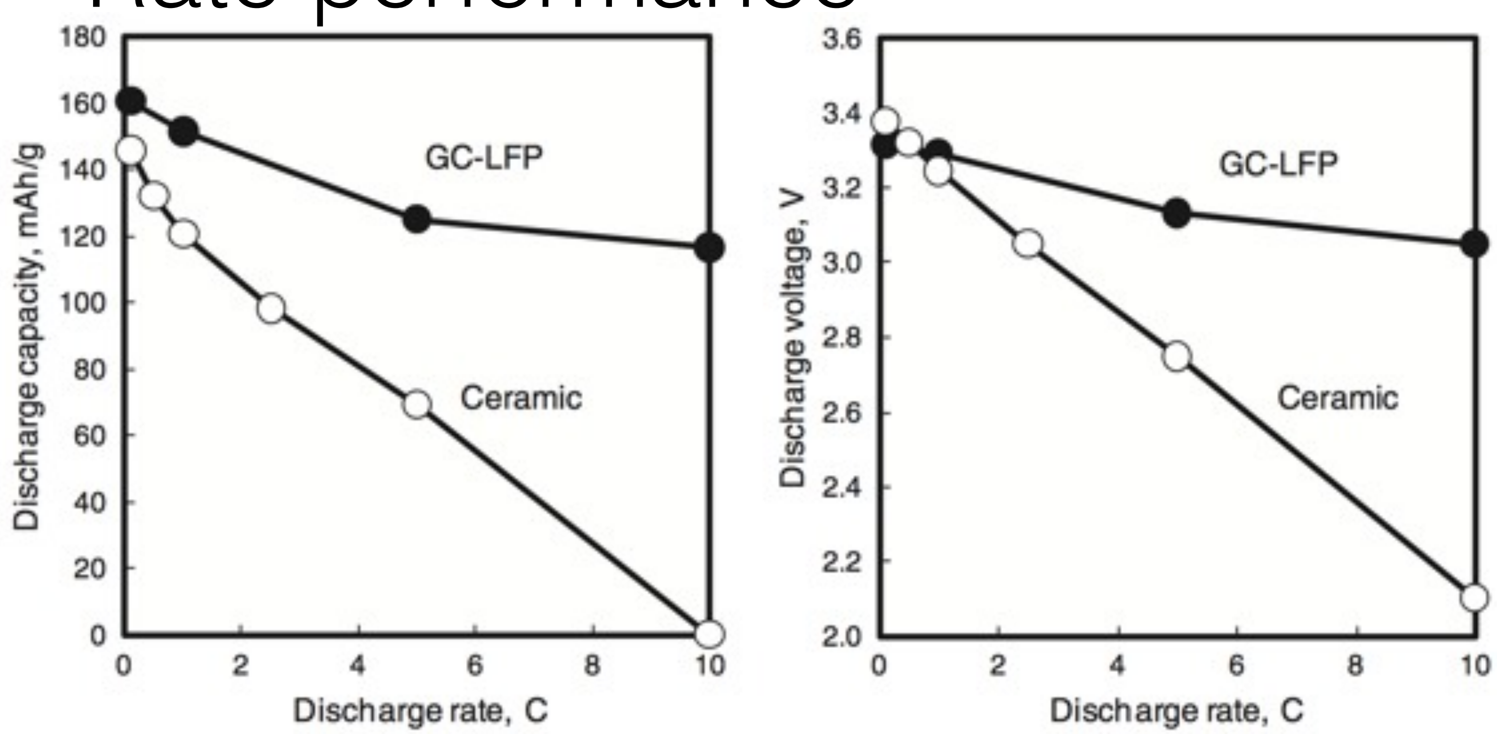
Discharge curve



Cycle performance



Rate performance



Nagakane et. al., Solid State Ionics, 206 78 (2012)

$LiFePO_4$ Glass-Ceramics

- Materials cost
  Inexpensive materials are able to use
  ex) $LiPO_3$, Fe_2O_3
- Production cost
  Short time melting (<30min)
  and crystallization (~2h)
  Simultaneous carbon coating process
- Battery performances
  Much better than that made by solid state reaction

Sodium ion batteries (NaB)

Why NaB?

Minor metals for Lithium ion batteries

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for cathode
for anode
for collector

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*1	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	*2	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
*1	La	Ce	Pr	Nd	Pm	Sm	Eu	Gb	Tb	Dy	Ho	Er	Tm	Yb	Lu			
*2	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

- depends on many kinds of minor metals

Mining of Lithium resources

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ニューストップ | 動物 | 古代の世界 | 環境 | 文化 | 科学&宇宙 | 風変わりニュース

リチウム、次世代の電池技術

ツイート　B!　SN　チェック　いいね！ 34　+1 4

友人に教える

National Geographic News
September 21, 2012

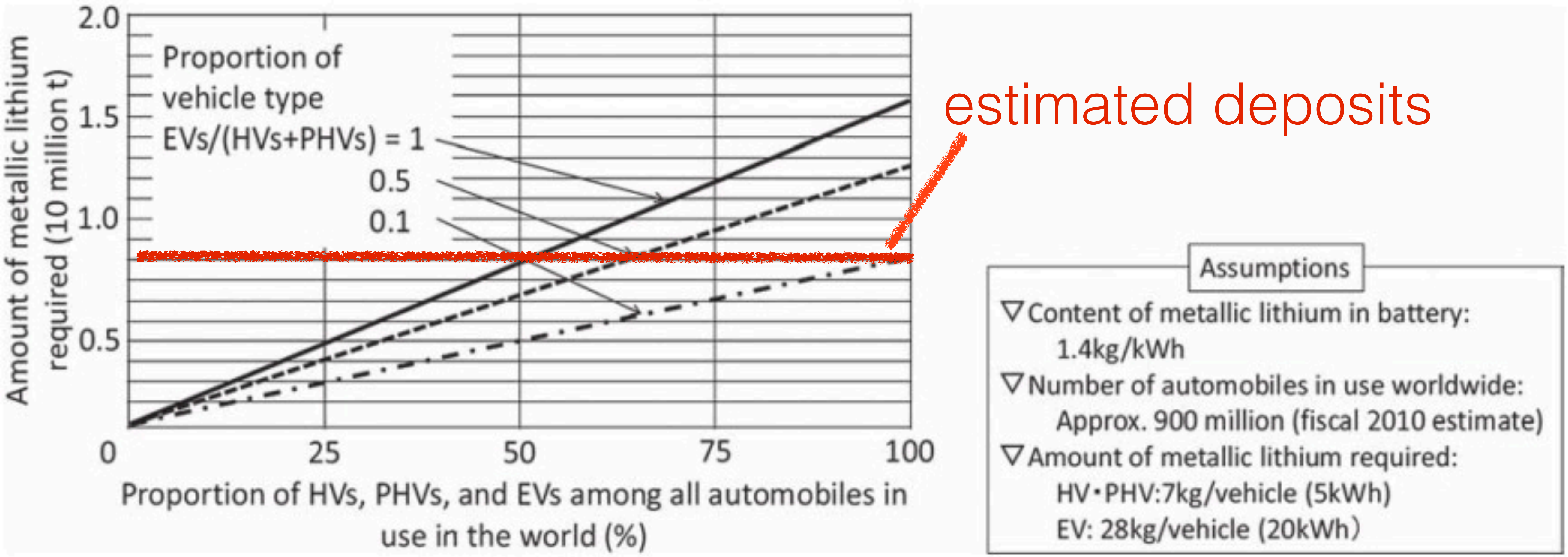
チリ北部、アタカマ塩原のリチウムを採掘する重機。充電可能な携帯電子機器や、電気自動車（EV）には欠かせないレアメタルだ。

Major producing country

Chile、Bolivia、China

http://www.nationalgeographic.co.jp/news/news_article.php?file_id=2012091907
http://diamond.jp/articles/-/7534

Lithium resources are enough?



Adv. Energy Mat., 2, 710 (2012)

Problems in huge size LiB

Safety performance, Lifetime

Hard to keep quality as 18650 type cell

Non-toxic materials must be use to avoid trouble

Total costs

Target <300$/kWh

18650 type：400～500$/kwh

Laminate type：800～1000$/kwh

Resource

By use of minor metals, cost cut is difficult

Lithium and Sodium

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	Lithium	Sodium
Deposits	maldistribution (20ppm)	infinite
ion radius	60pm	95pm
weight	6.9g/mol	22g/mol
Voltage vs SHE	-3.03V	-2.7V

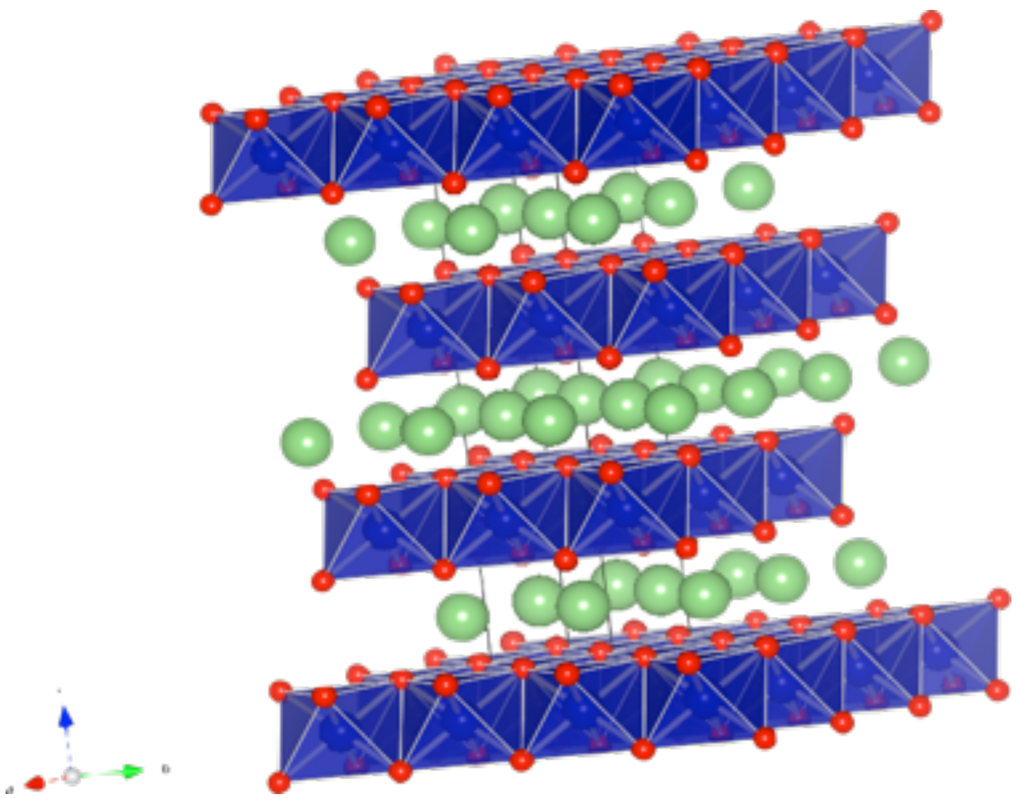
Sodium ion Batteries

High energy density batteries with low cost

It must be

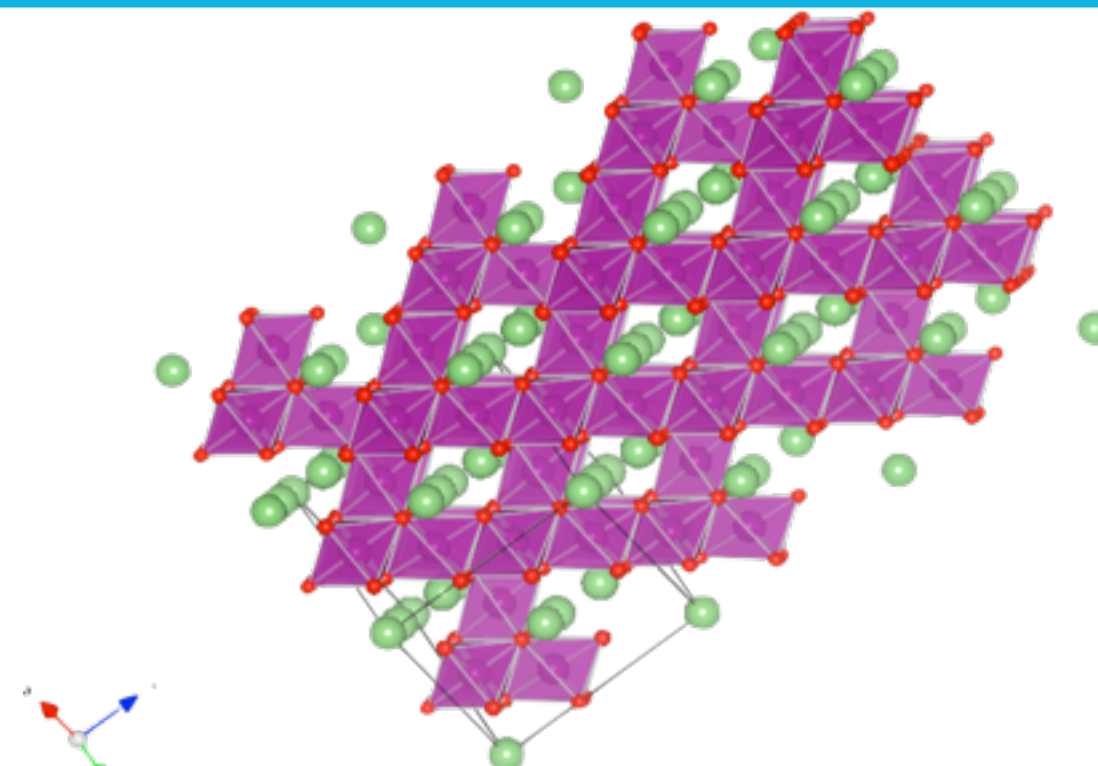
- good sodium ion conduction
- safe than LiB

Typical cathode structure

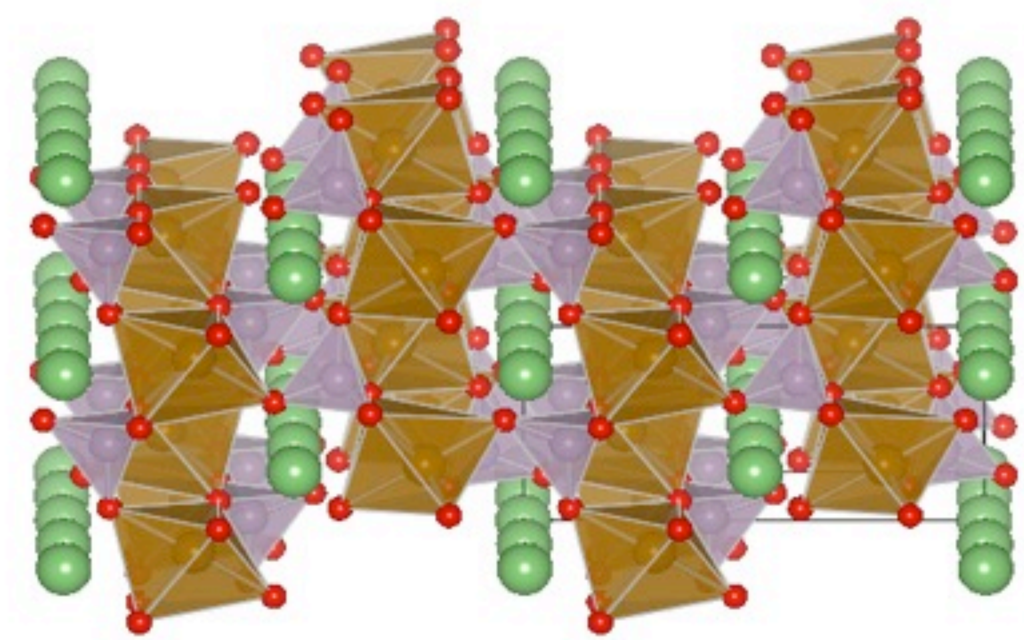


rock salt type

($LiCoO_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$)



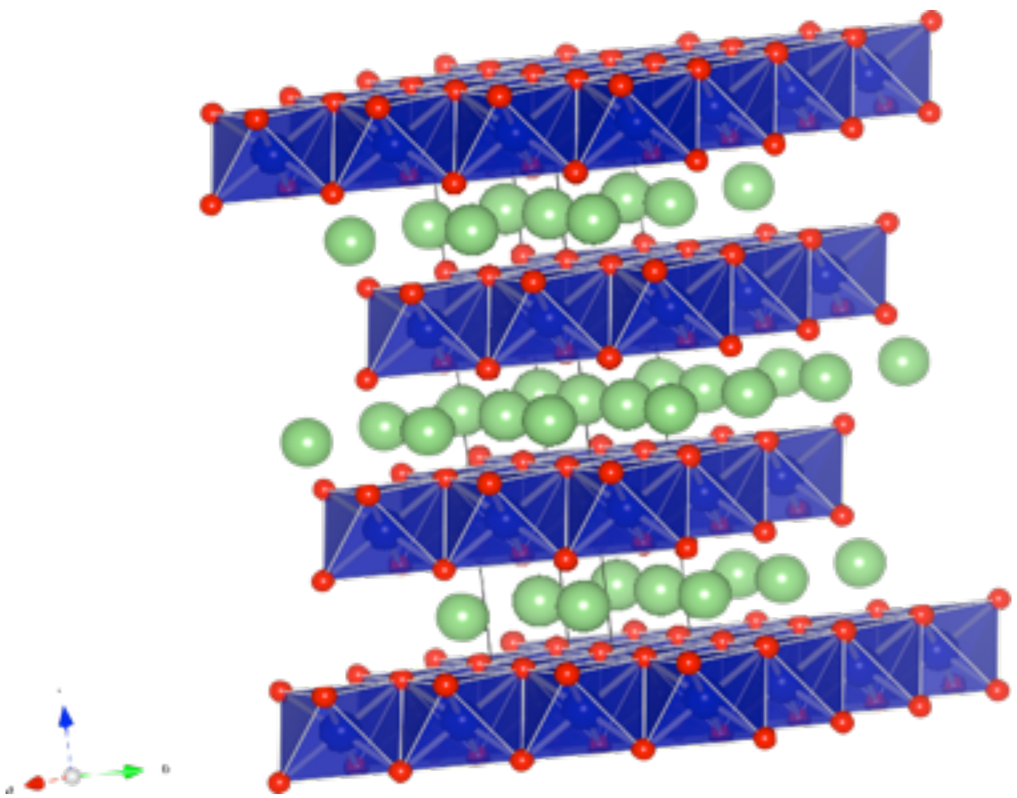
spinel type($LiMn_2O_4$)



olivine type($LiFePO_4$)

olivine		spinel		rock salt
strong	⟸	stability	⟹	weak
insulator	⟸	electrical conductivity	⟹	good

Typical cathode structure



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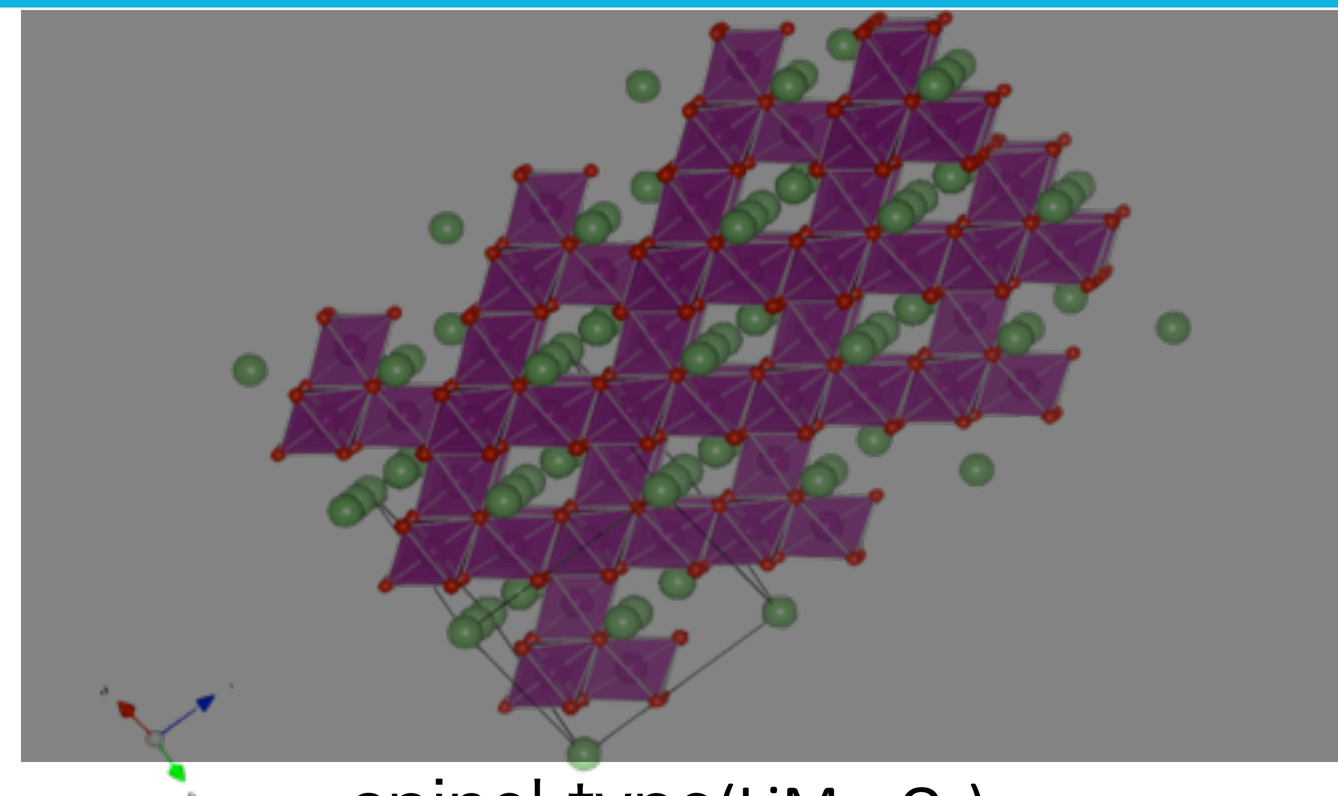

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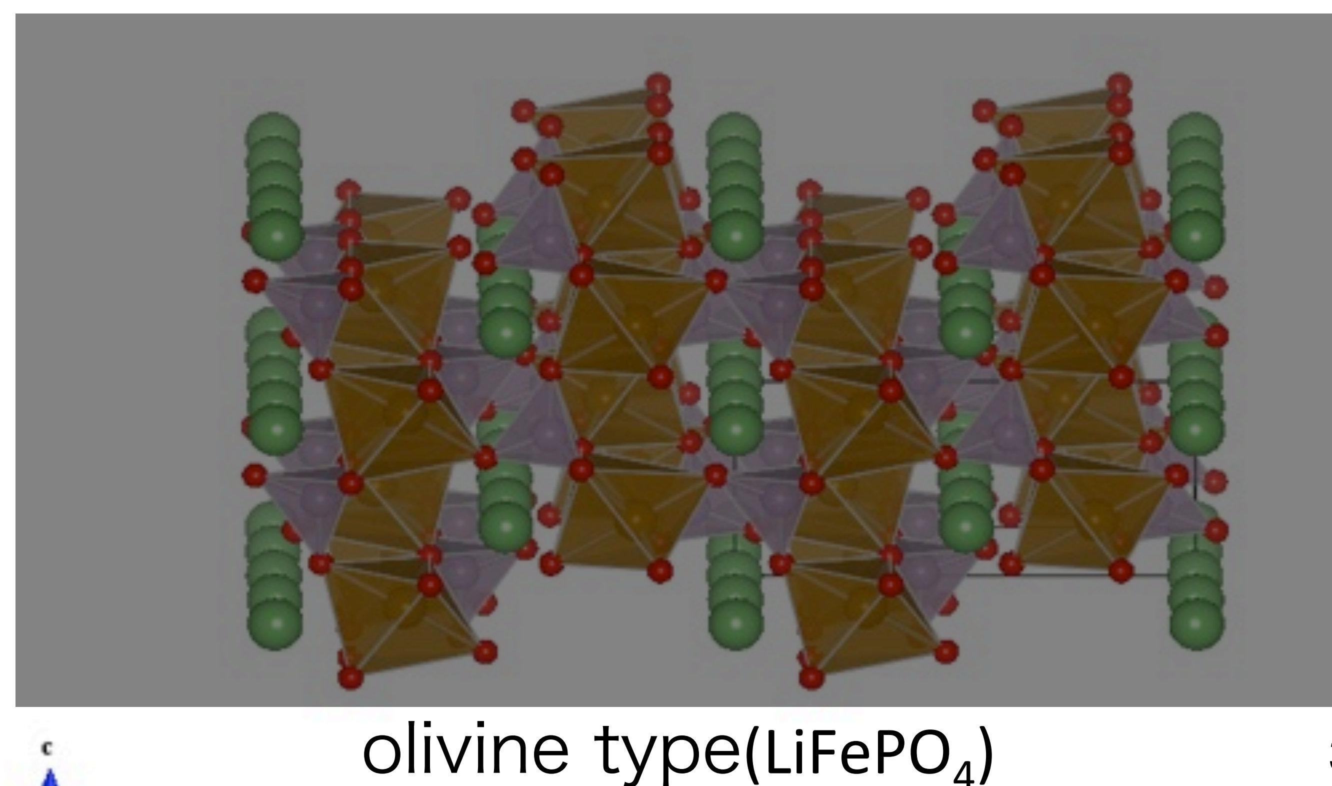

olivine type($LiFePO_4$)

olivine		spinel		rock salt
strong	←	stability	→	weak
insulator	←	electrical conductivity	→	good

Problem in $NaMO_2$ rock salt

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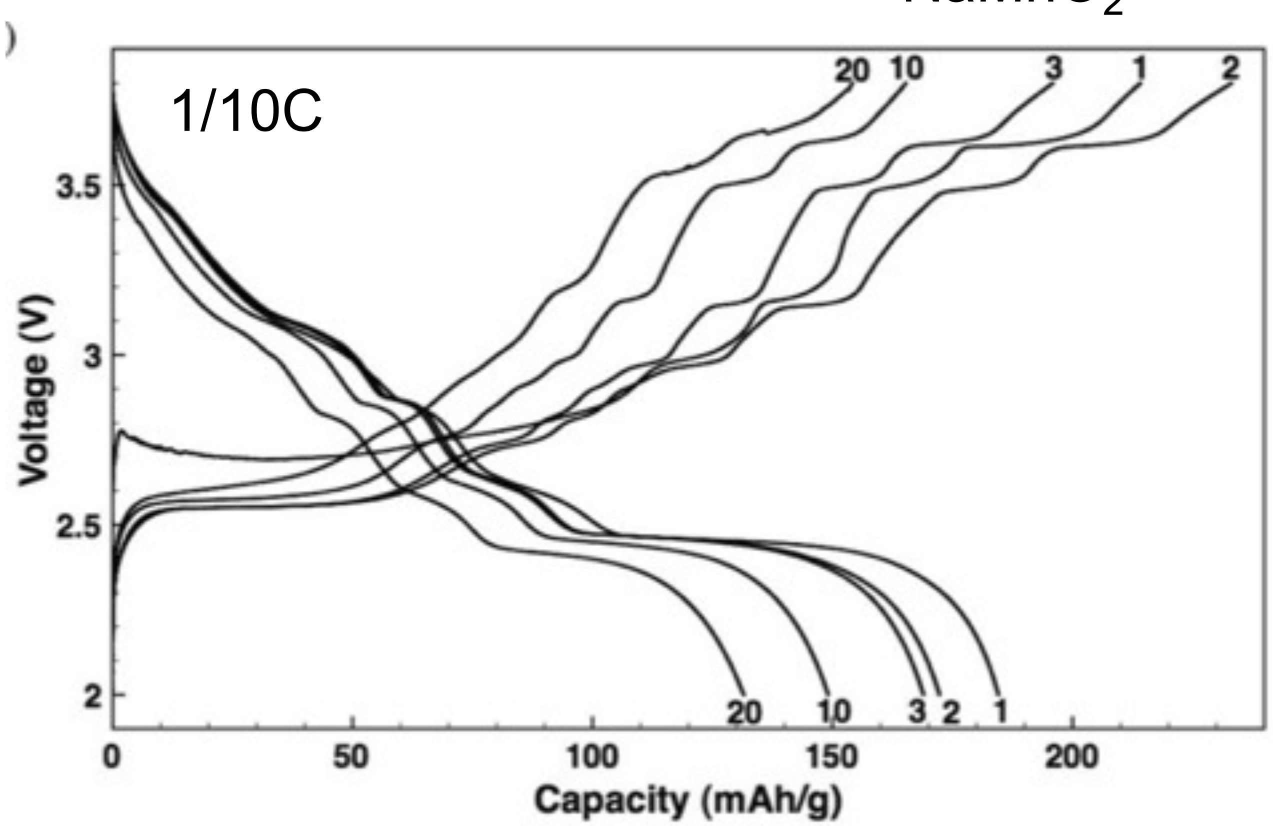
$NaFeO_2$[1], $NaMnO_2$[2], $NaNi_{0.5}Mn_{0.5}O_2$[3], $NaCrO_2$[4]…

[1]Takeda et al., Mat. Res. Bull. 29 659 (1994)
[3]Komaba et al., 214th ECS meet. Abstract (2008)

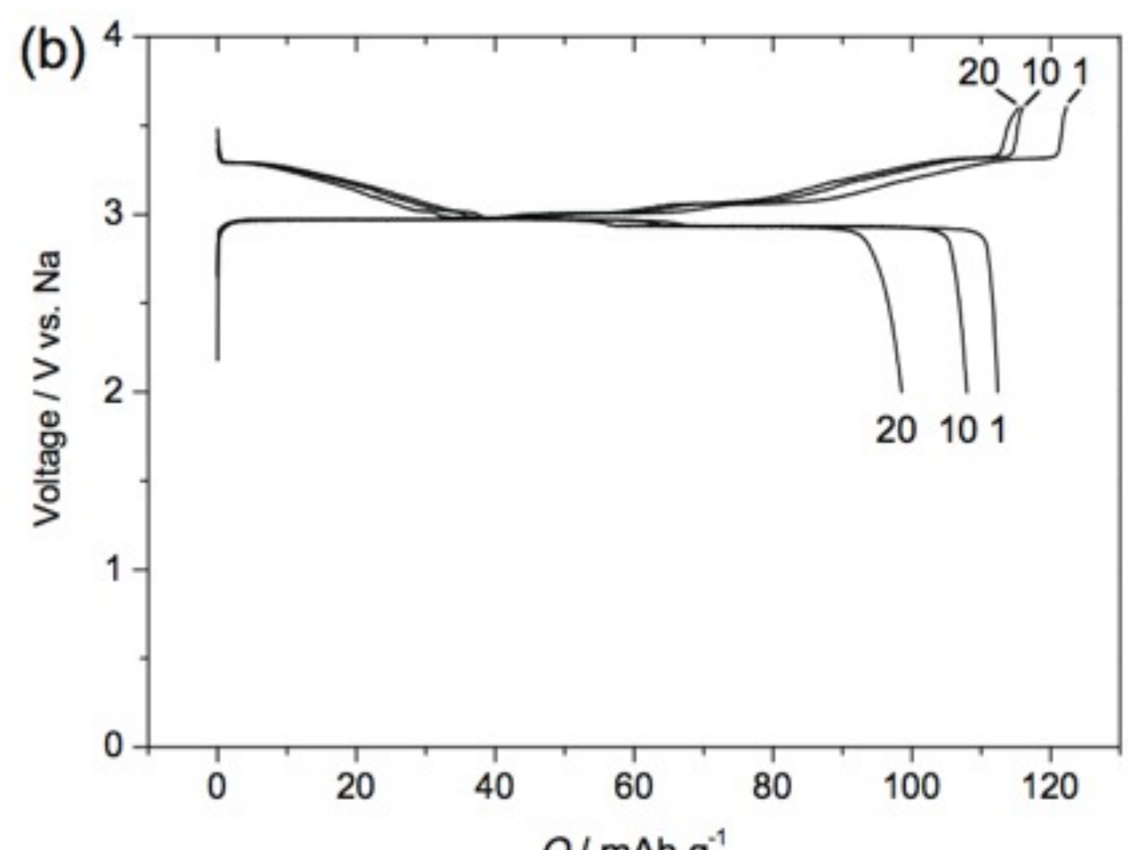
Good electronic conductivity, however...

- Chemical durability is much poor
- safety : not tested
- thermal stability: not tested

$NaMnO_2$



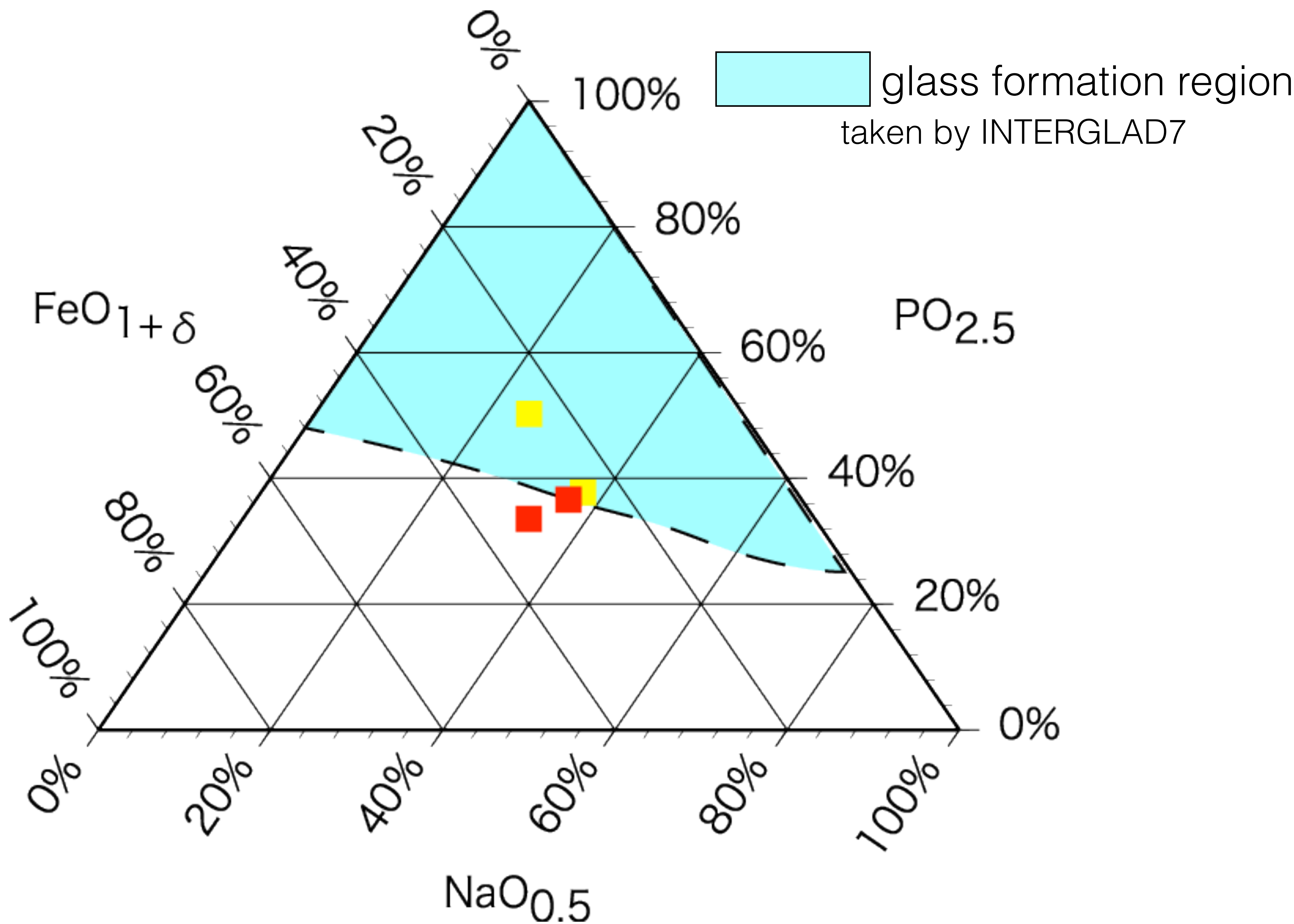
$NaCrO_2$



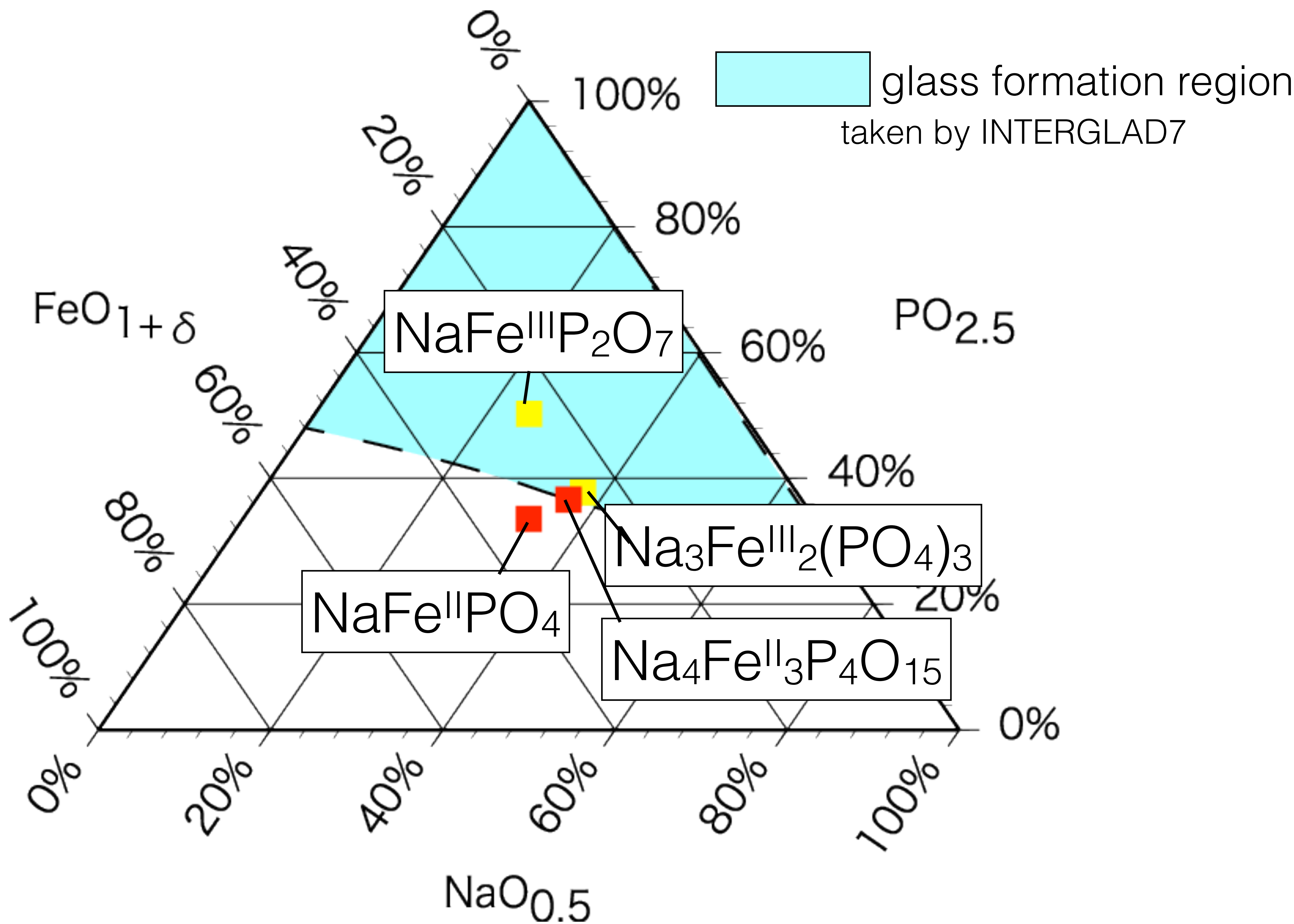
[2]Xiaohua et al., JES 158 A1307 (2011).

[4]Komaba et al., Electrochem. Comm.,12 355 (2010).

Cathode candidate in Na_2O-Fe_2O_3-P_2O_5 system

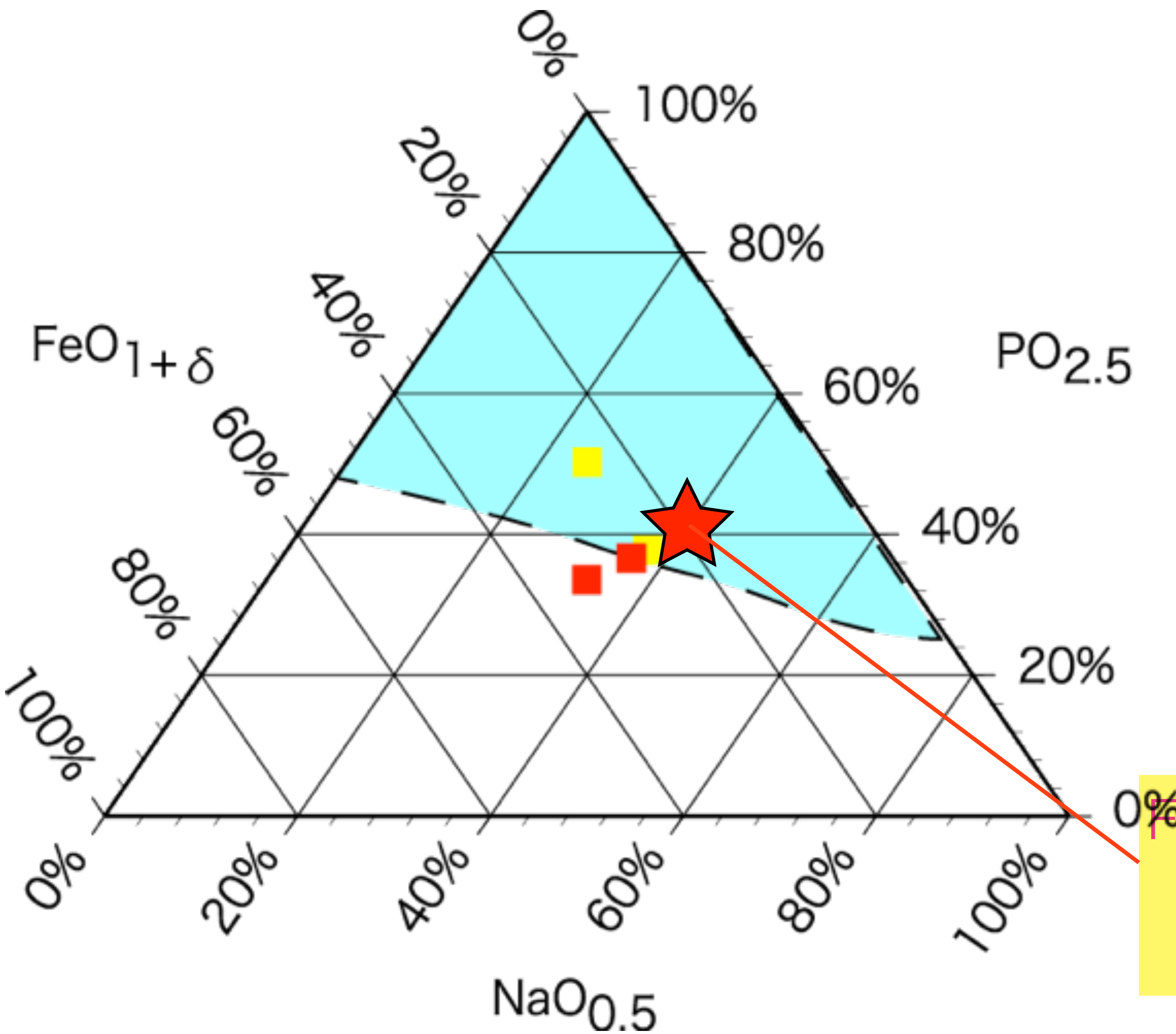


Cathode candidate in Na_2O-Fe_2O_3-P_2O_5 system



Purpose on this study

Fabrication of new cathode candidate by glass-ceramics method in the system Na_2O-Fe_2O_3-P_2O_5



- It must contain M^{2+}
- carbon coat

We found new crystalline phase around Na:Fe:P=2:1:2

Focus on Na:Fe:P=2:1:2 ($Na_2FeP_2O_7$)

- crystallization behavior
- electrochemical properties

Experiments

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Nagaoka University of Technology

【Glass preparation】

Starting reagents
($NaPO_3$, Fe_2O_3)

mix

melt — 1100˚C, 15min

cast

milling — Ball mill 700rpm 60min

glass powder

【Fabrication of $Na_2FeP_2O_7$/C composite】

glass powder:90% glucose 10%

crystallization — 620˚C, 3h $Ar\text{-}H_2$

$Na_2FeP_2O_7$/C composite

Advantages

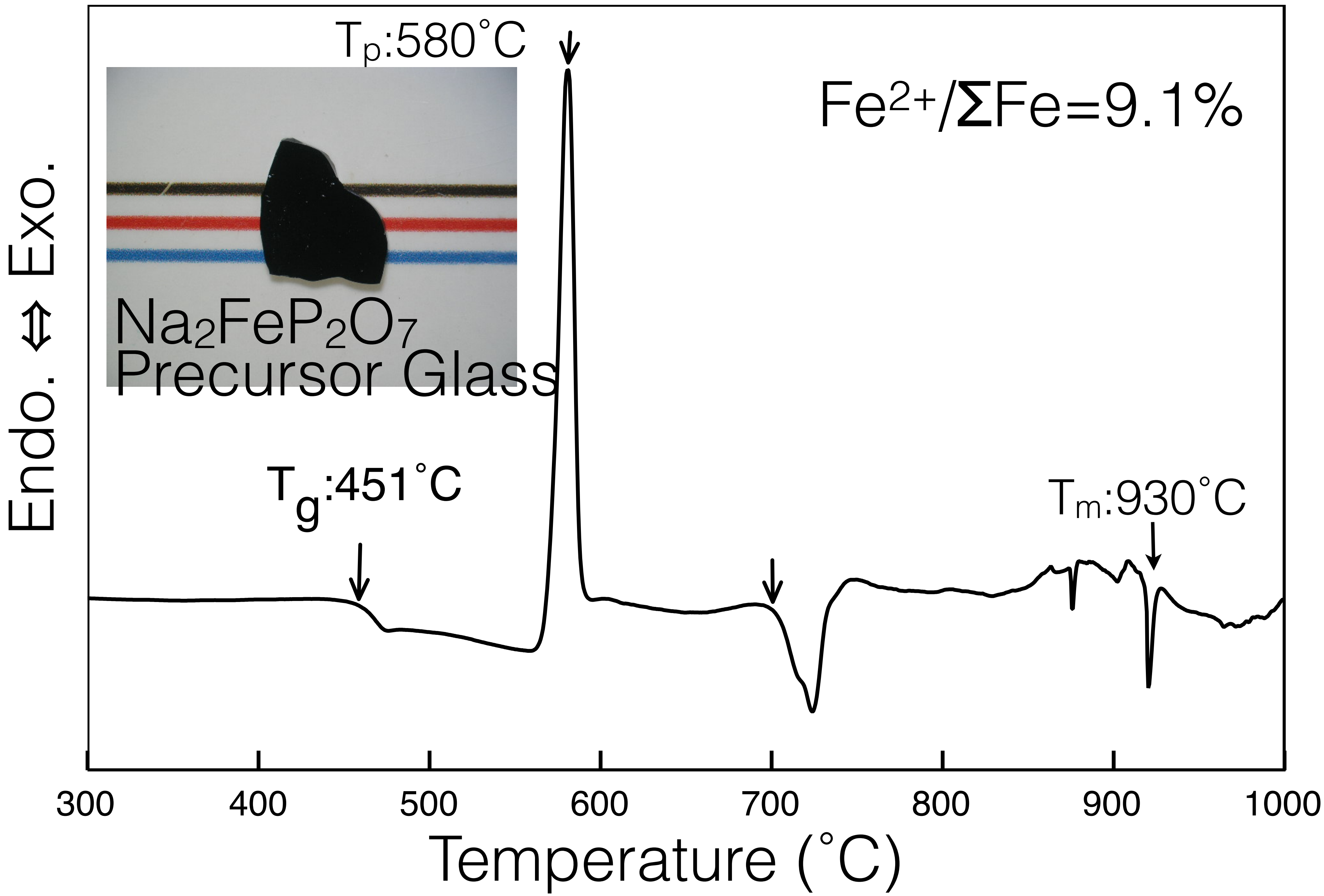
- Fe_2O_3 is available as raw materials
- Operation under air conditions

【Characterization】

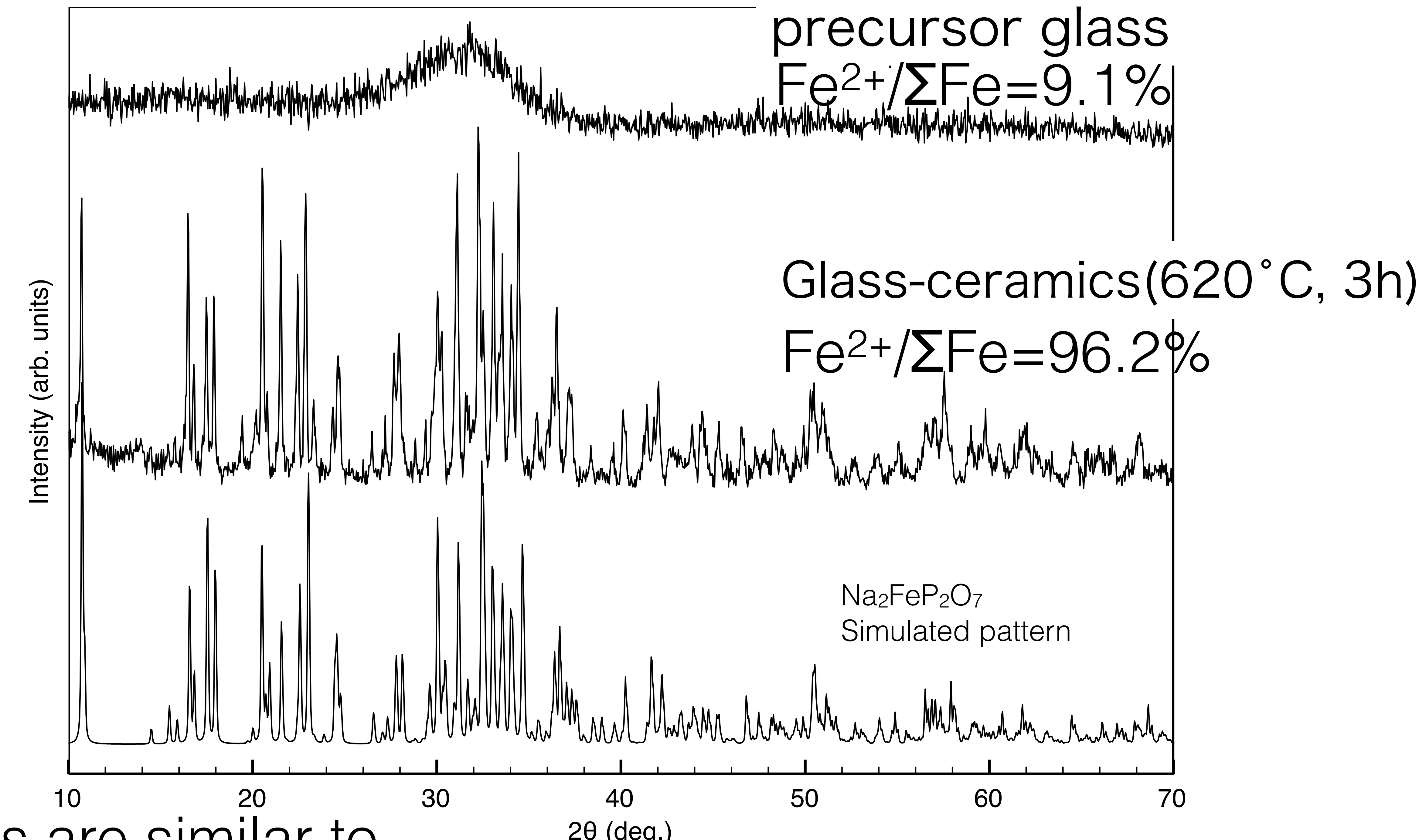
Red-ox titration,TG-DTA, XRD
SEM, STEM-EDS, Battery testing

Thermal properties

DTA curve　in Air　heating:10K/min



XRD pattern for glass and GC

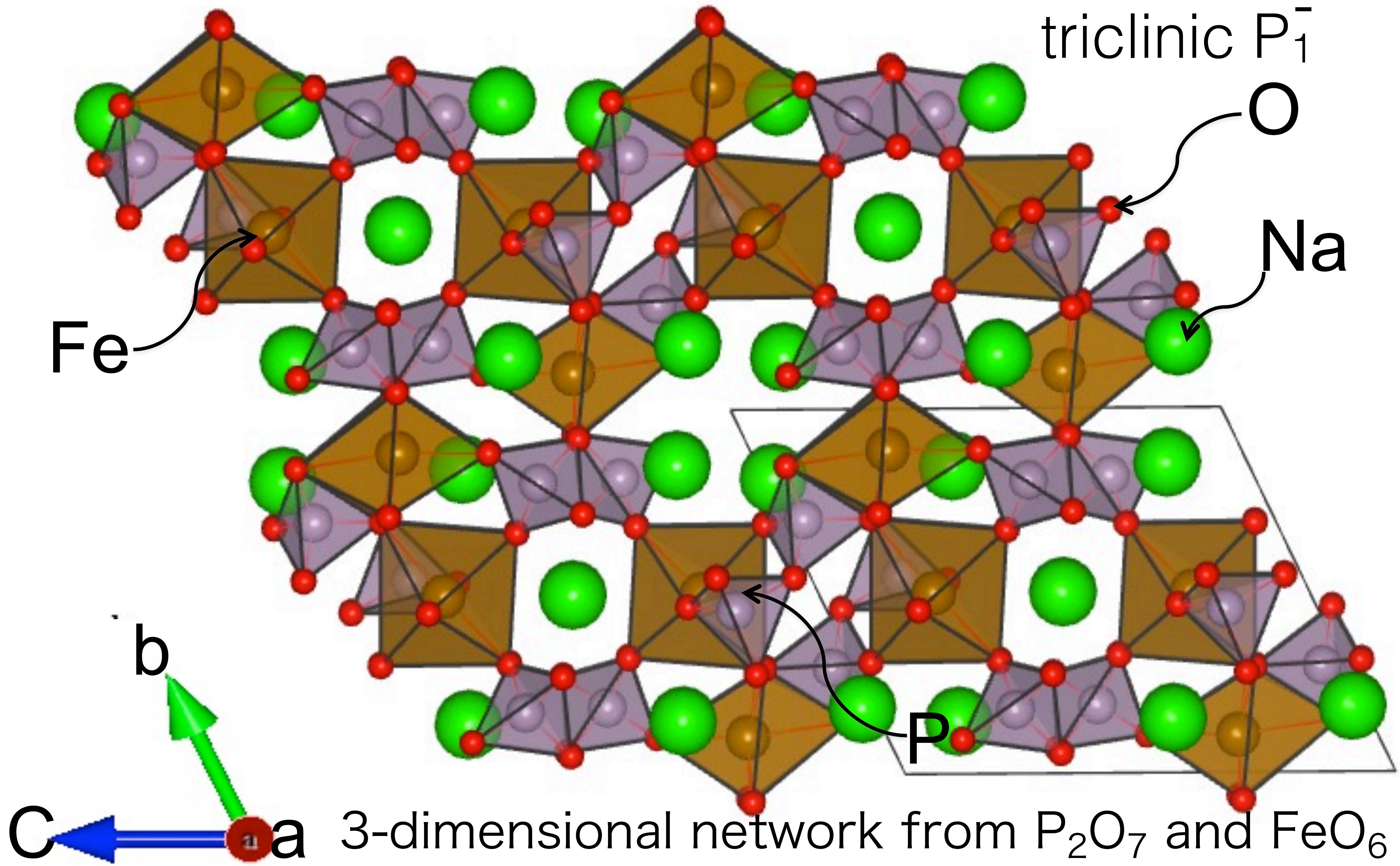


Patterns are similar to $Na_{3.12}Fe_{2.44}(P_2O_7)_2$

Eur. J. Solid State Inorg. Chem. 32 335 (1995)

a=0.640nm, b=0.938nm, c=1.097nm, α=64.53˚, β=86.05˚, γ=73.06

New cathode candidate $Na_2FeP_2O_7$



3-dimensional network from P_2O_7 and FeO_6

Morphology of GC/C composite

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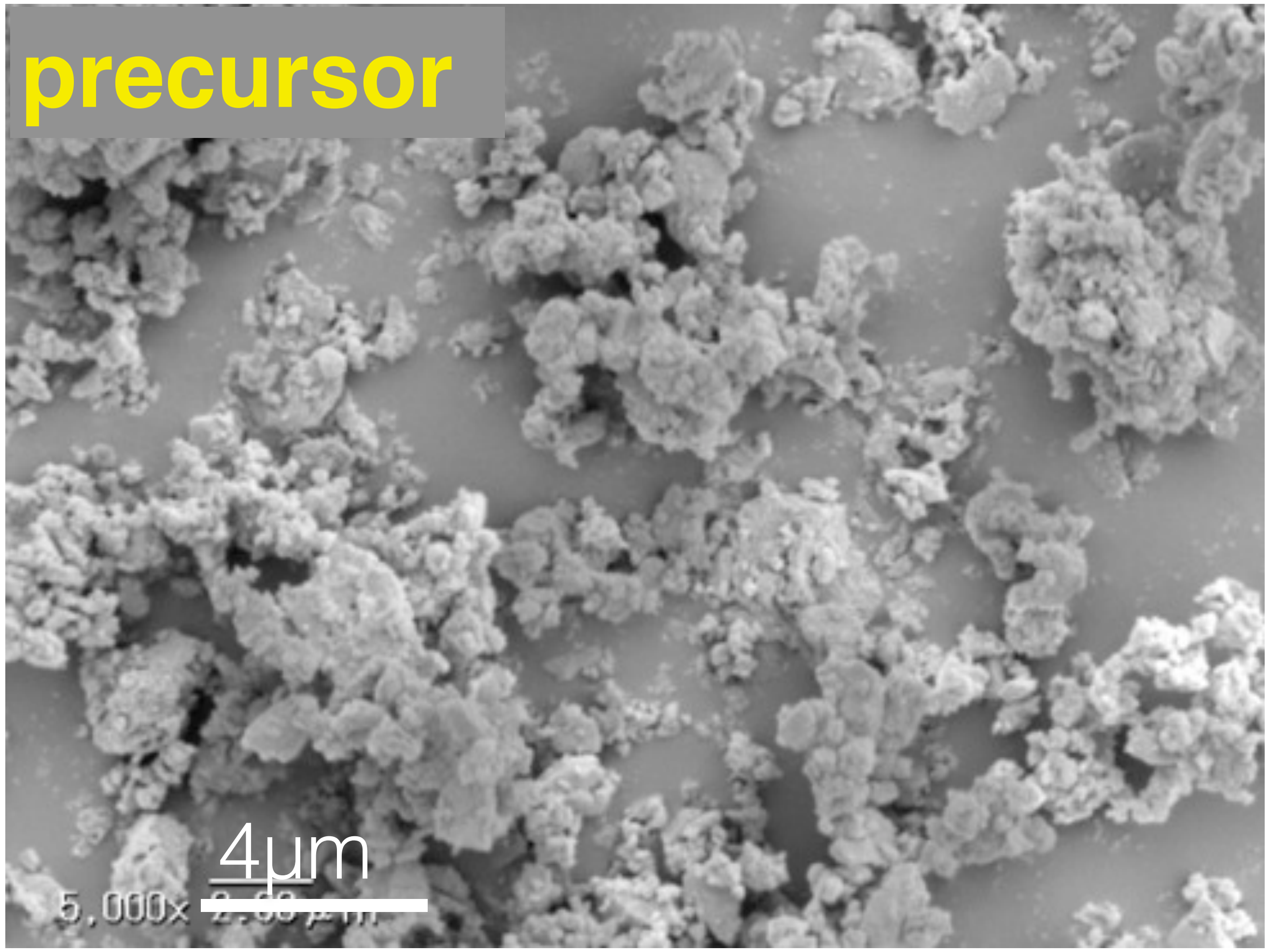
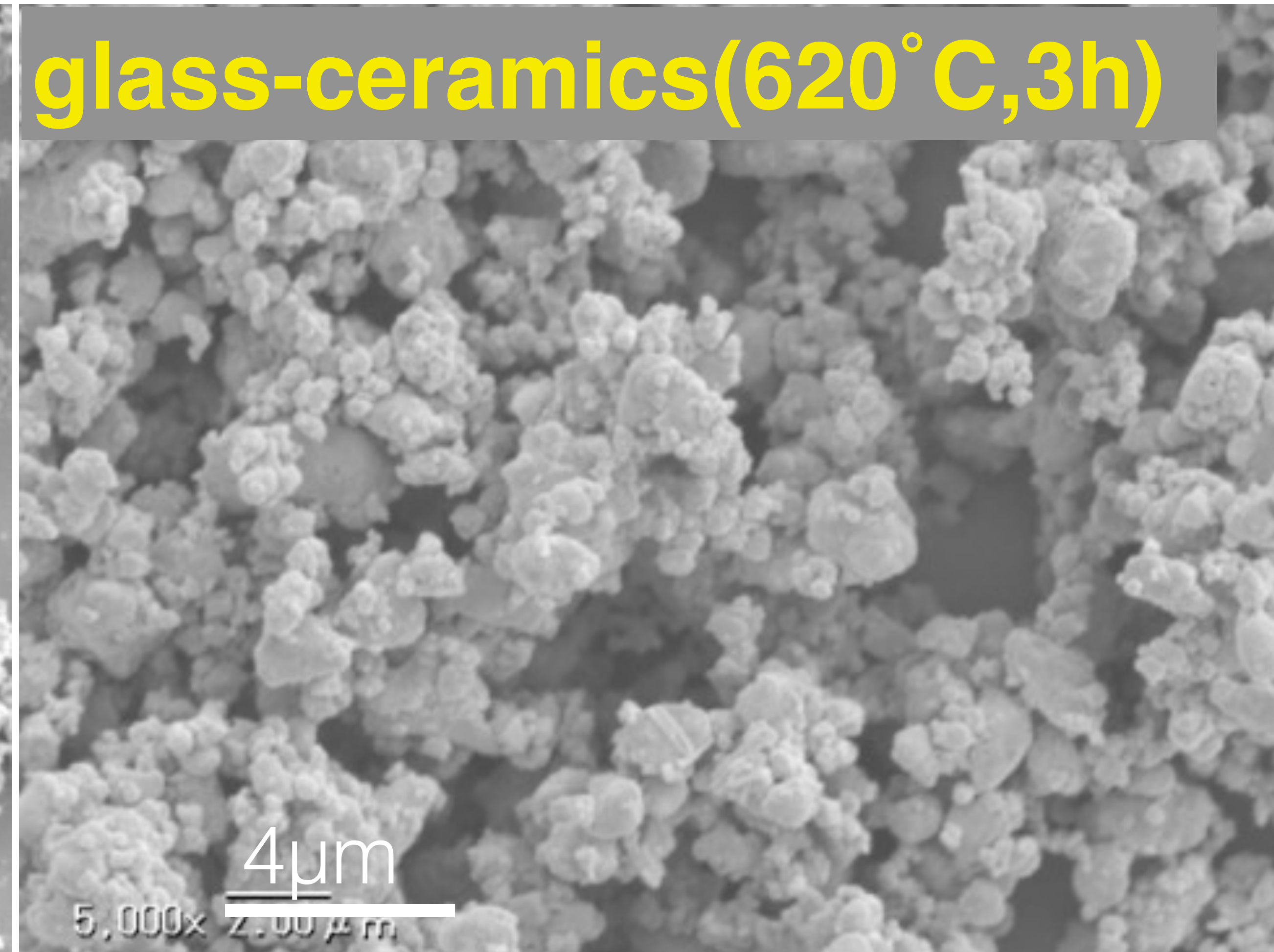
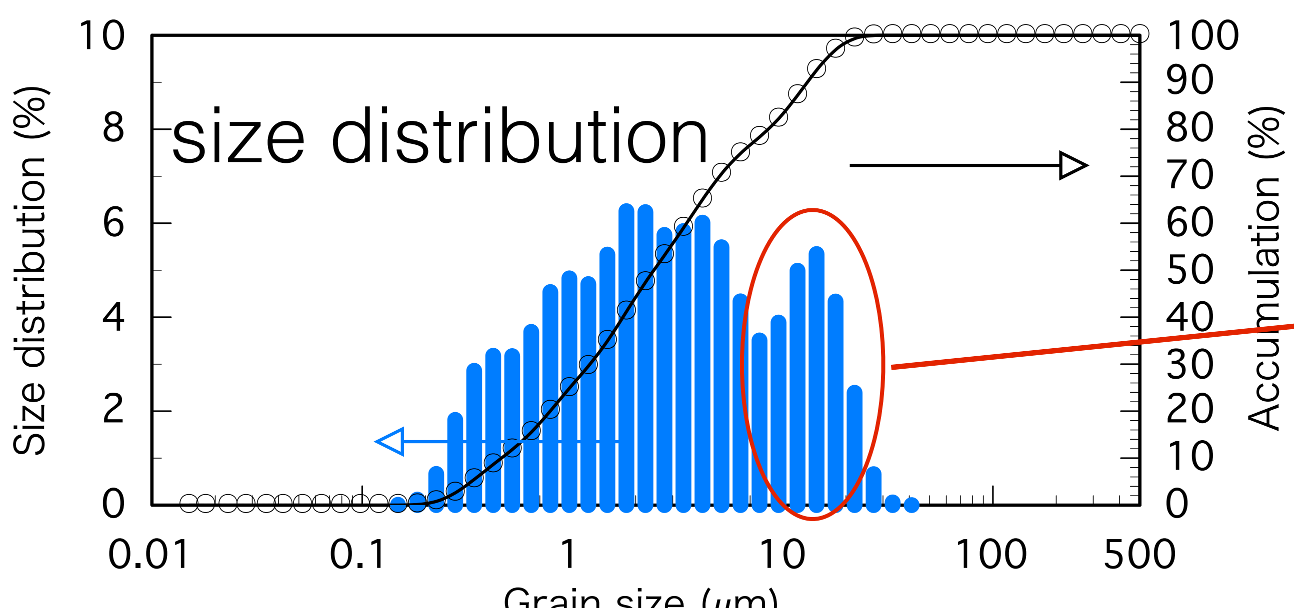
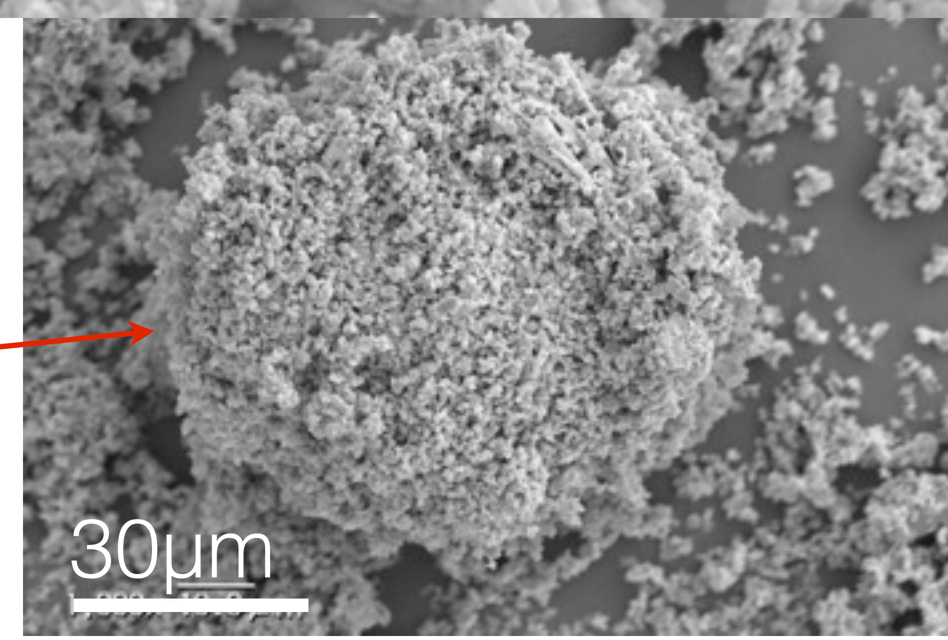
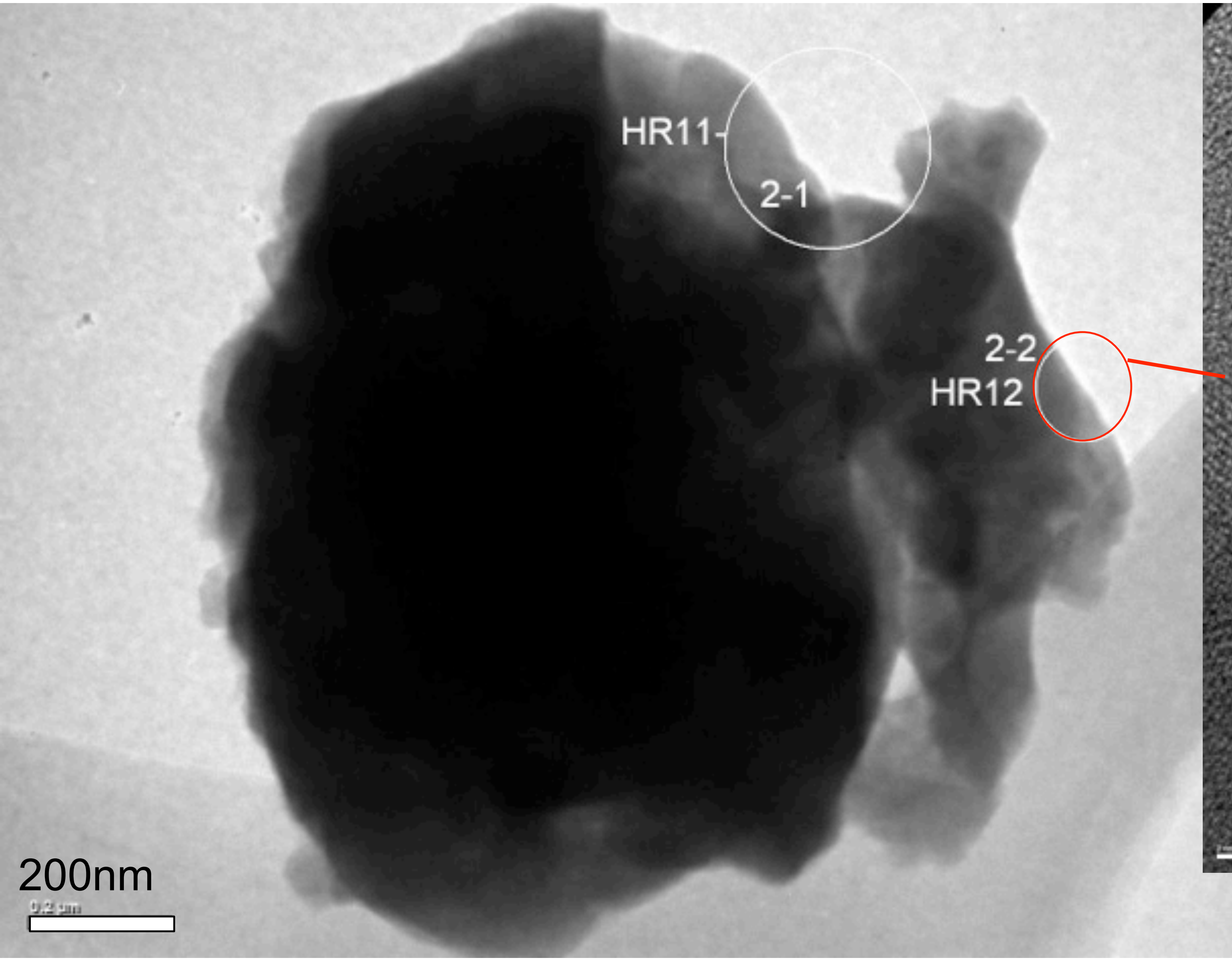


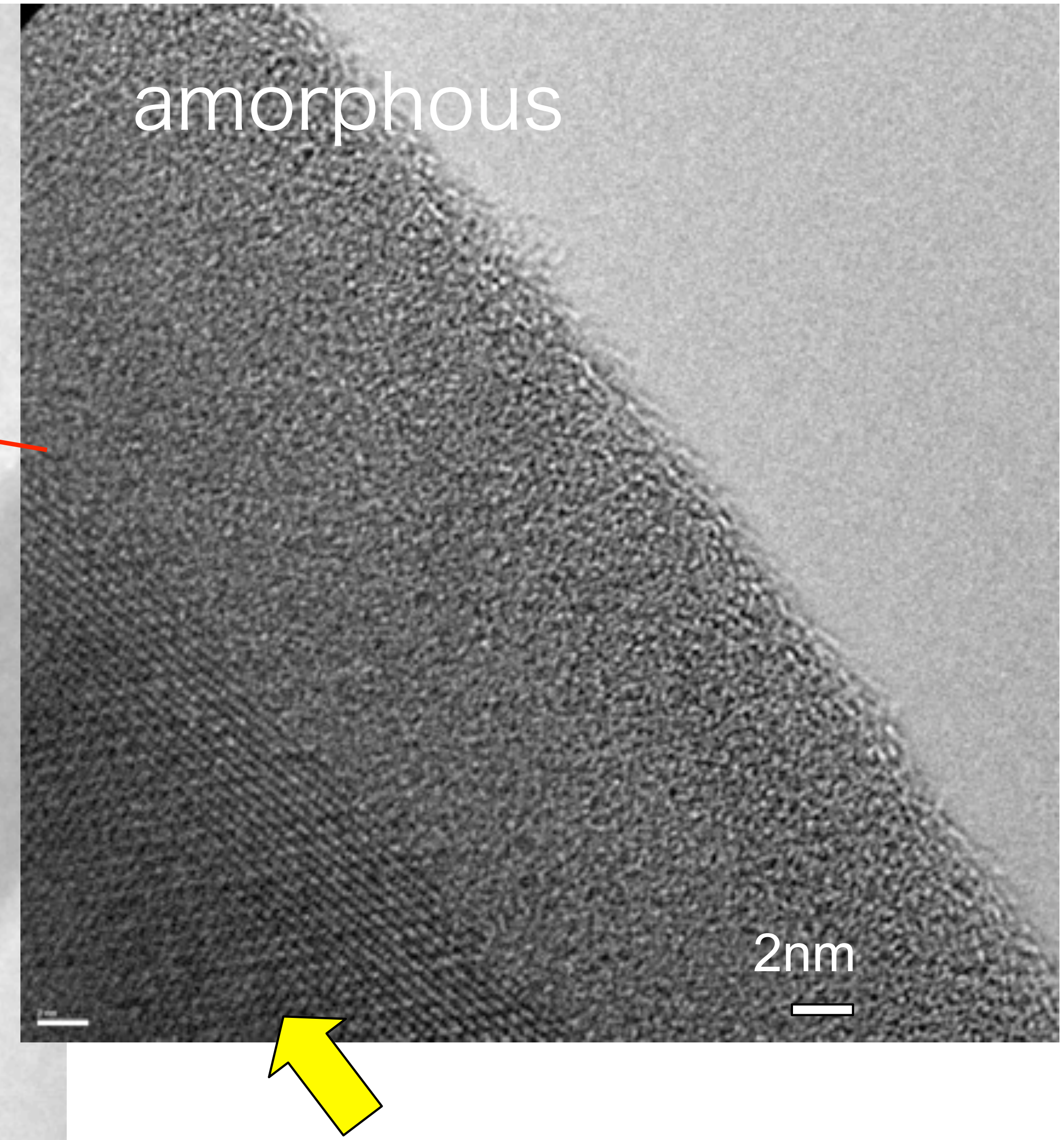






morphology of GC grain





$Na_2FeP_2O_7$ crystal

NFP grains are covered with amorphous carbon

Water durability

Under room temperature
soaked powder sample (1g) in water (100ml)

pH of Water : 7.7

	precursor	$Na_2FeP_2O_7/C$	$NaFeO_2$
pH after 17h	9.17	9.93	13.17
Color of solution	transparent	transparent	brown

Water durability is much higher than that of $NaFeO_2$

Charge-discharge profile(0.1C, 1-10times)

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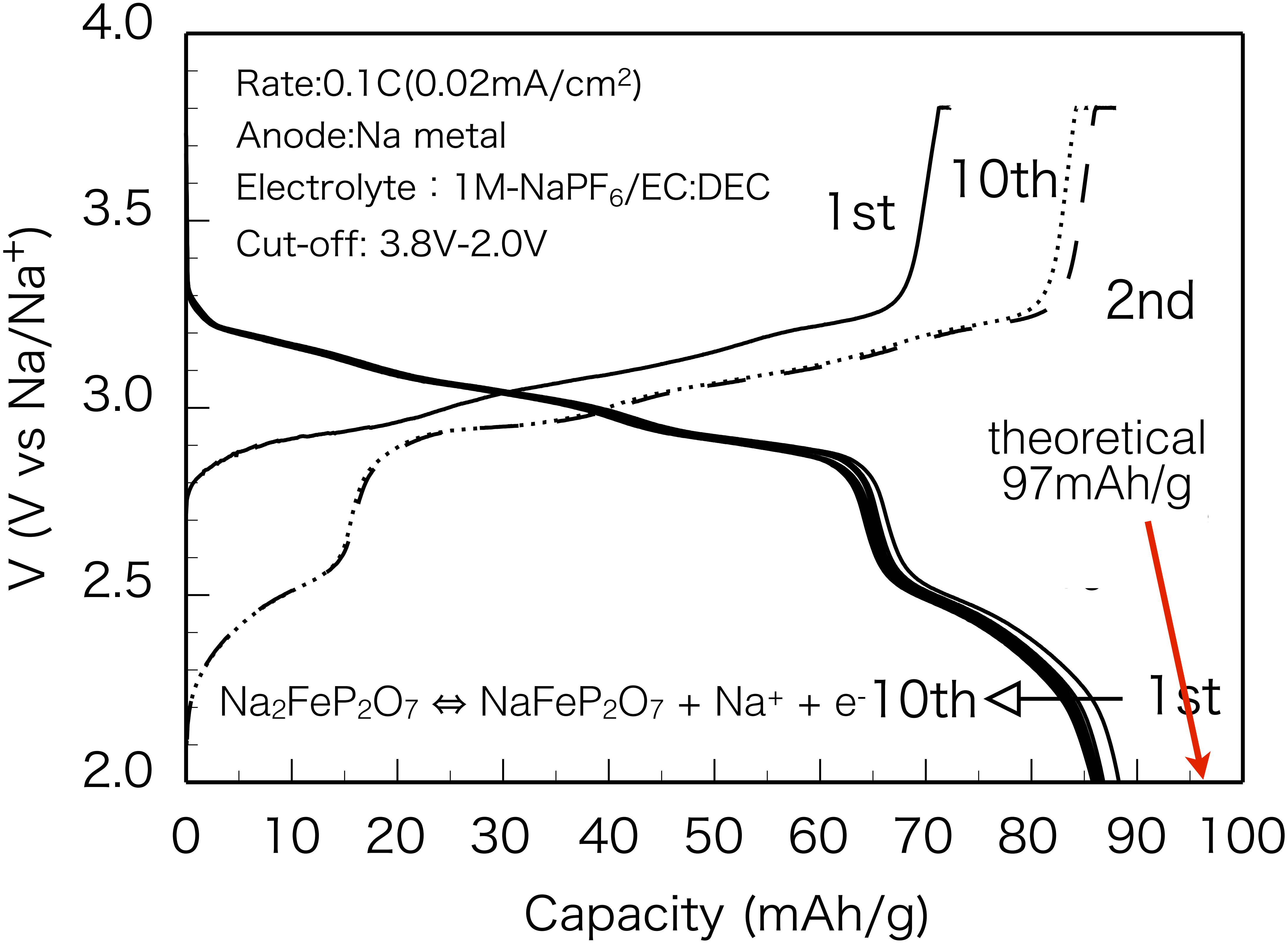
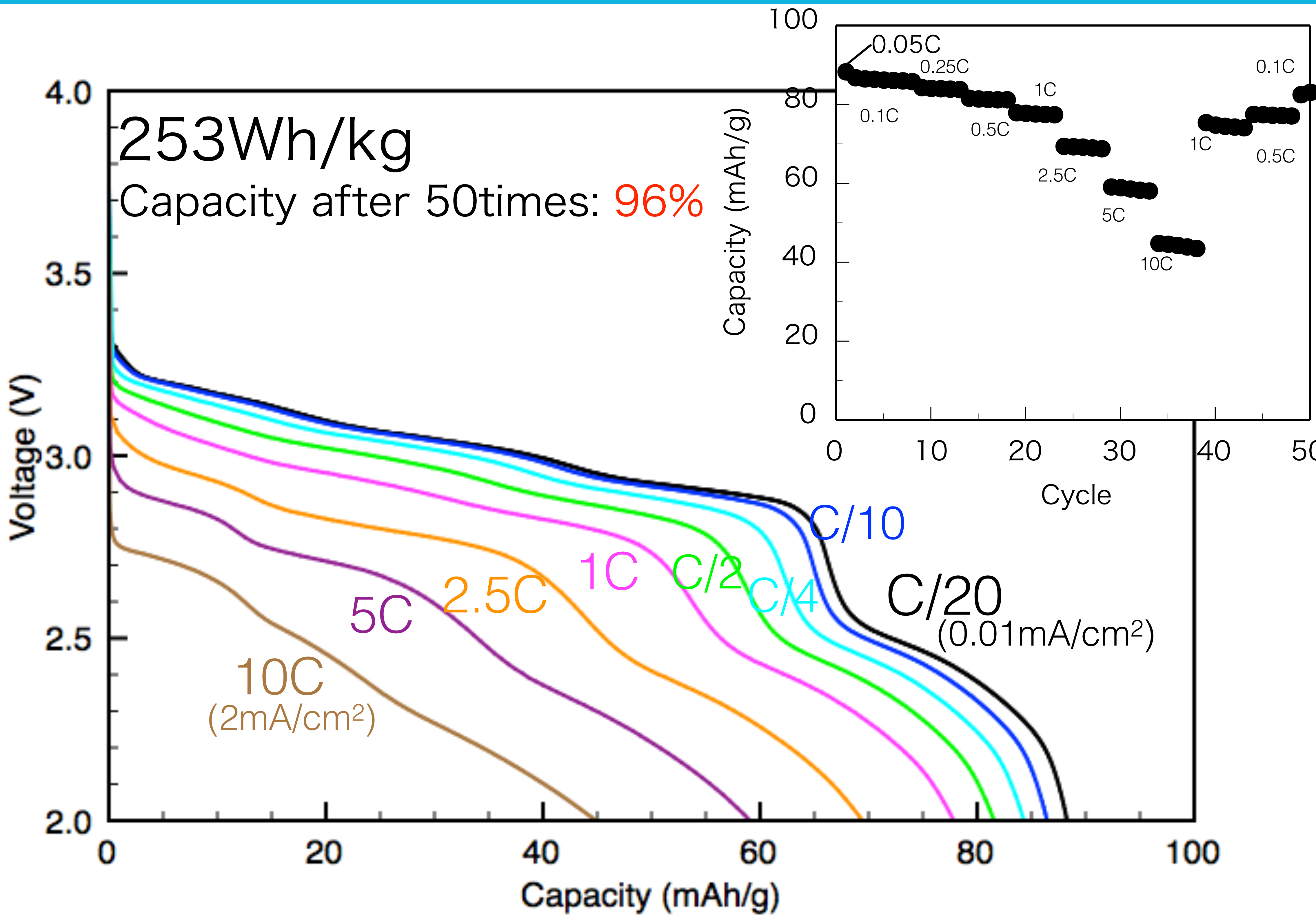
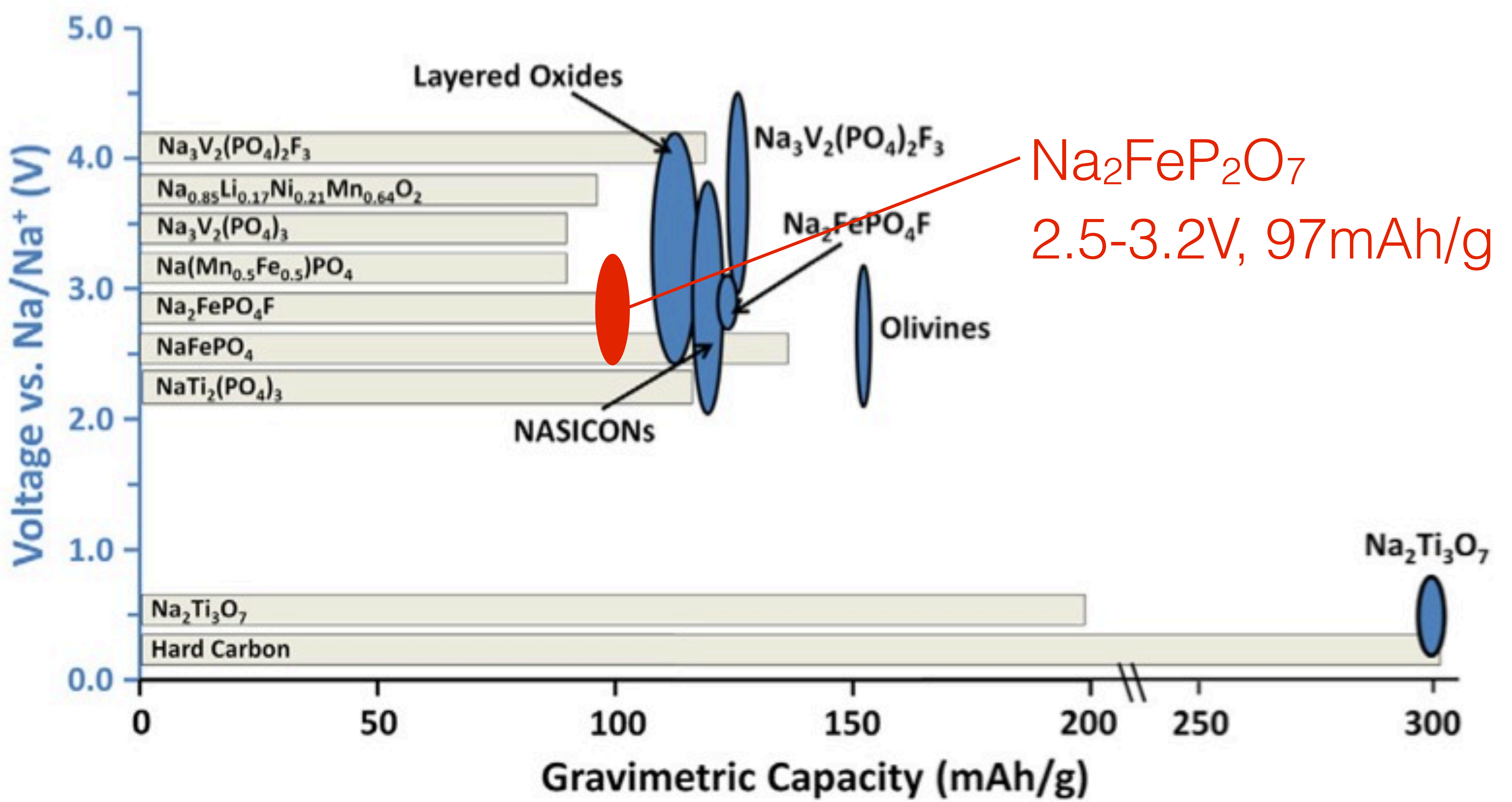


Rate performance



T.Honma et al., J. Power Sources 227 31(2012).

Cathode candidate for NaB



Brian L. Ellis, Linda F. Nazar, Solid State and Materials Science, 16 168-177 (2012)

Electron distribution in $Na_2FeP_2O_7$

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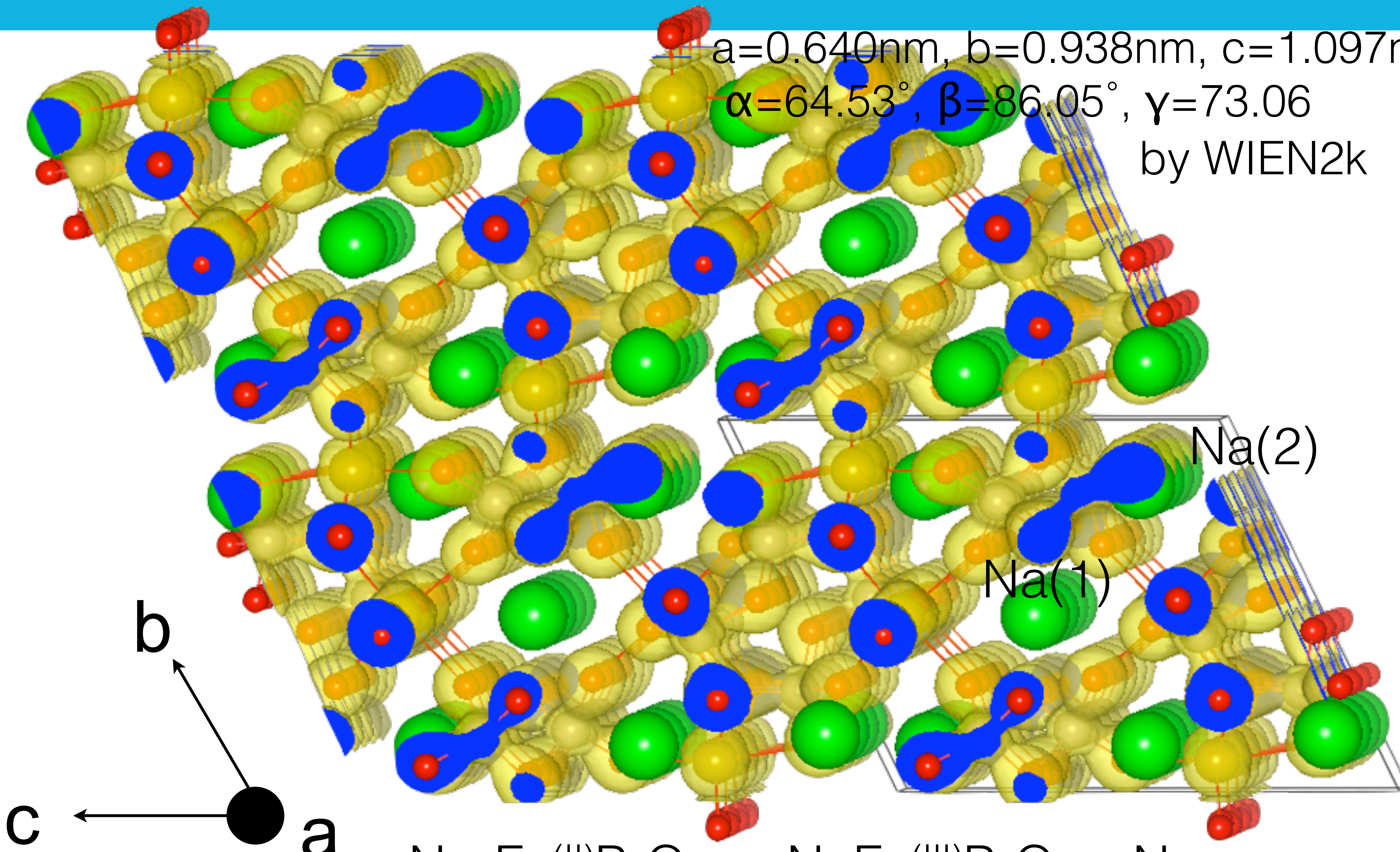


$Na_2Fe^{(II)}P_2O_7 \rightarrow NaFe^{(III)}P_2O_7 + Na^+ + e^-$

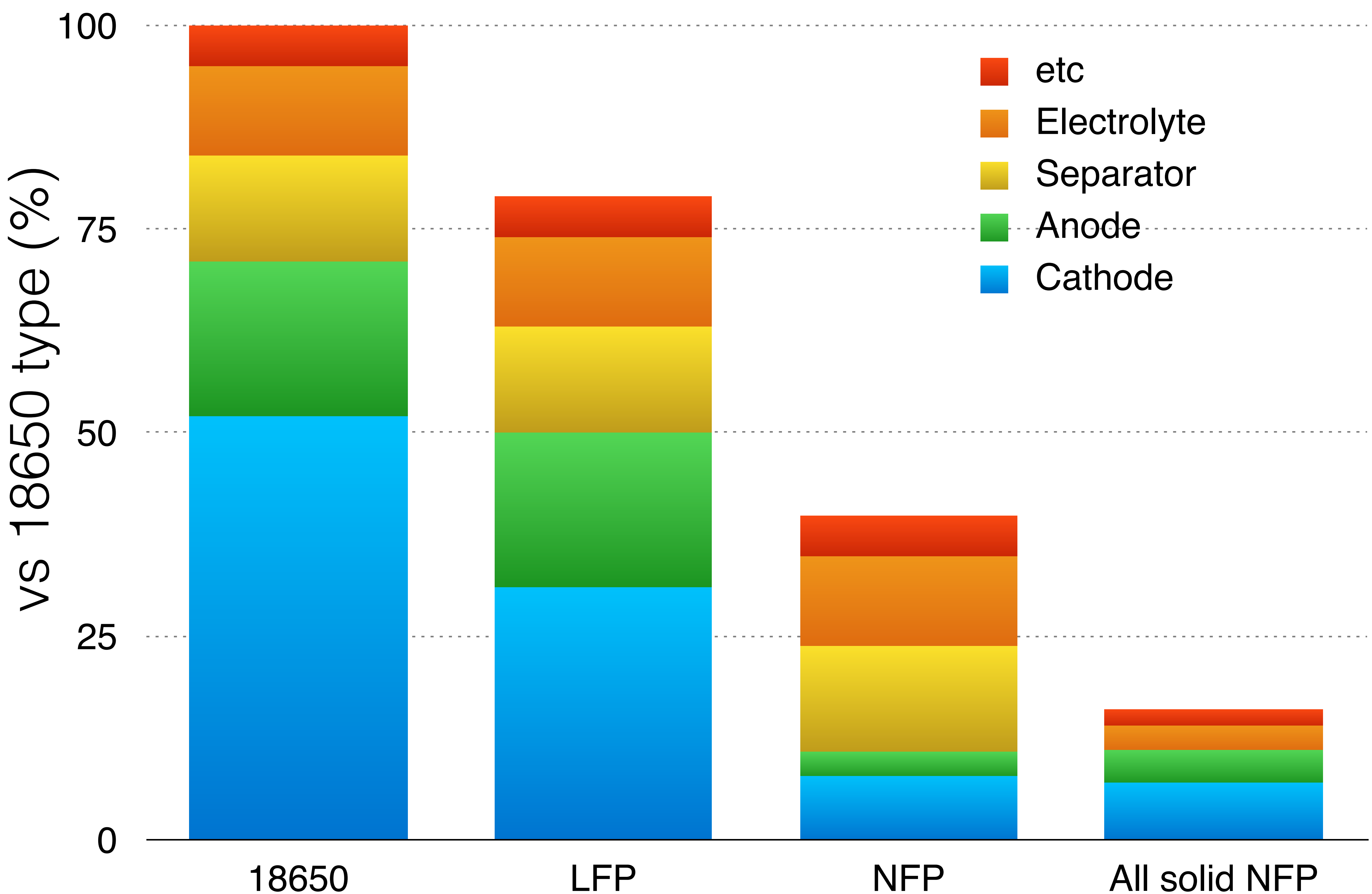
Conclusion

Fabrication of $Na_2FeP_2O_7$ glass-ceramics for rechargeable sodium ion battery

1. Triclinic $Na_2FeP_2O_7$ was formed by reduction heat-treatment.
2. $Na_2FeP_2O_7$ grains are covered with amorphous carbon layer, which assists electronic conduction in materials.
3. The reaction is expressed as

$$Na_2FeP_2O_7 \Leftrightarrow NaFeP_2O_7 + Na^+ + e^-$$

Cut down Mat. Costs



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Thank you for your attention