At noon Jan. 04, 2013 in Nagaoka
Glass-ceramics for the Innovative Secondary Batteries

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

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

J. E. Chem. Soc. 144, 1188(1997) cited 3563

**Na$_2$FeP$_2$O$_7$**
for Na-ion batteries
reported at first by us (2012)
1. Introduction
   • About Li-ion batteries
     - advantages and the problems
   • Typical cathode active materials
   • Iron phosphate base LiFePO₄
2. Glass-ceramics for LiB
   • Sample preparation
   • Properties
3. Sodium ion batteries (NaB)
   • New cathode candidate Na₂FeP₂O₇ by glass-ceramics method
   • Battery performance
4. Conclusion
Lithium ion batteries

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

In residential

~12kWh/day
XEVs

HV

Plug-in HV(PHV)

TOYOTA priusPHV, 4.4kWh

Plug-in HEV(PHEV)

TOYOTA prius, 1kWh

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

Cu foil  anode  Li\(^+\)  cathode  Al foil

Discharge: Li\textsuperscript{+} moves from cathode to anode

Charge: Li\textsuperscript{+} moves from anode to cathode

Cathode: LiCoO\(_2\) transition metal oxides
Anode: Carbon black
Collector: Al foil for cathode
Cu foil for anode
Breakdown of Materials cost

- Cathode: 52%
- Anode: 19%
- Separator: 13%
- Electroyte: 11%
- etc.: 5%

Materials cost is dominated by electrode.

We need valuable materials with cheap price.

Co$_3$O$_4$
LiCO$_3$
Al foil

http://www.jst-lcs.jp
Typical cathode structure

- **Rock salt type**
  - (LiCoO$_2$, LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$)

- **Spinel type** (LiMn$_2$O$_4$)

- **Olivine type** (LiFePO$_4$)

**Comparison:**
- Olivine: strong insulator with poor electrical conductivity and stability
- Spinel: moderate stability and electrical conductivity
- Rock salt: poor conductivity and stability
Olivine type LiFePO$_4$
A new cathode material without using cobalt oxide
Low cost
High theoretical capacity
170mAh/g
Redox potential
$\sim$3.5V
Poor electrical conductivity
$\sigma_{elec}\sim10^{-9}$Scm$^{-1}$
$\sigma_{ion}\sim10^{-11}$Scm$^{-1}$
Conventional: Solid-state, sol-gel, hydrothermal method etc.

LiCoO$_2$ (in use)
Li conduction is allowed along 1D axis

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

Our group has applied a Glass-Ceramics processing
Simple process and cheap reagents
Olivine type LiFePO$_4$
A new cathode material without using cobalt oxide

- Low cost
- High theoretical capacity: 170mAh/g
- Redox potential: ~3.5V
- Poor electrical conductivity: $\sigma_{\text{elec}} \sim 10^{-9}\text{Scm}^{-1}$
- Poor ionic conductivity: $\sigma_{\text{ion}} \sim 10^{-11}\text{Scm}^{-1}$

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

- Long processing time
- High-cost reagents
- Complicated process

Our group has applied a *Glass-Ceramics processing*

*Simple process and cheap reagents*
Glass-Ceramics (GC) processing

Li$_2$O-FeO-P$_2$O$_5$-Nb$_2$O$_5$  
K. Hirose et al.

Addition of Niobium Oxide
Double Al$_2$O$_3$ crucible + carbon

Li$_2$O-Fe$_2$O$_3$-P$_2$O$_5$  
T. Honma et al.

Melting in air is available
Cheap Fe$_2$O$_3$
Fe$^{2+}$/Fe$^{3+}$ mixed valence
i.e. Fe$^{3+}$/Fe=0.86
Reduction during crystallization

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

\[ \text{LiPO}_3 + \text{Fe}_2\text{O}_3 \]

quenching

\[ \text{LiFePO}_4 \text{ precursor glass} \]
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

1. Millling
2. Screening
3. Addition sugar (5-10%)
4. Baking (700°C)

LFP Glass Powder
Thermal property

Thermal property depends on valence state

Fe$^{2+}$/(Fe$^{2+}$+Fe$^{3+}$) = 0.87

Fe$^{2+}$/(Fe$^{2+}$+Fe$^{3+}$) = 0.8

Fe$^{2+}$/(Fe$^{2+}$+Fe$^{3+}$) = 0.31

Ratio Fe$^{2+}$ ions vs total Fe in glass
Glass formation tendency

Thermal stability ($\Delta T$) of precursor glass

$\Delta T = T_c - T_g$

- Fe$^{3+}$ rich 4-coordination
- Fe$^{2+}$ rich 6-coordination
Glass formation tendency

Thermal stability ($\Delta T$) of precursor glass

$\Delta T = T_c - T_g$

- $\Delta T / ^\circ C$
  - 150
  - 125
  - 100
  - 75
  - 50
- $0$ to $1$
- $\text{Fe}^{2+} / (\text{Fe}^{2+} + \text{Fe}^{3+})$
- $\text{Fe}^{3+}$ rich
  - 6-coordination
- $\text{Fe}^{2+}$ rich
  - 4-coordination
effect of sugar addition

Li₃Fe(III)₂(PO₄)₃

T.Honma et al., JNCS 356 3032 (2010)
HR-TEM image

350°C

HR-TEM image

Carbon coating

LiFePO₄

LiFePO₄

surface

By EDS

Amorphuos phase

C, Fe, P, O

2 nm
Crystallization mechanism

- At 350°C:
  - LFP glass
  - $\text{Fe}^{3+}$-rich

- At 700°C:
  - LiFePO$_4$
  - $\text{Fe}^{2+}$-rich site
  - Amorphous

One pot reaction:
- Reduction of $\text{Fe}^{3+}$
- Crystallization
- Carbon coat

References:
Preparation of LiB Cell

LFP:CB:PvDF=85:10:5

electrolyte
EC:DEC=1:1
1M LiPF$_6$

application

dry

press

punching

anode

stainless cell

Li foil

cathode

separator

electrolyte

cathode
Battery performance of LiFePO$_4$ glass-ceramics

Discharge curve

Cycle performance

Rate performance

LiFePO$_4$ Glass-Ceramics

- **Materials cost**
  Inexpensive materials are able to use
  ex) LiPO$_3$, Fe$_2$O$_3$

- **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

|   | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|
| 1 | H |   |   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |
| 2 | Li| Be|   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |
| 3 | Na| Mg|   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |
| 4 | K | Ca|   |   |   |   |   |   |   |    |    |    |    |    |    |    |    |    |
| 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|    |    |    |    |    |    |

- **for cathode**
- **for anode**
- **for collector**

• depends on many kinds of minor metals

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*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
Mining of Lithium resources

Major producing country

Chile、Bolivia、China

http://diamond.jp/articles/-/7534
Lithium resources are enough?

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
18650 type: 400～500$/kwh
Laminate type: 800～1000$/kwh
Target <300$/kWh

Resource
By use of minor metals, cost cut is difficult
## Lithium and Sodium

<table>
<thead>
<tr>
<th></th>
<th>Lithium</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposits</td>
<td>maldistribution (20ppm)</td>
<td>infinite</td>
</tr>
<tr>
<td>Ion radius</td>
<td>60pm</td>
<td>95pm</td>
</tr>
<tr>
<td>Weight</td>
<td>6.9g/mol</td>
<td>22g/mol</td>
</tr>
<tr>
<td>Voltage vs SHE</td>
<td>-3.03V</td>
<td>-2.7V</td>
</tr>
</tbody>
</table>

### 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**
  - \( \text{LiCoO}_2, \text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \)

- **Spinel type** (\( \text{LiMn}_2\text{O}_4 \))

- **Olivine type** (\( \text{LiFePO}_4 \))

**Properties**
- **Olivine**
  - Insulator
  - Strong
  - Good electrical conductivity

- **Spinel**
  - Stability
  - Weak
  - Good conductivity

- **Rock salt**
  - Insulator
  - Strong
  - Weak stability

**Chemical Formulas**
- LiCoO₂, LiCo₁/₃Ni₁/₃Mn₁/₃O₂
- LiMn₂O₄
- LiFePO₄
Typical cathode structure

- Rock salt type: 
  \( \text{LiCoO}_2, \text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \)
- Spinel type: 
  \( \text{LiMn}_2\text{O}_4 \)
- Olivine type: 
  \( \text{LiFePO}_4 \)

- Properties:
  - Olivine: strong insulator, good electrical conductivity
  - Spinel: stability, weak electrical conductivity
  - Rock salt: weak electrical conductivity, strong insulator
Problem in NaMO₂ rock salt

NaFeO₂[1], NaMnO₂[2], NaNi₀.₅Mn₀.₅O₂[3], NaCrO₂[4]…


Good electronic conductivity, however...

- Chemical durability is much poor
- Safety: not tested
- Thermal stability: not tested

NaMnO₂

NaCrO₂

Cathode candidate in Na$_2$O-Fe$_2$O$_3$-P$_2$O$_5$ system

glass formation region taken by INTERGLAD7
Cathode candidate in Na$_2$O-Fe$_2$O$_3$-P$_2$O$_5$ system

- NaFe$^{III}$P$_2$O$_7$
- Na$_3$Fe$^{III}$$_2$(PO$_4$)$_3$
- Na$_4$Fe$^{II}$$_3$P$_4$O$_{15}$

Glass formation region taken by INTERGLAD7
Fabrication of new cathode candidate by glass-ceramics method in the system Na$_2$O-Fe$_2$O$_3$-P$_2$O$_5$

- 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$_2$FeP$_2$O$_7$)
- crystallization behavior
- electrochemical properties
Experiments

【Glass preparation】
Starting reagents (NaPO₃, Fe₂O₃)

1. mix
2. melt
3. cast
4. milling

玻璃粉末

【Fabrication of Na₂FeP₂O₇/C composite】

glass powder: 90%
glucose 10%

crystallization
620°C, 3h Ar-H₂

Na₂FeP₂O₇/C composite

Advantages
- Fe₂O₃ 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

Precursor Glass

$\text{Na}_2\text{FeP}_2\text{O}_7$

$T_p$: 580°C

Fe$^{2+}$/ΣFe = 9.1%

$T_g$: 451°C

$T_m$: 930°C

$\text{Fe}^{2+}$/ΣFe = 9.1%
XRD pattern for glass and GC

Patterns are similar to Na$_{3.12}$Fe$_{2.44}$(P$_2$O$_7$)$_2$


precursor glass
Fe$^{2+}$/ΣFe=9.1%

Glass-ceramics(620°C, 3h)
Fe$^{2+}$/ΣFe=96.2%

Na$_2$FeP$_2$O$_7$
Simulated pattern

$\theta$ (deg.)

a=0.640nm, b=0.938nm, c=1.097nm,
$\alpha$=64.53°, $\beta$=86.05°, $\gamma$=73.06
New cathode candidate Na$_2$FeP$_2$O$_7$

3-dimensional network from P$_2$O$_7$ and FeO$_6$
Morphology of GC/C composite

precursor

glass-ceramics(620°C, 3h)

size distribution

0.01 0.1 1 10 100 500

0 2 4 6 8 10

Size distribution (%)

Grain size (µm)

Accumulation (%)
morphology of GC grain

Na$_2$FeP$_2$O$_7$ 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

<table>
<thead>
<tr>
<th></th>
<th>precursor</th>
<th>Na$_2$FeP$_2$O$_7$/C</th>
<th>NaFeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH after 17h</td>
<td>9.17</td>
<td>9.93</td>
<td>13.17</td>
</tr>
<tr>
<td>Color of solution</td>
<td>transparent</td>
<td>transparent</td>
<td>brown</td>
</tr>
</tbody>
</table>

Water durability is much higher than that of NaFeO$_2$
Charge-discharge profile (0.1C, 1-10times)

Rate: 0.1C (0.02 mA/cm²)
Anode: Na metal
Electrolyte: 1M-NaPF₆/EC:DEC
Cut-off: 3.8V-2.0V

Na₂FeP₂O₇ ↔ NaFeP₂O₇ + Na⁺ + e⁻

theoretical 97 mAh/g
Rate performance

253Wh/kg
Capacity after 50 times: 96%

Voltage (V)

Capacity (mAh/g)

Cathode candidate for NaB

Na$_2$FeP$_2$O$_7$
2.5-3.2V, 97mAh/g
Electron distribution in Na$_2$FeP$_2$O$_7$

Na$_2$Fe$^{(II)}$P$_2$O$_7$ $\rightarrow$ NaFe$^{(III)}$P$_2$O$_7$ + Na$^+$ + e$^-$

$a=0.640\text{nm}$, $b=0.938\text{nm}$, $c=1.097\text{nm}$,
$\alpha=64.53^\circ$, $\beta=86.05^\circ$, $\gamma=73.06^\circ$

by WIEN2k
Conclusion

Fabrication of Na$_2$FeP$_2$O$_7$ glass-ceramics for rechargeable sodium ion battery

1. Triclinic Na$_2$FeP$_2$O$_7$ was formed by reduction heat-treatment.
2. Na$_2$FeP$_2$O$_7$ grains are covered with amorphous carbon layer, which assists electronic conduction in materials.
3. The reaction is expressed as

$$\text{Na}_2\text{FeP}_2\text{O}_7 \leftrightarrow \text{NaFeP}_2\text{O}_7 + \text{Na}^+ + \text{e}^-$$
Cut down Mat. Costs

vs 18650 type (%)
Thank you for your attention