Development of Fe− and Mn−based cathode materials

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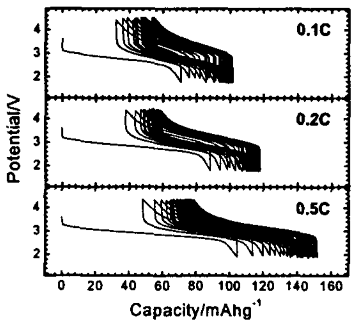
1. Introduction

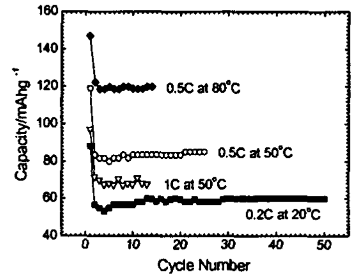
Development of Cathode Materials for Li-ion Batteries

Past 10 years		Alternatives		New Materials
- $LiCoO_2$: high cost - $LiNiO_2$: safety problem - $LiMn_2O_4$: capacity fade	⇨	- $LiMnO_2$: capacity fade - V_2O_5 : low voltage - $LiM_{0.5}Mn_{1.5}O_4$: high voltage	⇨	- $LiFePO_4$: good cyclability, low cost - Li-Ni-Mn-O : high capacity

2.1 Amorphous $FePO_4 \cdot xH_2O$

Electrochemical properties of new Fe-based cathode material a-$FePO_4$





Good cyclability but low capacity!!

2.2 New cathode materials with high capacity?

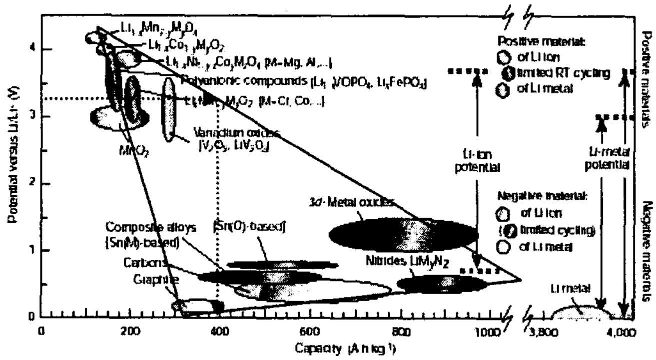


Fig. V vs. capacity for cathode and anode materials for the next generation of Li batteries. Note the huge difference in capacity between Li metal and the other negative electrodes, which is the reason why there is still great interest in solving the problem of dendrite growth.

J.-M. Tarascon and M. Armand, Nature, 2001, 414(15), 359

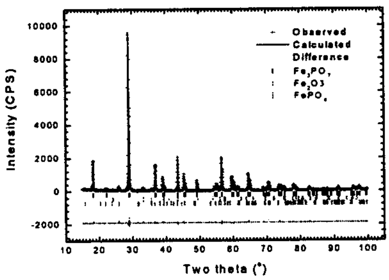
3V class cathode material with a capacity of 400 mAh/g

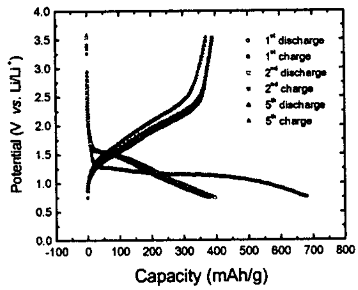
Is it possible ??

2.2.1 Crystalline Fe_3PO_7

From JCPDS-ICDD Search

XRD and electrochemical properties of new Fe-based cathode material Fe_3PO_7





1. **Trigonal(*R3m*) *a*=8.003, *c*=6.860 Å, Impurities : Fe_2O_3, $FePO_4$**
2. **High initial capacity of 700 mAh/g and stable cyclability with 400 mAh/g, but low voltage**
3. **Proposed Li insertion/extraction mechanism : $Fe_3PO_7 + 9Li \rightarrow Li_3PO_4 + 3Li_2O + 3Fe$**

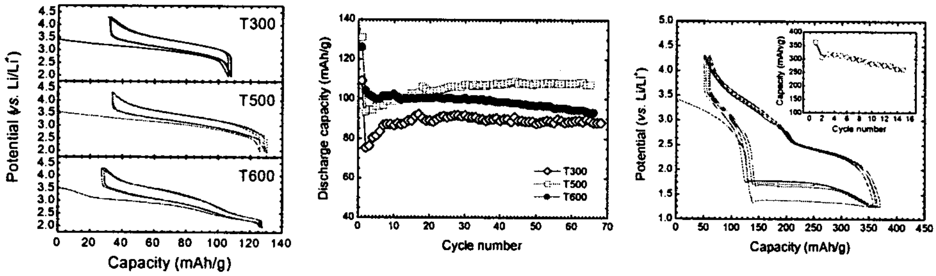
2.3 New Candidates from Mineral Search

Name	Formula	M.W		Capacity
Ag	Fe4As2O11	549.2	48.8	195
'Apatelite'	Fe3(SO4)2(OH)5 0.5H2O	444.7	60.3	181
'Avasite'	5Fe2O3 2SiO2 9H2O	918.6	29.2	292
'Azovskite'	Fe3(PO4)(OH)6	364.6	73.5	221
'Beldongr	Mn18Fe2O33 8H2O	1628.6	16.5	329
Beraunite	FeFe5(PO4)4(OH)5 6H2O	800.0	33.5	168
Bernalite	Fe(OH)3 nH2O	106.9	250.8	251
'Calcium-Jarosite'	CaFe6(SO4)4(OH)12	963.5	27.8	167
Chalcophanite	(Zn,Fe,Mn)Mn3O7 3H2O	332.7	80.6	242
Chalcosiderit	*CuFe6(PO4)4(OH)8 4H2O*	*914.6*	*29.3*	*176*
Cuzticite	Fe2TeO6 3H2O	335.3	79.9	160
Diadochite	Fe2PO4SO4(OH) 5H2O	319.7	83.8	168
Ferrihydrite	Fe5O7OH H2O	408.2	65.7	328
Ferrisicklerite	*(Fe,LiMn)PO4*	*150.8*	*177.7*	*178*
Giniite	FeFe4(PO4)3(OH)5 2H2O	645.1	41.5	166
Maricite	NaFePO4	157.8	169.9	170
Meurigite	KFe7(PO4)5(OH)7 8H2O	1023.9	26.2	183
Phosphosiderite	*FePO4 2H2O*	*150.8*	*177.7*	*178*
Purpurite	*(Mn,Fe)PO4*	*150.8*	*177.7*	*178*
Rodolicoite	FePO4	150.8	177.7	178
Schwert	Fe16O16(OH)12(SO4)2	1545.7	17.3	277
Sicki	Li(Mn,Fe)PO4	157.8	169.9	170
Strengite	*FePO4 2H2O*	*150.8*	*177.7*	*178*
'Strengite-Variscite Series'	FePO4 2H2O - AlPO4 2H2O	150.8	177.7	178
'Tietaiyangite'	Fe4FeTiO9	471.1	56.9	228
Tinticite	Fe4(PO4)3(OH)3 5H2O	559.3	47.9	192
Triphyl	LiFePO4	157.8	169.9	170
JCPDS_synthetic	Fe3PO7		86.3	259

2.3.1 Diadochite $Fe_2(PO_4)(SO_4)OH$

ETRI

Electrochemical properties of new Fe-based cathode material diadochite



1. Heat treatment at 300, 500, 600°C → good cyclability
2. When the cutoff voltage was down to 1.2V, the other plateau at 1.7V appeared.

2.4 Synthesis of $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$

ETRI

Mixed Hydroxide Method

- Dripping of (Ni,Mn) solution into LiOH solution
- Filtering and Washing
- Drying at 180°C
- Mixing of $(Ni,Mn)(OH)_x$ and LiOH
- Pelletizing
- Calcination at 480°C
- Heating at 900°C
- Quenching

Sol-Gel Method

- Adding of (Li,Ni,Mn) solution into chelating solution
- pH adjusting by NH_4OH
- pH control and evaporation
- Decomposition at 480°C
- Pelletizing
- Heating at 900°C
- Quenching

Simple Combustion Method

In this work

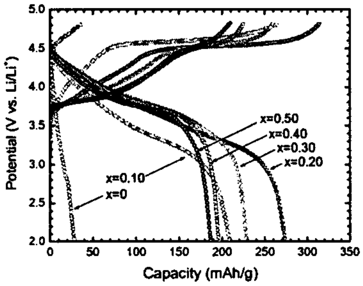
- (Li,M,Mn) solution (M=Ni,Cr)
- Evaporation
- Decomposition at 400°C
- Heating at 900°C
- Quenching

⇩

Easy and simple to prepare $Li[MLiMn]O_2$

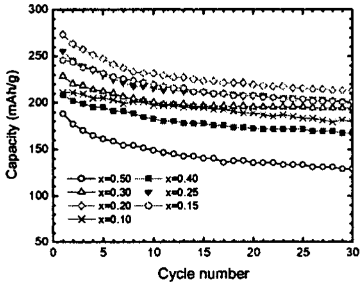
2.4.1 $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$

First Charge-Discharge Curve of $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$



Current density = 40mA/g, 4.8-2.0V
$LiNi_{0.20}Li_{0.20}Mn_{0.60}O_2$ (x=0.20)
Highest capacity of 272mAh/g

Discharge Capacity of $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$

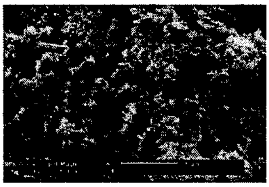


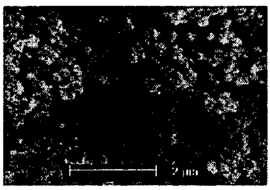
Cyclability should be improved

2.4.2 $Li[Ni_{0.20}Li_{0.20}Mn_{0.60}]O_2$

SEM Photograph

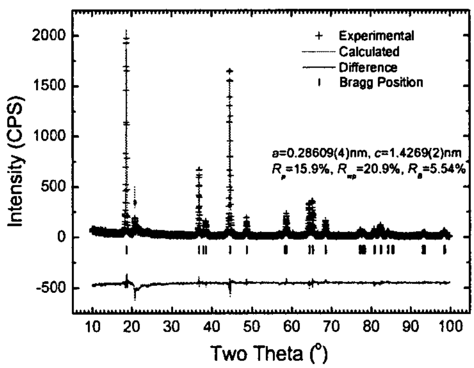
100-200nm in size, homogeneous





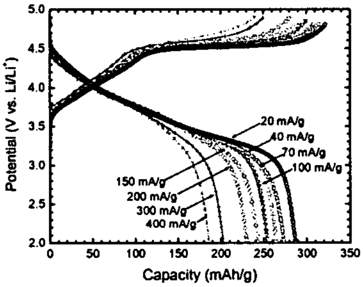
Rietveld Analysis

Well Crystallized XRD pattern



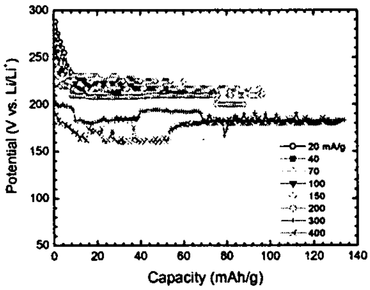
2.4.3 Rate Capability of $Li[Ni_{0.20}Li_{0.20}Mn_{0.60}]O_2$

Rate Capability



At a lower current density of 20mA/g → Excellent capacity of 290mAh/g

Discharge Capacity



At a higher current density → Excellent cyclability

2.4.4 Comparison

	J.R. Dahn Mixed oxide method	Our result Simple combustion method
Current density	5 mA/g	> 40 mA/g
Voltage range	2.0 – 4.8 V	2.0 – 4.8 V
Percent of active material	74%	80 – 90 wt%
Measuring temperature	30 °C	30 °C
Optimum composition	x = 1/3	x = 0.20
Initial capacity	250 mAh/g (5 mA/g)	290 mAh/g (20 mA/g)
Particle size	Several μm	0.15 μm
Morphology	Irregular	Homogeneous, spherical shape

3. Conclusion

1. Fe-based phosphate and/or sulfate is good cathode candidate for EV battery.
2. Li-Ni-Mn-O system is promising cathode candidate for portable electronics.