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LiFeO<sub>2</sub>와 LiFeO<sub>2</sub>-Li<sub>x</sub>MnO<sub>2</sub> 시스템의 합성  
및 전기화학적 특성

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# Synthesis and Electrochemical Characterization of $\text{LiFeO}_2$ and $\text{LiFeO}_2\text{-Li}_x\text{MnO}_2$ System

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## [ PART I ]

### Synthesis of $\text{o-LiFeO}_2$ and its unique structural change during cycling

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## The characteristics of conventional $\text{LiFeO}_2$

	$\alpha\text{-LiFeO}_2$	$\beta\text{-LiFeO}_2$	$\gamma\text{-LiFeO}_2$
Structure	Cubic ( $Fm\bar{3}m$ )	Monoclinic ( $C2/c$ )	Tetragonal ( $I4_1/amd$ )
Lattice Constant (Å)	a = 4.158	a = 4.158 b = 11.589 c = 5.147 $\beta = 145.7^\circ$	a = 4.057 c = 8.759
Synthetic Method	Solid-State, Hydrothermal	Hydrothermal	Hydrothermal, Post-annealing
Capacity (mAh/g)	5-10 (obtained at > 600 °C)	–	–
Reference	<ul style="list-style-type: none"> <li>• Anderson et al.</li> <li>• Tabuchi et al.</li> <li>• Kanno et al.</li> </ul>	<ul style="list-style-type: none"> <li>• Barriga et al.</li> <li>• Tabuchi et al.</li> </ul>	<ul style="list-style-type: none"> <li>• Hewston et al.</li> <li>• Anderson et al.</li> </ul>

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## The characteristics of layered- $\text{LiFeO}_2$

	$\alpha\text{-NaFeO}_2$ Type	Corrugated type
Structure	Hexagonal ( $R\bar{3}m$ )	Orthorhombic ( $Pnma$ )
Lattice constant (Å)	a = 2.963 c = 14.636	a = 4.061 b = 2.962 c = 6.032
Synthetic method	Ion-exchange, Hydrothermal	Ion-exchange, Hydrothermal
Discharge capacity (mAh/g)	60-140 (0.1 mA/cm <sup>2</sup> )	80-100 (0.4 mA/cm <sup>2</sup> )
Reference	<ul style="list-style-type: none"> <li>• Tabuchi et al.</li> <li>• Sakurai et al.</li> </ul>	<ul style="list-style-type: none"> <li>• Kanno et al.</li> <li>• Tabuchi et al.</li> <li>• Sakurai et al.</li> </ul>

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## Some questions of previous studies

Complexity	Cycle Performance	No report
of the synthetic process ; a long reaction time & many reaction steps. (ion-exchange)	impossible to fully insert/extract Li ions into the conventional $\alpha$ -LiFeO <sub>2</sub> compound	showing an excellent cycle performance of <i>corrugated</i> LiFeO <sub>2</sub> in the long-term cycling

### Goal of this Research

Synthesis of LiFeO<sub>2</sub> Material  
(Simple, High, and Good)

◆ Y.S.Lee et al. *Electrochem. Comm.* 4(9), 727 (2002).



## The starting point of this research

◆ Kanno et al. (*cor*-LiFeO<sub>2</sub>) ;

- ◆ LiOH +  $\gamma$ -FeOOH
- ◆ Ion-exchange method (100-150 °C)
- ◆ 100-120 mAh/g at RT.

◆ Y.S. Lee et al. (*o*-LiMnO<sub>2</sub>) ;

- ◆ LiOH +  $\gamma$ -MnOOH
- ◆ Quenching method (1000 °C)
- ◆ 200-210 mAh/g at RT and HT.

; Y.S. Lee et al. *Electrochem. & Solid-State Lett.*, 4(10), A116 (2001).

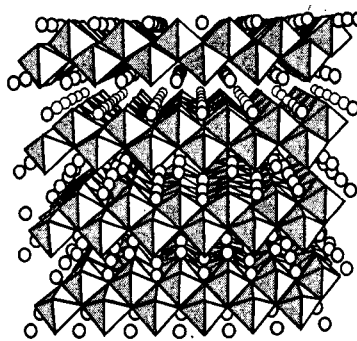
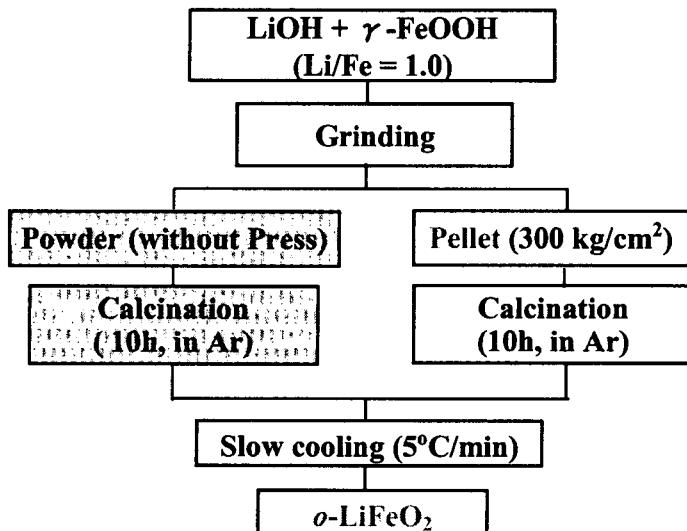


Fig. Structure of *cor*-LiFeO<sub>2</sub>

- ◆ *Cor*-LiFeO<sub>2</sub> has been successfully synthesized by ion exchange method at 150°C. → If so, is it possible to synthesize *o*-LiFeO<sub>2</sub> with advanced battery performance by solid-state method?



## Synthetic procedure of $\alpha$ -LiFeO<sub>2</sub> material



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### ● The effect and role of pelletizing

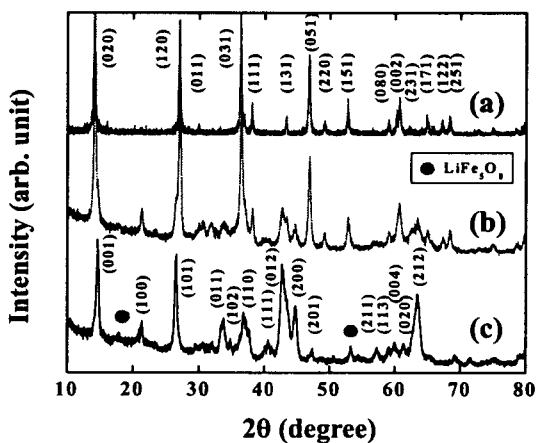


Fig. X-ray diffraction patterns of (a)  $\gamma$ -FeOOH, (b) LiFeO<sub>2</sub> without pelletizing, and (c) LiFeO<sub>2</sub> with pelletizing.

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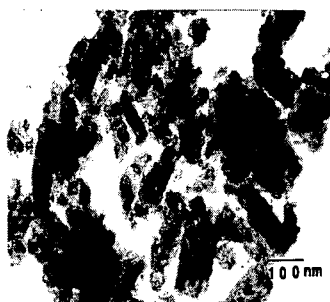
## Properties and chemical analysis of $\delta$ -LiFeO<sub>2</sub>

	a (Å)	b (Å)	c (Å)	Composition
LiFeO <sub>2</sub>	4.039	2.976	6.078	LiFeO <sub>2.02</sub>

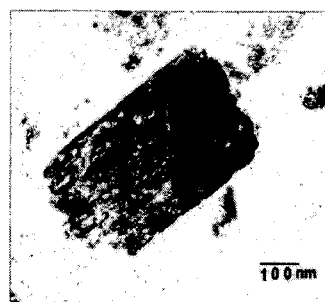
- The role of pelletizing during synthesis  
; in accelerating the slow reaction of lithium and  $\gamma$ -FeOOH particles at low synthetic temperature.
- The optimum synthetic condition  
; the calcination of LiOH and  $\gamma$ -FeOOH mixture with pressing for 10 h at 150 °C in Ar atmosphere.



## TEM analysis of $\delta$ -LiFeO<sub>2</sub> material



(a)

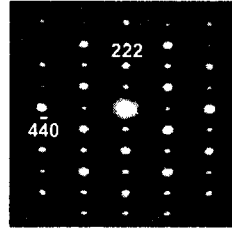
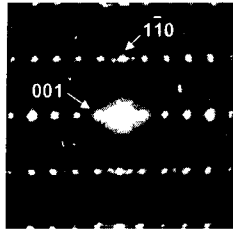


(b)

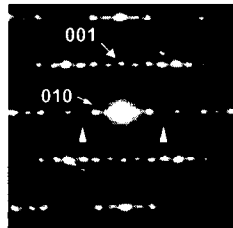
Fig. Bright field TEM image of the (a) LiFeO<sub>2</sub>, (b) LiFeO<sub>2</sub> particle with stacking fault.



### SAD patterns of *o*-LiFeO<sub>2</sub> material



Orthorhombic LiFeO<sub>2</sub> in [110] Spinel β-LiFe<sub>5</sub>O<sub>8</sub> in [112]

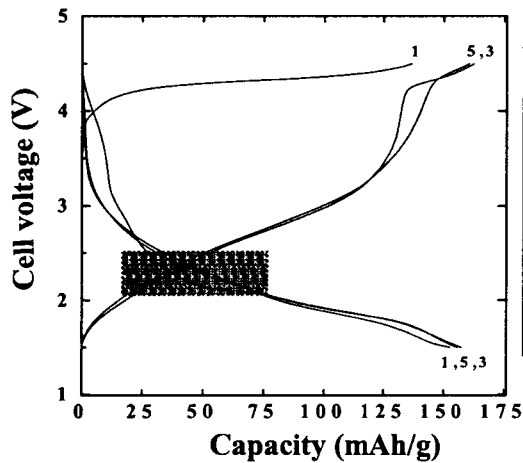


Orthorhombic  
+  
Spinel  
+  
(defective orthorhombic)  
; was mixed with 3 phases

Defective *o*-LiFeO<sub>2</sub> in [100]



### Cycle behavior of *o*-LiFeO<sub>2</sub> material

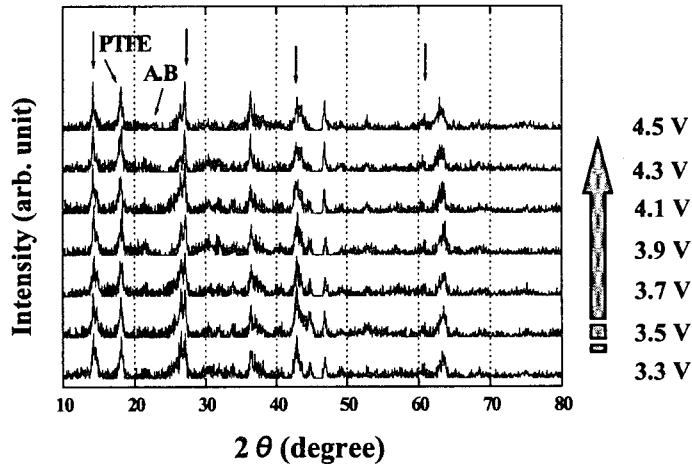


- ◆ Test condition
- 4.5~1.5V(Li/Li<sup>+</sup>)
- LiPF<sub>6</sub>-EC/DMC (1:2 vol.)
- Anode : Li metal
- Separator : P · P
- C · D : 0.1 mA/cm<sup>2</sup>

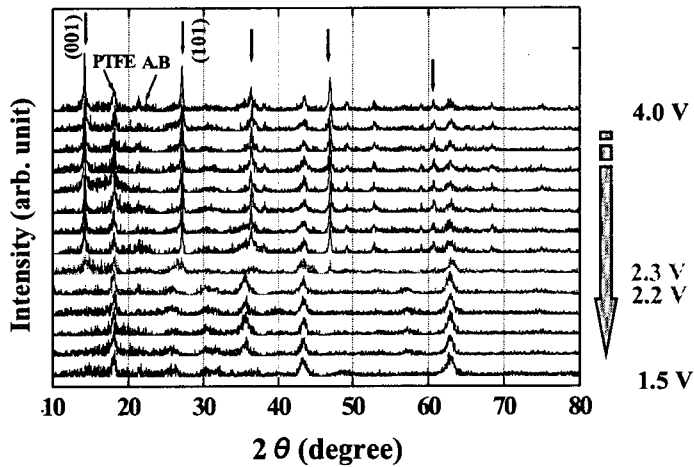




### *In-situ XRD of $o$ -LiFeO<sub>2</sub> in the 1<sup>st</sup> charge*

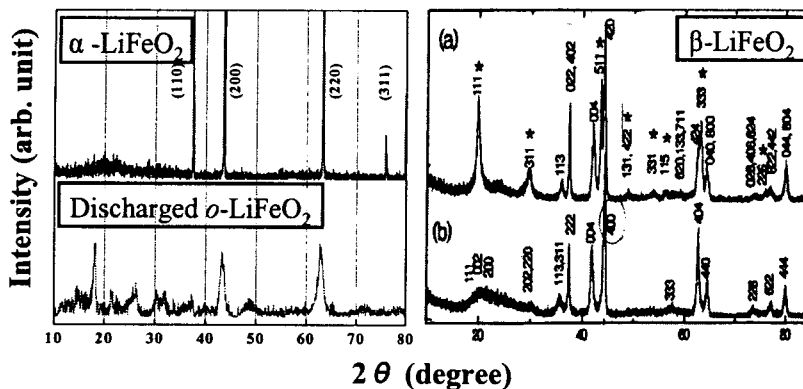


### *In-situ XRD of $o$ -LiFeO<sub>2</sub> in the 1<sup>st</sup> discharge*





## XRD patterns of various $\text{LiFeO}_2$ materials



● Reference ; M. Tabuchi et al.  
*Solid State Ionics*, 79 (1995) 220-226

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## Field dependence of the Magnetization of $o$ - $\text{LiFeO}_2$

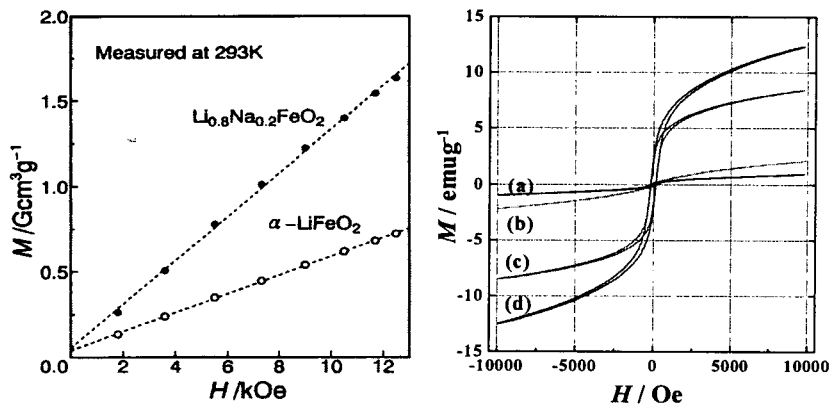


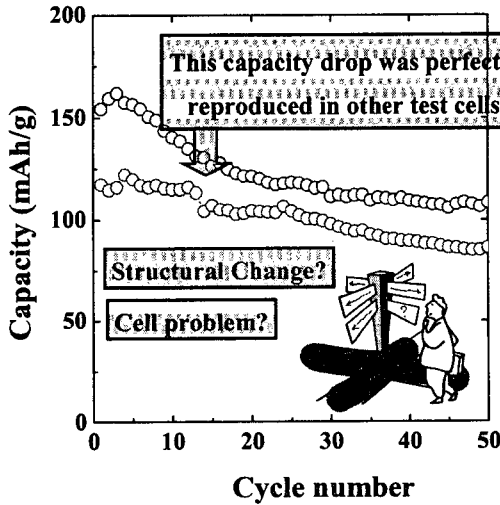
Fig. Magnetic field ( $H$ ) dependence of the magnetization ( $M$ ) for (a)  $\alpha$ - $\text{LiFeO}_2$ , (b) As-prepared  $o$ - $\text{LiFeO}_2$ , (c) the first charged electrode, and (d) the first cycled electrode.

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## Cycle performance of *o*-LiFeO<sub>2</sub> material



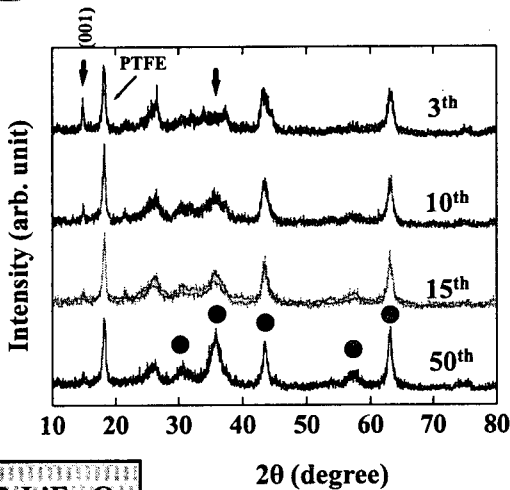
### ◆ Test condition

- ◆ 4.5~1.5V (Li/Li<sup>+</sup>)
- ◆ LiPF<sub>6</sub>-EC/DMC (1:2 vol.)
- ◆ Anode : Li metal
- ◆ Separator : P / P
- ◆ C.D. : 0.1 mA/cm<sup>2</sup> / 0.4 mA/cm<sup>2</sup>

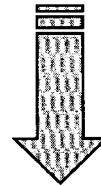
◆ We still have no concrete proof about abrupt capacity drop on 13<sup>th</sup> cycle, however,



## Ex-XRD patterns of *o*-LiFeO<sub>2</sub> after cycling



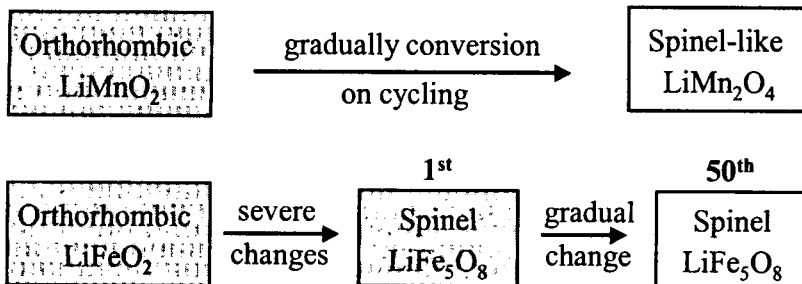
Orthorhombic



Structural change



## The summary of structural change Li/o-LiFeO<sub>2</sub>



- Croguennec et al., *J. Electrochem. Soc.*, **144**, 3323 (1997).
- Y.I. Jang, B. Huang, H. Wang, D.R. Sadoway, Y.M. Chiang, *J. Electrochem. Soc.*, **146**, 3217 (1999).



## Conclusion

- Orthorhombic LiFeO<sub>2</sub> compound was synthesized using LiOH and  $\gamma$ -FeOOH at 150 °C under an Ar atmosphere by Solid-State Method.
- LiFeO<sub>2</sub> in this study was mixed with well-crystallized orthorhombic LiFeO<sub>2</sub>, spinel  $\beta$ -LiFe<sub>5</sub>O<sub>8</sub>, and defective LiFeO<sub>2</sub> phases.
- Li/LiFeO<sub>2</sub> cell underwent a structural change to the spinel phase in the first cycle. Especially it showed severe structural changes during the first discharge process.
- Li/LiFeO<sub>2</sub> cell exhibited a unique abrupt drop near the 13<sup>th</sup> cycle. The cycle retention rate was 97 % from the 1<sup>st</sup> to 13<sup>th</sup> cycles and 99.4 % from the 13<sup>th</sup> to 25<sup>th</sup> cycles.



## [ PART II ]

### Synthesis of $\text{LiFeO}_2\text{-Li}_x\text{MnO}_2$ Solid-Solution System



## Recent research of $\text{LiFeO}_2$ material

### ◆ Y.S. Lee et al. (*o*- $\text{LiFeO}_2$ );

- ◆  $\text{LiOH} + \gamma\text{-FeOOH}$
- ◆ Solid-state method (150 °C)
- ◆ 150-160 mAh/g at RT (0.1 mA/cm<sup>2</sup>).

; Y.S. Lee et al. *Electrochem. Commun.*, 4, 727 (2002).

### ◆ Kanno et al. (*tunnel*- $\text{LiFeO}_2$ );

- ◆  $\text{LiOH} + \beta\text{-FeOOH}$
- ◆ Ion-exchange reaction (~ 250 °C)
- ◆ 160-170 mAh/g at RT (0.1 mA/cm<sup>2</sup>).

; R. Kanno et al. *J. Electrochem. Soc.*, 149(12), A1509 (2002).

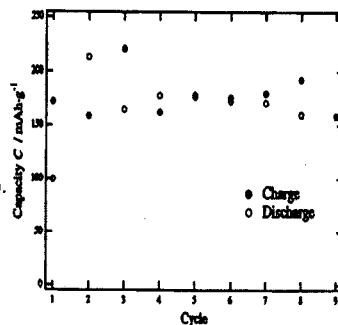


Fig. Cycle performance of  $\text{Li//LiFeO}_2$  cell

### > Common Problem !

- ◆ Low working voltage region (at about 2.0 V).
- ◆ Poor cycling performance.



## XRD patterns of $\text{LiFe}_{1-x}\text{Mn}_x\text{O}_2$ material

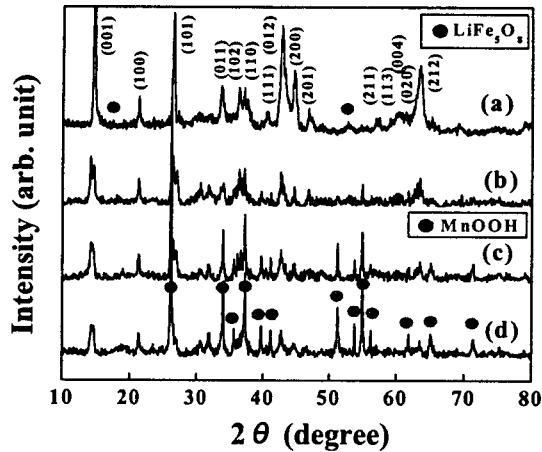


Fig. X-ray patterns of  $\text{LiFe}_{1-x}\text{Mn}_x\text{O}_2$  materials obtained at  $150\text{ }^\circ\text{C}$  (a)  $x = 0.0$ , (b)  $x = 0.1$ , (c)  $x = 0.3$ , and (d)  $x = 0.5$ .



## Cycle behavior of $\text{Li}/\text{LiFe}_{1-x}\text{Mn}_x\text{O}_2$ cell

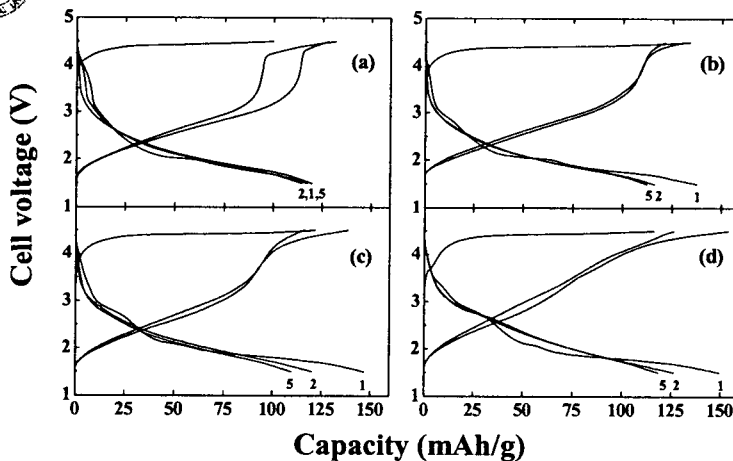
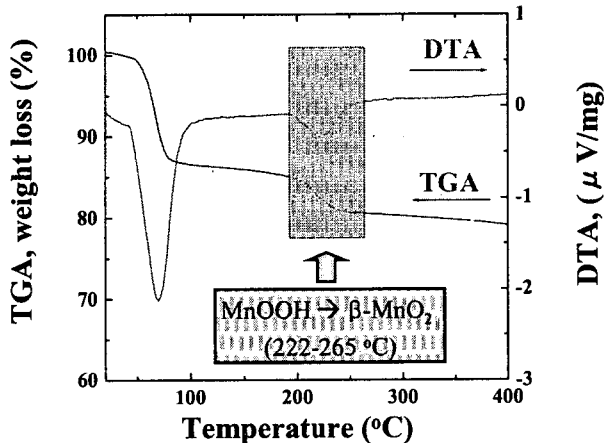


Fig. Charge/discharge curves of  $\text{LiFe}_{1-x}\text{Mn}_x\text{O}_2$  materials (a)  $x = 0.0$ , (b)  $x = 0.1$ , (c)  $x = 0.3$ , and (d)  $x = 0.5$ .



## Thermal analysis of precursor

(LiOH +  $\gamma$ -FeOOH +  $\gamma$ -MnOOH = 1 : 0.9 : 0.1)



● LiNO<sub>3</sub> (solid) + MnOOH (solid)  $\rightarrow$  *o*-Li<sub>0.3</sub>MnO<sub>2</sub> (Pnam) + HNO<sub>3</sub>  
 Y. Xia and M. Yoshio, *J. Power Sources*, 57 (1995), 125.



## The starting point of this research

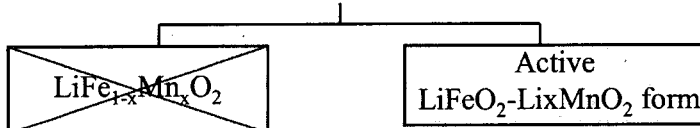
● Tabuchi et al. (the solid solution of LiFeO<sub>2</sub>-Li<sub>2</sub>MnO<sub>3</sub>);

- Inactive  $\alpha$ -LiFeO<sub>2</sub> + Li<sub>2</sub>MnO<sub>3</sub>  $\rightarrow$  Active solid-solution for 4 V.
- Hydrothermal & Solid-State Method.
- 100-150 mAh/g at Room temperature.

; M. Tabuchi et al. *J. Electrochem. Soc.*, 149(5), A509 (2002).

● Y.S. Lee et al. (the solid solution of LiFeO<sub>2</sub>-Li<sub>1-x</sub>MnO<sub>2</sub>);  
 ; the calcination at 300-350  $^{\circ}$ C

● Active *o*-LiFeO<sub>2</sub> +  $\gamma$ -MnOOH



; Y.S. Lee et al. *Electrochem. Commun.*, in press.

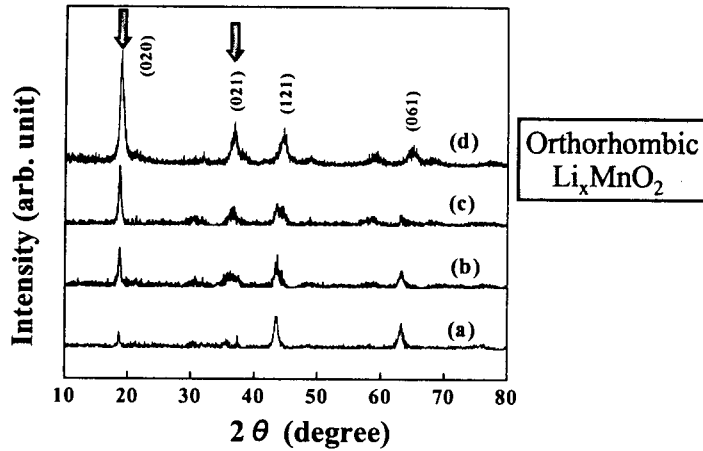


Fig. X-ray patterns of (a) 10%, (b) 30%, (c) 50% Mn-substituted,  $\text{LiFeO}_2$ , and (d)  $\text{Li}_x\text{MnO}_2$ . These materials were obtained at 350 °C.



### SEM analysis of $\text{LiFeO}_2$ - $\text{Li}_x\text{MnO}_2$ materials

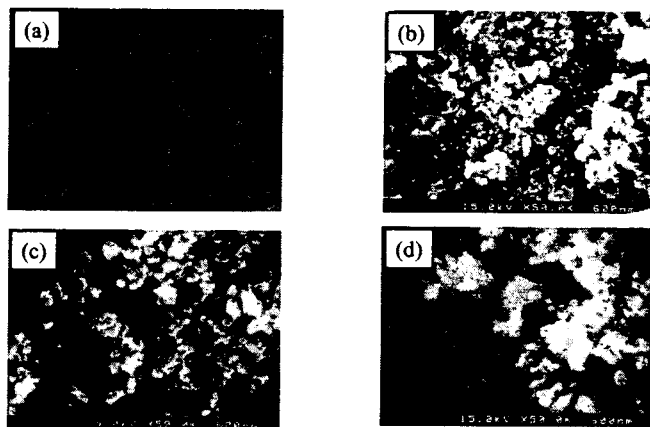


Fig. Scanning electron micrographs of (a)  $\text{LiFeO}_2$  (150 °C), (b) 10%, (c) 30%, (d) 50% Mn-substituted  $\text{LiFeO}_2$  powders obtained at 350 °C.





## Cycle behavior of Li/LiFeO<sub>2</sub>-Li<sub>x</sub>MnO<sub>2</sub> cells

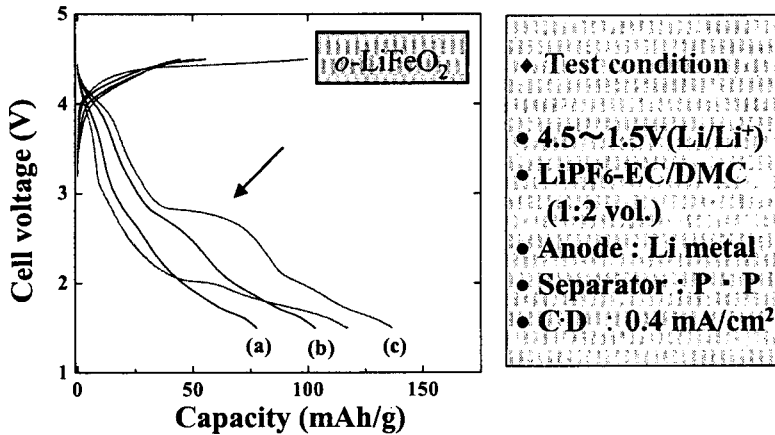


Fig. The initial charge/discharge curves of (a) 10%, (b) 30%, and (c) 50% Mn-substituted LiFeO<sub>2</sub> cell.



## Cyclic voltammogram

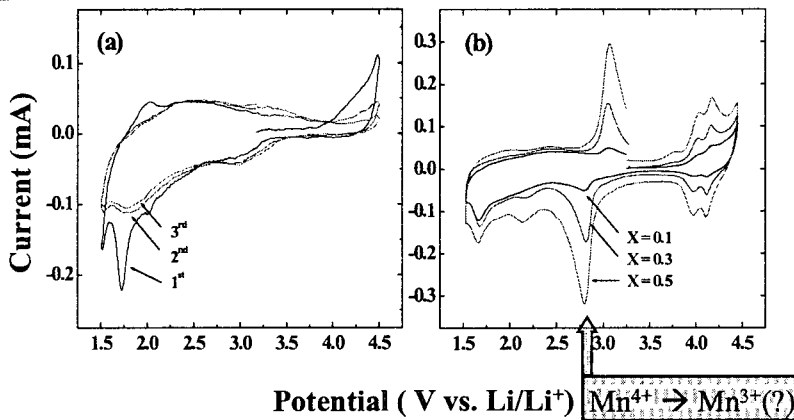


Fig. Cyclic voltammogram of (a) LiFeO<sub>2</sub> and (b) Mn-substituted LiFeO<sub>2</sub> cell.



## Cycle performance of Li/LiFeO<sub>2</sub>-Li<sub>x</sub>MnO<sub>2</sub> cells

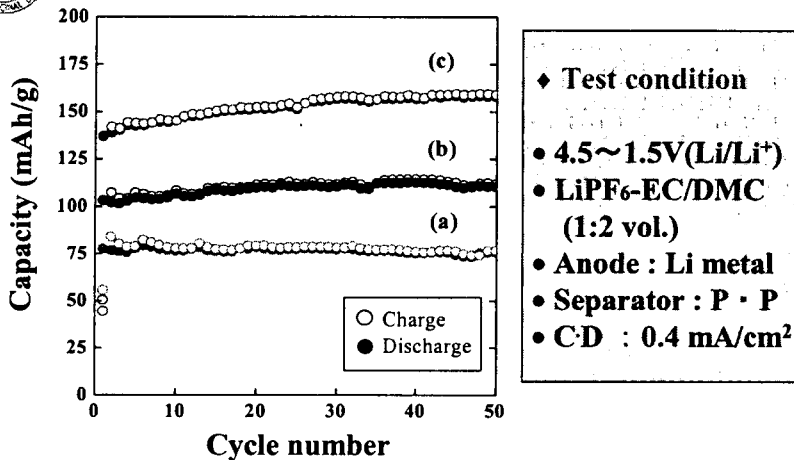


Fig. Discharge capacity vs. cycle number for Li/Mn-substituted LiFeO<sub>2</sub> cells. (a) 10%, (b) 30%, and (c) 50% Mn-substituted LiFeO<sub>2</sub>.



## Conclusion

- A new type of LiFeO<sub>2</sub>-Li<sub>x</sub>MnO<sub>2</sub> solid solution was synthesized at 350 °C under argon flow by solid-state reaction.
- The XRD pattern of the 50% Mn-substituted LiFeO<sub>2</sub> was very close to that of orthorhombic Li<sub>x</sub>MnO<sub>2</sub> compound.
- 50% Mn-substituted LiFeO<sub>2</sub> was composed large particles of about 500-600 nm and small particles of about 100-200 nm, which were distributed among the larger particles.
- Li/50% Mn-substituted LiFeO<sub>2</sub> cell exhibited not only a distinct voltage plateau in the 2.8 V region, but also an excellent cycle performance up to 50 cycles (> 99%).
- It was considered that this unique voltage plateau resulted from the redox reaction from Mn<sup>4+</sup> to Mn<sup>3+</sup> in the 3 V region.