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고체 NMR을 이용한 리튬이차전지의  
양극화 물질 연구

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이 영 주 박사  
(LG 화학)



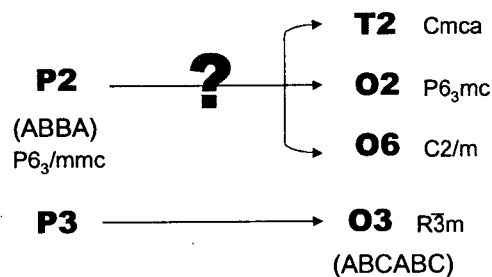
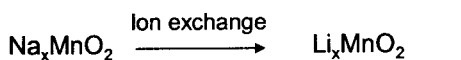
# MAS NMR Studies of Cathode Materials for Lithium Cells

이영주

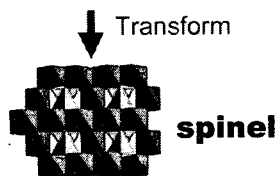
Elton J Cairns, Jeffrey Reimer,  
Marca Doeff, Tom Eriksson

Lawrence Berkeley National Laboratory  
Berkeley, California

## New Layered $\text{Li}_x\text{MnO}_2$ Phases

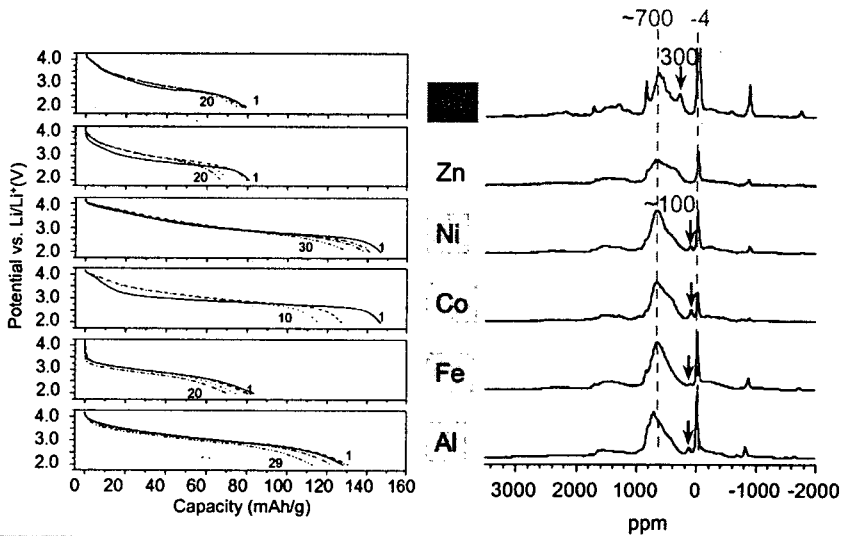


- P(prismatic), O(octahedral), T(tetrahedral) : coordination environment of alkali ion
- 2,3,6: number of  $\text{MO}_2$  sheets in the unit cell



Ref) P. G. Bruce et al., *Chem. Mater.*, 2002, 14,710.  
 J. Dahn et al., *J. Electrochem. Soc.*, 1999, 146, 3560.

# O2 Type $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_{2.05}$



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## Li on the Particle Surface vs. in the Lattice

$^7\text{Li}$ NMR shift (ppm)	-5	100	300	700
$T_1$ (ms)	1538.16	2.87	1.45	1.94

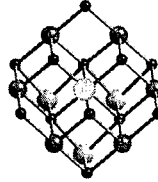
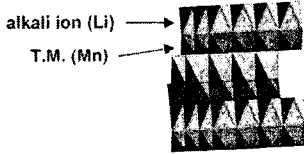
◆ Spin-lattice relaxation time,  $T_1$ , is short for the paramagnetic materials due to the coupling between the electrons and nuclear moment.

◆ Long  $T_1$  of the resonance at -5 ppm suggests that the lithium cations reside on the surface of the particle rather than inside the lattice.

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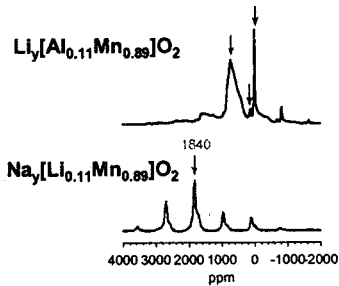
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# Presence of Li in the T.M. Layer?



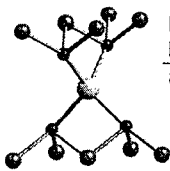
## Li in the T.M. layer

- ◆ 1500 ~1800 ppm for  $\text{Li}_2\text{MnO}_3$   
( =  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  )  
Ref) Y.J.Lee and C.P.Grey, JPC.B, 2002, 106, 3576  
Morgan et al. J. Chem. Soc., Chem. Commun, 1994, 1719
- ◆ ~1840 ppm for  $\text{Na}_y[\text{Li}_{0.11}\text{Mn}_{0.89}]\text{O}_2$
- ◆ Spinning sideband pattern characteristic of close to axial symmetry
- ◆ Lithium cations do not intercalate into T.M. layer during the ion-exchange process.



# Local Environments of T2 vs. O2

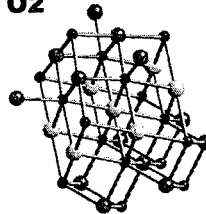
## T2



Li-O-Mn bond angle	# of Mn
83°	2
112°	4
153°	4

→ 270-430 ppm

## O2



Li-O-Mn bond angle	# of Mn
75°	1
93°	3
132°	6
169°	3

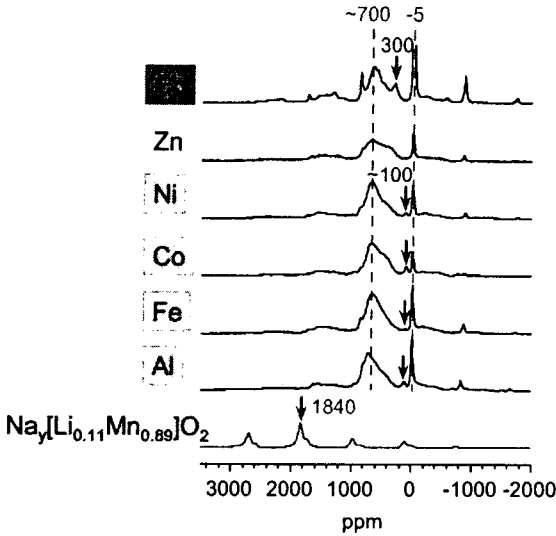
→ 940-1160 ppm

Ref) Y.J.Lee, F.Wang, and C.P.Grey, JACS, 1999, 120,12601  
Each Mn with Li-O-Mn 90° bonds : 250-300 ppm  
180° bonds : -100 ppm  
121° bonds : 43 ppm (for Mn<sup>3.5+</sup>)

O3  $\text{Li}_x\text{Mn}_y\text{O}_2$  (x≈0.6, y=0.9~1): 133 ppm

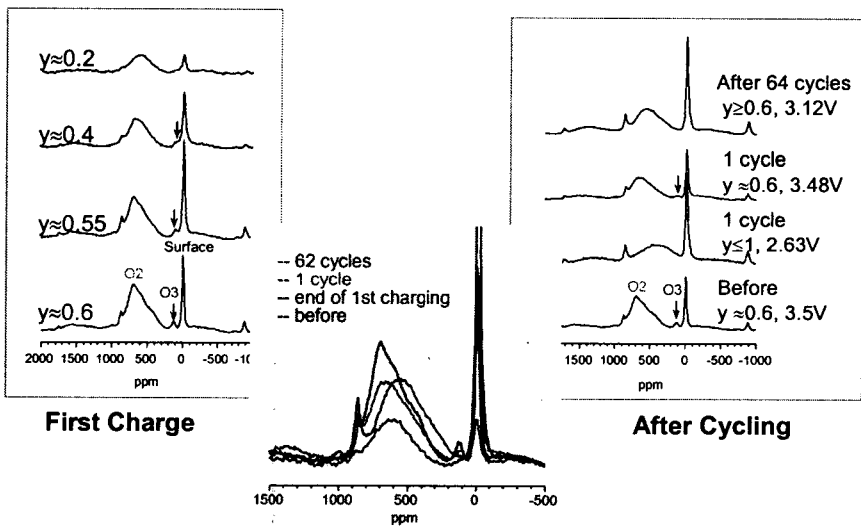
Ref) Bruce et al., 11<sup>th</sup> IMLB Conference, 2002, Monterey, California.

# Structure of O2 Type $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_{2.05}$



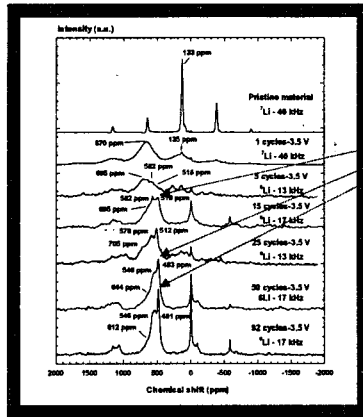
- ◆ No ordering between Mn and substituent atoms in the T.M. layer.
- ◆ No Li cation substitution in the T.M. layer.
- ◆ Assignment
  - ~700 ppm: O2 type env.
  - ~300 ppm: T2 type env.
  - ~100 ppm: O3 type env
  - 5 ppm: particle surface
- ◆ Ni, Co, Al, Fe: mixture of O2 & O3 environments
- ◆ Cu: mixture of O2 & T2 environments
- ◆ Zn: Only O2 type env.

# The Effect of Cycling on $\text{Li}_y[\text{Al}_{0.11}\text{Mn}_{0.89}]\text{O}_{2.05}$



# O<sub>3</sub> Li<sub>x</sub>Mn<sub>y</sub>O<sub>2</sub> (x≈0.6, y=0.9~1)

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Progressive formation of a spinel phase (Li in tetrahedral site) over repeated cycles.

Ref) Bruce et al., 11<sup>th</sup> IMLB Conference, 2002, Monterey, California.

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# Summary of O<sub>2</sub> Type Li<sub>y</sub>[M<sub>0.11</sub>Mn<sub>0.89</sub>]O<sub>2</sub>

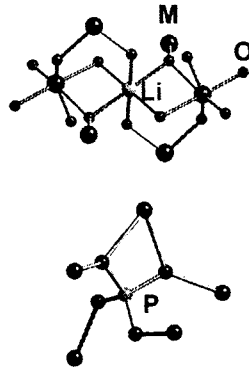
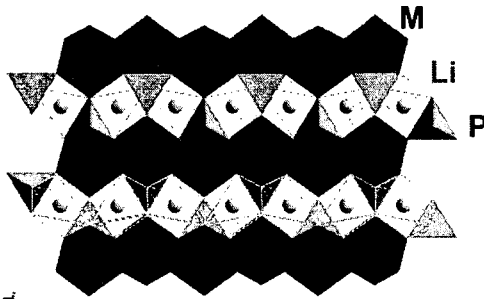
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- ◆ <sup>7</sup>Li NMR spectroscopy is very useful in determining the structure of Li<sub>y</sub>[M<sub>0.11</sub>Mn<sub>0.89</sub>]O<sub>2</sub> materials.
- ◆ The materials can be categorized into three different combinations of Li environments based on the differences in the NMR spectra and this correlates with the cycling performance.
- ◆ Depending on the metal substituent, three discrete resonances are observed at 700, 300, and 100 ppm and these can be assigned to O<sub>2</sub>, T<sub>2</sub> and O<sub>3</sub> type local environments, respectively. The resonance at -4 ppm is assigned to the lithium cations on the particle surface (SEI layer).
- ◆ No ordering between the Mn and the substituent atoms in the T.M. layer is observed.
- ◆ No Li cation substitution in the T.M. layer is observed.
- ◆ The electrodes which contain both O<sub>2</sub> and O<sub>3</sub> environments show higher capacity. The electrode which contain O<sub>2</sub> and T<sub>2</sub> type environments show good capacity retention, but, low capacity. Thus, optimization of the ratio between these environments should improve both specific capacity and capacity retention.
- ◆ The O<sub>2</sub> structure is retained after cycling, whereas the O<sub>3</sub> environment is lost. Transformation to the spinel phase is not observed.

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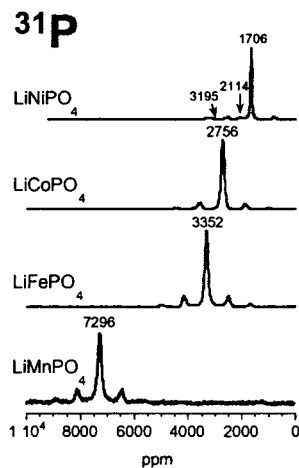
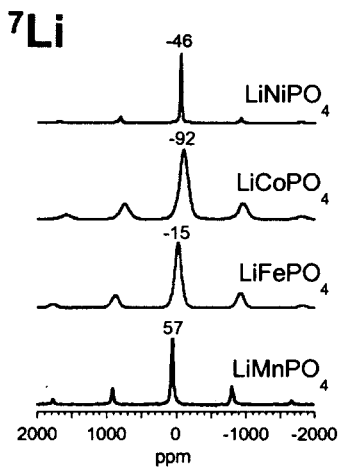
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# Crystallographic Structure of $\text{LiMPO}_4$



(M1M2) $\text{XO}_4$  Olivine  
 hcp oxygen array  
 M1=Li, M2=Ni, Co, Fe, Mn, X=P  
 Hexagonal analog of cubic spinel  $\text{XM}_2\text{O}_4$

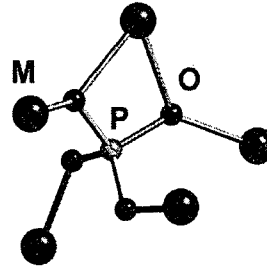
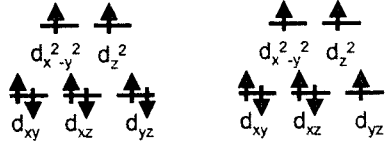
# $^7\text{Li}$ and $^{31}\text{P}$ NMR of $\text{LiMPO}_4$



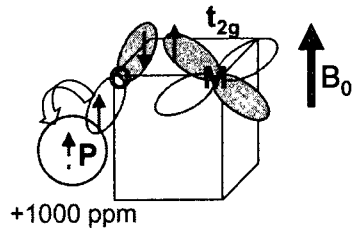
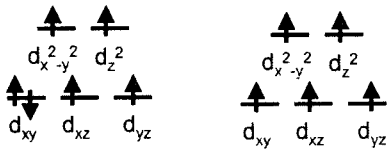


# <sup>31</sup>P Hyperfine Shift of LiMPO<sub>4</sub>

Ni<sup>2+</sup> 1700 ppm    Co<sup>2+</sup> 2700ppm

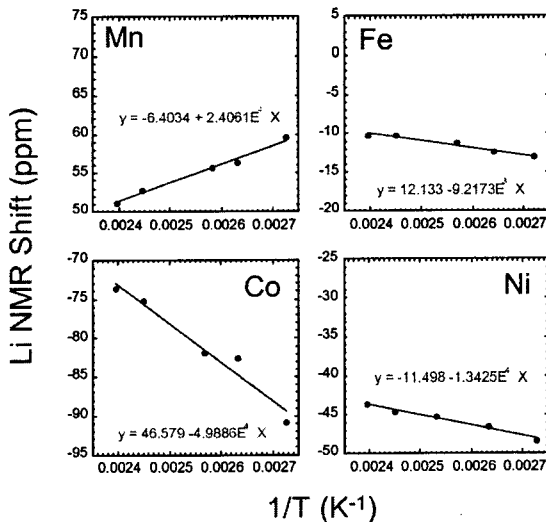


Fe<sup>2+</sup> 3400ppm    Mn<sup>2+</sup> 7300ppm



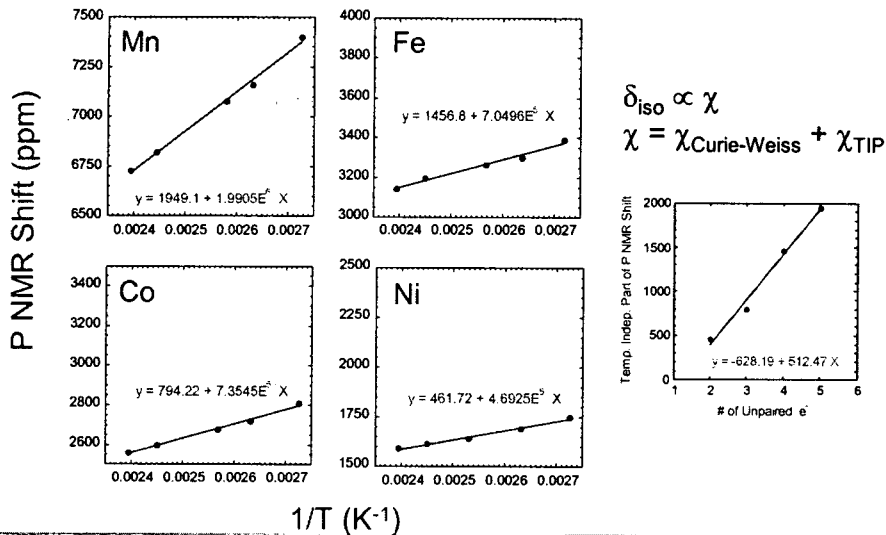
Fe<sup>3+</sup>PO<sub>4</sub> (d<sup>5</sup>): <sup>31</sup>P resonance is expected at 4700 ppm.

# <sup>7</sup>Li VT NMR of LiMPO<sub>4</sub>



# <sup>31</sup>P VT NMR of LiMPO<sub>4</sub>

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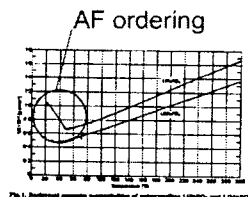
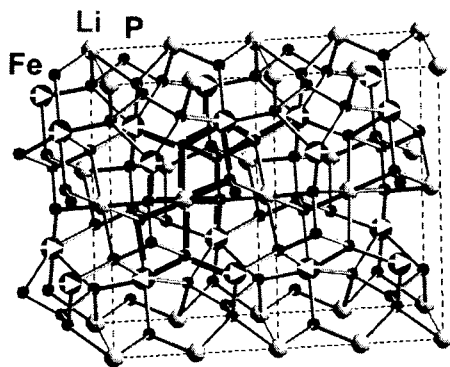


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# AF Correlation btw Metals

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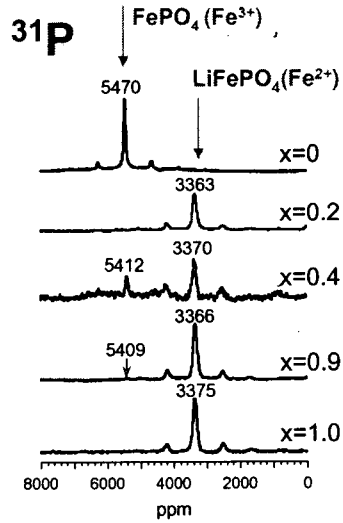
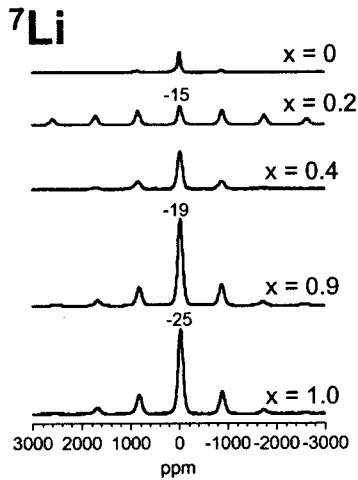


Ref) Santoro et al. *Acta. Cryst.* 1967, 22,344  
 Santoro et al. *J. Phys. Chem. Solids*, 1966, 27, 1192

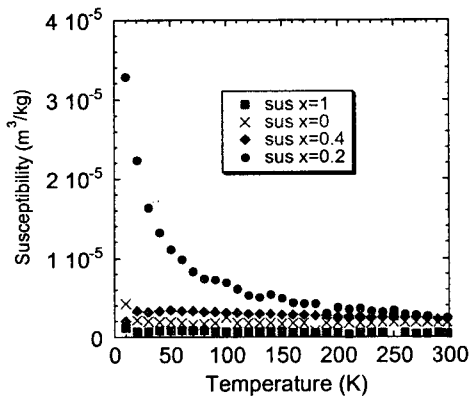
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# NMR of $\text{Li}_x\text{FePO}_4$ During Charging

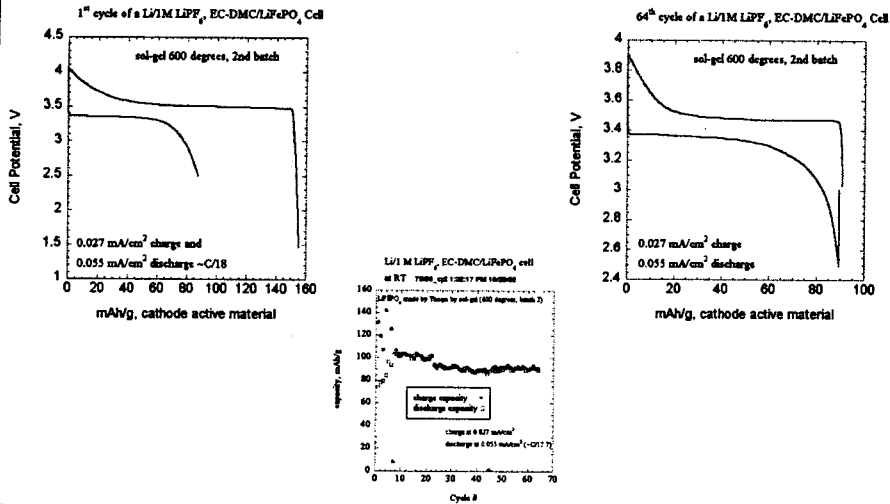


# Magnetic Susceptibility of $\text{Li}_x\text{FePO}_4$



x	1	0.4	0.2	0
Weiss const (K)	-370	-800	-20	-1960

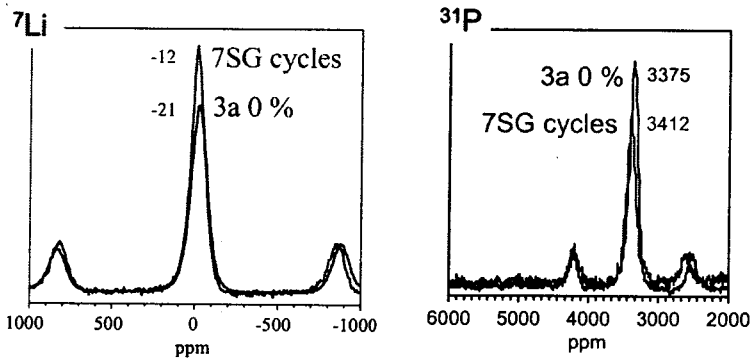
# Cycling of the $\text{Li}_x\text{FePO}_4$ electrode



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# $\text{Li}_x\text{FePO}_4$ after Many Cycles



No structural change after many cycles (64 cycles).  
A slight increase in average oxidation state of Fe and/or an increase in covalency after many cycles. But, no separate  $\text{FePO}_4$  phase is observed.

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## Summary of LiMPO<sub>4</sub>

- ◆ <sup>31</sup>P NMR shows a broader range of hyperfine shift than <sup>7</sup>Li NMR for LiMPO<sub>4</sub> olivines. <sup>7</sup>Li NMR hyperfine shift is less sensitive to the electronic environment and local structure and this can be ascribed to (1) the less covalent character of Li-O-M bonds compared to P-O-M bonds and (2) AF correlation between the metals in these layered compounds.
- ◆ <sup>31</sup>P NMR has been shown to be very informative to study LiMPO<sub>4</sub> electrodes.
- ◆ During the electrochemical intercalation/deintercalation process of LiFePO<sub>4</sub>, two discrete <sup>31</sup>P resonances were observed; one (3400 ppm) due to P in LiFePO<sub>4</sub> and the other (5400 ppm) due to P in FePO<sub>4</sub>. This is consistent with the two-phase behavior observed by XRD.
- ◆ NMR results show that there are no structural changes in the cycled electrode after repeated cyclings.
- ◆ <sup>31</sup>P NMR data suggest that there is a slight increase in the average oxidation state of Fe and/or covalency after repeated cyclings. However, no separate FePO<sub>4</sub> phase was observed within NMR detection limit. Recent X-ray absorption study confirms the increase in the oxidation state of Fe.