

Concepts in Design of Olivine-Type Cathodes

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Since the demonstration of reversible electrochemical lithium insertion-extraction for LiFePO_4 in 1997 [1], lithium transition metal phosphates with ordered-olivine structure, LiMPO_4 ($M=\text{Co}, \text{Ni}, \text{Mn}, \text{Fe}, \text{Cu}$), have attracted much attention as promising new cathode materials for rechargeable lithium batteries [2-8]. The presence of large tetrahedral polyanion $(\text{PO}_4)^{3-}$, and a use of M^{3+}/M^{2+} redox couple are distinctive natures of Olivine class cathodes from the ordered rock-salt system as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 . The $\text{P}_{\text{tet}}\text{-O-M}_{\text{oct}}$ linkage in the structure induces the superexchange interaction that tunes the M^{3+}/M^{2+} redox energy to useful levels (3.4V, 4.1V, and 4.8V for $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$, and $\text{Co}^{3+}/\text{Co}^{2+}$, respectively), which is called "inductive effect" [1].

Among the olivine-type LiMPO_4 family, the solid-solution, $\text{Li}(\text{Mn}_y\text{Fe}_{1-y})\text{PO}_4$, looks promising because of the voltage compatibility with the present lithium-ion battery system [1]. The optimization was performed in our laboratory based on the careful investigations of charge-discharge reaction, and the very promising cathode performances as in Fig. 1 were achieved at room temperature [5-7]. The stable nature of the olivine-type structure having a $(\text{PO}_4)^{3-}$ polyanion with a strong P-O covalent bond provides not only excellent cycle-life but also a safe system when the battery is fully charged; the reactivity is low for the combustion reaction with the organic electrolyte (Fig. 2) [5]. The stability under the high-temperature storage (ca. 80°C) at any depth of discharge is also excellent. The energy density is equal to that of presently used materials, based on the charge-discharge capacity as high as the theoretical value, ca. 170mAh/g [5].

In the optimization process, it was clarified that the inherent low conductivity for both Li-ions and electrons should be overcome [5]. Additionally, the local Jahn-Teller distortion around Mn^{3+} (Fig. 3), which is much more severe than the average lattice distortion, disturbs the charge-discharge reaction [6, 8].

In this paper, the essential strategies for a design of practical olivine-type cathode will be discussed, particularly on the importance of (1) the powder engineering of the electrode composites, and (2) the choice of the appropriate compositions. The discussion will be based on the systematic presentation of the data measured by x-ray diffraction, Mössbauer spectroscopy, electrochemical technique, x-ray absorption spectroscopy, and differential scanning calorimetry, with an aid of the first-principle calculation.

References

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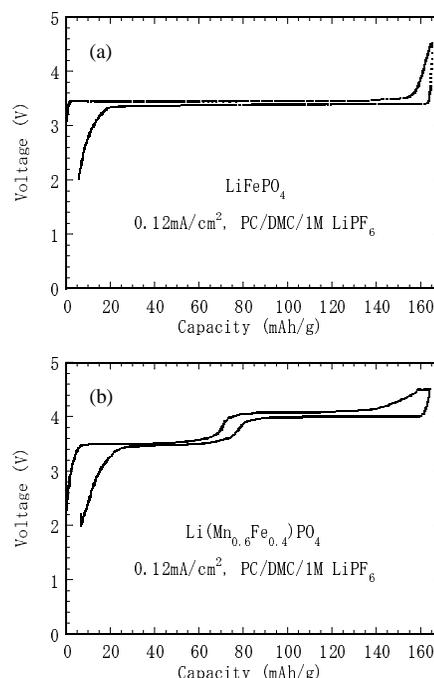


Fig. 1 Charge-discharge profiles of the optimized LiFePO_4 and $\text{Li}(\text{Mn}_{0.6}\text{Fe}_{0.4})\text{PO}_4$

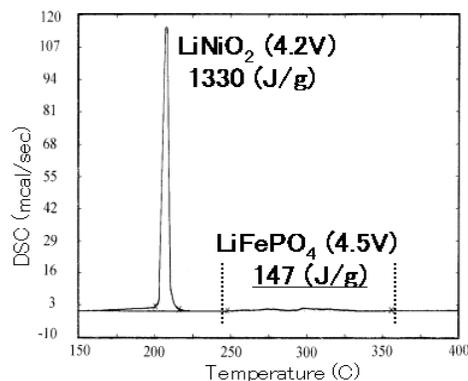


Fig. 2 DSC traces of the charged cathodes of LiNiO_2 and LiFePO_4 with electrolyte

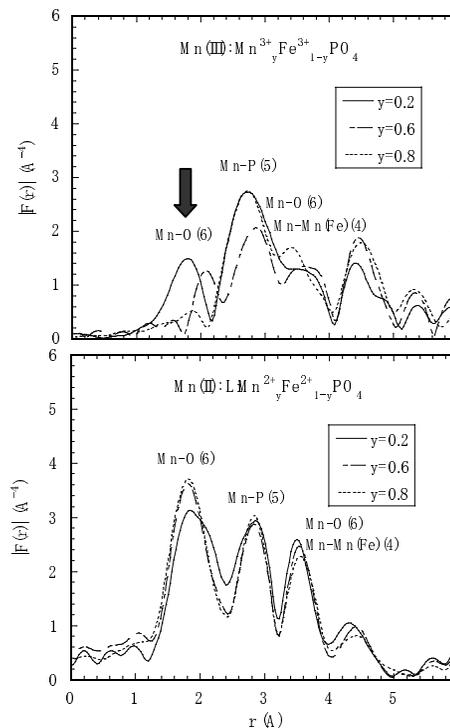


Fig. 3 Radial distribution function around Mn in $(\text{Mn}^{3+}_y\text{Fe}^{3+}_{1-y})\text{PO}_4$ and $\text{Li}(\text{Mn}^{2+}_y\text{Fe}^{2+}_{1-y})\text{PO}_4$