Ab initio study on Li$_2$MSiO$_4$ (M=Mn, Fe, Co, Ni) as cathode materials of lithium ion battery

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1. BACK GROUND

Li$_2$MSiO$_4$ is one of the promising cathode materials of the lithium ion battery because not only it has stable poly-anion structures, but also it possibly has a larger capacity than existing cathode materials. There are extensive studies about this new material by experimental or theoretical methods. However, from these studies, some defects of this material such as structural instability or lower capacity than the theoretical prediction have been reported, and these materials are not practically used yet. In this situation, our purpose of this research is to investigate the change and the stability of materials upon lithiation or dilithiation, to estimate the electric properties, and to discuss how these properties affect on the performance of batteries. We study these issues by using density functional theory (DFT) based calculations.

2. METHODOLOGY

All calculations were performed by the Vienna ab initio simulation package (VASP) within the projector augmented wave (PAW) method. The exchange correlation energies were approximated using Generalized Gradient Approximation (GGA) of the Perdew, Burke and Ernzerhof (PBE), using Hubbard parameter correction for the transition metals. The energy cut off for the plane wave basis set was kept at 500 eV and reciprocal space sampling was done with k-point grids of $4 \times 4 \times 4$. We focused on the Li$_2$MSiO$_4$ which has space group of *Pmn2$_1$* and its unit cell contains double amount of atoms of its formula unit (Fig.1), and it has a layered structure (Fig.2).The initial crystal structure of Li$_2$FeSiO$_4$ is taken from experimental parameters [1], and the cell shape and atomic coordinates are fully relaxed using the conjugate gradient (CG) method. The transition metal was changed from Fe to Mn, Co, Ni or the combinations of two of these metals. Then the amount of Li was reduced from 2 to 1.5, 1, 0.5 and 0, and the energy of each compound was calculated.
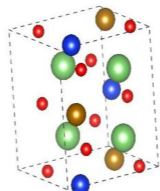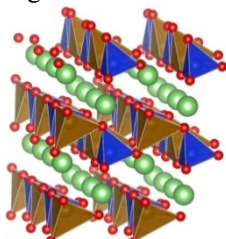

Fig.1 unit cell

Fig.2 layered structure

## 3. RESULT AND DISCUSSION

Optimized structure

First, we optimized the geometries of all crystals and confirmed the calculated lattice parameters are in good agreement with the experimental values [1] [2] [3]. The result also indicates that some materials will change their crystal structures and lose the reversibility upon the process of delithiation. Fig.3 (a) shows the optimized structure of Li$_{0.5}$FeSiO$_4$, which keep the original layered structure. In this structure, transition metal Fe has tetrahedral coordination with O. However, in Fig.3 (b), which has lost its original structure, Mn and Ni have 5 bonds with oxygen.

Electric properties

Secondly, we estimated the electric properties on charge and discharge from the calculated energies. In Fig.4, the calculated electric properties of Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$ are shown. The former has a step-like profile and the latter has a flat one, and these tendencies are very similar to the experimental data [4]. Other materials also showed similar properties to the experimental results, which indicates that our calculated results are accurate enough.

Relationship between electronic states and properties

Finally, we will discuss the relationship between these structural or electric properties and their electronic states, particularly the states of 3d electrons of the transition metals which may affect the crystal properties directly. Based on these discussions, we may conclude the potentiality of these materials as the cathode.
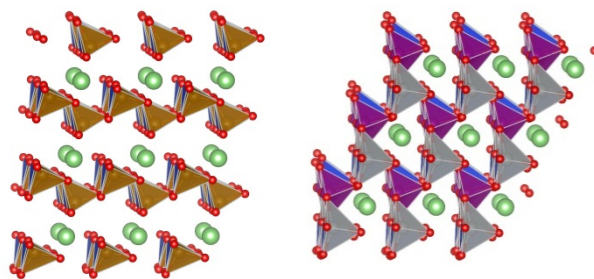
(a)Li$_{0.5}$FeSiO$_4$, keep its original structure

(b)Li$_{0.5}$Mn$_{0.5}$Ni$_{0.5}$SiO$_4$, lost its original structure
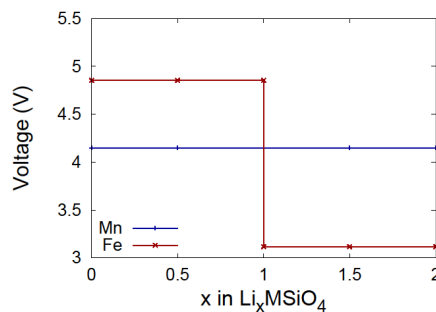
Fig.3 optimized structures

Fig.4 calculated electric properties of Li$_x$MSiO$_4$ (M=Fe, Mn)

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