Reaction Analysis of the Battery for Automobiles using First-principles Calculation and Molecular Dynamics Method

Project Representative

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Abstract

Using first principles molecular dynamics (FPMDs), time dependent behaviors of Li, Mn, and O of $Li_{2-x}MnO_3$(x = 0.5 and 1.0) were investigated as an aim of elucidating the reaction mechanism of solid solution cathode materials (Li_2MnO_3-$LiMO_2$: M = Co and Ni, etc.) in the future. Both of Li in Li layers and Li in Mn-Li layers can hop to another layer and return the layer belonged originally, by means of Li vacancies. The FPMDs simulation demonstrates such Li behavior enables Li to move in the cathode crystal along ab planes. The FPMDs calculation indicates that the Mn-O octahedra, cooperated with layer's periodic fluctuation, were tilted and distorted, and finally frozen as MD steps increased. The amount of Li displacement for a, b, and c directions at early charging stage also discussed.

Keywords: first-principles calculation, molecular dynamics, lithium-ion rechargeable battery, cathode material, diffusion

1. Introduction

Development of Li-ion rechargeable batteries has been a key technology to accomplish the greener sustainable society. Recently, it was reported that a solid solution system (Li_2MnO_3-$LiMO_2$: M = Co and Ni, etc.) has high capacity with maintaining durability. Because Li_2MnO_3 is the mother material of the solid solution systems, the investigation of the instability of Li_2MnO_3 at charge-discharge cycles has been important. Though the oxidation mechanism and Li configuration has been analyzed using XAFS and NMR, respectively, time evolution process such as diffusion and the related phenomenon have been unveiled. In this report, we then discussed the time dependent behaviors of Li, Mn, and O of $Li_{2-x}MnO_3$ (x = 0.5 and 1.0) using FPMDs.

2. Results and discussion

VASP and VASP-MD were adopted for geometrical optimization and FPMDs calculation, respectively [1]. The FPMDs calculation was carried out at 5 fs every one step under 3000 K. The crystal structure of $Li_{2-x}MnO_3$ has monoclinic system (C2/m). The arrangement of Li vacancies was shown in Figure 1. Assuming no vacancy, a Li was surrounded by six metal atoms.

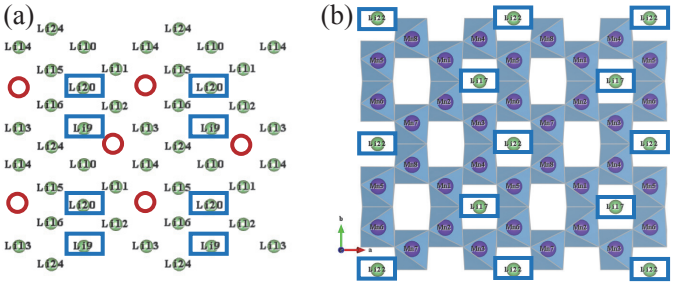


Figure 1. The view of ab plane, showing the configurations of Li vacancy. (a) Li layer. (b) Mn-Li Layer. Red open circle shows the Li vacancy at $Li_{1.5}MnO_3$. Blue open rectangle shows the extracted Li at forming $Li_{1.0}MnO_3$ model from $Li_{1.5}MnO_3$ model. Blue shading rectangle indicates the Mn-O octahedra.

Typical movement of Li in Li layers and in Mn-Li layers are shown in Figure 2. All Li in Li layers can hop to Mn-Li layer perpendicularly. The probability of Li hopping was 100 % at this model. Some Li can be back to the Li layer. Similary, Li in Mn-Li layers can jump to Li layers. Three-fourth of Li in Mn-Li layers jumped to Li layer and moved within the Li layer. One-fourth of Li in Mn-Li, with comings and goings among Li layers, strolled in ab plane.

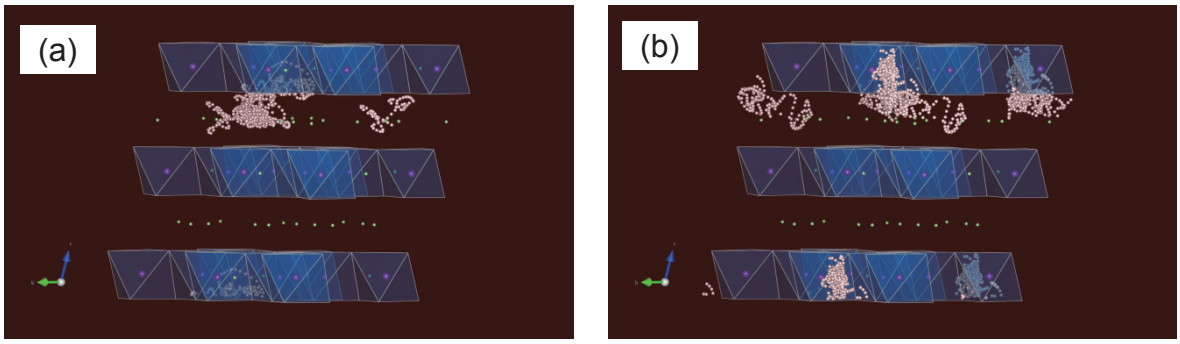
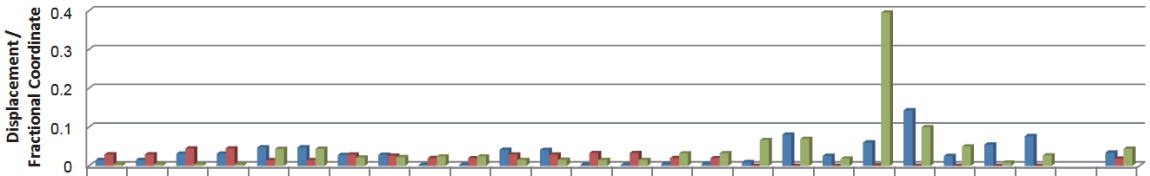


Figure 2. Consecutive motions of Li atoms. (a) A Li in Li layer. (b) A Li in Mn-Li layer.

Figure 3 shows displacement of each Li .The displacements for a direction of No.9, 10, 13, and 14 Li were zero. These Li were surrounded by five Li and one vacancy. In this case, a rectangular vacancy region which has the major axis along a-direction and minor axis along b-direction was formed at right side of No.9 Li(Figure 1(a)). Therefore, the vacancy region is responsible for dull motion of the No.9 Li to a-direction. Regarding b-direction, the displacements of No.17-24 Li were zero. These Li were surrounded by six metal atoms. Namely diffusion path is not vacancy but interstitial layer among atoms. The interstitial layer was expanded along a-direction and shrunk along b-direction. Therefore the displacement of the Li for b- direction might be almost zero.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24		a.v.
a direction	0.02	0.02	0.03	0.03	0.05	0.05	0.03	0.03	0	0	0.04	0.04	0	0	0.01	0.01	0.01	0.08	0.03	0.06	0.14	0.03	0.05	0.08		0.03
b direction	0.03	0.03	0.04	0.05	0.01	0.01	0.03	0.03	0.02	0.02	0.03	0.03	0.03	0.03	0.02	0.02	0	0	0	0	0	0	0	0		0.02
c direction	0	0	0	0	0.04	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.07	0.07	0.02	0.4	0.1	0.05	0.01	0.03		0.04

Figure 3. Displacement of each Li. The number of each Li corresponds to that in Figure 1.

References

1) G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).