Correlation between Performance and Electronic Structure of Cathode Materials for Lithium Ion Battery

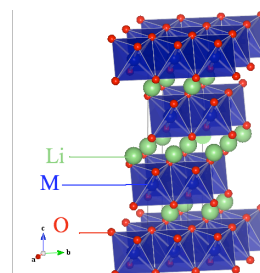Department of Advanced Materials Science 47-106038 Hiroki Matsuura

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Introduction

Lithium-ion battery (LIB) is one of the hottest topics and being subject of the most intensive research, due to its low environmental load, remarkably high voltage, high energy density, and capacity. Taking advantage of these properties, LIB is widely used for the portable devices.[i] It is important to clarify what kinds of parameters are key factors for good performance of LIB.

In this report, I have focused on correlations between the electronic structures of the positive electrode and performance of LIB. We can expect that the electronic states determine the properties of the electrodes as shown in Fig. 2 and Fig. 3. In these graphs, the

Fig. 1 structure of the layered LiMO$_2$

characteristics of the electrodes are plotted against the number of d-electrons. The points are almost on the approximate line, but the some are off. We explain them by taking the orbital occupation into account. We pursue the goal of showing that band calculation is applicable to the research of LIB.
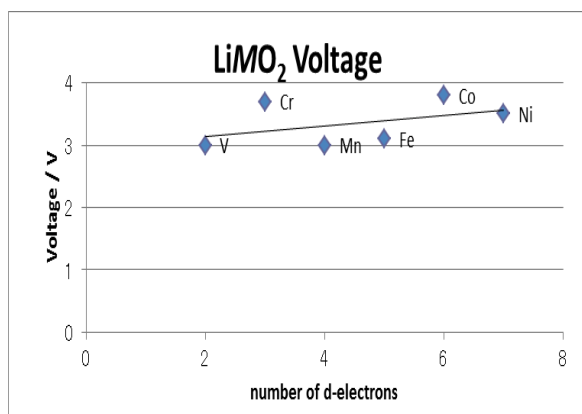
Fig. 2 Voltage of LiMO$_2$ plotted against the number of d-electrons
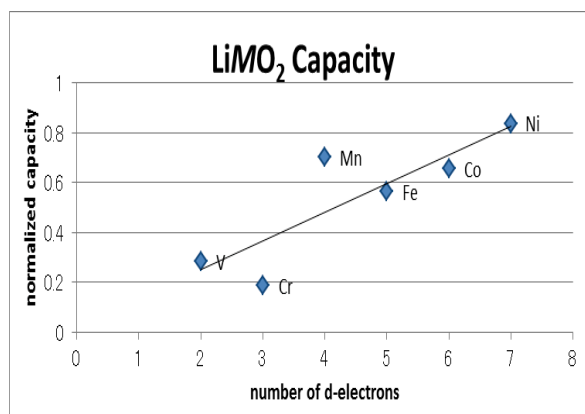
Fig. 3 Capacity of LiMO$_2$ plotted against the number of d-electrons

Experiment

The band structures of the positive-electrode-materials are obtained by first-principle calculations with WIEN2k [ii], the band calculating software. The band structures have close relationship with the characteristics of the positive electrodes of LIB. For example, the voltage of a battery is related to the difference of electrochemical potential between positive- and negative-electrodes. The electronic states around the Fermi level could be expected to have much contribution to the characteristics of electrodes.

In this report, I have focused on the relationship between the voltage of LIB and d-orbital band energy

against the p-orbital band energy, which is one of the main components around the Fermi energy. Then, I have investigated correlation between the capacity of the electrode and the electronic structure around the Fermi level, which consists of 2p-orbital of oxygen atoms and 3d-orbital of transition metal atoms. I have calculated the center energy of p-orbital band of O (ε_p) and d-orbital band of M (ε_d), and I estimated the energy difference ($\Delta\varepsilon = \varepsilon_d - \varepsilon_p$). I have compared capacity of LIB with the difference of center energies ($\Delta\varepsilon$), which are expected to reflect the relative Fermi energy position and the degree of 2p-3d hybridization.

   In this paper, layered LiMO$_2$ (Fig1. M denotes transition metal atoms, V〜Ni) is shown as representative example. The other materials, LiM_2O$_4$, LiMPO$_4$, LiMM'O$_4$ and Li$M_{1/2}M'_{1/2}$O$_2$ groups would be discussed in the report.

Results and Discussion

   In Fig.4, the voltage of LIB[i][iii][iv][v][vi] with LiMO$_2$ is plotted against the energy difference of ε_p and ε_p close to the Fermi level. As shown in Fig.4, the LIBs of the later series of transition metal oxides have higher voltage than that of earlier series of transition metal oxides.

   Smaller $|\Delta\varepsilon|$ seems to give us the larger voltage. It is because that the d-orbital energy becomes lower in the later series of transition metal ion and leads to lower Fermi level. In this situation, since the energy difference between Li-metal (anode) and transition metal oxide (cathode) becomes larger, the high voltage of LIB is obtained.

   Figure 5 displays $|\Delta\varepsilon|$ dependence of the normalized capacity, which is the ratio of the experimentally observed capacity[vii][viii][ix][x][xi] to the theoretical capacity, of LIB with LiMO$_2$. Theoretical capacity is the ideal capacity, which is obtained when all Li ions are removed from LiMO$_2$. I have found that high capacities appear for LiMO$_2$ with small $\Delta\varepsilon$. This result indicates that p-d hybridization is an effective parameter for LIB performance, since p-d hybridization should be strong for small $\Delta\varepsilon$. The observed correlation could be explained by following scenario. When a Li-ion extracted from the positive electrode LiMO$_2$, the transition metal atoms in the crystal change their valence. This valence change would induce lattice distortion and make the system unstable. However, if there is strong p-d hybridization, both oxygen and transition metal atoms can share valence change. This effect could moderate lattice distortion and makes Li-ion to extract more easily. Therefore, the p-d hybridization is expected to be an important factor for the performance of LIB. We could regard p-d hybridization as the key factor of positive electrode for good LIB performance.
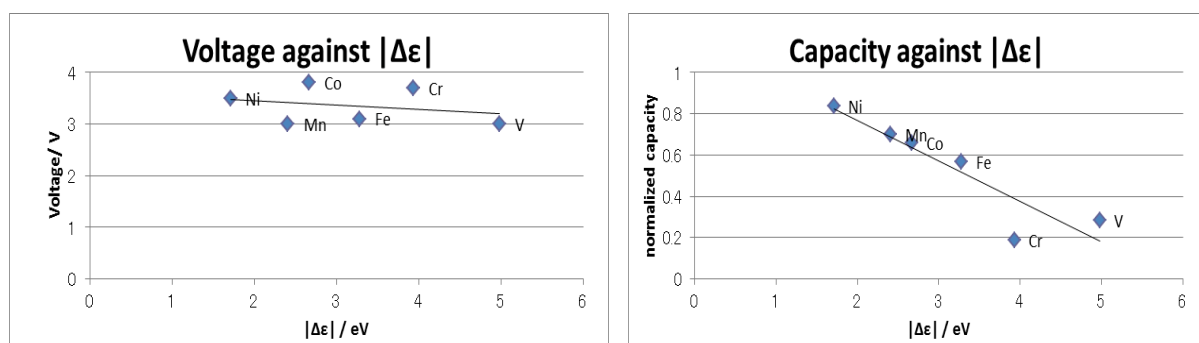
Fig. 4 Voltage of LiMO$_2$ plotted against the Fig. 5 Capacity of LiMO$_2$ plotted against

   To explain low capacity of LiCrO$_2$ in Fig. 5, we should focus on the stability of transition metal ion. The capacity gives large value when Li ion is easy to move. When the system is delithiated, the valence of the

transition metal changes. In this case, following reaction occurs when the battery is charged.

$$Li\mathit{M}O_2 \rightarrow Li_{1-x}\mathit{M}O_2 + Li^+ + xe^-$$
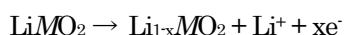
So, if the number of d-electrons is stable ones, it makes lithium difficult to be extracted. In other words, stability works negatively. The small capacity of $LiCrO_2$ can be explained based on this logic. The number of d-electron in $LiCrO_2$ is 3, and Cr^{3+} is stable. So, the extraction of lithium is difficult.

Future works

If similar correlations are found in other material groups such as polyanion groups (materials including BO_3^{2-}, SiO_4^{2-}, $P_2O_7^{4-}$ etc.), the argument would be asserted stronger. The investigation for other positive electrode materials would help us to construct better hypothesis and theory of electrodes form the view point of the electronic structures.

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