First principle calculation of lithiation/delithiation voltage in Li-ion battery materials

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A first principle method, based on the density functional theory, was used to investigate the average voltage of lithiation/delithiation for Li-ion battery materials across 7 categories and 18 series, including LiMO_2 , LiMn_2O_4 , LiMPO_4 , Li_2MSiO_4 and graphite. The average voltage of lithiation/delithiation in the relevant electrode materials was obtained by comparing the total-energy difference, before and after an electrochemical reaction. The calculated values were in good agreement with experimental data. The systematic difference between the simulated and experimental values could be explained in terms of the binding energy on the surface of the lithium electrode. This type of calculation method could be applied as an easy and effective tool for predicting the potential performance of new lithiation/delithiation materials.

first principle, Li-ion batteries, average voltage of lithiation/delithiation

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Since the development of the lithium-ion (Li-ion) battery by Sony of Japan in the 1990s, a significant amount of research has focused on the electrochemical performance of electrode materials. First principle calculations have become one of the primary methods applied in Li-ion research [1]. A first principle calculation does not require hypothetical or personal factors, and only uses fundamental physical constants and structural lattices of materials. The total energy of the relevant system can be acquired after solving the Schrödinger equation by self-consistent calculations. Therefore, a first principle calculation, in conjunction with experiments, has the ability to predict the properties of the novel materials and probe their kinetic mechanisms throughout charge and discharge processes. First principle simulation can assist in the design of high performance battery materials.

First principle calculations have been extensively applied in the field of Li-ion batteries, but the materials investigated to date have been limited to a narrow area. Their calculation

methods have not been very clear. Reimers [2] applied the first principle calculation to the voltage curve of $\text{Li/Li}_x\text{Al}$ in 1995 and predicted unknown materials $\text{LiMM}'\text{O}_2$ ($M, M'=\text{Co, Ni, Mn and V}$). Ceder et al. [3] used a similar method to study Al-doped $\text{Li}(\text{Co, Al})\text{O}_2$ materials. They proposed that such materials would have a higher voltage, a lower density and reduced cost. Using the GGA+U method, Zhou et al. [4] calculated the average voltage of delithiation for LiMSiO_4 olivine. The calculated output matched well with the experimental results, but suspiciously different U values were introduced before and after the delithiation. In addition, the Li migration energy was calculated as a rather small value for LiFePO_4 , suggesting the delithiation process was more important [5]. The calculated results varied widely, even for the same materials and methods. In this instance, some models and parameters were selected unsystematically, often with unfounded conceptions.

In this study, a first principle simulation based on the density functional theory is employed to systemically investigate the average voltage of lithiation/delithiation in widely

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used Li-ion battery materials. We found this method to be very effective for investigating the average voltage of lithiation/delithiation, with a good agreement between calculated and experimental results. This method could prove beneficial in the study and prediction of the lithiation/delithiation properties of unknown systems.

1 Method

For charging or discharging the voltage of electrode materials, a Li metal anode and an electrode material cathode such as LiMO_2 form the half-cell. When the battery is charging, the Li ion is extracted from the cathode to deposit the Li electrode. On the discharging process, the Li ion is removed from the anode and returns to the cathode. Based on this experimental design, Aydinol et al. [6] introduced a calculation method based on the average voltage of delithiation of the Li ion battery, LiMO_2 . The average voltage was obtained by calculating the energy difference between the reactants and products. For example, for Li/LiMO_2 electrochemical cells, the reaction is expressed as

The average voltage is

$$\bar{V}_{\text{Theory}} = -\frac{E_{\text{Defect}} + xE_{\text{Li}} - E_{\text{Perfect}}}{xF}, \quad (2)$$

where E_{Perfect} and E_{Defect} correspond to the energy of the complete structure (LiMO_2), before and the defective structure ($\text{Li}_{1-x}\text{MO}_2$) after delithiation, respectively. The E_{Li} is the energy of a single Li atom. According to the above defini-

tion, we construct a universal crystal model, as shown in Figure 1. The energy column on left hand side corresponds to the energy of the complete structure before delithiation. This energy is relatively lower than that after delithiation. As shown in the column on the right hand side of Figure 1, the energy of defective structure comprises contributions from a Li defect and a single Li atom. After delithiation, the total energy, for the defective structure and the isolated Li atom, increases. The average voltage of lithiation/delithiation can then be calculated from this difference in total energy, before and after delithiation, represented as $\bar{V}$ in Figure 1.

The total energy, in the present study, is calculated using the CASTEP module [7], part of Materials Studio software (Accelrys, Inc, San Diego, USA). We initially build the simulation models corresponding compounds based on experimental results (Table 1). We then calculate their total

Figure 1 Simulated energy change in LiMO_2 , before and after delithiation.

Table 1 Lattice parameters, calculated voltages, and experimental voltages of lithium-ion battery materials^{a)}

Structure	System	Lattice parameters [*]			Calculated voltages ^{**} (V)	Experimental voltages (V)	Ref.
		<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)			
Layer	LiCoO_2	0.2816	0.2816	1.4054	4.46	3.93	[9]
	LiNiO_2	0.2887	0.2887	1.4200	4.20	3.57 [10]	[11]
	LiVO_2	0.2910	0.2910	1.4230	4.18	3.00 [12]	[13]
	$\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$	0.2864	0.2864	1.4252	4.05	3.30	[14]
Spinel	LiMn_2O_4	0.8245	0.8245	0.8245	5.38	4.00 [15]	[16]
	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	0.8352	0.8352	0.8352	3.18	1.55	[17]
	LiFePO_4	1.0330	0.6012	0.4702	4.74	3.50 [18]	[19]
	LiMnPO_4	1.0437	0.6096	0.4742	5.51	4.10 [20]	[19]
Olivine	LiNiPO_4	1.0037	0.5867	0.4680	6.06	5.00	[21]
	LiCoPO_4	1.0193	0.5917	0.4695	5.75	4.80 [22]	[19]
	$\text{Li}_2\text{FeSiO}_4$	0.6266	0.5330	0.5015	4.46	3.20	[23]
Monocline	$\text{Li}_2\text{MnSiO}_4$	0.6308	0.5377	0.4988	5.44	3.90	[24]
	$\text{Li}_2\text{CoSiO}_4$	0.6159	0.5440	0.4988	5.37	4.10	[25]
	$\text{Li}_2\text{NiSiO}_4$	0.6333	0.5334	0.4899	6.00	4.67	[26]
Alloy	InSb	0.6479	0.6479	0.6479	2.15	0.75	[27]
	Cu_6Sn_5	1.1022	0.7282	0.9827	1.77	0.40	[28]
Graphite	C	0.2464	0.2464	0.6711	1.35	0.20	[29]
Tetragonal	LiFeAs	0.3772	0.3772	0.6357	1.86	0.45	[30]

a) *, Experimental parameters; **, the values calculated by eq. (2) are about 1 V higher than the experimental values.

energies and obtain the average voltage of lithiation/delithiation using eq. (2).

All calculations were carried out using the plane wave pseudo-potential method, within density functional theory, as implemented in the CASTEP module. All calculations were performed within the generalized gradient approximation and parameterized by the Perdew-Burke-Ernzerhof formula [8] for the exchange correlation energy. The cut-off energy for the plane wave is set to 380 eV. The maximum root-mean-square convergent tolerance is less than 1.0×10^{-5} eV atom⁻¹.

2 Results and discussion

We calculated the average voltage of lithiation for different types of cathode material using lattice values obtained from previous studies, including layered structures, LiMO_2 ($M=\text{V}$, Mn , Co , Ni); a spinel structure, LiMn_2O_4 ; olivine structures, LiMPO_4 ($M=\text{Fe}$, Mn , Co , Ni); monocline structures Li_2MSiO_4 ($M=\text{Fe}$, Mn , Co , Ni) and some other common Li-ion anode materials. Table 1 presents the lattice parameters, and the calculated and experimental average voltages, respectively. In our computational models, we do not adopt any U values because the U value only changes the energy gap of the system and hardly influences the energy difference before and after lithiation/delithiation.

The correlation between calculated average voltage, V_{Theory} and experimental voltage, V_{exp} for seven types of material are shown in Figure 2. A good linear relationship is evident, $V_{\text{Theory}}=0.94 \times V_{\text{exp}}+1.38$. The pertinent coefficient reaches 0.94, very close to 1, implying that the simulation results match experimental values very closely. The calculated values are generally higher than the experimental values, with a systematic shift of 1.38 V, obtained from the intercept value of the equation of the line of best fit in Figure 2. This systematic shift may be explained by the mechanism of surface energy. The extraction and insertion of Li ions

occurs on the surface of the Li electrode. It is clear that the Li atom is not alone. The binding energy between the Li atom and the electrode matrix needs to be considered. However, the Li atom is simply described as an isolated and unbound atom in eq. (2). As a result, the E_{Li} term is inevitably amplified, meaning the calculated values are higher than the experimental values.

To explain this difference, we went on to calculate the energy required to remove Li atoms from solid Li, with a body-centered structure ($E_{\text{Li_Binding}}=2.70$ eV). The binding energy between the atom at the surface and the matrix is considered as a half of the binding energy within the lattice of Li metal ($E_{\text{Li_surface}}=1/2 E_{\text{Li_Binding}}=1.35$ eV), because half of the chemical bonds have been broken for the atoms on the surface. Therefore, considering the surface binding energy of 1.35 eV, the systematic shift between calculated and experimental values can be explained. On the other hand, we independently calculated the surface binding energy of Li, which was similar to the half of the energy for extracting Li from the internal lattice. As a result, we have modified eq. (2) to define E_{Li} as the bound energy of Li metal, rather than the energy of isolated Li atoms (E_{Li}). The energy difference between them (the bound energy of Li metal and E_{Li}) is the surface binding energy, $E_{\text{Li_surface}}$, and the average voltage should be

$$\bar{V}_{\text{exp}} = \bar{V}_{\text{Theory}} - E_{\text{Li_Surface}} \quad (3)$$

The energy of deintercalation formation is associated with the degree of the Li extraction. The plateau voltage is also not fixed, and varies with changes in Li capacity. Therefore, a differentiation of the structure is necessary for the further study. In addition, a phase transition will occur during the charge and discharge processes in some electrode materials, thus a correction to the method will be required to calculate the voltages for lithiation/delithiation caused by the phase transition. Moreover, the energy of lithiation/delithiation formation is very small in some electrode materials, much smaller than the activation energy of Li migration. Hence, a study into Li migration may also be necessary.

3 Conclusions

A first principle method based on the density functional theory was used to investigate the average voltage of lithiation/delithiation in widely used Li-ion batteries. The calculated results indicate that the average voltage of lithiation/delithiation in relevant electrode materials can be obtained by calculating the total-energy differences before and after electrochemical reactions. Considering the surface binding energy, the calculated values are in good agreement with the experimental ones. Therefore, this type of calculation method presents an easy and effective way to predict the potential of new battery systems.

Figure 2 Linear relationship between calculated and experimental voltages.

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