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Influences of Li Intercalation on the Electronic Structures of O2p and V3d Orbitals in α -V₂O₅

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The influence of Li intercalation on the electronic structures of oxygen and vanadium ions in α -V₂O₅ was investigated using first-principles calculations based on the density functional theory with local density approximation. Two different intercalation sites for Li in the V₂O₅ lattices were considered. The calculation results demonstrate that intercalated Li ions at different sites show different effects on the electronic structures of O2p and V3d orbitals. But in both cases Li intercalation will weaken the V=O1 bonding and cause the split-off in V3d valence band to narrow or even disappear and simultaneously broaden the O2p conduction band. Further, the average electron transfer number from per intercalated Li2s to V3d orbitals is determined to total be about 0.52.

Key words: V₂O₅, Li intercalation, Electronic structure

I. INTRODUCTION

Due to its small and highly anisotropic *n*-type electrical conductivity, V₂O₅ has been a promising material in many technological applications. For example, it has been used in the gas and humidity sensors [1] and electronic information displays [2]. Moreover, V₂O₅ was widely used in electrochemical charge storage and electrochromic devices owing to its high charge capacity [3-8]. For these applications, the cycling life of Li intercalation/deintercalation into/from V₂O₅ lattices is the most critical factor that influences the performance of these devices. To improve the cycling life, a better understanding of the intercalation process and consequent influences on the electronic structures of V₂O₅ host as well as the subtle effects on the V3d and O2p orbitals is necessary. Figure 1 show the layered structure of V₂O₅ and the fivefold coordination of V with O ions. V₂O₅ crystallizes in an orthorhombic structure with large V-O separation along the crystallographic *c* direction. Three different types of O ions exist in V₂O₅: one terminal (vanadyl) oxygen, O1, which forms one strong bond at a distance of only 1.58 Å, one bridging oxygen (O2) in the center of two V ions at a V-O distance of 1.78 Å with a V-O2-V angle of 125.8°, and three chain oxygens, O3, which form two bonds at 1.88 Å and another one at 2.02 Å. Due to the layered structure, V₂O₅ can accommodate elements with small radii to form intercalated compounds such as: Na [9],

Mg [10], and Li [11]. The intercalation of Li into V₂O₅ has been intensively studied [12,13]. Most of the previous experimental studies were focused on the electrochemical and electrochromic properties and did not explain the intercalation mechanism or answer why/how the change of the V and O ions electronic structure happens during the intercalation of Li. Theoretical calculations might partly solve these problems, but few theoretical works have been reported on this topic [14,15], although the theoretical investigation of the electronic structure of V₂O₅ itself is abundant [16-24]. The influences of Li intercalation and oxygen vacancies on the electronic structures of V₂O₅ host were studied [25,26], the aim of this work was to increase the understanding, at the atomic level, of the changes of the electronic structures taking place in the O2p and V3d orbitals during the intercalation of Li into V₂O₅ host.

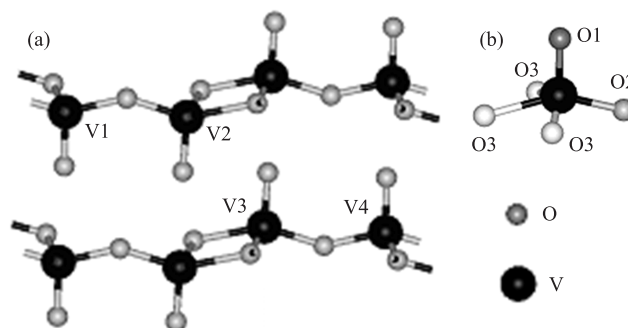


FIG. 1 (a) The layered structure of V₂O₅, (b) the five-fold co-ordination of V by O ions.

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II. THEORETICAL METHOD

We employed density functional theory (DFT) to undertake electronic structure calculations utilizing the Vienna *ab initio* simulation package (VASP) with local density approximation (LDA). DFT plane wave pseudopotential methods have recently been successfully used to model lithium vanadate materials [27]. VASP is a complex package for performing *ab initio* quantum-mechanical molecular dynamic simulations with plane wave basis sets and ultra-soft Vanderbilt pseudopotentials. The electron-core interaction is described by the projector augmented wave (PAW) method [28]. Compared to conventional pseudopotentials, PAW has the advantage that the exact shape of the valence wave function is taken into account, and this in turn can improve the description of transition metals. The primitive cell comprises two V_2O_5 formula units, which is displayed in Fig.1(a). The k -mesh used in this study is $4 \times 4 \times 4$; the convergence criteria for electron and ion are 0.1 and 1 meV, respectively; and the cut-off energy is 400 eV. The lattice parameters for V_2O_5 are taken from experimental data reported previously [29]: $a=11.510$ Å, $b=3.563$ Å, and $c=4.369$ Å, because the calculated lattice parameters for V_2O_5 agree extremely well with experimental data.

III. RESULTS AND DISCUSSION

According to previous studies [14,25,30], two possible intercalation sites for Li have been considered: one on the line between O1 and V ions (model 1), and the other on the line between two O2 ions (model 2) at the sequential V_2O_5 layers. The schematic diagrams of model 1, and model 2 are shown in Fig.2, respectively. The chemical stoichiometry for both models is thus $Li_{0.5}V_2O_5$. The V=O1 bond lengths for V_2O_5 , model 1 and model 2 are 1.57, 1.50, and 1.61 Å. When Li lies on the line between O1 and V ions, the V=O1 bond length becomes shorter; on the contrary, when Li sits on the line between two O2 ions, the V=O1 bond length is longer compared with that of V_2O_5 . For the transition metal oxides, shortening the bond length between metals and O ions will strengthen their bonding. It seems that intercalation of Li on the line between O1 and V ions will increase the bonding of O1 and V ions.

Figure 3 shows the total density of state of V_2O_5 , model 1, and model 2. The total DOS of V_2O_5 shows that its electronic states are mainly distributed in the two energy regions, one from -5.12 eV to 0.00 eV which corresponds to the valence band (VB) and the other from 1.61 eV to 4.03 eV where the conduction band (CB) appears. The VB is dominated by O2p states, and the CB mainly consists of V3d states [20]. A narrow so-called split-off CB [31] with a width of 0.65 eV lies below the broad higher conduction band separated by an additional gap of about 0.54 eV. This is because

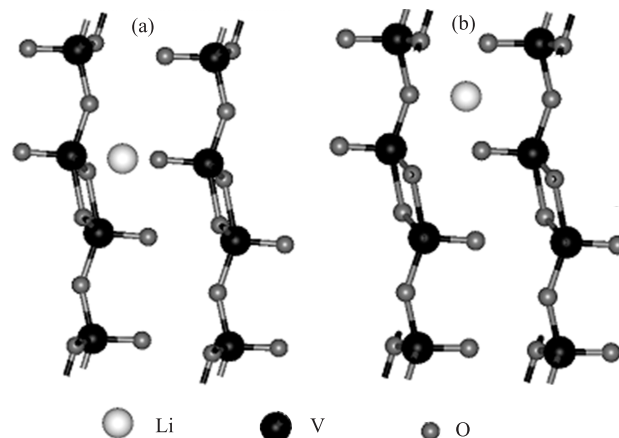


FIG. 2 The locations of intercalated Li ions in the V_2O_5 layers. (a) model 1: Li ion on the line of O1 and V, (b) model 2: Li ion on the c axis between two O2 ions at sequential layers.

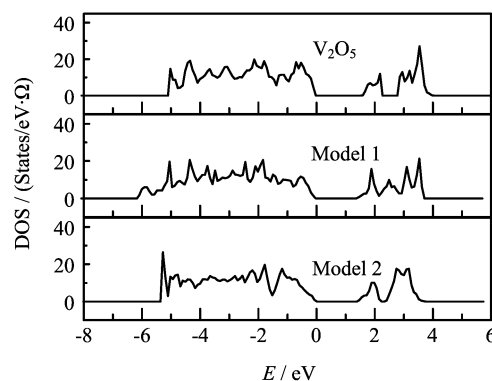


FIG. 3 The total density of state of V_2O_5 , model 1 and model 2.

of the splitting of partial DOS of V3d orbitals into the lower (t_{2g}) and the upper (e_g) manifolds due to the crystal field (see in Fig.4(b)). It is obvious that the narrow split-off CB in V_2O_5 completely disappears in model 1, whereas it still remains in model 2, though it becomes narrower. This result suggests that the intercalated Li on the line between O1 and V ions shows a stronger influence on the electronic structure of V3d states. The disappearance of the split-off in CB may be because the interaction between V and O1 ions decreases due to the intercalation of Li and consequently weakens the orbital split of V3d orbital caused by the crystal field (the V=O1 bond is the strongest bonding in the V_2O_5). This is inconsistent with the above result derived from the V=O1 bond length. The VB region of model 1 ranges from -6.17 eV to 0.00 eV, which is about 1.05 eV wider than that of V_2O_5 , which is very close to the experimental data shown in Fig.5 indicating that the VB of $Li_{0.5}V_2O_5$ is about 1.15 eV wider than that of V_2O_5 [10].

The VB region of model 2 is from -5.35 eV to 0.00 eV,

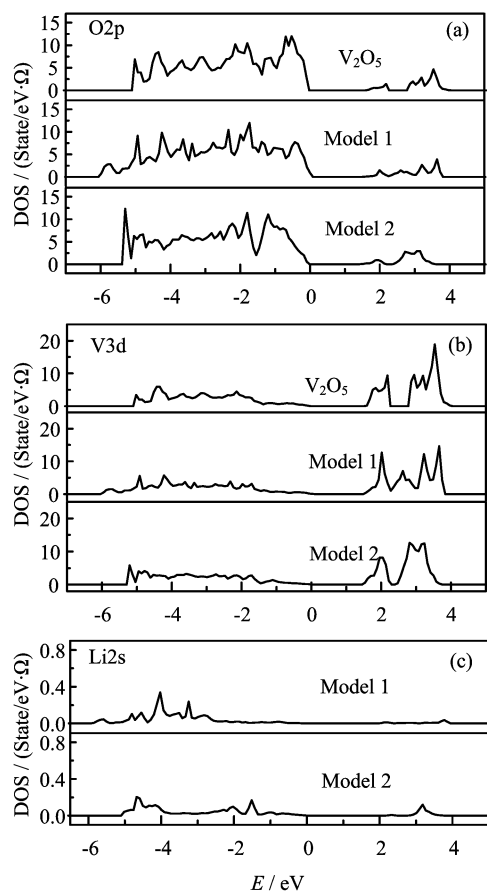


FIG. 4 The partial density of state of O2p (a) and V3d (b) orbitals of V_2O_5 , model 1, and model 2 together with Li2s orbitals (c) for both models.

which is only about 0.23 eV wider than that of V_2O_5 . This phenomenon implies that intercalation of Li ions on the line of O2 ions has also a smaller effect on the electronic structure of the O2p orbitals. In order to better understand the influence of intercalated Li on the electronic structures of O and V ions, the changes of partial DOS of O2p and V3d orbitals after Li intercalation were investigated. Figure 4 displays the partial DOS of O2p and V3d orbitals for V_2O_5 , and model 1 and model 2 together with Li2s state of model 1 and model 2. In model 1, the VB of O2p states becomes broader and shifts to lower energies. Consequently, due to the high hybridization between O2p and V3d orbitals, the VB of V3d state in model 1 also shifts to lower energies. It is obvious that the split-off in V3d VB completely disappears. In model 2, the VBs of O2p and V3d orbitals become only slightly broader. It is surprising to find that for model 2 the CBs of these orbitals (O2p and V3d) move to lower energy. This suggests that due to the intercalation of Li the anti-bonding level (e_g) of O2p and V3d orbitals would shift to lower energy [20]. The stability of intercalated compounds depends dramatically on whether the acceptor

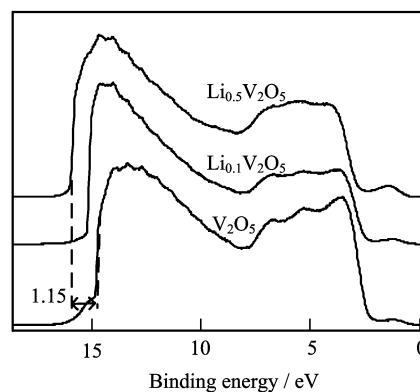


FIG. 5 The valence band spectra of V_2O_5 , $Li_{0.1}V_2O_5$, and $Li_{0.5}V_2O_5$ [11].

TABLE I The electron number distribution around the V3d orbitals for V_2O_5 and model 1 and model 2, the positions of V1, V2, V3, and V4 are shown in Fig.1(a), V_T3d is the sum of the electron numbers of V1, V2, V3, and V4 3d orbitals, $V_{EI}3d$ is the average electron number increase for per V ion in model 1 and model 2 compared with that in V_2O_5 .

	Electron number		
	V_2O_5	Model 1	Model 2
V1 3d	3.12	3.23	3.29
V2 3d	3.12	3.40	3.29
V3 3d	3.12	3.22	3.22
V4 3d	3.12	3.21	3.22
V_T^a3d	12.48	13.06	13.00
V_{EI}^b		0.14	0.13

^a The total electron numbers of the four V ions.

^b The average electron number increases for the four V ions.

level is bonding, antibonding or non-bonding. When Li intercalates into V_2O_5 lattices, the Li ion shares an O2p orbital with V ions; oxygen at the vertex of an octahedron is connected through $2p_x$, $2p_y$, and $2p_z$ orbitals to the 2s orbital of a Li atom. For model 1, when the Li is close to the O1 ions, the Li2s state is strongly hybridized with O2p orbitals, and also due to the electronic coupling between Li and V ions because of the close geometric space, the CB of Li2s for the model 1 is nearly empty compared with that of model 2 (see in Fig.4(c)). Contrarily, in model 2, the Li is much farther away from the O and V ions, and its influence on the O2p and V3d orbitals is thus smaller. It has actually been found that the alkali metals (Na, Li) valence electrons are transferred to the lowest unoccupied transition metal V3d states during the intercalation processes by photoemission spectroscopy [9,11].

In order to approximately calculate the electron transfer number from intercalated Li2s to V3d states, the electron number above the Fermi level accumulating

around the V3d orbitals before and after Li intercalation are integrated and listed in Table I. The V1, V2, V3 and V4 ions are labeled in Fig.1(a). It is clear that, for model 1, the electron number around the V2 3d orbitals increases much more than the other V ions (from 3.12 to 3.40), because it is the closest one to the intercalated Li. For model 2, the electron numbers of the V3d states for all four V ions increase slightly in comparison with V ions in V₂O₅, but those of V1 3d and V2 3d states increase a little more than those of V3 3d and V4 3d states. The above results imply that the intercalated Li will transfer more electrons to the closer V ions. This is the main reason that causes the weakening of O1=V bond for both model 1 and model 2 after intercalation of Li. V_T were then calculated to be 12.48, 13.06, and 13.00 for V₂O₅, and model 1 and model 2, respectively. It seems that more electrons will transfer to V3d from Li2s when Li intercalates on the line between O1 and V ions. V_{EI} increases for the V ions after Li intercalation for both models are thus calculated as,

$$V_{EI} = \frac{1}{4}[(V_{T3d})_{\text{Model 1, Model 2}} - (V_{T3d})_{V_2O_5}] \quad (1)$$

From the data in Table I, we know that when Li intercalates on the line between two O2 ions, there are about 0.13 electrons transferring from Li2s to four V3d states on average. This result means that the electron transfer number from per intercalated Li2s to total V3d states is about 0.52. We also calculate the average electron number of O2p states, which are 32.19, 32.24, and 32.20 for V₂O₅ and model 1 and model 2, respectively. This suggests that the intercalation of Li has a smaller effect on the electron numbers of O2p states compared with V3d states. The determination of electron transfer is an important step for characterizing the intercalation mechanism. The extents of charge transfer from intercalated alkali into the host has been a matter of debate for a long time, and still no complete agreement has been reached. The electrons of Li2s orbitals have higher energy than the Fermi level of V₂O₅ (see Fig.6). The 2s orbital electrons will transfer to V₂O₅ unoccupied states (V3d) due to a difference in work functions to form much more stable system. Guo and Liang found a transfer of only 0.45 electrons per Li atom to the TiS₂ host using rigid-bond model calculation. However, this charge transfer is probably significantly underestimated due to the large spherical size used to count the Li charge [32]. Moreau *et al.* obtained an even smaller charge transfer (0.24) from Li atom to the same compound from a Mulliken population analysis in an extended Hückel model [33]. This result is most likely due to the somewhat artificial charge assignment made in the Mulliken population analysis. The exact electron transfer number from Li2s to V3d orbitals needs to be further studied by advanced experimental techniques.

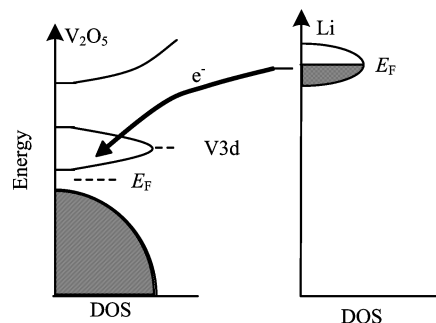


FIG. 6 The schematic diagram of the electron transfer process from the Li2s orbitals to the empty state of V₂O₅ host.

IV. CONCLUSION

In summary, it was found that the intercalated Li has localization effects on the electronic structures of O2p and V3d orbitals. In particular, when Li sits on the line of between O1 and V ions, the electronic structures of the nearest V ion are strongly altered. The intercalation of Li will weaken the bonding between V and O1 ions mainly by reducing the oxidation state of V ions. The electron transfer number from per intercalated Li2s to V3d orbitals is about 0.52 when the intercalated Li ions are located between the two O2 ions, whereas slightly more electron transfer is proposed from Li2s to V3d orbitals when the intercalated Li ions are sited on the line between O1 and V ions. This makes it possible to control the band filling of the host materials by varying the intercalated Li content. In electrochromic applications band filling is used to adjust electronic and optical properties.

V. ACKNOWLEDGMENTS

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