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Electronic band structure and migration of lithium ions in LiCoO_2

Key words: electrochemical battery, LiCoO_2 , electronic band structure, activation energy of lithium ion self-diffusion

Introduction

Lithium cobalt oxide LiCoO_2 has founded application in rechargeable lithium ion batteries mainly as a cathode [1, 2]. This material possesses the layered crystal structure, which has rhombohedral symmetry and belongs to the space group $R\bar{3}m$. This circumstance is favorable to the accommodation lithium in concentrations, which may change over a relatively large range [3]. Applications of LiCoO_2 with deintercalated lithium Li_xCoO_2 ($x < 1$) as cathode material in solid-state batteries are also taken place widely.

To build adequate mathematical model of the solid-state battery one should take into account numerous phenomena [4, 5]. One of the crucial points of these models is an achievement of the low activation energy for electric transport of solid electrodes and electrolytes. This activation energy depends generally on the electronic structure of the material [6], which may be modified by changing of the chemical elements contained, and external influences. The electronic band structure of LiCoO_2 was studied previously by using first principles methods [7 - 15]. The

near band gap E_g valence and conduction bands formed mainly by the hybridized d -states of cobalt and p -states of oxygen. The experimentally observed values of band gap E_g are about 1.7 – 2.7 eV [16 - 20, 23].

A common and important problem in theoretical chemistry and in condensed matter physics is the identification of a lowest energy path for a rearrangement of a group of atoms from one stable configuration to another. Such a path is often referred to as the ‘minimum energy path’ (MEP). This problem is closely related to the migration of lithium in solids suitable for the lithium ions batteries. One of the parameters of such MEP for lithium ions migration is the activation energy E_a .

In the present study we have calculated the electronic band structure and the activation energy E_a for Li-ions migration in LiCoO_2 . The latter value was calculated using the nudged elastic band (NEB) method and *ab-initio* molecular dynamics (MD). The dielectric permittivity of LiCoO_2 originated from the electronic polarizability was also investigated. These issue can be used to study the correlation between the properties of Li-ion diffusion in a host crystalline matrix and the corresponding change of the electronic polarizability. Such a correlation may supply additional knowledge for deeper understanding of the Li-ions migration in the diffusion process. The importance of the electronic polarizability for the analysis of structural features of Li-containing materials is discussed in Ref. [24].

Method of calculations

Band structure calculations were performed using the CASTEP code (Cambridge Serial Total Energy Package) [25] based on density functional theory (DFT) and a plane-wave basis set with ultrasoft pseudopotentials [26]. To take into account the exchange and correlation effects the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional (GGA-PBE) was used [27]. The eigen-energy convergence tolerance at self-consistent electronic minimization was chosen to be $2.4 \cdot 10^{-7}$ eV and the tolerance for the electronic total energy convergence during the structural optimization was $1.0 \cdot 10^{-5}$ eV. At structural optimization, the maximum ionic force tolerance was $3 \cdot 10^{-2}$ eV/Å and the maximum stress component tolerance was $5 \cdot 10^{-2}$ GPa. All values originated from the electronic structure, such as the total energy E , band dispersion $E(k)$, density of states (DOS), and dielectric functions $\epsilon(E)$ were computed at the respectively optimized crystal structure. For electronic structure calculations, 110 k -points in the irreducible Brillouin zone and a smearing of 0.1 eV were used.

VASP (Vienna *ab-initio* Simulation Package) [28] was used to calculate the activation energies E_a for Li-ion migration in LiCoO_2 (using NEB and MD) as well as the electronic dielectric permittivity ϵ . Here the projector-augmented wave method with the GGA-PBE exchange and correlation functionals were used. A cutoff energy E_{cutoff} of 520 eV for the plane waves, 10 irreducible k -points and a

smearing of 0.2 eV were used for the calculations on the crystal supercell of the size $2 \times 2 \times 1$ (the volume of the supercell corresponds to $V_{sc} = 394.4 \text{ \AA}^3$).

Results and discussion

We have calculated non-spin electronic band structure of LiCoO₂ because in normal conditions, the material does not reveal magnetic properties. Features of the non-spin-polarized band structures (Fig. 1) are in good agreement with the references [8, 13, 16]. The band gap E_g (red arrow in figure 1) at the GGA-PBE exchange-and-correlation approximation is near 1.02 eV (Fig. 1). This is close to the corresponding values in transition metal oxides such as NiO or CoO, where the gap is below 1 eV with PBE [29]. The underestimation of the band gap with standard functionals such as PBE is due to the not taking into account the artificial electronic self-interaction. The experimental values are in the range of $E_g = 1.7\text{--}2.7$ eV [16-20, 23]. The present results of band structure are in good agreement with the previous studies based on the same functionals [16]. The optical band gap E_g of LiCoO₂ is found to be indirect along the LZ-direction in the Brillouin zone, at the relaxed crystal structure (Fig. 1). The characteristic features of LiCoO₂ band structure are the following: (1) the three top valence bands and the two bottom conduction bands of LiCoO₂, being mainly of *d*-character, are characterized by a relatively small dispersion $E(\mathbf{k})$; (2) the six deeper valence bands, being mainly of oxygen *p*-character, show a larger dispersion. This is evident from the electronic density of states for of LiCoO₂ presented in figure 2. Main input into the density of electronic states of the crystal in the range -8 eV to 8 eV (this energy range contains the band gap E_g) originates from *p*O and *d*Co states (Fig. 2). The relative participation of the orbital states *s*Li, *s*Co, *s*O, and *p*Co is much smaller.

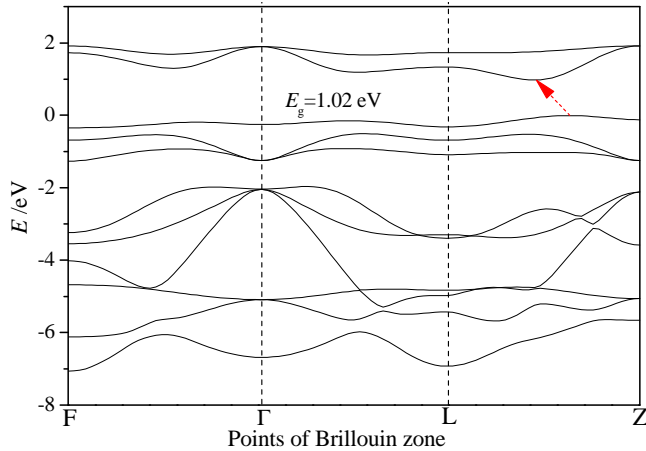


Fig. 1. Band structures of LiCoO₂

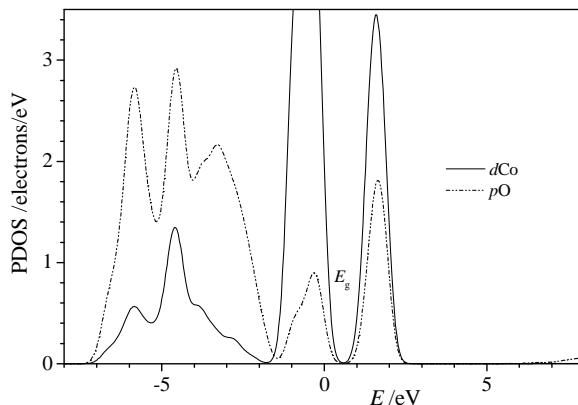


Fig. 2. Partial density of pO and dCo states of $LiCoO_2$.

The nudged elastic band (NEB) is a method for finding saddle points and minimum energy paths between known reactants and products. The method works by optimizing a number of intermediate images along the reaction path. Each image finds the lowest energy possible while maintaining equal spacing to neighboring images. [30].

$LiCoO_2$ is a material widely used in solid state batteries, and therefore a study of Li-ions transport properties is important. One of the approaches used by us to study the energy changes of the material at migration of Li ions is NEB method in non-spin polarized calculations, employing the VASP code [28]. A supercell containing $2 \times 2 \times 1$ units of the crystallographic unit cell of $LiCoO_2$ ($a = b = 5.698 \text{ \AA}$, $c = 14.023 \text{ \AA}$) was generated. The supercell contains 47 atoms and one lithium vacancy ($Li_{0.917}CoO_2$). The NEB images were obtained by moving a Li-ion along the a -axis in the xy -plane towards the vacancy (Fig. 3). The unit cell dimensions were kept fixed during the NEB calculations. The Li-ion migration path from the initial site to the closest vacancy obtained has been found slightly deviated from the straight line. The path and the computed energy barrier obtained $\Delta E = 0.44 \text{ eV}$ (Fig. 4) are in good agreement with the reference results [6, 31].

The Bader electronic charges of the Li ions in the three lithium layers of the supercell calculated along the path as a function of the distance between the same NEB images are also characterized by the extremum-like character (Fig. 5). It was found that at the saddle point, where the total energy is at its maximum, the Bader electronic charge for lithium is about $-2.136 |e|$ (the total charge is $0.864 |e|$) (Fig. 5). Thus, the total charge of lithium ion is here of the smallest absolute magnitude in relation to charges at other NEB images along the migration path. This means that $LiCoO_2$ here is least ionic. Here, the lithium – oxygen distances become the smallest, that probably influences this reduced ionicity of the material. As a

result, the electronic charge of the anions CoO_2 will thus be reduced at the saddle point, which may decrease its electronic polarizability.

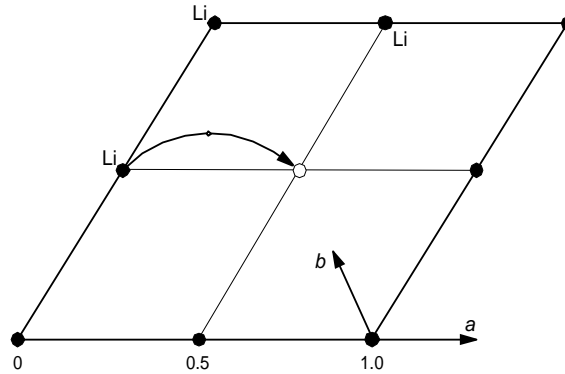


Fig. 3. Positions of Li-atoms (black circles) and Li-vacancy (white circle) in one z -cut of a $2 \times 2 \times 1$ supercell of $\text{Li}_{0.917}\text{CoO}_2$ and path of Li-ion migration path.

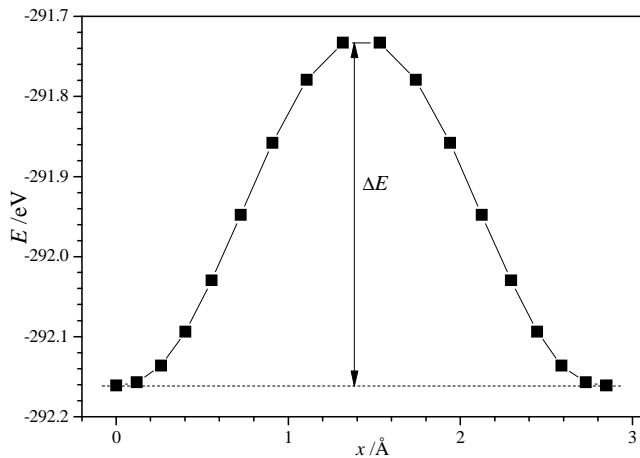


Fig. 4. Dependencies of the total energy E of $2 \times 2 \times 1$ supercell of $\text{Li}_{0.917}\text{CoO}_2$ on the position x of the migrating Li ions: the energy barrier is equal to $\Delta E = 0.44$ eV. The values of $x = 0$ and 5.7 Å correspond to the crystallographic positions $(0, 0, 0)$ and $(0, 0, 1)$ in the $2 \times 2 \times 1$ supercell.

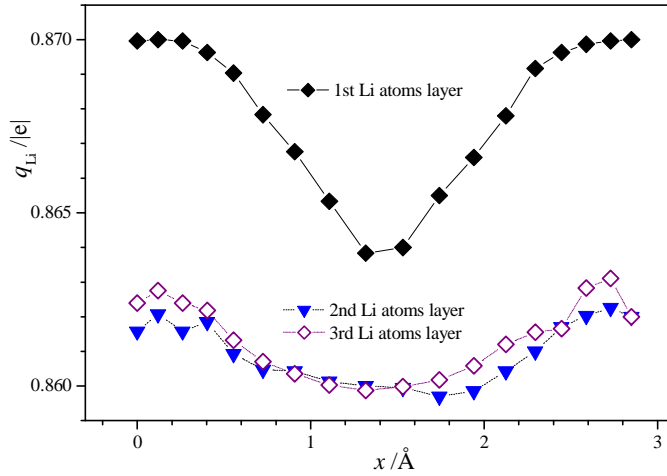


Fig. 5. The electronic polarizability α of a material may be estimated on the basis of the dielectric permittivity ϵ using the the Clausius–Mossotti relation [32].

The electronic polarizability α of a material may be estimated on the basis of the dielectric permittivity ϵ using the the Clausius–Mossotti relation [32],

$$\frac{M_{\text{unit-cell}}}{\rho} \frac{(\epsilon - 1)}{(\epsilon + 2)} = \frac{4\pi N_A}{3} \alpha_{\text{unit-cell}} \quad (1)$$

This relation indicates for the proportionality of these two values, α and ϵ . The real part of the dielectric permittivities $\epsilon_1^{(xx)}$ and $\epsilon_1^{(yy)}$ and $\epsilon_1^{(zz)}$ was calculated as function of the position of the lithium NEB image in the doped system $\text{Li}_{0.917}\text{CoO}_2$. Analysis of DOS and spectral dependencies of dielectric permittivity of the crystal have indicated that it mainly depends on the valence and conduction bands originating from CoO_2 anion. We have found that the dielectric permittivity as function of NEB image is characterized by minimum (Figs. 6, 7), that indicates decrease of the electronic polarizability of CoO_2 anions at saddle point of NEB lithium ions path. The anisotropy, $\epsilon_x \approx \epsilon_y > \epsilon_z$ is very high (Figs. 6, 7), that is expected in view of the layered character of the material.

The relative changes of the dielectric permittivity $\Delta\epsilon/\epsilon$ is maximal in z -direction, $\Delta\epsilon_z/\epsilon_z = 0.054$ (Fig. 7), that is 5 to 8 time larger than those in x - and y -directions, $\Delta\epsilon_x/\epsilon_x = 0.011$, $\Delta\epsilon_y/\epsilon_y = 0.007$ (Fig. 6).

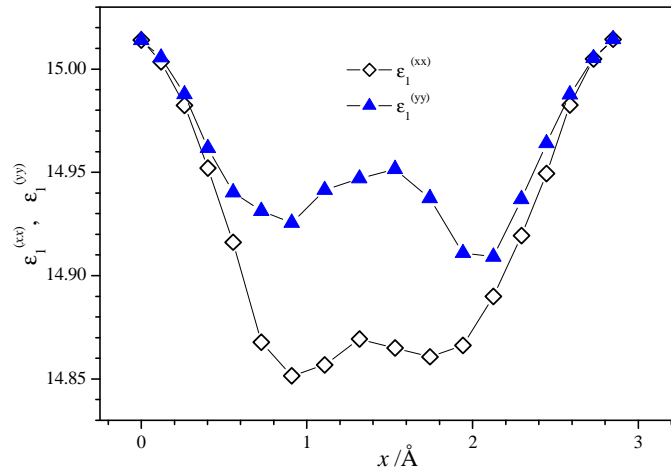


Fig. 6. Dependencies of the real part of the dielectric permittivity $\epsilon_1^{(xx)}$ and $\epsilon_1^{(yy)}$ of $\text{Li}_{0.917}\text{CoO}_2$ on the position of the lithium ion. The values of $x = 0$ and 5.7 \AA correspond to the crystallographic positions $(0, 0, 0)$ and $(0, 0, 1)$ in the $2 \times 2 \times 1$ supercell.

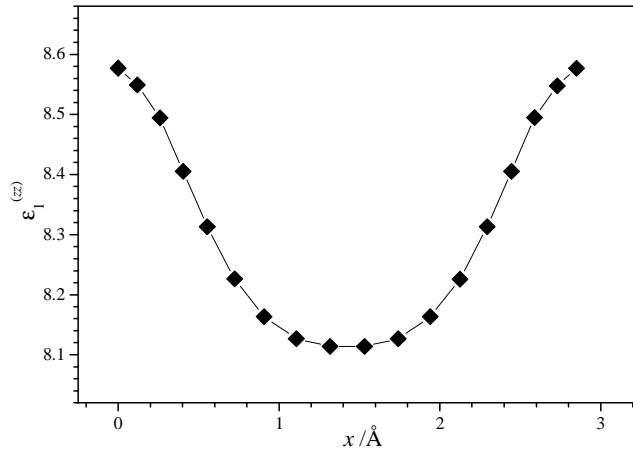


Fig. 7. Dependencies of the real part of the dielectric permittivity $\epsilon_1^{(zz)}$ of $\text{Li}_{0.917}\text{CoO}_2$ on the position of the lithium ion. The values of $x = 0$ and 5.7 \AA correspond to the crystallographic positions $(0, 0, 0)$ and $(0, 0, 1)$ in the $2 \times 2 \times 1$ supercell.

An alternative approach to evaluate the transport properties is a using of the molecular dynamics simulations. Therefore, we have performed *ab initio* molecular dynamics (AIMD) for the undoped LiCoO_2 in a $4 \times 4 \times 1$ supercell, employing the VASP program suite. These calculations were performed at the NVE ensemble at the temperatures 2000 K and 2300 K. The duration of AIMD and the time step were

5 ps and 1 fs, correspondingly. Slope of the linear dependency between the mean square displacement (MSD) of lithium ions and the simulation time is the diffusion coefficient D . The activation energy E_a and the value D_0 were calculated on the basis of AIMD results at two temperatures mentioned above using the relation of the Arrhenius law type

$$D = a^2 \omega \cdot \exp(-E_a/k_B T), \quad (2)$$

where a is the hopping distance ($a \approx 3 \text{ \AA}$ for LiCoO_2), ω is the hopping frequency ($\omega \approx 1 \cdot 10^{13} \text{ s}^{-1}$), and k_B is Boltzmann's constant [33]. Activation energy E_a is one of the main characteristics presenting suitability of a material to the lithium ions batteries. The activation energy obtained in such a way was found to be $E_a = 0.5 \text{ eV}$. This value is close to the similar one obtained using the NEB method (Fig. 4).

Conclusions

Main parameters of the electronic band structure of LiCoO_2 have been calculated using *ab initio* calculations within the density functional theory. The computed band gap is found to be $E_g = 1.02 \text{ eV}$ using the GGA-PBE exchange-and-correlation functional.

Using the nudged elastic band method, the minimal energy barrier of 0.44 eV for lithium ions migration in LiCoO_2 has been obtained, that is in agreement with reference data. The electronic polarizability of LiCoO_2 , which is proportional to the corresponding dielectric permittivity, was found to have a minimum at the trajectory point corresponding to the maximum of total crystal energy. The reduced polarizability of CoO_2 observed here takes place due to the reduced ionicity of LiCoO_2 found from the Mulliken charges of the material.

The activation energy for lithium ion displacement was also calculated using the molecular dynamics method. Assuming an Arrhenius law, the activation energy of $E_a^{(\text{Li})} = 0.5 \text{ eV}$ was deduced, being close to the value obtained with the nudged elastic band method (0.44 eV).

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Abstract

In view of search the effective materials for the electrochemical sources of energy, the density functional theory (DFT) based approach has been applied to the computational study of lithium ion migration in LiCoO_2 . Apart the standard first principles study of band structure and density of electronic states of the crystal, the material was studied using the nudget elastic band (NEB) and the *ab initio* molecular dynamics (AIMD) methods. The activation energy E_a of the lithium ions self-diffusion in LiCoO_2 , as one of the main characteristic of the material for the electrochemical sources of energy, has been obtained using NEB (0.44 eV) and AIMD (0.5 eV).

Streszczenie

Ze względu na poszukiwanie efektywnych materiałów do baterii elektrochemicznych, zostały wykonane obliczenia komputerowe z pierwszych zasad na bazie teorii funkcjonału gęstości (*density functional theory*) struktury elektronowej oraz migracji jonów litu w kryształ LiCoO_2 . Oprócz standardowych obliczeń struktury pasmowej i gęstości stanów elektronowych, przeprowadzono także badania materiału metodami NEB (*Nudget Elastic Bands*) i AIMD (*Ab Initio Molecular Dynamics*). Otrzymano jeden z głównych parametrów migracji litu w kryształ LiCoO_2 , stosowanym w bateriach elektrochemicznych - energię aktywacji samodyfuzji E_a . Ta wielkość okazała się być w granicach od 0.44 eV (NEB) do 0.5 eV (AIMD).