Effect of Strain on Polaron Hopping and Electronic Conductivity in Bulk $LiCoO_2$

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We apply the concept of the “elastic dipole tensor” to study the effect of strain on polaron hopping and electronic conductivity in ionic crystals. As a model system, we choose the commercially used cathode material for Li-ion batteries, namely, $LiCoO_2$, which has a layered structure with alternating planes of oxygen, lithium, oxygen, and cobalt. It is demonstrated that the electronic conductivity of $LiCoO_2$ increases (decreases) exponentially with compressive (tensile) strains. The results of the analytical elastic-dipole-tensor method are shown to be in good agreement with a direct approach in which migration barriers of polaron hopping as a function of strain are evaluated using density-functional-theory-based nudged elastic-band calculations. In a broader sense, the presented analytical approach can be used to study the effect of any induced or applied elastic strain field on the electronic conductivity of polarizable semiconductors and insulators.

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I. INTRODUCTION

Electron and hole transport in many insulator and semiconductor materials takes place via self-trapped small-polaron hopping [1–5]. Examples of these materials are ceramics and polymers, which are widely used and/or investigated in energy storage as electrode or electrolyte materials [6–11]. Li-containing transition-metal oxides such as $LiCoO_2$ (commercially used cathode material in Li-ion batteries) are generally p-type semiconductors. Electronic conductivity in these materials is therefore expected to occur via hole-polaron hopping. Experimental studies [12,13] indicate that the electronic conductivity of Li_xCoO_2 with $x > 0.95$ is Li-content dependent. The activation energy for hole migration increases with x from about 10 meV to 100–300 meV [14,15]. The large difference between the reported values of the energy barrier of polaron migration (ΔE_b) is due to the fact that ΔE_b depends strongly on the concentration of Li vacancy (i.e., the level of delithiation). *In situ* conductivity-potential profiles and cyclic voltammograms reveal that the electronic conductivity of Li_xCoO_2 decreases exponentially with x or potential (from 2.7 to 4.0 V) during Li insertion [16]. The mobility of electrons and holes in Li transition-metal oxides depends strongly on the potential well created by the displacement of ions close to the charge carriers, as well as coupling between the d orbitals of transition metals. Both of these factors can be affected by strain that is applied purposely or induced by the lattice mismatch at interfaces between different phases of Li_xCoO_2 with different values of x [17–23] or between Li_xCoO_2 and solid electrolytes or a binder.

Theoretical investigations are needed to uncover the relation between electronic conductivity and strain. A theoretical study by Lee *et al.* showed that a 4% tensile strain can change ionic and electronic conductivity of $LiFePO_4$ by 50 and 15 times, respectively, at 300 K [24].

Recently, the concept of the elastic dipole tensor was used to investigate the influence of strain on ionic mobility in materials. For example, Goyal *et al.* applied this method within transition-state theory to investigate mobility of single and divacancies of uranium in UO_2 [25]. They found that a 2% homogeneous strain can change the diffusion barrier of U ions by 0.4 eV [25]. In this paper, we study the influence of strain on hole-polaron mobility and electronic conductivity in $LiCoO_2$ using a density-functional theory (DFT)-based elastic dipole tensor approach and DFT-based nudged-elastic-band (NEB) calculations (see Ref. [26] for more details) and find a good agreement between these two methods. Migration of Li vacancy can be coupled to that of a polaron. Study of the effect of strain or stress on ionic conductivity, coupling between ionic and polaron migration, and the effect of strain or stress on this coupling in $LiCoO_2$ will be a topic of our future work.

To localize holes on one Co cation, we have (i) deliberately broken the symmetry by slightly displacing O

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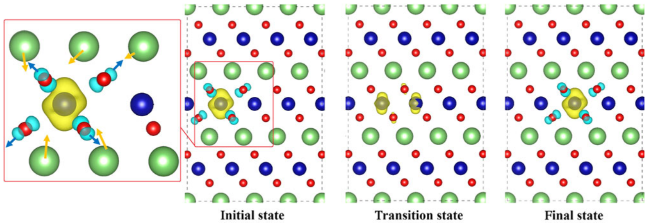

FIG. 1. Spin densities and atomic structures of initial, transition, and final states of a hole-polaron hopping between Co cations in $LiCoO_2$. Arrows show the displacement direction of ions close to the trapped hole in the initial state. Li, Co, and O ions are in green, blue, and red, respectively. Note that the *a*-*b* plane is perpendicular and the *c* axis is parallel to the sheet.

anions and (ii) used the generalized-gradient approximation with the Hubbard U parameter exchange-correlation functional with $U - J = 4.91$ (the Dudarev method [27]). The $U - J$ value which is used in this work has also been applied to this system in previous studies [28,29]. Figure 1 shows the trapped hole (in yellow) on one Co cation in bulk $LiCoO_2$. The bond lengths between octahedral O anions and the Co cation with the hole expand, while those between Li cations and O anions shrink. Note that the total energy of $LiCoO_2$ with a trapped hole is more favorable than that with a delocalized hole (a structure without deliberately broken symmetry). Structures of initial, transition, and final states of hole hopping between Co cations are also presented in Fig. 1. The calculated activation barrier for migration of a hole in the strain-free $LiCoO_2$ structure is 0.35 eV, which is slightly larger than the reported experimental value of 0.30 eV [14,15]. The reason of this difference can be due to the existing of stress in the system during the experimental measurements and also the nature approximation of the XC functional in the DFT calculations. Afterwards, we calculate the energy barrier for hole migration as a function of both lateral and longitudinal strains from −2% to +2% by performing climbing nudged-elastic-band (Cl-NEB) calculations (hereafter called the direct method). The results show (see Fig. 2, black points) that the diffusion barrier increases (decreases) by 7% and 5% for each 1% tensile (compressive) strain along the *a*-*b* plane and *c* axis, respectively. The effect of a 1% strain on Li-ion migration barrier in $LiCoO_2$ is about 15% and 23% in the *a*-*b* plane and along the *c* axis, respectively [30]. This means that the strain-induced (percentage) change in the migration barrier of holes is almost 2 to 4 times smaller than that of Li ions in $LiCoO_2$.

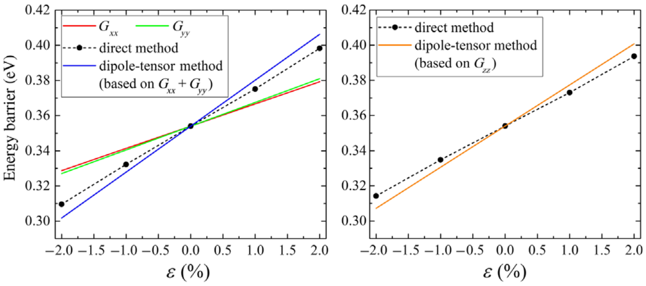

FIG. 2. Migration-energy barrier (in eV) of hole polarons in $LiCoO_2$ as a function of strain along (left panel) the *a*-*b* plane and (right panel) the *c* axis calculated using the direct and elastic-dipole-tensor methods.

In the following, the elastic-dipole-tensor method to predict the migration barrier of holes in $LiCoO_2$ is summarized. Existence of a hole in a crystal can cause (i) short-range and (ii) long-range distortions in which (i) the ions that are close to the hole displace and (ii) the dimensions of the crystal lattice change. The latter distortion leads to a volume change which can be evaluated by the so-called elastic dipole tensor [31]. The energy barrier for migration of holes with a density of $n_h = N_h/V$ (N_h is the number of holes per volume V) in a crystal with an applied strain field (ϵ) is the difference between the total energy of the transition and initial states,

$$\Delta E_b(n_h, \epsilon) = E_T(n_h, \epsilon) - E_I(n_h, \epsilon). \tag{1}$$

The total energies can be written as Maclaurin series

$$\begin{aligned} E(n_h, \epsilon) = {} & E^p(\epsilon = 0) - n_h \mu_h + n_h E_f \\ & + \frac{1}{2} n_h^2 \frac{\partial^2 E}{\partial n_h^2} + \cdots + \sum_{ij} \epsilon_{ij} \frac{\partial E}{\partial \epsilon_{ij}} \\ & + \frac{1}{2} \sum_{ij} \epsilon_{ij} \epsilon_{kl} \frac{\partial^2 E}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \\ & + \cdots + \sum_{ij} \epsilon_{ij} n_h \frac{\partial^2 E}{\partial n_h \partial \epsilon_{ij}}. \end{aligned} \tag{2}$$

Here, $E^p(\epsilon = 0)$ and μ_h are the total energy of pristine $LiCoO_2$ (polaron-free and stress-free) and the chemical potential of the holes. The third term is the formation energy of a hole (E_f) in $LiCoO_2$. The second and higher derivatives of E correspond to the interaction energy between holes, which is negligible for low contents of the hole polaron (n_h). Since we use a large supercell of $4 \times 4 \times 1$ (11.30 Å × 11.30 Å × 13.97 Å) for $LiCoO_2$, the hole concentration is very low, and the second and higher derivatives of E ($\epsilon = 0$) are therefore expected to be very small. Even if they are not negligible, they cancel out to a large extent when we calculate $\Delta E_b(n_h, \epsilon)$ [see Eq. (1)]. In Eq. (2), $\{[\partial E]/(\partial \epsilon_{ij})\}$, $\{[\partial^2 E]/(\partial \epsilon_{ij} \partial \epsilon_{kl})\}$, and $\{[\partial E]/(\partial n_h \partial \epsilon_{ij})\}$ are the stress (σ_{ij}) stiffness tensor (C_{ijkl}) and elastic dipole tensor ($-[(\partial \sigma_{ij})/(\partial n_h)] = G_{ij}$). Moreover, σ_{ij} is almost zero for hole-polaron-free $LiCoO_2$. Thus, Eq. (2) can be rewritten as

$$E(n_h,\epsilon) \approx E^p(\epsilon=0) - n_h\mu_h + n_hE_f + \frac{1}{2}\sum_{ij} C_{ijkl}\epsilon_{ij}\epsilon_{kl} - n_h\sum_{ij} G_{ij}\epsilon_{ij}. \quad (3)$$

By using Eq. (3) for initial and transition states in Eq. (1), $\Delta E_b(n_h,\epsilon)$ is

$$\Delta E_b(n_h,\epsilon) \approx [E_T(\epsilon=0) - E_I(\epsilon=0)] - n_h[G^T_{ij}\epsilon_{ij} - G^I_{ij}\epsilon_{ij}]. \quad (4)$$

In Eq. (4), we assume that μ_h and C_{ijkl} remain unchanged during the hole-polaron hopping and we replace the formation energies of holes by the total energies of hole-containing $LiCoO_2$.

To obtain the elastic dipole tensor which is needed in Eq. (4), we use the first derivative of $E(n_h,\epsilon)$ from Eq. (3) with respect to strain:

$$\sigma_{ij} \equiv \frac{\partial E}{\partial \epsilon_{ij}} = \sum_{kl} C_{ijkl}\epsilon_{kl} - n_hG_{ij}. \quad (5)$$

The elastic dipole tensor (G_{ij}) can then be calculated with the following equation:

$$G_{ij} = -\frac{\partial \sigma_{ij}}{\partial n_h} = -\frac{1}{n_h}(\sigma^h_{ij} - \sigma^0_{ij}) = -V(\sigma^h_{ij} - \sigma^0_{ij}), \quad (6)$$

where σ^h_{ij} is the induced stress due to the trapped hole in a supercell with a volume of V, and σ^0_{ij} is the stress of the hole-free system. The latter is very close to zero for an optimized unit cell. According to this definition, σ_{ij} and G_{ij} have opposite signs. A positive stress corresponds to a tensile stress. Please note that in Eq. (6) we have assumed that stiffness is independent of hole concentration.

The geometries of the initial and transition states from the direct method are then used to calculate the elastic dipole tensor using Eq. (6), followed by the calculation of diffusion barriers using Eq. (4). The extracted elastic-dipole-tensor matrices (in eV) for the initial and transition states are as follows:

$$G_I = \begin{bmatrix} 0.293 & -0.173 & -0.196 \\ -0.123 & 0.117 & 0.116 \\ -0.093 & 0.136 & -1.050 \end{bmatrix}$$

$$G_T = \begin{bmatrix} 1.557 & -0.124 & -0.102 \\ -0.124 & 1.466 & 0.118 \\ -0.102 & -0.118 & 1.290 \end{bmatrix}.$$

We find an anisotropic elastic dipole tensor for hole polarons in $LiCoO_2$. The calculated values of G_I show that a low content of holes, namely, $n_h = 5.6\times10^{20}$ cm^{-3}, tends to expand the crystal along the c axis (with a negative sign for G_{ij} or a positive sign for σ^h_{ij}). However, there is only a slight tendency to contract along the two orthogonal directions (along the a-b plane, with a positive sign for G_{ij} or a negative sign for σ^h_{ij}). These changes in lattice parameters result in an increase of total crystal volume. A comparison between the G_{ij} of polaronic defects and that of ionic defects in ionic crystals, such as UO_2 and $SrTiO_3$ ($2 < |G_{ij}| < 17$ in eV) [25,31–33], indicates that polaron-induced stresses are weaker than ion-induced ones. However, the effect of strain on the diffusion barrier depends not only on G_I but also on G_T. Migration barriers of hole polarons in the a-b plane and the c axis as a function of strain [$\Delta E_b(n_h = 5.6\times10^{20}$ cm$^{-3}, \epsilon)$] calculated with the elastic-dipole-tensor method (the blue and orange lines, respectively) are illustrated in Fig. 2. It can be seen that the difference between elastic-dipole-tensor and direct methods is less than 2%.

Afterwards, we estimate the electronic conductivity of Li_xCoO_2 as

$$\sigma = n_he\mu_h = n_he\frac{ega^2\nu_0}{k_BT}\exp\left(\frac{-\Delta E_b(n_h,\epsilon)}{k_BT}\right). \quad (7)$$

Here, n_h, e, g, a, ν_0, k_B, and T are the concentration of holes, the charge of an electron, the geometric prefactor, the jump distance, the characteristic phonon frequency, the Boltzmann constant, and the temperature, respectively. The concentration of holes is expected to be equal to the concentration of Li^+ vacancies (V^-_{Li}) (i.e., the level of delithiation). Because the creation of V^-_{Li} during the delithiation process should be compensated for mainly by the formation of holes and not by the formation of V^{+2}_O. Thus, the value of n_h for $Li_{0.98}CoO_2$, i.e., one hole per $4\times4\times1$ supercell (theoretical unit-cell parameters of 11.30 Å × 11.30 Å × 13.97 Å), is 5.6×10^{20} cm^{-3}. The value of $(ega^2\nu_0)/k_BT$ at $T = 300$ K for a variety of materials is almost equal to 1 cm^2/V s [1]. The variation of a and ν_0 with n_h and ϵ is expected to be much smaller than that of $\exp\{[-\Delta E_b(n_h,\epsilon)]/k_BT\}$. Therefore, using $\{[(ega^2\nu_0)/k_BT\} \approx 1$, we evaluate the conductivity as a function of strain at 300 K with the two abovementioned methods (see Fig. 3). It is found that without applying stress or strain, the value of conductivity for $Li_{0.98}CoO_2$ is 2.03×10^{-4}, which is close to the experimental value of approximately 10^{-4} reported by Levasseur *et al.* [34] for $Li_{0.96}CoO_2$. Moreover, Fig. 3 indicates that the electronic conductivity of $LiCoO_2$ decreases (increases) by a factor of 5.5 and 4.7 for 2% tensile (compressive) strain along a-b plane and c axis, respectively. The difference between the direct method and the elastic-dipole-tensor approach is only around 2%, showing that the latter method can predict the electronic conductivity of $LiCoO_2$ (and similar systems) with a reasonable accuracy and less computational effort.

In summary, we study in this paper the effect of strain on the polaron-hopping energy barrier and the electronic conductivity of bulk $LiCoO_2$ using a computationally

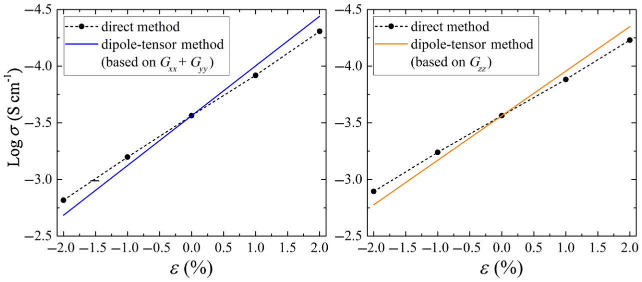

FIG. 3. Electronic conductivity of $Li_{0.98}CoO_2$ as a function of strain along (left panel) the *a*-*b* plane and (right panel) the *c* axis calculated using the direct and elastic-dipole-tensor methods for $T = 300$ K.

efficient analytical model based on the elastic-dipole-tensor concept. By comparing the results to those obtained by a direct approach in which the polaron-hopping energy barrier as a function of strain is obtained through DFT-NEB calculations, it is shown that the elastic-dipole-tensor method can be used to study strain-induced change in electronic conductivity of materials. This work suggests that the elastic-dipole-tensor approach can be used to estimate the energy barrier of polaron hopping and the electronic conductivity of ionic crystals for any given strain field with low computational and time efforts.

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[26] The spin-polarized DFT calculations are performed using the DFT code Vienna *ab initio* simulation package (VASP) [G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, Phys. Rev. B **54**, 11169 (1996)] with plane-wave basis sets, projector-augmented-wave pseudopotentials, and the Perdew-Burke-Ernzerhof+Hubbard U parameter exchange-correlation functional. A Gaussian smearing with a width of 0.05 eV is used. Convergence criterions for energy is set at 10^{-4} eV. We do not consider any symmetry constraints implemented in VASP. Hole-polaron migration is calculated using the Cl-NEB method implemented in VASP with nine images. The Monkhorst-Pack k-point mesh of $3 \times 3 \times 3$ including the Γ point (due to the hexagonal structure of $LiCoO_2$) and an energy cutoff of 500 eV are used for all of the calculations. For the direct method, to model the case of 0% strain, we optimize the unit cell in the charged state to release all of the residual stresses due to the formation of a polaron. To model the strained cases, we apply different strains (within the linear elastic regime) to the system containing the polaron. For the elastic-dipole-tensor method, according to Eq. (6), we need the stress tensor of the system in the ideal (polaron-free) and defective (polaron-containing) states. The system is neutral for the ideal case. The stress tensor for the defective case is calculated with the optimized unit cell of the ideal system. We do not consider the correction for the charged cell since this correction is expected to be very similar in the transition and initial states. Therefore, we expect the effect of this correction on the activation barrier of polaron migration, which is the energy difference between the transition and initial states, to be canceled out.

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