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Simultaneous enhancement of electronic and Li^+ ion conductivity in $LiFePO_4$

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Enhancing the electronic and ionic conductivity in Li compounds can significantly impact the design of batteries. Here, we explore the influence of biaxial strain on the electronic and Li^+ ion conductivities of $LiFePO_4$ by performing first-principles calculations. We find that 4% biaxial tensile strain (BTS) leads to 15 times increase in electronic conductivity and 50 times increase in Li^+ ion conductivity at 300 K, respectively. Electronic conductivity is enhanced because BTS softens lattice distortions around a polaron, resulting in a reduction of the activation barrier. The extra volume introduced by tensile strain also reduces the barrier of Li^+ ion migration. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4737212]

Extensive research is currently under way to explore the atomic-scale physics of energy-related materials, aiming to improve their performance. $LiFePO_4$ is a promising candidate for rechargeable Li-ion battery electrodes. The material is known for its structural and chemical stability, high intercalation voltage, high theoretical discharge capacity, environmental friendliness, and potentially low costs.[1–3] However, the intrinsic low electronic and Li^+ ion conductivities restrict its extensive applications. Methods to improve the low conductivity, such as size minimization and intimate carbon coating,[4,5] have had only partial success, but these methods do not alter the intrinsic nature of low electronic conductivity. Furthermore, high processing costs associated with the manufacturing of carbon-coated $LiFePO_4$ nanoparticles make it less competitive than other materials.

Doping is the most direct method to modify the intrinsically low electronic conductivity.[6,7] Li-site doping by a group-II element can in principle improve the electronic conductivity. However, the Li^+ ion conductivity is then reduced because dopants at Li sites block the one-dimensional Li migration pathway. Fe-site doping is an alternative option to avoid blocking the migration pathway.[8] On the other hand, trivalent, tetravalent, or pentavalent doping at Fe sites is not energetically favorable as the energy required for such substitution is too high.[9] The substitution of Fe by divalent dopants like Mg, Mn, Co, or Ca is energetically favorable, but such doping does not introduce excess carriers and thus does not improve the electronic conductivity. Therefore, doping is not a practical method to improve the intrinsic electronic conductivity of $LiFePO_4$.

Electronic transport in olivine $LiFePO_4$ is mostly dominated by polaron hopping, i.e., the carriers are accompanied by a self-induced local lattice distortion that may cause self-trapping.[10–12] Therefore, we expect the electronic transport in $LiFePO_4$ to be susceptible to changes in the lattice structure.

Strain engineering is one method to change the lattice distortion around polarons. It is known that the electronic and structural properties of a number of 3*d* transition metal oxides are unusually sensitive to mechanical strain.[13–15] For instance, a colossal change of the *electronic conductivity* by several orders of magnitude has been observed in ferromagnetic $La_{0.7}Sr_{0.3}CoO_3$ films due to a strain-induced static Jahn-Teller-type deformation of the CoO_6 units.[16] Additionally, an eight-orders-of-magnitude increase in *ionic conductivity* has been reported in yttria stabilized zirconia (YSZ)/$SrTiO_3$ heterostructures due to the extreme oxygen sublattice disorder at the YSZ/$SrTiO_3$ interface that is caused by 7% lattice-mismatch strain.[17,18]

In this letter, we explore the influence of biaxial strain on the electronic and Li^+ ion conductivities of $LiFePO_4$ by performing first-principles calculations. We find that 4% BTS leads to 15 times increase in electronic conductivity and 50 times increase in Li^+ ion conductivity at 300 K, respectively. We find that the BTS softens lattice distortions around a polaron quite remarkably, resulting in a reduction of the polaron binding energy and consequently a decrease of the activation barrier, which improves the electronic conductivity. Simultaneously, in accord with recent observations in other system,[19] the excess space that accompanies BTS allows Li^+ ions to migrate more easily, resulting in enhanced Li^+ ion conductivity.

The calculations were performed using density functional theory (DFT) in the generalized gradient approximation (GGA) and the projector-augmented wave method with a plane-wave basis as implemented in the Vienna *ab initio* simulation package (VASP) code.[20] We used a kinetic energy cut-off of 500 eV, $1 \times 2 \times 2$ supercell to reduce interactions between either lithium vacancies or polaron images and a minimal Γ-centered $1 \times 1 \times 1$ and $2 \times 2 \times 2$ *k*-point grid for polaron and lithium diffusion calculations, respectively. We applied a Hubbard U correction with U = 4.3 eV to improve the description of the Fe-3d states. A U_{eff} (U-J) value of 4.3 eV was chosen based on the average values for Fe^{2+} (U_{eff} = 3.7 eV in $LiFePO_4$) and Fe^{3+} (U_{eff} = 4.9 eV for $FePO_4$) calculated by Zhou *et al.*[21]

In order to generate a hole polaron into $LiFePO_4$, an electron is removed from one of the Fe ions at the $LiFePO_4$ supercell and then atomic relaxation is carried out.[22,23] Polaron hopping occurs only in the yz plane as depicted in Fig. 1(a) because the Fe interlayer distance along the x axis is too large for hopping. Let q_A represent the relaxed ion coordinates

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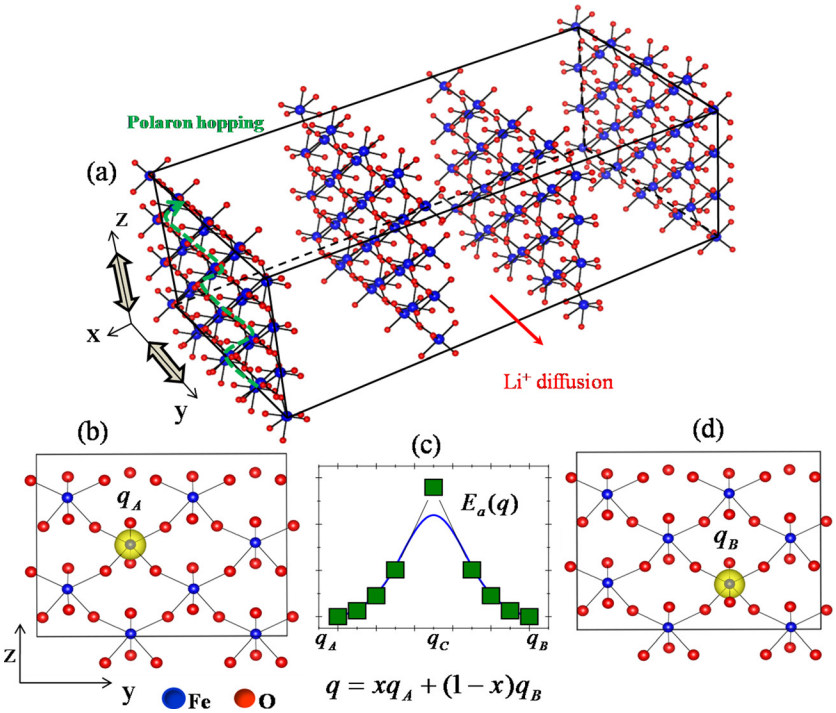

FIG. 1. (a) Schematic showing biaxial strain in the yz plane of $LiFePO_4$. (b) Equilibrium configuration with polaron represented as q_A. (c) Schematic of the activation energy along the polaron migration path linearly interpolated between two fully relaxed equilibrium configurations. (d) Equilibrium configuration with polaron represented as q_B.

when the polaron is localized at an Fe site A, which is indicated by the yellow circle in Fig. 1(b). q_B are the coordinates of an adjacent equivalent position (Fig. 1(d)). Since the transfer of a hole polaron occurs by hopping between two fully relaxed equilibrium configurations, the migration path of the polaron can be linearly interpolated between q_A and q_B as $q = (1-x)q_A + xq_B$, where $0 < x < 1$. On the migration path from q_A to q_B, a configuration q_C exists where the total energy reaches a maximum value defining a transition state. The difference between the total energy at the transition state at q_C and the initial state at q_A defines the activation energy as shown in Fig. 1(c).

In order to directly alter the polaron hopping distance, we consider a biaxial strain in the yz plane. Such a biaxial strain is imposed by altering the simulation cell in the y and z directions and relaxing the cell dimension in the x direction.

The polaronic conductivity (σ) in $LiFePO_4$ is described by the general formula proposed by Mott[10,11]

$$\sigma = c_n(c_n - 1)\frac{e^2\nu_e}{k_B T}\frac{\exp(-2\alpha R)}{R}\exp\left(-\frac{E_a}{k_B T}\right), \qquad (1)$$

where α is the rate of the wave function decay for Fe ion ($\alpha = 1.5\,\text{Å}^{-1}$) and R is the distance between two neighboring Fe ions in $LiFePO_4$ ($R = 3.87$ Å) corresponding to the hopping distance. ν_e is the attempt electronic frequency ($\nu_e = 10^{15}$ Hz), and c_n is the ratio of the concentration of Fe^{3+} ions over the total amount of Fe ions in the matrix. This ratio depends on the Li vacancy concentration.[24] E_a is the activation barrier of the polaron. Naively, biaxial compressive strain in the yz plane is likely to enhance the electronic conductivity because it results in a shorter hopping distance R. A 4% biaxial compressive strain in the yz plane contracts the hopping distance by 0.15 Å (ΔR) compared to that in the unstrained structure. However, such a small change leads to at most a 1.6 fold increase in polaron conductivity. Instead of the hopping distance R, we find that the activation barrier E_a is highly sensitive to biaxial strain as shown in Fig. 2(a). The 4% BTS reduces the activation barrier by 0.07 eV relative to the unstrained case and by more than 0.12 eV relative to the 4% compressively strained case. We estimate the ratio of the conductivity in the strained phase to that in the unstrained (pure) phase, as

$$\frac{\sigma_{strained}}{\sigma_{pure}} \sim \exp\left(-\frac{\Delta E_a}{k_B T}\right). \qquad (2)$$

where ΔE_a is the activation barrier difference between the strained and the unstrained phase. The 15-times increase in polaron conductivity at 4% BTS is evaluated at 300 K as shown in Fig. 2(b). Even 2% BTS gives an increase by a factor of 4.

We now investigate why the activation barrier E_a is highly susceptible to strain in $LiFePO_4$. The electronic structure of the states involved in a polaron transfer process is illustrated for 4% compressive and 4% tensile strained cases in Fig. 3(a). In the equilibrium configuration q_1, the polaron is formed at one particular Fe site and Ψ_1 represents the polaron 1 state depicted in thick solid line (olive color), while in configuration q_2, the polaron has moved to an adjacent site and Ψ_2 represents the polaron 2 state. The solid round symbols represent the polaron activation barrier calculated along the migration path. According to the linear approximation of the electron-phonon interaction, the activation energy E_a is equal to half of the polaron binding energy E_b.[25] If, however, there is an interaction between neighboring polaron states, the degeneracy is lifted and the activation energy is lowered by an interaction energy t. Thus, the real E_a is related to $E_b/2$-t as depicted in Fig. 3(a). The polaron binding

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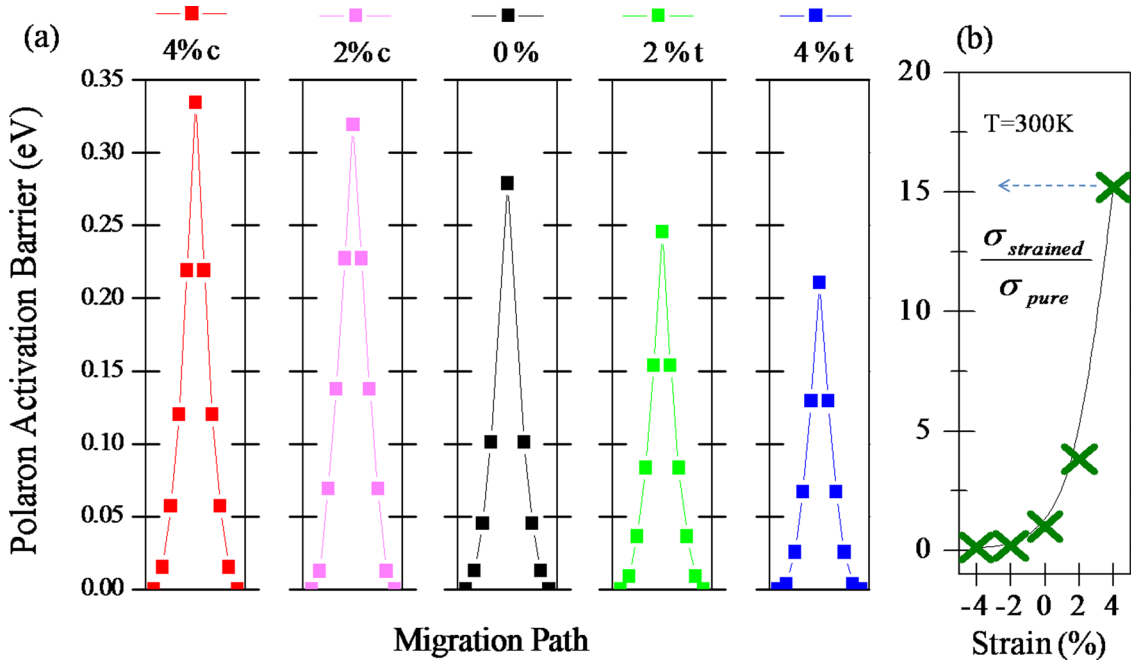

FIG. 2. (a) The variation of polaron activation barrier of $LiFePO_4$ as a function of strain. (b) Expected ratio of the polaron conductivity in the strained phase to that in the unstrained phase at 300 K.

energy E_b (Fig. 3(b)) is evaluated from the difference between the ground-state energy of a free polaron E_{free} and that of a bound polaron E_p for each strained $LiFePO_4$, $E_b = E_{free} - E_p$.

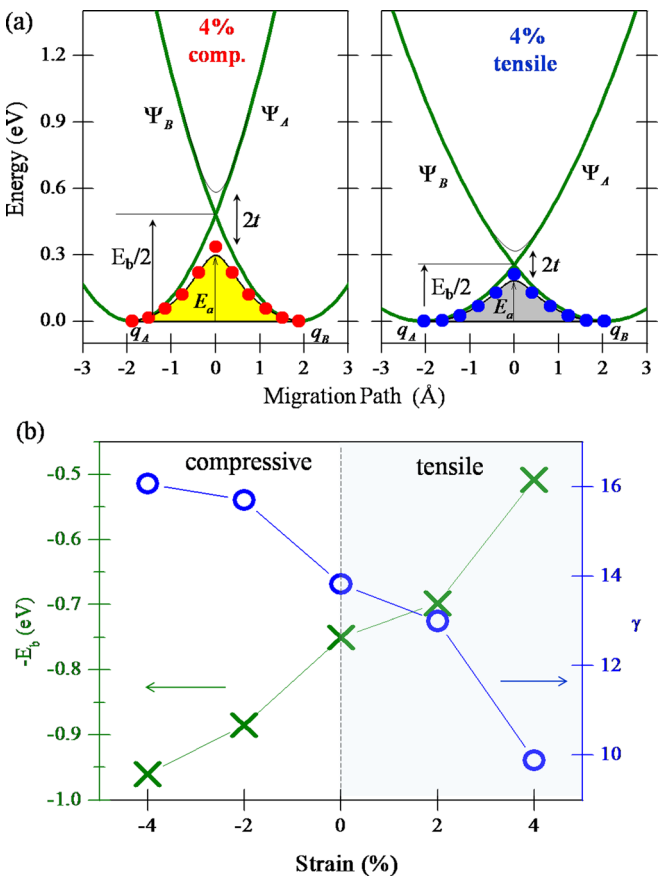

FIG. 3. (a) The polaron energy surface and activation barrier along the polaron migration path. The symbols are defined in the text. (b) The variation of polaron binding energy and electron-phonon constant as a function of strain.

Polaron transport is known to be related to a certain phonon mode with specific phonon energy.[26] For $LiFePO_4$, the two Fe sites involved in the polaron transfer share bridging oxygen atom; the phonon mode that corresponds to the transfer exhibits an asymmetric displacement of the bridging atoms.[27,28] This is the mode that is captured in a linearized approximation of the polaron transfer coordinate. In order to calculate the vibrational frequency of asymmetric Fe-O-Fe mode (E_{ph}), the frozen phonon method is used for each strained $1 \times 2 \times 2$ supercell of $LiFePO_4$ (see S1 in the supplementary information[29]) and the electron-phonon coupling constant, γ, is calculated using the relation $\gamma = E_b/E_{ph}$ (Refs. 25 and 30–32). The values of γ decrease from 16 (for 4% compressive strain) to 10 (for 4% tensile strain) as shown in Fig. 3(b), which are in the range of polaronic transport.[25,32] Therefore, the electron-phonon coupling gets weaker as the biaxial tensile strain increases, resulting in an increase in electronic conductivity due to the reduction of the polaron binding energy E_b (and activation barrier E_a).

We also explored how biaxial strain affects the Li^+ ion conductivity in $LiFePO_4$. We find the 4% BTS reduces the migration barrier by about 0.1 eV (see Fig. 4(a)), which leads to a 50-fold increase in Li^+ ion conductivity at 300 K as indicated in Fig. 4(b). The increase of volume in the strained phase (Fig. 4(c)) provides a possible explanation for migration-barrier decrease, as recently suggested by Han and Yildiz.[19]

Given the fact that all kinds of epitaxial structures have been reported for transition-metal oxides, we expect a [100] oriented $LiFePO_4$ thin film can be epitaxially grown on suitable substrates. Interface chemistry may help or hinder, but a number of materials with cubic perovskite structure appear as good candidates as substrates to achieve the proposed strain in epitaxial films. For example, almost 4% biaxial tensile strain can in principle be achieved using $SrTbO_3$ as a substrate. Alternatively, the [100] oriented surface can be

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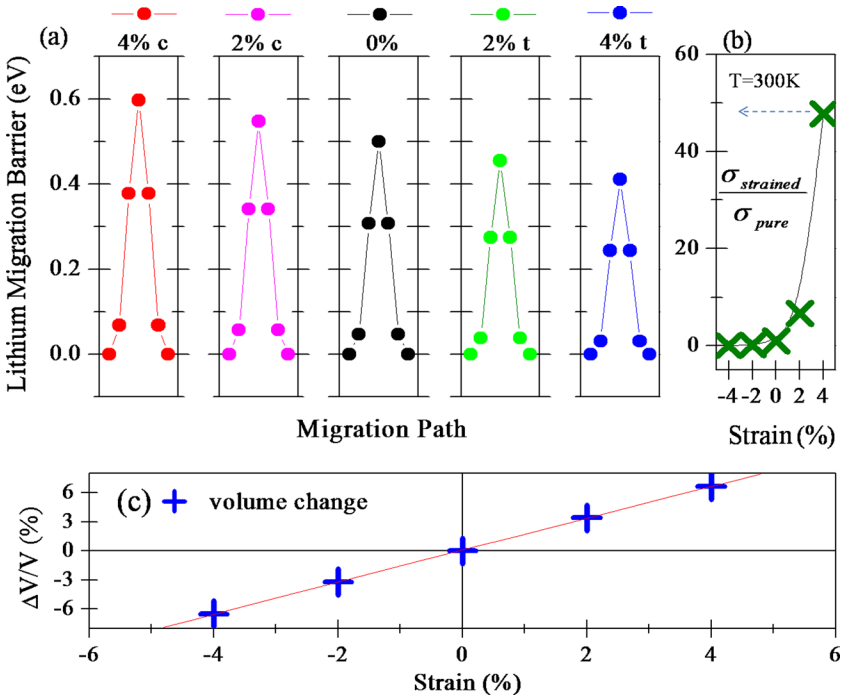

FIG. 4. (a) The variation of Li^+ ion migration barrier as a function of strain (b) Expected ratio of the Li^+ ion conductivity in the strained phase to that in the unstrained phase at 300 K. (c) The variation of the volume ratio in the strained phase to that in the unstrained phase as a function of strain.

obtained by cutting the $LiFePO_4$ single crystal into slices along (100) plane and then BTS can be generated by applying pressure along the x axis.

In summary, we showed 4% BTS leads to 15 times increase in electronic conductivity and 50 times increase in Li^+ ion conductivity at 300 K, respectively. We find the electron-phonon coupling gets weaker as the biaxial tensile strain increases, resulting in a reduction of polaron binding energy and activation barrier. We also find the volume in the strained phase increases as the biaxial tensile strain increases, results in the reduction in Li^+ ion migration barrier because more vacant space due to volume expansion allows Li^+ ions to migrate more easily. Consequently, we expect that this strain-engineering can be a promising approach to optimize lithium-based energy storage for electric vehicles requiring high power.

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