First-principles Calculations on Electronic Properties of LaNiO$_3$ in Solid Oxide Fuel Cell Cathodes

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Abstract: First-principles calculations based on the density functional theory are used to study the electronic structure of LaNiO$_3$ perovskite for application of cathode material in solid oxide fuel cell. Our results show that bulk LaNiO$_3$ exhibits metallic behavior. For 1x1x1 LaNiO$_3$ unit cell, increasing in-plane strain leads to the increase in the density of states (DOS) at the Fermi level. On the other hand, the DOS at the Fermi level for 2x2x2 LaNiO$_3$ supercell first increases with the strain up to 3% and then decreases for larger values of the strain. The difference between the electronic structure of the 2x2x2 supercell and that of the 1x1x1 unit cell is attributed to the rotations of NiO$_6$ octahedra.

Keywords: Solid oxide fuel cell, density functional theory, LaNiO$_3$ perovskite, electronic structures, strain.

1. Introduction

The perovskite LaNiO$_3$ is frequently used as cathode material for solid oxide fuel cells due to its high temperature stability, acceptable thermal expansion, and the ability to enhance oxygen reduction reaction [1-4]. At cathode-electrolyte interface, the induced strain caused by lattice mismatch between LaNiO$_3$ and electrolyte materials is expected to give rise to the reconstructions of the electronic structures of LaNiO$_3$. Such electronic reconstructions could be important as they are tightly linked with the formation of oxygen vacancy and the conduction of oxygen ions, which greatly affect the operation of the fuel cell. On the other hand, previous publications have reported that the NiO$_6$ octahedra rotated in bulk LaNiO$_3$, alternating the electronic structure [5, 6]. As a result of the induced strain at the cathode-electrolyte interface, such octahedral rotations can be enhanced or suppressed. In this paper, we investigate the electronic structure and NiO$_6$ octahedral rotations of LaNiO$_3$ under epitaxial strain using first-principles calculations.

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2. Computational details

All calculations are performed based on the density functional theory [7] using plane-wave basis sets [8] as implemented in the Quantum Espresso package [9]. The exchange-correlation interaction is treated using local density approximation (LDA) with the Perdew-Zunger parametrization [10], and the electron-ion interaction is described by Vandebilt ultrasoft pseudopotentials [11].

The computational models of 1x1x1 unit cell and 2x2x2 supercell of LaNiO₃ are shown in Fig. 1. Periodic boundary conditions are imposed in all dimensions. The kinetic energy cutoff for wavefunctions is chosen at 680 eV and sufficient k-point sampling is employed in the Brillouin zone. Structural optimizations are performed until all remaining forces acting on each atom are less than 0.03 eV/Å.

3. Results and discussion

The optimized lattice parameters of the 1x1x1 LaNiO₃ unit cell are found to be \( l_{\text{cal}} = l_x = l_y = l_z = 3.749 \) Å, which are 2.3% smaller than the published experimental data [3]. The underestimation of the lattice parameters is typical of LDA calculations [15, 16].

Figure 2 shows the out-of-plane strain \( u_z = l_z/l_{\text{cal}} - 1 \) as a function of the in-plane strain \( u_{xy} = l_x/l_{\text{cal}} - 1 \) for the 1x1x1 LaNiO₃ unit cell, where \( l_x \) and \( l_z \) are the in-plane and out-of-plane lattice parameters, respectively.
respectively, and \( l_{\text{ref}} \) is the non-strained equilibrium one. It can be seen that \( u_z \) declines (almost linearly) by 0.6% for each 1.0% increase in \( u_{xy} \). The computed out-of-plane strain of LaNiO\(_3\) on SrTiO\(_3\) substrate is found to be 1.0% as compared to the experimental value of 0.7% [5].

![Figure 2](image1.png)  
**Fig. 2.** Calculated out-of-plane strain \( u_z \) vs in-plane strain \( u_{xy} \): x: experimental value for a LaNiO\(_3\) film grown on SrTiO\(_3\) substrate. Vertical arrows designate in-plane strains of commercially available substrates, from left to right: LaAlO\(_3\), SrTiO\(_3\), and KTaO\(_3\).

![Figure 3](image2.png)  
**Fig. 3.** Total DOS of 1x1x1 LaNiO\(_3\) unit cell for various values of in-plane strain \( u_{xy} \). The Fermi level is chosen at 0 eV.

Figure 3 presents the total DOS of 1x1x1 LaNiO\(_3\) unit cell for various in-plane strains. As one can see, LaNiO\(_3\) keeps the metallic behavior, and the total DOS near the Fermi level is enhanced with the strain. Specifically, the DOS is increased by 2.7 times as \( u_{xy} \) increases from -2% to 5%. Previous publications have shown that states near the Fermi level of bulk LaNiO\(_3\) are formed by the hybridization between Ni 3\(d\) and O 2\(p\) orbitals [2, 17-19]. Thus, we plot in Fig. 4 the projected DOS of strained LaNiO\(_3\) onto Ni \(t_{2g}\) and \(e_g\) orbitals. For the non-strained case, \(t_{2g}\)-derived states are completely filled, and the \(e_g\)-derived states are occupied by one electron. For \(u_{xy} > 0\%), \(t_{2g}\)-derived states become partially occupied as a result of the changes in Ni-O bond distances. In the vicinity of the Fermi level, the density of \(t_{2g}\)-derived states increases with increasing \(u_{xy}\), whereas that of \(e_g\)-derived states first increases and then decreases as \(u_{xy}\) is larger than 3%. As the changes in the density of \(t_{2g}\)-derived states are substantial compared to those of \(e_g\)-derived states, the total DOS at the Fermi level increases with the in-plane strain.

For the 2x2x2 LaNiO\(_3\) supercell, the electronic structure is expected to deviate from that of the 1x1x1 unit cell. The rotations of NiO\(_6\) octahedra inside the supercell change the Ni-O-Ni bonding angles (see Fig. 1(b)) and thus alter the hybridization between Ni 3\(d\) and O 2\(p\) orbitals. Figure 5 indicates the dependence of Ni-O-Ni angles along the \(z\) direction (\(\alpha_z\)) and in the \(xy\) plane (\(\alpha_{xy}\)) on the in-plane strain. It is noted that the in-plane strain in the case of 2x2x2 supercell is the same as that in 1x1x1 unit cell. By increasing \(u_{xy}\), \(\alpha_z\) (\(\alpha_{xy}\)) decreases (increases), implying the reduction (enhancement) of the \(p-d\) hybridization. Thus, a competition in the contributions of \(p-d\) hybridized states along the \(z\) direction and in the \(xy\) plane to the electronic structure is expected. We plot in Fig. 6 total DOS of the 2x2x2 LaNiO\(_3\) supercell with respect to the in-plane strain. In contrast to the 1x1x1 unit cell case, where the DOS at the Fermi level increases with increasing \(u_{xy}\) (see Fig. 3), the DOS at the Fermi level of the 2x2x2 supercell first increases with \(u_{xy}\) up to 3% and then decreases. This behavior can be attributed to the rotations of NiO\(_6\) octahedra, which alters the electronic structure in the vicinity of the Fermi level.
4. Conclusions

First-principles calculations are employed to investigate the electronic structure of bulk LaNiO$_3$ under epitaxial strain. By applying strain, the Ni $t_{2g}$-derived states of the 1x1x1 unit cell become partially occupied. In the vicinity of the Fermi level, the density of the $t_{2g}$-derived states increases with $u_{xy}$ while that of the $e_g$-derived states increases for $u_{xy} < 3\%$ and then decreases for larger $u_{xy}$. In addition, the variation of density of the $t_{2g}$-derived states is much larger than that of the $e_g$-derived states, resulting in the increase of the total DOS at the Fermi level with respect to the in-plane strain. For the 2x2x2 LaNiO$_3$ supercell, rotations of the NiO$_6$ octahedra are observed, altering the $p$-$d$ hybridization. The total DOS at the Fermi level first increases for values of the in-plane strain lower than 3\% and then decreases for larger strain. Our results are the first step towards further calculations regarding oxygen-defected LaNiO$_3$ systems and migration paths of oxygen ions.
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References