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Anisotropic oxygen diffusion in tetragonal La$_2$NiO$_{4+\delta}$: molecular dynamics calculations

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Molecular dynamics simulations, used in conjunction with a set of Born model potentials, have been employed to study oxygen transport in tetragonal La$_2$NiO$_{4+\delta}$. We predict an interstitialcy mechanism with an activation energy of migration of 0.51 eV in the temperature range 800–1100 K. The simulations are consistent with the most recent experiments. The prevalence of oxygen diffusion in the $a$–$b$ plane accounts for the anisotropy observed in measurements of diffusivity in tetragonal La$_2$NiO$_{4+\delta}$.

Introduction

A number of oxides are presently being investigated for solid-oxide fuel cell (SOFC) electrode applications. These materials must have improved performance at lower temperatures and resistance to degradation during operation. In this regard, perovskite-related materials such as the Ruddlesden-Popper (RP) series of layered oxides (formula $A_{n+1}B_nO_{3n+1}$) are important candidate materials for the next generation of SOFCs because of their electrochemical, electrical and catalytic properties in synergy with their thermal and mechanical stability. In particular, La$_2$NiO$_4$ and related materials with the K$_2$NiF$_4$ structure (A$_3$BO$_4$ or the first members of the RP series) are considered for oxygen sensors, oxygen separation membranes and as cathodes for intermediate temperature SOFCs (ITSOFCs).$^{1–12}$ These materials exhibit an oxygen hyperstoichiometry that significantly influences the oxygen transport (see for example ref. 3 and references therein). Interestingly, previous experimental studies report a wide range of determined activation energies, from 0.19 eV to 0.90 eV and the mechanism of diffusion is not well defined.$^{2,5,13}$ This range includes both studies of total diffusion and $a$–$b$ plane and $c$ direction partial diffusions measured for single crystals and/or thin films.

The knowledge of the crystal structure, stoichiometry and the effect of different A and B atoms are important in the study of diffusion mechanisms.$^{10,14}$ Oxides possessing the K$_2$NiF$_4$ structure have been extensively investigated since the observation of high-temperature superconductivity in La$_{2–x}$Ba$_x$CuO$_4$ by Bednorz and Müller.$^{15}$ La$_2$NiO$_4$ exhibits various structural polymorphs that are dependent on temperature and subtle changes in stoichiometry; the effect of the cooperative tilting of the NiO$_6$ octahedra has also been previously studied.$^{5,11–16,18–19}$ Skinner$^{18}$ determined with the use of in situ high temperature neutron powder diffraction that La$_2$NiO$_4$ exhibits the tetragonal symmetry (space group $I4/mmm$) above 423 K and up to at least 1073 K. At room temperature La$_2$NiO$_4$ exhibits the orthorhombic symmetry (space group $Cmca$).$^{20}$

Atomistic simulation techniques provide detailed information concerning the diffusion mechanisms of materials.$^{21–25}$ The aim of the present study is to predict the oxygen diffusion mechanism and activation energy of migration in tetragonal La$_2$NiO$_{4+\delta}$ using molecular dynamics (MD). The results are discussed in view of recent experimental evidence.

Methods

MD simulations are the iterative solution of Newton’s equations of motion for an ensemble of particles that interact through potential energy functions. The classical Born-like description of the ionic crystal lattice is used.$^{26}$ The interactions between ions $i$ and $j$ are described by a long-range Coulombic (summed using Ewald’s method$^{27}$) and a short-range parameterized Buckingham pair potential.$^{28}$ The Buckingham pair potential is summed to the cut-off value of 10.5 Å, beyond which the influence of the potential is considered negligible. The lattice energy is given by,

$$E_L = \sum_{j>i} \left[ \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}} + A_{ij} \exp \left( -\frac{r_{ij}}{\rho_j} \right) - \frac{C_{ij}}{r_{ij}^{12}} \right] \tag{1}$$

where $r_{ij}$ is the interionic separation, $q_i$ is the charge of ion $i$, $A_{ij}$, $\rho_j$ and $C_{ij}$ are the short-range parameters of the Buckingham pair potential (see Table 1) and $\varepsilon_0$ is the permittivity of free space. The short-range parameters used here were reported in previous studies,$^{19,29}$ and their efficacy has been established for La$_2$NiO$_4$ (see ref. 3 and 7) and other oxide materials.$^{30–32}$

The present simulations are based on the high temperature tetragonal structure of La$_2$NiO$_{4+\delta}$ determined by Skinner.$^{11}$ The periodic crystal lattice is constructed from a supercell of $10 \times 10 \times 4$ unit cells (containing 5600 ions) tessellated throughout space through the use of periodic boundary conditions as defined by the crystallographic lattice vectors. Thermogravimetric analysis of La$_2$NiO$_{4+\delta}$ (ref. 33–35) has revealed a number of oxygen hyperstoichiometries that were dependent upon the thermal

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$A_{ij}/eV$</th>
<th>$\rho_j/Å$</th>
<th>$C_{ij}/eV Å^6$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^{2-}$–O$^{2-}$</td>
<td>9547.96</td>
<td>0.2072</td>
<td>32.00</td>
<td>29</td>
</tr>
<tr>
<td>La$^{3+}$–O$^{2-}$</td>
<td>2119.79</td>
<td>0.3459</td>
<td>23.25</td>
<td>3</td>
</tr>
<tr>
<td>Ni$^{2+}$–O$^{2-}$</td>
<td>905.40</td>
<td>0.3145</td>
<td>0.00</td>
<td>3</td>
</tr>
</tbody>
</table>
The incorporation of oxygen interstitials and their migration in $La_2NiO_4+$ was studied previously in detail using static atomistic simulation techniques. Interestingly, Read et al. predicted that the oxidation reaction in $La_2NiO_4$ is exothermic. Frayret et al. using density functional theory in conjunction with Bader’s atoms in molecules theory, predicted that the interstitial oxygen in $La_2NiO_4+$ is doubly negatively charged ($O^{2-}$). In the present work we consider only $O^{2-}$ ions that we initially distribute randomly.

Ionic transport was determined by monitoring the mean square displacement (MSD) of ions, as a function of time, for a range of defect temperatures. To ensure adequate statistical sampling extensive simulation times of 300 ps were used. The MSD of an ion $i$ at a position $\mathbf{r}_i(t)$ at time $t$ with respect to its initial position $\mathbf{r}_i(0)$ is defined by

$$\langle \mathbf{r}_i^2(t) \rangle = \frac{1}{N} \sum_{j=1}^{N} [\mathbf{r}_j(t) - \mathbf{r}_i(0)]^2$$

(2)

where $N$ is the total number of ions in the system. During the simulations lanthanum and nickel cations oscillate around their equilibrium positions. Conversely, especially at higher temperatures, oxygen ions demonstrate an increasing MSD with time. Therefore, oxygen self-diffusion is far more significant compared to cation self-diffusion on the time scales considered. Although there is no available experimental data on cation migration of $La_2NiO_4+$, previous studies in perovskite-type oxides have determined that cation diffusion coefficients are orders of magnitude lower than oxygen diffusion coefficients.

The oxygen diffusion coefficient, $D$, is calculated from the slopes of MSD for a range of temperatures (here 800–1100 K) using

$$\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle = 6Dt + B$$

(3)

where $[\mathbf{r}_i(t) - \mathbf{r}_i(0)]$ is the displacement of an oxygen ion from its initial position and $B$ is an atomic displacement parameter attributed to thermal vibrations.

Fig. 1 is an Arrhenius plot comparing the predicted diffusivities for $\delta = 0.055$ and 0.12, with previous experimental results. The latter $\delta$ value is closer to the experimentally determined values at high temperatures. The predicted values are in excellent agreement with the experimental data. Fig. 1 predicts an activation energy of migration is 0.51 eV, whereas previous experimental activation energies are: 0.85 eV for the dense ceramic and 0.88 eV for the single crystal. Notably, however, recent experimental work of Sayers et al. predicted that an activation energy for oxygen diffusion of 0.54 eV (see Table 2). The diffusivities of Sayers et al. are in the same order of magnitude as the predicted and experimental diffusivities of Fig. 1. Interestingly, in tetragonal $La_{1.85}Sr_{0.15}CuO_4$ Savvin et al. predicted, using MD, oxygen diffusivities that were higher by several orders of magnitude compared to the tracer study of Routbort et al. on dense polycrystalline samples. Nevertheless, for $La_{1.85}Sr_{0.15}CuO_4$ their predicted activation energy of diffusion, 0.86 eV, is in excellent agreement with the determined value of 0.84 eV.

### Table 2: Activation energies of oxygen self-diffusion in $La_2NiO_4+$

<table>
<thead>
<tr>
<th>Methodology</th>
<th>$E}$/eV</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>0.19</td>
<td>Epitaxial thin film</td>
<td>13</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.54</td>
<td>Polycrystal, TOF-SIMS</td>
<td>33</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.88</td>
<td>Single crystal, $a-b$ plane</td>
<td>5</td>
</tr>
<tr>
<td>Static atomistic simulation</td>
<td>0.55a</td>
<td>Vacancy mechanism</td>
<td>7</td>
</tr>
<tr>
<td>Molecular dynamics</td>
<td>0.51</td>
<td>Interstitial mechanism</td>
<td>Present study</td>
</tr>
</tbody>
</table>

$a$ Activation energy of migration.
In the recent work by Cleave et al.,7 who considered stoichiometric tetragonal La2NiO4, a number of vacancy migration pathways along the a–b plane and the c-axis were considered as well as an O2/C0 interstitial migration mechanism. These predictions indicate that the most energetically favorable mechanism for oxygen migration is the vacancy mechanism in the a–b plane.7 In this mechanism the oxygen vacancy is transported between equatorial sites and the overall migration activation energy is 0.55 eV.7 This mechanism is supported by previous simulations in the related tetragonal La2CuO4+δ.49,51 Using static atomic simulation techniques Cleave et al.7 considered the interstitial migration mechanism of the O2/C0 ion to be 0.86 eV. This value is in excellent agreement with the activation energy of migration for O2 predicted by Minervini et al.3 using the same atomistic simulation technique in orthorhombic La2NiO4+δ. Frayret et al.6 predicted, using DFT, a migration energy barrier via the oxygen interstitial mechanism of 1.2 eV. However, in addition to the small cell used in their study Frayret et al.6 only considered a direct path between the two interstitial sites, whereas in Fig. 2 we note a significant deviation from the most direct route between the lattice and interstitial site.

At this juncture it is also important to consider that vacancy mediated diffusion necessitates the formation of oxygen vacancies. Therefore, as oxygen interstitials will dominate in La2NiO4+δ over the temperature range considered, these additional oxygen ions will be accommodated in interstitial sites in the lattice (see ref. 3 and references therein). This supersaturation of oxygen interstitials greatly reduces the concentration of oxygen vacancies, through the oxygen Frenkel reaction.

In the recent work by Cleave et al.,7 who considered stoichiometric tetragonal La2NiO4, a number of vacancy migration pathways along the a–b plane and the c-axis were considered as well as an O2– interstitial migration mechanism. These predictions indicate that the most energetically favorable mechanism for oxygen migration is the vacancy mechanism in the a–b plane.7 In this mechanism the oxygen vacancy is transported between equatorial sites and the overall migration activation energy is 0.55 eV.7 This mechanism is supported by previous simulations in the related tetragonal La2CuO4+δ.49,51 Using static atomic simulation techniques Cleave et al.7 considered the interstitial migration mechanism of the O2– ion to be 0.86 eV. This value is in excellent agreement with the activation energy of migration for O2– predicted by Minervini et al.3 using the same atomistic simulation technique in orthorhombic La2NiO4+δ. Frayret et al.6 predicted, using DFT, a migration energy barrier via the oxygen interstitial mechanism of 1.2 eV. However, in addition to the
equilibrium, leading to the minimisation of diffusion by vacancy mechanisms. We also note that here, when MD simulations were carried out on perfect stoichiometric La$_2$NiO$_4$ (i.e. without the prior presence of either oxygen vacancies or interstitials) the oxygen diffusivities were not significant for the temperature range and time scales considered.

For a range of oxygen hyperstoichiometries, all the present predicted oxygen density profiles support an interstitialcy mechanism of diffusion in the $a$-$b$ plane (see Fig. 2). In particular, the oxygen interstitial displaces an apical oxygen ion from the NiO$_6$ octahedron, which in turn progresses to an adjacent oxygen interstitial site. Consistent with Skinner, we observe that the equatorial site has a strongly anisotropic thermal ellipsoid. Additionally, simulations suggest a highly anisotropic motion of the La site out of the $a$-$b$ plane.

We show an example of the time resolved diffusion process in Fig. 3. Here, representative snapshots of a single simulation show ions actively involved in a single diffusion process. We note in the initial configuration (Fig. 3a) the significant tilting of the neighbouring NiO$_6$ octahedra away from the single interstitial oxygen ion. The apical ion from one of these octahedra is able to move upwards towards an unoccupied interstitial site with the corresponding relaxation of the existing interstitial ion towards the formerly occupied site. The intermediate state is shown in Fig. 3b and exists only briefly before the original interstitial ion reforms the NiO$_6$ octahedron and the apical ion takes up residence in an adjacent interstitial site. The final configuration (Fig. 3c) is equivalent to the initial configuration aside from the translation of a single interstitial ion in the $a$-$b$ plane.

The intermediate state (Fig. 3b) where both ions are in interstitial sites, has a very brief residency time (~1 ps), however it is still possible to observe subsequent distortion of the equatorial oxygen ions towards the interstitial layer. This is the origin of the strongly anisotropic thermal ellipsoid reported from the diffraction measurements of Skinner. It is also possible that these transient states may provide a conduction pathway for oxygen ions out of the equatorial plane. We did not observe such motion in La$_2$NiO$_{4+t}$, although other compounds with less significant anisotropy in their oxygen diffusivity may provide such a route.

Experimental evidence for oxygen interstitial transport in the $a$-$b$ plane of related tetragonal materials is scarce. Notably, however, Yashima et al. recently observed an interstitial mechanism in tetragonal (Pr$_{0.9}$La$_{0.1}$)$_2$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_4$-$t$. More particularly, Yashima et al. employed neutron scattering experiments and analysis based on the maximum entropy method to demonstrate that oxygen atoms move via an interstitial process along a two-dimensional network in the $a$-$b$ plane. Diffusion of O$^2-$ ions across the $a$-$b$ plane is also consistent to the MD studies of Savvin et al. in tetragonal La$_2$-xSr$_x$CuO$_{4-t}$.

Conclusions

In summary, MD calculations confirm the highly anisotropic nature of oxygen diffusion in tetragonal La$_2$NiO$_{4+t}$. We predict an $O^2-$ interstitialcy mechanism in the $a$-$b$ plane with migration activation energy of 0.51 eV. The effect of oxygen hyperstoichiometry on the activation energy is not significant. Previous theoretical evidence supports the view that charge-transfer phenomena in La$_2$NiO$_{4+t}$ are negligible. Nevertheless, possible compensation mechanisms that could influence the oxygen transport are presently under investigation.

Acknowledgements

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