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A Molecular Dynamics Study of Anisotropic Oxygen Diffusion in $La_2NiO_{4+\delta}$

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1. Introduction

Perovskite-related materials such as the Ruddleston-Popper (RP) series of layered oxides (formula $A_{n+1}BnO_{3n+1}$) are important candidate materials for the next generation SOFC. In particular, La_2NiO_4 and related materials of the K_2NiF_4 structure (A_2BO_4 or the first members of the RP series) are considered for oxygen sensors, oxygen separation membranes and as cathodes for intermediate temperature SOFC. These materials exhibit an oxygen hyperstoichiometry that influences significantly the oxygen transport. Interestingly, in previous experimental work there is a wide range of determined activation energies, from 0.19 eV to 0.90 eV and the mechanism of diffusion is not well defined [1-3]. The aim of the present study is to predict the oxygen diffusion mechanism and activation energy of migration in tetragonal $La_2NiO_{4+\delta}$ using molecular dynamics (MD).

The interactions between ions *i* and *j* are described by a long-range Coulombic and a short-range parameterized Buckingham pair potential. The periodic crystal lattice is constructed from a supercell of 10 x 10 x 4 unit cells (containing 5600 ions). Up to 250000 time steps (each time step of the order of 1 fs) were used to investigate oxygen diffusion in the temperature range 800-1100 K. Both the NPT and the NVT ensembles were applied to predict the diffusion properties.

2. Mechanism of Oxygen Diffusion

MD calculations confirm the highly anisotropic nature of oxygen diffusion in tetragonal $La_2NiO_{4+\delta}$. We predict an O^{2-} interstitialcy mechanism in the *a-b* plane with migration activation energy of 0.51 eV [4]. The effect of oxygen hyperstoichiometry on the activation energy is not significant.

Experimental evidence for oxygen interstitial transport in the *a-b* plane of related tetragonal materials is rare. Yashima *et al.* [5] recently observed an interstitial mechanism in tetragonal $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$. More particularly, Yashima *et al.* [5] 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.* [6] in tetragonal $La_{2-x}Sr_xCuO_{4-\delta}$.

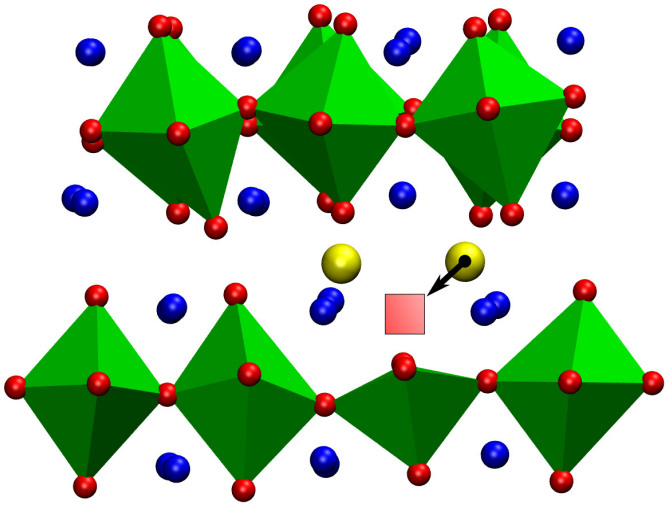

Fig. 1: The observed oxygen interstitialcy mechanism in La2NiO4+δ [4].

3. Conclusion

MD calculations confirm the highly anisotropic nature of oxygen diffusion in tetragonal La2NiO4+δ. We predict an O2- 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.

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