

Review

Self-Diffusion in Perovskite and Perovskite Related Oxides: Insights from Modelling

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Abstract: Perovskite and perovskite related oxides are important materials with applications ranging from solid oxide fuel cells, electronics, batteries and high temperature superconductors. The investigation of physical properties at the atomic scale such as self-diffusion is important to further improve and/or miniaturize electronic or energy related devices. In the present review we examine the oxygen self-diffusion and defect processes in perovskite and perovskite related oxides. This contribution is not meant to be an exhaustive review of the literature but rather aims to highlight the important mechanisms and ways to tune self-diffusion in this important class of energy materials.

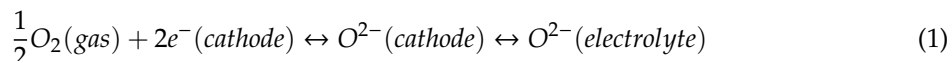
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1. Introduction

Diffusion is a fundamental process that impacts material and device properties in semiconductors, oxides and metals [1–30]. Perovskite (refer to Figure 1) and perovskite related oxides have been widely studied for applications including electronics, batteries, solid oxide fuel cells (SOFC) and superconductors [31–60]. As paradigms of the insights of the governing dynamics gained by the application of atomistic modelling, we consider here perovskite and perovskite related oxides employed in SOFC technology and batteries.

The importance of SOFCs is their potential for high efficiency energy conversion accompanied with reduced emission of greenhouse gases as compared to fossil fuel-based power generation [61,62]. For high operating temperatures (up to 1000 °C), SOFCs can operate with hydrogen and/or natural gas efficiently converting the chemical energy to electricity. SOFCs are applied in combined heat and power applications, but the high operating temperatures can result to materials issues and increased cost [63–65]. In particular, high temperatures lead to thermal cycling, performance degradation and the use of expensive materials in interconnects [65]. To alleviate these issues, the community aims to lower the operating temperatures of SOFCs to the intermediate temperature range (500–700 °C).

Regrettably, however, this reduction in temperature leads to the increase in the losses for reaction and transport kinetics in the active layers of the SOFC, and in particular the cathode and electrolyte. This in turn motivated the community to investigate new classes of materials that have high oxygen diffusivities at 500–700 °C. It should be stressed that oxygen diffusivities are significant because at the intermediate temperature range the oxygen reduction reaction in the cathode and the oxygen diffusion in the cathode and electrolyte have to be accelerated (to alleviate for the lower temperature). This can be represented by the following reaction:



This relation describes the reduction of oxygen on the cathode surface, the diffusion of oxygen in the cathode and finally the diffusion of oxygen on the electrolyte. It is acknowledged that in the traditional SOFC materials (for example $La_{1-x}Sr_xMnO_{3-\delta}$) the reduction of temperature will lead to electrical energy losses [66]. A way to overcome this problem is to use alternative materials such as the mixed ionic-electronic conductors (MIEC) [33,66,67], in which the oxygen reduction kinetics in MIEC electrodes is contributed by both the oxygen surface exchange and diffusion. Although oxygen diffusion needs also to be high at electrolytes there low, electronic conductivity is needed. Numerous studies in recent years have addressed oxygen diffusion in cathode and electrolyte materials [51,68–74].

The second example considered in the present review is battery materials. Demand for electrical energy storage is ever increasing particularly for mobile applications. As the requirement is to have high energy densities and capacities there is a lot of scientific and technological interest on solid state rechargeable Li-ion batteries [75]. In these devices, the solid electrolyte is a key component and this has been the driving force for numerous theoretical and experimental studies [75]. Increasing the ionic conductivity by replacing the solvent electrolytes with solid materials is a way to overcome the restrictions emerging in electrochemical applications. Additionally, the electrolyte has to be compatible with the electrode materials and be able to withstand the diffusion of ions during the battery life cycle [76].

Ionic diffusion can be influenced and even tuned by numerous parameters including the (i.e., crystal structure, doping and composition) and external parameters (i.e., elastic strain). Atomic scale modelling has the advantage that it can deconvolute the individual contributions of these parameters thus offering a way to gain insights on their impact in physical properties such as self-diffusion. This in turn can lead to progress in the selection of materials of technological importance and the rapid tuning of their properties, leading experimental work to the most promising systems [77,78].

In the present review article, we focus on ionic diffusion mechanisms and the related energetics of SOFC and battery materials. The main emphasis is to demonstrate how atomic scale modelling can provide insights of ionic diffusion in structurally complicated systems. The review is structured as follows. First, we briefly discuss diffusion mechanisms and the atomistic scale methodologies. Thereafter, cathode and electrolyte SOFC materials are considered with particular focus on the Ruddlesden–Popper series (for example La_2NiO_4) and double perovskites (for example $GdBaCo_2O_{5+\delta}$). Then the focus is on disordered oxides such as lithium lanthanum titanates ($La_{2/3-x}Li_{3x}TiO_3$) and the importance of methodological advances to gain insights on their complicated mechanisms of diffusion. The final part is concerned on the future directions to optimise the ionic diffusion including the promising ideas of grain boundary engineering.

2. Diffusion Mechanisms

Diffusion in materials is a fundamental and complicated phenomenon. The added complexity in oxide materials, as compared to metals, is the anion and cation sublattices. These sublattices can restrict the ionic diffusion to its own sublattice, however, the cation sublattice may have a significant impact upon the anion diffusion. In oxides oxygen self-diffusion is typically orders of magnitude faster than cation self-diffusion [79–82].

For net diffusion to occur in a crystalline material atoms have to migrate away from their equilibrium positions towards neighbouring equilibrium positions. For this process to occur point defects (interstitials and/or vacancies) are necessary [34]. For the materials considered in the present review there are mainly three mechanisms: the interstitial, the interstitialcy and the vacancy mechanisms. There are also mechanisms, which are based upon the point defects but also involve cooperative motion of the local polyhedral structures.

Considering first the vacancy mechanism of diffusion, in which an ion diffuses by migrating to a neighbouring vacancy [81,83]. The vacancy mechanism necessitates the presence of lattice vacancies, with their concentration in the lattice and migration energy barriers effectively controlling the transport kinetics. The vacancy mechanism is common for oxygen self-diffusion in a number of oxygen hypostoichiometric oxides that are of interest to SOFC (for example fluorite- and perovskite-related systems) [84].

In the interstitial mechanism, interstitial ions migrate from one interstitial site to a neighbouring interstitial site. Conversely, to the vacancy mechanism in the interstitial mechanism when a jump between interstitial sites is completed there is no net displacement of the other ions. Additionally, the interstitial mechanism does only require the interstitial ions and no other point defects. Finally, the interstitialcy mechanism is distinct from the interstitial mechanism, as the interstitial ion displaces another ion from its equilibrium lattice site. Following this the displaced ion moves to another interstitial site and so on.

In the vacancy mechanism, the migration enthalpies for the thermally activated vacancy hopping is the critical factor determining how low a temperature the electrolyte and cathode can effectively function at. According to transition state theory, the rate of vacancy hops, ν , is given by the Boltzmann relationship,

$$\nu = \nu_0 \exp\left(\frac{-E_M}{k_B T}\right), \quad (2)$$

where E_M is the migration barrier and ν_0 is a constant.

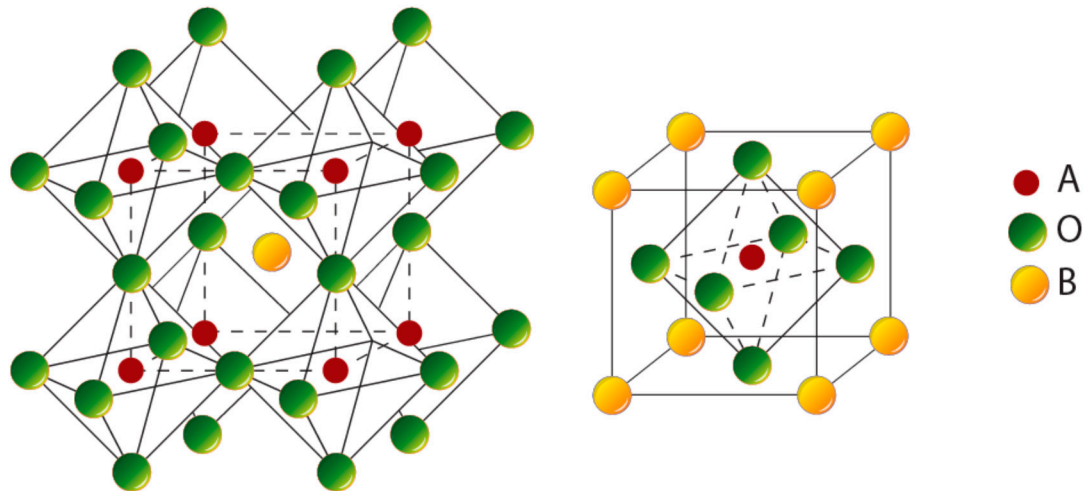


Figure 1. A schematic of the cubic perovskite structure ABO_3 .

The vacancy diffusivity, D_v , is related to the mean square displacement $\langle R^2 \rangle$ of the vacancies via the Einstein relation,

$$\langle R^2 \rangle = 6D_v t. \quad (3)$$

It should be noted that D_v exponentially depends on the energy barrier for oxygen vacancy migration. The oxygen diffusivity, D_O , is connected to D_v via the following relation,

$$D_O = \frac{c_v}{1 - c_v} D_v, \quad (4)$$

where c_v is the vacancy concentration fraction.

3. Atomistic Simulation Methodology

As the focus of the present review is the diffusion in energy materials, we will briefly introduce here molecular dynamics (MD) and density functional theory (DFT) methods. The quantum mechanical formulation offers the most complete description, however, the analytical solution of Schrödinger's equation for a large number of electrons is practically impossible due to the complexity of many-electron interactions [85]. DFT is in essence an approximation that allows the efficient modelling of solids [86,87]. Presently in DFT, the common way to address the exchange-correlation energy is by the local density approximation (LDA), the generalized gradient approximation (GGA) and hybrid functional, which incorporate a part of the exact exchange from Hartree–Fock theory [88]. Typically, a plane-wave basis set is used with the pseudopotential method, with the core electrons being described by effective potentials (known as pseudopotentials) and the valence electrons evolving explicitly. Diffusion energetics and mechanisms can be investigated using DFT as the activation energy of diffusion can be calculated by identifying the minimum energy path, using methods such as the nudged elastic band (NEB) [89]. The main issue of DFT simulations is the relatively small number of atoms that can be modelled (presently a few hundred atoms) and this is an issue particularly when modelling complicated diffusion mechanisms (for example, involving the cooperative motion of local polyhedral structures in the lattice).

MD using classical potentials is a very common method to study the energetics of diffusion in energy materials. MD the state of the system can be described by the positions and the momenta of all the constituent particles, with Newton's equations of motion for an ensemble of particles being solved iteratively. The interactions between particles is through potential energy functions, typically within the classical Born-like description of the crystal lattice [90]. In these the ionic interactions are defined by a long-range Coulombic term and by a short-range parameterized pair potential (for example the Buckingham potential [91]). The key advantage of MD as compared to DFT is that extended systems can be modelled, however, this is not a method that can be used when the description of the electronic structure of the system becomes important [92–96]. In essence, not unlike experimental techniques different methodologies are more appropriate for different length scales and properties.

Finally, it should be stressed that the use of thermodynamic models (for example the cBΩ model) can be used to gain further insights from the experimental and computational modelling methods as it was demonstrated for other systems in previous work [97–113].

4. Ruddlesden–Popper Layered Oxides

Ruddlesden–Popper series oxides have been considered for intermediate temperature oxide fuel cells and in particular cathodes for a number of years [114–117]. They can be described by the formula $A_{n+1}B_nO_{3n+1}$. The first members ($n = 1$) of the series include the widely studied La_2NiO_4 . La_2NiO_4 is tetragonal (space group $I4/mmm$) [117] at a wide temperature range (423–1073 K) including the temperature that are important of Intermediate temperature solid oxide fuel cells (IT-SOFC). For completeness, La_2NiO_4 is orthorhombic ($Cmca$) at room temperature [118]. As a side line it should be mentioned La_2NiO_4 is in the K_2NiF_4 structure that is widely known as it is the structure of $La_{2-x}Ba_xCuO_4$ the archetypal material for high temperature superconductivity [119].

The intricacy in these materials is that oxygen concentration can have a significant impact on the oxygen diffusion properties. This is because self-diffusion is dominated by oxygen and oxygen vacancies (in oxygen deficient or hypostoichiometric oxides) or oxygen interstitials (in oxygen excess or hyperstoichiometric oxides) act as the vehicles for diffusion. More formally and in Kröger–Vink notation [120] this can be described by:

$$D_O = D_V[V_O''] + D_i[O_i''] \quad (5)$$

where D_0 is the oxygen diffusion coefficient, D_V is the vacancy diffusion coefficient, D_i is the interstitial diffusion coefficient, $[V_O'']$ is the oxygen vacancy concentration and $[O_i'']$ is the oxygen interstitial concentration.

Considering La_2NiO_4 is oxygen hypostoichiometric, the excess oxygen is typically related to the experimental conditions of the samples [70,121,122]. For numerous years the experimentally determined activation energies of diffusion in lanthanum nikelate were in a wide range 0.19–0.90 eV [40,115,122–125], whereas there was no agreement on the diffusion mechanism. Classical molecular dynamics work [124] calculated an activation energy of diffusion of 0.51 eV in excellent agreement with the time of flight secondary ion mass spectrometry (ToF-SIMS) study of Sayers et al. [122] (0.54 eV). Additionally, the MD study proposed the interstitialcy in the a-b plane diffusion mechanism for oxygen self-diffusion (refer to Figure 2) [125]. An analogous interstitialcy mechanism in the a-b plane was also proposed in the experimental (neutron scattering experiments with analysis based on the maximum entropy method) work by Yashima et al. [74] in the related tetragonal $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$.

It should be noted that research on the Ruddlesden–Popper series oxides continues to attract the interest of the research community and although self-diffusion is well characterised theoretically and experimentally, the focus is on proton diffusivity, doping and structural/electronic/magnetic properties [126–135].

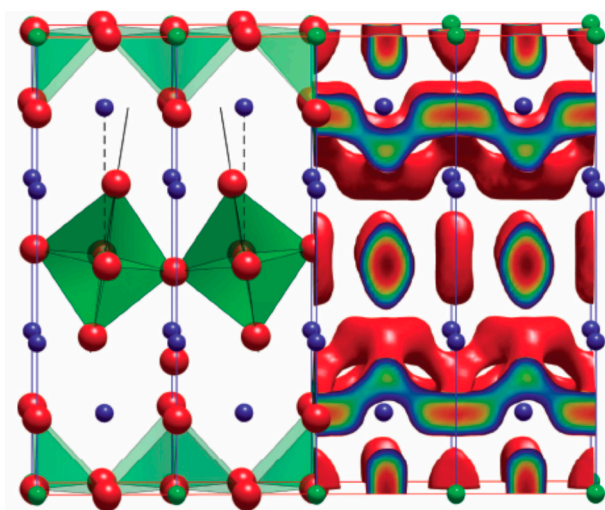


Figure 2. In the left part of the figure the tetragonal $\text{Pr}_2\text{NiO}_{4+\delta}$ where O is in red, NiO_6 octahedra in green and Ni in blue (c-axis is the vertical axis). The right part of the figure represents the isosurface connecting the O diffusion sites in the a-b plane as derived using molecular dynamics at 1100 K and $\delta = 0.09875$ Reproduced by permission from the Owner Societies [125].

5. Double Perovskites

The interest on double perovskite materials ($\text{AA}'\text{B}_2\text{O}_{5-\delta}$) as cathodes for SOFC was motivated by the seminal studies of Taskin et al. [69,136]. The secondary ion mass spectrometry work by Tarancon et al. [73] confirmed the high oxygen self-diffusion of oxygen in $\text{GdBaCo}_2\text{O}_{5+\delta}$ and determined a tracer diffusion coefficient of 0.6 eV. This is also in agreement with the classical molecular dynamics work of Parfitt et al. [137] with the calculated activation energy of diffusion of 0.5 eV as the 0.1 eV difference can be traced in the methodological errors. Additionally, Parfitt et al. [137] showed that the oxygen self-diffusion mechanism is in the a-b- plane. In particular the MD calculations revealed that oxygen migration in this double perovskite is highly anisotropic taking place in the Gd-O and the adjacent Co-O layers. The energetics and mechanisms of oxygen self-diffusion in double perovskites are also supported by the MD studies of Hermet et al. [138] and experimental work [139]. The classical atomistic and MD studies of Seymour et al. [53] showed that oxygen diffusion in $\text{PrBaCo}_2\text{O}_{5+\delta}$ is analogous but with a lower activation energy of diffusion (0.35 eV) constituting this material very promising. An interesting feature of the double perovskites is the antisite disorder in the cation sublattice. The impact of cation ordering on oxygen diffusion was experimentally observed by Taskin et al. [69,136] in the related material $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3\pm\delta}$. In particular, Taskin et al. [69,136] determined a significant increase in the oxygen

diffusion coefficient in the cation ordered perovskite as compared to the cation disordered perovskite. The question that arises is: how does the antisite disorder in the cation sublattice impact the energetics and mechanism of oxygen self-diffusion in the double perovskite system? Parfitt et al. [137] used classical MD calculations to show that the self-diffusion of oxygen in $\text{GdBaCo}_2\text{O}_{5+\delta}$ is highly dependent on the cation disorder. In particular, for ordered $\text{GdBaCo}_2\text{O}_{5.5}$, the oxygen diffusion mechanism is anisotropic along the a-b plane, whereas disorder in the cation sublattice (formation of Ba and Gd antisites) results to a reduction of the oxygen diffusivity and diffusion in the c-axis (refer to Figure 3) [137]. The higher the disorder in the cation sublattice, the more isotropic the mechanism of oxygen self-diffusion [137]. From a technological viewpoint this implies that the thermal history of the material and sample preparation are important parameters that could impact the energetics and mechanism of diffusion of these systems. For SOFC applications ordered double perovskites should be preferred.

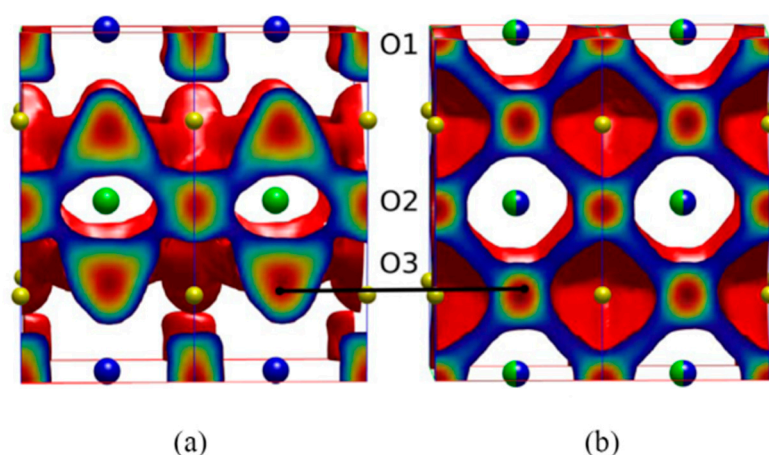


Figure 3. A schematic representation of the MD calculated oxygen density profiles for $\text{GdBaCo}_2\text{O}_{5.5}$. (a) when ordered (anisotropic diffusion) and (b) fully disordered (isotropic diffusion) [137]. Blue and green spheres represent Ba and Gd ions respectively (Copyright 2011 Royal Society of Chemistry).

6. Others Perovskite Systems

It has been 34 years since the discovery of high temperature superconductivity by Bednorz and Müller [119] and many thousands of studies have taken place but there is still no unambiguous explanation of superconductivity and related phenomena (i.e., pseudo gap state, linear dependence of electrical resistance) [140–149]. Although $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are very important perovskite-related materials (crystal structure is a combination of perovskite and rock salt units) with superconducting properties (high critical temperatures) [140–149] they will not be reviewed in detail here as the focus is on materials with fast oxygen self-diffusion. Oxygen vacancies (in the Cu-O planes) and oxygen vacancy diffusion in these materials is of importance as it can impact the structure and superconducting properties [140–149]. The activation energies of oxygen self-diffusion of $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are typically in the range 0.76–0.98 eV [150–155]. An important observation is that in $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ there is an increase in the activation energy and pre-exponential factor of oxygen self-diffusion (refer to [51] and references therein).

There is a large amount of experimental and theoretical investigations on the materials properties of perovskite and related materials. As it was demonstrated in the Ruddlesden–Popper series example, the experimental determination of the self-diffusion properties and in particular the diffusion mechanism can be a challenge and, in that respect, computational modelling work can provide useful and complementary information. This becomes even more pronounced when considering disordered perovskite related structures such as lithium lanthanum titanates ($\text{La}_{2/3-x}\text{Li}_{1/3+x}\text{TiO}_3$, LLTO). In what follows we will describe how computational modelling techniques involving the fruitful marriage of classical molecular dynamics with genetic algorithms can describe the complicated Li self-diffusion in LLTO. $\text{La}_{2/3-x}\text{Li}_{1/3+x}\text{TiO}_3$ has high ionic conductivities and exhibits non-Arrhenius behaviour. Through MD analysis insights can be gained on the three-dimensional network of diffusion pathways via which

ions migrate in different directions. Importantly in this perovskite cations form low La content (La_{poor}) and high La content (La_{rich}) atomic layers, which in turn will impact the lithium migration [156]. Jay et al. [59] introduced the ordering degree in the crystal using the following relation [59]:

$$S = \frac{R_{\text{La-rich}} - R_{\text{dis}}}{1 - R_{\text{dis}}} \quad (6)$$

where R_{dis} ($R_{\text{La-rich}}$) is the occupancies of the A -sites by the exact amount of La^{3+} ions for the disordered (La-rich) layered structure. Therefore, for $S = 0$ the system's structure is completely disordered. Figure 4 represents LLTO with La_{poor} and La_{rich} layers coloured in blue and yellow respectively. For $S = 0$ the MD calculations by Jay et al. [59] revealed that lithium diffusion is completely homogeneous and isotropic. From an atomistic point of view this can be explained as lithium diffusion in LLTO is facilitated by vacancies, therefore the stoichiometry and the ordering degree that constitute the percolating network (refer to Figure 4) are key [59]. Given the number of possible combination of La_{poor} and La_{rich} layers it becomes computationally intractable to consider all the different possibilities for large number of atoms. To overcome this hurdle Jay et al. [59] investigated the impact of the structure on the conductivity of LLTO using MD combined with a genetic algorithm (GA) (refer to Figure 5). This approach was the first to reproduce the experimental results in this material [157], and more importantly it is an effective defect engineering strategy to maximise the lithium diffusivity by tailoring the lanthanum content of the layers. This approach is a paradigm and in essence transferable thus it can lead to the design of advanced materials with optimised properties particularly in disordered systems with a wide range of possible compositions and stoichiometry [158–163]. The trend is on machine learning techniques to encounter difficult problems in science and engineering [164].

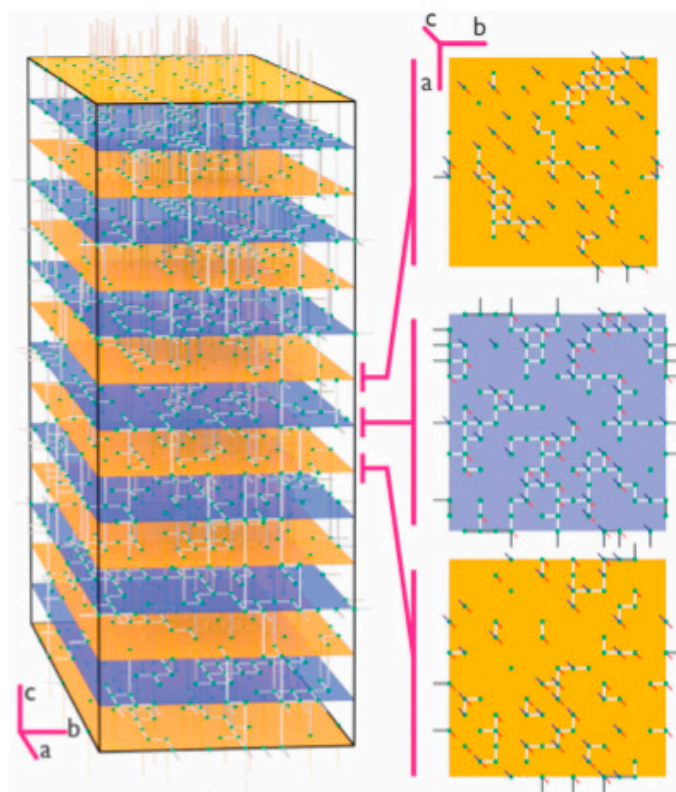


Figure 4. A schematic representation of diffusion pathways in lithium lanthanum titanate. Here the pathways in the ab directions are shown for every La_{poor} and La_{rich} layer. This is an example of how insights can be gained by the synergetic application of molecular dynamics with genetic algorithms. Reproduced by permission from the Owner Societies [59].

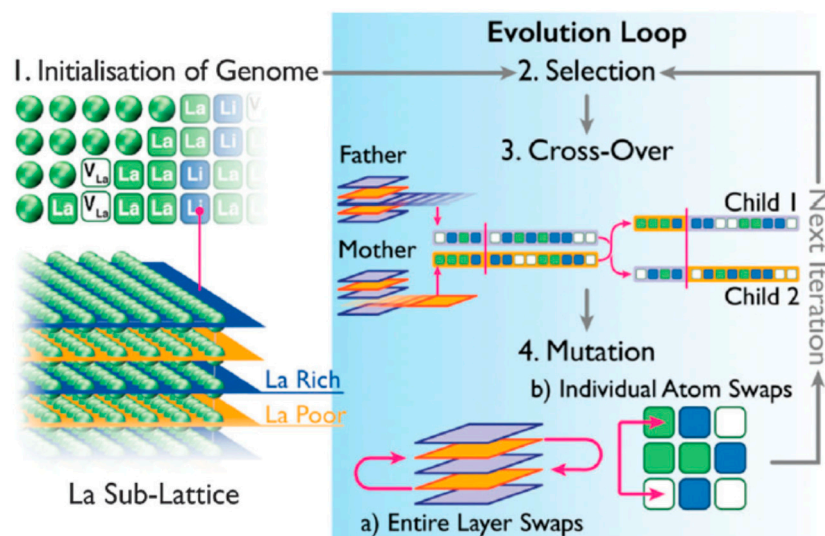


Figure 5. A schematic representation describing how the genetic algorithm favors “inheritance” from structures having high diffusivity to yield the iterative refinement of structures. Reproduced by permission from the Owner Societies [59].

7. Summary

In the present review, we have considered the diffusion processes of perovskite and related oxides. These materials are technologically important for a range of applications including sensors, SOFC and batteries. Although they have been investigated by the community for numerous decades, recent experimental and theoretical methodological advances (such as ToF-SIMS and DFT) provided insight and have accelerated progress.

Considering the paradigm of disordered ionic conductors can be an effective way to proceed given the advantages (for example blocked pathways do not affect diffusion) and the new compositional and structural possibilities for the discovery of new materials. The latter could benefit by the fruitful combination of atomistic simulation (MD and/or DFT) with machine learning.

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