

Review

# The Evolution of Solid Oxide Fuel Cell Materials

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**Abstract:** Solid oxide fuel cells (SOFCs) are a key component of the future energy landscape. Although there is considerable research on the physical properties and technology of classic oxide materials for electrode and electrolytes in SOFCs, the field is very active as new experimental and theoretical techniques are now available that can improve these systems. In the present review, we consider key systems such as perovskite-related materials, the impact of strain and interfaces and advanced concepts that can improve the properties of SOFC materials. In particular, we consider the oxygen diffusion properties of perovskite-related materials and focus on  $\text{La}_2\text{NiO}_{4+\delta}$  and the double perovskites such as  $\text{GdBaCo}_2\text{O}_{5.5}$ . Then, we review the importance of interfaces and strain as a way to engineer defect processes. Finally, we consider advanced concepts to form designed structures that explore the effect of local high entropy on lattice stabilization.

**Keywords:** defect engineering; solid oxide fuel cells; atomistic simulation



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## 1. Introduction

SOFCs have been considered for decades and have a vast number of applications including mobile (cars and buses) and industrial uses. In the past years, there has been a trend to introduce more efficient systems for energy conversion and storage and this includes SOFCs, batteries, supercapacitors, solar cells, etc. [1–25]. The main interest in SOFC technology is because of its very efficient energy conversion in conjunction with reduced emission of the so-called greenhouse gases as compared with the typical power generation routes [1,3]. Typically, SOFCs operate efficiently at high temperatures (up to 1000 °C), with hydrogen and fossil fuels converting chemical energy to electricity; however, they can also be used in combined heat and power applications [26,27]. A consequence of the high temperatures in which SOFCs operate is the high materials costs (materials issues include thermal cycling, chemical degradation, etc.) due to expensive interconnects and heat exchangers [28]. The impact of high temperature can be mitigated by lowering the operating temperatures to 500–700 °C (known as the intermediate temperature range). Nevertheless, SOFC thermal-activated processes (i.e., diffusion) are affected by the reduction in temperature, and this is particularly problematic for the cathode and electrolyte. This leads to the requirement of advanced materials with high rates of oxygen self-diffusion at these reduced temperatures. In particular, it is necessary to accelerate the oxygen diffusion in the cathode and electrolyte of the SOFC.

It should be stressed that the more conventional cathodes, for example,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ , that are considered to be competent electronic conductors are not appropriate because of their low bulk ionic conductivity ([10] and references therein). This has led to the use of another group of materials called mixed ionic–electronic conductors (MIECs) as the oxygen reduction reaction (ORR) in MIEC electrodes is ruled by the oxygen surface exchange and

oxygen diffusion [10]. Similarly to cathodes, electrolytes for SOFCs also need to possess high ionic conductivity but with low electronic conductivity [10].

Oxygen diffusion is therefore fundamentally and technologically important for the cathode and electrolyte materials of SOFC [1–25]. Oxygen self-diffusion in these systems is a complicated phenomenon that is influenced by the composition, crystal structure, oxygen stoichiometry, doping and elastic strain ([10] and references therein). In that respect, predictive computational modelling can be used synergistically with experimental work to ensure an efficient design route for fast oxygen ion diffusion in SOFCs. Essentially, the complexities constitute the determination of the defect processes and the impact of various factors on these difficulties when using experiments and simulations at the atomic scale can offer detailed insights.

In this review, the focus is on the oxygen diffusion mechanisms of SOFC materials moving from more common materials (perovskite-related materials) to novel concepts, considering the latter emphasis is given on recent theoretical (refer to Section 2.2) and associated experimental results highlighting the importance of strain, interfaces and architectures on the enhancement of the diffusion properties of oxide materials for SOFC applications.

## 2. Methodology

### 2.1. Recent Developments

In the past decades there has been more intensive use of experimental and theoretical techniques. In particular, the advancement of secondary ion mass spectrometry (SIMS) (and variants such as time-of-flight (ToF) SIMS) has led to the very precise determination of self- and dopant diffusion in energy and electronic materials [29,30]. From a theoretical viewpoint, the development of molecular dynamics (MD) and density functional theory (DFT) in conjunction with ever-increasing computational resources is a powerful and complementary tool [31–34]. It is a complementary tool given that atomistic simulations can more efficiently quantify migration energy barriers and point defect processes at different planes and directions [35–39]. If these techniques are combined with advanced techniques such as cluster expansion and special quasirandom structures (SQS), structurally and compositionally complicated systems can be considered [40–55]. Finally, thermodynamic techniques including the  $cB\Omega$  model by Varotsos and Alexopoulos can benefit from the understanding of the point defect chemistry and provide predictions for a vast range of temperatures and pressures [56–62].

### 2.2. Atomistic Simulation

The most common ways to investigate the defect processes on SOFC materials at the atomistic level is via classical MD and DFT, as has been shown in previous theoretical studies [63–70]. Classical MD has been a popular way to investigate the atomic scale properties of inorganic materials for over 40 years. The present computational resources allow the MD simulations of many millions of atoms and therefore research can include extended defects such as grain boundaries. This is important as polycrystalline material processes can be dominated or severely impacted at the extended defects. Classical MD is a fairly simple method where the state of the system is predicted by considering the positions and the momenta of the particles using Newton's equations of motion, which are solved iteratively in order to calculate the evolution of the system. Interparticle interactions are described using the potential energy function. For SOFC, the ionic systems are modelled within the classical Born-like description [71,72]. Typically, the ionic interactions can be modelled by a Coulombic term (long-range) and by a short-range parameterized pair potential [73,74]. Although MD calculations in ionic systems can work very well and can be a useful tool when considering dynamical properties such as diffusion, they cannot calculate the electronic structure of the system.

When considering electronic properties, DFT calculations are advantageous over MD. It is acknowledged that the quantum mechanical description is the most complete depiction of nature. What is also acknowledged is that the analytic solution of the Schrödinger

equation for practical systems (i.e., a substantial number of electrons and nuclei) is intractable due to the complexity of many-electron interactions [75–77]. The DFT method was discovered to address these issues via the description of the exchange-correlation energy of electrons through approximations (typically the local density approximation (LDA), the generalized gradient approximation (GGA) or with hybrid functionals) [75,76]. A key aspect of DFT is to use a plane-wave basis set with the pseudopotential method, where the core electrons can be modelled by effective potentials and the valence electrons can evolve explicitly [75–77]. Although DFT is at zero kelvin and diffusion typically occurs at high temperatures, there are ways to gain information for the energetics of diffusion using this approach. For example, formation energies (the energy to form a point defect) of ionic systems can be easily modelled, whereas for the activation energy of migration (i.e., the energy barrier that the ion has to overcome to move from one minimum energy site to the next), methods such as the nudged elastic band method can be employed. An issue with the DFT study of ionic materials is the supercell size, as it needs to be extended enough so that periodic images have little effect upon the calculated energies. This is particularly important for extended and charged defects. Finally, it should be considered that the *ab initio* MD can overcome many of the problems of classical MD (for example, the inability to calculate electronic properties) and DFT (i.e., it is dynamic and can model high temperatures); however, it is a technique that is very computationally intensive, so it is typically limited to small number of atoms.

### 3. Materials Systems

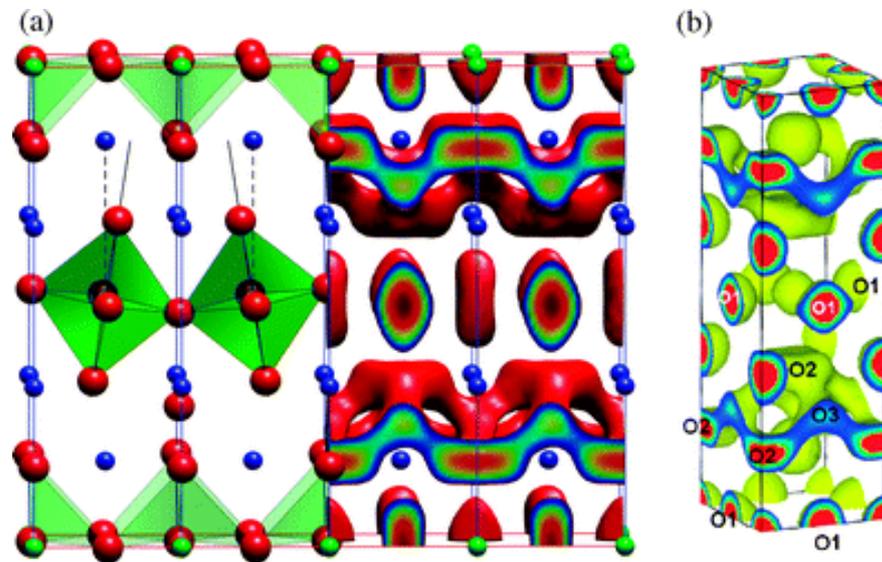
#### 3.1. Perovskite-Related Materials

Perovskite and perovskite-related materials are particularly important for a range of applications from SOFC to high-temperature superconductivity [78–87]. For example, the community has investigated the  $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (where Re = rare earth element or Y) system following the discovery of high-temperature superconductivity [78]. Through doping and external conditions, these systems showed improvements in the critical temperature of superconductivity ( $T_c$ ) [80,81]. In fact, these systems are still also being investigated for fusion applications [85–87]. Regarding materials for SOFC lanthanum nickelate ( $\text{La}_2\text{NiO}_{4+\delta}$ ), gadolinium barium cobaltate ( $\text{GdBaCo}_2\text{O}_{5+\delta}$ ) and other perovskite-related systems have been considered in the past two decades [29,35,88–100].

Considering first oxygen self-diffusion in  $\text{La}_2\text{NiO}_{4+\delta}$ , it should be considered that the experimental determination of its energetics and mechanism is difficult due to its crystal structure and oxygen hypo- or hyperstoichiometry. For example, it was difficult to determine the energetics and mechanism of oxygen self-diffusion in  $\text{La}_2\text{NiO}_{4+\delta}$  [10,29]. Experimental time-of-flight secondary ion mass spectrometry investigations on  $\text{La}_2\text{NiO}_{4+\delta}$  by Sayers et al. [29] determined an activation energy of oxygen migration of 0.54–0.56 eV in excellent agreement with the classical MD work (0.51 eV [89]). MD also revealed that the dominant oxygen self-diffusion mechanism in  $\text{La}_2\text{NiO}_{4+\delta}$  is the interstitialcy mechanism (in the a–b plane) in which oxygen interstitials displace apical oxygens from the  $\text{NiO}_6$  octahedron, which are thereafter promoted to adjacent oxygen interstitial sites [89].

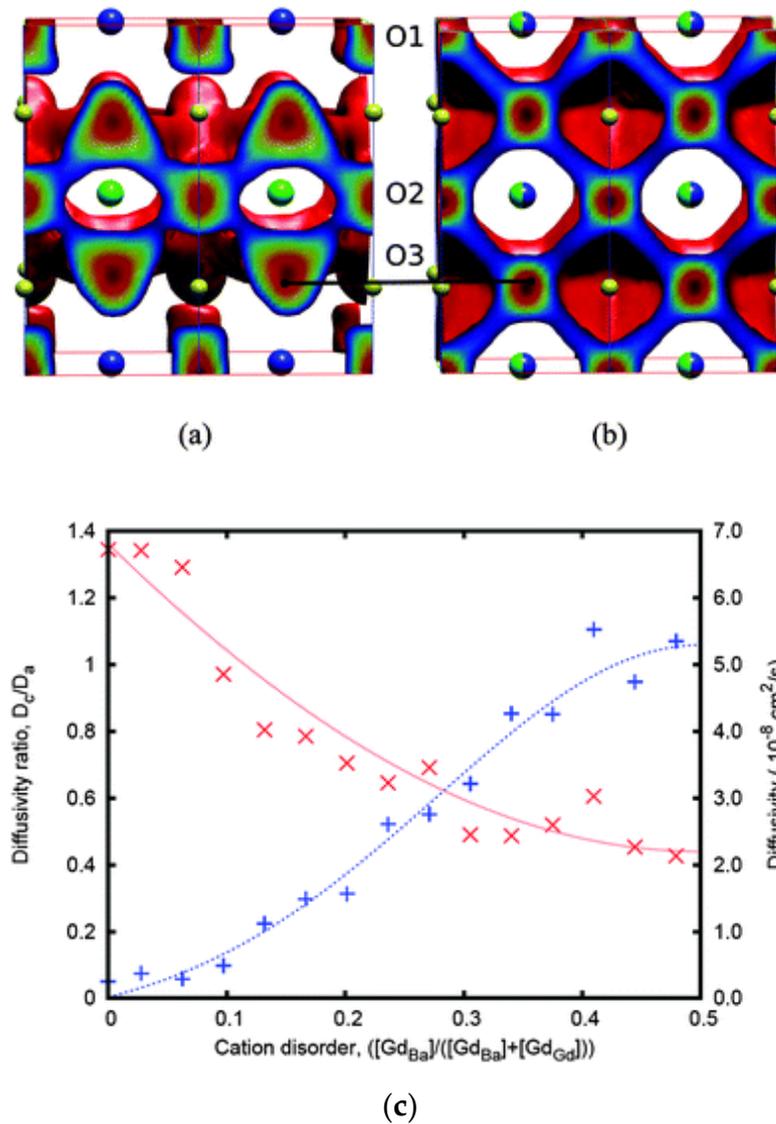
Although praseodymium (Pr) has a very negative effect in perovskite-related high- $T_c$  superconductivity, Pr-based perovskite materials such as  $\text{PrBaCo}_2\text{O}_{5+\delta}$  or  $\text{Pr}_2\text{NiO}_{4+\delta}$  were considered by the SOFC community due to their high oxygen self-diffusion [90,93]. In the intermediate temperature range,  $\text{Pr}_2\text{NiO}_{4+\delta}$ , similarly to the isostructural  $\text{La}_2\text{NiO}_{4+\delta}$ , has a tetragonal crystal structure (I4/mmm space group, refer to Figure 1a). This structure can be described as perovskite layers ( $\text{PrNiO}_3$ ) intergrown with rock salt layers (PrO) [90]. There is a mismatch between the layers which leads to the introduction of oxygen interstitials in the  $\text{Pr}_2\text{O}_2$  bilayers [90]. This, in turn, leads to the local distortion of the  $\text{NiO}_6$  octahedra (refer to Figure 1a) due to the Coulombic repulsion between the oxygen interstitial and the apical ions in the  $\text{NiO}_6$  octahedra [89]. This effect is key if the aim is to understand the mechanism of oxygen self-diffusion of  $\text{Pr}_2\text{NiO}_{4+\delta}$  at the atomic level. The interstitialcy oxygen self-diffusion mechanism in the a–b plane in  $\text{Pr}_2\text{NiO}_{4+\delta}$  is common with related

systems such as  $\text{La}_2\text{NiO}_{4+\delta}$ , as mentioned above, and  $\text{La}_2\text{CoO}_{4+\delta}$  [92]. Figure 1a is based on classical MD calculations and shows the isosurface connecting the oxygen diffusion sites in the a–b plane [90]. This isosurface is in agreement with the maximum entropy method results reported in a related system (Figure 1b, reference [90] and references therein).



**Figure 1.** The structure and oxygen self-diffusion in  $\text{Pr}_2\text{NiO}_{4+\delta}$ . (a) The crystal structure, where  $\text{NiO}_6$  octahedra are green, Ni ions are blue and O ions are red (c-axis is the vertical axis); MD calculations at 1100 K and  $\delta = 0.09875$  predicting the isosurface of the O diffusion sites (in the a–b plane) and (b) maximum entropy method results [90].

The community has also investigated the impact of intrinsic point defects such as antisites on the diffusion properties in perovskite materials for SOFCs. An interesting example is  $\text{GdBaCo}_2\text{O}_{5+\delta}$  (double perovskite structure), which has high oxygen diffusivity with an activation energy of 0.5 eV [91]. In ordered  $\text{GdBaCo}_2\text{O}_{5+\delta}$ , oxygen self-diffusion is highly anisotropic and takes place primarily in the Gd–O and adjacent Co–O layers [91]. This is shown using MD results in Figure 2a [91]. What the MD results by Parfitt et al. [91] showed is that cation disorder in the Gd–Ba sublattice will result in a decrease in the oxygen diffusivity with the diffusion becoming more isotropic (there is now significant diffusion in the c-axis). Figure 2c quantifies the differences in the oxygen self-diffusion in the c-axis and the a–b plane with respect to the level of cation disorder [91]. In the left y-axis of this figure is the ratio of the diffusivity in the c-axis over the diffusivity in the a–b plane, whereas the right y-axis represents the total diffusivity [91]. The x-axis corresponds to the antisite disorder, i.e., the ratio of Gd atoms occupying a Ba site over the Gd atoms occupying a Ba or Gd lattice site. Considering the zero of the x-axis, that is when there is no antisite disorder, there is in essence no diffusivity in the c-axis (anisotropic diffusion) [91], whereas the total diffusivity (predominantly in the a–b plane) is maximum [91]. At the other extreme (i.e., for the x-axis value of 0.5) where there is maximum antisite disorder, the total diffusivity is minimized, whereas the left y-axis is nearly 1 (i.e., diffusion becomes isotropic) [91]. What can be deduced is that cation disorder in the double perovskites will minimize oxygen self-diffusion [91]. Therefore, for SOFCs, these systems should be ordered and oriented in a way that they benefit from the maximum oxygen diffusion in the a–b plane. In essence, cation antisite disorder is a design parameter that can be used to tune the energetics of diffusion and direct the diffusion mechanism. The key findings and activation energies for the perovskite-related materials considered here are summarized in Table 1.



**Figure 2.** (a) Classical MD results of the oxygen diffusion pathways in (a) ordered and (b) disordered  $GdBaCo_2O_{5.5}$  for  $\delta = 0.5$  at  $T = 900$  K. (c) The ratio of diffusivities in the a- and c-axis ( $D_c/D_a$  represented by + and the blue line) with respect to the cation disorder for  $\delta = 0.5$  at  $T = 1200$  K. The second y-axis represents the diffusivity values ( $\times$ , red line) with respect to the cation disorder [91].

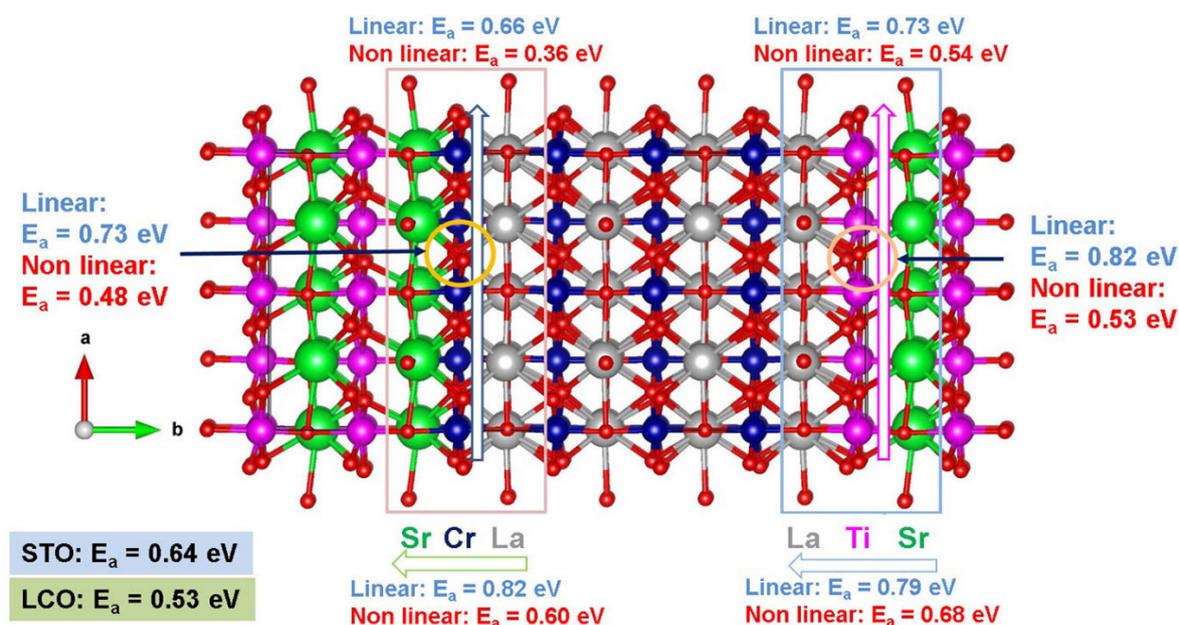
**Table 1.** The activation energies of oxygen diffusion and comments on the mechanism of oxygen diffusion in representative oxides.

Material	Activation Energy/eV	Comments
$La_2NiO_{4+\delta}$	0.51	[29], Classical MD, anisotropic mechanism along the a–b plane, interstitialcy mechanism
$La_2NiO_{4+\delta}$	0.54–0.56	[29], Experiment
$GdBaCo_2O_{5+\delta}$	0.50	[91] Classical MD, anisotropic mechanism along the a–b plane. Cation antisite disorder retards diffusion, makes it more isotropic
$Sr_{0.75}Y_{0.25}CoO_{2.625}$	1.56	[8], Classical MD, isotropic mechanism, vacancy mechanism

### 3.2. Interfaces and Strain

Understanding the impact of strain and interfaces is key for the development of more efficient and sustainable materials for SOFC applications [101–110]. The intriguing study of Garcia-Barriocanal et al. [4] determined that in nanostructured SrTiO<sub>3</sub>/YSZ/SrTiO<sub>3</sub> heterostructures, there is colossal conductivity. In particular, in this heterostructure, yttria stabilized zirconia (ZrO<sub>2</sub> with 8 mol% Y<sub>2</sub>O<sub>3</sub>) layers under 7% tensile strain have conductivities eight orders of magnitude higher than bulk YSZ [4]. This extreme enhancement in ionic conductivity was treated with skepticism from the community but it nevertheless led to numerous studies in SrTiO<sub>3</sub>/YSZ/SrTiO<sub>3</sub> and related heterostructures [5,9,103,104]. Cavallaro et al. [103] determined that in the SrTiO<sub>3</sub>/YSZ/SrTiO<sub>3</sub> heterostructure, the total conductivity dependence is inconsistent with ionic diffusion in YSZ, whereas the DFT work by Kushima and Yildiz [9] in biaxially strained bulk YSZ predicted ionic enhancement by up to four orders of magnitude. Notably, in that study, the migration energy barriers were calculated using the nudged elastic band (NEB) method in relatively small supercells [9]. What is profound in the studies following the work by Garcia-Barriocanal et al. [4] is that tensile strain does significantly increase ionic conductivity but this does not translate to an eight-order of magnitude increase in ionic diffusion. Nevertheless, there is increased interest in the oxygen diffusion properties at oxide interfaces [105–109]. Lee et al. [24] employed ionic interfaces to produce a nonstoichiometric oxygen vacancy concentration. This in turn is very important as oxygen vacancy concentrations at equilibrium are limited, and, therefore, there is a requirement to increase their content as oxygen vacancies are the vehicles of oxygen diffusion in these systems. Lee et al. [24] used the oxide nanobrush architecture to form a substantial nonequilibrium oxygen vacancy concentration at the interface between CeO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>. This is an important example of how the material architecture (here, the designed interfacial oxide) can be used to increase the formation and tune the diffusion properties of defects. With a similar objective but with a more fundamentally scientific viewpoint, the investigation by Chiabrera et al. [22] showed that the modification of nonstoichiometry in grain boundaries can be employed to tune the diffusion properties. Chiabrera et al. [22] effectively determined that point defects induced by strain in the grain boundaries of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3±δ</sub> increase the oxygen diffusivity and diminish the electronic and magnetic order.

Kuganathan et al. [109] employed static atomistic simulations to examine the minimum energy oxygen diffusion pathways and activation migration energies at the STO–LCO interface (refer to Figure 3). It was predicted by these calculations that curved pathways have lower migration energies [109]. Kuganathan et al. [109] showed that at the Sr–Cr–La interface layer, the fastest oxygen transport occurs along the a-axis (i.e., in the Cr layer) with an activation energy of migration of 0.36 eV. This migration energy is significantly smaller than the 0.53 eV calculated for oxygen diffusion in bulk LCO using the same methodology [109]. Considering the c-axis of the Cr layer, the activation energy of migration for oxygen is 0.48 eV, i.e., lower by only 0.05 eV as compared to the activation energy of migration in LCO bulk [109]. Therefore, oxygen will preferentially diffuse along the a-axis in the interface layer. In the La–Cr–Sr layer, the b-axis oxygen activation energy of migration is 0.60 eV, which is not significantly lower than the activation energy of migration (0.64 eV) calculated in bulk STO [109]. Finally, at the Sr–Ti–La interface layer, the activation energies of migration predicted along the a-axis and the c-axis in the Ti layer are lower by about 0.10 eV as compared to bulk STO [99]. At the b-axis of the Sr–Ti–La layer, there is a considerable increase in the activation energy of migration in comparison to bulk STO (by 0.04 eV) or bulk LCO (by 0.15 eV) [109].



**Figure 3.** Static atomistic simulation results of the activation energies of migration calculated in the STO-LCO interface [109].

### 3.3. Advanced Concepts

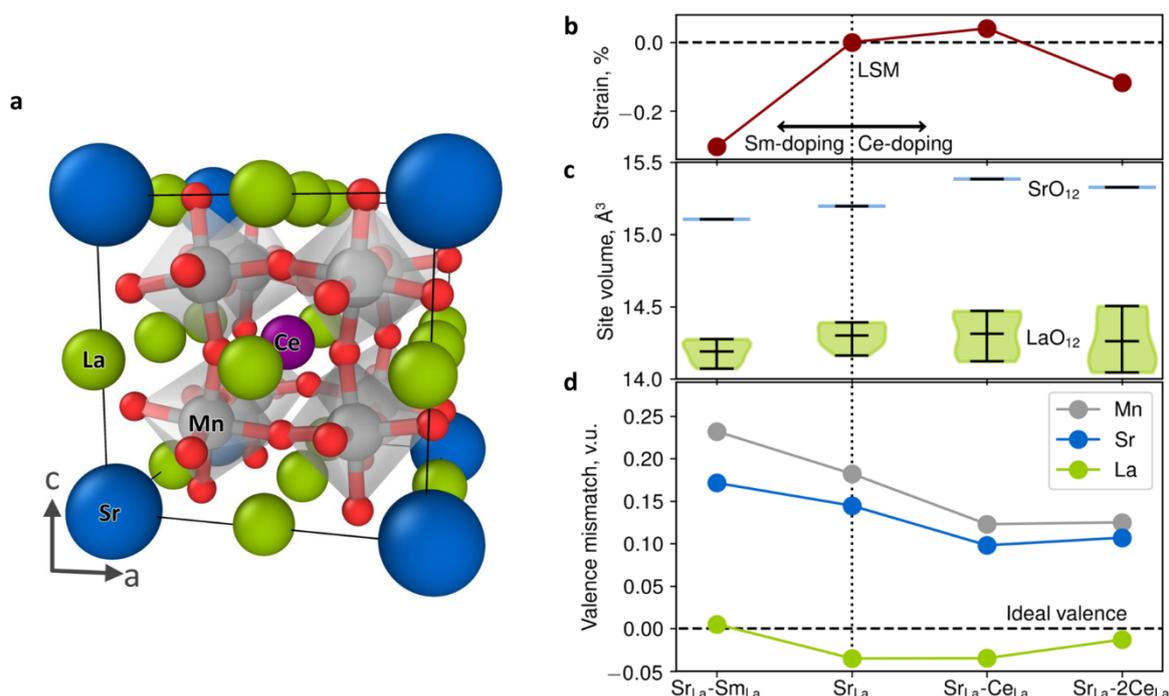
In order to attain improved performance and downscaling so as to be compatible with the design specifications that will be required, solid oxide cells (SOC) need to benefit from beyond-state-of-the-art concepts for nanoengineering materials [111]. In essence, practical applications will need to approach the scaling rate of Moore's Law as it has been observed in microelectronics for many decades. In reality, this is hindered by the poor thermochemical stability, limited electrode catalytic activity and the difficulties in the efficient introduction of nanoscale materials, all of which undermine the use of SOCs as a portable energy source. The improvement of the SOC air electrode can be achieved using scarce materials or by the introduction of advanced ceramic nanostructures formed using mixed ionic–electronic conducting oxides (MIECs) such as doped cobaltites, ferrites and manganites [112]. It is critical in MIEC materials to balance the free energy of the oxygen redox cycle and the enthalpy of oxide reduction as this will ensure significant electrocatalytic activity over the free surface combined with enhanced oxygen diffusion [113]. In thin-film MIECs, the dense microstructure leads to significant in-plane percolation, and the potential of nanostructuring through cutting-edge thin-film techniques is a way to unravel nanoscale effects (i.e., fast oxygen reduction kinetics diffusion) [23]. MIEC thin films are beneficial for SOC functional layers as they do not have areas with high oxygen chemical potential gradients or high electronic current density that are deleterious for device performance; however, there are still issues that need to be considered such as dopant segregation toward the surface that can lead to limited thermal stability [114]. Controlling and limiting cation self-diffusion is important to limit the formation of insulating secondary phases and also to retain surface activity in the long term [115,116]. The community has addressed the improvement of MIEC thin films' performance through chemical doping, inclusion of interfaces, surface decoration and strain engineering [117–121]. The difficulty that emerges is to mitigate cation segregation and to improve the oxygen reduction reaction (ORR) kinetics [122].

To improve the oxygen diffusion at intermediate temperatures, MIEC can be paired with oxygen conductors to form nanocomposites, with applications as SOC electrodes and dual-phase membranes for oxygen separation. Nanocomposites are structurally stable and have the benefit of ionic and electronic species transport [123,124]. Vertically aligned nanostructures (VANs) are considered as an alternative to the nanocomposite electrode functional

layers [125]. VANs have been studied for nearly a decade and, in particular, nanocolumn in matrix mesostructures exhibited important functionalities such as controlled resistive switching, enhanced ionic diffusion and photocatalytic properties [126–129]. The interplay of interfacial effects (elastic strain ionic and electronic redistribution) inspired the investigation of self-assembled MIEC–fluorite thin-film vertical nanocomposites for applications in SOFCs [37,130,131]. The benefit of these studies is the realization of the VAN approach; however, their inclusion of inert model substrates and unrealistic electrolyte layers leads to incoherent interfaces with low interface density, and these in turn restrain the potential of VANs and inhibit their use in realistic electrochemical devices. The recent study by Baiutti et al. [25] described the construction of a self-assembled thin-film VAN nanocomposite using an electronic conductor ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM)) and an ionic conductor ( $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  (SDC)). Importantly, VAN has long-range order and phase alternation with nanosized column width ( $\approx 10$  nm) [25]. Using a yttria-stabilized zirconia (YSZ) electrolyte as support, this nanostructure is compatible as a functional oxide nanomaterial for high-temperature electrochemical devices (i.e., as a SOC functional electrode layer given the high stability against cation migration and accelerated ORR kinetics) [132]. Importantly, the introduction of nano-engineered composite oxides can lead to further ways for the development of new functional materials with improved electrochemical properties [25].

Interestingly, the Baiutti et al. study [25] employed DFT calculations to study the effects of local high entropy on lattice stabilization. In particular, they used spin-polarized DFT on a confined cubic perovskite supercell (refer to Figure 4), aiming to gain insights into the thermal stability of the LSM-SDC VAN. This is not trivial; however, the study focused on the high degree of cation (Sm and Ce) intermixing. The ability of DFT to decouple between the different contributions and to quantify energy and strain differences is valuable to gain insights that are not feasible via experiment. The study by Baiutti et al. [25] showed that the determined isotropic compressive strain of LSM in the VAN structure is due to the introduction of Sm from the SDC layers. Importantly, spontaneous cation interdiffusion leads to Sr segregation suppression, whereas LSM can be considered a six-element high-entropy oxide [25]. This is also consistent with the results by Yang et al. [133], who have determined entropy-induced stabilization for bulk LSM. Figure 4 illustrates the DFT-derived results, showing the lattice strain due to doping, the mean and distribution of site volumes around the La and Sr sites and the bond valence mismatch of the ionic positions for the different cation dopants [25]. In  $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ , it is predicted that the Sr ion is significantly overbonded (i.e., the surrounding oxygen ions are closer), whereas La ions are slightly underbonded [25]. This valence mismatch in conjunction with electrostatic effects can be key for the exchange of overbonded Sr ions with underbonded La ions on the surface [25]. This incoherency is balanced by cationic intermixing (refer to Figure 4c,d) [25]. The incorporation of Ce will effectively increase the Sr–O site volume and reduce the Sr–O overbonding compared to the La–O polyhedral [25]. This will result in a decrease in the elastic driving force for Sr surface segregation. That is, the configurational entropy increase leads to more stable LSM via local lattice distortion, consistent with theoretical studies [25,134]. VAN structures are (a) self-assembled and therefore their composition and interfaces at a growth temperature are thermodynamically stable, and (b) they can accommodate Ce contents beyond the solubility limit [25,135].

In essence, the whole approach is based on using VANs for the combination of the very good oxygen exchange properties of LSM and the fast oxygen diffusion of SDC to form an advanced designed electrode functional layer for SOCs. The heavily codoped manganite phase in the VAN is a high-entropy oxide which is stable and obstructs Sr segregation from the surface. The consequence is very long-term durability. The study by Baiutti et al. [25] determined (via isotopic exchange depth profiling based on APT) that there is a fast oxygen diffusion pathway along the SDC phase. This is a paradigm of the use of VAN nanocomposites as a tool to fix current kinetic limitations of existing electrodes. The VAN architecture is relatively easy to form and leads to prolonged thermal stability and fast oxygen reduction kinetics [25,136–138].



**Figure 4.** DFT-derived results illustrating (a) the relaxed positions of the Mn (gray), Sr (blue), La (green), O (red) and Ce (purple) ion in the 40-atom periodic supercell  $La_{0.75}Sr_{0.125}Sm_{0.125}MnO_3$ . (b) The predicted lattice strain due to doping, (c) the mean and distribution of site volumes around the La (green) and Sr (blue) sites and (d) bond valence mismatch of the ionic positions for the different cation dopants [25].

### 3.4. Perspectives

It should be stressed that this review is not exhaustive but rather aimed at highlighting some key SOFC materials, properties and theoretical ways to predict them. The research community is very active on these systems, as can be seen through the very high publication rate (refer for example to [99,100,139–152] and references therein).

## 4. Summary and Future Outlook

In the present energy landscape, there is increased need for efficient energy conversion combined with reduced emissions, and this is where SOFC technology thrives. Although typical material systems for these technologies have been investigated for decades, there has been renewed interest in the past few years as SOFCs can play a more mainstream role, and there is the desire to move to intermediate temperatures and hence more advanced materials that can operate efficiently at these lower temperatures. The investigations in the past 20 years have benefited from the advanced computational techniques (and substantial computational power) and the advances in experimental techniques (for example, ToF-SIMS). Presently, experiment and theory are synergistically employed, as they can provide complementary information that can accelerate progress and guide the community to more fruitful systems. The computational techniques allow the prediction of the point defect processes, early recognition of defect engineering strategies, the diffusion mechanisms and energetics. Commonly, the quest for more efficient SOFC research is focused on compositionally and structurally complicated materials.

The community is working towards a path for the development of next-generation functional oxides for SOFC and electrochemical applications. Vertically aligned nanostructures can be used to form electrode functional layers for SOFCs, taking advantage of the excellent oxygen exchange properties of LSM in conjunction with the good diffusivity of SDC. With the spontaneous formation of a high entropy oxide in the VAN, a stable compound is formed, which limits cation segregation to the surface, increasing

the long-term durability of solid oxide electrochemical cells. It is determined that VAN nanocomposites can solve kinetic limitations of electrodes and, in general, can be an efficient strategy for oxide electrochemistry (combining fast oxygen reduction kinetics with long-term thermal stability).

What is also important is to avoid expensive, unsustainable and scarce materials, which can be a bottleneck for the use of the technology. It is common in research to use rare earths and other expensive materials; however, the limitations in the production and their availability require a reduction in the dependence on these materials. In this respect, the use of more efficient architectures such as VAN to improve properties is very positive. Whatever the technological solutions, the future development of energy conversion, storage and production systems will require the understanding and optimization of all intermediate steps from cradle to grave.

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