In Search of Enhanced Electrolyte Materials: A Case Study of Doubly Doped Ceria

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Abstract

Various compositions of gadolinium-praseodymium doubly doped ceria (GPDC) have been studied to elucidate the effect of two co-dopants in enhancing the ionic conductivity. A Kinetic Lattice Monte Carlo (KLMC) model of vacancy diffusion in GPDC has been developed, which uses activation energies obtained from DFT-calculations for vacancy migration in gadolinium-doped ceria (GDC) and praseodymium-doped ceria (PDC) as input. In order to identify the optimal composition of electrolyte materials for solid oxide fuel cells, three different classes of GPDC were studied; (i) Gd rich (ii) Pr rich and (iii) equal Gd-Pr content. It is assumed that the Gd and Pr are 100% ionized to Gd³⁺ and Pr^{3+} . KLMC simulations showed that GPDC compositions with ≈ 0.20 mole fraction to 0.25 mole fraction of total dopant content exhibited the maximum ionic conductivity. Among the three classes studied, Gd-rich GPDC is found to have the highest conductivity for the temperature ranging 873 K to 1073 K. The optimal co-doped compositions were found to be slightly temperature dependent. Analysis of vacancy migration pathways for millions of jump events show that GPDC has a slightly higher number of next neighbor jumps, which seems to explain most of the reason why GPDC has a higher ionic conductivity than PDC or GDC. The current KLMC calculations present a novel approach to study doubly doped ceria, as so far the theoretical results for ceria-based materials have been limited to mono-doped ceria.

1. Introduction

Solid oxide fuel cells (SOFCs) are an efficient, combustion-less, pollution-free power source, and are promising for both stationary and mobile applications (auxiliary power sources). Identifying the best electrolyte material is imperative for the development of next generation SOFCs. As a result, several new electrolyte materials for SOFCs have been proposed. Among these materials, doped ceria is recognized as one of the most promising solid electrolyte materials for the operation of SOFCs in the intermediate temperature range, 773 K to 1073 K.¹ A brief overview regarding the role of lanthanide-doped ceria as a potential candidate for electrolyte materials in SOFCs is presented in our previous papers ^{2,3,4} and references therein.

In the last decade, ceria mixed with more than one aliovalent dopant has received major attention. One proposed mechanism for the observed improvements in conductivity is that the co-dopant suppresses the ordering of the oxygen vacancies, which will decrease the activation energy for oxygen vacancy diffusion leading to an increase in oxygen-ion conductivity.^{1,5,6} Another proposed mechanism is that the binding enthalpy of the oxygen vacancies and dopant ions will be lowered, leading to higher ionic conductivity.⁷ A few other favorable effects that might be observed due to the addition of co-dopants are increase in configurational entropy, steric changes (due to the presence of larger co-dopants ions, some of the vacancy migration pathways are more favorable) and modification in grain boundary composition.⁷ As singly doped GDC is considered as one of the most promising electrolyte material for SOFCs,^{2,8,9,10} a general practice involved in synthesizing double doped ceria has been to use GDC and a small amount of a co-dopant, such as- Sm,^{5,6,7,11,12,14} Ca,¹³ Pr,^{14,16,17,18,19,20}

Nd,^{7,11,12,14,15} Y,⁷ Bi,^{11,12} La^{11,12,14} and Mg¹⁵ etc. Samarium-doped ceria (SDC), which exhibits high oxygen ion conductivity, has also been mixed with other co-dopants including Ca,¹³ Sr,²¹ Pr,²² Mg¹⁵ and Nd^{15,23} to maximize the ionic conductivity. In most cases doubly doped ceria has a somewhat higher ionic conductivity compared to singly doped ceria. Nevertheless, controversial results on the effect of co-dopants have been reported¹ and the mechanism(s) by which the co-dopants affect ionic conductivity has not been well understood.

Computational studies have investigated the effect of one aliovalent dopant on the oxygen-ion conductivity in doped ceria, but there has not been an investigation of the effect of co-dopants. A detailed survey of the computational studies involving singly doped ceria can be found elsewhere.^{2,3} In the past, we performed a systematic study for predicting the optimal dopant concentration for maximum conductivity in GDC^{2,8} and PDC.^{3,4} GDC and PDC are well known for their applications as electrolyte materials, and experimental reports suggest that Pr used as a co-dopant in GDC increases the ionic conductivity.^{16,18} It has been claimed that the addition of Pr to GDC decreases the grain boundary resistance leading to an increase in conductivity as Pr reduces the segregation of Gd₂O₃ at the grain boundaries.¹⁶ On the contrary, another report claims that the addition of Pr as a co-dopant to GDC increases the tendency for segregation of rare-earth dopants at the grain boundaries, which may have a positive effect on the electrochemical activity.²⁰ Two independent studies have found that Pr co-dopant in GDC resulted in somewhat decreased electronic conductivity,^{18,19} but two other studies did not find such an effect.^{14,17}

In light of the conflicting experimental reports of the effect of Pr co-dopant in GDC, it would be valuable to computationally investigate the effect of Pr as a co-dopant to GDC. Moreover, density functional theory (DFT) calculations have predicted that a combination of Gd/Pr dopants should lead to an ionic conductivity that is higher than either of them alone.²⁴ Furthermore, it is critical to predict the optimal operating temperature range of various electrolyte materials used in SOFCs. Hence, our current effort is not just aimed at finding materials that show higher conductivity, but also to predict the temperature ranges in which they show optimum behavior.

We have developed and applied a KLMC model for mono-doped ceria to predict the optimal dopant content in PDC⁴ and GDC.⁸ The model uses as input the oxygen vacancy diffusion data obtained from DFT+*U* calculations for PDC³ and GDC.² In this article, we used a slightly modified KLMC model that can include two dopants, and present KLMC results for ionic conductivity in GPDC, as a function of dopant concentration, dopant ratio, and temperature. Details of the KLMC vacancy-repelling model for mono- doped ceria can be found elsewhere.⁴ The current KLMC simulations were conducted using the activation energies for oxygen vacancy migration in GDC² and PDC³ calculated using DFT+*U*.

2. Computational Methodology

KLMC simulations based on a set of kinetic atomic-scale processes can describe the evolution of mesoscopic systems up to macroscopic times. In this way, we have developed a 3-D KLMC model of vacancy diffusion in GPDC. In the KLMC model, all atoms are assumed to occupy lattice sites that coincides with the local potential minimum with a potential barrier, E_{xy} , separating the adjacent lattice sites. The only

meaningful events in KLMC simulations are those involving transfer or exchange of atoms from one lattice site to another. In this paper we focus on a vacancy diffusion mechanism, wherein we only track the oxygen vacancies, and assume all other sites are occupied. In events where $E_{xy} \ll k_BT$, the transition rate of a vacancy moving from lattice site *x* to *y* is evaluated by the hopping mechanism governed by the Arrhenius Law:

$$q_{xy} = v_{xy} e^{(-E_{xy}/k_BT)} \quad (1)$$

where, v_{xy} represents the attempt frequency for an atom hopping from lattice site *x* to *y*. This model will further enable us to calculate ionic conductivity in GPDC as a function of temperature, dopant and co-dopant content. Most of the vacancies in ceria-doped materials are generated to maintain the charge balance due to the addition of aliovalent dopants. For instance, the addition of Gd⁺³ or Pr⁺³ to CeO₂ results in an oxygen vacancy for every two ionized dopants (since the stoichiometric vacancy to dopant ratio is 0.5). The KLMC model uses the calculated activation energies for oxygen vacancy migration along distinct pathways (Figure 1) in GDC and PDC, which can be found elsewhere.^{2,3} In this article, the uncertainty in calculated energies using DFT+*U* is \approx 10 meV. For GDC, the oxygen vacancy prefers a first nearest neighbor (1NN) site to the dopant ion,² whereas for PDC,³ it prefers the 2NN site. This means that many types of jump events need to be included (1NN \rightarrow 2NN, 2NN \rightarrow 1NN, 2NN \rightarrow 2NN, 2NN \rightarrow 3NN, etc.) to properly model the complexity of diffusional processes in GPDC (Figure 1).

The KLMC model comprises a number of ordered events which take place in a sequence as detailed in our earlier work [4]. In the KLMC model, vacancies are picked randomly and allowed to move one by one in a random jump direction. The acceptance criterion of the jumping vacancy is governed by equation 1, which is influenced by the local environment and simulation temperature. Furthermore, in the KLMC vacancy-repelling model, the vacancies are not allowed to move adjacent (1NN) to any other vacancies in the simulation cell, nor into an existing vacancy. We computed the mean square displacement of all the vacancies in the simulation cell (accounting for crossing periodic boundaries) and used the results to calculate the diffusion coefficient of oxygen vacancies as follows:

(2)
$$D_{v} = \lim_{t \to \infty} \sum_{i=1}^{N} \frac{|R_{i}(t) - R_{i}(0)|^{2}}{6t}$$

where *t* is the sum of all the time steps Δt , for each jump event and $R_i(t)$ is the position of the *i*th vacancy at time *t*. Here, $|R_i(t) - R_i(0)|^2$ is the mean square displacement of the vacancy. The time step (seconds) is chosen small enough so that no more than one jump event will occur, on average, for the fastest event in the system. During that time step, every vacancy in the system has the possibility of executing a single jump, based on the rate of the jump event which is randomly chosen. Following the computation of oxygen vacancy diffusion coefficient (cm²/s), the ionic conductivity (S/cm) was calculated using the Nernst-Einstein relation given as

$$\sigma_i = \frac{D_v C_i (qe)^2}{k_B T} \quad (3)$$

where σ_i is the ionic conductivity, C_i is the concentration of ionic carriers (vacancies for the present case) and *qe* their charge.

Further details of the current methodology and a flowchart outlining the working of the KLMC vacancy-repelling model are given in our previous work.⁴ All the results presented in this article are generated using the KLMC vacancy-repelling model, but the term KLMC will be used henceforth for brevity. For GPDC, we used a 10×10×10 cell (consisting of 12,000 sites) built from a conventional 12-atom cubic unit cell of ceria using the theoretically optimized lattice constant of 0.5494 nm for bulk ceria.^{2,3} Among these 12,000 positions, 4,000 are available for cation dopant placement, which are assumed to be immobile. The vacancies are formed on the oxygen sublattice consisting of 8,000 sites, and are allowed to hop to adjacent sites, subject to certain constraints, such as vacancy repelling factor and the hopping mechanism governed by Arrhenius law. The simulation cell was repeated periodically along the three axes to simulate a 3-D lattice of effectively infinite extent. The dopant and vacancy concentration were varied in order to maintain a stoichiometric vacancy to dopant ratio of 0.5, as all the dopant ions are assumed to be trivalent. This assumption is appropriate for Gd, but at equilibrium, Pr reportedly exists in roughly equal concentration of Pr³⁺ and Pr⁴⁺. This will be explained in detail in the results section, but throughout the simulations, all the dopants used are trivalent i.e. Pr³⁺ and Gd³⁺.

For every composition, ten simulations were performed, each with a different dopant distribution, with approximately 1,000,000 or more jump events for each configuration. This resulted in achieving a statistical average with a precision of $\approx 2 \%$ for various dopant concentrations. The slight discrepancy in the results obtained using

ten different initial configurations are shown in Figure 2 by the use of error bars. Considering the difference of the order of ≈ 2 % in ionic conductivity for the simulations involved, the sampling did not require additional runs for each configuration. The simulations were performed for temperatures ranging from 773 K to 1073 K and approximately equal diffusion distances were used to calculate the final diffusion coefficients.

The current simulations are performed using the KLMC vacancy-repelling model. This model was developed to incorporate the effect of vacancy repelling in ceria related materials.^{4,8} The three different classes of GPDC i.e. (i) Gd-rich (ii) Pr-rich and (iii) equal Gd-Pr, are studied to establish a general preference for co-dopants and understand the mechanism which leads to a particular composition exhibiting improved oxygen ion conductivity. For all cases considered, Gd-rich GPDC corresponds to 75 % Gd and 25 % Pr content of the total dopant content. Similarly, Pr-rich GPDC corresponds to 75 % Gd content, and equal Gd-Pr GPDC corresponds to 50 % Pr and 50 % Gd content of the total dopant content. For instance, if the total dopant content is 0.20 mole fraction, then Gd-rich, Pr-rich and equal Gd-Pr GPDC can be expressed as Ce_{0.80}Gd_{0.15}Pr_{0.05}O_{1.90}, Ce_{0.80}Gd_{0.05}Pr_{0.15}O_{1.90} and Ce_{0.80}Gd_{0.10}Pr_{0.10}O_{1.90}, respectively.

The KLMC model used for doubly doped GPDC assumes that every additional Gd/Pr dopant ion in the vicinity of the migrating vacancy will have an additive effect towards the activation energy for vacancy migration. This assumption is similar to the one involved in simulating GDC⁸ and PDC.⁴ This is a reasonable first-order approximation that greatly simplifies the complexity of the problem. Previous studies have shown that the effect of dopants on oxygen vacancy migration is reasonably linear

for the two dopants individually,^{2,3} so the same trend for co-dopants should be reliable to approximately 10 meV, especially at lower dopant concentrations. We have not explicitly calculated the activation energies for oxygen vacancy migration in presence of two different species of dopant ions, i.e. Gd and Pr, but instead, have used equation 4 for computing the change in activation energies.

$$\Delta \mathsf{E} = \Delta \mathsf{E}_{\mathsf{Gd}}(\mathsf{NN} \Longrightarrow \mathsf{NN}) + \Delta \mathsf{E}_{\mathsf{Pr}}(\mathsf{NN} \Longrightarrow \mathsf{NN}) \tag{4}$$

$$\Delta \mathsf{E}_{\mathsf{Gd}(i\mathsf{NN} \Longrightarrow j\mathsf{NN})} = \mathsf{E}_{\mathsf{Gd}(i\mathsf{NN} \Longrightarrow j\mathsf{NN})} - \mathsf{E}_{\mathsf{Bulk}}$$
(5)

$$\Delta \mathsf{E}_{\mathsf{Pr}(i\mathsf{NN} \Longrightarrow j\mathsf{NN})} = \mathsf{E}_{\mathsf{Pr}(i\mathsf{NN} \Longrightarrow j\mathsf{NN})} - \mathsf{E}_{\mathsf{Bulk}} \tag{6}$$

where i and j are the nearest neighbor positions with respect to the dopant ion. E_{Gd} and E_{Pr} are the activation energies for the vacancy migrating from i to j with respect to the dopant ion and E_{Bulk} is the bulk migration energy in pure ceria. For example, let's assume that an oxygen vacancy is positioned at 1NN to a Gd ion and 2NN to a Pr ion. If this vacancy is moving away towards a position that is 1NN to the Pr ion and 2NN to the Gd ion, the change in activation energy can be summed as $\Delta E_{Gd}(1\rightarrow 2) + \Delta E_{Pr}(2\rightarrow 1)$. Due to the above assumption, we do not require recalculating the activation energies for vacancy migration in presence of Pr and Gd in the same supercell using first-principles as those calculated for GDC^{2,8} and PDC^{3,4} are adequate.

3. Results

Figure 2 shows the variations in ionic conductivity as a function of total dopant and co-dopant content in the three classes of GPDC, Gd-rich, Pr-rich and equal Gd-Pr, using the KLMC model, for temperatures ranging from 773 K to 1073 K. Small error bars in Figure 2 correspond to the slight difference in the results obtained using ten different initial configuration for each dopant concentration. The small error bars also illustrate that the final diffusion coefficient for a given dopant concentration is independent of the initial dopant arrangement. For comparison, ionic conductivity data for GDC⁸ and PDC⁴ at respective temperatures are also included. For all temperatures and all compositions, the ionic conductivity initially increases with dopant concentration, since higher dopant concentration results in higher vacancy concentration, and then decreases. The decrease in ionic conductivity after reaching a maximum can be attributed to (i) increase in binding of vacancies to dopants, (ii) vacancy-vacancy repulsion, resulting in fewer available sites for the vacancies to migrate to.^{4,8}

At 1073 K (Figure 2(a)), Gd-rich and equal Gd-Pr exhibit a maximum in conductivity at 0.25 total mole fraction, whereas Pr-rich exhibit a maximum at 0.20 total mole fraction of dopant content. At the same total dopant content, mono-doped GDC and PDC show lower conductivity. The calculated conductivity for equal Gd-Pr material falls between Gd-rich and Pr-rich, showing superior performance of Gd-rich materials at 1073 K.

Pr is known to have mixed valence at atmospheric pressure and hence an equilibrium between Pr^{4+} and Pr^{3+} exists determined by the temperature and oxygen pressure.^{25,26,27} Hence, only approximately half of the dopant ions are Pr^{3+} . This condition ensures that almost twice the Pr dopant content will be required to generate a reasonable oxygen vacancy concentration and for achieving maximum conductivity.⁴ For instance, an effective 0.20 mole fraction of dopant content in Pr-rich GPDC will essentially require \approx 0.35 mole fraction of total dopant content. Not only will the material cost increase due to the high dopant content but it can also be unstable due to a

possible departure from the fluorite phase. Moreover, PDC is claimed to have mixed electronic and ionic conductivity that is advantageous for anode materials and membranes for oxygen separation, but is not very useful for application as an electrolyte material.^{25,28,29} These could be some of the possible reasons why most of the experiments predicting the properties of electrolyte materials are performed for materials with small addition of Pr co-dopant in GDC^{14,16,17,18,19,20} rather than Gd as co-dopant in PDC.

At 973 K (Figure 2(b)) and 873 K (Figure 2(C)), the trend in maxima for the calculated conductivity for the different classes of GPDC is similar to the one observed at 1073 K. At these temperatures, Gd-rich GPDC exhibits the maximum conductivity among the different classes of GPDC, and in comparison with GDC and PDC. But, the net increase in the absolute value of conductivity for the different classes of GPDC, compared to PDC and GDC, slowly decreases from 1073 K to 873 K. Also, at 873 K, the highest conductivity is calculated for Gd-rich followed by Pr-rich and equal Gd-Pr. This is in contrast with the results at 1073 K and 973 K, wherein Pr-rich material was found to exhibit a lower conductivity than equal Gd-Pr.

At 773 K (Figure 2(d)), the results are slightly different than those at higher temperatures. Among the different classes of GPDC, Pr-rich exhibits maximum conductivity, followed by Gd-rich and equal Gd-Pr, but the difference in the absolute value of conductivity is negligible. Furthermore, all classes of GPDC show slightly lower conductivity than singly doped PDC. For Pr-rich and equal Gd-Pr, 0.20 total mole fraction of dopant content shows maximum conductivity, whereas for Gd-rich the optimal content is 0.25 mole fraction. For the temperatures ranging from 1073 K to 873

K, one consistent behavior observed is that the doubly doped Gd-rich exhibits higher conductivity in comparison to single doped GDC and PDC. At 773 K, Gd-rich GPDC exhibits higher conductivity than GDC, but slightly lower in comparison to PDC.

4. Discussion

The most favorable position for oxygen vacancy formation depends on the type of dopant ion, i.e. 1NN position is favorable in GDC² and 2NN position is favorable in PDC.³ Depending on the preference of vacancy formation, the most favorable vacancy migration pathway in GDC is 1NN \rightarrow 2NN, whereas that in PDC is 2NN \rightarrow 1NN. A comparative analysis of the various migration pathways traced by oxygen vacancies in GPDC, GDC and PDC provide a reasonable description of the conducting pathways and help us identify the reasons for the change in conductivity due to the addition of codopants. The percent (%) difference in various migration pathways (as showed in Figure 1) traversed by vacancies during the KLMC simulations for GPDC (Gd-rich, Pr-rich and Equal Gd-Pr) in comparison with GDC and PDC at 1073 K are listed in Table 1. In mono-doped ceria (GDC/PDC), the pathway XNN \rightarrow YNN corresponds to a vacancy migrating from XNN to YNN with respect to one particular dopant (Gd/Pr) ion, whereas in GPDC, it corresponds to the cumulative effect of the presence of both Gd and Pr ions. For instance, in GPDC, the final value for 1NN \rightarrow 1NN jumps traversed by a vacancy near Gd and Pr ion is calculated by adding the total number of 1NN \rightarrow 1NN jumps near both, the Gd and Pr ion. The total mole fraction of dopant content is kept fixed at 0.20 mole fraction for all the materials. The analysis is performed using data for \approx 1,000,000 jump events to provide a valid comparison.

In Gd-rich GPDC, there is a 7 % decrease in the total number of 1NN \rightarrow 1NN jumps as compared to GDC. This is due to the presence of larger Pr co-dopant in Gdrich GPDC, near which a 1NN \rightarrow 1NN jump is less probable due to the higher activation energy (0.78 eV) required as compared to GDC (0.59 eV). The other migration paths in GPDC, more importantly the 1NN \rightarrow 2NN and 2NN \rightarrow 1NN are traversed more than those in GDC, which leads to higher conductivity in co-doped materials. This shows that for the same total mole fraction of dopant content, in Gd-rich GPDC, the minimum energy pathways increases, due to the presence of Pr ions, leading to higher conductivity. One of the numerous possible situations arising due to the presence of codopants is portrayed in Figure 3, where two similar arrangements are presented for GDC (Figure 3(a)) and Gd-rich GPDC (Figure 3(b)). For GDC, the change in vacancy migration energy along the paths E_{ab} and E_{ac} are -0.08 eV and 0.05 eV, respectively. For a similar case, if one of the Gd ions is substituted by a Pr ion, the vacancy migration energy along the paths E_{ab} and E_{ac} are -0.17 eV and -0.04 eV, respectively. This decrease in activation energies can be attributed to the presence of dissimilar favorable migration pathways in the presence of Gd and Pr ions. Due to the presence of both types of dopant, one preferred the 1NN position to a vacancy and the other the 2NN, therefore the number of minimum energy pathways increased. We wish to point out that this is just one of the many possible cases where a vacancy is in the vicinity of two different dopant ions. In reality, there could be several different dopants ions and vacancies present in the material at any instant. Also, there could be other possible arrangements where the activation energy barriers might be lower in GDC as compared to Gd-rich GPDC. But in terms of describing the average behavior for long time

diffusion, the presence of these minimum energy pathways is more likely in the double doped ceria.

In addition to the jump analysis for Gd-rich co-doped ceria, listed in Table 1, is the data for Pr-rich and equal Gd-Pr. A similar trend as observed for Gd-rich, is found to be true for Pr-rich and equal Gd-Pr GPDC. In conclusion, the number of $1NN \rightarrow 2NN$ and $2NN \rightarrow 1NN$ jumps increases in all the three classes of GPDC in comparison to GDC and PDC. The number of $1NN \rightarrow 1NN$ jumps primarily depends on the Gd and Pr content in the co-doped material. The higher the amount of Pr content, the lower are the number of $1NN \rightarrow 1NN$ jumps and the higher the amount of Gd content, the higher the number of $1NN \rightarrow 1NN$ jumps. The numbers of jumps along most of the migration pathways in all the three classes of GPDC are found to increase in comparison to GDC and PDC, which lead to the increase in conductivity in double doped ceria.

5. Comparison with experiment

The current results obtained using KLMC simulations predicting the increase in conductivity in Gd-rich GPDC are in qualitative agreement with two experimental studies for double doped $Ce_{0.80}Gd_{0.20-x}Pr_xO_{1.90}$ (x = 0.01, 0.02, 0.03,¹⁶ x = 0.01, 0.03, 0.06,¹⁸ and x = 0.02¹⁹), where Pr addition was found to increase conductivity, but disagree with one set of experiments which did not find an increase (Kim *et al.*¹⁴ for $Ce_{0.80}Gd_{0.20-x}Pr_xO_{1.90}$, (x = 0.01, 0.03, 0.05)). There is no experimental data available for Pr-rich or equal Gd-Pr. For PDC and GDC, previous results of the KLMC model found reasonable agreement with experimental results.^{2,8}

Figure 4 shows ionic conductivity values as a function of inverse temperature for the three different classes of GPDC. For comparison, the data for GDC and PDC are

also included. The total mole fraction of dopant content is fixed at 0.20 for all the materials. The Arrhenius type behavior of the ionic conductivity for these materials is visible with all KLMC data lying on a straight line. No experimental results are included in the plot as most of the experiments are performed at very low co-dopant concentration. Moreover, we have performed simulations for three broad categories of GPDC to elucidate the general behavior of these materials and evaluate the effect of co-dopants. We have calculated the average activation energy for the three classes of GPDC with a total mole fraction of dopant content of 0.20. The calculated activation energies for Gd-rich, Pr-rich and equal Gd-Pr are 0.43 eV, 0.40 eV and 0.42 eV, respectively. The corresponding values for GDC⁸ and PDC⁴ are 0.46 and 0.40 eV respectively. The calculated decrease in average activation energy for Gd-rich GPDC in comparison with GDC is in qualitative agreement with the experimental findings where addition of small amount of Pr in GDC leads to a decrease in activation energy.¹⁶ Another study reported no significant change in activation energy.¹⁸ This slight decrease in activation energy has a minor effect towards increasing the conductivity in Gd-rich GPDC as compared with GDC. Moreover, similar to the results observed for GDC⁸ and PDC,⁴ the average activation energies in all the three classes of GPDC increased slightly with the increase in total mole fraction of dopant content.

4. Conclusions

Double doped ceria has been studied using KLMC simulations to comprehend the effect of co-dopants in increasing the conductivity of mono-doped ceria. KLMC model developed in this work for double doped ceria is an extension of our previous work on mono-doped ceria. Three different classes of GPDC were studied; (i) Gd rich

(ii) Pr rich and (iii) equal Gd-Pr content, to ensure an exhaustive search for identifying the best combination. The three classes of GPDC show a maximum in conductivity at \approx 0.20 to 0.25 mole fraction of total dopant content. Gd-rich GPDC is found to be the most promising due to its higher conductivity in comparison to GDC, which is one of the most widely used electrolyte materials in SOFCs and due to the practical applications of Gd-rich GPDC. A detailed analysis of the various types of jump events revealed that the migration paths $1NN \rightarrow 2NN$ and $2NN \rightarrow 1NN$ are traversed more in double doped ceria as compared to GDC and PDC, which contribute towards higher conductivity. In future, the novel KLMC model developed for double doped ceria can be used for investigating the role of other lanthanide co-dopants in ceria-based materials.

Acknowledgements

This paper is based upon the work supported by the Department of Energy under the Grant No. DE-PS02-06ER06-17. The authors gratefully acknowledge the Fulton High Performance Computing Initiative (HPCI) at the Arizona State University for the computational resources. P.P.D wishes to thank Shahriar Anwar for stimulating discussions.

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Table 1. The percent (%) difference in various migration pathways traced by vacancies during the KLMC simulations for GPDC (Gd-rich, Pr-rich and Equal Gd-Pr) in comparison with GDC and PDC at 1073 K. The total mole fraction of dopant content of 0.20 was kept fixed for all the cases. For the different pathways, a positive (+) or negative (-) sign implies that GPDC has x % more or x % less jumps respectively, in comparison to the mono-doped ceria. The given numbers are approximate as the analyzed data is averaged over 10 simulation runs with each simulation being performed for \approx 1000,000 jumps. The vacancies never traversed along the pathways 1NN \rightarrow 3NN and 3NN \rightarrow 1NN. The activation energies (eV) for vacancy migration in GDC and PDC are provided. The activation energy for vacancy migration in undoped ceria is 0.47 eV.

Migration pathway	GDC (eV)	PDC (eV)	Gd-rich		Pr-rich		Equal Gd-Pr	
			vs. GDC	vs. PDC	vs. GDC	vs. PDC	vs. GDC	vs. PDC
$1NN \rightarrow 1NN$	0.59	0.78	- 7 %	+ 90 %	- 62 %	+ 75 %	- 35 %	+ 86 %
1NN → 2NN	0.50	0.41	+ 13 %	+9%	+ 11 %	+6%	+ 12 %	+7%
$2NN \rightarrow 1NN$	0.36	0.43	+ 13 %	+9%	+ 11 %	+6%	+ 12 %	+7%
$2NN \rightarrow 2NN$	0.48	0.47	+ 22 %	- 20 %	+ 35 %	- 4 %	+ 33 %	- 8 %
$2NN \rightarrow 3NN$	0.49	0.57	+ 20 %	+ 23 %	+7%	+ 11 %	+ 16 %	+ 18 %
$3NN \rightarrow 2NN$	0.46	0.44	+ 21 %	+ 19 %	+ 11 %	+9%	+ 18 %	+ 15 %
3NN → 3NN	0.47	0.47	+ 14 %	+ 24 %	+ 5 %	+7%	+ 11 %	+ 19 %



Figure 1. Top view of a $2\times2\times2$ GPDC supercell. The blue, red, green and pink balls represent Ce, O, Gd and Pr ions, respectively. Black box corresponds to an oxygen vacancy. Numbers 1, 2 and 3 represent 1NN, 2NN and 3NN oxygen ions with respect to the Gd ion, respectively. (X, Y) represents an oxygen vacancy jump from XNN to YNN with respect to the Gd ion. Similar jumps can be drawn with respect to Pr ion.



Figure 2. Calculated ionic conductivity in Gd-rich, Pr-rich and Equal Gd-Pr GPDC as a function of total dopant content for temperature range 1073 K to 773 K. For comparison, data for GDC [8] and PDC [4] generated using KLMC model is also shown. (a) 1073 K.



(b) 973 K



(c) 873 K



(d) 773 K



Figure 3. Calculated activation energies for oxygen vacancy migration along two of the possible migration pathways in (a) GDC, $E_{ab} = -0.08$ eV and $E_{ac} = 0.05$ eV (b) GPDC, $E_{ab} = -0.17$ eV and $E_{ac} = -0.04$ eV. Here, E_{ab} and E_{ac} are the activation energies required for vacancy to move from positions *a* to *b* and *a* to *c* respectively.



Figure 4. Plot showing the Arrhenius behavior of calculated ionic conductivities for the three different classes of GPDC. Data for GDC [8] and PDC [4] are also included for comparison. The data is for 20 % total mole fraction of dopant content. No error bars are shown as they are indistinguishable due to the scale of y-axis.