Optimizing oxygen diffusion in cathode materials for solid oxide fuel cells

A. I. Chroneos[1,2], D. Parfitt[2]

department of Materials Science and Metallurgy, University of Cambridge,
Cambridge CB2 3QZ, United Kingdom
Department of Materials, Imperial College London,
London SW7 2AZ, United Kingdom

Recent investigations have revealed that the Ruddlesden-Popper series ($A_{n+1}B_nO_{3n+1}$) and the layered perovskite $LnBaCo_2O_5+s$ (Ln = rare-earth cations) are promising as cathodes for intermediate temperature solid oxide fuel cells. For these to be economical the oxygen diffusion must be maximized. In the present investigation we propose strategies for optimizing oxygen diffusion in these materials by modifying the oxygen stoichiometry, the composition and cation disorder.
Keywords: $LnBa_{1-x}Sr_xCo_2O_5+s$; Molecular dynamics; Oxygen migration; Anisotropy

Introduction

Solid Oxide Fuel Cell (SOFC) technology is characterized by the potential for high efficiency energy conversion in conjunction with reduced emission of green house gases compared to other more traditional power generation routes [1-16]. An active field of research is aiming at lowering the operating temperature of SOFCs to the intermediate temperature range (500-700) °C [1]. This operating temperature range will result in more economic SOFCs, however, it is necessary to maintain their performance. The key is to improve the catalytic activity of cathode materials as these can become a significant source of electric losses at lower temperatures [2,3]. The main factors affecting cathode performance is the high electronic conductivity, the surface exchange rate and the oxygen diffusion coefficient [4,5]. The development of novel cathode materials has focused on perovskite-related materials such as the first members of the Ruddlesden-Popper (RP) series (i.e. A_2BO_4) [6-8], and the layered perovskite $LnBaCo_2O_5+s$ (Ln = rare-earth cations) [9-12].

Molecular dynamics (MD) simulations enable the calculation of the energetic of diffusion (i.e. activation energy of diffusion and diffusivity of ions) as well as the mechanism of diffusion of complex systems, which are difficult to investigate experimentally [17,18]. The aim of the present study is to identify how oxygen diffusion in cathode materials can be maximized by varying the oxygen stoichiometry, the composition and cation disorder. Paradigms include the first members of the RP series (A2BO4) and the archetypal double perovskite, $GdBaCo_2O_5+s$.

Methodology

Classical MD simulations were used in the Born description of the ionic crystal lattice [19]. Ions interact via simple short-range parameterised pair potentials and the long range Coulombic interactions are summed using the Ewald method [20]. The short range interactions were described using parameterised Buckingham potentials [21], which were previously established by comparison to experimental work [18,2224]. The DL POLY simulation package was used for all the calculations [25]. For the $GdBaCo_2O_5+s$, initial configurations we used 8 x 8 x 4 supercells for the high temperature phase to give a total
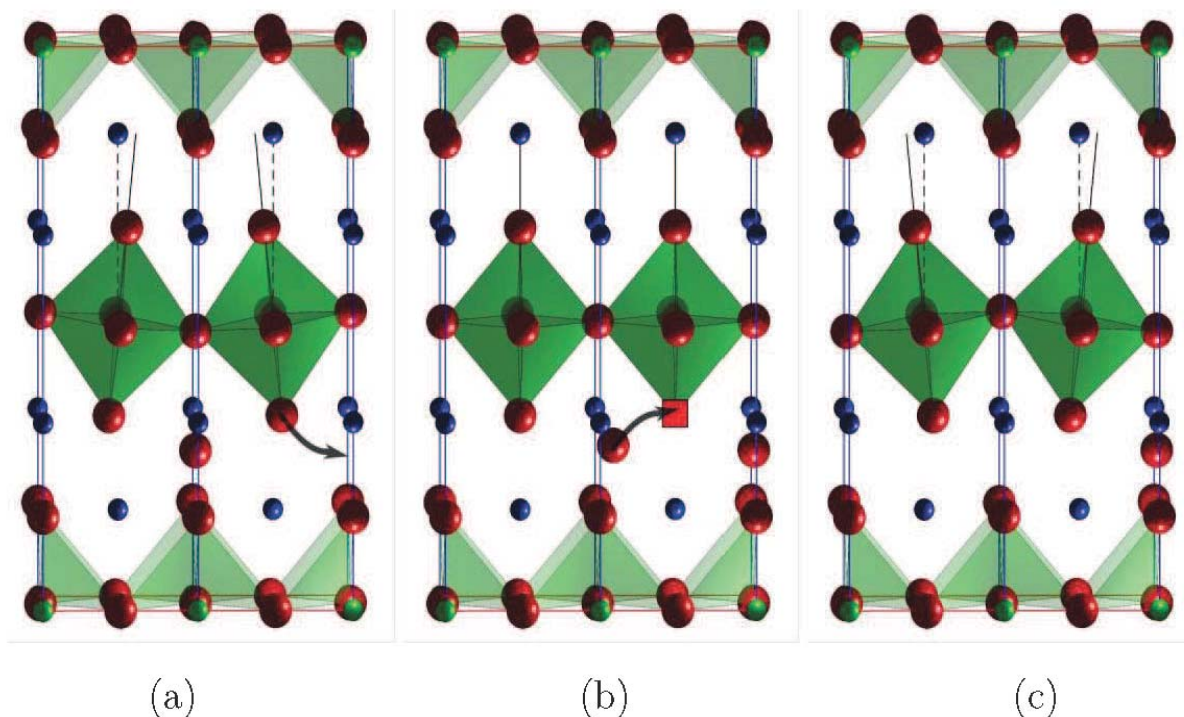
Fig. 1 Characteristic snapshots of the oxygen (red spheres) interstitialcy diffusion mechanism predicted by MD calculations for the diffusion of Pr2NiO4+8. Praseodymium ions are represented by blue spheres, the oxygen vacancy by a red square, nickel-oxygen polyhedral in green.

of around 5000 ions. The partial occupancy of the oxygen sites was handled by taking an appropriately sized random sample of fractionally occupied oxygen sites in each layer. To predict the oxygen diffusion mechanism, stoichiometrics of 8 = 0.5 were studied in a wide temperature range (T = 800-1400K). Initial calculations were performed for 10000 timesteps with the atoms coupled to a barostat allowing the cell parameters to change at each timestep. Thereafter, a further 10000 timesteps were performed under constant volume conditions to allow the cell to come into equilibrium at the new volume. Data collection runs were restarted from these final simulations and lasted for 10 ps to ensure adequate statistical sampling. The temperature and pressure were corrected using the Nose-Hoover Thermostat [26,27].

Results and discussion

MD simulations clarified the landscape regarding oxygen ion diffusion in the RP materials La_2NiO_{4+8}, Pr_2NiO_{4+8} and La_2CoO_{4+8}. It was calculated that oxygen migrates via a highly anisotropic interstitialcy mechanism in the a-b planes (refer to Figure 1) [8,28-30]. This is consistent with the recent ToF-SIMS results of Sayers et al. [31] for oxygen transport in $La_2NiO_4+_8$ with an activation energy of 0.54 eV again in excellent agreement with the MD results (0.51 eV, Ref. 8). Parfitt et al. [28] calculated the oxygen activation energy of $Pr_2NiO_{4+}S$ over a range of hyperstoichiometries. These results were again in excellent agreement with the experimental work of Boehm

Table 1. Activation energies of oxygen self-diffusion in $A_2BO_{4+\delta}$.

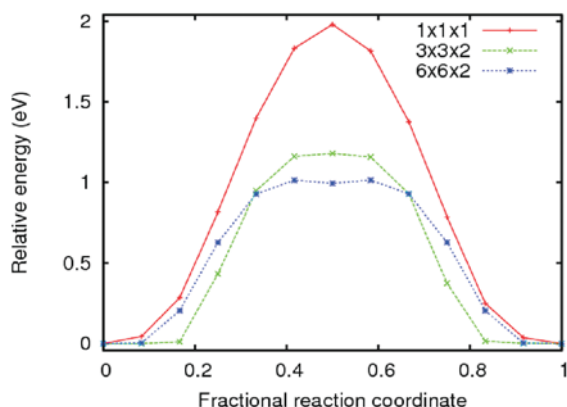| Material	E_a (eV)	Methodology	Comment	Reference
$La_2CoO_{4+\delta}$	0.73–0.80	DFT	Interstitialcy mechanism	29
$La_2CoO_{4+\delta}$	0.31	MD	Interstitialcy mechanism	29
$Pr_2NiO_{4+\delta}$	0.49–0.64	MD	Interstitialcy mechanism	28
$Pr_2NiO_{4+\delta}$	0.6	Experimental	Interstitialcy mechanism	6
$La_2NiO_{4+\delta}$	0.51	MD	Interstitialcy mechanism	8
$La_2NiO_{4+\delta}$	0.54	Experimental	Polycrystal, TOF-SIMS	31

Fig. 2. Relative energies of each nudged elastic band image showing the variation of calculated transition barrier for a single oxygen interstitial as a function of supercell size. The start and end points of the pathway are at the same minimised structure for each supercell and are offset to zero energy.

et al. [6] (Table 1). The MD work of Parfitt et al. [28] highlights that the activation energy of oxygen migration is strongly dependent upon the degree of hyperstoichiometry ranging from 0.49eV (for δ = 0.025) to 0.64 eV (for δ = 0.20)]. The oxygen diffusivity, D, at a temperature T can be described by, $D = [Oi] f \exp(-Em/kBT)$. This links D with the concentration of oxygen interstitials, [Oi] and the energy barrier to migration, Em [28]. f is the correlation factor and kB is Boltzmann's constant [28]. The rise of $[O_i]$ will result in a rapid increase of the diffusivity and this is not surprising as it is the interstitials that mediate

the oxygen diffusion process in these materials [28-31]. At high enough $[O_i]$ (here $\delta \sim 0.02$, [28]) the diffusivity levels off. This is due to the rise in the effective migration barrier due to the increased formation energy of oxygen interstitials (because of the presence of other pre-existing neighbouring interstitials). This leads to the stiffening of the lattice as the NiO6 sub-lattice is pinned as a consequence of the additional oxygen interstitials. This reduces the ease with which the NiO_6 octahedra tilt to accommodate the diffusion of oxygen ions (see Figure 1). We tested this by performing static and atomistic simulations in conjunction with the nudged elastic band method for $La_2CoO_4+_\delta$ another promising RP compound (Figure 2) [29,32].

In Figure 2 we show the results of the interstitialcy mechanism calculated for a single oxygen interstitial for varying tessellations of the original tetragonal unit cell. Defect-defect interactions are significant in these layered compounds; this is both a result of Coulomb repulsion between oxygen interstiatials and the interaction of strain fields surrounding the defects. Figure 2 demonstrates that the migration energy barrier depends quite strongly upon the concentration of oxygen interstitials. For the higher [Oi] (smaller cell, 1x1x1, Figure 2) the migration energy is about double compared to the migration energy of the larger cells (6x6x2, Figure 2).

In ordered $GdBaCo_2O_5+_\delta$ the activation energy was calculated to be 0.5 eV (for T = 800-1400 K). This is in excellent agreement with the determined value of 0.6 eV that was obtained by using isotopic exchange techniques in the temperature range 600K to 1000K [9,32]. Notably
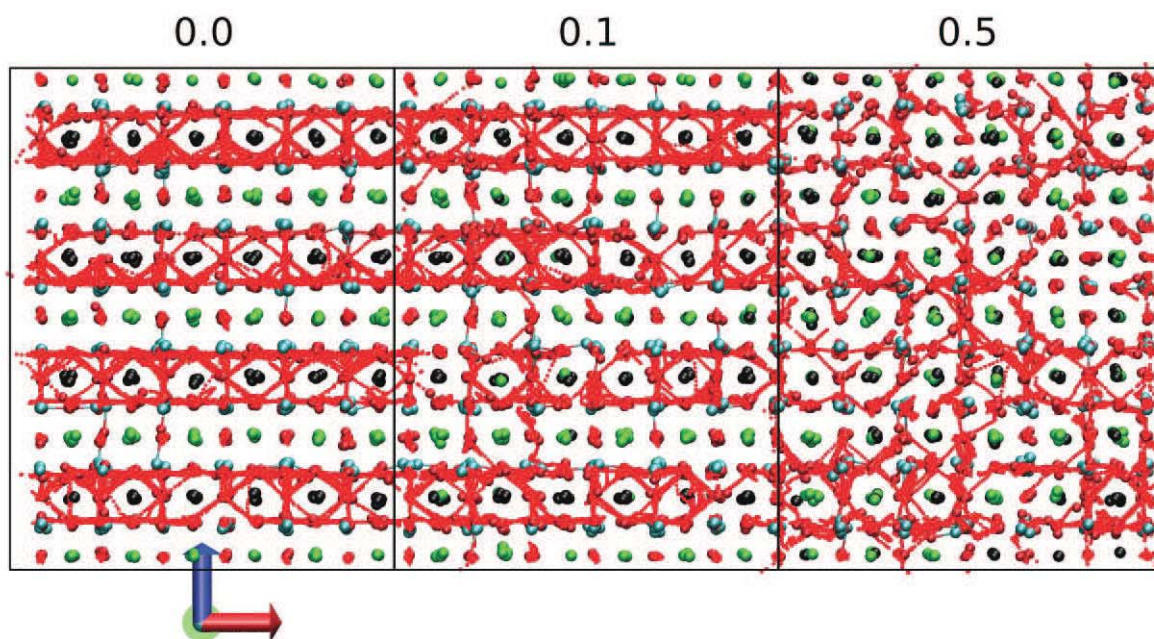

Fig.3. The impact of disorder in the Gd/Ba sublattice on the oxygen diffusion mechanism in $GdBaCo_2O_{55}$. For no disorder in the Gd/Ba sublattice (i.e. F = 0.0) diffusion is anisotropic and prevalent in the ab-plane, whereas as disorder increases case (i.e. from F = 0.1 to F = 0.5) diffusion is becoming more isotropic.

the high temperature tetragonal phase of $GdBaCo_2O_5+_\delta$ exhibits a highly anisotropic oxygen diffusion long the a-b plane [33]. This is facilitated by oxygen vacancies consistently with experimental results [9].

In $GdBaCo_2O_5+_\delta$ there is antisite disorder between the Gd and Ba cations. This can be quantified via a parameter F = $[Gd_{Ba}]/([Gd_{Ba}]+[Gd_{Gd}])$, which represents the probability of finding a Gd ion on a Ba site. Here [MN] represents the concentration of M ions on an N site. The fully disordered case corresponds to F = 0.5 in which there is a 50% probability of either site being occupied by a Gd or Ba ion. Conversely for the fully ordered case F = 0.

Figure 3 schematically illustrates the effect of cation disorder upon the oxygen diffusion mechanism for ordered (F = 0) and as disorder increases (i.e. from F = 0.1 to F = 0.5) $GdBaCo_2O_{5+\delta}$. It is evident that the formation of cation disordered defects leads to migration pathways along the c-axis and thus the increase of disorder results to the reduction of anisotropy of oxygen diffusion in $GdBaCo_2O_5+_\delta$. Interestingly for F = 0.5 there is a decrease in the oxygen diffusivity and the diffusion mechanism is almost isotropic. This can appear to be counterintuitive as it would be anticipated that order in the oxygen sublattice would be consistent with order in the cation sublattice as they are interknitted in each other in an oxide. This would in turn imply that cation sublattice ordered oxides would have limited oxygen diffusion. Interestingly, Norby [34] has previously investigated these issues and calculated that there are oxides with cation order and anion disorder, which demonstrate high oxygen diffusivities. The key is that in the disordered oxides defect trapping can lower the measured diffusivity. In a recent static atomistic simulation study by Seymour et al. [35] it was calculated that there is significant defect trapping between oxygen vacancies and Ba in a Ln site antisites in $LnBaCo_2Os_+\delta S$ (where Ln = rare-earth) double perovskites. This in turn may lower the diffusivity. As the levels of cation disorder are important, experimental conditions such as sample preparation and thermal history can be very used to tune the anisotropy of the material.

Other issues need to be also considered when selecting materials for SOFC cathodes. Notably, Kim et al. [11] propose the application of intermediate rare-earth cations such as samarium to avoid the decrease in the thermal expansion coefficient, which can be associated with the smaller rare-earth cations. Substituting barium with strontium in $GdBaCo_2O_5+_\delta$ leads to $GdBa_{1-x}Sr_xCo_2O_5+_\delta$, which has an increased oxygen content [12]. These substitutions may also affect the diffusion properties and are presently under investigation.

Conclusions

To conclude, atomic scale modelling is valble in the optimisation and design of cathode materials for SOFC.

In the RP series the composition influences high oxygen diffusion, with $La_2CoO_4+_\delta$ having the lowest activation energy of diffusion. In these materials the increase of the oxygen hyperstoichiometry (i.e. the oxygen interstitials that mediate diffusion) also affect the energetics of oxygen transport. This effect, however, soon levels-off as the hyperstoichiometry is increased. In $GdBaCo_2O_5+_\delta$ and related compounds cation disorder is of critical importance not only for the energetics of diffusion but also for the diffusion mechanism. The more disordered the material the more isotropic oxygen transport will become. As a design criterion we need an ordered GdBaCo2O5+δ to optimise the oxygen diffusion. A second design criterion valid for all the materials considered here is that we need to grow crystals along the ab-plane to optimise the oxygen diffusion properties. Investigations are in progress to quantify the impact of cation disorder on the oxygen diffusivity in GdBaCo2O5+δ and to clarify further the energetics of oxygen self-diffusion in La2CoO4+δ.

1. B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345.

2. J. Fleig, Ann. Rev. Mater. Res. 33 (2003) 361.

3. Z. Shao, S.M. Haile, J. Ahn, P.D. Ronney, Z. Zhan, S.A. Barnett, Nature 435 (2005) 3676.

4. S.B. Adler, J.A. Lane, B.C.H. Steele, J. Electrochem. Soc. 143 (1996) 3554.

5. S.B. Adler, Solid State Ionics 111 (1998) 125.

6. E. Boehm, J.M. Bassat, P. Dordor, F. Mauvy, J.C. Grenier, Ph. Stevens, Solid State Ionics 176 (2005) 2717.

7. M. Burriel, G. Garcia, J. Santiso, J.A. Kilner, R.J. Chater, S.J. Skinner, J. Mater. Chem. 18 (2008) 416.

8. A. Chroneos, D. Parfitt, J.A. Kilner, R. W. Grimes, J. Mater. Chem. 20 (2010) 266.

9. A. Tarancon, S.J. Skinner, R.J. Chater, F. Hernandez-Ramirez, J.A. Kilner, J. Mater. Chem. 17 (2007) 3175.

10. C.J. Zhu, X.M. Liu, C.S. Yi, D. Yan, W.H. Su, J. Power Sources 185 (2008) 193.

11. J.H. Kim, A. Manthiran, J. Electrochem. Soc. 155 (2008) B385.

12. J.H. Kim, F. Prado, A. Manthiran, J. Electrochem. Soc. 155 (2008) B1023.

13. A.A. Taskin, A.N. Lavrov, Y. Ando, Appl. Phys. Lett. 86 (2005) 91910.

14. D.J. Liu, J. Almer, Appl. Phys. Lett. 94 (2009) 224106.

15. J. Hermet, G. Geneste, G. Dezanneau, Appl. Phys. Lett. 97 (2010) 174102.

16. A. Aguadero, J.A. Alonso, R. Martinez-Coronado, M.J. Martinez-Lope, M.T. Fernandez-Diaz, J. Appl. Phys. 109 (2011) 034907.

17. G.N. Mazo, S.N. Savvin, Solid State Ionics 175 (2004) 371.

18. D. Rupasov, A. Chroneos, D. Parfitt, J.A. Kilner, R.W. Grimes, S.Ya. Istomin, E.V. Antipov, Phys. Rev. B 79 (2009)

172102.

19. M. Born, J.E. Mayer, Z. Phys. 75 (1932) 1.

20. P.P. Ewald, Ann. Phys. 64 (1921) 253.

21. R.A. Buckingham, Proc. Royal Soc. London Series A, Math. Phys. Sci. 168 (1938) 264.

22. R.W. Grimes, D.J. Binks, A.B. Lidiard, Philos. Mag. A 72 (1995) 651.

23. R.W. Grimes, G. Busker, M.A. McCoy, A. Chroneos, J.A. Kilner, S. P. Chen, Ber. Bunsenges. Phys. Chem. 101 (1997) 1204.

24. M.R. Levy, C.R. Stanek, A. Chroneos, R.W. Grimes, Solid State Sci. 9 (2007) 588.

25. W. Smith, T.R. Forester, J. Mol. Graphics 14 (1996) 136.

26. S. Nose, J. Chem. Phys. 81 (1984) 511.

27. W.G. Hoover, Phys. Rev. A 31 91985) 1695.

28. D. Parfitt, A. Chroneos, J.A. Kilner, R.W. Grimes, Phys. Chem. Chem. Phys. 12 (2010) 6834.

29. A. Kushima, D. Parfitt, A. Chroneos, B. Yildiz, J.A. Kilner, R.W. Grimes, Phys. Chem. Chem. Phys. In press.

30. E.N. Naumovich, V.V. Kharton, J. Molec. Struct.: THEOCHEM 946 (2010) 57.

31. R. Sayers, R.A. De Souza, J.A. Kilner, S.J. Skinner, Solid State Ionics 181 (2010) 386.

32. C.N. Munnings, S.J. Skinner, G. Amow, P.S. Whitfield, I.J. Davidson, Solid State Ionics 176 (2005) 1895.

33. D. Parfitt, A. Chroneos, A. Tarancon, J.A. Kilner, J. Mater. Chem. In press.

34. T. Norby, J. Mater. Chem. 11 (2001) 11.

35. I. Seymour, A. Chroneos, J.A. Kilner, R.W. Grimes unpublished results.