Correlating oxygen mobility with thermochemical CO₂-splitting efficiency in A-site substituted manganite perovskites

Mahesh Muraleedharan Nair^a and Stéphane Abanades^{a*}

The effect of lattice geometric parameters of perovskite oxides on thermochemical redox CO₂-splitting process was highlighted. Experimentally-derived amounts of O₂ and CO evolved were found to correlate with critical radius per unit cell volume (Rc.u) and specific free volume (V_{F,s}) respectively, in a series of phase pure A-site substituted perovskites. These findings demonstrate the possibility to design new oxygen carrier materials based on geometric parameters while predicting their CO₂-splitting activity during two-step cycles.

Thermochemical redox processes for solar fuel production from H₂O and CO₂ splitting are recently emerging as one promising approach to harvest and store solar energy.¹⁻⁶ Concentrated solar heat captured using specific optical devices is used to drive high temperature multi-step endothermal reactions enabling H₂ production, CO₂ conversion or biomass gasification. Development of cost-effective, efficient, and stable oxygen carriers is a major requirement for such processes to act as redox intermediates for the storage and transport of oxygen. To date, CeO₂ is considered as the state-of-the-art material and alternative materials exhibiting superior performance are strongly desired.^{1,3} Owing to their enhanced compositional flexibility, perovskite-structured mixed oxides (ABO₃) are receiving tremendous attention.⁴⁻⁸ Stringent efforts are ongoing to identify optimum perovskite formulations with noteworthy redox performance and enhanced thermal stability. In the ABO₃ structure, the A-site is usually occupied by a lanthanide, alkali metal or alkaline earth metal, and the B-site by a transition metal. In general, the B-site mostly governs the activity of the material whereas the A-site composition contributes towards structural stability aspects. Studies so far concerning thermochemical redox processes clearly indicate that manganese is the most preferred B-site cation whereas for A-site, a combination of lanthanum with calcium, strontium or barium can be suitable.⁴⁻⁹

Since the perovskite structure can partially or completely accommodate a large number of metal cations, studies are still

necessary to further advance the development of adequate oxygen carrier materials with commercial relevance. Trial and error-based evaluations of all possible combinations of cations in the ABO₃ structure are rather time and energy consuming. In parallel to ongoing sophisticated computational investigations, developing simple design methods based on correlating experimental data with structural and compositional parameters can be a convenient approach.⁴ For instance, calculated values of transition metal electronegativities were recently found to be correlated with the oxygen storage capacity of a series of perovskite oxides.¹⁰

As far as oxygen carriers are concerned, facile surface-bulk oxygen ion mobility is one pre-requisite. Cook *et al.* and Sammells *et al.* previously suggested two empirical parameters named critical radius (Rc) and lattice free volumes (V_F) as representative metrics for oxygen mobility in perovskites.^{11,12} Even though perovskite structure can accommodate a large number of metallic elements substitutions, only a few of them were found to be practically efficient for thermochemical two-step CO₂ splitting. Limited reduction/re-oxidation extents, poor kinetics, irreversible phase changes, or carbonate formation under representative experimental conditions are the major hurdles.⁶⁻⁹ In this work, four perovskite oxides with varying A-site composition were synthesized. The thermochemical oxygen release capacity and CO₂ splitting efficiency of the synthetic La_{0.5}Sr_{0.5}MnO₃ (LSM), La_{0.5}Ca_{0.5}MnO₃ (LCM), La_{0.5}Ba_{0.5}MnO₃ (LBM), and Y_{0.5}Sr_{0.5}MnO₃ (YSM) oxygen carriers were then evaluated. The suitability of the aforementioned geometrical parameters (Rc and V_F) to effectively correlate the amounts of O₂/CO evolved and the respective reaction rates was investigated.

All the materials used in this study were synthesized by following the conventional solid-state method. Precursors (SrCO₃, BaO, CaO, La₂O₃, and MnO₂) in appropriate amounts according to the desired perovskite composition were ground **Fig. 1** Powder X-ray diffraction (XRD) patterns in the wide-angle region for A-site substituted perovskite oxygen carriers used in this study. All the materials were calcined at 1500 °C.

and calcined at 1000 °C. In order to ensure the formation of the desired phase, the materials were recovered, ground well and subjected to an additional annealing step at 1500 °C under air, for two hours. The calcination temperature being higher than the reaction temperature (1400 °C) warrants suitable structural and phase stability during the reaction. The

^a Processes, Materials and Solar Energy Laboratory, PROMES-CNRS (UPR 8521), 7 Rue du Four Solaire 66120, Font-Romeu, France.

E-mail: Stephane.Abanades@promes.cnrs.fr

Tel: +33-(0)4-68-30-77-30

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formation, purity, and crystallinity of the desired perovskite phase were determined by carrying out X-ray diffraction (XRD) analysis. The obtained XRD profiles are given in Fig. 1 and all the observed reflection peaks in the wide-angle region can be assigned to the characteristic perovskite structure. Minor variations in observed peak positions can be attributed to variations in the cationic composition. Absence of additional peaks indicates that the presence of secondary phases, if any, was negligible below the detection limit. Average crystallite sizes were then calculated using Scherrer equation and no significant variations were evidenced from the obtained values (Table S1), thus confirming structure stabilization during the synthesis.

Thermochemical redox experiments were carried out by thermogravimetric analysis (TGA, SETARAM SETSYS Evolution device) for high precision quantification of redox activity. Oxide mass variations during reduction and re-oxidation steps were monitored continuously as a function of time over approximately 100 mg of perovskites. The resultant mass evolution profiles are shown in Fig. S1. Ideally, the overall reaction takes place in two steps as shown in eqns (1) and (2).^{6,7,13}

Oxygen release experiments were conducted at a temperature of 1400 °C (with a heating rate of 20 °C.min⁻¹) for all the materials. The amounts of O₂ released are compiled in Table S1. As evidenced by the resulting oxygen evolution profiles shown in Fig. 2(a) and Fig. S2(a), a clear influence of the A-site composition was observed on the amount of oxygen evolved and the reaction rate. A combination of lanthanum and barium was found to be the least effective whereas a combination of yttrium and strontium exhibited superior

Fig. 2

Thermochemical O₂ (a) and CO (b) evolution profiles for A-site substituted perovskite oxygen carriers used in this study. O₂ release experiments were conducted at 1400 °C and CO release experiments were conducted at 1050 °C. The dashed line in (a) represents the variation in temperature during heating (20 °C.min⁻¹) up to 1400°C.

performance for oxygen release. The maximum values of reaction rates were obtained by performing numerical differentiation of the oxygen evolution profiles. Similar to the amounts of O₂ evolved, the values of O₂-releasing rates were also found to depend on the variations in the A-site composition. The partially reduced perovskite oxides were further re-oxidized using CO₂ as an oxidant at 1050 °C (isothermal) and the resultant amounts of CO produced are given in Table S1. The observed trends in CO evolution and oxidation reaction rates were different from those observed during the O₂ evolution step. If the amount of O₂ evolved during reduction was playing a decisive role, YSM should exhibit maximum efficiency for CO₂ splitting. In contrast, YSM exhibited the lowest extent of re-oxidation with extremely low values for both CO evolved and re-oxidation rate. A maximum amount of CO evolution was observed in the case of LSM, along with a higher oxidation rate. The performance of LBM and LCM was found to be intermediate. The resultant CO evolution profiles along with reaction rates are provided in Fig. 2(b) and Fig. S2(b). It can be concluded that different parameters influence the thermochemical reduction and re-oxidation reactions in perovskites.

Enhancing surface/bulk oxygen mobility while maintaining the overall crystal structure is an important aspect of redox reactions involving non-stoichiometric oxides. In the materials used in this study, B-site cation remains unchanged (Mn), along with the method of synthesis and calcination temperature. Therefore, the observed trends on O₂/CO

Fig. 3 Evolution of (a) O₂ and (b) reduction rate as a function of critical radius per unit cell volume for A-site substituted perovskite oxygen carriers

evolution can be solely attributed to the variations in A-site composition. In other words, the geometrical defects put forward by the changes in A-site composition can promote or hinder the surface/bulk mobility of oxygen ions, thereby controlling the redox activity of the oxygen carriers. Such effects were previously found to influence the ion conductivity in perovskites.¹⁴⁻¹⁷ Moreover, the energy profiles of the ion migration paths can be crucial. The anion (O²⁻) migration in perovskites follows a vacancy mechanism involving the octahedral edge sites.¹⁸⁻²⁰ It was previously shown that the anion migration takes place through a saddle point formed by a triangle comprising two A-site cations and one B-site cation.¹⁸⁻²² The radius of the imaginary circle encompassing the space in between is called critical radius (Rc). Anions with radius smaller than Rc, will pass through without any barrier. In general, the higher the value of critical radius, the smaller will be the activation energy of ion migration.

Critical radius is dependent on the cation radii and can be calculated using the following equations:

$$[3/4a_0^2 - R_A^2 + R_B^2 - \sqrt{2}a_0R_B] / [2(R_A - R_B) + \sqrt{2}a_0] \quad (3)$$

$$a_0 = 2.15R_B + 2.47 - 1.40(S^{-1} - 1) \quad (4)$$

where R_A and R_B are the radii of cations, a_0 is the pseudo cubic lattice parameter and S is the tolerance factor.^{11,12,14,21,22} Ionic radii used for calculations were directly taken from Shannon.²³ The calculated Rc values for the four perovskite oxygen carriers used in the present study were found to be between 1.4-1.5 Å. Since the radius of O²⁻ ion is smaller (1.35 Å) than the obtained Rc values, facile surface-bulk transport of oxygen ions can be expected during reduction and re-oxidation steps.

However, the observed correlations for the Rc values with the amounts of O₂ evolved and the reduction rates were found to decrease with an increase in critical radius Fig. S3. This result contradicts the generally accepted fact that an increase in critical radius facilitates ion transport in perovskites.^{12,14,21} Possibly, Rc value itself cannot explain the thermochemical oxygen release trends observed in the reduction reaction. As the next step, the contribution of critical radius per unit cell volume (Rc.u) was deduced for all the materials used in this study. Interestingly, both the amounts of O₂ evolved and the reaction rates correlate well with this parameter in this case, as shown in Fig. 3. Thus, rather than the value of Rc, the value of Rc.u seems to be an appropriate descriptor that effectively portray the thermochemical reduction behaviour of A-site substituted perovskite oxygen carriers. Critical radius actually represents a 3D spherical region in the oxide lattice.²¹ Therefore, it is reasonable to assume that a portion of that region identified by the unit cell volume can reflect the oxygen transport. Similar efforts were made to elucidate the influence of Rc and Rc.u on the amounts of CO evolved and the re-oxidation rate. Unfortunately, neither of these parameters successfully described the observed re-oxidation trends for the series of materials used in this study (Fig. S4 and Fig. S5).

The migration of oxide ions also depends on the volume of free space in the lattice facilitating transport.^{11,12,14-16} The free volume (V_F) can be defined as the difference between the total unit cell volume and the volume occupied by the atoms constituting the lattice. The availability of a larger free space can lower the activation energy of ion transport. The experimentally obtained values of O₂ evolved were plotted as a function of calculated values of V_F . Here again, the observed correlation was in the reverse order indicating that smaller values of V_F facilitate lattice O₂ release (Fig. S6). Furthermore, the values of specific free volumes ($V_{F,S}$), defined as the free volume per unit cell volume, were obtained. However, similar unreasonable trends for O₂ release were also observed in this case (Fig. S7). Even though the amounts of CO evolved during re-oxidation were found to increase with an increase in V_F , the overall correlations were found to be poor (Fig. S8). Further analysis clearly indicated that specific free volume can play a more decisive role during re-oxidation. In this case, excellent trends and correlations were observed for $V_{F,S}$ with the amount of CO evolved and re-oxidation rate (Fig. 4). In other words, the variations in specific free volume can depict the re-oxidation tendencies of perovskite oxygen carriers in presence of CO₂. Hayashi *et al.* previously reported specific free volume as a measure of ion mobility in perovskites.¹⁵

Several effects can contribute to the reversed trend observed in the case of Rc. Probably, there exists a threshold value for critical radius, beyond which other factors take over. For instance, changes in oxygen stoichiometry, existence of an unusual valence in the B-site, vacancy concentration, lattice polarizability, etc, can arise with substitution of A-site. To confirm this statement, more A-site substituted perovskites would need to be studied. However, the practical suitability

Fig. 4 Evolution of (a) CO and (b) re-oxidation rate as a function of specific free volume for A-site substituted perovskite oxygen carriers.

and relevance of such possible formulations in thermochemical CO_2 conversion was previously ruled out as mentioned before and hence, other relevant A-site cation substitutions need to be identified for this application.

Perovskite oxides are well known for their versatility and ability to accommodate a large number of elements substituted in varying proportions in their lattice. Even though deviations from ideal cubic structure are inevitable, the resultant orthorhombic, rhombohedral, etc, variants exhibit excellent structural stability, as required for a variety of applications. Among these, only limited ones are known to overcome the efficiency and thermochemical stability issues concerning solar thermal CO_2 conversion. To propose a simple performance descriptor for CO_2 conversion, the redox properties of four A-site substituted perovskites were studied. The effect of critical radius per unit cell volume ($R_{c.u}$) was found to be dominant during thermal reduction. On the other hand, specific free volume ($V_{F.S}$) played a decisive role during CO_2 -induced re-oxidation. Overall, geometrical variance induced by the variations in perovskite composition can influence the thermochemical redox properties of these materials. It is to be noted that thermochemical solar redox cycles involve material exposure to extreme temperatures ($> 1000^\circ\text{C}$). Under these conditions, adequate materials must preserve their microstructure and morphology during cyclic operation. Ion diffusion mechanisms, reversibility and thermochemical stability need to be optimized to maintain reactivity of the oxygen carriers for several redox cycles. Therefore, additional effects such as sintering may pose serious morphological stability issues in the long run and are to be managed separately. The design of adequate oxygen carrier materials thus remains challenging. The geometric parameters considered in this study ($R_{c.u}$ and $V_{F.S}$) offer a more

customized initial selection of perovskites to be used as oxygen carriers in thermochemical redox processes. This method represents an attractive tool for the design of robust oxygen carriers and can be used to predict their redox activity in two-step cycles, provided the additional thermal stability concerns are successfully overcome. Further work is necessary to deduce nature of relationships existing between the lattice geometry and the thermochemical redox efficiency of perovskites. A more challenging task will be to utilize such parameters to predict the possible stability concerns (e.g.: irreversible phase changes). Such valuable insights can aid in developing robust oxygen carriers for practical applications in solar thermochemical energy utilization.

Author contributions

Conceptualization, M.M.N. and S.A.; data curation, M.M.N. and S.A.; formal analysis, M.M.N. and S.A.; investigation, M.M.N. and S.A.; methodology, M.M.N. and S.A.; project administration, S.A.; supervision, S.A.; validation, M.M.N. and S.A.; visualization, M.M.N.; writing original draft, M.M.N.; writing review and editing, S.A.

Conflict of interests

The authors declare no conflict of interests. References

- W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile, A. Steinfeld, *Science*, 2010, **330**, 1797.
- C. L. Muhich, B. W. Evanko, K. C. Weston, P. Litchy, X. Liang, J. Martinek, C. B. Musgrave, A. W. Weimer, *Science*, 2013, **341**, 540.
- P. Furler, J. R. Scheffe, A. Steinfeld, *Energy Environ. Sci.*, 2012, **5**, 6098.
- J. Vieten, B. Bulfin, P. Huck, M. Horton, D. Guban, L. Zhu, Y. Lu, K. A. Persson, M. Roeb, C. Sattler, *Energy Environ. Sci.*, 2019, **12**, 1369.
- A. H. McDaniel, E. C. Miller, D. Arifin, A. Ambrosini, E. N. Coker, R. O'Hayre, W. C. Chueh, J. Tong, *Energy Environ. Sci.*, 2013, **6**, 2424.
- M. Kubicek, A. H. Bork, J. L. M. Rupp, *J. Mater. Chem. A*, 2017, **5**, 11983.
- M. M. Nair, S. Abanades, *Sustainable Energy Fuels*, 2018, **2**, 843.
- M. M. Nair, S. Abanades, *Energy Technol.*, 2021, **9**, 2000885.
- A. Demont, S. Abanades, *J. Mater. Chem. A*, 2015, **3**, 3536.
- L. Liu, D. D. Taylor, E. E. Rodriguez, M. R. Zachariah, *Chem. Commun.*, 2016, **52**, 10369.
- R. L. Cook, A. F. Sammells, *Solid State Ionics*, 1991, **45**, 311.
- A. F. Sammells, R. L. Cook, J. H. White, J. J. Osborne, R. C. MacDuff, *Solid State Ionics*, 1992, **52**, 111.
- M. M. Nair, S. Abanades, *ChemistrySelect*, 2016, **1**, 4449.
- S. Li, W. Jin, P. Huang, N. Xu, J. Shi, *Ind. Eng. Chem. Res.*, 1999, **38**, 2963.
- H. Hayashi, H. Inaba, M. Matsuyama, N. G. Lan, M. Dokiya, H. Tagawa, *Solid State Ionics*, 1999, **122**, 1.
- M. Mogensen, D. Lybye, N. Bonanos, P. V. Hendriksen, F. W. Poulsen, *Solid State Ionics*, 2004, **174**, 279.
- H. He, X. Huang, L. Chen, *Electrochim. Acta*, 2001, **46**, 2871.

- 18 M. S. Islam, M. Cherry, C. R. A. Catlow, *J. Solid State Chem.*, 1996, **124**, 230.
- 19 M. Cherry, M. S. Islam, C. R. A. Catlow, *J. Solid State Chem.*, 1995, **118**, 125
- 20 J. A. Kilner, P. Barrow, R. J. Brook, *J. Power Sources*, 1978, **3**, 67.
- 21 J. A. Kilner, R. J. Brook, *Solid State Ionics*, 1982, **6**, 237.
- 22 N. Xu, H. Zhao, X. Zhou, W. Wei, X. Lu, W. Ding, F. Li, *Int. J. Hydrogen Energy*, 2010, **35**, 7295.
- 23 R. D. Shannon, *Acta Crystallogr. A*, 1976, **A32**, 751.