Structural and thermodynamic study of Ca A- or Co B-site substituted \( \text{SrFeO}_3-\delta \) perovskites for low temperature chemical looping applications†

Giancarlo Luongo, Felix Donat and Christoph R. Müller

Perovskite-structured materials, owing to their chemical–physical properties and tuneable composition, have extended their range of applications to chemical looping processes, in which lattice oxygen provides the oxygen needed for chemical reactions omitting the use of co-fed gaseous oxidants. To optimise their oxygen donating behaviour to the specific application a fundamental understanding of the reduction/oxidation characteristics of perovskite structured oxides and their manipulation through the introduction of dopants is key. In this study, we investigate the structural and oxygen desorption/sorption properties of \( \text{Sr}_{1-x}\text{Ca}_x\text{FeO}_3-\delta \) and \( \text{SrFe}_{1-y}\text{Co}_y\text{O}_3-\delta \) (\( 0 \leq x \leq 1 \)) to guide the design of more effective oxygen carriers for chemical looping applications at low temperatures (i.e. 400–600 °C). Ca A- or Co B-site substituted \( \text{SrFeO}_3-\delta \) show an increased reducibility, resulting in a higher oxygen capacity at \( T \leq 600 \) °C when compared to the unsubstituted sample. The quantitative assessment of the thermodynamic properties (partial molar enthalpy and entropy of vacancy formation) confirms a reduced enthalpy of vacancy formation upon substitution in this temperature range (i.e. 400–600 °C). Among the examined samples, \( \text{Sr}_{0.5}\text{Ca}_{0.5}\text{FeO}_3-\delta \) exhibited the highest oxygen storage capacity (2.15 wt%) at 500 °C, complemented by excellent redox and structural stability over 100 cycles. The thermodynamic assessment, supported by in situ XRD measurements, revealed that the oxygen release occurs with a phase transition perovskite-brownmillerite below 770 °C, while the perovskite structure remains stable above 770 °C.

Although CAS is a very mature technology for the production of \( \text{O}_2 \) technoeconomic studies of oxy-fuel combustion estimate that conventional CAS (specific power consumption of 0.24 kW h kg\( \text{O}_2 \)^{−1}) consumes ~10% of the net oxy-fuel thermal power plant output and represents in addition ~40% of the total equipment costs. \(^{10-13}\) A potentially more cost-efficient method to produce pure \( \text{O}_2 \) is chemical looping air separation (CLAS), which dates back to the original Brin process. \(^{14}\) The CLAS process utilises metal oxides (referred to as oxygen carriers, OCs) capable of releasing gas phase \( \text{O}_2 \) at elevated temperatures (up to 1000 °C). \(^{9,15,16}\) The CLAS process consists of two steps that occur in a cyclic fashion: first, \( \text{O}_2 \) is released (uncoupling, reaction (1) by the metal oxide. Each metal oxide, \( \text{Me}_x\text{O}_y \), possesses an equilibrium \( \text{O}_2 \) partial pressure (\( p\text{O}_2,\text{eq} \)) for a given temperature at which the transition to a lower oxidation state, \( \text{Me}_x\text{O}_{y-2} \), occurs. Gaseous \( \text{O}_2 \) is thus released when the \( \text{O}_2 \) partial pressure (\( p\text{O}_2 \)) in the given environment is lower than the respective thermodynamic equilibrium value (i.e. \( p\text{O}_2,\text{eq} \)). The metal oxide is regenerated (reaction 2) at lower temperatures and/or higher \( p\text{O}_2 \) (typically using air).

\[
\text{Me}_x\text{O}_y(s) \rightarrow \text{Me}_x\text{O}_{y-2}(s) + \text{O}_2(g) \quad (1)
\]

\[
\text{Me}_x\text{O}_{y-2}(s) + \text{O}_2(g) \rightarrow \text{Me}_x\text{O}_y(s) \quad (2)
\]
A series of experimental and techno-economic modelling studies have suggested that CLAS could produce O₂ at 40–70% lower costs than CAS. In fact, power costs for CLAS at an industrial scale have been estimated to be as low as 0.06 kWh/kgO₂, against the benchmark 0.24 kWh/kgO₂ of a conventional cryogenic system.

A key challenge for CLAS is finding OCs with suitable thermodynamic properties. The pO₂,eq, the reaction enthalpy of a given OC and its oxygen storage capacity (OSC) largely determine its suitability for CLAS. For example, low values (<1 wt%) of the OSC (defined as the mass of redox-active lattice O₂ of an OC divided by the total mass of the OC) imply that an OC would have to be regenerated (eqn (2)) more frequently in a given time compared to an OC with a high OSC. Further, the OC should have a stable reactivity over multiple redox cycles, besides being low cost and environmentally friendly. Typical OCs that have been demonstrated to be conceptually suitable for CLAS are based on the monometallic transition metal oxides CuO, Co₃O₄ or MnO₂. Transition metal oxides often require high temperatures (up to 1000 °C) to release gaseous O₂. Under operation, metal oxides may thus reach temperatures close to their melting points, leading to sintering and in turn a decline in their redox activity and stability. To mitigate sintering, the metal oxide is often stabilized by an inert support, e.g. calcium aluminate.

To lower the energy costs of the CLAS processes further, it is desirable to identify metal oxides with suitable thermodynamic properties (reaction enthalpy and pO₂,eq) that are capable of releasing O₂ at lower temperatures than typical CLOU temperatures, i.e. in the range 400–600 °C. However, operation at such temperatures may reduce the rates of the redox reactions, implying larger system volumes (and in increased capital costs) of the CLAS process. An interesting class of materials that determine its suitability for CLAS is one of the most extensively investigated perovskites but in spite of a reasonably high OSC of ~1 wt% it undergoes an irreversible phase transformation to Ca₂MnO₄ and CaMn₂O₄ when exposed to repeated cycles of air and N₂ at high temperatures (i.e. T = 1170 °C), as these two latter phases are thermodynamically more stable than the parent CaMnO₃ under the given operating conditions. The phase transition from perovskite to spinel is accompanied by a gradual decrease of the OSC, which makes such compositions unattractive for industrial applications.

From an application point of view, OCs must possess excellent structural stability and reactivity. CaMnO₃, for example, is one of the most extensively investigated perovskites but in spite of a reasonably high OSC of ~1 wt% it undergoes an irreversible phase transformation to Ca₂MnO₄ and CaMn₂O₄ when exposed to repeated cycles of air and N₂ at high temperatures (i.e. T = 1170 °C), as these two latter phases are thermodynamically more stable than the parent CaMnO₃ under the given operating conditions. The phase transition from perovskite to spinel is accompanied by a gradual decrease of the OSC, which makes such compositions unattractive for industrial applications.

Among the large number of possible non-stoichiometric oxides, strontium and iron-based perovskites have been identified as suitable OCs for low-temperature applications. For example, Miura et al. found that A-site substitution of the SrFeO₃ system by Ca improves the OSC when operating cyclically between 5% O₂ and air, identifying Sr₀.₇₆Ca₀.₂₄FeO₃₋δ with an OSC of 1.1 wt% at 550 °C as an attractive OC (the OSC of the undoped SrFeO₃₋δ was only 0.6 wt%). In addition, substitution of the B-site of SrFeO₃ with Co was investigated by Ikeda et al. and they found that the substitution of 85% of Fe with Co allows the release of O₂ at temperatures as low as 300 °C instead of 600 °C for the unsubstituted SrFeO₃₋δ. Dou et al. recently showed that the A- and B-site co-substitution in SrFeO₃ of Sr and Fe by Ca and Co, respectively, lowers the activation energy of oxygen diffusion and surface oxygen exchange i.e. faster redox kinetics compared to the unsubstituted perovskite. In particular, they found that Sr₀.₈Ca₀.₄Fe₀.₂O₃₋δ releases 1.2 wt% at 400 °C, even under when the pO₂ was relatively high (i.e. 0.05 atm).
As outlined above, the thermodynamic properties of the OC play an important role in the design of the CLAS process and the identification of the optimal working conditions. Although Sr1−xCaFeO3−δ and SrFe1−xCo3−δ perovskites have been shown to possess promising chemical-physical properties, thermodynamic data for such materials is scarce or non-existent albeit critical for process modelling and further material optimisation.

Motivated by the promising results reported by Miura et al. and Ikeda et al., we focused in our study on the thermodynamic and structural analysis of Ca A-site or Co B-site substituted SrFeO3 (Sr1−xCaFeO3−δ and SrFe1−xCo3−δ, 0 ≤ x ≤ 1) aiming at elucidating changes in the chemical-physical properties (i.e. OSC, thermodynamics, structural stability) upon substitution. This work shall provide guidelines for the design of more effective OCs for chemical looping applications at low temperatures.

The selected ones resulted in partially molten samples. Sr1−xCaFeO3−δ and SrFe2−xCo0.8O3−δ was individuated as the most promising OC for CLAS application due to its ability to release a high amount of O2 (OSC of 1.1 wt%) at temperatures as low as 500 °C, while among the Co-substituted perovskites, SrFe0.2Co0.8O3−δ was individuated as the most promising OC for CLAS application due to its ability to release a high amount of O2 (OSC of 1.1 wt%) at 500 °C in atmospheres containing as much as 5% O2.

2. Experimental methods
Synthesis of the oxygen carriers
Sr1−xCaFeO3−δ and SrFe1−xCo3−δ (0 ≤ x ≤ 1) materials were synthesised by dissolving stoichiometric amounts of Sr(NO3)2 (Sigma Aldrich, ACS reagent, 99.9%), Fe(NO3)3·9H2O (Sigma Aldrich, ACS reagent, ≥98%) and Ca(NO3)2·4H2O (Sigma Aldrich, 99%) or Co(NO3)2·6H2O (Sigma Aldrich, 99%) in deionised water together with citric acid (3:1 molar ratio of citric acid to metal ions) and ethylene glycol (1:2:1 molar ratio of ethylene glycol to citric acid). The solution was heated to 80 °C and held at this temperature until a gel formed. The gel was dried at 130 °C for 10 h in an oven and subsequently crushed to a fine powder. The powder was calcined in air in two steps: the first calcination step was performed with a heating rate of 3 °C min−1 and holding at 500 °C for 7 h. The second calcination step was performed with a heating rate of 5 °C min−1 and holding at 1000 °C (for Sr1−xCaFeO3−δ) or 1200 °C (for SrFe1−xCo3−δ) for 10 h. Calculation temperatures higher than the selected ones resulted in partially molten samples.

Characterisation
All gases used in this study were provided by Carbagas from cylinders (grade 5.0) and thus contained small quantities of impurities, such as ~10 ppm O2 in N2. The flow rates of gas were measured and controlled at normal temperature and pressure (NTP) using mass flow controllers (Bronkhorst EL-Flow).

X-ray powder diffraction (XRD). X-ray diffractograms of the materials were collected using a PANalytical Empyrean X-ray powder diffractometer equipped with a X’Celerator Scientific ultra-fast line detector and Bragg–Brentano HD incident beam optics using Cu Kα radiation (45 kV and 40 mA). The scans were collected in the 2θ range of 10–90° with a scanning speed of 0.022° s−1 and a step size of 0.016°. In situ XRD measurements were performed in the same diffractometer using an Anton Paar XKR 900 reactor chamber (Macor sample holder) in a reflection geometry, with gas flow through the sample and uniform temperature control. Each sample was heated up to 900 °C under a flow of air and then investigated under different temperatures.

Inductively coupled plasma – optical emission spectroscopy (ICP-OES). The actual extent of the substitution of the A- or B-site of the perovskite with Ca or Co, respectively, was quantified by ICP-OES using an Agilent 5100 VDV. A multi-element standard (Sigma Aldrich) was utilised for the calibration.

Nitrogen physisorption. A Quantachrome NOVA 4000e N2 adsorption analyser was used to determine the pore volume of the OCs used in the fixed bed experiments. Each sample was degassed at 250 °C for 2 h prior to the measurements. The BJH model was used to calculate the pore volume of the materials.

Electron microscopy. Transmission electron microscopy (TEM) was performed on an FEI Talos F200X operated at 200 kV. The instrument was equipped with SuperX EDX comprising four SDD detectors. The morphology of the fresh OCs was investigated using scanning electron microscopy (FEI Quanta 200F).

Iodometric titration. The actual oxygen content of the as-synthesised OCs was determined by iodometric titration. An OC sample (250.0 mg) was dissolved in 50 mL HCl (6 M). A portion of the solution (10 mL) was placed in an Erlenmeyer flask and 1.00 g of potassium iodide (KI) was added. After a few minutes, the solution was diluted with DI water and the liberated iodine was titrated with sodium thiosulfate Na2S2O3 (0.05 M). Sodium thiosulfate was always standardised against KIO3 before each series of titration. The titration end-point was detected using a
starch-indicator, which was introduced into the solution before the titration.

Each titration was repeated at least twice and the values reported represent an average of the individual measurements. All reagents used were of analytical grade.

**Thermogravimetric analyser (TGA).** The OSC of the materials was determined using a TGA (Mettler Toledo TGA/DSC 3+). A small amount of the sample (~30 mg) was placed in an alumina crucible (70 μL), heated to 900 °C at a rate of 25 °C min⁻¹ and held for 150 min. The total flow rate of gas was 150 mL min⁻¹ and included a constant N₂ flow of 25 mL min⁻¹ over the microbalance. During that isothermal period, the gas atmosphere was altered to three different pO₂ by using either pure N₂ (125 mL min⁻¹), a gas mixture of N₂ and air (60 mL min⁻¹ and 65 mL min⁻¹, respectively) or only air (125 mL min⁻¹). The resulting pO₂ were 7.09 × 10⁻⁵ bar, 9.96 × 10⁻² bar and 2.09 × 10⁻¹ bar. The same procedure was repeated for temperatures ranging from 800 °C to 450 °C in decrements of 50 °C. The temperature range in which the OCs release O₂ was determined through temperature-programmed reduction (TPR) experiments. In these experiments, the sample was heated to 1000 °C at a rate of 5 °C min⁻¹ in N₂ and held for 30 min.

To determine the thermodynamic properties of the OCs, a high pressure thermobalance (LINSEIS L81PT High Pressure TGA-DTA/DSC) was used. Blank experiments were performed before the analysis of the material to correct for the effect of buoyancy on the balance. About 300 mg of sample, placed in an alumina crucible (500 μL), was used in each experiment. The sample sat on top of a layer of quartz wool to reduce the depth of the crucible and to minimise gas diffusion effects. First the sample was heated to 125 °C under a flow of synthetic air at a total flow rate of 1 L min⁻¹ and held for 30 min to remove adsorbed water. The temperature program of each experiment consisted of four consecutive temperature segments: 800, 700, 600 and 500 °C. At each temperature, the gas environment was varied to obtain seven different pO₂. At the beginning and at the end of each temperature segment, the pO₂ was identical to assess whether irreversible structural changes occurred. For each sample, experiments were performed at an absolute pressure of 1, 5 or 7 bar, covering a wide range of pO₂ (i.e. from 7.09 × 10⁻⁵ to 1.4 bar). Additionally, a constant N₂ flow of 1.5 L min⁻¹ was used to purge the balance. The change in oxygen non-stoichiometry Δδ was calculated from the recorded weight changes as:

\[ \Delta \delta = \Delta m_\text{OC} \frac{M_\text{OC}}{M_\text{O}_2} \]

(4)

where Δmₐ is the measured weight loss, calculated as the difference between the mass at the set point temperature (i.e. before switching to pure N₂) and the mass at the investigated pO₂.

The standard partial molar Gibbs free energy change for reduction (eqn (3)) is defined as:

\[ \Delta g^R_\text{O}(\delta, T) = -\frac{1}{2}RT \ln \left( \frac{p_{O_2}}{p^*} \right) \]

(5)

where \( p^* \) is the standard pressure (1 bar), \( T \) is the temperature (K) and \( R \) is the ideal gas constant (8.314 J K⁻¹ mol⁻¹). \( \Delta g^R_\text{O} \) can be related to the standard partial molar enthalpy (\( \Delta h^R_\text{O} \)) and entropy change (\( \Delta s^R_\text{O} \)):

\[ \Delta g^R_\text{O}(\delta, T) = \Delta h^R_\text{O}(\delta) - T \Delta s^R_\text{O}(\delta) \]

(6)

Eqn (5) and (6) can be combined such that \( \Delta h^R_\text{O} \) and \( \Delta s^R_\text{O} \) are expressed as a function of \( p_{O_2} \) and temperature, for a constant oxygen non-stoichiometry \( \delta \):

\[ -\ln \left( \frac{p_{O_2}}{p^*} \right) = \frac{1}{T} \frac{\Delta h^R_\text{O} \delta}{R} - \frac{\Delta s^R_\text{O} \delta}{R} \]

(7)

Accordingly, plotting the logarithm of \( p_{O_2}/p^* \) over the inverse of temperature (Arrhenius plot) for constant \( \Delta \delta \) allows extracting the thermodynamic properties of the OCs (i.e. the standard partial molar enthalpy and entropy change) from the slope \( 2\Delta h^R_\text{O}/R \) intercept and \( 2\Delta s^R_\text{O}/R \).

**Cyclic redox experiments.** The cyclic redox stability of the OCs Sr₀.₈Co₀.₂FeO₃₋₅ and SrFe₀.₈Co₀.₂O₃₋₅, i.e. the two most promising materials of the Ca- and Co-substituted materials, respectively, were investigated also in a fixed bed reactor over 100 cycles. Here, a quartz tube reactor (ID 10 mm, 30 cm long) was loaded with 3 g of the OC (sieved to 180–250 μm), which was held in the centre of the tube by means of a plug of quartz wool, giving a bed of length 20 mm. The OC was heated to 600 °C in air (50 mL min⁻¹) by using a tubular furnace controlled via an N-type thermocouple. Each redox cycle consisted of 40 min reduction under a flow of N₂ (50 mL min⁻¹) followed by 20 min oxidation in air (50 mL min⁻¹). The fraction of O₂ in the gas stream at the outlet of the reactor was determined by means of a paramagnetic analyser (ABB EL3020, Magnos 206). A blank experiment was performed at 600 °C under a flow of N₂ (50 mL min⁻¹) using the same quartz tube reactor filled with an inert material (SiC) to account for mixing effects in the gas sampling system when switching between gases. The total amount of O₂ released by the OC in each cycle was quantified using eqn (8):

\[ N_{O_2} = \int_{t_1}^{t_2} \frac{x_{O_2}}{1 - x_{O_2}} \, dt \]

(8)

where \( N_{O_2} \) is the total molar flowrate of N₂, t₁ and t₂ are the time when the gas flow rate is switched from air to N₂ and when \( x_{O_2} = 0 \), respectively, and \( x_{O_2} \) is the mole fraction of O₂ measured at the outlet of the reactor when flowing only N₂, after subtraction of the blank measurement.

**3. Results and discussion**

**Characterisation of the oxygen carriers**

Fig. 1 shows the XRD patterns of as-prepared SrFe₁₋ₓCoₓO₃₋₅ and Sr₁₋ₓCaₓFeO₃₋₅ at ambient temperature. The diffraction patterns of the samples with composition SrFe₁₋ₓCoₓO₃₋₅ (0 ≤ x ≤ 0.8) and Sr₁₋ₓCaₓFeO₃₋₅ showed good agreement with the reference perovskite cubic structure (PDF 39-0954)
(0 ≤ x ≤ 0.25), and no impurity phases were detected. For Co B-site substitution and x = 1, additional diffraction peaks were observed corresponding to hexagonal SrCoO$_2$ with previous reports. In the case of Ca A-site substitution, the samples with a composition 0.3 ≤ x ≤ 1 revealed reflections due to further oxide phases that were identified as CaO and the brownmillerite phase Ca$_{1.5}$Sr$_0.5$Fe$_2$O$_5$. In an attempt to enhance the purity of the perovskites with Ca substitutions in the range 0.3 ≤ x ≤ 1, higher calcination temperatures (i.e. 1100 °C or 1200 °C, for 10 h) were used, yet the same extent of impurity phases was observed, in agreement with other works.

In agreement with other works, 29,39 attempts to enhance the purity of the perovskites with Ca substitutions in the range 0.3 ≤ x ≤ 1, higher calcination temperatures (i.e. 1100 °C or 1200 °C, for 10 h) were used, yet the same extent of impurity phases was observed, in agreement with previous reports. High signal-to-noise X-ray diffractograms of some of the samples (Fig. S1, ESI†) were collected also at the ID31 beamline of the European Synchrotron Radiation Facility (ESRF), confirming the formation of a phase-pure perovskite structure only in the range 0 ≤ x ≤ 0.8 for SrFe$_{1-x}$CoO$_3$ and 0 ≤ x ≤ 0.25 for Sr$_{1-x}$Ca$_x$FeO$_3$. For each sample in this range of substitution, the actual ratio of the single elements was determined by ICP-OES analysis. The values obtained are in good agreement with the expected values based on the amount of nitrates used in the preparation method, confirming the successful synthesis of phase-pure materials (Table S1 of the ESI†).

The microscopic distribution of the elements composing the OCs was probed by energy dispersive X-ray spectroscopy (EDS) coupled with scanning transmission electron microscopy (STEM). Fig. 1(c) shows a high-angle annular dark-field (HAADF) image and the corresponding EDS maps of Fe, Ca and Sr, confirming a homogeneous dispersion of all elements. Agglomerates or impurity phases were not observed. For compositions that, according to XRD, do not yield a phase-pure perovskite phase (Sr$_{0.2}$Ca$_{0.8}$FeO$_{3-δ}$, Fig. 2(d)), a non-homogenous distribution of the elements was observed, due to the formation of additional (segregated) mixed oxide phases.

The following investigations consider phase-pure perovskites only to exclude the influence of the impurity phases on the observed reduction/oxidation behaviour.

**Oxygen desorption properties**

When heating from ambient temperature to the set point temperature in a flow of air, all samples exhibited a significant weight loss that suggests their $p_{O_2}$ increases with temperature (Fig. S2, ESI†). The effect of the composition of the perovskite on their $p_{O_2}$ and thermodynamic properties is discussed in more detail in the next section.

Thermogravimetric analysis revealed a strong influence of the perovskite composition (for both A- and B-site substitution) on the amount of desorbed/sorbed O$_2$ in the temperature range 400–900 °C.

The measured oxygen storage capacity (OSC$_m$) for each temperature was evaluated as the weight change at equilibrium (eqn (9)) after changing the atmosphere from air ($p_{O_2} = 2.09 \times 10^{-1}$ bar) to N$_2$ ($p_{O_2} = 7.09 \times 10^{-3}$ bar), and is reported in Fig. 2(a) and (b) for SrFe$_{1-x}$CoO$_{3-δ}$ (x = 0, 0.2, 0.4, 0.6, 0.8) and Sr$_{1-x}$Ca$_x$FeO$_{3-δ}$ (x = 0.1, 0.2, 0.25), respectively.

\[
\text{OSC}_m = \frac{m_{\text{air}} - m_{\text{N}_2}}{m_{\text{N}_2}} \times 100
\]

where $m_{\text{air}}$ and $m_{\text{N}_2}$ are the weight of the OC measured at equilibrium in air and N$_2$, respectively.

![XRD patterns of as-prepared samples](image1)

**Fig. 1** XRD patterns of as-prepared (a) SrFe$_{1-x}$CoO$_{3-δ}$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) and (b) Sr$_{1-x}$Ca$_x$FeO$_{3-δ}$ (x = 0, 0.1, 0.2, 0.25, 0.4, 0.6, 0.8, 1). HAADF images and elemental composition of (c) Sr$_{0.8}$Ca$_0.2$FeO$_{3-δ}$ and (d) Sr$_{0.2}$Ca$_0.8$FeO$_{3-δ}$.
The variation in the OSC with the composition of the perovskites was more evident in the temperature range 300–700 °C, showing that the substitution of A or B-site cations promotes the release of O₂ at low temperatures. Fe B-site substitution by Co by 20% increased the observed OSC from 0.8 wt% (when \( x = 0 \)) to 1.25 wt% at 500 °C. Increasing the amount of Co further resulted in an even higher OSC, reaching 1.42 wt% for \( x = 0.6 \) at 500 °C. In the case of Sr A-site substitution by Ca, the highest OSC of 2.15 wt% was observed for \( x = 0.2 \) at 500 °C. The substitution of Sr by Ca did not yield an increased OSC at high temperatures (700–900 °C), likely due to the high \( pO_2 \text{eq} \) in this temperature range.

The dependence of the composition of the perovskite on the amount of O₂ released as a function of temperature was assessed further by temperature programmed reduction (TPR).

For samples of composition SrFe₁₋ₓCoₓO₃₋ₓ, \( 0 \leq x \leq 0.8 \), a mass loss due to the release of O₂ at low temperatures as \( 330 °C \) (Fig. 2[c]). Importantly, an increased substitution of Fe by Co resulted in an increased rate of mass loss (with a maximum rate for \( x = 0.6 \)), i.e. an increased reducibility of the metal oxide at low temperature. To summarise, B-site substitution of Fe by Co represents a possibility to release O₂ at relatively low temperatures compared to the original material. In the case of Ca (A-site) substituted perovskites (Sr₁₋ₓCaₓFeO₃₋ₓ, \( 0 \leq x \leq 0.25 \)), reported in Fig. 2(d), an increasing quantity of Ca in the perovskite increased the rate of reduction in \( N_2 \) compared to the original SrFeO₃₋ₓ.

Similar to the case of Co B-site substitution, the range of temperatures in which the materials released the entire quantity of O₂ decreased from 330–750 °C (SrFeO₃) to 330–550 °C.

The cyclic redox stability of the OCs Sr₀.₈Ca₀.₂FeO₃₋ₙ and SrFe₀.₂Co₀.₈O₃₋ₙ, i.e. the two most promising materials of the Ca- or Co-substituted materials, respectively, was studied using both a TGA and a fixed bed reactor. Fig. 3 plots the oxygen capacity of Sr₀.₈Ca₀.₂FeO₃₋ₙ over 30 cycles (TGA at 500 °C). There was no measurable loss in the performance of Sr₀.₈Ca₀.₂FeO₃₋ₙ and the cyclic OSC was ~2.1 wt% in all cycles but the first two, in which the OSC was ~2 wt%. Similarly, the morphology of the material remained unaltered during the cyclic test, as observed by SEM (Fig. 3).

XRD patterns collected before and after the cycling experiment did not show any substantial difference (Fig. S3(a), ESI†), in particular no phase separation was observed. Rietveld full pattern refinement confirmed an unchanged cell parameter (Fig. S3(b), ESI†). The cyclic redox stability of SrFe₀.₂Co₀.₈O₃₋ₙ was also investigated in the TGA at 500 °C over 30 redox cycles (Fig. S4, ESI†). For SrFe₀.₂Co₀.₈O₃₋ₙ we observed an activation period over the first 10 cycles during which the amount of O₂ absorbed by the OC increased with cycle number. This activation period was followed by a stable reactivity with no loss in performance with cycle number. Similar to Sr₀.₈Ca₀.₂FeO₃₋ₙ, when comparing the XRD patterns of SrFe₀.₂Co₀.₈O₃₋ₙ before and after the cycling experiment no apparent change in the structure of the OC was observed (Fig. S5(a), ESI†). The Rietveld refinement of the full XRD pattern of the OC collected after the cyclic experiment confirmed its unchanged crystal structure (Fig. S5(b), ESI†). This suggests that the observed activation of the OC was not related to a chemical phenomenon, but possibly a physical phenomenon, such as an improved mass transport within the material. Indeed, a slight increase in the pore volume and porosity of the OC SrFe₀.₂Co₀.₈O₃₋ₙ (but not Sr₀.₈Ca₀.₂FeO₃₋ₙ) was observed upon cycling (Table S2, ESI†), which may explain the observed activation period for this material.

In the fixed bed experiments, the number of redox cycles was increased to 100. Fig. 4, plots the \( pO_2 \) for the OC Sr₀.₈Ca₀.₂FeO₃₋ₙ as a function of time over 100 redox cycles performed at 500 °C. For comparison, the \( pO_2 \) of the blank experiment (reactor filled with SiC of the same volume as in the experiment with OC) is given by empty circles. Sr₀.₈Ca₀.₂FeO₃₋ₙ shows no significant difference in the measured \( pO_2 \) between cycle 1 (red) and cycle 100 (black), confirming the stable cyclic performance of the material, observed in the previous TGA experiments. The area between the \( pO_2 \) profiles obtained from the OC and the blank experiment using SiC allows to calculate...
The activation phase (first 10 cycles) of the O₂ release was followed by a stable reactivity for the remaining 90 cycles. Fig. S7 (ESI) compares the TGA-determined OSC (OSCₘ = 1.2 wt%) with the respective evolution of Δρ (dashed lines) for cycle numbers 1 and 100; no apparent difference between the two cycle numbers is observed.

The same type of cyclic experiment was performed also for Sr₀.₈Ca₀.₂FeO₃₋ₓ (Fig. S6, ESI†). In agreement with what has been observed in the TGA, the pO₂ profiles for cycle 1 (green) and cycle 100 (black) were different. The amount of O₂ released by Sr₀.₈Ca₀.₂FeO₃₋ₓ increased from cycle 1 to 10 from ~67% to ~96% of the total O₂ that could be released based on the TGA-determined OSC (OSCₘ = 2.15 wt%). Fig. 4 also plots the evolution of the oxygen non-stoichiometry Δρ (dashed lines) for cycle numbers 1 and 100.

Thermodynamic assessment

A thermodynamic analysis was performed on SrFe₁₋ₓCoₓO₃₋₀.₃ to assess the suitability of the investigated oxides for CLAS. Fig. S8 (ESI†) shows an overview of the thermogravimetric measurements (weight change as a function of time, temperature and pO₂) acquired for SrFe₁₋ₓCoₓO₃₋₀.₃, with x ranging from 0 to 0.8. It was observed that upon heating from ambient temperature to 800 °C the materials with a higher degree of substitution of Fe by Co (Fig. S8, ESI†) released a lower amount of O₂ than unsubstituted SrFeO₃₋₀.₃. This suggests that the pO₂,eq of the substituted samples decreased with increasing x. In addition, the amount of O₂ released was fully recovered (i.e. the material could be fully reoxidised) at each temperature. Interestingly, the sample with the composition SrFe₀.₂CoₓO₃₋₀.₃ showed a very different behaviour compared to all the other samples in the temperature range 500–700 °C. The sample weight of this material did not change in the pO₂ range 9 × 10⁻⁴–1 × 10⁻¹ bar, which implies that it is not required to employ an atmosphere of extremely low pO₂ to extract a significant amount of O₂ from the OC. For example, when switching the gas atmosphere from air (pO₂ = 2.09 × 10⁻¹ bar) to N₂ (pO₂ = 7.09 × 10⁻⁵ bar), the OSC of SrFe₀.₂CoₓO₃₋₀.₃ was 1.21 wt% at 500 °C, while the OSC reduced only marginally to 1.1 wt% when operating between air and 5% O₂ (pO₂ = 5 × 10⁻² bar). For comparison, the OSC of unsubstituted SrFeO₃₋₀.₃ at 500 °C decreased from 0.8 wt% (when switching the gas atmosphere between air and N₂) to 0.1 wt% (when switching between air and 5% O₂). From a practical standpoint, SrFe₀.₂CoₓO₃₋₀.₃ represents a good candidate for CLAS due to its ability to release and take up O₂ at relatively low temperatures (i.e. <600 °C) even in “oxygen-rich” environments (for example for pO₂ between 0.1 and 0.2 bar). In contrast, other compositions and the unsubstituted SrFeO₃₋₀.₃ require very low – and practically difficult to realise – pO₂ to release a large quantity of O₂, which would lower the economic attractiveness of CLAS.

The initial oxygen non-stoichiometry δ₀ of all samples was determined by iodometric titration at ambient temperature and is reported in Table S2 (ESI†). The substitution of the B-site cation Fe by Co (up to 60% substitution) yielded only a slight change in the initial δ₀ (δ₀ ≈ 0.22), while in the case of 80% substitution, δ₀ ≈ 0.32. On the other hand, substitution of A-site Sr by Ca strongly increased the available amount of O₂ (i.e. δ₀ ≈ 0.15) compared to the original SrFeO₃₋₀.₃ (δ₀ ≈ 0.22). The increased amount of available redox-active lattice oxygen compared to the original SrFeO₃₋₀.₃ when partially substituting the A- or B-site of the perovskite is reflected by the overall higher OSC of the substitute material, as shown in Fig. 2.

Fig. 5(a) shows exemplarily the evolution of the oxygen non-stoichiometry (symbols) of SrFe₁₋ₓCoₓO₃₋₀.₃ (0 ≤ x ≤ 0.8) as a function of pO₂ at 500 °C (the dotted lines represent qualitative guidelines). The initial value of δ of each sample at 500 °C was higher than that measured at ambient temperature due to the increase of pO₂,eq with temperature; i.e. there was a release of O₂ upon heating the sample. Generally, all Co-substituted...
samples showed a similar behaviour, except for the case of $x = 0.8$, for which the oxygen non-stoichiometry decreased sharply at relatively high oxygen partial pressures (i.e. $p_{O_2} = 1 \times 10^{-1}$ bar). Importantly, the value of $3 - \delta$ was found to be $\sim 2.5$ at low $p_{O_2}$ (i.e. $p_{O_2} = 7.09 \times 10^{-5}$ bar, pure $N_2$) for all materials at 500 $^\circ$C. This suggests that the perovskite structure was completely reduced to its defect-order variant brownmillerite (ABO$_{2.5}$). In the absence of a strongly reducing gas (e.g. H$_2$) that would thermodynamically enable a further reduction, the $O_2$ released from the perovskite structure corresponds to the maximal amount of lattice oxygen that can be released for this class of materials. Overall, the trend of the oxygen non-stoichiometry as a function of $p_{O_2}$ recorded at 600 $^\circ$C and 700 $^\circ$C (Fig. S9(a) and (b), ESI†) was qualitatively similar to the behaviour at 500 $^\circ$C. Increasing the temperature further to 800 $^\circ$C (Fig. S9(c), ESI†), no significant difference in the evolution of $3 - \delta$ with $p_{O_2}$ could be observed between each sample. Moreover, at 800 $^\circ$C, the measured values of $3 - \delta$ were always greater than 2.5 (i.e. $\sim 2.54$) for the lowest oxygen partial pressure studied (i.e. $p_{O_2} = 7.09 \times 10^{-5}$ bar), suggesting that a phase change to brownmillerite did not occur at this temperature. In situ XRD measurements confirmed that at 800 $^\circ$C the release of $O_2$ occurred without any phase transition (this is discussed in detail in the following section).

The respective thermogravimetric experiment for Sr$_{1-x}$Ca$_x$FeO$_{3-\delta}$ in which the A-site Sr was substituted by Ca, is reported in Fig. S10 (ESI†) while the measured $3 - \delta$ values as a function of $p_{O_2}$ for Sr$_{1-x}$Ca$_x$FeO$_{3-\delta}$ ($x = 0, 0.1, 0.2, 0.25$) are reported in Fig. S11(a)–(d) (ESI†). Generally, the evolution of $3 - \delta$ with $p_{O_2}$ for the A-site substituted materials was found to be similar to the B-site substituted materials. All the A-site substituted perovskites gave $3 - \delta = 2.5$ at the lowest $p_{O_2}$ studied (i.e. $7.09 \times 10^{-5}$ bar, pure $N_2$) at 500 $^\circ$C, 600 $^\circ$C and 700 $^\circ$C, suggesting the transition to brownmillerite at this oxygen partial pressure. Increasing the temperature to 800 $^\circ$C, a value of $3 - \delta = 2.5$ was observed only in the case of Sr$_{0.8}$Ca$_{0.2}$FeO$_{3-\delta}$ at the lowest $p_{O_2}$ studied (i.e. $7.09 \times 10^{-5}$ bar, pure $N_2$), while the measured values of $3 - \delta$ for the other samples were $\sim 2.57$ at this $p_{O_2}$, suggesting that a phase change to brownmillerite did not occur at this temperature.

To extract the partial molar enthalpy and entropy of vacancy formation from the TGA measurements of the substituted perovskites, the negative natural logarithm of $p_{O_2}$ as a function of the inverse absolute temperature (Arrhenius plot) for constant $\Delta \delta$. Fig. 5(b)) exemplarily shows the Arrhenius plot for SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$. The Arrhenius plot of all the other Co-substituted samples can be found in the ESI† (Fig. S12(a)–(d)). As we increase the temperature range compared to related works (albeit on different materials)$^{35,41-43}$ we observe two distinct regimes, both of which can be approximated by a linear relationship. Similar observations were made also for Ca-substituted materials. For all samples investigated in this work, the transition temperature between the two regimes (linked to a structural change of the bulk perovskite phase) was $\sim 770$ $^\circ$C. Similarly, for SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ Liu et al.$^{44}$ identified also $770$ $^\circ$C as the temperature above which the $O_2$ release occurs without a phase transition from perovskite to brownmillerite, known as order-disorder transition.$^{40}$ From the Arrhenius plot, the thermodynamic properties of the OCs (i.e. the standard partial molar enthalpy and entropy of vacancy formation) were determined as a function of the change in the oxygen non-stoichiometry $\Delta \delta$. The partial molar enthalpy of formation as a function of $\Delta \delta$ for SrFe$_{1-x}$Co$_x$O$_{3-\delta}$ ($0 \leq x \leq 0.8$) is shown in Fig. 6(a) and (b), for the low ($T < 770$ $^\circ$C) and high ($770$–$900$ $^\circ$C) temperature range, respectively. Generally, the samples in which Fe was substituted by Co showed smaller partial molar enthalpy of formation compared to the unsubstituted SrFeO$_{3-\delta}$, when $T < 770$ $^\circ$C. Additionally, in the same range (i.e. $T < 770$ $^\circ$C), an increase in the oxygen non-stoichiometry yielded an increase in $\Delta h^\circ_{f}$ for SrFe$_{1-x}$Co$_x$O$_{3-\delta}$ with $x = 0, 0.2, 0.4, 0.6, 0.8$, consistent with what has been found in thermodynamic studies performed on perovskites such as La$_{1-x}$(Ca,Sr)$_x$Mn$_{1-y}$Al$_y$O$_3$. For the unsubstituted sample SrFeO$_{3-\delta}$ gave the highest partial molar enthalpy of formation of $\sim 40$ kJ mol$^{-1}$, when $\Delta \delta = 0.09$. The smaller values of the partial molar enthalpy of formation of the Co-substituted samples compared to the original SrFeO$_{3-\delta}$.
explain their increased reducibility at low temperatures \((T < 770 \, ^\circ C)\). The partial molar entropy of vacancy formation was generally constant (\(~7 \, J \, mol^{-1} \, K^{-1}\)) with increasing \(\Delta S\) when at \(T < 770 \, ^\circ C\) (Fig. 6(c)). In the high temperature range \((770–900 \, ^\circ C)\), the partial molar enthalpy of vacancy formation decreased with increasing \(\Delta S\) for all the Co-substituted samples, a result also reported for lanthanum manganites in the context of solar thermochemical water splitting.42,43 Overall, in the temperature range \(770–900 \, ^\circ C\), higher values of \(\Delta h_o\) compared to the unsubstituted \(\text{SrFeO}_3\) were found for each \(\Delta S\), translating into a decreased reducibility of the substituted samples in this temperature range. In the same temperature range, an increase in the oxygen non-stoichiometry yielded an increase in The partial molar entropy of vacancy formation (Fig. 6(d)) showed generally increasing values with increasing \(\Delta S\). Interestingly, the Co-substituted samples show higher \(\Delta S_o\) compared to the unsubstituted sample.

The Arrhenius plots and the thermodynamic properties (partial molar entropy and enthalpy of formation of vacancies) obtained for \(\text{Sr}_{1-x}\text{Ca}_x\text{FeO}_3\) are given in Fig. S13 and S14 (ESI†). In the low temperature range (i.e. \(T < 770 \, ^\circ C\)), the partial molar enthalpy of formation was relatively constant (\(~20 \, kJ \, mol^{-1}\)) with increasing \(\Delta S\) for all substituted samples. Dou et al.18 found similar values (i.e. \(~25 \, kJ \, mol^{-1}\)) for \(\text{Sr}_{0.8}\text{Ca}_{0.2}\text{FeO}_3\)\(_{\delta}\). Similarly, to the case of substitution of Fe by Co, smaller values of \(\Delta h_o\) compared to unsubstituted \(\text{SrFeO}_3\) confirmed an increased reducibility induced by the substitution of Sr by Ca. In the temperature range \(700–900 \, ^\circ C\), higher values of \(\Delta h_o\) compared to unsubstituted \(\text{SrFeO}_3\)\(_{\delta}\) were found for each \(\Delta S\). Table S3 in ESI† summarises the extrapolated partial molar enthalpy and entropy of vacancy formation for all samples.

Fig. 6(e) and (f) exemplary show the resulting partial molar Gibbs free energy change of vacancy formation \(\Delta g_o = \Delta h_o – T \Delta s_o\) when \(\Delta S = 0.025\). It was found that \(\Delta g_o\) was always smaller for all substituted samples compared than the unsubstituted \(\text{SrFeO}_3\)\(_{\delta}\) when \(T < 770 \, ^\circ C\). Note that this is consistent with the increased reducibility of all substituted samples observed in this temperature range compared to the unsubstituted \(\text{SrFeO}_3\)\(_{\delta}\). In the high temperature range (i.e. 770–900 \, ^\circ C), \(\Delta g_o\) of the substituted samples was always smaller than \(\text{SrFeO}_3\)\(_{\delta}\).

**In situ XRD measurements**

**In situ XRD** was performed for all the substituted perovskites (and the reference, unsubstituted perovskite) to probe the evolution of the crystal structure as a function of temperature. The measurements were performed isothermally at different temperatures in pure \(\text{N}_2\) \((p_{\text{O}_2} = 7.09 \times 10^{-5} \, \text{bar})\). Fig. 7(a) shows an exemplary result of the evolution of the structure of \(\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_3\)\(_{\delta}\) with scan number under a flow of pure \(\text{N}_2\) \((p_{\text{O}_2} = 7.09 \times 10^{-5} \, \text{bar})\) at 600 \, ^\circ C. With scan number (i.e. with the progress of \(\text{O}_2\) release) the main peak of the perovskite phase (110) shifted towards lower diffraction angles (indicating an increase in the perovskite unit cell parameter) due to the release of \(\text{O}_2\). When all the \(\text{O}_2\) was released from the perovskite, a phase transition to brownmillerite occurred at this temperature (i.e. 600 \, ^\circ C). The same experiment, performed at 900 \, ^\circ C (Fig. 7(b)), shows that only the position of main perovskite peak (110) changed as \(\text{O}_2\) was being released, but no separate reflections corresponding to brownmillerite were observed (in agreement with TG experiments). When reducing \(\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_3\)\(_{\delta}\) under \(\text{N}_2\) at different temperatures, the in situ XRD measurements showed that for temperatures \(\leq 750 \, ^\circ C\) the release of \(\text{O}_2\) occurred through a phase transition from perovskite to brownmillerite, while for temperatures > 750 \, ^\circ C only the perovskite peak was observed, implying that no brownmillerite phase was formed.

Bulk phase transitions during reduction (and oxidation) are often an undesired characteristic in chemical looping applications (i.e. CLAS) as they may induce abrupt volume changes in the materials affecting negatively their mechanical stability. For large scale processes where, for example, fluidised beds may be...
used, a poor mechanical stability can result in attrition and loss of material. The change in the molar volume upon phase transition from the perovskite structure to brownmillerite is <1.5% and hence mechanical stresses within the particles may be less of a concern.

Turning back to SrFe_{1-x}CoO_{3-δ} (x = 0, 0.4, 0.6, 0.8) and Sr_{1-x}CaFeO_{3-δ} (x = 0.1, 0.25), Fig. S14 (EIS), the formation of a brownmillerite phase when releasing O_2 (in N_2) was observed for all samples at T < 750 °C, while the perovskite structure remained stable for T > 750 °C. Only in the case of 20% substitution of Sr by Ca a phase transition from perovskite to brownmillerite was observed also at T > 750 °C (Fig. 8(a) and (b)), consistent with the measured δ = 2.5 for this sample (Fig. S10(d), ESI†). For both substituted and unsubstituted perovskites, the regeneration of the perovskite structure was possible only in air (pO_2 = 2.09 × 10^{-1} bar).

4. Conclusions

We have studied the influence of Ca A- or Co B-site substitution of SrFeO_3 on the materials’ chemical–physical properties at temperatures ranging from 400 to 900 °C, relevant for chemical looping applications. We have shown that phase pure materials can be obtained when limiting the substitution of A- or B-site cations to the range of 0 ≤ x ≤ 0.8 or 0 ≤ x ≤ 0.25 for Co B-site or Ca A-site substitution, respectively. Thermogravimetric analysis revealed that the chemical–physical properties (quantity of oxygen released, desorption/sorption rate and reducibility) of the materials are altered by the partial substitution of their A- or B-site cations. In particular, it was found that the substitution of Fe by Co increased the reducibility of the metal oxide in the low temperature regime (i.e. T = 400–600 °C) when compared to the unsubstituted SrFeO_3. Our quantitative thermodynamic assessment confirmed a decreased partial molar enthalpy of formation of SrFe_{1-x}CaO_{3-δ} in this temperature range. Among the Co-substituted samples, SrFe_{0.5}Co_{0.5}FeO_{3-δ} showed a high OSC ~1.1 wt% when operating between air and 5% O_2 at 500 °C. The ability to effectively release and take up O_2 at relatively low temperatures (i.e. <600 °C) without the need for gas atmospheres of extremely low pO_2 makes this material a good candidate for CLAS.

Sr A-site substitution by Ca improved the OSC and among all the materials investigated, Sr_{0.8}Ca_{0.2}FeO_{3-δ} exhibited the highest OSC (2.15 wt%) at 500 °C when operating between air and N_2. The redox cyclic stability of SrFe_{0.5}Co_{0.5}FeO_{3-δ} and Sr_{0.8}Ca_{0.2}FeO_{3-δ} was investigated over up to 100 redox cycles in a fixed bed reactor and no apparent alteration in the crystalline structure nor loss in activity was observed.

When probing the evolution of the oxygen non-stoichiometry as a function of temperature and pO_2, two regimes were observed for the substituted perovskites. The transition temperature between the two regimes is ~770 °C. For T < 770 °C the O_2 release in N_2 (pO_2 = 7.09 × 10^{-5} bar) was accompanied by a phase transition from a perovskite to a brownmillerite phase, while the perovskite structure remained stable for T > 770 °C, as confirmed by in situ XRD measurements. The only exception was Sr_{0.8}Ca_{0.2}FeO_{3-δ} that showed a phase transition during the reduction in N_2 over the entire temperature range studied (500–900 °C).

Lastly, our results show that in spite of the high OSC of the perovskite materials studied, the challenge to obtain a constant flow of O_2 released remains as the O_2 release varies with the oxygen non-stoichiometry δ. This intrinsic feature of non-stoichiometric materials would require engineering solutions (e.g. moving bed reactor design in a counter-current flow configuration) to control the variation in the oxygen non-stoichiometry and, therefore, ensure a constant flow of O_2 at the outlet of the reactor if demanded by the chemical looping process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to acknowledge the Swiss Federal Office of Energy (BFE, SI/501590-01) for financial support. We also thank the Scientific Centre for Optical and Electron Microscopy (ScopeM) at ETH Zürich for providing training and access to scanning electron microscopes. The authors are grateful to the beamline scientist Dr Agnieszka Poulain of ID31 at the European Synchrotron Facility (ESRF) for the provided support. Dr Paula M. Abdala is acknowledged for assisting with the analysis of the in situ XRD measurements. Dr Agnieszka Kierzkowska is acknowledged for performing SEM and EDX measurements.

Notes and references

1 M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, J. P. Hallett, H. J. Herzog, G. Jackson, J. Kemper, S. Krevor, G. C. Maitland, M. Matuszewski, I. S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D. M. Reiner, E. S. Rubin, S. A. Scott, N. Shah, B. Smit, J. P. M. Trusler, P. Webley, J. Wilcox and N. Mac Dowell, Energy Environ. Sci., 2018, 11(5), 1062–1176.

2 S. Fuss, W. F. Lamb, M. W. Callaghan, J. Hilaire, F. Creutzig, T. Amann, T. Beringer, W. De Oliveira Garcia, J. Hartmann, T. Khanna, G. Luderer, G. F. Nemet, J. Rogelj, P. Smith, J. L. Vicente, J. Wilcox, M. Del Mar Zamora Dominguez and J. C. Minx, Environ. Res. Lett., 2018, 13(6), 063002.

3 J. C. Minx, W. F. Lamb, M. W. Callaghan, S. Fuss, J. Hilaire, F. Creutzig, T. Amann, T. Beringer, W. De Oliveira Garcia, J. Hartmann, T. Khanna, D. Lenzi, G. Luderer, G. F. Nemet, J. Rogelj, P. Smith, J. L. Vicente, J. Wilcox and M. Del Mar Zamora Dominguez, Environ. Res. Lett., 2018, 13(6), 063001.

4 B. Mckee, Solutions for the 21st century, zero emissions technologies for fossil fuels, Technology status report, Energy, DOI:10.1016/B978-0-12-802748-6.01001-9.

5 H. I. Mathogka, B. O. Oboirien and B. C. North, Int. J. Energy Res., 2016, 40(7), 878–902.
