
Johnston SRW, Ray B, Hu W, Metcalfe IS. [An investigation into the stability and use of non-stoichiometric \$\text{YBaCo}_4\text{O}_{7+\delta}\$ for oxygen enrichment processes](#). *Solid State Ionics* 2018, **320**, 292-296.

DOI link

<https://doi.org/10.1016/j.ssi.2018.03.016>

ePrints link

<http://eprint.ncl.ac.uk/246784>

Date deposited

27/03/2018

Embargo release date

21/03/2019

Copyright

© 2018. This manuscript version is made available under the [CC-BY-NC-ND 4.0 license](#)

Licence

This work is licensed under a [Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International licence](#)



An investigation into the stability and use of non-stoichiometric YBaCo₄O_{7+δ} for oxygen enrichment processes

S.R.W.Johnston, B.Ray, W.Hu, I.S.Metcalf

School of Chemical Engineering and Advanced Materials

Newcastle University

Newcastle upon Tyne NE1 7RU

E-mail: ian.metcalf@ncl.ac.uk

Keywords: Air separation, Non-stoichiometric materials, stability investigations.

Abstract

YBaCo₄O_{7+δ} has been reported to have a large oxygen capacity which can be accessed on practical timescales by both temperature and pressure swings below 400 °C. One potential use of this oxygen capacity is for oxygen enrichment of process gas streams for e.g. application in oxy-fuel combustion and auto-thermal reforming. In this work, YBaCo₄O_{7+δ} powders were produced by a solid state synthesis and their material properties studied with a view to use as a process stream oxygen enricher. The stability of the material as a function of temperature in both CO₂ and reducing gases (CO and H₂) was investigated. The kinetics of oxygen uptake and release was studied by following the response to swings in oxygen partial pressure (pO₂) and temperature. To demonstrate the potential for employing this reversible oxygen capacity, the material was successfully used to supply oxygen into a gas stream with a pO₂ of 0.31 bar after oxidation in an air stream (pO₂ = 0.21 bar).

1. Introduction

Oxygen enrichment of process gas streams can be useful in many chemical processes such as the oxygen enhanced water gas shift reaction (OWGS) [1-2], auto-thermal reforming of methane (ATR) [3], the removal of H₂S from a gas stream (Claus reaction) [4-5], ammonia synthesis [6] and oxy-fuel combustion. The characteristics and potential benefits of such processes are summarised in Table 1.

Table 1 – List of processes potentially benefited by the addition of controlled amounts of oxygen

Process	Process characteristic of oxygen addition
OWGS	In the presence of a suitable catalyst, a small amount of O ₂ co-fed with the WGS feed can selectively improve the conversion of CO whilst maintaining a high yield of H ₂ in the product stream [1-2]

ATR	Partially combusts methane to provide the heat required for the otherwise endothermic methane reforming [3].
Claus process	Oxygen used to convert H ₂ S to SO ₂ and water which can be further processed to allow recovery of sulphur and removal of acid gas from exhaust streams [4-5]
Ammonia synthesis	Oxygen enrichment can be used to control the nitrogen to hydrogen ratio during ammonia synthesis, improving the efficiency of the reactor [6]
Oxy-fuel combustion	Combustion of fuel in a stream of CO ₂ and O ₂ instead of air can produce a CO ₂ -rich exhaust that can be easily captured with minimal gas separation and treatment [7]

One process of particular interest to the current work is oxy-fuel combustion. In this process, the fuels are combusted in a stream of CO₂ and O₂ instead of air [8]. The major advantage of this process is that it prevents nitrogen from entering the combustion system, yielding an exhaust rich in CO₂ (as opposed to N₂ in a traditional air-fed furnace) which can be readily captured. Additionally, the absence of N₂ reduces the amount of NO_x formed during combustion, potentially removing the need for additional treatments (unless an N-rich fuel is used) [10]. Part of the CO₂ exhaust is recycled and oxygenated to a high enough pO₂ (typically 0.3 bar) for combustion. Studies have shown that a pO₂ lower than 0.3 bar cannot sustain the flame due to the higher specific heat capacity of CO₂ [11-12].

There are several different processes currently used for oxygen enrichment. The simplest of these methods involves the use of cryogenic distillation or pressure swing absorption (PSA) to produce oxygen which is subsequently injected into a process stream. However, cryogenic distillation is energy intensive and the purity of oxygen produced by PSA is lower, typically ~95% [13-14]. Additionally, both methods generally operate on a large scale, and it is uncommon for smaller stationary units to be present for use at an individual process site. Oxygen separation using membranes which allow the selective transport of oxygen into a process stream can be a local, small-scale alternative for oxygen production. Although these units suffer from high operating costs, relatively low mechanical stability and the requirement of large areas of operation [15].

Oxygen separation through redox cycling of an oxygen storage material has the potential to improve on several of these issues. These materials can be used to selectively uptake oxygen (e.g. from air) during an oxidation step before releasing this incorporated oxygen into a process stream during an oxygen release step, caused by a change in the temperature or pO₂. Two classes of materials have been studied for this thermo-chemical oxygen production. Simple transition metal oxides such as Mn₂O₃, Co₃O₄ and

CuO have relatively high oxygen transfer capacities, up to ~ 10 wt% of the material, but suffer from sintering [16]. On the other hand, non-stoichiometric oxides, primarily perovskites, are much more resistant to sintering, albeit offering lower oxygen transfer capacities [17]. Both types of materials typically operate at temperatures above 800°C due to either kinetic or thermodynamic limitations.

YBaCo₄O_{7+δ} is an oxygen hyper-stoichiometric material which has been shown to reversibly incorporate a large excess of oxygen ions into its crystal structure in ambient air, at temperatures between 300 and 400 °C, which is lost upon further heating [18-21]. In-situ x-ray diffraction (XRD) investigations of the material have shown that in a pO₂ of 1 bar the material undergoes complex crystallographic changes, namely a transition from a hexagonal to an orthorhombic space group upon oxygen incorporation at 300 C. Further heating of the sample to temperatures above 400 °C returns the original hexagonal structure [22]. The oxygen storage capacity of this material is one of the highest among non-stoichiometric materials investigated so far, approximately 3.5% by weight (equal to a change in δ of 1.5) [23]. Furthermore, as the operating temperature of the material is only ~400 °C, much lower than its synthesis temperatures of 1200 °C, it is likely that YBaCo₄O_{7+δ} would be less prone to further thermal sintering during operation. Whilst the potential of YBaCo₄O_{7+δ} for oxygen separation has been demonstrated qualitatively, no detailed study of how the release of oxygen from the material changes in different pO₂'s has been conducted.

In this work, a feasibility study was conducted to demonstrate how YBaCo₄O_{7+δ} could be used for oxygen enrichment processes. This work aims to find suitable operating conditions for both oxygen incorporation and release, in order to demonstrate the ability of this material to incorporate oxygen from air (pO₂ of 0.21 bar) and to release this oxygen at a higher pO₂ of 0.31 bar over reasonable timescales, using a small temperature swing to create a driving force. Additionally, the material stability in various reactive gases is investigated to elucidate for which oxygen enrichment processes this material may be suitable.

2. Experimental

2.1 Sample synthesis

Powders of YBaCo₄O_{7+δ} were produced by a solid state synthesis described in ref. [24]. Stoichiometric amounts of Y₂O₃, Co₃O₄ and BaCO₃ (Sigma Aldrich, 99.99, 99.7 and 99%+ purity respectively) were ground together by mortar and pestle and underwent a two stage calcination in air with intermittent grinding. The first calcination step occurred at 1000 °C and lasted 12 hours and the second calcination was performed at 1200 °C for 12 hours with the sample cooled to room temperature in-between. A heating and cooling rate of 1 °C/min between room temperature and the target temperature was used for both steps.

2.2 Sample characterisation

X-ray powder diffraction (XRD) of the as-synthesised and used material was performed at ambient conditions with a Panalytical X'Pert Pro diffractometer using CuK α radiation (40 kV, 40 mA) for 2 θ between 10 and 90° with a step size of 0.033°. EDX analysis of samples were conducted using a Rontec Quantax unit.

Thermogravimetric analysis (TGA) of the material was conducted using a Rubotherm dynTHERM unit. The gas molar flow rates of all TGA experiments were regulated at 8.8×10^{-3} mol/min with Brooks mass flow controllers and a sample of particles with mass between 200 and 400 mg and size between 80 and 160 microns was used for each experiment. For each experiment, the sample was pre-treated by heating in helium (BOC, 99.995% purity) to 500 °C and dwelling for 4 hours to achieve a stable final mass (δ change < 0.001 over 1 hour) corresponding to $\delta = 0$ according to other studies [25] and subsequently cooled to the required starting temperature.

Two types of TGA experiments were conducted in this work- temperature programmed reactions (TPR) in a constant atmosphere, and oxygen cycling experiments.

To investigate the stability of the material in CO, H₂ and CO₂, TPR experiments were performed in 5 mol% CO in He, 5 mol% H₂ in He and 50 mol% CO₂ in He respectively provided by BOC, from 100 to 500 °C (800 °C in the case of CO₂) with a heating rate of 1 °C/min.

To determine the effect on pO₂ on the temperature at which oxygen release begins, a set of experiments were conducted where the pre-treated samples were first exposed to different pO₂'s ranging from 0.05 and 0.42 bar at 300 °C for 10 hours, followed by step changes in temperature in 5 °C increments up to 430 °C, allowing for 1 hour between each change.

Oxygen cycling experiments were conducted in order to measure the rate of incorporation and release of oxygen as a function of temperature. During these experiments, after the sample underwent the helium pre-treatment, the sample was cooled in helium to the required starting temperature. Once the required starting temperature, between 280 and 370 °C, was reached, the gas environment was switched from helium to the required pO₂ where the material was allowed to dwell for 1 hour for oxidation. After oxidation the gas environment was switched to helium and held for another hour to release oxygen from the sample.

To fully demonstrate the potential of the material for oxygen enrichment, a sample of YBaCo₄O_{7+ δ} was allowed to dwell for 2 hours in an air stream (pO₂ = 0.21 bar) at 310 °C to incorporate oxygen before a temperature swing in a pO₂ of 0.31 bar was used to release this incorporated oxygen. During this oxygen release step, the sample was heated at a rate of 20 °C/min to 430 °C, starting at the same time as the gas switch.

The stability of the material in water vapour was also examined by exposing 1 g of the material in a packed bed (internal diameter 5 mm) to a $p_{\text{H}_2\text{O}}$ of 0.05 bar, balanced in Ar (99.995% purity) at 450 °C for 3 hours, with a flow rate of 2×10^{-3} mol/min controlled by Brooks mass flow controllers.

3. Results and discussion

3.1 Material stability

The results of several TPRs of $\text{YBaCo}_4\text{O}_{7+\delta}$ in common reactive gases found in an exhaust stream from a potential oxy-fuel combustion process are shown in Figure 1.

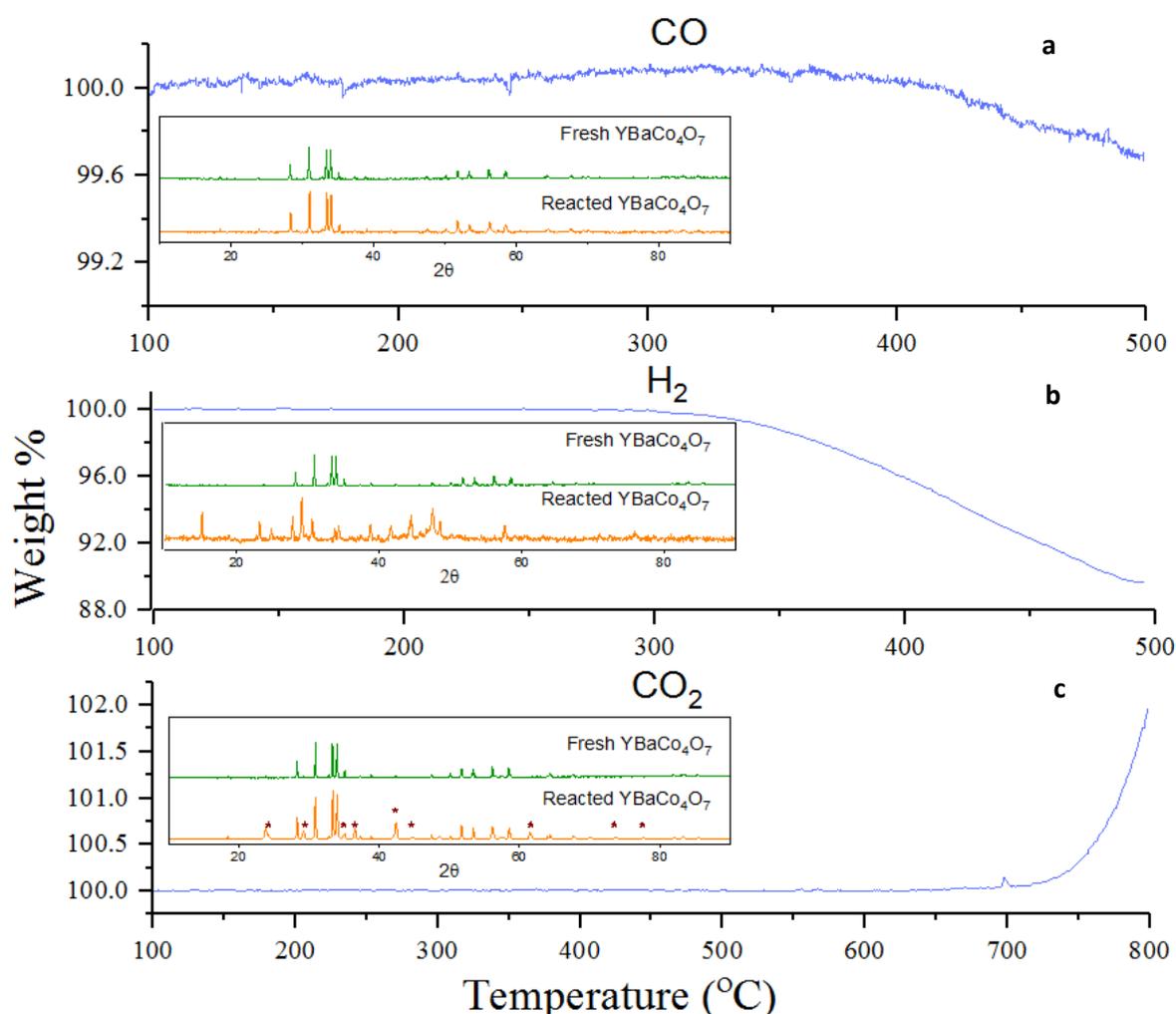


Figure 1 – Dynamic TG curves showing the mass change versus temperature of $\text{YBaCo}_4\text{O}_{7+\delta}$ heated at a ramp rate of 1 °C/min in (a), $p_{\text{CO}} = 0.05$ bar, (b), $p_{\text{H}_2} = 0.05$ bar, (c), $p_{\text{CO}_2} = 0.5$ bar (balance He). Inserts show XRD results of fresh powder and powder after each treatment. Peaks corresponding to barium carbonate are identified by a ★

It can be seen from Figure 1(a) that during TPR with $p_{\text{CO}} = 0.05$ bar, the sample maintained a constant mass until approximately 250 °C, after which a small weight gain of approximately 0.1% was observed. This gain was attributed to carbon deposition on the material via the Boudouard reaction and was

confirmed by EDX measurements which showed an increased carbon loading on the material compared to fresh powder. Between 350 °C and 500 °C, the sample mass decreased slightly to 99.6% of the initial mass, most likely due to the reduction of the material by CO. The insert in Figure 1(a) compares XRD patterns of a sample treated in helium only and the sample after the treatment in CO with no new peaks being detected.

As shown in Figure 1(b), the material is stable in $p_{H_2} = 0.05$ bar until approximately 300 °C. Further heating caused a decrease in the sample mass at a constant rate until the sample mass stabilised at approximately 480 °C, at which point approximately 10% of the sample mass was lost. The insert in Figure 1(b) shows multiple new peaks forming, along with the loss of peaks belonging to $YBaCo_4O_{7+\delta}$, indicating significant phase changes had occurred with the reduction.

Figure 1(c) presents the weight change of $YBaCo_4O_{7+\delta}$ heated at a rate of 1 °C/min in a p_{CO_2} of 0.5 bar. The figure shows the sample mass was stable until approximately 650 °C, 250 °C higher than the likely operating temperature of the material. Upon further heating the sample mass increased by 2%, likely due to the formation of barium carbonate, which is supported by the XRD patterns shown in the insert in Figure 1(c).

In addition to the TPR investigations, the stability of the material in water vapour was also examined by exposing 1 g of the material in a packed bed (internal diameter 5 mm) to a p_{H_2O} of 0.05 bar, balanced in Ar (99.995% purity) at 450 °C for 3 hours, with a flow rate of 2×10^{-3} mol/min. After treatment the sample was cooled in argon and the XRD pattern of the treated sample showed no new phases being produced.

3.2 Investigation into the effect of p_{O_2} on the useful oxygen release of $YBaCo_4O_{7+\delta}$

To investigate the effect of p_{O_2} on the temperature of the material's oxygen release, a sample was held at 300 °C for 10 hours in different p_{O_2} 's ranging from 0.05 to 0.42 bar before being heated in the same p_{O_2} in 5 °C steps, each lasting 1 hour. The results of this experiment can be seen in Figure 2 and show how the temperature of oxygen release changes with changing p_{O_2} . Heating the sample above the oxygen release temperature for a given p_{O_2} allows the material to release additional oxygen into the gas environment, enriching the oxygen content of the gas stream.

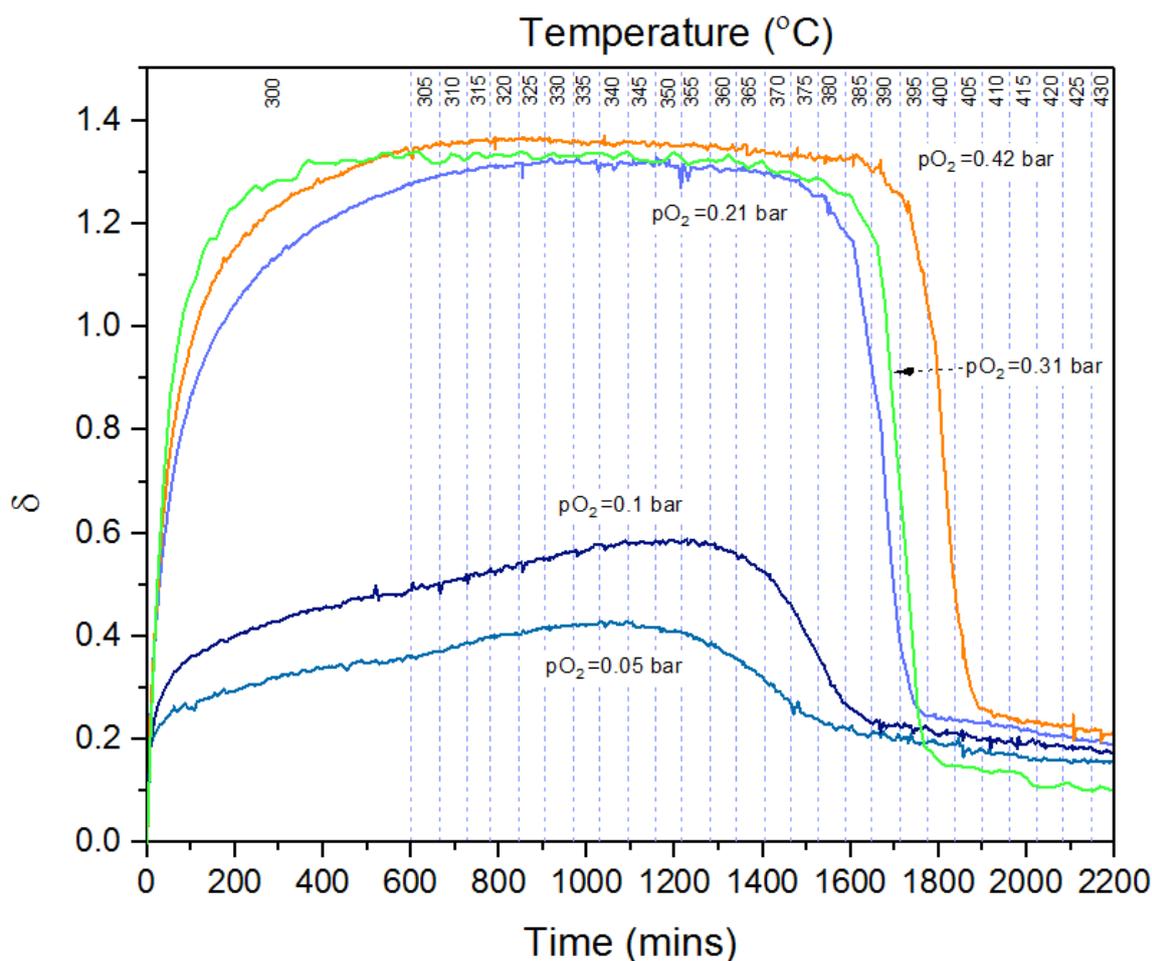


Figure 2 –TG curves showing δ versus time for $\text{YBaCo}_4\text{O}_{7+\delta}$ heated in hour long 5°C steps from 300 to 430°C with $p\text{O}_2$'s ranging from 0.05 to 0.42 bar after an initial 10 hour oxygen annealing in the same $p\text{O}_2$

Each curve in this figure follows a similar trend, with large amounts of O_2 being incorporated at low temperatures (between 300 and 320°C). The sample maintains this δ upon heating until 370°C in a $p\text{O}_2$ of 0.21 bar, at which point the sample began to release oxygen. The temperature at which oxygen release occurs increases upon increasing the $p\text{O}_2$. In a $p\text{O}_2$ of 0.3 bar (the minimum for the oxy-fuel process) the material will begin to release oxygen when heated above 380°C , meaning that the higher $p\text{O}_2$'s required for oxy-fuel combustion are accessible in practical timescales using this material above approximately 390°C .

3.3 Isothermal oxygen incorporation/release experiments

To investigate the rate of oxygen incorporation/release for $\text{YBaCo}_4\text{O}_{7+\delta}$, isothermal experiments were conducted in a TGA at temperatures ranging from 270 to 330°C . A sample was left for 1 hour in an air flow of 8.8×10^{-3} mol/min for oxygen incorporation, before the gas feed was switched to helium to release this oxygen. The results can be seen in Figure 3, with Figure 3(a) showing the oxidising

isotherm, and Figure 3(b) showing the change in δ after this oxidising step when the gas environment was switched to helium.

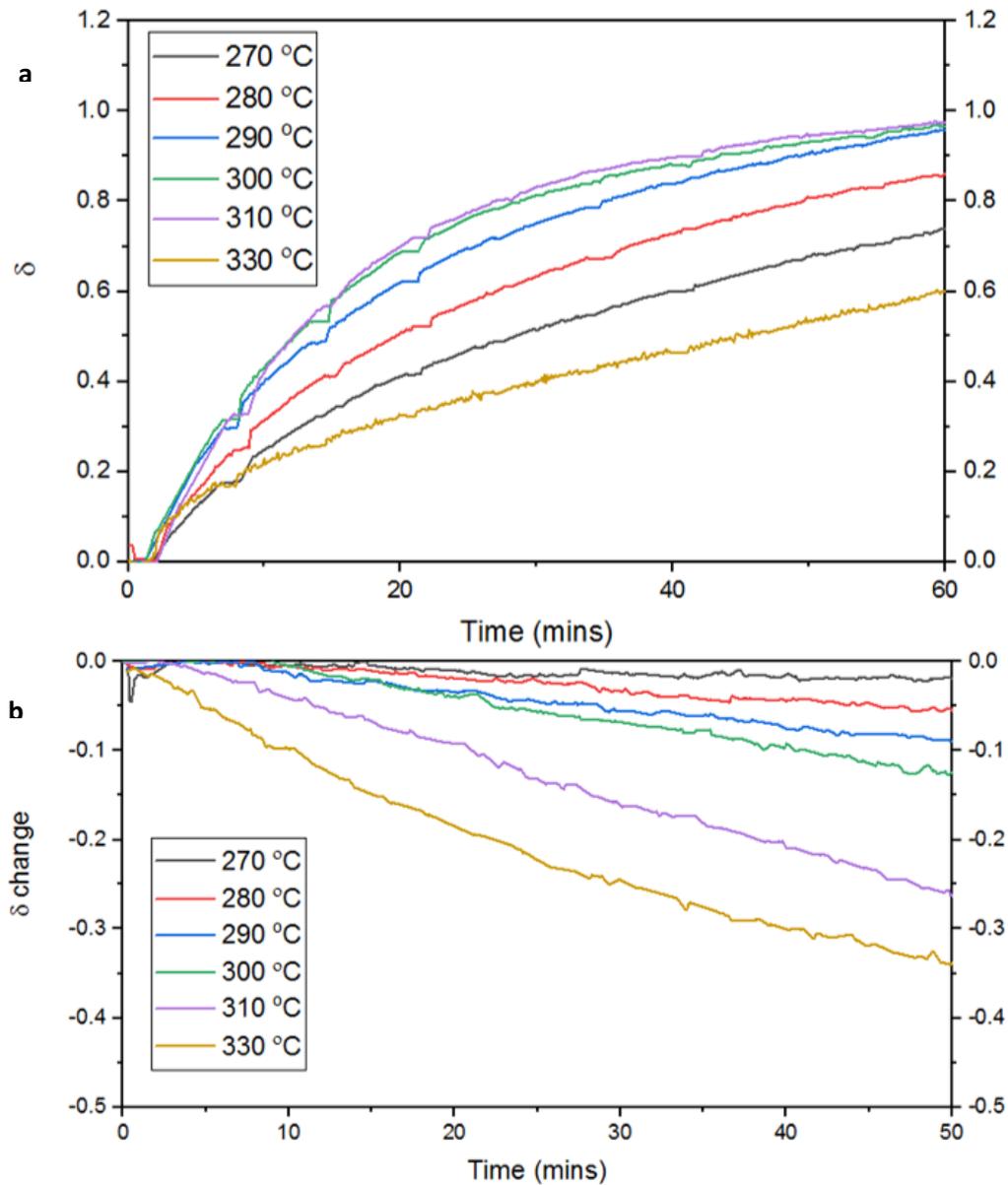


Figure 3(a) - TG curves showing δ versus time for isothermal holds of $\text{YBaCo}_4\text{O}_{7+\delta}$ held in a $p\text{O}_2$ of 0.21 bar between 270 and 330 °C, (b) – TG curves showing δ change versus time for isothermal holds of $\text{YBaCo}_4\text{O}_{7+\delta}$ held in helium at temperatures between 270 and 330 °C after oxygen incorporation shown in Figure 3(a)

Figure 3(a) shows how the oxygen incorporation of $\text{YBaCo}_4\text{O}_{7+\delta}$ changes with temperature. The fastest rate of oxygen incorporation occurred between 290 and 310 °C and the oxygen non-stoichiometry of the sample, δ , increased by 0.96 and 0.98 respectively after 1 hour. A further increase in temperature to 330 °C caused the rate of oxygen incorporation to reduce significantly and 25% less oxygen was incorporated. Figure 3(b) shows how the oxygen release from $\text{YBaCo}_4\text{O}_{7+\delta}$ changes with temperature.

The rate of oxygen release was slow at temperatures below 280 °C, with an equivalent change in δ less than 0.02 over 1 hour.

Overall, a maximum rate of oxygen incorporation of $\text{YBaCo}_4\text{O}_{7+\delta}$ in air occurred at 310 °C, whilst the rate of oxygen release increased monotonically with temperature. Thus, it would be more favourable to operate the material at different temperatures for oxygen incorporation and release. Considering further that to produce oxygen for a viable oxy-fuel combustion process, a $p\text{O}_2$ of 0.3 bar is required, it would be necessary to release oxygen at temperatures higher than 380 °C as shown in Figure 2 and re-oxidise the material in air at around 310 °C.

4. Discussion

The effects of $p\text{O}_2$ and temperature on the oxygen incorporation/release behaviour of $\text{YBaCo}_4\text{O}_{7+\delta}$ have been investigated and show clear potential for $\text{YBaCo}_4\text{O}_{7+\delta}$ to be used for oxygen enrichment processes. The clearest method of use for oxygen enrichment utilises a temperature swing, incorporating oxygen at 310 °C and release this incorporated oxygen above 380 °C as shown in Figures 2 and 3. For demonstration, a sample was cycled between an oxidising step at 310 °C in a $p\text{O}_2$ of 0.21 bar before undergoing heating to 430 °C in a $p\text{O}_2$ of 0.31 bar to release this incorporated oxygen, shown below in Figure 4.

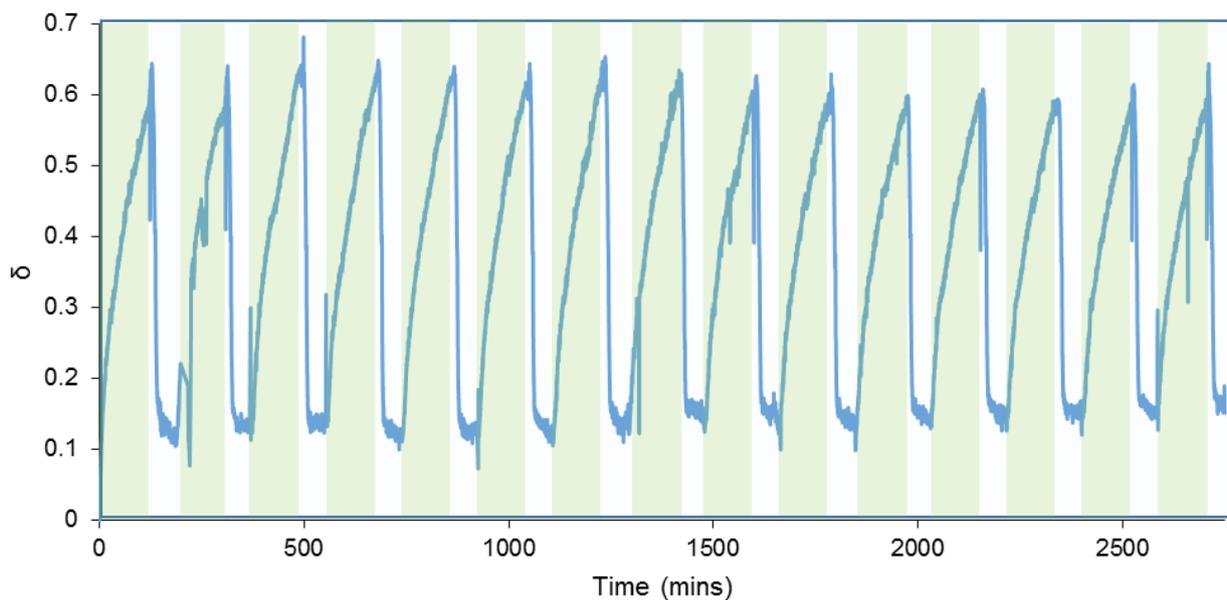


Figure 4 - TG curves showing δ versus time for $\text{YBaCo}_4\text{O}_{7+\delta}$ cycling between 120 minute long holds in a $p\text{O}_2$ of 0.21 bar at 310 °C (pale green rectangles) before being heated at a rate of 20 °C/min to 430 °C in a $p\text{O}_2$ of 0.31 bar with gas flow rate of 1.7×10^{-2} mol/min (pale blue rectangles)

During this temperature swing the sample oxidised to a δ of approximately 0.6 during the oxidation step before releasing the incorporated oxygen equal to a change in δ of 0.45 during the heating phase in a $p\text{O}_2$ of 0.31 bar to give a final δ of 0.15. This change in δ is equivalent to approximately 1.5 % of

the sample mass and clearly demonstrates $\text{YBaCo}_4\text{O}_{7+\delta}$ is suitable for use for oxygen enrichment processes such as oxy-fuel combustion.

Figure 4 however shows a drop in the capacity of $\text{YBaCo}_4\text{O}_{7+\delta}$ with the amount of oxygen incorporated and released decreasing over 15 cycles (45 operational hours). Table 2 compares the maximum and minimum value of δ obtained during the 3rd and 11th cycle. These cycles were chosen as the 3rd cycle incorporated and released the most oxygen during the experiment and the 11th cycle showed the greatest drop in capacity compared to the previous cycles. The 11th cycle also appears representative of the subsequent cycles which do not show further loss of performance.

Table 2 – List of δ values obtained during the 3rd and 11th oxygen incorporation and release cycles shown in Figure 4

Parameter	Cycle 3	Cycle 11
δ Max	0.64	0.57
δ Min	0.12	0.15
Change in δ	0.52	0.42

The decrease in the amount of oxygen transferred during the first 10 cycles suggests there may be potential issues with long term stability of the material. This loss of activity was unexpected due to the low operating temperatures of the material and further investigations into the cause are required.

5. Conclusion

In this study $\text{YBaCo}_4\text{O}_{7+\delta}$ powders were produced by a solid state synthesis and the oxygen enrichment properties of the material were investigated. The effect of temperature on oxygen incorporation and the necessary operational temperatures for oxygen release to obtain specific $p\text{O}_2$'s were found by TGA methods.

A temperature swing was conducted to mimic how $\text{YBaCo}_4\text{O}_{7+\delta}$ could be used to oxygenate a CO_2 stream for the oxy-fuel combustion process, driving oxygen incorporated from an air stream at a $p\text{O}_2$ of 0.21 bar into a stream of 0.31 bar – the minimum operating $p\text{O}_2$ for the process. The material was shown to be suitable for oxygen enrichment processes. During operation the material underwent 15 oxygen incorporation/release cycles or 45 hours of operation with a 19% drop in the amount of oxygen incorporated and released during the first 10 cycles. During the final 5 redox cycles no notable changes in the amount of oxygen incorporated and released were observed.

Material stability in CO₂, CO and H₂O was shown up to 420 °C showing the potential for use in an exhaust stream. Coking was seen in the presence of CO between 250 and 350 °C which may cause operational issues for the process. The material was also seen to decompose readily in hydrogen at temperatures above 300 °C.

Acknowledgments

Thanks go to Dr Evangelos. I. Papaioannou from Newcastle University for his review, comments and support for this work. Thanks also go to Maggie White for performing the XRD experiments.

We thank Professor Truls Norby for bringing this material to our attention.

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement Number 320725 and from the EPSRC via Grant EP/J016454/1, EP/K014706/1, EP/K014706/2, EP/K029649/1, EP/P007767/1, EP/P024807/1. Data supporting this publication is openly available under an 'Open Data Commons Open Database License'. Additional metadata are available at: <http://dx.doi.org/10.17634/154300-64>. Please contact Newcastle Research Data Service at rdm@ncl.ac.uk for access instructions.

References

- [1] J. Kugaia, J. T. Miller, N. Guob, C. Song - Oxygen-enhanced water gas shift on ceria-supported Pd–Cu and Pt–Cu bimetallic catalysts, *Journal of Catalysis*, 277(2011), 1, 46-53
- [2] J. Kugaia, E. B. Fox, C. Song - Kinetic characteristics of oxygen-enhanced water gas shift on CeO₂-supported Pt–Cu and Pd–Cu bimetallic catalysts, *Applied Catalysis A: General*, 497, (2015), 31–41
- [3] R.Horn, K.A.Williams, N.J.Degenstein, A.Bitsch-Larsen, D.Dalle Nogare, S.A. Tupy, L.D.Schmidt - Methane catalytic partial oxidation on autothermal Rh and Pt foam catalysts: Oxidation and reforming zones, transport effects, and approach to thermodynamic equilibrium, *Journal of Catalysis*, 249, (2007), 380–393
- [4] B.M.Khudenko, G.M.Gitman, T.E.P.Wechesler - Oxygen Based Claus Process for Recovery of Sulfur from H₂S Gases, *J. Environ. Eng.*, 1993, 119(6): 1233-1251
- [5] M.Sassi, A.K.Gupta - Sulfur Recovery from Acid Gas Using the Claus Process and High Temperature Air Combustion (HiTAC) Technology, *American Journal of Environmental Sciences* 4 (5): 502-511, 2008

- [6] A.Bensakhira, M.Leturia - Natural gas oxy-combustion with flue gas recycling for CO₂ capture
Chemical Engineering Transactions, Vol.21, 2010
- [7] A.Kontopoulos, J.Koenig - "Oxygen and nitrogen injection for increasing ammonia production"
" U.S. Patent application no WO1998045211 A1
- [8] - B.J.P. Buhre, L.K. Elliott, C.D. Sheng, R.P. Gupta, T.F. Wall, Oxy-fuel combustion technology
for coal-fired power generation, Progress in Energy and Combustion Science, 2005, 31, 283-307
- [9] - D Singh, E Croiset, PL Douglas, MA Douglas – Techno-economic study of CO₂ capture from an
existing coal-fired power plant: MEA scrubbing V.s. O₂/CO₂ recycle combustion, Energy Convers
Manage 2003, 44, 3073-3091
- [10] – K Kimura, K Omata, T Kiga, S Takano, S Shikisima - Characteristics of pulverised coal
combustion in O₂/CO₂ mixtures for CO₂ recovery. Energy convers manage 1995, 36, 805-808
- [11] – T Kiga - O₂/RFG combustion-applied pulverised coal fired plan for CO₂ recovery, Advanced
coal combustion, Nova Science Publishers, Inc; 2001. P. 185-41
- [12] – T Kiga, S Takano, N Kimura, K Omata, M Okawa, T Mori et al. - Characteristics of pulverised
coal combustion in the system of oxygen/recycled flue gas combustions. Energy convers Manage 1997,
38. S129-s34
- [13] - Yang Q, Lin YS, - High temperature sorption separation of air for producing oxygen enriched
CO₂ stream ALChE J, 2006, 52, 574-584
- [14] - Yang Q, Lin YS, - Fixed bed performance for production of oxygen enriched carbon dioxide
stream by perovskite type ceramic sorbent, Sep. Purif. Technol 2006, 49, 27-35
- [15] A.R.Smith, J.Klosek - A review of air separation technologies and their integration with energy
conversion processes. Fuel Process Technol (2001) 70 (2): 115–134
- [16] Q.Imtiaz, D.Hosseini, C.R.Muller - Review of Oxygen Carriers for Chemical Looping with
Oxygen Uncoupling (CLOU): Thermodynamics, Material Development, and Synthesis, Energy
Technology, (2013), 1, 11, 633-647
- [17] A.Murugan , A.Thursfield, I.S.Metcalf - A chemical looping process for hydrogen production
using iron-containing perovskites, Energy Environ. Sci., 2011, 4, 4639-4649
- [18] - M. Valldor, M. Andersson - The structure of the new compound YBaCo₄O₇ with a magnetic
feature, Solid State Sci. 4 (2002), p.923.

- [19] - M. Karppinen, H. Yamauchi, S. Otani, T. Fujita, T. Motohashi, Y.-H. Huang, M. Valkeapää, and H. Fjellvåg - Oxygen Nonstoichiometry in $\text{YBaCo}_4\text{O}_{7+\delta}$: Large Low-Temperature Oxygen Absorption/Desorption Capability, *Chem. Mater.* 2006, 18, 490-494
- [20] - H. Hao, J. Cui, C. Chen, L. Pan, J. Hu, X. Hu - Oxygen adsorption properties of YBaCo_4O_7 -type compounds, *Solid State Ionics*, 2006, 177, 631–637
- [21] -K.Zhang, Z.Zhu, R.Ran, Z.Shao, W.Jin, S.Liu,- Layered perovskite $\text{Y}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_{7+\delta}$ as ceramic membranes for oxygen separation, *JACS*, 2010, 492, 528-558
- [22] – M. Valkeapa, M. Karppinen, T. Motohashi,, R. Liu, J. Chen, H. Yamauchi2 - In Situ and Ex Situ Monitoring of Oxygen Absorption in YBaCo_4O_7 , *Chemistry Letters* Vol.36, No.11 (2007)
- [23] –S.Räsänen, T.Motohashi, H.Yamauchi, M.Karppinen - Stability and oxygen-storage characteristics of Al-substituted $\text{YBaCo}_4\text{O}_{7+\delta}$ *Journal of Solid State Chemistry*, 2010, 183, 692-695
- [24] - M.Vallador - Syntheses and structures of compounds with YBaCo_4O_7 -type structure, *Solid State Sciences*, 2004, 6, 251-266
- [25] - H.Hao, X.Hu, H.Hou - Oxygen adsorption/desorption behaviour of $\text{YBaCo}_4\text{O}_{7+\delta}$ and its application to oxygen removal from nitrogen, *Journal of rare earth metals* 2009 (27) 815-818