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Carbon Dioxide Decomposition Through Gas Exchange in Barium Calcium Iron Niobates

Harriet Kildahl^{*a}, Zhongbo Li^{*b}, Hui Cao^{a, †}, Peter Slater^c, Yulong Ding^a

^a School of Chemical Engineering, University of Birmingham, Birmingham, United Kingdom

^b Beijing District Heating Group, China

^c School of Chemistry, University of Birmingham, Birmingham, United Kingdom

[†] Corresponding author: h.cao@bham.ac.uk

^{*}Both authors contributed equally to this manuscript

Abstract

A number of metal oxides and perovskites are capable of being reduced at high temperatures and then re-oxidised in the presence of CO₂ or H₂O to form CO or H₂. Barium calcium iron niobates have been found to be redox-active in this way. The redox activity of these perovskites was explored, and the chemical and physical stability was investigated using EDX and SEM imaging, respectively. The most promising, Ba₂Ca_{0.66}Nb_{0.34}FeO_{6-δ} (BCNF1), showed mass changes of 0.45% after five cycles of reduction with N₂ and re-oxidation with 10% CO₂. BCNF1 is chemically stable as it shows no changes in XRD and shows no evidence of sintering, although cracking of the pellets was observed after re-oxidation. The low enthalpy of re-oxidation of BCNF1 coupled with the high and sustained mass change makes this perovskite suitable for chemical looping use for energy storage and conversion systems.

Keywords: Carbon dioxide conversion, perovskite, CO₂ reduction, chemical looping, barium calcium iron niobates

1. Introduction

With the shift towards a 100% renewable future well underway, there are still areas where gains in efficiency and decreases in losses can be made. One of these areas is industrial waste heat. There are many industries which require heat such as chemical, food and drink, textiles and metal processing. The 28 members of the European Union required 1820 TWh of energy as heat across all industries in 2018, which amounts to around 70% of total energy consumption by industry[1]. More than 48% of this heat is over 500 °C with up to 28% hotter than 1000 °C. The iron and steel industries are particularly attractive for waste heat recovery or usage since the temperatures can be up to 2000 °C[2]. Industrial-scale demonstrations have been built to store the waste heat in thermal energy and later on reuse it for industrial/domestic heating[3]. A recently proposed novel concept of exploiting this waste heat is to use a thermochemical cycle where changes in temperature are used to decompose small molecules such as CO₂ or H₂O into CO and H₂[4]. Carbon monoxide and hydrogen can be used as syngas for the Fischer-Tropsch process, to produce essential chemicals without the need for crude oil[5], or as a fuel in a fuel cell device. The iron and steel industries also have high CO₂ emissions, such as 1.22 tonnes of CO₂ per tonne of product produced in a blast furnace[6]. Therefore, both heat and increased CO₂ concentrations could be found in these industries, which would be ideal for the implementation of a thermochemical material and help to reduce direct emissions. CO production from carbon dioxide by a thermochemical cycle was found to be more than 2.5 times more efficient than algae-based biomass conversions when using waste heat from industry[7].

A thermochemical cycle works through the addition of heat, causing reduction of the material. Oxygen is released from the material resulting in the formation of oxygen vacancies throughout the structure (Equation 1). Upon the addition of CO₂ or H₂O, the material is re-oxidised, often at a lower temperature, and the oxygen vacancies are filled while CO or H₂ is released (Equation 2). As can be seen from Equation (1) and (2), fuel production is increased with an increase in the oxygen non-stoichiometry, δ . Therefore, the efficiency and fuel production yield can be increased by aiding the diffusion of gases throughout the material. If oxygen is lost throughout the material rather than only the surface, more oxygen vacancies

can be formed. This greater level of reduction leads to deeper oxidation as there are more oxygen vacancies to be filled. This leads to a greater decomposition of CO_2 or H_2O and therefore greater fuel production. The diffusion of gases within the material can be aided by increases in porosity or surface area to volume ratio.

The two main classes of materials capable of undergoing a thermochemical cycle are simple metal oxides or mixed metal oxides, such as perovskites. Of the simple metal oxides, the most researched is ceria (cerium oxide) which can split both carbon dioxide and water with good yields; however, it requires high temperatures such as 1400°C for reduction and 900°C for oxidation[8]. Ceria is a non-stoichiometric oxygen carrier meaning that less than one mole of oxygen is released per mole of ceria. Other metal oxides include the volatile metal oxides and iron oxides. Volatile metal oxides are stoichiometric oxygen carriers and have melting temperatures of the pure metal lower than the reduction temperature of the metal oxide. For example, ZnO has a reduction temperature of 2000°C but a melting temperature of 420°C , meaning that the gaseous zinc must be quenched quickly to avoid recombination with oxygen[9]. Pure iron oxide (Fe_3O_4) can be reduced at 2200°C ; however, it can be oxidised easily by water at 175°C [10].

Perovskites are non-stoichiometric mixed metal oxides with an ideal formula of ABO_3 . The most researched perovskite for thermochemical cycles is the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ family, which can be reduced at about 1400°C and oxidised at around 900°C with up to ten times higher fuel yields than ceria[11]. $\text{Ba}_2\text{Ca}_{0.66}\text{Nb}_{1.34-x}\text{Fe}_x\text{O}_6$ ($x = 0, 0.34, 0.66$ and 1) is a double perovskite-type and can be reduced and made to decompose CO_2 at 700°C [12]. This paper will investigate the barium calcium iron niobate perovskite family for their ability to split carbon dioxide at 700°C . The redox activity of these materials will be measured predominantly by mass change during the thermochemical cycles along with tracking of changes to the crystal structure and surface morphology during the reaction.

2. Experiment

2.1 Material Synthesis

$\text{Ba}_2\text{Ca}_{0.66}\text{Nb}_{1.34-x}\text{Fe}_x\text{O}_6$ perovskites were synthesised through a solid-state reaction as performed previously[12]. Four perovskites were synthesised by varying the concentrations of niobium and iron in the B-site while maintaining the concentration of calcium in the B-site and barium in the A-site. The four perovskites tested are $\text{Ba}_2\text{Ca}_{0.66}\text{Nb}_{1.34}\text{O}_{6-\delta}$ ($x = 0$, named BCNF0), $\text{Ba}_2\text{Ca}_{0.66}\text{NbFe}_{0.34}\text{O}_{6-\delta}$ ($x = 0.34$, named BCNF0.34), $\text{Ba}_2\text{Ca}_{0.66}\text{Nb}_{0.68}\text{Fe}_{0.66}\text{O}_{6-\delta}$ ($x =$

0.66, named BCNF0.66) and $\text{Ba}_2\text{Ca}_{0.66}\text{Nb}_{0.34}\text{FeO}_{6-\delta}$ ($x = 1$, named BCNF1). Stoichiometric ratios of the precursors (BaCO_3 (Alfa Aesar, 99%), CaCO_3 (Alfa Aesar, 99.5%), Nb_2O_5 (Alfa Aesar, 99.5%), Fe_2O_3 (J.T.Baker, 99%)) were mixed in a ball mill (Fritsch Pulverisette) at 350 rpm for 30 minutes. The resulting powder was calcined in air at 1000 °C for 12 hours (Carbolite, HTF18/27) before ball milling again. The powder was pressed into 13mm diameter pellets with isostatic pressure of 120 MPa (Lloyd Instruments, LS100Plus) and sintered at 1400 °C for 24 hours.

2.2 Material Characterisation

X-ray diffraction (XRD) was performed on a Bruker d8 Advance X-ray Diffractometer with Cu K α radiation ($\lambda=1.54$ Å) over the 2θ range between 10° and 80° with a step size of 0.02° and 3 seconds per step. The pellets were measured whole. Lattice parameters were calculated by solving the least-squares of 2θ , using Bragg's Law and the plane spacing equation. Scanning electron microscopy (SEM) (Hitachi TM3030) with energy dispersive X-ray (EDX) was used to investigate the surface structure of the pellets and the composition of the surface layers. Helium Pycnometry (Accupyc II 1340) was used to determine the density and porosity of the perovskite pellets. Microcomputer tomography (Micro CT) (Bruker SkyScan 2211) was used to visualise the 3D structure of the pellets to investigate gas exchange.

2.3 Thermal Cycle of Perovskites

The perovskites were tested for catalytic ability in a tubular furnace with controlled gas flows (Elite Thermal Systems Ltd TSH15/50/450). The pellets were inserted into the furnace, and the furnace was heated to 700 °C with a nitrogen flow of 50 ml/min. The pellets were reduced for 24 hours before being weighed and characterised with SEM, EDX and XRD. The pellets were heated again to 700 °C with a 10% CO_2 /90% N_2 flow of 50 ml/min and left to react for 24 hours. The pellets were weighed again, and characterisation with SEM, EDX and XRD was repeated. Simultaneous thermal analysis (Linseis STA PT1600/800) was used to calculate the enthalpy of the CO_2 reaction. The experimental flowchart is shown in Figure 1 (a). Thermal cycling was performed by alternating 24 hours of reduction under nitrogen at 700 °C with 24 hours of oxidation under 10 % CO_2 / 90 % N_2 at 700 °C for five cycles. After each step of the cycle, the pellets were cooled to room temperature and weighed.

3. Results and Discussion

3.1 Material Characterisation

Characterisation of the as-prepared perovskites was undertaken to confirm their phase formation. The as-prepared pellets can be seen in Figure 1(b). The iron-containing perovskites (BCNF1 (1), BCNF0.66 (2) and BCNF0.34 (3)) are black while BCNF0 (4) which contains no iron is white. Helium pycnometry (Table 1) shows an increase in density with increasing niobium content due to the higher molecular weight of niobium compared to iron. Porosity also generally increases with increasing niobium content, and it can be seen in Figure 1(b) that the BCNF0 pellets are slightly larger than the iron-containing pellets (BCNF0.34, BCNF0.66 and BCNF1), despite being made in the same mould, indicating less shrinkage on sintering. This correlates with the much higher pore volume in BCNF0. This is in agreement with the literature where doping with larger atomic radii elements results in greater porosity[13].

Figure 1. (a) Experimental workflow, (b) Visual representation of the as-synthesized pellets, (1) BCNF1, (2) BCNF0.66, (3) BCNF0.34 and (4) BCNF0

Table 1. Helium pycnometry results showing density, pore volume and porosity

Sample	Mass (g)	Density (g/cm ³)	Pore volume (cm ³ /g)	Porosity (%)
BCNF1	0.472	6.1003	0.1687	50.70
BCNF0.66	0.462	6.2382	0.2512	61.04
BCNF0.34	0.468	6.3966	0.2278	59.31
BCNF0	0.441	6.6309	0.3231	68.18

SEM images with x1000 magnification of the as-prepared perovskites can be seen in Figure 2. The as-prepared BCNF0 perovskite without iron (a) had an average grain size around

10 μ m with no grains larger than 20 μ m and pores of around 1 μ m. BCNF0 had the smallest variation in grain sizes of any of the perovskites. The BCNF0.34 perovskite (d) had an average grain size below 5 μ m with a high density of pores. The as-prepared BCNF0.66 perovskite (g) had larger grains than BCNF0 or BCNF0.34 with an average size of around 20 μ m and a few large pores around 8 μ m. The grain sizes in the as-prepared BCNF1 (j), the perovskite with the most iron, are not distinguishable.

Figure 2. SEM images of as-prepared, after reduction and after re-oxidation of the four perovskites, BCNF0, BCNF0.34, BCNF0.66 and BCNF1

The Micro CT scans (Figure 3) of the four perovskites reveal that the core of the pellets has a higher density than the outer edges of the pellets, which likely occurred during the high-pressure moulding of the pellets. Additionally, the faces of the pellets are textured rather than smooth, showing that the surface is porous, as was seen in the SEM images and confirmed by helium pycnometry.

Figure 3. Micro Computer Tomography Reconstructed Images of (a) BCNF0, (b) BCNF0.34, (c) BCNF0.66, and (d) BCNF1.

XRD data of the as-prepared perovskites (Figure 4) shows that all perovskites had a double-perovskite type face centred cubic structure with an $Fm\bar{3}m$ space group. The average lattice parameters and miller indexing can be seen in Table 2. The perovskites synthesised here showed similar XRD patterns and crystal structures as other Barium Calcium Iron Niobates synthesised in the literature[12,14,15], with some variations in relative intensities of peaks, which may relate to some preferred orientation of the crystallites within the pellets. None of the impurities seen in the literature of these compounds could be identified here, including $BaCO_3$, Fe_2C , C and Fe_3O_4 [15], supporting the purity of the samples in the present study.

Figure 4. X-ray diffraction patterns of as-synthesized BCNF1, BCNF0.66, BCNF0.34 and BCNF0.

Table 2. Indexed XRD data for BCNF1, BCNF0.66, BCNF0.34 and BCNF0 with d spacing and intensity

			BCNF1		BCNF0.66		BCNF0.34		BCNF0	
h	k	l	d(Å)	I(%)	d(Å)	I(%)	d(Å)	I(%)	d(Å)	I(%)

1	1	1	4.831	7	4.852	5	4.831	4	5.089	2
2	0	0	4.174	15	4.198	11	4.182	6	4.166	13
2	2	0	2.950	100	2.962	100	2.958	100	2.952	41
2	2	2	2.404	19	2.417	16	2.414	13	2.404	5
4	0	0	2.081	21	2.092	24	2.091	29	2.086	100
4	2	0	1.861	6	1.870	5	1.869	4	1.862	2
4	2	2	1.699	23	1.706	28	1.706	34	1.702	17
4	4	0	1.470	10	1.477	11	1.478	14	1.472	6
6	0	0	1.385	4	1.392	3	1.393	2	1.388	2
6	2	0	1.314	8	1.321	9	1.319	6	1.318	16
6	2	2	1.253	4	1.259	5	1.260	2	1.258	2
4	4	4	1.201	4	1.205	4	1.207	4	1.203	2
			a = 8.344Å		a = 8.377Å		a = 8.366Å		a = 8.345Å	

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165 The double-perovskite type crystal structures can be seen in Figure 5, with calcium, niobium
166 and iron occupying the B-sites and barium occupying the A-sites. The EDX scans in Figure 6
167 of as-prepared BCNF0, BCNF0.34 and BCNF0.66 show an even distribution of all elements,
168 which suggests a uniform sample. On the other hand, BCNF1 shows small clumps of calcium
169 with many areas containing no calcium at all. Since XRD analysis shows that the correct
170 perovskite was synthesized, it can be suggested that the calcium seen in lumps on the surface
171 of the perovskite does not represent the spread of elements within the whole pellet. There are
172 many small patches of around 4µm on the surface, which through EDX analysis are seen to
173 contain high concentrations of calcium. The CaCO₃ starting material had a powder size less
174 than 5µm and so these patches are highly likely to be unreacted CaCO₃ starting material.

Figure 5. Crystal Structures of (a) BCNF0, (b) BCNF0.34, (c) BCNF0.66 and (d) BCNF1

Figure 6. EDX Scans of as-synthesized BCNF1, BCNF0.66, BCNF0.34 and BCNF0

3.2 Reduction and Oxidation

The average mass change during reduction and re-oxidation of the perovskites in the tubular furnace at 700 °C can be seen in Figure 7, and error bars showing one standard deviation are shown in red. Firstly, BCNF0 showed no mass change during reduction or re-oxidation, supporting that iron is needed in the barium calcium iron niobates. This finding has also been confirmed in the literature[12]. BCNF0.34 and BCNF0.66 lost 0.28 and 0.21 % mass during

reduction respectively; however, both showed no mass gain during re-oxidation. In fact, BCNF0.34 showed a minimal amount of mass loss during re-oxidation, perhaps since nitrogen was used during the reduction step and 90 % nitrogen with 10 % carbon dioxide was used during re-oxidation. This could suggest that a higher concentration of carbon dioxide is necessary for the re-oxidation of BCNF0.34 and BCNF0.66. The 10% carbon dioxide mixture used for re-oxidation was chosen to mimic flue gases from iron and steel processing industries. BCNF1 showed the highest mass loss during reduction, 1.14 %. This high level of reduction suggests that oxygen vacancies are forming easily, likely due to the high iron content, allowing more oxygen vacancies to form. Re-oxidation of BCNF1 with 10 % carbon dioxide resulted in a 0.2 % increase in mass. It is common that perovskites are not completely re-oxidised during the re-oxidation reaction [16–19]. This suggests that not all oxygen vacancies formed during reduction are filled during the re-oxidation step. This could be due to the low carbon dioxide content (10 %) which could mean that carbon dioxide was not coming into contact with the oxygen vacancies in the material. Secondly, the low extent of re-oxidation could be due to the high density of the pellets, as seen in the Micro CT images in Figure 3, particularly in the core of the pellet, meaning that gas exchange was likely not possible within the pellet but rather just on the surface. Reactivity of the four perovskites had an inverse relationship with porosity, suggesting that gas exchange was not the limiting factor but rather the material itself, particularly in the case of BCNF0. It is likely that increasing the porosity of BCNF1 would increase its reactivity; this will be investigated in future research. It must be noted that the position in the tubular furnace is not linked to the extent of reduction or oxidation for any of the perovskites.

Figure 7. Average Mass Change of the Four Perovskites During Reduction and Re-oxidation

The difference in the reactivities of the four perovskites can be partially explained by the enthalpy of oxidation calculated from STA measurements (Table 3). A negative enthalpy of oxidation suggests an exothermic reaction which a positive enthalpy suggests an endothermic reaction. The enthalpy of the oxidation reaction for BCNF1 is -45 J/g, which is very small compared to the energy required to raise the perovskite to the reaction temperature of 700 °C, which is around 2570 J/g. This energy likely incorporates the enthalpy of reduction and the energy required to heat the perovskite. This energy requirement is likely much higher for BCNF1 because it contains more iron and can therefore form more oxygen vacancies. Part of this large enthalpy could be rearrangement within the crystal structure to allow oxygen to move from within the material to the surface of the material. This would allow more oxygen to be released during the reduction step; this was observed in the experimental studies. In order to elucidate the effect reduction is playing on the magnitude of this energy, future research using STA will maintain the perovskite at 700 °C while cycling between nitrogen and carbon dioxide atmospheres in order to separate the enthalpy of reduction. However, the low enthalpy of re-oxidation of BCNF1 means that when the perovskite is kept at 700 °C, the energy required to cycle between the oxidation and reduction reactions is very small, which should lead to a high level of energy storage with very little energy lost to the reaction. Since the enthalpy of oxidation for BCNF1 is exothermic, this suggests that the products (the oxidised perovskite and carbon) are more stable than the reactants (the reduces perovskite with oxygen vacancies and carbon dioxide) and therefore the oxidation reaction is energetically favourable. However, the enthalpy of oxidation for BCNF0.66 and BCNF0.34 are only around -1J/g, likely the difference in stability is not large enough to make the reaction favourable. BCNF0 has an endothermic reaction enthalpy, meaning the products are

less stable than the reactants and therefore the reaction is less favourable. The enthalpy results also explain the fact that compounds similar to BCNF0 are unable to split carbon dioxide in the literature[12,14,15,20–23].

Table 3. Enthalpy calculations of the four perovskites calculated from simultaneous thermal analysis.

Perovskite	Energy to heat from 25 to 750 °C (J/g)	Enthalpy of oxidation (J/g)
BCNF1	2570.89	-45.11
BCNF0.66	2046.13	-1.04
BCNF0.34	1337.06	-1.11
BCNF0	458.85	0.14

EDX analysis (Figure 6) of the pellets after oxidation in 10% CO₂ were used to visualise carbon deposition on the surface of the pellets. BCNF0 (e) clearly shows the least carbon deposition on its surface compared to the other three perovskites. This small amount of carbon on the surface could be due to the carbonate salts used in the synthesis of the perovskite, suggesting that the carbonate was not completely reacted during calcining and sintering. Moving from BCNF0.33 (j) to BCNF0.66 (o) and BCNF1 (t) there is an increase in the size of the carbon deposition particles, with large patches forming in BCNF1. Given that there was no mass gain during re-oxidation for BCNF0.34 and BCNF0.66, this carbon deposition could again be due to improper removal of carbonate salts during synthesis or very minimal surface deposition. The large clumps of carbon deposition on BCNF1 are not likely to be from the carbonate salts since it does not present this way in any other perovskite. This suggests that some of the CO₂ has been split into carbon on the surface of BCNF1, showing the high activity of this phase for CO₂ reduction.

3.3 Perovskite stability

XRD scans (Figure 9) of the perovskites as-prepared, after reduction and after re-oxidation were taken to investigate the chemical stability of the perovskites throughout the cycle. For BCNF0 (1), it can be seen that there were very little changes throughout the cycle, as expected from the lack of redox activity in this material. BCNF0.34 (2), BCNF0.66 (3) and BCNF1 (4) also showed no change in XRD pattern throughout the cycle showing that they are stable at 700 °C and under a 10 % CO₂ flow. In agreement with previous research, the BCNF1 perovskite did not show evidence of carbon deposition after re-oxidation (4c), usually visible as a small peak after the (422) reflection at around 55° [15]. In previous

research, this carbon peak was only seen after re-oxidation with pure CO₂ while the reaction with 2000ppm CO₂ did not show a carbon peak.

Figure 8. XRD Scans of (1) BCNF0, (2) BCNF0.34, (3) BCNF0.66 and (4) BCNF1 with (a) as-prepared, (b) after reduction and (c) after re-oxidation

SEM images (Figure 2) were taken of the as-prepared perovskites, after reduction and after re-oxidation to assess the structural stability of the perovskites. In BCNF0, after reduction (1b) the average grain size had decreased from around 10μm to less than 10μm and fewer pores were visible. There was also less definition between the grain boundaries. After re-oxidation (1c) the definition of the grain boundaries has increased, the grain size has grown to larger than 10μm, and there are more pores visible, most around 3μm. This suggests that sintering has occurred due to the increase in grain size. In BCNF0.34 after reduction (2b), the average pore size had increased from less than 5μm to around 10μm, and fewer pores are present, suggesting sintering has occurred. Additionally, there is a small amount of deposition on the surface which appears to have a high concentration of calcium through EDX analysis (Figure 6 (g)). After re-oxidation (2c), there are markedly fewer pores and less deposition on the surface, suggesting the calcium-containing deposits were reacted or incorporated into the structure. The average grain size remains unchanged through the re-oxidation step. The as-prepared BCNF0.66 (3a) perovskite had larger grains than BCNF0 or BCNF0.34. After reduction (3b), the grain boundaries are less pronounced, and the pore sizes have decreased from around 8μm to just a few microns. Overall, the grains are roughly the same size as the as-prepared sample; however, there is again some solid deposition. After re-oxidation (3c),

there is an increase in grain size, with some of the larger grains above $30\mu\text{m}$ and an increase in the number and size of pores. There is also a significant decrease in deposition on the surface, as seen in BCNF0.34 after re-oxidation. After reduction of BCNF1 (4b), the perovskite again has indistinguishable grain sizes, a few pores and deposition on the surface. After re-oxidation (4c), a large crack can be seen running the length of the scanned area and upon visual observation, many large cracks had appeared over the surface of the pellet. The cracking of the pellet suggests significant volume changes during the redox process; however, the cracks may help gas diffusion and penetration in later cycles.

Figure 9 shows the mass change observed through five cycles of reduction in 100% N_2 and re-oxidation in 10% CO_2 /90% N_2 for BCNF1. It can be seen that although the mass gain in the first re-oxidation cycle was only 0.2 %, from the second cycle, the mass changes stabilise at around 0.45 %. This increase in the reactivity of the CO_2 splitting reaction between the first and second cycle is likely due to morphological changes since no changes were seen in the XRD after the first cycle. Figure 2 shows that the pellet had cracks on the surface after the first cycle, which could have led to a larger surface area for the reaction to occur, resulting in a larger mass change in the second cycle. The lower mass change for the 3rd re-oxidation and 4th reduction is accompanied by a much higher standard deviation between the pellets, perhaps suggesting some human or mechanical error during weighing. This is likely the case because the mass change returns to 0.45% after these two points, making error more likely. However, the sustained mass change of 0.45 % is extremely promising in terms of potential applications of this material. This mass change can be converted to oxygen evolution and carbon monoxide production volumes, giving an average over five cycles of $140\text{ }\mu\text{mol}$ of O_2 per gram of perovskite and $160\text{ }\mu\text{mol}$ of CO per gram. This fuel yield is higher than many ceria-based materials[8].

Figure 9. Mass change of BCNF1 during five cycles of reduction and re-oxidation

4. Conclusion

The results presented here show that for the barium calcium iron niobate family of perovskites, the higher the iron content, the more successful for chemical looping and the decomposition of carbon dioxide. BCNF1, $\text{Ba}_2\text{Ca}_{0.66}\text{Nb}_{0.34}\text{FeO}_{6-\delta}$, showed an exceptionally high mass loss during reduction of 1.14%, equal to the loss of 0.34 moles of oxygen. The sustained mass change of 0.45 % after five cycles suggests this material could be suitable for use in chemical looping energy storage applications. More importantly, the low enthalpy change of oxidation of BCNF1 suggests that very little energy would be lost cycling the material, meaning more of the energy input can be regained.

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