The search for new materials for high-temperature carbon capture and storage

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A dissertation submitted for the degree of
Doctor of Philosophy
January 2015
Declaration

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except as specified in the text.

It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University of similar institution except as specified in the text.

It does not exceed the prescribed word limit for the Degree Committee of Physics and Chemistry.
Abstract

In this study a holistic approach to studying novel materials for carbon capture and storage is presented, encompassing the entire design of new materials from theoretical screening to experimental validation and \textit{in situ} studies to probe their performance in real time. In the first part, a high-throughput screening methodology was devised to function within the Materials Project database. The screening found 640 materials that could be potentially implemented in high temperature carbonate looping; the materials were subsequently ranked by the theoretical energy penalty associated with their use. The most promising candidates were synthesised and subjected to thermogravimetric and diffraction studies to determine their experimental carbonation behaviour, showing good agreement with the screening results.

The second part describes a study of the first perovskite-type material shown to reversibly react with CO$_2$, Ba$_4$Sb$_2$O$_9$. A combination of \textit{in situ} thermogravimetric, diffraction and imaging techniques were used to characterise the structural evolution of the material and its stability upon repeated carbonation cycles. Remarkably stable capacity retention over 100 cycles was found, a key improvement over currently used materials.

The final part details the use of novel solid-state nuclear magnetic resonance techniques to study how ion dynamics influence the CO$_2$ absorption properties of alkali oxides. Using measurements collected up to the high operating temperatures of these CO$_2$ capture materials, it was found at higher temperatures the Li and O ionic dynamic processes are correlated, and the range of increased mobility coincides with the range over which CO$_2$ absorption takes place. These results present initial insights into the underlying mechanism of CO$_2$ capture in these materials, and how ion dynamics influence their absorption kinetics.
Acknowledgements

First and foremost I would like to thank my supervisor, Professor Clare Grey, for her wisdom and guidance over the last three and a half years. This field is a somewhat new research area for both of us, but I have been fortunate to have a supervisor with such good ideas and a willingness to try ideas which were seemingly not so good!

I would like to thank Dr Frédéric Blanc, Dr John Griffin and Dr Michal Leskes who have been my mentors in all things NMR. Their patience and willingness to help me grasp the basics of both the theory and practice of solid state NMR has been truly invaluable. In particular, the CASTEP calculations on Li₂CO₃ and Li₂ZrO₃ were carried out by John Griffin, with assistance from Hannah Laeverenz Schlogelhofer, a Part III student within our group. Dr Tao Liu also helped to collect SEM images of some of the materials. I would also like to thank the rest of the Grey group for their assistance in various lab matters and for their excellent company.

The diffraction studies on Ba₄Sb₂O₉ were carried at the Australian synchrotron, with assistance from Dr Justin Kimpton, Dr Chris Ling, and Adriano Pavan. I thank them all for their help with the experiments, and the useful conversations that were had over the course of the research.

At the University of Cambridge, I have worked closely with Dr John Dennis and Dr Stuart Scott and their respective groups at the Department of Chemical Engineering and Biotechnology and Department of Engineering. In particular, I would like to thank Dr Wen Liu who taught me the fundamentals of thermogravimetric analysis. Dr Liu assisted with the SEM and TGA cycling studies on Ba₄Sb₂O₉, and also assisted with the data analysis for all the TGA experimental studies. I truly could not have finished this thesis without his kind and ever-patient help. I would also like to thank Dr Zlatko Saracevic in the Department of Chemical Engineering and Biotechnology for his assistance in collecting the BET surface area
measurements. Finally I would like to thank Dr Andrew Morris in the Department of Physics for coming in at the death and helping me with the AIRSS structural studies of calcium vanadate polymorphs.

The large scale screening was carried out in collaboration with Dr Kristin Persson, Dr Anubhav Jain and Dr Shyue Ping Ong of the Materials Project. In particular, both Anubhav and Shyue helped me a lot in the beginning in setting up the screening methodology, learning the pymatgen library which was used to perform the screening itself, and generally helping me to think about the various parts to consider in what was a completely new endeavour for me. I thank them wholeheartedly for their help.

Other collaborators whose work is not directly featured in this thesis, but who nonetheless were invaluable for their discussions and contribution, include: Professor Martin Dove and Serena Maugeri from Queen Mary University London for their help and company during neutron beamtime at ISIS; Dr Matt Tucker from Diamond for his help in designing an *in situ* experimental setup for the I15 beamline at Diamond, and his subsequent help in performing the experiments (which were sadly interrupted by beamline failure!); and Dr Paul Shearing and Dami Taiwo from University College London for their expertise and assistance in performing x-ray tomography experiments through the night at SLS. They have my deep gratitude for their immense knowledge and help that they all generously shared with me throughout my PhD.

I would also like to thank the Commonwealth Cambridge Trusts and Trinity College for funding, without which I wouldn’t have been able to come to Cambridge. Finally, I would like to thank my friends and family for their support, both those near and further away. In particular, I would like to thank my brothers Damien and Chris and my parents Catherine and Paul for their love and support at all times; Andrew for his immense knowledge and unending advice to do with all things to do with my work; and to Terezie for being there for me through the absolute best and worst of times, and loving me all the same.
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<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and storage</td>
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<tr>
<td>CT</td>
<td>Central transition</td>
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<tr>
<td>DEA</td>
<td>Diethanolamine</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Energy penalty</td>
</tr>
<tr>
<td>$E_{XC}$</td>
<td>Exchange-correlation functional</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EFG</td>
<td>Electric field gradient</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
</tr>
<tr>
<td>HK</td>
<td>Hohenberg-Kohn</td>
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<tr>
<td>HTC</td>
<td>Hydrotalcite-like compound</td>
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<tr>
<td>KS</td>
<td>Kohn-Sham</td>
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<tr>
<td>LDA</td>
<td>Local density approximation</td>
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<tr>
<td>MAS</td>
<td>Magic-angle spinning</td>
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<tr>
<td>MDEA</td>
<td>Methyl diethanolamine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
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<tr>
<td>MM</td>
<td>Molar mass</td>
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<tr>
<td>MOF</td>
<td>Metal-organic framework</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>PAW</td>
<td>Projector augmented wave (psuedopotential)</td>
</tr>
<tr>
<td>S-XRD</td>
<td>Synchrotron x-ray diffraction</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>------------------------------------------------</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>ST</td>
<td>Satellite transition</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed decomposition</td>
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<tr>
<td>VASP</td>
<td>Vienna Ab Initio Simulation Package</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>ZIF</td>
<td>Zeolitic imidazolate framework</td>
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<td>$C_Q$</td>
<td>Quadrupolar coupling constant</td>
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<tr>
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<td>Enthalpy of carbonation</td>
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<td>Quadrupolar splitting parameter</td>
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<tr>
<td>$\tau_c$</td>
<td>Correlation time</td>
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<tr>
<td>$\omega_0$</td>
<td>Larmor frequency</td>
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Chapter 1

Introduction

Of the many environmental concerns that humanity faces as it moves into the 21st century, anthropogenic emissions of CO$_2$ into the atmosphere and the associated increase in mean global temperatures present one of the most pressing issues. To begin with, the annual total global emissions of CO$_2$ has increased over 80 % from 1970 to 2004 [1]. This problem is intimately connected with the ever-increasing amount of fossil fuels consumed for power generation and the CO$_2$ released within these processes.

The imperative to curtail CO$_2$ emissions without having to sacrifice power generation capacity has led to the development of initiatives designed to capture and sequester CO$_2$ within the Earth [2]. These strategies are collectively known as Carbon Capture and Storage (CCS) schemes. Considering the ambitious goals to reduce CO$_2$ emissions (at present member states of the European Union have agreed to a collective 40 % decrease in CO$_2$ emissions domestically by 2030), CCS strategies are clearly necessary to achieve these goals, which cannot be met by increases in renewable sources of energy alone. Producing pure streams of CO$_2$ for capture is not a straightforward task however. Fossil fuels are often combusted in air rather than in pure oxygen, leading to the inclusion of unwanted gases in the waste stream such as methane and N$_2$. N$_2$ and CO$_2$ have very similar sizes, and so are difficult to separate physically. Moreover, the waste gas streams are very hot exiting the combustion chamber, and energy often has to be spent cooling the gases prior to separation and capture [3]. A further constraint is that any material that would be used in a CCS application must be renewable, otherwise whatever global reserves from which the materials are made will be rapidly depleted [4].
Various methodologies have been proposed for the efficient capture and storage of CO$_2$ over the past two decades, each with their own advantages and disadvantages. Whilst it is more favourable to simply halt the use of fossil fuels, and use sources of energy that do not produce CO$_2$ such as solar, wind or nuclear power, this scenario is unlikely to happen. In reality, consumers will always want to pay the least for the energy that they use, and this ensures we will continue to use fossil fuels until they run out [5].

The technology being developed for CCS, especially that which involves chemical absorption of CO$_2$, is also important for other applications. One broad category of application is towards zero-emission pre-combustion or oxyfuel strategies for using coal and other fossil fuels. For example, one specific process is in the hydrogasification of coal [6], where adding a material to remove CO$_2$ in situ would improve the efficiency of the water-gas shift reaction component. This process, as well as other industrial applications outside of traditional postcombustion CCS, means that emerging technologies may be viable depending on the nature of the CCS application they are being used for.

1.1 Current technological approaches for CCS

1.1.1 Post-combustion amine scrubbing

The most extensively studied and researched method for post-combustion CO$_2$ capture is amine scrubbing, which is based on the reaction of CO$_2$ gas with an aqueous solution of monoethanolamine (MEA). It was first developed by Girdler Co. in 1930 [7], where an aqueous amine solution (25-30 wt. %) is pumped into a tower into which CO$_2$ gas is introduced. At 313 K the amine reacts with CO$_2$ to form a carbamate ion via a zwitterion intermediate [8]. This mixture is then pumped out into another tower where steam is introduced and the mixture is heated to 373–413 K to reverse the initial absorption reaction and form hydrogen carbonate. The regenerated MEA is pumped back into the absorption tower and the process is repeated, cycling the absorbent throughout the entire system.

This mature technology is already being retrofitted to a number of coal-fired power plants as a form of post-combustion CCS. In fact, as of December 2014, there were over 200 different experimental and pilot plants in operation around the world [9]. However, there are still fundamental issues that need to be overcome as it moves to becoming a more widely implemented technology. Firstly, even considering the efficiency gains over
the past decade of active CCS research, the process still consumes between 20-30% of the energy generated by the power plant (known as the energy penalty) due to the relatively high temperatures required to regenerate the MEA or other amine derivatives [10]. In addition to the difficult regeneration process, the low partial pressure of CO$_2$ in flue gases (typically between 4–14%) means that large volumes of gases need to be treated, requiring large and expensive equipment [11]. There are also issues of solvent degradation that occur when there are impurities in the combustion gas stream such as SO$_x$ or NO$_x$, which further increase the cost of separation. Finally, the process requires that the gas stream be cooled prior to capture, as temperatures higher than 673 K lead to thermal decomposition of the MEA.

1.1.2 Pre-combustion carbon capture

An alternative approach to CCS is to separate and store CO$_2$ prior to the actual combustion, that is to convert carbon to a non-carbon containing fuel stock as H$_2$. This, along with the oxyfuel combustion process (described in Section 1.1.3), is a particularly attractive option as this process is run under high partial pressures of CO$_2$, increasing the efficiency of the absorbent, and can be performed at much higher temperatures with the appropriate materials, saving energy formerly used to cool the exhaust gases in amine scrubbing.

In pre-combustion carbon capture, a fuel source is initially converted to methane at high pressures and temperatures: $C_{(s)} + 2H_2 \rightarrow CH_4$. Then the methane is reformed with steam to form a mixture of hydrogen gas and carbon monoxide, $H_2O_{(g)} + CH_4 \rightarrow CO + 3H_2$. The final step of the reaction is a water-gas shift, where the carbon monoxide reacts with excess steam to form hydrogen and carbon dioxide $H_2O_{(g)} + CO \rightleftharpoons CO_2 + H_2$. The overall process produces pure CO$_2$ ready for storage, and is also a source of H$_2$ for other applications such as fuel cells.

A CO$_2$ absorbent material is crucial in driving the equilibrium towards the right in the water-gas shift. In fact, in the presence of an efficient absorbent the reaction essentially goes to completion (and in doing so also performs the useful function of separating the CO$_2$ and H$_2$ gas streams). The absorbent can be cycled in and out of the reaction chamber, into a second chamber where it can be regenerated at higher temperatures or CO$_2$-free environments.
The main advantage of pre-combustion CCS is the conversion of a carbon-based fuel to a carbon-free fuel. Hydrogen burns much more cleanly without sacrificing much of the high chemical energy of coal or natural gas, and does not have the problem of producing sulfur or nitrous oxides. As both the pressure and concentration of CO$_2$ in the process is much higher than in post-combustion capture plants, the equipment used can be much smaller and less expensive, further enhancing the viability of such a process [11].

1.1.3 Oxyfuel combustion processes

Oxyfuel combustion CCS is a modified post-combustion process where the fuel is combusted in a stream of pure O$_2$ rather than air. There are several advantages to this approach over conventional combustion. Firstly, the concentration of CO$_2$ in the flue gas is much higher, usually around 80 %, and this improves the efficiency of the carbon capture step [11]. Physical absorbents are able to be used rather than large amounts of potentially hazardous solvents, leading to possible improvements in the energy penalty of the process and a longer lifetime for the absorbents used. Combustion under pure oxygen also reduces the production of NO$_x$, reducing the energy required for its separation from CO$_2$ prior to storage.

At the present moment, the main barrier to wide deployment of oxyfuel combustion within power plants is the cost of retrofitting existing infrastructure. There is also a significant energy penalty incurred during the production of O$_2$ through cryogenic separation, equal to approximately 11.5 % with current technology [12]. To date, there has been one pilot plant constructed in 2008 in Germany by Vattenfall, a company that has since completed another pilot plant in 2010 to test pre-combustion CCS in the Netherlands [13]. However, oxyfuel is still the least developed technology compared to other post- and pre-combustion systems, with much work still remaining in order to develop new strategies for low-cost O$_2$ production.

1.2 Separation methods

Common to all of the technologies described above is the requirement for a method to separate and capture CO$_2$ gas from a flue gas stream, and then release this purified gas in a suitable manner to be liquified, transported and ultimately stored. These current viable separation processes are either physical or chemical, with the main methods involving absorption, adsorption, or gas separation membranes. These methods all have their own inherent
advantages and disadvantages to their use and cost of implementation. It is not the intention of this section to give an exhaustive review of the methods being developed, but rather to give a general understanding of the state of the field, and so that comparisons can be made to the materials which this thesis will focus on.

An overall concern when it comes to the development of new materials for CO$_2$ separation is the cost. It should be noted that this metric encompasses more than just the actual cost of obtaining the sorbent, either through synthesis or extraction of naturally occurring materials. The capacity of a sorbent is also important, and is usually compared across materials as a measurement of the weight of CO$_2$ absorbed per gram of sorbent (the gravimetric capacity). From a more fundamental viewpoint, it can also be expressed as a molar conversion rate of the sorbent to give some indication as to how much of the sorbent actually reacts with CO$_2$. A final important aspect of cost is the lifetime of the sorbent, and for how long the sorbent can be recycled and still maintain its activity. The initial cost of a sorbent can be balanced out if it has a sufficiently long lifetime, and the frequency of replacement of the sorbent and the process by which it is regenerated should be considered when assessing the total cost.

### 1.2.1 Absorbent materials

The primary absorption method used commercially in chemical absorption is the amine scrubbing process described above in Section 1.1.1. This process can be modified to use diethanolamine (DEA) or methyl diethanolamine (MDEA) instead, which can alter the reactivity and capacity for CO$_2$ absorption by the solvent. For example, MDEA displays a slightly higher loading capacity for CO$_2$, but with a lower rate of reaction. It displays slower rates of degradation than those seen for MEA and requires slightly less energy to regenerate the amine [8]. In fact, using a mix of MEA and MDEA results in a solvent with overall improved properties compared to either of the pure amines [14, 15]. The use of many other types of mixes of amines has been proposed, but the overall chemical reaction and problems remain the same, especially the relatively high energy penalty.

In comparison to chemical absorption, there have been promising results for the use of physical absorbents such as Selexol (a mix of diethyl ethers and glycol) and Rectisol (methanol at 233 K). These are established technologies used in natural gas sweetening and have an advantage over solvent based processes in that they require less energy to regenerate. Regenera-
tion can even be achieved through sufficient pressure reduction, known as flash distillation [16]. In addition to these increases in energy efficiency, Rectisol in particular is non-corrosive and does not suffer the same degradation problems over many cycles as compared to MEA. However, Selexol has a high affinity for hydrocarbons, and its use would result in hydrocarbon losses, and the complexity of the Rectisol absorption process would make its implementation in plants very costly [11].

1.2.2 Adsorbent materials

Adsorption processes differ from absorption processes in that they rely on a thermodynamically favourable interaction for molecules in the gas phase to attach themselves to the surface of a solid material. The basic method consists of exposing the adsorbent to a gas stream containing CO$_2$ for some time followed by its removal and regeneration, either through lowering the pressure (pressure-swing) or raising the temperature (temperature-swing). Some methods also regenerate materials electrochemically by passing an electric current through the material (electrical-swing). A desirable material will have fast adsorption and regeneration kinetics, a large capacity for adsorbed CO$_2$, stability over a wide range of temperatures, pressures and atmospheres, and excellent cyclability over a long time [17]. Ultimately, materials will always be a compromise of varying performances against the different criteria, and will be suitable for different applications.

There are several main classes of materials that are being used for CCS applications, with the main types investigated being zeolites, metal oxides, hydrotalcite-like compounds (HTCs), metal-organic frameworks (MOFs), and activated carbons.

Metal-organic framework (MOF) materials, consisting of a three-dimensional network of metals coordinated to organic ligands, were first shown by Yaghi et al. to be able to exist without solvent forming a material with significant porosity [18]. Since then, these materials have been investigated as possible adsorption and storage materials for a variety of gases. Subsequent research has shown that the shape and size of the pores can be controlled through careful choice of ligands, and this ability to control the porosity has allowed even larger gas molecules such as methane to be adsorbed by MOFs [19]. There have been several studies investigating CO$_2$ adsorption capacity with a variety of MOFs [20, 21, 22, 23, 24]. The results of these studies were promising, showing certain MOFs to have comparable adsorption capacities to zeolites at medium to high CO$_2$ partial pressures. However, at low
pressures the adsorption kinetics slow considerably, making MOFs unsuitable for post-combustion processes. Furthermore, the adsorption capacity decreases with increasing temperature [25]. To date, there has been little research into multi-cycle stability and regeneration characteristics of MOFs, and this ongoing work will ultimately determine their suitability for future CSS applications.

1.2.3 Gas separation membranes

Membranes for gas separation and purification are attractive due to their low cost, the comparatively small energy penalty incurred in their operation, and the flexibility they offer in being retrofitted to existing power plants. A wide range of materials have been considered including inorganic materials such as perovskite oxides, MOFs, zeolites, molecular sieves and organic materials including cellulose acetate, various polymers and hollow fibers with very large surface area to volume ratios [26]. Materials such as perovskites have little permeability to CO\(_2\), but their ability to allow the passage of other gases such as O\(_2\) and water vapour enables the concentration of CO\(_2\) through the specific removal of contaminant gases. The efficiency and effectiveness of membranes depends on two main factors: their gas permeability and their selectivity to the gas molecule of interest. These transport and separation factors are inversely related, and much of the current work in developing and implementing new membranes relies on maximising these two properties simultaneously [4].

Much progress has been made, especially in regards to organic polymeric membranes and zeolites, in tuning the chemical and/or physical properties of the membrane to improve its selectivity towards CO\(_2\). Polymers derived from cellulose acetate, as well as those based on polysulfone and polyimide have already been used extensively in natural gas sweetening, separating CO\(_2\) from CH\(_4\) [27]. Inorganic metallic oxide membranes have also shown promise as an alternative to cryogenic oxygen separation in oxyfuel combustion, being able to separate oxygen from a gas mixture through ionic transport of oxide ions through the membrane [28].

Two main problems persist when it comes to the use of membranes for CCS applications. Firstly, the partial pressure of CO\(_2\) in the feed gas is often very low, and thus provides little driving force for efficient separation through a membrane. The gas would have to be compressed to achieve acceptable rates of separation, and this compression would result in an increased energy penalty for the process which is better avoided [29].
Additionally, membrane surfaces are especially susceptible to changes in porosity and surface area from particles present in the gas mixture, as well as possible degradation due to impurities.

1.3 CO$_2$ looping

Recently a new approach to CCS has emerged, that of CO$_2$ or carbon looping cycles. According to Anthony et al. [30], a looping cycle is defined as one that uses a solid carrier substance to either bring oxygen to the fuel gas or removes CO$_2$ from the combustion or gasification gases that is later released as a pure CO$_2$ gas stream for sequestration. Crucially, this method also involves the regeneration of the carrier so that the material can be cycled and reused.

The main difference between this method and some of the CCS methods described previously is that CO$_2$ looping avoids gas phase separation either before or after combustion, potentially avoiding one of the most energy intensive parts of the process.

In this work the primary concern is with intermediate to high-temperature CO$_2$ looping, where a solid sorbent is used to remove CO$_2$ from the environment, storing it as a solid carbonate in a carbonation reaction (shown in Equation (1.1) for a general M$^{2+}$ ion). The sorbent is regenerated usually through heating or changing the CO$_2$ partial pressure.

\[
\text{Carbonation} : \ MO + \ CO_2 \rightarrow MCO_3 \quad (1.1)
\]
\[
\text{Calcination}(\text{Regeneration}) : MCO_3 \rightarrow MO + CO_2 \quad (1.2)
\]

To optimise the efficiency of a power plant operating with a CO$_2$ looping system, is it possible to locate the two separate reactions in different reactors, maintained at different temperatures. Such a system usually employs a fluidized bed system, which has separate reactors containing beds of absorbent particles, and allows gas flow through the particles [31, 32]. It also has the additional benefit of allowing the easy transport of sorbent particles from the carbonation reactor to the regeneration reactor, fundamental to the overall concept of CO$_2$ looping. The ease of implantation of such a technology into existing power generation systems is aided by the fact that large atmospheric and pressurised systems have already been developed for use in other applications [33, 34].

While the overall method for CO$_2$ looping is well understood and theoretically more energy efficient than other CCS processes, its implementation
1.3. \( \text{CO}_2 \) looping

is reliant on finding a suitable sorbent material, which needs to satisfy several criteria: high capacity and selectivity for \( \text{CO}_2 \) absorption; moderate to good reaction kinetics for both carbonation and regeneration; and the ability to retain its capacity over many cycles [17, 35, 36]. This is especially true for the use of synthetic sorbents, which are more costly and less sustainable than naturally occurring compounds, especially given the recent focus to synthesise new materials with the desired properties [37].

The first main aim of this work is to investigate new synthetic materials for use in \( \text{CO}_2 \) absorption, especially with regards to \( \text{CO}_2 \) looping, focussing on inorganic oxide materials whose carbonation and calcination reactions occur in the intermediate temperature range of 673–1273 K. There are two main reasons for seeking reactions at these higher temperatures. Firstly, it avoids the need to cool the flue gases entering or exiting the reaction chambers, increasing the efficiency of the overall process. Secondly, as the carbonation reaction is exothermic, the heat produced there can be used to reduce the heat required for the calcination reaction, also increasing the efficiency of the system [32].

The following sections provide an overview of the materials investigated so far in previous research, and assesses their relative advantages and disadvantages against the criteria for a good sorbent described above, before describing which materials will be the focus of the present work.

1.3.1 Group II metal oxides

The oldest material used in \( \text{CO}_2 \) looping is limestone, \( \text{CaCO}_3 \), with its background in the use of gas separation going back to 1867, when its role in aiding the gasification of steam was patented by DuMontay and Marechall [38]. As a naturally occurring mineral, limestone has the advantage of being widely available at low cost, making it suitable for large scale applications. Dedman et al. studied the reaction of \( \text{CO}_2 \) with \( \text{CaO} \) over the temperature range 373–873 K, finding that the reaction progressed in two distinct stages, with an initial rapid reaction leading to the formation of \( \text{CaCO}_3 \) at the surface, followed by a second slower process that appeared to correspond to \( \text{CO}_2 \) diffusion along grain boundaries [39]. Earlier studies at higher temperatures supported these observations, noting that the amount of \( \text{CO}_2 \) absorbed in the initial rapid process increased as a function of temperature [40, 41, 42]. Later studies on the influence of the carbonate product layer on the rate of carbonation raised the possibility that the underlying reason for the slower second rate was to do with the necessity for carbonate and/or
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oxygen ions to have to diffuse through the product layer rather than along
grain boundaries, and that this mechanism was influenced by the applied
CO$_2$ partial pressure [43, 44].

More recently, Han, Silaban and Harrison first showed how the reversible
carbonation reaction of CaO with CO$_2$ could be used to separate CO$_2$ at
high temperatures to ultimately produce hydrogen [45, 46]. This was fol-
lowed by work describing how to implement this process within a larger
scale fluidized bed operation and also as a chemical heat pump, both of
which involved studies of the reversibility and stability of the reactants over
many cycles [31, 47].

Based on the stoichiometric reaction described in Equation (1.1), the
maximum theoretical CO$_2$ absorption capacity for CaO is 17.8 mmol g$^{-1}$.
The observed experimental capacities are lower than this, despite the capac-
ity still being larger than for other sorbents [17]. The absorption capacity
was found to depend on the size and morphology of the CaO particles,
with experiments showing that the experimental capacity decreased to 13.4
mmol g$^{-1}$ for 10 µm particles compared to 16.6 mmol g$^{-1}$ for 10 nm parti-
cles [48, 49]. Further studies revealed that the capacity also varies depend-
ing on whether the sorbent is prepared from naturally occurring dolomite
and limestone [50], or from calcined materials prepared from decarbonating
limestones that were almost pure CaCO$_3$ [51].

Other studies attempted to improve the capacity through doping CaO
with other alkali metals [52]. It was observed that doping 20 wt % with an
alkali metal (Li, Na, K, Rb and Cs) increased the absorption capacity in
all cases (except for Li). This was attributed to the increase in the number
of basic sites on the sorbent surface increasing the reactivity with acidic
CO$_2$ [53]. The observed positive gradient between capacity increase and
the dopant’s ionic radii would suggest the electropositivity of the metal
influences the changes in a doped sorbent’s capacity.

The other main criteria to evaluate the effectiveness of CaO is the kinet-
ics and cyclability of the carbonation and calcination reactions. The many
studies of the reversibility of these reactions suggest that the calcination
reaction is relatively fast and goes to completion given sufficient thermal
energy [31, 46, 47, 48, 51, 54, 55]. However, the carbonation reaction ap-
ppears to be quite different, and poses problems for its use in CO$_2$ looping.

As mentioned earlier in this section, the carbonation reaction goes through
two distinct stages: a first stage characterised by rapid absorption at the
surface with gaseous CO$_2$, followed by a much slower period of bulk absorp-
tion. Given the relatively minor contribution to the total amount of CO$_2$
absorbed by the second stage, the maximum capacity of the material can be determined by the absorption taking place in the first phase, which typically is over within a few minutes of the reaction commencing [51]. The fact that there are two different absorption regimes is not in itself a problem, as the material can be cycled so that only the first stage occurs. The real problem lies in the reversibility of the reaction, especially in the sintering processes that reduce the capacity of this first process. In the studies referenced earlier, it was found that as a natural CaO sorbent is cycled, its capacity decreases rapidly, so much so that within 20 cycles it has been reduced to a quarter of its original value (a carbonation conversion of 0.2 as compared to a fresh sorbent with a conversion factor of 0.8) [31, 46, 47, 48, 51, 54]. These studies link this effect with the corresponding change in morphology and porosity of the sorbent after many cycles, with the reduction in the number of smaller pores present in the material leading to less surface area being available for the first stage of the reaction.

Current research efforts have focussed on improving upon the cyclability of CaO by either pretreating limestone, searching for an optimal natural Ca-based material [56], or by developing new synthetic CaO-based materials. Ideas for pretreatment include reactivating the limestone under pure CO$_2$ or using Na-based additives [55, 57], and using steam hydration to increase the number and size of the pores of the cycled limestone [58, 59]. These were mostly found to lead to small improvements in cyclability, but did not stop the overall degradation of the sorbent over the long term.

Studies by Li et al. on a 3:1 weight percentage mixture of CaO and Ca$_{12}$Al$_{14}$O$_{33}$ (mayenite) showed the material to have a good initial capacity for CO$_2$ absorption (0.45 g g$^{-1}$ of sorbent, $\sim$73 % of the maximum theoretical uptake of CaO), and maintained this capacity over 13 cycles [60]. Subsequent studies on a similar material (an 85:15 weight percentage mixture) have shown it to actually increase its capacity as a function of cycle number, have an increased capacity under higher partial pressures of CO$_2$, and to resist changes in surface area and porosity over many reaction cycles [37, 61, 62, 63]. Similar studies by Aihara et al. showed that mixing CaO with some amount of CaTiO$_3$ improved the regenerability of the sorbent overall [47]. In any case, the addition of inert support materials shows much promise in improving upon one of the most significant disadvantages of CaO for use in CO$_2$ looping.

The final issue is that of the high temperatures required to calcine and regenerate the sorbent, which is around 1173 K in the case of CaO [64]. While there can be some efficiency gains from operating at high temperatures with
heat integration from the carbonation chamber, the high temperature still requires a relatively large amount of energy to maintain. Any way to modify the sorbent so that it could regenerate at lower temperatures would be useful in reducing the overall energy cost.

MgO-based sorbents have recently been considered for use in CO$_2$ looping applications, especially because the temperature to calcine MgCO$_3$ (~648 K) is considerably lower than CaCO$_3$ (~1173 K). MgO behaves much like CaO with regards to its carbonation and calcination reactions, except for the temperature ranges in which these reactions are active. Lee et al. found that MgO could absorb CO$_2$ at as low a temperature as 333 K in the presence of water vapour, and only required a calcination temperature of 623 K to be fully regenerated [65]. While MgO has a higher theoretical capacity than CaO, the use of pure MgO is unlikely, given its relatively small CO$_2$ absorption capacity in practice and the difficulty to regenerate it fully over many cycles [66].

The low temperature of operation for MgO has made it suitable to act as a support for other promising sorbents at low to intermediate temperatures, such as K$_2$CO$_3$ and Al$_2$O$_3$. It was found that a MgO/Al$_2$O$_3$ mixture with 10 % MgO could have capacities as high as 0.97 mmol g$^{-1}$ at 333 K with a dry gas mixture containing 13 vol % CO$_2$, which increased to 1.36 mmol g$^{-1}$ once the water vapour concentration was increased to 13 vol % [67]. This improved behaviour under moist conditions is especially important given that flue gases typically contain 8–17 vol % H$_2$O and 10–15 vol % CO$_2$, showing the sorbent to be able to perform in gas mixtures similar to those in industrial conditions [68, 69]. Further studies have found that a similar MgO/Al$_2$O$_3$ mesoporous composite material had CO$_2$ absorption capacities of 1.67 mmol g$^{-1}$ and 2.85 mmol g$^{-1}$ at 473 K in the absence and presence of water vapour respectively, with the ability to be regenerated at 873 K [70].

Other work has been done to make MgO-based sorbents from naturally occurring minerals as a low-cost alternative to synthetic sorbents. For example when dolomite, which is naturally around 44 % MgCO$_3$ and 54 % CaCO$_3$ by weight, was pretreated at above the MgCO$_3$ calcination temperature (but below the CaCO$_3$ calcination temperature) and promoted by the addition of K$_2$CO$_3$, it displays a high reactivity and capacity for CO$_2$ absorption between 573–723 K and was able to be fully regenerated above 723 K [71].

MgO-based sorbents thus present an excellent alternative to CaO-based sorbents, especially at lower temperatures and in humid operating condi-
tions. Either way, their use can cover a wide spectrum of expected industrial setups, and their attractive low cost has seen them become the most promising class of materials for intermediate to high temperature CO$_2$ looping applications.

### 1.3.2 Group I metal oxides

More recently lithium-based oxides (and to a lesser extent, sodium-based oxides) have become the subject of much interest with regards to CCS applications. These materials, with their high capacities for CO$_2$ absorption, thermal stability in the temperature ranges of interest (673–973 K), and excellent cyclic stability have led to many studies of their possible use in industrial processes [72].

The first material to be extensively studied in this context was Li$_2$ZrO$_3$, by Nakagawa and coworkers in the 1990s [73, 74]. Li$_2$ZrO$_3$ reacts with CO$_2$ at approximately 673–773 K to form lithium carbonate and zirconium oxide:

$$\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{ZrO}_2$$  \hspace{1cm} (1.3)

The original Li$_2$ZrO$_3$ can be regenerated by heating the products formed to a sufficiently high temperature, between 873–1073 K depending on the CO$_2$ partial pressure [73].

It should be immediately noted that already this reaction scheme differs from the Ca and Mg-based absorbents in that the carbonation reaction produces two different solid phases, and this will be common in all the sorbents discussed in this section (with the exception of the pure oxides Li$_2$O and Na$_2$O). This has important ramifications on how the reaction progresses, and presents different challenges to those faced with CaO and MgO. Additionally, the volume expansion after absorption of Li$_2$ZrO$_3$ (34 %) is much smaller than for the rare earth oxides such as MgO, which has a volume expansion after absorption of 149 % [35].

The main difficulty in using Li$_2$ZrO$_3$ is its poor carbonation reaction kinetics, which have been shown to be too slow for industrial processes [17, 75]. Accordingly, subsequent studies of this material have sought to improve both the capacity of Li$_2$ZrO$_3$ as a CO$_2$ sorbent, as well as increasing its rate of reaction. Previous studies found that the morphology and structure of Li$_2$ZrO$_3$ has a strong influence on its CO$_2$ absorption properties, with experiments testing Li$_2$ZrO$_3$ powders with different particle sizes showing a dependence between the rate of the reaction and the particle
Chapter 1. Introduction

sizes of the samples [76]. For example, Xiong et al. showed that a sorbent with an average particle size of 5 \( \mu m \) absorbed \( CO_2 \) four times faster than powders with an average particle size of 15 \( \mu m \) [3]. It has also been shown that \( Li_2ZrO_3 \) in its tetragonal phase absorbs more \( CO_2 \) and at a faster rate than in its monoclinic phase, an observation which suggests a correlation between absorption kinetics and conductivity of lithium, oxygen or carbonate ions through the sorbent (this will be revisited in Section 1.3.4) [77, 78]. Morphology of the sorbent particles and the presence of steam during the reaction have also been shown to influence the reaction kinetics [79, 80, 81].

Further studies involved doping \( Li_2ZrO_3 \) with other materials such as \( K_2CO_3 \) or \( Na_2CO_3 \) in the hope of improving reaction rates. The addition of \( K_2CO_3 \) has been shown to lead to faster carbonation rates as compared to undoped \( Li_2ZrO_3 \) [75, 82, 83, 84], with the proposed explanation that potassium and lithium can form a eutectic mixture on the surface of sorbent particles which aids lithium and oxygen ion conduction [3]. Doping with Na to form mixtures of \( Li_2ZrO_3 \) and \( Na_2ZrO_3 \) also created sorbents with improved reaction kinetics [85, 86], with absorption rates approximately twenty times faster for 5 % doped \( Li_2ZrO_3 \) [87]. In this case, it was inferred that the formation of the solid solution \( Li_{1-x}Na_xZrO_3 \) and the substitution of Na atoms on Li sites leads to a weakening of the Li-O bonds and an increase in the relative reactivity towards \( CO_2 \).

Following the initial work on \( Li_2ZrO_3 \), many other lithium and sodium based oxides have been studied as \( CO_2 \) absorbents. Foremost of these is lithium orthosilicate, \( Li_4SiO_4 \), which carbonates through the following reaction:

\[
Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3
\]  

(1.4)

There have been numerous studies done to examine the capacity, kinetics and reversibility of the reaction, as well as the effect of synthetic methods on the physical properties of the sorbent [88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98]. The first main advantage over \( Li_2ZrO_3 \) is that \( Li_4SiO_4 \) can be synthesised from \( SiO_2 \) rather than from \( ZrO_2 \), making it lighter and cheaper. Thermogravimetric analysis (TGA) experiments at 773 K and 20 % \( CO_2 \) showed \( Li_4SiO_4 \) to absorb approximately 50 % more \( CO_2 \) over 50 minutes, and at an initial rate that was thirty times quicker than for \( Li_2ZrO_3 \). Even at 2 % \( CO_2 \), \( Li_4SiO_4 \) still showed a similar weight increase compared to the 20 % case, whereas at the same low \( CO_2 \) partial pressures \( Li_2ZrO_3 \) showed no clear weight increase, and this result was replicated even
1.3. CO$_2$ looping

at room temperature under an ambient atmosphere [97]. Gibbs free energy calculations indicate that the regeneration temperature for Li$_4$SiO$_4$ is much lower than for CaO (993 K as compared to 1173 K for CaO), leading to lower energy costs for regeneration [98].

Much like Li$_2$ZrO$_3$, the addition of sodium dopant atoms was shown to improve the CO$_2$ absorption properties of Li$_4$SiO$_4$, leading to an increased total capacity and carbonation rate with as little as $\sim$2.5 % doping [92]. Another study investigated the effects of vacancy vs interstitial doping by synthesising Al- and Fe-doped Li$_4$SiO$_4$ with different Si:Al and Si:Fe ratios and lithium content [93]. It was found that Li$_{4,1}$Al$_{0,1}$Si$_{0,9}$O$_4$, Li$_{3,7}$Al$_{0,1}$SiO$_4$ and Li$_{3,7}$Fe$_{0,1}$SiO$_4$ all showed enhanced absorption capacity as compared with pure Li$_4$SiO$_4$. The higher reactivity of Li$_{3,7}$Al$_{0,1}$SiO$_4$ indicated vacancy doping to be more effective than interstitial doping, most likely due to the improved O$^{2-}$ mobility through the crystal structure (further discussed in Section 1.3.4). The Fe-doped sample also showed the highest absorption rate at 773 K of the samples in the study, perhaps due to the overall weaker Fe-O bonds compared to Si-O.

Li$_2$ZrO$_3$ and Li$_4$SiO$_4$ are only the beginning of the research efforts to investigate the many different alkali metal oxides that have potential as CO$_2$ capture materials. Considering the promising results obtained when both Li$_2$ZrO$_3$ and Li$_4$SiO$_4$ are doped with other elements, there is much work still to be done to find an optimal composition for CCS applications. Other materials studied have included alkali metal metasilicates (Li$_2$SiO$_3$, Na$_2$SiO$_3$ and K$_2$SiO$_3$) [99, 100, 101], Li$_2$O [102], Na$_2$O [103, 104], LiOH [105], Na$_2$ZrO$_3$ [106, 107, 108], Li$_6$Zr$_2$O$_7$ and Li$_8$ZrO$_6$ [109, 110, 111], Li$_4$TiO$_4$ [112, 113], Li$_2$CuO$_2$ [114, 115, 116], Li$_5$AlO$_4$ [117, 118] and Li$_5$GaO$_4$ [119]. The true test will be to find a sorbent with optimised properties that can compete with CaO on cost and reaction kinetics. Nonetheless, the capacity for optimisation and the already excellent properties shown by this class of materials represents an excellent opportunity for further research.

1.3.3 Perovskites

Perovskites (with the general formula ABO$_3$) have been used widely in fuel cell and mixed ionic-electronic conducting applications, where their inherent flexibility in structure and composition make them well suited to a wide variety of chemical processes. However, there have been few studies into the suitability of perovskites as CO$_2$ absorbent materials. They are potentially a rich source of many novel materials for CSS applications, as
they are readily doped to refine their physical and chemical properties to optimise their performance over a wide range of operating conditions.

Some of the earliest studies by Nomura et al. reporting CO$_2$ absorption by mixed Ba and Ca oxides containing Fe and Co were discovered during studies of these materials for other applications such as oxidative coupling of methane [120, 121, 122, 123]. As such, research into CO$_2$ absorption properties of these materials was usually connected to optimising their performance as membranes or catalysts rather than optimising these materials specifically for CO$_2$ absorption. Despite this there have been a few studies investigating the effect of different parameters on the CO$_2$ absorption properties of perovskites. Yang et al. studied the kinetics of CO$_2$ absorption of La$_{0.1}$Sr$_{0.9}$Co$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ powders sintered at different temperatures, finding that those samples sintered at higher temperatures exhibited denser microstructures and slower rates of absorption [124]. Using a homogeneous reaction model they proposed that more porous samples can react faster with CO$_2$ as this reaction could take place within the whole particle as opposed to only on the surface for denser samples. Further studies identified Sr$_{0.5}$Ca$_{0.5}$Co$_{0.5}$Fe$_{0.5}$O$_{2.47}$ as the optimal composition for a coupled carbonation and oxygen desorption reaction at 973 K, also showing good stability after the first few cycles [125]. Experiments at higher temperatures found that the CO$_2$ absorption capacity decreased markedly above 1023 K, putting forward the explanation that above this temperature the solid carbonates formed decompose to their respective oxides, releasing previously absorbed CO$_2$ [126].

More recently, there have been a few studies specifically addressing the reversible CO$_2$ absorption by perovskite related materials. Galven et al. reported the first Ruddleston-Popper phases shown to absorb CO$_2$, Li$_2$SrTa$_2$O$_7$ and Li$_2$SrNb$_2$O$_7$ [127, 128]. In the presence of water and at 413 K, protons displace Li$^+$ in the layered structure, and the displaced lithium is able to react with CO$_2$ to form Li$_2$CO$_3$ (described below as for the Ta analogue):

\[
\text{Li}_2\text{SrTa}_2\text{O}_7 + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{CO}_2 \rightarrow \text{LiHSrTa}_2\text{O}_7 + \text{Li}_2\text{CO}_3 \tag{1.5}
\]

The reverse reaction is activated at elevated temperatures ($\sim$973 K), with TGA results confirming the occurrence of complete regeneration.

The structural stability of perovskites, even when atoms such as Ba or Li are removed from their structure, pose an interesting alternative to the simple binary and ternary metal oxides described above for CO$_2$ looping.
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Many of the problems with the former materials, such as their deterioration over many cycles and large volume changes, are obviated by perovskites, which act as an inert framework for the movement of the active ions into and out of the structure. Future research is hoped to be able to find a perovskite that is able to be cycled for CO$_2$ looping.

1.3.4 Mechanisms of CO$_2$ absorption

Despite the progress being made in developing new materials for CO$_2$ looping processes, the underlying mechanism by which these materials undergo carbonation and calcination is still poorly understood. Previous studies have mainly found empirical evidence for the influence of different parameters on the activity and kinetics of the absorption processes, especially for CaO, Li$_2$ZrO$_3$ and Li$_4$SiO$_4$, but it has been difficult to directly observe the effect of these different conditions on the progress of the reaction itself.

It is commonly agreed that the initial process taking place in the carbonation reaction is a surface reaction between gaseous CO$_2$ and reactive sites on the surface of the oxide to form a carbonate product layer. This corresponds to the most rapid part of the carbonation reaction, and proceeds until no reactive surface is available. Understanding exactly how the morphology of the sorbent particle influences when the absorption changes from the fast to the slow regime has been studied extensively for CaO [32, 51, 129, 130, 131, 132, 133, 134]. In general, cycled samples of CaO showed virtually no pores of diameter <220 nm compared to fresh samples, leading to a conclusion that the reduced capacity of CaO over time corresponds to the reduced surface area available for reaction. It was found that the addition of water or steam improved the regeneration of these smaller pores during calcination, and also led to particle cracking producing smaller sorbent particles overall, even if the exact mechanism by which this occurs is not completely known [71, 134, 135].

Additives such as Al$_2$O$_3$ or mayenite (Ca$_{12}$Al$_{14}$O$_{33}$) are added to hopefully provide an inert support phase to reduce the progression of sintering with subsequent cycling of the material, but again there is little experimental evidence to show how these influence the carbonation and calcination reactions on an atomic level [37, 60, 61, 62, 134]. It is experimentally observed that sintering does not progress for an infinite amount of time even in pure CaO, with some CO$_2$ absorption capacity remaining even after many cycles, and while the mechanism is yet to be elucidated, a model was proposed for the formation of an inert interconnected CaO framework that acts
as a framework for the outer reactive CaO layer [136].

One of the earliest studies to consider the mechanism of the reaction of CO$_2$ with CaO was that of Bhatia et al. in 1983 [43]. They measured the effective product layer (CaCO$_3$) diffusivities for different CaO samples, and the activation energies for the corresponding carbonation reactions. The observation that the activation energies for the slower reaction regime are large combined with the relatively low diffusion rates in the carbonate product layer indicated a process that was inconsistent with simple gas molecule diffusion. They also observed a change in activation energy at 788 K, which would suggest a solid-state process is involved considering that the Tammann temperature for CaCO$_3$ is approximately 800 K [137]. The Tammann temperature is an empirically determined value which marks when the mobility of atomic species into a crystalline lattice changes significantly at a temperature between 30 % to 75 % of the material’s absolute melting point (with 50 % as a reasonable first approximation). The proposed mechanism of Bhatia et al. was that ionic conduction of either Ca$^{2+}$ or CO$_3^{2-}$ ions through the carbonate layer facilitated ongoing carbonation after the initial surface reaction, and they reasoned that it was more likely to be CO$_3^{2-}$ as it best matched the measured conduction observed for pure CaCO$_3$ at the time [138]. If it is accepted that CO$_3^{2-}$ is mobile through the carbonate layer, then there must be a matching counter-current of O$^{2-}$ ions to preserve charge neutrality, leading to the following reaction scheme [43]:

\[
\text{Pore Surface : } \text{CO}_2(\text{gas}) \leftrightarrow \text{CO}_2(\text{adsorbed})
\]

\[
\text{CO}_2(\text{adsorbed}) + \text{O}^{2-} \rightarrow \text{CO}_3^{2-}
\] (1.6)

\[
\text{CaO-CaCO}_3 \text{ interface : } \text{CO}_3^{2-} + \text{CaO} \rightarrow \text{CaCO}_3 + \text{O}^{2-}
\] (1.7)

In the temperature range above 788 K, the measured activation energy of 179.2 kJ mol$^{-1}$ is very similar to the heat of decomposition of CaCO$_3$ (178.5 kJ mol$^{-1}$), leading Bhatia et al. to infer that a different diffusion mechanism is activated at higher temperatures, one carried out by sequential carbonate ion decomposition. The decomposition of a carbonate ion into CO$_2$ and O$^{2-}$ would allow the movement of CO$_2$ to another vacated site in the carbonate structure, while another CO$_2$ molecule reacts with O$^{2-}$ to reform a carbonate ion. In this way, the carbon dioxide molecule is able to move through the CaCO$_3$ layer in a mechanism much akin to vacancy hopping.

A similar shell model has been proposed for the carbonation reactions of the lithium oxide based sorbents, albeit with some differences due to the
much lower melting point of Li$_2$CO$_3$ compared to CaCO$_3$ [139]. Ida et al. compared the carbonation reaction of pure Li$_2$ZrO$_3$ and that of potassium-doped Li$_2$ZrO$_3$, finding that pure Li$_2$ZrO$_3$ had a very slow absorption rate at 773 K (similar to the rate of the modified sorbent at 673 K) but that modified Li$_2$ZrO$_3$ showed absorption rates 40 times faster at 773 K. Analysing the modified sorbent further, they found an excess Li-K carbonate mixture on the surface of the particles, and that this mixture melted at 771 K, approximately the same temperature at which rapid CO$_2$ absorption was seen for modified Li$_2$ZrO$_3$. This is in contrast to the Li$_2$CO$_3$ formed in the carbonation of pure Li$_2$ZrO$_3$, which formed in the solid state due to its higher melting point. These results suggest an ionic diffusion mechanism, in which the rate of CO$_2$ diffusion is much faster through the molten carbonate layer than a solid.

Ida et al. proposed a double shell model, in which the initial rapid reaction of CO$_2$ with Li$_2$ZrO$_3$ forms an outer layer of Li$_2$CO$_3$ and ZrO$_2$ covering a core of unreacted Li$_2$ZrO$_3$ [139]. After this first absorption process, carbonation can continue, but requires the movement of Li$^+$ and O$^{2-}$ ions through the Li$_2$CO$_3$ and ZrO$_2$ layer, a process facilitated by defects and oxygen vacancies in the oxide layer as previously studied for ionic conductor applications (Figure 1.1) [140]. They also explained the similar calcination rates for both samples by reasoning that at the desorption temperature of 1053 K, the outer carbonate layer for both species is molten, and thus exhibits similar ionic conduction rates. This theory of eutectic formation explains well the many experimental results showing absorption kinetic improvements for potassium and sodium-doped sorbents.

Kato et al. in their comparative studies of the CO$_2$ absorption properties of Li$_2$ZrO$_3$ and Li$_4$SiO$_4$, expand upon the connection between crystallographic structure, ionic conduction and absorption capacity and kinetics [98]. Their reasoning behind the observed superior CO$_2$ absorption properties of Li$_4$SiO$_4$ over Li$_2$ZrO$_3$, being able to absorb CO$_2$ faster at lower partial pressures and lower temperatures, is that the crucial factor is the improved Li$^+$ mobility due to more available sites for lithium-hopping. There are six crystallographically distinct Li sites in ordered Li$_4$SiO$_4$, each with partial occupancy factors between $\frac{1}{3}$ and $\frac{2}{3}$, and taken together they form a continuous network constructed from edge and corner sharing LiO$_4$, LiO$_5$ and LiO$_6$ polyhedra [141]. Consistent with this analysis, introducing Li vacancies through doping with P or S or Li interstitials with Al greatly improves the ionic conductivity of Li$_4$SiO$_4$ through activation of these lithium ion conduction pathways [142]. Cruz et al. performed some structural analysis
Figure 1.1: Proposed CO$_2$ diffusion mechanism during the carbonation reaction of Li$_2$ZrO$_3$ [139]. After the initial surface reaction with CO$_2$ to form a layer of Li$_2$CO$_3$, both Li and O ions need to be transported across the Li$_2$CO$_3$ and ZrO$_2$ layer to allow the reaction to continue.

using x-ray diffraction (XRD) to model the transformation of Li$_4$SiO$_4$ to Li$_2$SiO$_3$, finding that after carbonation, Li$_2$SiO$_3$ is produced along a preferred growth direction resulting in the formation of long chains of (SiO$_3$)$_2^-$ units [94]. Understanding the altered ionic conduction properties in phases with such preferred orientations would help to model the actual conduction pathways used during the carbonation reaction.

The influence of crystallographic structure on CO$_2$ absorption can also be seen in the studies comparing the monoclinic and tetragonal forms of Li$_2$ZrO$_3$ [76, 77, 78, 79]. While it is not always possible to completely separate the influences of particle size and crystallographic structure across the different studies, the overall trend definitely indicated that the tetragonal phase had a higher capacity and faster carbonation rate than the monoclinic phase. However, there have been no subsequent studies to identify the features of the tetragonal structure that aid in CO$_2$ absorption. Considering the studies of Li$_4$SiO$_4$ discussed above, it would seem likely that these differences could be traced to different rates of lithium ion conduction through the respective phases, but this is yet to be conclusively determined. It may also be influenced by the relative stabilities of the two polymorphs, which could be investigated through theoretical calculations.

The composition of the external shell around an unreacted core may
1.3. CO$_2$ looping

also change the rate of ionic diffusion during carbonation, even in the solid state. In the work of Pfeiffer et al., it is assumed that after carbonation, the external shell contains a mixture of carbonate and other oxide phases rather than a strict outer and inner layer [35, 143]. They divide the possible compositions into three broad categories: external shells composed of pure Li$_2$CO$_3$, shells composed of Li$_2$CO$_3$ and a metal oxide (such as ZrO$_2$ in the case of Li$_2$ZrO$_3$), and shells containing Li$_2$CO$_3$ and another lithium oxide-based phase (such as Li$_2$SiO$_3$). In these analyses, the rate-limiting factor was assumed to be the materials present in the external shell, and their positive or negative effect on the overall lithium diffusion throughout the shell. This assumption was supported by comparative TGA results of differently doped samples of Li$_4$SiO$_4$, which would form different carbonation products with different inherent lithium diffusivities.

While these studies support the theory that lithium ionic diffusion is the controlling parameter during the bulk CO$_2$ absorption regime at higher temperatures, they neglect other parameters that could affect ionic conduction such as particle morphology and grain boundaries, conduction through the pristine material, and the diffusion of other species, most importantly that of O$^{2-}$. It is possible that the overall ionic diffusion is influenced far more by the structural changes introduced by doping with aliovalent species than by the different decomposition phases produced on the surface.

The experiments of Gauer et al. would appear to support the inference that oxygen mobility is just as important as lithium mobility, if not more so. Comparing the observed absorption properties for the vacancy-doped Li$_{3.7}$Al$_{0.1}$SiO$_4$ and Li$_{3.7}$Fe$_{0.1}$SiO$_4$ and the interstitial-doped Li$_{4.1}$Al$_{0.1}$Si$_{0.9}$O$_4$ shows the former doping to result in a much faster reaction rate, as much as four times more [93]. This improvement is attributed mainly to the increased availability of sites for oxygen conduction through the lattice, leading to the conclusion that O$^{2-}$ diffusion is the limiting factor. The similar performance of the interstitial-doped material over pure Li$_4$SiO$_4$ appears to support the idea that lithium ion mobility is far from the only contributing variable in determining CO$_2$ absorption rate. In the case of Li$_{3.7}$Fe$_{0.1}$SiO$_4$, the doping also was shown to improve the regenerability of the solvent (but not for Li$_{3.7}$Al$_{0.1}$SiO$_4$), meaning that further studies are needed to ascertain the role of iron in the process.

There have been very few studies into the mechanisms of CO$_2$ absorption (or degradation) of perovskites, with the exception of a recent study by Yi et al. on mixed barium oxides [144]. Through sputtering the surface of the oxide with gold, and then carbonating at 1173 K, SEM images showed
that the BaCO$_3$ layer formed through outward growth of the surface of the particle. This led to the inference that Ba$^{2+}$ diffusion, rather than CO$_2$, was the underlying mechanism for carbonate formation. This is a surprising result considering the relative size of Ba cations compared to Li, but it shows that similar carbonation and calcination reactions are definitely possible for perovskites composed of larger cations.

Another important observation by Yi et al. is that doping with successively more acidic metal cations (as reported by Jeong et al. [145]) improves a material’s resistance to CO$_2$. While such resistance is not desirable for a CO$_2$ absorbent material, it does add a further parameter to consider in the development of new materials, and for analysing the observed differences in previously studied sorbents. Systematic substitution of more basic metal cations into existing oxide materials could potentially provide new insights into the effect of acid-base affinities on the kinetics and capacities of CO$_2$ absorption reactions.

It is difficult to ascertain a consensus view in the literature as to what is the most important parameter influencing the mechanisms of CO$_2$ absorption. However, it is very likely that a combination of many factors, including chemistry, structure, thermodynamics and morphology are important to consider. What is definitely required are more careful studies directed at observing these parameters in situ during the reaction to ascertain their relative importance.

1.4 Theoretical screening of novel materials

The ability to discover new materials with desirable properties, in this instance CO$_2$ absorption, has been dramatically improved with the advent of high-throughput computing methods. It is now accepted that through solving the underlying fundamental physical equations, many important properties of materials can be predicted through the use of quantum chemical approximations such as those implemented in density functional theory (DFT) [146, 147, 148]. Utilising DFT allows the simulation of completely new materials in silico, enabling the use of various computational approaches to design materials with optimal properties. There have been a number of different approaches used to discover novel structures and materials, including simulated annealing [149], genetic algorithms [150, 151], and ab initio random structure searching (AIRSS) [152, 153] amongst many others.
At the same time, high throughput data mining approaches have harnessed information technology concepts in concert with computational calculations to screen many thousands of compounds for potential new uses in applications ranging from topological insulators, to catalysis and lithium-ion batteries. This dissertation follows this approach, with the Materials Project database [154] being utilised to perform a large scale screening aimed at discovering new materials for use in CO$_2$ capture.

Underpinning this work is an understanding of how DFT theory is employed to calculate the structures and energies of target compounds \textit{in silico}, and how this theory is applied particularly to the entries within the Materials Project database.

### 1.4.1 Density functional theory (DFT)

The development of density functional theory essentially seeks to find more efficient ways to compute the energy and wavefunction of a given molecule or compound. This is motivated by the fact that the time independent Schrödinger equation (used to determine the energy and wavefunction of the system) has three times the number of parameters as the sum of all the nuclei ($N_N$) and electrons ($N_e$) in the system (corresponding to the degrees of freedom for all components in the system), and for even moderately simple molecules this equation is impossible to solve computationally.

The first step towards simplifying the problem comes from the Born-Oppenheimer approximation, which states that due to the relative masses of electrons and nuclei, the latter can effectively be considered static on the timescale of electronic dynamics. This leads to being able to break the wavefunction into its electronic and nuclear components:

\[
\Psi_{total} = \psi_{\text{electronic}} \times \psi_{\text{nuclear}}
\]

Under the Born-Oppenheimer approximation, each wavefunction can be solved separately, considering the other part static and exerting a constant external potential on the system. This reduces the complexity of the constituent Schrödinger equations substantially, each being dependent separately on $N_N$ and $N_e$. Unfortunately, even with this approximation, $\psi_{\text{electronic}}$ is still a many body problem consisting of $N_e$ electrons with $3N_e$ degrees of freedom, and for systems with many atoms solving the ground state wavefunction computationally is still a very difficult task.

DFT seeks to address this problem and enable the computation of much more demanding systems, with the key points in the development of DFT
coming from the theorems of Hohenberg and Kohn (HK) [148]. Their first proof essentially states that there exists a functional $E[n(r)]$ from which you can obtain the exact solution to the Schrödinger equation (and hence the ground state energy) if you know the exact electron density, and that the ground state electronic configuration has a unique electron density associated with it. This reduces the many body problem described from one with $3N_e$ to 3 degrees of freedom corresponding to the three spatial coordinates of the electron density. It is useful to express $n(r)$ in terms of individual electron wave functions $\psi_i(r)$ (especially when considering the Kohn-Sham theory presented later):

\[
n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \tag{1.9}
\]

where the summation expresses the probability that an electron in each individual wave function $\psi_i(r)$ is located at position $r$, and the whole sum is multiplied by two because each wave function can be occupied by two different electrons provided they have different spins (by the Pauli exclusion principle).

The second HK theorem deals with knowing whether a given density is the true ground state density. It states that the functional $E[n(r)]$ delivers the lowest energy if and only if the input density $n(r)$ is really the ground state density. Therefore if we minimise the energy of $E[n(r)]$ over all electron densities, we will get the exact ground state energy of the system.

$E[n(r)]$ can be expressed as a combination of a universal function $F[n]$, which is common to all systems, and a term that includes the external potential exerted by the nuclei of the system:

\[
E[n(r)] = F[n] + \int V(r)n(r)d^3r \tag{1.10}
\]

Furthermore, $F[n]$ can be expressed in terms of the single electron wave functions ($\psi_i$) described above in Equation (1.9):

\[
F[\psi_i] = -\frac{\hbar^2}{m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r - r'|} d^3r d^3r' + E_{\text{XC}}[\psi_i] \tag{1.11}
\]

where the terms in order correspond to the kinetic energies of the electrons, the electrostatic energy of the system, and the remaining many-body interactions between the electrons, known as the exchange-correlation functional $E_{\text{XC}}[\psi_i]$. Even considering if it were possible to find an exact ana-
lytical form of the unknown exchange-correlation functional, this does not guarantee that these sets of equations will be able to be computationally solved.

Fortunately in 1965 Kohn and Sham [147] showed that it was possible to map these many-electron functionals to a set of equations involving the single electron wave functions in such a way that these equations would yield the same ground state electron density. The Kohn-Sham (KS) equations have the form:

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right) \psi_i(r) = \eta_i \psi_i(r) \quad (1.12)
\]

which contains three potentials: \( V(r) \), \( V_H(r) \) and \( V_{XC}(r) \) (as well as the first term representing the kinetic energy of the non-interacting electrons). The first potential, \( V(r) \), corresponds to the known interaction between an electron and field generated by the nuclei. The second potential, \( V_H(r) \), is called the Hartree potential and describes the Coulomb repulsion between the individual electrons in the single electron wave functions and the total electronic density:

\[
V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3 r' \quad (1.13)
\]

The use of this potential introduces an unphysical interaction, known as self-interaction, due to the fact that because each electron is part of the overall electron density and therefore \( V_H(r) \) includes interactions between electrons and themselves. In practice, the correction to the self-interaction problem is included in the exchange-correlation functional, \( V_{XC}(r) \), which formally is the functional derivative of the \( E_{XC} \) functional encountered in Equation (1.11).

With the KS equations, it is possible to arrive at a solution to the total electron density in an iterative fashion, which is necessary due to the fact that to be able to solve the KS equations requires knowledge of the Hartree potential, which in turn requires knowledge of the electron density, which in turn requires us to solve the KS equations to find the single electron wave functions. First a trial electron density is used to solve the KS equations and find the single electron wave functions, and then these wave functions are used to calculate the electron density using Equation (1.9). If the two electron densities agree to within a certain energy tolerance, then we have the correct answer, if not, the calculated electron density is used as the input for the next iteration.
The final difficulty lies in obtaining an approximate form of the exchange-correlation functional. In the first instance the local electron density can be approximated as a uniform electron gas, which treats the density as a slowly varying function. This use of the local density at each electron as an approximation to the real electron density is the basis for the local density approximation (LDA) functional, one of the many functionals used to estimate the unknown $E_{XC}$. Another widely used class of functionals are known as generalised gradient approximation (GGA) functionals [155]. These functionals depend not only on the density at the electron’s location, but also the gradient of the density at that point, and generally give more accurate optimised structures and energies than LDA (although not always).

The systems we are interested in calculating in this work are principally periodic crystals, consisting of (approximately) infinite lattices of atoms, rather than isolated molecules. As such, it is advantageous to use periodic functions to represent the electron density to mirror the periodicity of the crystal system and minimise the number of variables that need to be considered in the calculations. The accuracy of such a simplication was proved by Felix Bloch, who states in his theorem that for wave functions $\psi$ (called Bloch waves) of the form

$$\psi(r) = e^{ik\cdot r}u(r)$$

where $k$ is a real number denoted as the crystal wave vector and $u(r)$ is a periodic function with the same periodicity as the crystal, the ground state energies of electrons in a periodic crystal can be written as Bloch waves [156]. In this way, an infinite number of electrons within a crystal can be considered instead as a finite number of Bloch waves. In reality, only a finite number of values for $k$ can be computed, but various methods have been developed to efficiently sample them to provide an accurate approximation to the true wave functions [157].

A further addition to the DFT described so far is the use of pseudopotentials to decrease the computational time to calculate the total energies of the compounds involved. In the pseudopotential approximation, the electrons in a system are split into two categories, the core and valence electrons, with the former being replaced by a simpler pseudopotential function rather than being treated explicitly. Core electrons have a shorter wavelength and thus higher energy, and as pseudopotentials remove these components, it is possible to use a lower energy cutoff, reducing the total computational time.
required. This approximation is generally valid as the core electrons nearer the nucleus rarely interact with electrons on neighbouring nuclei and do not influence the physical properties and chemistry of the system. A type of pseudopotentials called projector augmented wave (PAW) pseudopotentials are commonly used [158], and need to be individually optimised for each of the different elements involved in a calculation.

1.4.2 The Materials Project and DFT

The Materials Project* is a large database containing the structural information of thousands of compounds, as well as their calculated total energies [154]. To calculate these energies, DFT is used as described in the previous section, with the program of choice being the Vienna Ab Initio Simulation Package (VASP) [159]. However, there are a number of additional parameters that need to be considered when optimising the use of DFT for the high-throughput calculation of so many varied compounds.

The first important part is the choice of functional to approximate $E_{XC}$. As discussed in Section 1.4.1, LDA is the simplest approach, using the uniform density from the electron gas to approximate the real electron density at each electron. For the Materials Project, as for many other studies, GGA functionals generally give more accurate results across the wide range of materials being calculated and hence were the functionals of choice.

However, GGA can perform poorly for compounds in which the electrons are largely localised on the nuclei, and interact strongly with each other, as in the case with compounds containing transition metals and rare earth elements. In these cases, the DFT+U methodology is employed, which adds an additional parameter $U$ to take into account the localised electron interactions [160, 161]. The value of $U$ is different for each element, and can be obtained either \textit{ab initio} through using a linear response approach [162], or by optimising $U$ so as to best fit experimental physical properties measurements. In the case of the Materials Project, $U$ values are obtained for each element by fitting to experimental binary formation enthalpies [163] as this parameter tends to give the most accurate reproduction of phase stabilities. Furthermore, depending on the phases involved in different chemical systems, sometimes all GGA or all GGA+U calculations are used if appropriate. However, when there is a mixture of phases with very different electronic properties (such as a metal and an insulator), a hybrid approach is used where both GGA and GGA+U energies are used, and a correction

*www.materialsproject.org
is applied to the GGA+U terms to make them comparable to the GGA results [164].

1.5 Experimental determination of \( \Delta H \)

Thermogravimetric analysis (TGA) is the primary tool to experimentally determine the carbonation equilibrium for a given material. Samples are placed in a crucible made of alumina or platinum (depending on the material and the temperatures used in the experiment), and then placed on a cantilever-style balance within a furnace. Different mixtures of gases can be supplied to flow over the sample as the reactive gas during experiments, controlled by a system of flowmeters leading to the reaction chamber. The design of a typical reaction chamber is shown in Figure 1.2.

\[ K_p = p_{CO_2} = A \exp(-\frac{B}{T}) \]  

where \( p_{CO_2} \) is the CO\(_2\) partial pressure in atm, \( T \) is the calcination temperature in K, and \( A \) and \( B \) are constants specific to each reaction, which can be obtained by plotting a logarithmic curve of \( 1/T \) measured at different \( p_{CO_2} \).
Combining two expressions for the Gibbs free energy in terms of the equilibrium constant, and the enthalpy and entropy of the reaction,

\[ \Delta G_r = -RT \ln K_p \] (1.16)

\[ \Delta G_r = \Delta H_r - T \Delta S_r \] (1.17)

and assuming that both \( \Delta H_r \) and \( \Delta S_r \) are invariant over the temperature range of the reaction, we can obtain values for \( \Delta H_r \) and \( \Delta S_r \) from the fitting constants determined previously:

\[ K_p = \exp(\Delta S_r / R) \cdot \exp(-\Delta H_r / RT) \] (1.18)

\[ A = \exp(\Delta S_r / R) \] (1.19)

\[ B = \Delta H_r / R \] (1.20)

A different method to measure \( \Delta H \) for a particular reaction is differential scanning calorimetry (DSC), which directly measures the heat flow that occurs in a sample under changing temperature or even isothermally. It is possible to derive \( \Delta H \) by the following relationship:

\[ \Delta H = \int_{1}^{2} \frac{dH}{dt} \, dt \] (1.21)

where \( \Delta H \) is measured in J, the integral is taken between times 1 and 2, and \( \frac{dH}{dt} \) is the measured heat flow that flows to the sample. It is usual to perform a regular TGA trace simultaneously to the DSC experiment, allowing the \( \Delta H \) in kJ mol\(^{-1}\) to be calculated given the mass increase due to CO\(_2\) absorption.

### 1.6 Diffraction

Diffraction occurs as a result of constructive and destructive interference of incident waves (x-rays, neutrons or electrons) following reflection from regularly spaced lattice planes of a crystalline material. These diffracted waves can be detected with an appropriate instrument, such as a charge-coupled device detector, to produce a diffraction pattern. The condition for constructive interference is known as Bragg’s Law:

\[ n\lambda = 2d \sin \theta \] (1.22)
Where $n$ is an integer, $\lambda$ is the wavelength of the incident wave, $d$ is the spacing between atomic lattice planes and $\theta$ is the angle between the incident beam and the scattering lattice planes. Diffraction patterns are normally presented as diffracted intensity vs the experimentally measured scattering angle $2\theta$.

Laboratory powder x-ray diffraction (XRD) is the main method used in solid-state synthetic chemistry to efficiently and accurately monitor the progress of reactions. Modern laboratory x-ray diffractometers are able to analyse samples in very short times with little preparation or degradation of the sample. Typically, patterns can be measured over a range of $3\text{–}80^\circ 2\theta$ and provide sufficient resolution to characterise progressive changes in the sample such as the changing ratio of starting materials to desired product.

1.6.1 Synchrotron XRD

The primary difference between laboratory and synchrotron XRD (S-XRD) is the source of the x-rays themselves. In laboratory diffractometers x-rays are produced through irradiation of a single metallic anode, which produces x-rays with a specific set of wavelengths dependent upon the metal used. In a synchrotron, x-rays over a wide range of energies are produced from the acceleration of electrons as they move at extremely high speeds around a ring.

Synchrotron radiation offers several advantages over its laboratory counterpart. Firstly, the x-ray flux is much higher than what is able to be produced in a laboratory instrument. This leads to stronger Bragg diffraction peaks with a higher signal-to-noise ratio. This is important in accurately identifying and quantifying weaker peaks that might have formerly been masked by the background. Furthermore, in our \textit{in situ} gas flow experiments, being able to acquire high quality data rapidly allows the reaction profile to be measured with better time resolution as well. Finally, the x-rays can be monochromated to have a much better energy (and hence wavelength) resolution. This means the peaks in the diffraction pattern have a better shape and narrower peak width, allowing better resolution and identification of reflections with a similar $d$-spacing. It is also possible to tune or select monochromatic x-rays to avoid problems (e.g. absorption) that arise from the use of particular wavelengths with a sample, or to exploit a particular wavelength such as one on or near the absorption edge of an element in the sample (the underlying principle used in x-ray absorption spectroscopy).
1.6.2 Rietveld refinement

The concept of structural refinement against powder diffraction data was pioneered by Hugo Rietveld in 1969 [165]. The main difference between it and single crystal methods is that Rietveld is a whole pattern fitting technique, including the background, whereas single crystal methods only seek to match the intensities of the Bragg diffraction peaks. The Rietveld refinement process essentially involves the least-squares minimisation of a function $M$ which describes the difference between an observed diffraction pattern and a calculated diffraction pattern simulated from a crystallographic model:

$$\text{M} = \sum_i W_i (y_i^{\text{obs}} - \frac{1}{c} y_i^{\text{calc}})^2$$

(1.23)

where $W_i$ is the weight given to each point in the pattern and is defined as $W_i = \frac{1}{\sigma_i^2(y_i^{\text{obs}})}$ and $c$ is a scaling factor that accounts for the overall difference in intensity between the observed and calculated patterns. This technique was unique at the time in that it could resolve peak intensity in powder diffraction data where there were a number of overlapping peaks.

Much like single crystal refinement, the Rietveld method starts from an initial model of which numerous structural parameters can be varied. In this case, the goal is to minimise $M$ to get the best fit between the observed and calculated intensities across each point in the $2\theta$ range.

Different programs are available to perform Rietveld refinements which have different advantages and disadvantages depending on the type of diffraction data you are refining and the type of refinement you are performing. The program used in this work was GSAS with the EXPGUI interface [166, 167]. In GSAS, the refinement performs a least squares minimisation on the weighted profile factor:

$$R_{wp} = \left[ \frac{\sum_i W_i (y_i^{\text{obs}} - y_i^{\text{calc}})^2}{\sum_i W_i (y_i^{\text{obs}})^2} \right]^{\frac{1}{2}}$$

(1.24)

When considering this quantity, it is also helpful to calculate the best possible value which $R_{wp}$ can take, where there is no discrepancy between the calculated and observed diffraction patterns. This is termed the “expected R factor” or “expected weighted profile factor” and is denoted $R_{\text{exp}}$. $R_{\text{exp}}$ depends on the number of degrees of freedom in the refinement, $n - p$, where $n$ is the number of data points and $p$ is the number of refined parameters.
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ters. In reality the number of parameters can be omitted from the expression if \( n \) is sufficiently large, which is the case in most powder experiments [168].

\[
R_{\text{exp}} = \left[ \frac{n - p}{\sum_i W_i (y_{i}^{\text{obs}})^2} \right]^{\frac{1}{2}}
\]

(1.25)

The agreement between the model and the data can be measured via the Bragg R-factor and \( \chi^2 \). Each is calculated in a different way, and together are a best indication of the accuracy of the model.

The Bragg R-factor is calculated in a very similar way to the crystallographic R-factor, \( R_f \), except that instead of structure factors, it relies upon the measured intensities at each point in the \( 2\theta \) range. Similar values are expected to that of \( R_f \), namely \(<0.15\).

\[
R_{\text{Bragg}} = \frac{\sum ||I_{\text{obs}}| - |I_{\text{calc}}||}{\sum |I_{\text{obs}}|}
\]

(1.26)

\( \chi^2 \) is simply the square of the ratio of \( R_{wp} \) to \( R_{\text{exp}} \), and should minimise to one rather than zero:

\[
\chi^2 = \left( \frac{R_{wp}}{R_{\text{exp}}} \right)^2
\]

(1.27)

It is important to view these statistical measurements within the context of the refinement that is being run and the experimental data being used. For example, as Toby [168] notes, if the background contributes a significant amount to the total measured intensity of a diffraction pattern, then excellent values of \( R_{\text{Bragg}} \) and \( \chi^2 \) can be obtained by simply fitting the background well regardless of the model tested. This is shown best in synchrotron x-ray data, where the signal to noise ratio is considerably better than in laboratory x-ray powder data. For these data it is very difficult to obtain very low \( R_{\text{Bragg}} \) and \( \chi^2 \), regardless of how accurate the tested model might be, as even small deviations from the observed pattern will have large contributions to the difference in intensities and therefore on the statistical measures of refinement reliability.

1.7 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) experiments measure the precession frequency of nuclear spins in a magnetic field. This frequency is very sensitive to the local chemical environment; therefore NMR can provide a highly sensitive probe of local structure and dynamics, which is complementary
1.7. Nuclear magnetic resonance

to the long-range structural information derived from diffraction experiments. In this particular case, local structural information is particularly important to study the changes in environment as we move through the different reaction fronts within sorbent particles. It can also provide valuable information about rates and paths of ionic conduction that will help in identifying the role structure plays in the physical properties of carbonation and calcination.

It is not the intention to give a complete introduction to the theory behind NMR in this section, but rather to focus on the different interactions and experiments that were employed in this work.

1.7.1 Quadrupolar NMR

In this work, the NMR studies were concerned with quadrupolar nuclei, that is nuclei with spin \( I > \frac{1}{2} \). For these nuclei, in addition to the local environment, the nuclear spins are also influenced by the interaction of the inherent quadrupole moment of the nuclei with the electric field gradient (EFG) present at the nucleus. Importantly, these interactions are not isotropic, and so for a solid powder sample these interactions give rise to broad resonances [169, 170].

The quadrupolar interaction of a particular nucleus can be described by a number of different parameters. Firstly we have the quadrupolar coupling constant, or \( C_Q \), which is a measure of the magnitude of the interaction and depends on the electric quadrupole moment of the nuclei and the EFG tensor. The electric field gradient is caused by the distribution of charges in a system, which for a first approximation can be modelled by the nearest coordinating atoms. \( C_Q \) is zero for an ideal octahedral, tetrahedral or cubic environment, becoming larger as the environment becomes less symmetric. This environment also influences the quadrupolar asymmetry parameter, \( \eta_Q \), which is a measure of how symmetric the cross-section of the EFG is at the nuclei of interest. For a cubic coordination environment, \( \eta_Q = 0 \), and can increase to 1 as the environment becomes more asymmetric. The quadrupolar splitting parameter, \( \nu_Q \), is directly related to the \( C_Q \):

\[
\nu_Q = \frac{3C_Q}{4I(2I-1)}
\] (1.28)

As a first approximation (neglecting other effects such as dipolar coupling), we can write the total Hamiltonian for the system as a sum of the chemical shift, or Zeeman interactions, and the quadrupolar interactions:
Total = \( H_Z + H_Q \) \hspace{1cm} (1.29)

The quadrupolar coupling constant is often much smaller than the Zeeman effect, and when this is the case (such as for \(^6\)Li or \(^7\)Li) we can approximate the influence of the quadrupolar moment on the Zeeman energy levels as a simple sum:

\[ E = E_Z + E_Q \] \hspace{1cm} (1.30)

For a half-integer nuclear spin, such as \( I = \frac{3}{2} \), this has an important consequence in that the central transition (CT), \( \frac{1}{2} \rightarrow -\frac{1}{2} \) occurs with the same energy as if we only had to consider Zeeman interactions, with satellite transitions (ST) due to the \( |\frac{1}{2}\rangle \leftrightarrow |\frac{3}{2}\rangle \) transitions appearing with shifts on either side of the CT (with their separation dependent upon the size of \( \omega_Q \)) (Figure 1.3).

![Figure 1.3: Energy levels for a \( I = \frac{3}{2} \) nuclei, considering only Zeeman and first-order quadrupolar interactions, and the resulting NMR spectra. Figure from ‘Introduction to Quadrupolar NMR’ by Sharon Ashbrook. [170]](image)

However, this approximation does not hold for cases where the quadrupolar interaction is large and on a similar scale to the Zeeman interaction (such as for \(^{93}\)Nb). In this case, we must correct the energy levels by including more terms to describe the quadrupolar interaction. In practice, including the second-order term \( E_Q^2 \) is sufficient as a good approximation:
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Figure 1.4: Energy levels for a $I = 3/2$ nuclei, considering the Zeeman, first-order and second-order quadrupolar interactions, and the resulting NMR spectra. Figure from ‘Introduction to Quadrupolar NMR’ by Sharon Ashbrook. [170]

$$E = E_Z + E_Q^1 + E_Q^2$$

(1.31)

While the size of the second-order term is much smaller than the first-order term, it still affects the energy levels of the system, and leads to a broadening of the central transition and added broadening to the satellite transitions (Figure 1.4).

1.7.2 Motional averaging and quadrupolar NMR

In experiments with $^7$Li ($I = 3/2$), fortunately the quadrupolar interaction is much smaller, and the second-order term does not have such a significant effect. As such, it is possible to remove the first-order quadrupolar broadening by acquiring spectra under magic-angle spinning (MAS). However, even under these conditions broadening is sometimes observed for the STs, which under MAS consist of a series of spinning sidebands. While this broadening can be caused by a number of different phenomena, a strong dependence on temperature generally indicates that it is due to motion in the solid [171]. In this case, this occurs as Li ions move between different crystallographic sites in a material.
The effect of dynamic exchange of Li ions between magnetically-inequivalent sites on the ST spinning sidebands can be understood by considering the frequency jump, $\Delta \nu$, in the quadrupolar splitting that results from the reorientation of the EFG tensor when a Li ion exchanges between two magnetically-inequivalent sites. It has been shown that if the rate constant, $k$, for the exchange process is comparable to $\Delta \nu$, significant broadening of the ST spinning sidebands can occur [172]. To determine $\Delta \nu$, it is necessary to consider the change in the $^7$Li quadrupolar splitting parameter, $\nu_Q$, upon exchange of a Li ion between two magnetically inequivalent sites. For a static single crystallite orientation, $\nu_Q$, is given by

$$\nu_Q = \nu_Q^{PAS}[D^2_{0,0}(\alpha, \beta, \gamma) + \frac{\eta_Q}{\sqrt{6}}(D^2_{0,-2}(\alpha, \beta, \gamma) + D^2_{0,2}(\alpha, \beta, \gamma))] \quad (1.32)$$

where $\eta_Q$ is the asymmetry parameter, $D^2_{m,m}(\alpha, \beta, \gamma)$ is a rank $l = 2$ Wigner rotation element describing the orientation of the principal axis system (PAS) of the EFG tensor in the laboratory frame in terms of Euler angles $\alpha$, $\beta$ and $\gamma$, and $\nu_Q^{PAS}$ is the quadrupolar splitting parameter in the PAS, with spin $I = 3/2$ for $^7$Li.

For a single crystallite orientation, the splitting between the $\pm 1/2 \leftrightarrow \pm 3/2$ quadrupolar satellite transitions and the central transition is equal to $2\nu_Q$. Exchange of a Li ion between two magnetically-inequivalent sites will cause a change in the orientation of the EFG tensor, resulting in a new quadrupolar splitting, $2\nu'_Q$. The change in quadrupolar splitting, $\Delta \nu$, resulting from movement of a Li ion between two magnetically-inequivalent sites is therefore given by

$$\Delta \nu = 2\nu_Q - 2\nu'_Q \quad (1.33)$$

where $\Delta \nu$ is a function of $\eta_Q$ and the Euler angles $\beta_1$ and $\gamma_1$ relating the original tensor to the laboratory frame, and $\nu'_Q$ is a function of $\Delta \nu$ and the Euler angles $\beta_2$ and $\gamma_2$ which relate the two tensors. In a powdered solid, there will be a distribution of $\Delta \nu'$ values owing to the dependence on the angles $\beta_1$ and $\gamma_1$, and the root-mean square (rms) frequency jump, $\Delta \nu^{rms}$, is considered as an appropriate mean of the powder distribution. This is obtained by integrating over $\beta_1$ and $\gamma_1$ angles between $0^\circ$ and $180^\circ$, and $0^\circ$ and $360^\circ$, respectively [173, 174].

Importantly this allows the calculation of $\Delta \nu^{rms}$ given the quadrupolar parameters $C_Q$ and $\eta_Q$ and the orientation of the EFG tensor for the different sites in a material (which can be obtained from DFT calculations), and
from this the motionally-averaged ST sideband linewidths can be simulated as a function of the rate constant \( k \) of ionic motion. Comparison with experimentally observed linewidths across a range of temperatures allows the extraction of \( k \) against temperature for the given ionic process, and subsequent fitting of this data can yield an activation energy for the ionic process.

## 1.8 Structure of the dissertation

Overall, this study has three main aims: synthesising new materials and testing their physical properties as potential CO\(_2\) absorbents; developing and using various \textit{in situ} techniques to gain data on the carbonation and regeneration reactions of various materials; and combining the knowledge from these new materials and the \textit{in situ} studies with other experimental techniques to understand the mechanism by which these materials operate, and the factors that influence their performance.

In Chapter 2, the process by which new materials for CO\(_2\) absorption were discovered through screening of the Materials Project database is explored. In Chapter 3, those materials that were found to have promising theoretical performance were subjected to thermogravimetric analysis to determine their experimental properties, and to validate the initial screening methodology.

In Chapter 4, a thorough \textit{in situ} experimental study of a novel perovskite capable of reversible CO\(_2\) absorption, Ba\(_4\)Sb\(_2\)O\(_9\), is presented based on the publication of Dunstan \textit{et al.} \cite{175}. Thermogravimetry, synchrotron x-ray diffraction and scanning electron microscopy is used to characterise the performance of the material, and to determine the origin of its remarkably stable CO\(_2\) absorption capacity over 100 cycles.

Finally, in Chapter 5 a novel technique utilising solid state NMR at variable temperatures is reported in order to study ionic motion in a prototypical material involved in CCS processes, Li\(_2\)CO\(_3\). Using both \(^{7}\)Li and \(^{17}\)O NMR it was possible to extract activation energies for both Li and O ionic motion, and to determine that these processes are linked to one another over the temperature range relevant to CO\(_2\) looping. This study is a first step in validating the underlying mechanism for continued carbonation via ionic transport that has been theorised to this point.
2.1 Introduction

There is much interest in developing new materials for high-temperature CO$_2$ looping, or modifying existing ones, because of the problems with capacity loss encountered when using a pure CaO-CaCO$_3$ system. There are a number of different parameters that influence the suitability of a material for use in CO$_2$ looping, including carbonation thermodynamics, CO$_2$ capture capacity, cycling stability of the material and cost [35]. In addition to this, there are a very wide range of alkali-based oxide materials that could potentially be used in developing an optimal process. Practically, synthesising and testing all possible materials is plainly not feasible, and therefore it is desirable to develop a computational screening methodology to identify the most promising candidates for the target application.

There have been a few examples of previous approaches utilising various theoretical methods to screen materials for applicability for CO$_2$ capture. Lin et al. generated a database of potential zeolite-like structures that were subsequently analysed via interatomic potentials to determine their thermodynamic stability [176]. CO$_2$ absorption isotherms were constructed using molecular simulations which allowed the calculation of the parasitic energy for the stable materials, corresponding to the penalty imposed on a power plant if fitted with a CCS process using the material. Their screening showed a theoretical limit to the minimum parasitic energy that can be obtained with zeolite and zeolitic imidazolate framework (ZIF) type mate-
Chapter 2. Large scale screening of novel materials for CCS

Several other studies have also been performed on similar materials, albeit on smaller sets, with some comparison between theoretical and experimental results for CO$_2$ uptake [177, 178, 179], along with high-throughput synthesis methods being used to find novel ZIF materials for CO$_2$ capture [180].

The group of Duan et al. has focused on lithium-based oxide materials for high-temperature CCS applications, using density functional theory (DFT) and phonon calculations to determine the carbonation reaction thermodynamics of these materials, and comparing them to tabulated experimental data [181, 182, 183]. Other studies have also outlined a possible screening process based on theoretical DFT and phonon calculations to filter out the most suitable materials given a large starting set, with screening performed on smaller sets of alkali-based oxides [184, 185]. The limitation of these previous studies is that they were applied to a relatively small number of materials, many of them already well known experimentally as being promising compounds for CO$_2$ capture. In our study, we sought to theoretically screen thousands of possible carbonation reactions from a very wide range of solid oxide based materials, both with the hope of discovering novel compounds for CCS applications, and that the screening results can help elucidate the underlying principles that can drive future design of CCS materials. For these novel materials, we also sought to experimentally validate the results proposed by the screening method so as to go beyond the theoretical framework used solely in previous studies (these studies are described in Chapter 3).

2.2 Computational Methods

In this work, we utilised the Materials Project\textsuperscript{*} database which contains structural, electronic and energetic data for over 50 000 compounds calculated using the Vienna Ab initio Simulation Package (VASP) [154, 159, 186]. Importantly, the contents of the database are accessible via the REST Materials API, which allows users to develop their own screening programs to search the database using an open-source Python library Pymatgen for materials analysis [187]. In this work a screening methodology was developed to search the database for suitable materials for high-temperature CO$_2$ capture and to predict the thermodynamic enthalpies and entropies for the \textit{in silico} carbonation reactions of these compounds. To rank these reactions

\textsuperscript{*}www.materialsproject.org
we used a similar energy penalty concept as previous studies [176], which favours materials whose use for CCS minimises the energy load imposed on a power station. We also screened materials based on their gravimetric CO$_2$ capacity as a preliminary measure of the material cost per unit of CO$_2$ captured, and also the net volume change of a material after carbonation as an indication of cycling stability.

Given the ground state energies of all the phases present in a given carbonation reaction, it is possible to calculate $\Delta E_{DFT}$ for the reaction, which is equivalent to $\Delta H_{\text{carbonation}}$ at 0 K and zero pressure. The first part of the screening process therefore is to determine this value for all possible reactions within a given subset of compounds. Furthermore, since these reactions will be performed at varying CO$_2$ partial pressures and temperatures, a single variable can be defined by considering all reactions under varying CO$_2$ chemical potential ($\mu_{\text{CO}_2}$), with a more negative value corresponding to either higher $T$ or lower $p_{\text{CO}_2}$.

The screening focused on oxide materials that were either binary or ternary compounds in this initial screening, as this not only drastically narrows the phase space within which the search is conducted, but it also excludes compounds with multiple components that are more likely to sinter and phase segregate during the cycles of carbonation and calcination. Furthermore, materials were limited to those containing elements from the 37 most abundant within the earth’s crust, as this realistically reflects concerns about cost and availability of a theoretically useful CCS material$^\dagger$. Finally, materials were only considered where at least one of the elements was an alkali metal ($A = \text{Li, Na, Mg, K, Ca, Rb, Sr, Ba}$), to hopefully find a material with acceptable reaction kinetics, especially considering that the initial screening does not account for the rate of reaction. The geometry optimised structures and ground state $E_{DFT}$ of the relevant materials were retrieved from the Materials Project database, having been previously calculated by the Materials Project using VASP [154].

The screening comprised of 640 unique compounds with a total of 1442 simulated carbonation reactions. To obtain all compounds that matched these initial criteria, quaternary phase diagrams of the form $A-M-O-CO_2$ were simulated, where $M$ is a non-alkali element, using the Phase Diagram app within the Pymatgen library [164, 188]. Because the primary interest lies in the evolution of the phases under reaction with CO$_2$, the approach found in previous studies that generated open phase diagrams with respect to $A$, $M$, and $O$ was followed.

$^\dagger$Sb was also included in the screening, despite not being within the most abundant elements, due to our work on a novel CCS material, Ba$_4$Sb$_2$O$_9$ [175].
to $\mu_{O_2}$ [188, 189] was adapted to study the phase equilibria under changing $\mu_{CO_2}$.

In order to construct these phase diagrams, and assuming that the system is closed with respect to every element except $CO_2$, which is reasonable given that $p_{CO_2} > p_{O_2}$ in the carbonator and calciner, it is necessary to use the $CO_2$ grand canonical potential which can be defined as

$$\phi(T, P, N_A, N_M, N_O, \mu_{CO_2}) = G - \mu_{CO_2}N_{CO_2} \approx E - TS + PV - \mu_{CO_2}N_{CO_2}$$  \hspace{1cm} (2.1)$$

where $G$ is the Gibbs free energy, $E$ is the internal energy, $T$ is the temperature, $S$ is the entropy, $P$ is the pressure, $V$ is the volume, and $N_i$ is the number of atoms of species $i$ in the system. If it is assumed that the $PV$ term is small relative to the $E$ and $TS$ terms for a reaction that primarily involves solid condensed phases, and $\phi$ is normalised so that the sum of the $A$, $M$ and $O$ components is equal to 1, Equation (2.1) can be rewritten as

$$\phi(T, P, x_A, x_M, x_{O_2}, \mu_{CO_2}) \approx \frac{E - TS - \mu_{CO_2}N_{CO_2}}{N_A + N_M + N_O}$$  \hspace{1cm} (2.2)$$

where $x_i$ is the component fraction of $i$ in the ternary phase diagram.

In order to construct these open phase diagrams it is normally necessary to calculate the entropy change in the solid and gas phases due to different vibrational, configurational and electronic excitations. For solid crystalline structures this would normally be approached through calculating the various phonon frequencies (and hence the phonon densities and dispersion curves) for individual phases and using these to derive the total entropy of the crystal at different temperatures. This approach is valid when it comes to studying a small number of phases and reactions, but in a screening study involving thousands of different compounds, these calculations are too expensive to be feasible.

Thankfully in this case, there are some assumptions which can be employed to simplify the calculation of the phase diagram. Given that all the reactions of interest involve $CO_2$ gas absorption, it is reasonable to assume that the reaction entropy is dominated by the $CO_2$ gas entropy, rather than changes due to solid-solid transformations. As such, the change in the $CO_2$ chemical potential can account for the effect of temperature on $\phi$. At a given temperature $T$ and $CO_2$ partial pressure $p_{CO_2}$, the chemical potential can be described as:
\[ \mu_{\text{CO}_2}(T, p_{\text{CO}_2}) = \mu_{\text{CO}_2}(T, p_0) + kT \ln \frac{p_{\text{CO}_2}}{p_0} \]  

(2.3)

where \( p_{\text{CO}_2} \) is the \( \text{CO}_2 \) partial pressure, \( p_0 \) is a reference \( \text{CO}_2 \) partial pressure (0.1 MPa) and \( k \) is Boltzmann’s constant. \( \mu_{\text{CO}_2}(T, p_0) \) can be rewritten as a Legendre transform of the internal energy:

\[ \mu_{\text{CO}_2}(T, p_{\text{CO}_2}) = E_{\text{CO}_2} + PV - T S_{\text{CO}_2}^{T, p_0} + kT \ln \frac{p_{\text{CO}_2}}{p_0} \]  

(2.4)

where \( S_{\text{CO}_2}^{T, p_0} \) is the \( \text{CO}_2 \) entropy, obtained from the NIST-JANAF thermochemical tables [190]. If we make a further ideal gas assumption, the PV term is equal to \( kT \), leaving the chemical potential to be dependent only on \( T \) and \( p_{\text{CO}_2} \). Furthermore, the expression for \( \phi \) can now be further simplified, given our assumption that the contribution of \( S_{\text{CO}_2} \) within \( \mu_{\text{CO}_2}N_{\text{CO}_2} \) dominates compared to S:

\[ \phi(T, P, x_A, x_M, x_O, \mu_{\text{CO}_2}) \approx \frac{E}{N_A + N_M + N_O} - \mu_{\text{CO}_2} \]  

(2.5)

It is possible then to interpret carbonation reactions as the evolution of phases over successive ternary phase diagrams \( A - M - O \) with different \( \mu_{\text{CO}_2} \), essentially tracking the decomposition of a given phase into different products under increasing temperature or \( \text{CO}_2 \) partial pressure. An example of this can be seen in Figure 2.1, showing different projections of the Li-Si-O-\( \text{CO}_2 \) phase space as constant \( \mu_{\text{CO}_2} \) slices. Further studies using an approach such as AIRSS [152, 153] to predict novel phases not in the database could potentially add more detail to the phase diagram and suggest different decomposition paths for a given material.

It is also necessary to obtain a more accurate estimation of the energy of the \( \text{CO}_2 \) molecule found in the database, due to the fact that the database entry for \( \text{CO}_2 \) is based on a solid, rather than gaseous \( \text{CO}_2 \). To this end we calibrated the database energy by comparing \( \Delta E_{\text{DFT}} \) and \( \Delta H_{\text{experimental}} \) at 293 K for a small set of basic binary alkali oxides, and a number of ternary Li-based oxides (Figure 2.2). These results validate the earlier assumption that \( \text{CO}_2 \) dominates the entropy change in these reactions, and that this approach in simulating carbonation at elevated temperatures is a good approximation. The average error between the theoretical and experimental values was added as a correction to \( E_{\text{CO}_2} \), and the corrected value was used for the screening. This correction will also account for some part of the solid entropy change between 0 and 300 K that is not taken into account in the calculations.
Figure 2.1: Ternary Li-Si-O phase diagrams under different $\mu_{\text{CO}_2}$ obtained by applying the CO$_2$ grand potential to the Materials Project database. The physical equivalent of increasing the chemical potential is either an isothermal reaction performed with increasing $p_{\text{CO}_2}$, or an isobaric reaction under decreasing temperature. Vertices that are present in the lefthand phase diagram but are not present in righthand phase diagram represent phases which have decomposed as a result of the change in $\mu_{\text{CO}_2}$. The product phases of this decomposition reaction with CO$_2$ are situated at the vertices at either end of the edge where the original phase was formerly located. For example, Li$_4$SiO$_4$ transforms to a mixture of Li$_2$CO$_3$ and Li$_2$SiO$_3$ with increasing $\mu_{\text{CO}_2}$.

Figure 2.2: Errors between $\Delta E_{\text{DFT}}$ and $\Delta H_{\text{experimental}}$ at 293 K for selected binary and ternary oxides. The average error was used as a correction to $E_{\text{CO}_2}$ in the Materials Project database.
2.3 Results

2.3.1 Comparison to other theoretical studies

There are previous theoretical results derived from a similar level of DFT theory to model $\Delta E_{DFT}$ for the carbonation reactions of binary oxides and some different reaction pathways for Li-based ternary oxides [181, 182, 185, 191]. To further validate the calculated energies in the Materials Project database, we compiled these previous results and compared the respective $\Delta E_{DFT}$ for the various reactions. As the comparison is with other 0 K calculations that have not optimised the CO$_2$ energy, the earlier correction to the CO$_2$ energy was not applied in order to have a more accurate comparison. The respective values for $\Delta E_{DFT}$ are shown in Figure 2.3.

![Figure 2.3: Comparison between the calculated $\Delta E_{DFT}$ for this work (blue), and with the studies of Duan et al. (red) [181, 182, 185, 191]. There is a significant difference between the two studies, with the Materials Project $\Delta E_{DFT}$ being 13 kJ mol$^{-1}$ higher than the previous study on average.](image)

It can be clearly seen that there is a very constant underestimation (less negative) of $\Delta E_{DFT}$ in this work compared to the previous studies, but the average error of 13 kJ mol$^{-1}$ is most likely due to the differing methods in determining $E_{CO_2}$, which obtain slightly different values of $-2225$ kJ mol$^{-1}$ and $-2219$ kJ mol$^{-1}$ for the Materials Project and the work of Duan et al. respectively [184].
2.3.2 Screened materials

The screening of the Materials Project database for compounds within the A-M-O-CO\textsubscript{2} open phase diagrams found 640 distinct compounds able to undergo reactions with CO\textsubscript{2}, with a total of 1442 distinct carbonation reactions. The difference in these numbers is due to some compounds being able to undergo several different decomposition pathways with increasing CO\textsubscript{2} chemical potential. A breakdown of these numbers into separate alkali metal compounds can be seen in Table 2.1.

Two subsequent filters were applied to the data to more realistically screen for materials that could be practically used for CO\textsubscript{2} looping applications. The first filter removed materials whose carbonation reactions occurred below 293 K, as practically a CCS process would have to occur at room temperature or above. The second filter used a similar open phase diagram construction as used previously in the original screening process, except this time with the open element being O\textsubscript{2}, to screen the materials for their stability at the very low pO\textsubscript{2} levels expected in the calciner (pO\textsubscript{2} < 0.01). Those materials that would oxidise even under these conditions were removed from the screening, as they would transform before the carbonation reaction had a chance to occur. The remaining distinct compounds, along with the number of distinct possible carbonation reactions, can be seen in Table 2.1.

<table>
<thead>
<tr>
<th>Alkali metal</th>
<th>Original Screening</th>
<th>After Filtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Compounds</td>
<td>Reactions</td>
</tr>
<tr>
<td>Ba</td>
<td>91</td>
<td>195</td>
</tr>
<tr>
<td>Ca</td>
<td>74</td>
<td>164</td>
</tr>
<tr>
<td>K</td>
<td>101</td>
<td>261</td>
</tr>
<tr>
<td>Li</td>
<td>57</td>
<td>118</td>
</tr>
<tr>
<td>Mg</td>
<td>48</td>
<td>84</td>
</tr>
<tr>
<td>Na</td>
<td>92</td>
<td>249</td>
</tr>
<tr>
<td>Rb</td>
<td>81</td>
<td>175</td>
</tr>
<tr>
<td>Sr</td>
<td>75</td>
<td>165</td>
</tr>
<tr>
<td>Non-alkali</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>Total</td>
<td>640</td>
<td>1442</td>
</tr>
</tbody>
</table>

Table 2.1: Total number of compounds and associated carbonation reactions found in the original screening, and after screening out compounds that either react with CO\textsubscript{2} below 293 K, or oxidise before carbonation.

These results show that our screening was able to find materials that
undergo carbonation reactions across all the different alkali metals used, and is certainly the largest number of solid oxide type materials ever to be considered for CCS applications in a single study. Interestingly, the smallest number of compounds were found in the database for the most abundant alkali metals, Ca and Mg. It is unlikely that this reflects a similar disparity in thermodynamically stable phases based on these elements as compared to the other alkalis, but rather suggests that part of the phase diagrams have not been extensively explored. Alternatively, the stability of the binary oxides CaO and MgO compared to the other alkali binary oxides could simply result in fewer stable tertiary phases with these elements. Predicting new compositions and structures based on Ca and Mg using the Structure Predictor module already present in the Materials Project system [192] would be a useful direction to explore this phenomenon further. This module uses a probabilistic function to determine ionic substitutions, trained on a set of known materials and their compositions to predict the crystal structures of entirely new compositions. These new compounds could then be run through the screening process to potentially discover novel materials with desirable properties for CCS.

2.3.3 Energy penalties

Using the relative energies of the reactant and product phases in each theoretical carbonation reaction it was possible to compute a value for $\Delta H_{\text{carbonation}}$ [164]. For a single compound, the multiple reactions essentially describe the same decomposition process, followed to different endpoints, with the order following increasing $\Delta H_{\text{carbonation}}$. Experimentally, we only observe the products of the first decomposition reaction, even on increasing $T$, and therefore the results could be further restricted to one carbonation reaction for each distinct compound, the reaction with the most negative $\Delta H_{\text{carbonation}}$.

To evaluate the potential use of these compounds in CCS applications, the overall parasitic energy penalty that would be imposed on a model power plant through the use of this material was considered, following the approach in previous studies [176]. If the temperatures for the carbonation and calcination reactors are set by the theoretical carbonation equilibrium of the material, the inlet $p_{\text{CO}_2}$ (chosen to be 0.15 for a typical flue gas) and the outlet $p_{\text{CO}_2}$ (chosen to be 1.00 for production of pure CO$_2$), then the total diverted energy from the power process per mole of CO$_2$ absorbed ($m_{\text{CO}_2}$) is given by:
\[
Q_{\text{loss}} = \frac{\Delta H_{\text{calcination}} + C_p(T_{\text{calcination}} - T_{\text{carbonation}})}{m_{\text{CO}_2}}
\]  

(2.6)

where \(C_p\) is the molar heat capacity of the sorbent material, \(T_{\text{calcination}}\) is the temperature of calcination, \(T_{\text{carbonation}}\) is the temperature of carbonation and \(\Delta H_{\text{calcination}} = -\Delta H_{\text{carbonation}}\). Assuming a Carnot efficiency, the work lost due to this diverted heat is

\[
W_{\text{loss}} = Q_{\text{loss}} \left(1 - \frac{T_{\text{environment}}}{\min(T_{\text{calcination}}, T_h)}\right)
\]  

(2.7)

where \(T_{\text{environment}}\) is chosen to be room temperature, 298 K, and \(T_h\) is the operating temperature of the power cycle, which was set to be 623 K.

However, there is a need to consider the amount of work that can be recovered by reintegrating the heat from the carbonator, which will reduce the total \(W_{\text{loss}}\). The heat rejected by the CCS process is given by:

\[
Q_{\text{recovered}} = Q_{\text{loss}} - \Delta H_{\text{CO}_2\text{flow}}
\]  

(2.8)

where \(\Delta H_{\text{CO}_2\text{flow}}\) is the net molar enthalpy flow between the \(\text{CO}_2\) inlet and outlet. Therefore the recovered work from this heat can be calculated:

\[
W_{\text{recovered}} = Q_{\text{recovered}} \left(1 - \frac{T_{\text{environment}}}{T_{\text{carbonation}}}\right)
\]  

(2.9)

and the total energy penalty, \(E_p\) is given by:

\[
E_p = W_{\text{loss}} - W_{\text{recovered}}
\]  

(2.10)

Using these calculations, the most commonly used high temperature CCS material, CaO, has a calculated energy penalty of 41.9 kJ (mol CO\(_2\))\(^{-1}\), and this sets a benchmark for the screening to obtain materials that will lead to efficiency gains for CCS applications. For reference, process engineering studies using CaO as a solid absorbent in a postcombustion CCS setup found this process imposes a 6–8 % energy penalty as compared to plants without CCS [193, 194, 195], and of that penalty, between 3–10 % is attributed to the energy to calcine \(\text{CaCO}_3\) to CaO. A commonly accepted goal for an economically viable CCS process set by the US Department of Energy is to have an energy penalty of 5 % or less, so if we assume that our calculated energy penalty mostly accounts for the calcination energy, this would mean finding a material in our screening with \(E_p < 35\) kJ (mol CO\(_2\))\(^{-1}\). This is still only a rough approximation, as any promising candidate would also
need to the subject of in-depth process engineering simulations to determine its realistic energy penalty in a CCS process.

From the stoichiometry of the reaction, it is also possible to output the CO$_2$ gravimetric capacity ($g_{\text{CO}_2\text{absorbed}}/g_{\text{sorbent}}$) of each theoretical carbonation reaction, as well as the volume change for the reaction (derived from the change in the unit cell volume of the optimised structures). Volume expansion is theorised to contribute to the cycling instability of CaO, with large volume changes causing pore closure and particle sintering and resulting in the rapid fading of the CO$_2$ capture efficiency over the first 10–20 cycles [46, 47, 51, 54]. Therefore, the compounds were screened based on the volume change with carbonation as a preliminary indication of the stability of the compound over multiple cycles.

These different parameters are plotted for each of the screened reactions in Figure 2.4. There is a direct correlation with $\Delta H$ and $E_p$, as is to be expected considering it is a dominant part of the $Q_{\text{loss}}$ and $Q_{\text{recovered}}$ terms used to determine the overall energy penalty. However, for less exothermic carbonation reactions, these terms become more on the scale of the heat capacity term. The approximate heat capacities of the compounds used in the screening were calculated using the Dulong-Petit law [196], this being a good approximation for solid state materials in high temperature regimes, and also being trivial to calculate as it only depends on the molar mass (MM) of the compound. In the lower energy penalty part of the plot, some materials are seen with similar $E_p$, but with $\Delta H$ that differ by as much as 0.5 eV. In this region we have some control over the balance between $\Delta H$ and MM to achieve a given $E_p$, and given that compounds with a lower MM will normally have a higher gravimetric CO$_2$ capacity, this means it is possible to select compounds on the basis of this parameter. Conversely, for a process that might prefer smaller $\Delta H$ to reduce heat flow in and out of the system, it is also possible to select compounds with a higher MM to achieve the same overall $E_p$. 
Figure 2.4: Overview of results from the screening of the Materials Project database for compounds that undergo carbonation. Each data point represents the carbonation reaction for each distinct compound with the most negative ΔH. The calculated energy penalty, $E_p$, for each reaction is plotted against $\Delta H_{carbonation}$ (top), CO$_2$ gravimetric capacity (middle) and volume change (bottom). The plots on the left are for the complete 640 distinct compounds in the screening, and the plots on the right are for specific compounds of interest.
2.4 Discussion

Regarding the gravimetric CO₂ capacity, CaO has one of the highest capacities amongst the compounds screened, with the other binary oxides also having very high gravimetric capacities due to their small MM. However, there are some ternary compounds that show comparable capacities, such as the compounds with very high alkali metal content Li₆MnO₄, Li₆CoO₄ and Mg₆MnO₈. While it is important to have a high theoretical CO₂ capacity, in practice a low $E_p$ is more desirable in terms of reducing costs, so a lower capacity can be offset with a lower $E_p$ to still produce a material that is promising for CCS applications.

If we take volume change to be a approximate guide to a compound’s resistance to capacity fading upon cycling, the spread of results confirms that there is a wide composition space in which to find more optimal materials with improved properties compared to CaO. In particular, CaO had one of the highest volume increases upon carbonation (124 %) out of all the materials screened, with only the binary compounds NiO, MgO and Li₂O having a larger volume expansion. Ideally the volume change should be as close as possible to 0, and there are many compounds in the screening that show volume changes less than 20 %, a significant improvement over the 124 % volume increase seen in CaO.

Figure 2.5 further filters the screened compounds to include only those where $A =$ Na, Li, Mg or Ca, to make a more direct comparision of our screening results with the kinds of materials that have been suggested previously in the literature (which are composed of these alkali metals). It is clear from Figure 2.5 that the carbonation equilibrium is greatly influenced by the choice of alkali metal atom, with Na-based compounds having the most negative $\Delta H_{\text{carbonation}}$ and hence the largest $E_p$, while Ca and Mg based compounds have a much lower $E_p$ generally. In particular, there seem to be many Mg-based materials with relatively low $E_p$ that could have a desirable carbonation equilibrium.

The range of $\Delta H_{\text{carbonation}}$ and $E_p$ within members of the same alkali metal group seems directly related to the relative stability of the corresponding binary alkali metal oxides, which are the reactive species in all of the carbonation reactions (regardless of what other metal atoms might be present), and in the majority of cases the addition of a ternary element increases $\Delta H_{\text{carbonation}}$ and decreases $E_p$. This would suggest that there is a good thermodynamic reason for pursuing ternary alkali compounds as novel CCS materials and moving beyond using simple binary oxides.
In terms of gravimetric CO$_2$ capacity, obviously the screening results reflect that the binary oxides have the highest capacities, which is why they are so attractive for further development. However, there are a suite of ternary compounds with significant capacity, especially amongst Li-based compounds. Some of these have already been explored, such as Li$_2$ZrO$_3$ [73], Li$_5$AlO$_4$ [118] and Li$_4$SiO$_4$ [97], but this screening has found many others, such as Li$_6$CoO$_4$, Li$_6$MnO$_4$ and Li$_5$FeO$_4$, that could be the subject of further research. The screening also found two ternary Mg-based compounds with very high gravimetric capacity: Mg$_2$SiO$_4$ or olivine, which is already been researched extensively as a geological CCS material [197] and Mg$_6$MnO$_8$, which is essentially a form of doped MgO, which has a simple cubic structure with ordered Mn atoms and O vacancies [198], but has never been studied before for CCS applications.

Volume change is perhaps the least important parameter to optimise for, as it is still not fully understood how large a role it plays in determining the cycling stability of a material. However, the best materials should have as little a change in volume as possible over the course of the carbonation reaction in order to minimise sintering and pore clogging, and these screening results show there are many materials with small (<20 %) volume changes across all of the different alkali metal compounds. Furthermore, it shows that the binary oxides are again the worst materials in terms of volume changes, further underscoring the necessity to pursue development of ternary alkali oxides as materials of interest.
2.4. Discussion

Figure 2.5: Screened materials containing Na, Li, Mg or Ca as their alkali atom. Each data point represents the carbonation reaction for each distinct compound with the most negative $\Delta H$. The calculated energy penalty, $E_p$, for each reaction is plotted against $\Delta H_{\text{carbonation}}$ (top), CO$_2$ gravimetric capacity (middle) and volume change (bottom). The respective binary oxides are circled for clarity.
2.5 Conclusions

Through the use of open phase diagrams and the Materials Project, the largest set ever of oxide compounds were screened for their theoretical thermodynamics of carbonation, as well as their theoretical gravimetric CO$_2$ capacity and volume change upon carbonation. The results were validated both against standard experimental values for known carbonation reactions, and against similar previous DFT studies, and good agreement was found with both. A single parameter, energy penalty, was used to assess the relative efficiency of using a compound in a model CCS process, and to provide a way to rank materials in terms of their suitability for further study.

Looking at the results from the screening gives new insights to implement in rational design approaches towards finding optimal CCS materials. Firstly, the use of ternary alkali metal oxide compounds is found to be advantageous both in being able to achieve lower energy penalties due to less negative $\Delta H_{\text{carbonation}}$, but also in avoiding very large volume changes that occur when carbonating the binary oxide compounds, which could lead to cycling instability through sintering and pore clogging.

The earth alkali metals Mg and Ca are found to be generally more favourable than compounds containing Li and Na mainly due to their lower energy penalty, and there are many compounds found in the screening that are suitable for further study. Two in particular that show very high theoretical gravimetric CO$_2$ capacity are Mg$_2$SiO$_4$ and Mg$_6$MnO$_8$, and these compounds among others will be the subject of more in-depth experimental tests.

These results show that large scale screening processes can employ a reasonably efficient level of DFT theory to achieve accurate results that give real information into overall trends that are important to designing novel functional materials.
Chapter 3

Thermogravimetric and structural characterisation of candidate CCS materials

3.1 Introduction

In concert with the screening methodology described in the previous chapter, validation of the results of that screening was carried out through measuring $\Delta H_{\text{carbonation}}$ and comparing it with the theoretical value obtained from the Materials Project. The experiments also allowed insight into the kinetics of carbonation and to the cycling stability of the candidate compounds.

The preliminary candidates were chosen for a number of different reasons. Firstly materials for which there had been no previous CO$_2$ capture properties reported were studied, to validate the claim that the screening could suggest truly novel materials for CCS applications. Ternary oxide materials were also chosen, given that the screening results suggested they gave lower energy penalties and better cycling capacities than simple binary oxides.

In this section experimental studies are presented on four materials: Ca$_3$V$_2$O$_8$, Na$_3$SbO$_4$, Li$_5$FeO$_4$ and Li$_6$CoO$_4$. Ca$_3$V$_2$O$_8$ and Na$_3$SbO$_4$ were chosen because they had similar, but lower $E_p$ values than that of CaO from the screening, and as such they are useful comparisons to this benchmark material, especially in comparing their cycling stability. Li$_5$FeO$_4$ and Li$_6$CoO$_4$ were chosen for their very high theoretical gravimetric CO$_2$ capac-
Chapter 3. Thermogravimetric and structural characterisation of candidate CCS materials

ities, and hopefully to be able to compare to previous studies on similar Li ternary oxides [73, 75, 97, 109, 118]. It should be noted however that most of these materials are unlikely to find use in CCS applications due to the cost of Sb and the toxicity of V, although Li₅FeO₄ is made from more abundant and safe elements and is thus particularly appealing. The relevant parameters obtained from the Materials Project screening for these materials are presented in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_p ) kJ (mol CO₂)(^{-1})</th>
<th>( \Delta H_{\text{carbonation}} ) kJ mol(^{-1})</th>
<th>CO₂ capacity ( g_{\text{CO₂}}/g_{\text{sorbent}} )</th>
<th>Volume change %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>41.9</td>
<td>-179.5</td>
<td>0.78</td>
<td>124.4</td>
</tr>
<tr>
<td>Ca₃V₂O₈</td>
<td>41.5</td>
<td>-172.2</td>
<td>0.13</td>
<td>24.0</td>
</tr>
<tr>
<td>Na₃SbO₄</td>
<td>40.7</td>
<td>-167.6</td>
<td>0.17</td>
<td>37.4</td>
</tr>
<tr>
<td>Li₅FeO₄</td>
<td>44.7</td>
<td>-208.7</td>
<td>0.57</td>
<td>59.9</td>
</tr>
<tr>
<td>Li₆CoO₄</td>
<td>44.6</td>
<td>-217.4</td>
<td>0.80</td>
<td>104.9</td>
</tr>
</tbody>
</table>

Table 3.1: Theoretical results from the Materials Project screening for CaO and the preliminary candidates in the experimental analysis. The respective carbonation reactions relating to the tabulated values are CaO + CO₂ → CaCO₃; Ca₃V₂O₈ + CO₂ → CaCO₃ + Ca₂V₂O₇; Na₃SbO₄ + CO₂ → Na₂CO₃ + NaSbO₃; 0.5Li₅FeO₄ + CO₂ → Li₂CO₃ + 0.5LiFeO₂; and 0.33Li₆CoO₄ + CO₂ → Li₂CO₃ + 0.33CoO.

These materials are presented as preliminary candidates to arise from the screening, but are not the only materials that were considered in experimental studies. Materials with much lower theoretical \( E_p \) and high gravimetric CO₂ capacity, such as Mg₆MnO₈ and Mg₂SiO₄, are the subject of ongoing experimental studies. These preliminary experiments have the primary aim of providing an experimental validation of the screening process, and providing further insight into the parameters which contribute to the kinetics and stability of the CO₂ looping process.

3.2 Experimental and theoretical methods

Pure polycrystalline samples of the candidate materials were prepared using a solid-state method. Briefly, Ca₃V₂O₈ was formed by solid-state reaction from CaCO₃ and V₂O₅, Na₃SbO₄ from Na₂CO₃ and Sb₂O₃, Li₅FeO₄ from Li₂O and Fe₂O₃ and Li₆CoO₄ from Li₂O and CoO. Prior to weighing, CaCO₃ was dried at 1000 K overnight to ensure there was as little moisture present in the compound as possible. The stoichiometric mixtures were
ground using an agate mortar and pestle, and the Ca$_3$V$_2$O$_8$ starting materials were calcined in air at 1173 K for 12 h, and then reground and calcined at 1273 K for 12 h twice, while the Na$_3$SbO$_4$ precursors were initially calcined (again in air) at 923 K for 12 h, before being calcined at 1173 K for 12 h, and then for a further 12 h at 1223 K. The Li$_5$FeO$_4$ and Li$_6$CoO$_4$ precursors were calcined under flowing argon at 973 K for 12 h. Phase purity of the samples was monitored by room-temperature x-ray powder diffraction (XRD), using a Panalytical Empyrean diffractometer utilising Cu K$_\alpha$ radiation. The Li$_5$FeO$_4$ and Li$_6$CoO$_4$ samples were seen to visibly react over the course of a day in air, as denoted by a distinct change in colour. This is most likely due to reaction with CO$_2$ in the air.

The carbonation and calcination reactions of the candidate materials were investigated using a thermogravimetric analyser (TGA/DSC 1, Mettler Toledo) operating at atmospheric pressure. In each experiment, a sample of $\sim$20 mg of powder was placed in a 70 $\mu$L Al$_2$O$_3$ or Pt crucible, supported on a cantilever-type balance. Gases were fed to the reaction chamber through three gas ports, viz. reactive gas, purge gas and protective gas. The reaction chamber is electrically heated by a tubular furnace surrounding the balance. Both the protective gas and the purge gas were N$_2$, and were fed to the TGA reaction chamber. The reactive gas was a stream of pure CO$_2$, which was fed by a capillary so that the gas could flow over the top of the crucible. The partial pressure of CO$_2$ at the surface of the solid sample was adjusted by varying the flow-rates of the protective and reactive gases respectively.

For the DSC experiments, the samples were first heated to 873 K under a flow of N$_2$, before being exposed to a pure gas stream of CO$_2$ for 10 minutes while being held at a constant temperature. Integration of the heat flow curves over this time interval with a baseline set to the heat flow prior to carbonation gave the accumulated heat in joules of the sample during carbonation.

The actual CO$_2$ concentration (partial-pressure) at the gas-solid interface was calibrated against the well-understood thermodynamic CaO/CaCO$_3$ carbonation equilibrium. For example, when a carbonated sample of pure CaO (98 wt %) was gradually heated in a specific mixture of CO$_2$ and N$_2$, the temperature at the onset of decomposition of CaCO$_3$ was recorded and the corresponding CO$_2$ partial pressure in contact with the solid phase was determined from the phase diagram of the CaO-CaCO$_3$-CO$_2$ system. In the TPD experiments, the samples were heated from 323 K to either 973 K (Li$_6$CoO$_4$ and Li$_5$FeO$_4$) or 1223 K (Ca$_3$V$_2$O$_8$ and Na$_3$SbO$_4$) under a specific partial pressure of CO$_2$, i.e. a specific N$_2$/CO$_2$ ratio. The equilibrium tem-
Chapter 3. Thermogravimetric and structural characterisation of candidate CCS materials

Temperature corresponding to a given partial pressure of CO$_2$ was determined by the temperature at which the material started to decompose (after possibly carbonating at a lower temperature), determined by the zero point of the first derivative of the mass curve.

The surface morphologies of the solid samples at various stages of the cycling experiments (viz. fresh, fully carbonated and fully regenerated) were examined ex situ by scanning electron microscopy (SEM). The samples were inspected in a field-emission gun SEM (Hitachi S-5500) with a secondary electron detector.

The porosity and specific surface area (SSA) of the candidate materials were determined using volumetric sorption measurements (TriStar3000 analyzer, Micromeritics) in N$_2$ at 77 K. The SSA was calculated using Brunauer-Emmett-Teller (BET) analysis using N$_2$ sorption [199]. Pore size distribution and pore volumes were determined by applying the Barrett-Joyner-Halenda (BJH) model using a 55 point adsorption-desorption isotherm.

Ab initio random structure searching (AIRSS) was carried out to generate possible unit cells for materials of unknown structure [152, 153]. DFT geometry optimizations of the atomic positions and cell vectors were performed on the cells generated, using a basis set containing plane waves up to 340 eV, a Brillouin zone sampling finer than $2\pi \times 0.07 \text{ Å}^{-1}$ and the PBE exchange correlation functional. Whilst these were not expected to give highly accurate energies, they are suitable for initial structure determination. The lowest energy structures were then relaxed at a higher level of accuracy using CASTEP on-the-fly pseudopotentials and a basis set up to 500 eV.

3.3 Results and discussion

3.3.1 Structural characterisation of Na$_3$SbO$_4$, Li$_5$FeO$_4$ and Li$_6$CoO$_4$

XRD patterns acquired of the as-synthesised Na$_3$SbO$_4$, Li$_5$FeO$_4$ and Li$_6$CoO$_4$ samples confirmed that all of these materials were phase pure (Figure 3.1). Further XRD patterns were then taken of these samples after being carbonated under $p_{CO_2} = 0.37$ bar at 973 K (Li$_5$FeO$_4$ and Li$_6$CoO$_4$) or 1223 K (Na$_3$SbO$_4$) in a thermogravimetric analyser (TGA) to identify the phases that formed upon carbonation, and to see if these match with the phases predicted by the screening. Carbonation temperatures were identified by an
3.3. Results and discussion

Initial TGA trace to pinpoint the range over which the samples carbonated and regenerated. Phases present in the pre- and post-carbonation samples could be indexed and their structures and cell parameters were refined using Rietveld refinement, as shown in Figure 3.1.

![Indexed XRD diffractograms](image)

Figure 3.1: Indexed XRD diffractograms (λ = 1.54056 Å) and refinements of the as-synthesized Na$_3$SbO$_4$, Li$_5$FeO$_4$ and Li$_6$CoO$_4$ samples, and after carbonation at 973 K (Li$_5$FeO$_4$ and Li$_6$CoO$_4$) or 1223 K (Na$_3$SbO$_4$) under $p_{CO_2} = 0.37$ bar. The experimental data points are shown in red, with the pattern obtained from the Rietveld refinements overlaid in black, and the difference curve below.

In the case of Na$_3$SbO$_4$, Li$_5$FeO$_4$ and Li$_6$CoO$_4$, the reaction products were confirmed to be as predicted from the prior screening, that being:
Chapter 3. Thermogravimetric and structural characterisation of candidate CCS materials

\[
\text{Na}_3\text{SbO}_4 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{NaSbO}_3 \quad (3.1)
\]

\[
0.5\text{Li}_5\text{FeO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + 0.5\text{LiFeO}_2 \quad (3.2)
\]

\[
0.33\text{Li}_6\text{CoO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + 0.33\text{CoO} \quad (3.3)
\]

For \( \text{Li}_5\text{FeO}_4 \) a significant amount of the original material remained after carbonation (19 % by weight), indicating that the reaction had not gone to completion.

### 3.3.2 Structural Characterisation of \( \text{Ca}_3\text{V}_2\text{O}_8 \)

Analysis of the \( \text{Ca}_3\text{V}_2\text{O}_8 \) sample showed that a majority of the sample adopted a different phase from the expected stoichiometry, and subsequent indexing of the powder XRD data suggested that the formed phase was the hexagonal phase \( \text{Ca}_{10}\text{V}_6\text{O}_{25} \). This phase exists in the ICDD database (JCPDS card, no. 52-0649), but only the unit cell and symmetry are reported. Despite multiple subsequent attempts to synthesise a pure sample of \( \text{Ca}_3\text{V}_2\text{O}_8 \), the majority phase that formed was always \( \text{Ca}_{10}\text{V}_6\text{O}_{25} \). In order to be able to compare the experimental results with the output of the screening process, it was therefore required to obtain the ground state energy of the \( \text{Ca}_{10}\text{V}_6\text{O}_{25} \) phase using the DFT methodology within the Materials Project. To determine a suitable structural model for \( \text{Ca}_{10}\text{V}_6\text{O}_{25} \) the \textit{ab initio} random structure searching (AIRSS) method was used to test thousands of initial atomic configurations, which was chosen due to its previous success in predicting new phases formed in other solid state systems such as batteries [200, 201].

Atoms corresponding to one formula unit were randomly placed in a generated unit cell with geometry matching that from the ICDD database \((a, b = 9.7574 \text{ Å}, c = 7.0045 \text{ Å}, \alpha = \beta = 90^\circ \text{ and } \gamma = 120^\circ)\). 6 vanadium, 25 oxygen and 10 calcium atoms were randomly placed within the cell, subject to constraints. Firstly, the screened cells were restricted to those that obeyed 6 (or more) symmetry operations to match the reported high symmetry of the phase \((P6_3/m)\). Secondly, the minimum distances between atoms were restricted to favour the formation of V-O and Ca-O bonds and disfavour structures with small V-V, Ca-Ca and O-O bond distances. The resulting unit cells were optimised using DFT as described in Section 3.2.

All the lowest energy structures obtained were in the \( P3 \) space group, a subgroup of the reported \( P6_3/m \) space group. They consisted of isolated \( \text{VO}_4 \) tetrahedra with an additional lone oxygen atom. The choice of this
3.3. Results and discussion

V:O ratio is justified by the white appearance of the compound indicative of a fully oxidised sample with all vanadium in the 5+ oxidation state.

The lowest energy structure is shown in Figure 3.2. The unit cell parameters are $a = 9.675$ Å and $c = 6.836$ Å, which agrees well with the previously reported lattice, and the lone oxygen is located along a channel in the structure parallel to the $c$ axis.

![Figure 3.2: Lowest energy structure obtained using AIRSS for Ca$_{10}$V$_6$O$_{25}$. Vanadium atoms and tetrahedra are shown in light red, calcium atoms in blue and oxygen atoms in red.](image)

This structure was used as a starting point for Rietveld refinements against XRD data. Initial refinements with a single oxygen located midway along the $c$ axis displayed incorrect ratios of intensities for certain reflections in the data. To try and correct this, various different configurations for the lone oxygen atomic position were tried and evaluated through comparison of the experimental and simulated diffraction patterns. The best fit to the data was obtained by splitting the oxygen site into two sites with half occupancies located at $(0, 0, 0.25)$ and $(0, 0, 0.75)$ respectively. The resulting refinement using this model is shown in Figure 3.3, with the refined structure of Ca$_{10}$V$_6$O$_{25}$ shown in Figure 3.4.

The refinements show that the nominally Ca$_3$V$_2$O$_8$ sample is in fact comprised mainly of the Ca$_{10}$V$_6$O$_{25}$ phase with some amount of the Ca$_3$V$_2$O$_8$ phase as well (the weight fractions from the refinement were 91 % and 9 % for the two phases respectively), along with some trace impurities that we were unable to characterise. More importantly, the good fit to the experimental data indicates that our structural model for the Ca$_{10}$V$_6$O$_{25}$ phase is a reasonable one.
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Figure 3.3: Indexed XRD diffractogram ($\lambda = 1.54056 \text{ Å}$) of the sample of nominal stoichiometry $\text{Ca}_3\text{V}_2\text{O}_8$. The experimental data points are shown in red, with the model obtained from the Rietveld refinements overlaid in black, and the difference curve below. From the indexing it can be seen that both $\text{Ca}_{10}\text{V}_6\text{O}_{25}$ and $\text{Ca}_3\text{V}_2\text{O}_8$ phases are present in the sample, with weight fractions of 91% for $\text{Ca}_{10}\text{V}_6\text{O}_{25}$ and 9% for $\text{Ca}_3\text{V}_2\text{O}_8$. There also are some peaks that were unable to be indexed.

Figure 3.4: Rietveld-refined structure for $\text{Ca}_{10}\text{V}_6\text{O}_{25}$. Vanadium atoms and tetrahedra are shown in orange, calcium atoms in blue and oxygen atoms in red. Additionally, the brown atoms represent oxygen atom sites with half occupancies.
Structures with the lone oxygen positioned at (0, 0, 0.25), (0, 0, 0.5) and (0, 0, 0.75) respectively were submitted to the Materials Project workflow to determine their optimised geometries and ground state energies, with the results of these calculations shown in Table 3.2. Encouragingly, the two configurations with the oxygen atom at the split positions (0, 0, 0.25) or (0, 0, 0.75) in our original model have a lower energy than the (0, 0, 0.5) configuration, further supporting our theory that oxygen is located at either of these sites in the structure.

Phase stability within the Materials Project is measured by comparing the energy of a new phase to the convex hull of the phase diagram within which it is located. The convex hull of a set of points (of energies and associated fractional compositions in this case) is the smallest convex set containing all the points. If a new phase lies below the hull, it is lower in energy than other phases in the phase diagram, and is considered stable. On the other hand, if a phase lies above the hull, it is considered unstable, and will spontaneously decompose into neighbouring phases that lie on the hull. In the case of Ca$_{10}$V$_6$O$_{25}$, an energy of -0.032 eV/atom below the hull is considered stable with comparison to the other phases that form in the Ca-V-O phase diagram within the Materials Project, which in this case is defined by the bounding phases Ca$_3$V$_2$O$_8$ and CaO.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Total energy (eV)</th>
<th>Energy above hull (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 0, 0.25)</td>
<td>-322.275</td>
<td>-0.032</td>
</tr>
<tr>
<td>(0, 0, 0.5)</td>
<td>-321.153</td>
<td>0.001</td>
</tr>
<tr>
<td>(0, 0, 0.75)</td>
<td>-322.275</td>
<td>-0.032</td>
</tr>
</tbody>
</table>

Table 3.2: Total energies determined by DFT+U within the Materials Project workflow for the different positions of the lone oxygen atom in the Ca$_{10}$V$_6$O$_{25}$ structure (described by fractional coordinates in the x, y and z directions). A negative energy above hull corresponds to a stable phase with respect to the other phases present in the Ca-V-O phase diagram, whereas a postive energy denotes an unstable phase.

Due to the mixed phases present in the nominally Ca$_3$V$_2$O$_8$ phase, from hence forth we will refer to this sample as Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$. 
3.3.3 Surface area analysis

The results from the BET SSA analysis are shown in Table 3.3. Unfortunately due to persistent problems with the instrument, it was only able to obtain results for a subset of materials including those synthesised specifically as a result of the screening (Na$_3$SbO$_4$ and Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$), and some materials previously reported as CO$_2$ absorption materials (Li$_4$SiO$_4$ and Li$_5$AlO$_4$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>BET SSA (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_3$V$_2$O$<em>8$/Ca$</em>{10}$V$<em>6$O$</em>{25}$</td>
<td>1.1230</td>
<td>0.005866</td>
</tr>
<tr>
<td>Na$_3$SbO$_4$</td>
<td>0.3787</td>
<td>0.001239</td>
</tr>
<tr>
<td>Li$_4$SiO$_4$</td>
<td>0.6778</td>
<td>0.004228</td>
</tr>
<tr>
<td>Li$_5$AlO$_4$</td>
<td>2.7585</td>
<td>0.015195</td>
</tr>
</tbody>
</table>

Table 3.3: Results of the SSA and total pore volume measurements for a number of different CO$_2$ absorption materials. The total pore volume was determined from N$_2$ absorption.

Compared to Li$_5$AlO$_4$, which has reported to have very fast absorption kinetics, as well as a large CO$_2$ capacity [117, 118], the other materials measured have a lower surface area. This might influence the kinetics of absorption for the screened materials, outside of any thermodynamic factors that were used in the screening. However, even Li$_4$SiO$_4$ is known to have a reasonable carbonation rate [90], so it is likely that Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$ should show reasonable absorption kinetics as well.

3.3.4 Carbonation experiments

TPD experiments were performed on the candidate materials to determine their carbonation enthalpy, with a typical TGA trace for Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ shown in Figure 3.5. The mass increase corresponds to a gravimetric uptake of $\sim$0.12 g$_{CO_2}$/g$_{sorbet}$, compared to the theoretical maximum gravimetric capacity of 0.13 g$_{CO_2}$/g$_{sorbet}$ for Ca$_3$V$_2$O$_8$ and 0.04 g$_{CO_2}$/g$_{sorbet}$ for Ca$_{10}$V$_6$O$_{25}$.

While the products created as a result of the TPD experiments on Na$_3$SbO$_4$, Li$_3$FeO$_4$ and Li$_6$CoO$_4$ were able to be characterised using XRD (Figure 3.1), it was difficult to accurately identify the products formed after carbonation of the Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ sample. Indexing of the patterns showed evidence for the formation of a range of phases including Ca$_{10}$V$_6$O$_{25}$,
3.3. Results and discussion

Figure 3.5: Temperature programmed decomposition (TPD) experiment for the nominally Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ sample at $p_{CO_2} = 0.37$ bar. The mass gains correspond to the carbonation reactions Ca$_{10}$V$_6$O$_{25}$ + CO$_2$ $\rightarrow$ CaCO$_3$ + 3 Ca$_3$V$_2$O$_8$ and Ca$_3$V$_2$O$_8$ + CO$_2$ $\rightarrow$ CaCO$_3$ + Ca$_2$V$_2$O$_7$, while the subsequent mass loss arises from the decomposition of CaCO$_3$ to form Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and CaO, as shown in Figure 3.6. Calculation of the zero points of the first derivative of the mass curve gives the temperature of the onset of carbonation and decomposition respectively.

Ca$_3$V$_2$O$_8$, Ca$_2$V$_2$O$_7$, CaCO$_3$, and CaO. A Le Bail fit to the experimental data was attempted, as shown in Figure 3.6, and while the fit does not completely match the observed data, it does confirm the presence of several new phases that form as a result of the carbonation reaction. For the two starting phases the products formed seem consistent with the carbonation reactions:

\[
\begin{align*}
\text{Ca}_{10}\text{V}_6\text{O}_{25} + \text{CO}_2 & \rightarrow \text{CaCO}_3 + 3 \text{Ca}_3\text{V}_2\text{O}_8 & (3.4) \\
\text{Ca}_3\text{V}_2\text{O}_8 + \text{CO}_2 & \rightarrow \text{CaCO}_3 + \text{Ca}_2\text{V}_2\text{O}_7 & (3.5)
\end{align*}
\]

It should be noted that the sample actually carbonates twice in this experiment, once upon heating and once upon cooling (Figure 3.5). At the highest temperature (1223 K), the sample decarbonates, and should reform the original material (in this case a mixture of Ca$_3$V$_2$O$_8$ and Ca$_{10}$V$_6$O$_{25}$) before carbonating again on cooling. The presence of CaO in the final sample indicates that the sample does not completely reform above 1223 K, and that some remnant CaO is formed after CaCO$_3$ decomposes. Some of this CaO should carbonate again on cooling, but it is probable that not all of it does, leading to CaO still being present in the final sample.
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Figure 3.6: Selected part of the indexed XRD diffractogram ($\lambda = 1.54056 \text{ Å}$) of the nominally Ca$_3$V$_2$O$_8$ sample after carbonation up to 1223 K and under $p_{\text{CO}_2} = 0.37$ bar, with a fit obtained from the Le Bail method. The experimental data points are shown in red, with the model obtained from the fitting overlaid in black, and the difference curve below. The indexed phases include Ca$_{10}$V$_6$O$_{25}$, Ca$_3$V$_2$O$_8$, Ca$_2$V$_2$O$_7$, CaCO$_3$ and CaO.

Future experiments are planned to monitor the structural evolution of the phases in situ during carbonation and calcination, to get more accurate information as to the phases forming during the reactions. In particular, high resolution S-XRD data is necessary to accurately quantify phases with lower symmetry such as Ca$_2$V$_2$O$_7$ (which has numerous overlapping reflections) and other phases that are present in very small amounts.

To order to determine $\Delta H_{\text{carbonation}}$ and $\Delta S_{\text{carbonation}}$, the equilibrium constants of the respective carbonation reactions as a function of temperature were measured experimentally by TPD in a TGA under various CO$_2$ partial pressures. As described in Section 1.5, the equilibrium curve for a carbonation reaction can be fit to an exponential curve of the form:

$$K_p = p_{\text{CO}_2} = A \exp\left(-\frac{B}{T}\right)$$  \hspace{1cm} (3.6)
3.3. Results and discussion

where $p_{CO_2}$ is the CO$_2$ partial pressure in atm, $T$ is calcination temperature in K, and $A$ and $B$ are constants specific to each reaction, which can be obtained by plotting a logarithmic curve of $1/T$ measured at different $p_{CO_2}$.

From these it is possible to calculate $\Delta H_{\text{carbonation}}$ and $\Delta S_{\text{carbonation}}$ from these fitting constants:

$$K_p = \exp(\Delta S_r/R) \cdot \exp(-\Delta H_r/RT)$$  \hspace{1cm} (3.7)

$$A = \exp(\Delta S_r/R)$$  \hspace{1cm} (3.8)

$$B = \Delta H_r/R$$  \hspace{1cm} (3.9)

The fits for the constants $A$ and $B$ for Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$ are shown in Figure 3.7, and then compared against the corresponding values obtained from the Materials Project screening in Table 3.4 (values are given for both the Ca$_{10}$V$_6$O$_{25}$ and Ca$_3$V$_2$O$_8$ reactions). For Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$, the decomposition onset temperature at a static ramp rate was extrapolated from onset temperatures measured with TPD experiments at heating rates of 2 K min$^{-1}$, 5 K min$^{-1}$ and 10 K min$^{-1}$, to correct for any errors due to variable heating rates. The Na$_3$SbO$_4$ data presented here was collected at a 10 K min$^{-1}$ ramp rate. Subsequent experiments with different ramp rates gave spurious results, which were attributed to degradation of the sample over multiple cycles while changing ramp rates. As such, this effect was minimised by measuring at a single ramp rate for each sample of Na$_3$SbO$_4$.

![Figure 3.7: Plot of ln($K_p$) against the inverse decomposition onset temperatures derived from TPD experiments for Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$. The linear fit to determine the constants $A$ and $B$ relating to $K_p$ is also shown on each plot.](image-url)
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<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_r$ kJ mol$^{-1}$</th>
<th>$\Delta S_r$ J mol$^{-1}$ K$^{-1}$</th>
<th>$\Delta H_r$ kJ mol$^{-1}$</th>
<th>$\Delta S_r$ J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>-170 ± 5</td>
<td>152 ± 5</td>
<td>-179.5</td>
<td>255</td>
</tr>
<tr>
<td>Ca$_{10}$V$<em>6$O$</em>{25}$</td>
<td>-177 ± 10*</td>
<td>153 ± 10</td>
<td>-8.3</td>
<td></td>
</tr>
<tr>
<td>Ca$_3$V$_2$O$_8$</td>
<td>-177 ± 10*</td>
<td>153 ± 10</td>
<td>-172.2</td>
<td>255</td>
</tr>
<tr>
<td>Na$_3$SbO$_4$</td>
<td>-175 ± 20</td>
<td>150 ± 20</td>
<td>-167.6</td>
<td>293</td>
</tr>
</tbody>
</table>

Table 3.4: Experimentally derived values and predicted values from the Materials Project screening of $\Delta H_{\text{carbonation}}$ and $\Delta S_{\text{carbonation}}$ for CaO, Ca$_{10}$V$_6$O$_{25}$, Ca$_3$V$_2$O$_8$ and Na$_3$SbO$_4$. The screening values are based on the following reactions: CaO + CO$_2$ $\rightarrow$ CaCO$_3$, Ca$_{10}$V$_6$O$_{25}$ + CO$_2$ $\rightarrow$ CaCO$_3$ + 3Ca$_3$V$_2$O$_8$, Ca$_3$V$_2$O$_8$ + CO$_2$ $\rightarrow$ CaCO$_3$ + Ca$_2$V$_2$O$_7$ and Na$_3$SbO$_4$ + CO$_2$ $\rightarrow$ Na$_2$CO$_3$ + NaSbO$_3$. *The single experimental value for both Ca$_3$V$_2$O$_8$ and Ca$_{10}$V$_6$O$_{25}$ comes from the results obtained from the Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ TPD experiment.

In the case of CaO and Na$_3$SbO$_4$, it is seen that there is very good agreement between the theoretical and experimental values for $\Delta H_{\text{carbonation}}$. In the case of CaO, this is to be expected because of the CO$_2$ energy correction applied which was derived from experimental values for binary oxide carbonation reactions. But for Na$_3$SbO$_4$, these results validate the accuracy of the screening process and its ability to correctly predict the carbonation equilibrium for as yet unstudied materials.

Unfortunately, the calculated energies of the optimised structures for Ca$_{10}$V$_6$O$_{25}$ underestimate $\Delta H_{\text{carbonation}}$ drastically, especially when compared to how well the TPD data fits to the predicted carbonation reaction of Ca$_3$V$_2$O$_8$. On one hand, there may be a large error with the proposed Ca$_{10}$V$_6$O$_{25}$ structure, but this goes against the relatively good fit to experimental XRD data. Another possibility is that under the conditions in the TGA, Ca$_{10}$V$_6$O$_{25}$ first decomposes to Ca$_3$V$_2$O$_8$ and CaO before Ca$_3$V$_2$O$_8$ reacts with CO$_2$ to give the measured carbonation equilibria. This would agree well with the appearance of CaO and Ca$_2$V$_2$O$_7$ in the XRD of the carbonated sample, and would explain why the observed equilibria matches the predicted carbonation thermodynamics of Ca$_3$V$_2$O$_8$ from the Materials Project. While we hope to undertake more detailed structural studies of this material in the future, for this initial screening phase it seems that the predicted value for Ca$_3$V$_2$O$_8$ best matches our experimental data.

There is a large error between the experimental and theoretical values of
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\(\Delta S_{\text{carbonation}}\) for \(\text{Ca}_3\text{V}_2\text{O}_8/\text{Ca}_{10}\text{V}_6\text{O}_{25}\) and \(\text{Na}_3\text{SbO}_4\), which is to be expected considering the simplifying assumptions that were made in calculating the entropy in the screening process. This would indicate that \(\Delta S_{\text{solid}}\) cannot be ignored in the calculations, and that methods to reintroduce this parameter into the calculations could improve the agreement with experiment. The challenge for further work is to include this term without having to do more expensive phonon calculations to determine \(\Delta S_{\text{solid}}\) more accurately.

![Figure 3.8: TGA traces for Li\(_5\)FeO\(_4\) and Li\(_6\)CoO\(_4\) under \(p\text{CO}_2 \approx 0.1\) bar.](image)

Attempts to perform a similar TPD analysis for Li\(_5\)FeO\(_4\) and Li\(_6\)CoO\(_4\) failed due to the fact that the phases formed in the carbonation reactions do not decompose before the melting point of Li\(_2\)CO\(_3\) at \(\sim 993\) K, even though the temperature of decomposition was predicted to be \(\sim 805\) K at \(p\text{CO}_2 = 1\) from the screening. TPD traces of Li\(_5\)FeO\(_4\) and Li\(_6\)CoO\(_4\) are shown in Figure 3.8, showing the mass gains as the materials react with CO\(_2\) to form Li\(_2\)CO\(_3\) and LiFeO\(_2\) and CoO respectively. On further heating however there is no mass loss, and therefore the same method of determining the carbonation equilibrium constant cannot be used. It is also seen in these TGA traces that the experimental CO\(_2\) capacity is much less than the theoretical value as obtained from the stoichiometry of the carbonation reaction. One reason for this may be that a large percentage of the sample had already reacted with CO\(_2\) in the air prior to the experiment, as it was not possible to keep the samples in vacuum when transferring in and out of the TGA itself. Furthermore, longer isothermal experiments should be performed in future studies to better elucidate the combined effect of thermodynamics and kinetics on the rate of these reactions.
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3.3.5 Determination of carbonation enthalpy by DSC

For materials that melt before decomposing, such as Li$_5$FeO$_4$ and Li$_6$CoO$_4$, DSC experiments provide an alternative way to determine $\Delta H_{\text{carbonation}}$ without melting the material. Integrated heat curves for the candidate materials and CaO derived from DSC are shown in Figure 3.9. By taking a TGA trace simultaneously, the mass change of the sample can be measured over the same time interval, and calculating the CO$_2$ absorbed in moles allows $\Delta H_{\text{carbonation}}$ in kJ mol$^{-1}$ to be derived (as described in Section 1.5). These results are shown in Table 3.5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>DSC  $\Delta H_r$</th>
<th>TPD  $\Delta H_r$</th>
<th>Screening $\Delta H_r$</th>
<th>Literature $\Delta H_r$</th>
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</thead>
<tbody>
<tr>
<td>CaO</td>
<td>-157(5)</td>
<td>-170 ± 5</td>
<td>-179.5</td>
<td>-169.4 [202]</td>
</tr>
<tr>
<td>Ca$_{10}$V$<em>6$O$</em>{25}$</td>
<td>-183(5)*</td>
<td>-177 ± 10*</td>
<td>-8.3</td>
<td></td>
</tr>
<tr>
<td>Ca$_3$V$_2$O$_8$</td>
<td>-183(5)*</td>
<td>-177 ± 10*</td>
<td>-172.2</td>
<td></td>
</tr>
<tr>
<td>Na$_3$SbO$_4$</td>
<td>-129(5)</td>
<td>-175 ± 20</td>
<td>-167.6</td>
<td></td>
</tr>
<tr>
<td>Li$_5$FeO$_4$</td>
<td>-197(5)</td>
<td>-208.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_6$CoO$_4$</td>
<td>-158(5)</td>
<td>-217.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5: Values of $\Delta H_{\text{carbonation}}$ obtained from DSC and TPD experiments compared with literature and the predicted values from the Materials Project screening. All values are in kJ mol$^{-1}$. *The single experimental value for both Ca$_3$V$_2$O$_8$ and Ca$_{10}$V$_6$O$_{25}$ comes from the results obtained from the Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ sample.

Figure 3.9: DSC obtained heat flow and cumulative heat traces for all samples, studied under $p$(CO$_2$) = 1 bar.
Comparing the $\Delta H_{\text{carbonation}}$ for CaO obtained from DSC, -157 kJ mol$^{-1}$, with the known experimental value of -169 kJ mol$^{-1}$ [202], it is seen that while the DSC method tends to underestimate $\Delta H_{\text{carbonation}}$ by $\sim 10\%$, it can still be used as an approximate experimental guide. For Li$_5$FeO$_4$ there is a reasonably good agreement between the experimental and theoretical values, within error. The same good agreement is seen between the experimental value for Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and the value obtained for Ca$_3$V$_2$O$_8$ from the Materials Project (further suprting the theory that it is Ca$_3$V$_2$O$_8$ and not Ca$_{10}$V$_6$O$_{25}$ that is actually undergoing carbonation). For Na$_3$SbO$_4$ a much lower value of -129 kJ mol$^{-1}$ for the experimental $\Delta H_{\text{carbonation}}$ is obtained than in the previous TPD analysis (which gave a $\Delta H_{\text{carbonation}}$ of -175 kJ mol$^{-1}$), compared to the value obtained from the Materials Project of -168 kJ mol$^{-1}$. For Li$_6$CoO$_4$ the theoretical value is $\sim 30\%$ higher than that obtained from the DSC experiment. Further thermogravimetric tests to gain a more accurate experimental value of $\Delta H_{\text{carbonation}}$ are ongoing, specifically TPD experiments under more precisely determined $p$ (CO$_2$) and ramp rates, which will allow greater confidence when comparing to the values obtained from the Materials Project.

### 3.3.6 CO$_2$ cycling capacity studies

To test the cyclic performance of Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$, the materials were heated between 923 K and 1173 K for 40 minutes each to sequentially carbonate and decarbonate the samples. The switches between temperatures were achieved by heating and cooling at constant rates of 20 K min$^{-1}$ and -20 K min$^{-1}$, respectively, all under a constant CO$_2$ partial pressure of 0.1 bar in contact with the solid sample. The results of the cycling experiments were analysed by estimating the CO$_2$ uptake ($g_{\text{CO}_2}/g_{\text{sorbent}}$) by the sorbent in each cycle according to:

$$\text{CO}_2 \text{ uptake} = \frac{m_{\text{max},i} - m_{\text{min},i}}{m_{\text{min},i}} \quad (3.10)$$

where $m_{\text{max},i}$ and $m_{\text{min},i}$ are the maximum and minimum mass of the sample in the $i$th cycle respectively. The profile of CO$_2$ uptake, as a function of cycle number, is plotted in Figure 3.10.

The results show that both materials carbonate at close to full theoretical capacity on the first cycle (if the Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ sample is compared to the theoretical capacity of Ca$_3$V$_2$O$_8$), but show capacity fading upon further cycling. In particular, the capacity of Na$_3$SbO$_4$ rapidly
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Figure 3.10: Gravimetric CO$_2$ capacity as a function of cycle number for Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$, measured by TGA under $p$(CO$_2$) = 0.1 bar. The full and dashed lines show the predicted capacity, based on the stoichiometry of the carbonation reaction. For both materials, they initially absorb CO$_2$ at close to full theoretical capacity, but their capacity quickly fades to between 25–35 % of that of the first cycle.

decreases even by the second cycle, which showed approximately half the CO$_2$ uptake compared to the first cycle. Both materials settle to a gravimetric capacity of $\sim$0.035 g$_{CO_2}$/g$_{sorbent}$ after 24 cycles, which is roughly half the gravimetric capacity displayed by CaO under similar conditions [51].

Further analysis of the maximum and minimum sample masses measured during each cycle for both materials reveals that the reduction in capacity is almost entirely due to the decreasing maximum sample mass measured in each cycle, compared to the minimum sample mass which stays relatively constant (Figure 3.11). The minimum mass corresponds to the mass of the fully regenerated sample, and as such these results indicate that the samples are regenerating fully upon each cycle. The reduction in the maximum sample mass shows that the capacity fading is primarily due to the reduced amount of carbonate being formed in each cycle.

These results indicate that volume change might not be sufficient to indicate materials which might have improved cycling stability, and that capacity fading is a more complex process than can be described by a single variable. Further cycling studies of a wider range of materials is hoped to allow more insight into the determining factors responsible for capacity fading and retention respectively.
3.3. Results and discussion

3.3.7 Morphological studies of materials upon cycling

To further investigate the reasons behind the degradation of CO$_2$ capacity experienced by both Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$ upon cycling, the samples were observed using SEM, as shown in Figure 3.12 and Figure 3.13.

The SEM results indicate that the fading in cycling capacity for both Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$ is connected to changes in the surface morphology of the sorbent particles, although this appears to be linked to different factors for the two samples. The fresh particles show a large amount of available surface area, allowing the maximum amount of reaction with gaseous CO$_2$. After the first carbonation cycle, the morphology of the particles changes to reflect the new carbonate phase forming on the surface. In the case of Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$, the two morphologies indicative of the presence of both Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and CaCO$_3$ seen in the carbonated sample persist in the sample even when it is fully regenerated after 20 cycles (which nominally should not contain any carbonate phase). The inability to fully regenerate the original oxide phase reduces the amount material that is available for future carbonation cycles, leading to a decrease in capacity. This is supported by the TGA cycling results (Figure 3.11) which show that the mass of the sample after regeneration slowly increases over successive cycles.

For Na$_3$SbO$_4$ it is much more difficult to distinguish two different phases in the carbonated samples, instead there appears to be a phase formed with a different morphology and reduced surface area and porosity. This is presumably Na$_2$CO$_3$, which is sintering due to the sample being heated so close...
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Figure 3.12: SEM images of the Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ sample under two different magnifications (left: x500, right: x1500): heated to 1223 K under N$_2$ (a) and (b); fully carbonated (c) and (d); and cycled 20 times, then fully regenerated under N$_2$ (e) and (f). After the reaction with CO$_2$ the appearance of the new CaCO$_3$ phase with a different morphology can be seen clearly in (d). Comparing the particle in (e) and (f) with the two previous stages of reaction shows that after extended cycling, a significant amount of CaCO$_3$ remains in the notionally regenerated particle, leading to a decrease in capacity as less of the original Ca$_3$V$_2$O$_8$ phase is available for reaction.
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Figure 3.13: SEM images of Na$_3$SbO$_4$ samples under two different magnifications (left: x500, right: x1500): heated to 1223 K under N$_2$ (a) and (b); fully carbonated (c) and (d); and cycled 20 times, then fully regenerated under N$_2$ (e) and (f). Compared to Ca$_3$V$_2$O$_8$, upon extended cycling Na$_3$SbO$_4$ shows a drastic decrease in both surface area and available porosity, which is likely responsible for its reduction in cycling capacity. The drastic reduction in surface area can be seen especially in the cycled material (f) as compared to the unreacted material (b), indicating that this is a key parameter influencing the cycling stability of Na$_3$SbO$_4$. 
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to its melting point. The images of the fully regenerated particle after 20 cycles shows that the morphology mirrors that of the carbonated phase, indicating that this sintering persists even upon regenerating the sample, and that multiple cycles appear to lock in this reduction of surface area and porosity. This would seem to explain the reduction in carbonation capacity of these cycled particles as there is less available surface area for CO$_2$ to react with. These two results taken together indicate that thermodynamic parameters influencing the ability to fully regenerate the original material, as well as finding ways to control the surface morphology of the sorbents over many cycles, are key to finding a material with a stable cycling capacity. Both parameters influence the overall behavior of a sorbent, and only focussing on a single aspect is insufficient to fully understand a material’s ability to withstand multiple carbonation cycles without losing capacity.

3.4 Conclusions

Using a variety of thermogravimetric techniques, experimental validation was provided for a small set of candidate materials suggested by the Materials Project screening. For some of the materials, such as Na$_3$SbO$_4$ and Li$_5$FeO$_4$, the experimental values of $\Delta H_{\text{carbonation}}$ were in good agreement with those calculated from the screening procedure, indicating that the output of that screening can predict the carbonation thermodynamics of materials from a theoretical standpoint. This experimental validation is vital to developing a robust screening procedure that is able to predict materials that function in realistic reaction conditions.

In the particular case of the Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ material, there are still a number of unresolved issues regarding its exact composition during carbonation. While a plausible structure was suggested for Ca$_{10}$V$_6$O$_{25}$ that appears to form upon trying to synthesise Ca$_3$V$_2$O$_8$, further high resolution XRD experiments are needed to fully characterise the phase. In addition, future in situ XRD experiments should be able to shed light on the behaviour of the material during carbonation, and most importantly identify the actual carbonation reaction that is occurring.

Unfortunately, poor agreement was found for the enthalpy value of Li$_6$CoO$_4$, suggesting that further work is needed to improve the theoretical accuracy of the screening process. That being said, the methods for experimentally determining $\Delta H_{\text{carbonation}}$, especially for compounds close to the melting points of one of their carbonation products also need to be
improved, and this is an area of ongoing research.

Cycling experiments on Ca$_3$V$_2$O$_8$/Ca$_{10}$V$_6$O$_{25}$ and Na$_3$SbO$_4$ showed that these materials suffer similar capacity fading as seen in the CaO-CaCO$_3$ system, despite these materials having much lower predicted volume expansions upon carbonation. SEM studies suggest that the decrease in available surface area of the cycled particles compared to those in the fresh sample contributes to this capacity fading, and that some amount of the carbonate phase does not regenerate in later cycles. Future studies on a wider range of compounds will hopefully assist in understanding the underlying parameters influencing the stability of these compounds over many cycles of carbonation.
Chapter 4

Reversible CO$_2$ absorption by the perovskite Ba$_4$Sb$_2$O$_9$

This chapter is adapted from a previously published article in Chemistry of Materials [175].

4.1 Introduction

Perovskites, and their ability to reversibly react with CO$_2$ to form carbonates even as atoms such as Ba or Li are removed from the structure, represent an interesting alternative to the binary and ternary metal oxides described above for CO$_2$ separation. Many of the problems with simple oxides, such as their deterioration over many cycles, and large volume changes occurring as the oxide is converted to carbonate, are obviated in perovskites, which act as a stable structural framework or maintain some structural motifs of the original structure despite the movement of active ions into and out of the structure. Many more perovskite materials, which have previously been shown to react with O$_2$ for oxygen chemical looping, may be able to be cycled for carbon chemical looping (such as LSCF) [203, 204].

Previously the high and low temperature structures of the 6H-perovskite Ba$_4$Sb$_2$O$_9$ were characterised, as well as its moderate mixed ionic and electronic conductivity properties [205]. The high temperature structure of Ba$_4$Sb$_2$O$_9$ is similar to that of the related 6H-perovskite material Ba$_4$Ta$_2$O$_9$ [206], adopting the ideal hexagonal $P6_3/mmc$ space group symmetry. Preliminary in situ diffraction measurements conducted under CO$_2$ showed
that 6H-Ba$_4$Sb$_2$O$_9$ decomposes between 923–1073 K, above which BaCO$_3$ was formed along with an unidentified phase, presumably a Sb-rich oxide, suggesting that the material had undergone a carbonation reaction [205]. Later results showed the product of this reaction to be another barium antimonate phase, BaSb$_2$O$_6$, with the relevant structures shown in Figure 4.1. This behaviour is similar to earlier results obtained from \textit{in situ} studies under CO$_2$ of phases of the related materials Ba$_4$Ta$_2$O$_9$ and Ba$_4$Nb$_2$O$_9$, which were also found to decompose to BaCO$_3$ and other oxides over a temperature range of 700–1300 K [207]. Upon further heating, however, Ba$_4$Sb$_2$O$_9$ was found to reform the crystalline high-temperature 6H-perovskite phase above 1173 K, whereas the other materials did not reform even upon heating to 1723 K.

![Figure 4.1: Crystallographic structures of Ba$_4$Sb$_2$O$_9$ (a) and BaSb$_2$O$_6$ along both the ab-plane and c axis (b). SbO$_6$ are drawn as blue polyhedra and Ba atoms as yellow spheres. O atoms have been omitted for the sake of clarity.](image-url)

In this chapter a detailed study of the reversible carbonation of Ba$_4$Sb$_2$O$_9$ is presented. Firstly, an investigation of the thermodynamic properties of the material under the influence of CO$_2$ was carried out, identifying the equilibrium curve for the carbonation reaction. Secondly, long-term cycling studies were undertaken to investigate the capacity of Ba$_4$Sb$_2$O$_9$ to alternately absorb and desorb CO$_2$. Finally \textit{in situ} S-XRD studies and \textit{ex situ} SEM were used to probe the structural evolution of the material during
cycling. Through these studies it is shown that $\text{Ba}_4\text{Sb}_2\text{O}_9$ can reversibly react with $\text{CO}_2$ between 923 K and 1223 K with negligible capacity loss over 100 cycles. In addition, it is possible to positively identify and characterise the phases formed upon carbonation that were unable to be determined in previous XRD studies [205]. It is also shown that the surface porosity of $\text{Ba}_4\text{Sb}_2\text{O}_9$ is recreated upon regeneration, leading to its excellent cycling stability in comparison to CaO.

4.2 Experimental methods

Pure polycrystalline samples of $\text{Ba}_4\text{Sb}_2\text{O}_9$ were prepared as described elsewhere [205]. Briefly, $\text{Ba}_4\text{Sb}_2\text{O}_9$ was formed by solid-state reaction in air from $\text{BaCO}_3$ and $\text{Sb}_2\text{O}_3$ (99.99% purity or greater). Prior to weighing, $\text{BaCO}_3$ was dried at 1000 K overnight. The stoichiometric mixture was ground using an agate mortar and pestle, calcined at 1073 K for 4 h, reground and calcined at 1273 K for 12 h. The sample was then reground and calcined for a further 12 h at 1273 K. Room-temperature and in situ high-temperature X-ray powder diffraction (XRD) data were collected on a Panalytical X’Pert Pro diffractometer using Cu K$_\alpha$ radiation.

The carbonation and regeneration reactions of $\text{Ba}_4\text{Sb}_2\text{O}_9$ were investigated using a thermogravimetric analyser (TGA/DSC 1, Mettler Toledo) operating at atmospheric pressure. The same process was used as for previous experiments, as detailed in Section 3.2.

Variable-temperature S-XRD data were collected at the Powder Diffraction beamline of the Australian Synchrotron using a wavelength $\lambda = 0.82354$ Å. Samples were placed in 0.5 mm diameter quartz capillaries and mounted in a gas flow cell under flowing $\text{CO}_2$. Data were collected at room temperature, then the sample was heated to 923 K at a ramp rate of 5 K min$^{-1}$. The sample was held at 923 K, and data continuously collected isothermally for 1 hour, then heated to 1173 K and again held for another hour. Finally, the sample was heated to 1223 K and monitored for a further hour. We performed sequential Rietveld refinements on the data using GSAS with the graphical interface EXPGUI [166, 167].

The surface morphologies of the solid samples at various stages of the cycling experiments (viz. fresh, fully carbonated, partially regenerated and fully regenerated) were examined ex situ by scanning electron microscopy (SEM). After sputter coating with Pt for 55 s (current = 40 mA), the samples were inspected in a field-emission gun SEM (6340F FEGSEM, JEOL)
with a secondary electron detector. Then, the elemental composition of the surface of a partially regenerated sample was analysed by energy-dispersive X-ray spectroscopy (EDX) using a variable-pressure SEM (5800 LV SEM, JEOL) under low-vacuum conditions.

4.3 Results

4.3.1 Thermogravimetric analysis

In order to determine the stoichiometry of the reaction during the carbonation of Ba$_4$Sb$_2$O$_9$, the results of the preliminary TGA experiment were analysed as shown in Figure 4.2. Some mass loss was seen during the heat treatment at 1023 K of the freshly-prepared sample, suggesting that Ba$_4$Sb$_2$O$_9$ might have reacted with the CO$_2$ in air under ambient conditions during storage. After approximately 130 min, the mass of the sample stabilised. The profile of sample mass as a function of time was therefore normalised by assuming that the sample at $t = 130$ min was 100% Ba$_4$Sb$_2$O$_9$. When a mixture of 42% CO$_2$ and 58% N$_2$ was introduced into the reaction chamber again at 1023 K, the sample gained mass rapidly due to the carbonation reaction, which gradually reached completion after approximately 4 hours. The mass of the sample at the end of the carbonation reaction was 13.75% greater than that of the pure Ba$_4$Sb$_2$O$_9$. Assuming that one of the solid products of carbonation is BaCO$_3$, the other solid product must have a stoichiometric formula BaSb$_{1.89}$O$_{5.72}$, which is in close agreement with the phase identified by XRD (BaSb$_2$O$_6$, shown later). Therefore, from this point onwards, the molar conversion of the carbonation of Ba$_4$Sb$_2$O$_9$ is calculated on the basis that 100% conversion corresponds to the complete reaction of:

$$ \text{Ba}_4\text{Sb}_2\text{O}_9 + 3 \text{CO}_2 \rightarrow 3 \text{BaCO}_3 + \text{BaSb}_2\text{O}_6 $$

(4.1)

To investigate further the nature of Equation (4.1), its equilibrium constant as a function of temperature was measured experimentally by TPD in a TGA under various CO$_2$ partial pressures. Due to limitations of the current TGA arrangement, there is a substantial difference between the concentration of CO$_2$ seen by the sample and the nominal concentration of the reactive gas input (i.e. the N$_2$ stream used to protect the TGA against corrosion and for purging); the mixing of CO$_2$ from the reactive gas stream with N$_2$ in the bulk gas phase along with mass transfer effects are also complex processes. Therefore, for each TGA experiment the actual CO$_2$ concentra-
Figure 4.2: Percentage sample mass change and sample temperature change as functions of time during the carbonation of a fresh sample of Ba₄Sb₂O₉ in a TGA. 100 % sample mass corresponds to the point where the sample is fully decomposed under N₂ at 1023 K.

The reaction (partial-pressure) at the gas-solid interface was calibrated against the CaO/CaCO₃ as described earlier in Section 3.2, and it was assumed that the rate of CO₂ uptake of Ba₄Sb₂O₉ was similar to that of CaO. The same gas mixture was then used for the TPD of a partially-carbonated sample of Ba₄Sb₂O₉ to find the corresponding temperature at the onset of weight loss, i.e., the regeneration of Ba₄Sb₂O₉. The measured gas-solid equilib-rium for the Ba₄Sb₂O₉-BaCO₃-CO₂ system as a function of pCO₂ is shown in Figure 4.3.

Using these equations outlined in Section 1.5, it was possible to calculate the enthalpy and entropy of the Ba₄Sb₂O₉ carbonation reaction from the series of TPD experiments to be 156(1) kJ mol⁻¹ and 131(1) J mol⁻¹ K⁻¹, respectively.

From Figure 4.3, it can be seen that the thermodynamic equilibrium of the Ba₄Sb₂O₉-BaCO₃-CO₂ system is similar to that of the CaO-CaCO₃-CO₂ system. Therefore pCO₂ = 0.42 bar is a reasonable condition under which Ba₄Sb₂O₉ can be cycled under constant pCO₂ by a temperature swing. In addition, when the measured equilibrium curves are compared to the calculated equilibrium curve for the BaO-BaCO₃-CO₂ system, based on the study by Basu and Searcy [208], as shown in Figure 4.3(b), it is obvious
that the equilibrium partial pressure for the pure BaO-BaCO$_3$-CO$_2$ system is too low to allow for regeneration under a realistic partial pressure of CO$_2$ over the temperature range of interest (873–1223 K). Thus, by using Ba$_4$Sb$_2$O$_9$, a barium-based sorbent becomes capable of almost mimicking the thermodynamic property of calcium-based sorbents.

The results of representative cycles of the cycling experiment are shown in Figure 4.4. During isothermal carbonation at 923 K, the carbonation reaction did not reach completion, and continued during temperature ramping from 923 to 1223 K. As the temperature was gradually raised, the rate began to accelerate, suggesting that the carbonation step was affected by an activated rate process as well as by the thermodynamic equilibrium. When the temperature of the sample exceeded $\sim$1133 K, the partially-carbonated sample started to lose weight as the thermodynamics started to favour regeneration. This observation is in good agreement with the measured equilibrium in Figure 4.3, which predicted the onset of regeneration at 1129 K. The sample was further decomposed at 1223 K for an additional 20 minutes before cooling to 923 K, at which point carbonation became feasible again.
4.3. Results

The profiles of mass change as functions of time during the 2nd and 100th cycles are distinctly different to those during the 10th, and 50th cycles, which almost overlap with each other. The reason for the apparently higher uptake of CO$_2$ in the 2nd cycle compared to later cycles is in fact an experimental artefact, which will be discussed later. The carbonation reaction appears to become increasingly faster from cycle 10 to 100 as seen from the more rapid onset of the carbonation reaction as the temperature is lowered below 1150 K, whereas the total CO$_2$ uptake by cycle before regeneration remains roughly the same as for all cycles. On the other hand, the rate of regeneration of the Ba$_4$Sb$_2$O$_9$ at 1223 K decreases slightly over cycles after cycle 50, but almost full decomposition was still reached before the subsequent carbonation reaction.

![Figure 4.4: Profiles of weight change as a function of time over selected cycles during the TGA cycling experiment.](image)

The results of the cycling experiments were further analysed by estimating the CO$_2$ uptake (g$_{CO_2}$/g$_{sorbent}$) by the sorbent in each cycle according to the procedure described earlier in Section 3.3.6. The profile of CO$_2$ uptake, as a function of cycle number is plotted in Figure 4.5.

The results shown in Figure 4.5 indicate that, overall, the barium based sorbent shows a very stable performance over 100 cycles. There is a rapid decay of CO$_2$ uptake from 100 mol% in the first cycle to 76.6 mol% in
Chapter 4. Reversible CO\textsubscript{2} absorption by the perovskite Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9}

Figure 4.5: Uptake of CO\textsubscript{2} by Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9} as a function of cycle number over 100 temperature swing cycles in a TGA, taken from the same experiment as shown in Figure 4.4, with the reactions occurring between 923–1223 K. 100 % CO\textsubscript{2} uptake on a molar basis corresponds to full conversion of Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9} to a mixture of BaCO\textsubscript{3} and BaSb\textsubscript{2}O\textsubscript{6}.

the fifth cycle. This is because, prior to cycling, the samples had been fully carbonated in CO\textsubscript{2}, resulting in 100 mol% uptake in the first cycle. In the subsequent cycles, the carbonation reactions were never allowed to reach completion, lasting only 60 minutes rather than the approximately 100 minutes required for full carbonation, giving rise to a dynamic change in the BaCO\textsubscript{3} content in the sample until an equilibrium between CO\textsubscript{2} uptake and CO\textsubscript{2} release was reached by the fifth cycle. From cycle 5 onwards, the CO\textsubscript{2} uptake was stable at around 73 mol% until the end of the cycling experiment. As discussed above, the less than 100 % CO\textsubscript{2} uptake during the remaining of the cycling experiments is a rate effect. The reproducibility of the weight curves as functions of time over many cycles suggests that the underlying mechanisms governing the cycling reactions were consistent, repeatable and reversible.

4.3.2 In situ XRD

In order to study the carbonation and calcination reactions of Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9}, variable-temperature in situ S-XRD results were collected under flowing CO\textsubscript{2}. Similar reaction temperatures as for the TGA studies were used, with carbonation at 923 K and calcination at 1223 K.
4.3. Results

The full S-XRD diffractograms at 923 K are shown in Figure 4.6. The indexing corresponds to the observed $\alpha$-Ba$_4$Sb$_2$O$_9$, 6H-Ba$_4$Sb$_2$O$_9$, BaSb$_2$O$_6$ and BaCO$_3$ phases. The gradual decrease of the phase fraction of Ba$_4$Sb$_2$O$_9$ matches well with the gradual increase of the BaCO$_3$ and BaSb$_2$O$_6$ phase fractions. Unlike earlier in situ S-XRD experiments utilising a flat-plate geometry for Ba$_4$Sb$_2$O$_9$ [205] where the Sb-rich decomposition product could not be identified, in this current experiment it was possible not only to identify all decomposition products, but also to track their evolution throughout the carbonation and calcination reactions. This is seen in the highlighted region of the isothermal diffractograms for the carbonation reaction in Figure 4.7. Sequential Rietveld refinements were performed and a representative refinement at 923 K after 6 minutes of carbonation is shown in Figure 4.8.

![Figure 4.6: Sequential isothermal synchrotron XRD diffractograms of Ba$_4$Sb$_2$O$_9$ ($\lambda = 0.82534$ Å) at 923 K. The rows of peak markers correspond to the BaSb$_2$O$_6$, BaCO$_3$, $\alpha$-Ba$_4$Sb$_2$O$_9$ and 6H-Ba$_4$Sb$_2$O$_9$ phases respectively.](image)
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Figure 4.7: Synchrotron X-ray diffractograms ($\lambda = 0.82354$ Å) of the products of the Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9} sample at 923 K under flowing CO\textsubscript{2}. Reflections indicating the presence of the formed phases BaCO\textsubscript{3} and BaSb\textsubscript{2}O\textsubscript{6} were indexed as shown.

Figure 4.8: Rietveld-refinement results for Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9} after 6 minutes of carbonation against synchrotron X-ray diffraction data ($\lambda = 0.82354$ Å) at 923 K. The rows of peak markers correspond to the phases, from top to bottom, BaSb\textsubscript{2}O\textsubscript{6}, BaCO\textsubscript{3}, $\alpha$-Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9} and 6H-Ba\textsubscript{4}Sb\textsubscript{2}O\textsubscript{9}.
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The phase behaviour during the carbonation reaction is close to what is expected from the earlier TGA experiments, with peaks due to the original 6H-perovskite $\text{Ba}_4\text{Sb}_2\text{O}_9$ phase slowly diminishing as it reacts with $\text{CO}_2$ to form orthorhombic $\text{BaCO}_3$. From the thermogravimetric analysis, the resulting secondary Sb-containing product phase was expected to have stoichiometry $\text{BaSb}_{1.89}\text{O}_{5.72}$, and from the diffractograms this product was identified as $\text{BaSb}_2\text{O}_6$. $\text{BaSb}_2\text{O}_6$ is a trigonal phase (space group $\text{P}\overline{3}1m$) first described by DeBoer et al. in 1994, consisting of infinite sheets of edge-sharing $\text{SbO}_6$ octahedra, with the $\text{Ba}^{2+}$ ions located in the cavities formed by these octahedra [209]. During refinement of the data, it was discovered that a small amount of the $\text{Ba}_4\text{Sb}_2\text{O}_9$ phase (approximately 25%) was in fact a different polymorph than that of the 6H hexagonal phase. Closer inspection revealed this phase to be isomorphic to the low temperature structure of related materials $\text{Ba}_4\text{Nb}_2\text{O}_9$ and $\text{Ba}_4\text{Ta}_2\text{O}_9$[206, 210], which is of the $\text{Sr}_4\text{Ru}_2\text{O}_9$ structure type [211].

In addition to the peaks corresponding to $\text{BaCO}_3$ and $\text{BaSb}_2\text{O}_6$, there is an increase in the background around $13^\circ 2\theta$ which indicates that some amount of amorphous phase is created during the reaction, and that this is likely to be $\text{BaCO}_3$ and/or $\text{BaSb}_2\text{O}_6$. This is mirrored in the refined phrase fractions shown in Figure 4.9, which show a lower amount of crystalline $\text{BaCO}_3$ being formed than would be expected from the reaction stoichiometry. The exact form of this amorphous content was difficult to determine.

Figure 4.9: Relative phase fractions obtained from sequential Rietveld refinements of the data collected at 923 K.
from the synchrotron diffractograms, but it should be noted that the peaks corresponding to $\text{Ba}_4\text{Sb}_2\text{O}_9$ broaden as they disappear, indicating that the reaction proceeds with a diminishing $\text{Ba}_4\text{Sb}_2\text{O}_9$ particle size.

Figure 4.10: Sequential isothermal synchrotron XRD diffractograms of $\text{Ba}_4\text{Sb}_2\text{O}_9$ ($\lambda = 0.82534$ Å) at 1223 K. The rows of peak markers correspond to the $\text{BaSb}_2\text{O}_6$, $\text{BaCO}_3$ (high temperature trigonal) and 6H-$\text{Ba}_4\text{Sb}_2\text{O}_9$ phases respectively.

The reverse reaction was expected to occur during the calcination process, where $\text{BaCO}_3$ and $\text{BaSb}_2\text{O}_6$ react together to regenerate the original $\text{Ba}_4\text{Sb}_2\text{O}_9$ phase. The complete sequential S-XRD diffractograms at 1223 K are shown in Figure 4.10, with highlighted segments of the patterns shown in Figure 4.11. Note that the change in the positions of the $\text{BaCO}_3$ peaks is due to its well known orthorhombic to trigonal phase transition at 1084 K [212]. Analysis of these diffractograms first shows the reappearance of peaks related to the $\text{Ba}_4\text{Sb}_2\text{O}_9$ phase, confirming the regeneration of the original material. However, this reappearance is not accompanied by a decrease in the crystalline $\text{BaCO}_3$ and $\text{BaSb}_2\text{O}_6$ phases, with peaks corresponding to these phases remaining even after 1 hour with little change in intensity. It therefore appears that $\text{Ba}_4\text{Sb}_2\text{O}_9$ reforms in these experiments without any noticeable reduction of the other crystalline phases present in the diffraction patterns, suggesting that the reaction does not go to completion, and that
possibly the reaction proceeds inhomogenously in the capillary, leading to unreacted regions being measured (Figure 4.11).

![Synchrotron X-ray diffractograms](image)

Figure 4.11: Synchrotron X-ray diffractograms ($\lambda = 0.82354$ Å) of the $\text{Ba}_4\text{Sb}_2\text{O}_9$ sample at 1223 K under flowing $\text{CO}_2$. Reflections indicating the presence of the formed phases $\text{BaCO}_3$ and $\text{BaSb}_2\text{O}_6$ are labelled. It can be seen that while the $\text{Ba}_4\text{Sb}_2\text{O}_9$ phase is reforming, the $\text{BaCO}_3$ and $\text{BaSb}_2\text{O}_6$ phases still persist, even after 1 hour of reaction.

### 4.3.3 SEM

To investigate the structural evolution of $\text{Ba}_4\text{Sb}_2\text{O}_9$ under cycling, four samples of pelletised $\text{Ba}_4\text{Sb}_2\text{O}_9$ were examined by SEM in various states of reaction: one sample was taken before the reaction started (Figure 4.12 a) while the other samples were cycled for 85 times and then fully-carbonated (Figure 4.12 b), fully carbonated and then partially regenerated (Figure 4.12 c) and fully regenerated (Figure 4.12 d).

In the unreacted sample, the primary particle sizes of the particles on the surface of the pellet were between 5–8 $\mu$m in diameter, similar particle sizes being observed in the fully regenerated sample, but with more defined particle shapes and larger porosity after 85 cycles. In contrast, in the fully carbonated sample, the morphology of the composite completely changes,
Figure 4.12: SEM images of pelleted Ba$_4$Sb$_2$O$_9$ samples: unreacted (a); cycled 85 times, then fully carbonated (b); fully carbonated and then partially regenerated (c); and fully carbonated and then fully regenerated (d). Comparison of (a) and (d) shows that the size of the surface particles and porosity of the Ba$_4$Sb$_2$O$_9$ pellets is similar (especially when compared against (b) or (c)), even after 85 cycles. From (b), we see that this porosity is destroyed upon carbonation, but is created again upon further regeneration (in (c) and (d)). In a higher magnification image of (b), long straight cracks can be observed to form on the surface of the BaCO$_3$ product layer, indicating strain being applied to the particle’s surface upon cooling, or during reaction.
4.3. Results

with most of the pores being filled by the product of the carbonation reaction. Upon partial regeneration a mix of these two states is observed, with the regions of hexagonal crystallites and porosity with dimensions of a similar scale as in the fully regenerated samples, and regions with smooth and dense surface analogous to that seen in the fully carbonated sample (shown in Figure 4.12(c)).

The higher magnification image of the fully carbonated sample (Figure 4.12 b) more clearly shows that well defined particles remain but they are almost completely covered by the smooth solid component. Long thin cracks are seen running down the surface of the particle, which are likely due either to the cracking of the ‘smooth’ phase upon cooling as the material contracts ex situ, or during reaction as large changes in volume cause internal stress on the formed carbonate phase.

EDX experiments were performed on the partially-regenerated sample (Figure 4.12 c) on selected areas (Figure 4.13) to analyse the chemical composition of the phases formed during cycling. The elemental analysis results are shown in Table 4.1. For the purposes of identifying the phases present, the most reliable value is the Ba:Sb atomic ratio, due to the better sensitivity of EDX to heavier elements. With Ba:Sb ratios of 2.3:1 and 2.4:1, both Ba$_4$Sb$_2$O$_9$ and BaSb$_2$O$_6$ crystallites must be contributing to spectra 1 and 4, while the phase with a compact, smooth morphology on the surface of the particle is BaCO$_3$. It should be noted that, owing to limitations of the experimental setup, it was difficult to keep the samples free from contamination by carbonaceous species in the atmosphere, therefore the carbon content shown in Table 4.1 may not correspond to the actual carbon content of the phases. Nevertheless, the negligible contribution from Sb in spectra 2 and 3 in Figure 4.13 confirms that the dense phase is indeed BaCO$_3$. This result is consistent with the observation in Figure 4.12 (b) that at full carbonation, the particle is covered by a layer of the product of carbonation, i.e. BaCO$_3$.

Based on the unit cell parameters calculated from refinements against in situ diffraction results, the molar volume of the solid reactant and products Ba$_4$Sb$_2$O$_9$, BaCO$_3$ and BaSb$_2$O$_6$ were calculated to be 261.88, 78.30 and 141.63 Å$^3$ respectively, i.e., a net increase in molar volume of 44 % is expected for the carbonation reaction. Therefore, the disappearance of the pore structure upon carbonation is attributed to the swelling due to the molar volume increase, which is typical for the carbonation of alkaline earth metal oxides such as CaO and BaO. As the material is cycled the apparent increase in porosity seen for the non-carbonated phase between
Figure 4.13: Higher resolution SEM image of partially regenerated Ba$_4$Sb$_2$O$_9$ (Figure 4.12 (c)), indicating from where different EDX spectra were taken. The results (see Table 4.1) verify that the nucleated crystals are Ba$_4$Sb$_2$O$_9$ (spectra 1 and 4), and the darker dense phase in the background is likely to be BaCO$_3$ (spectra 2 and 3).

<table>
<thead>
<tr>
<th>Spectra</th>
<th>C</th>
<th>O</th>
<th>Sb</th>
<th>Ba</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>20.6</td>
<td>47.6</td>
<td>9.6</td>
<td>22.2</td>
</tr>
<tr>
<td>2</td>
<td>34.3</td>
<td>44.0</td>
<td>0.6</td>
<td>21.2</td>
</tr>
<tr>
<td>3</td>
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<td>47.2</td>
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<td>18.5</td>
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<tr>
<td>4</td>
<td>17.9</td>
<td>45.0</td>
<td>10.8</td>
<td>26.2</td>
</tr>
</tbody>
</table>

Table 4.1: EDX results for four different locations on the surface of the partially regenerated particle of Ba$_4$Sb$_2$O$_9$ as shown in Figure 4.13. All values are atomic percentages, each with an uncertainty of ± 0.5 %. 
4.4. Discussion

the initial sample and 85 cycles is likely due to the continued swelling and then contraction that occurs during each cycle. The volume increase from the formed BaCO$_3$ might be expected to lead to a plugging of the porosity, giving an essentially non-porous composite (pellet) upon carbonation. Yet, despite the apparent lack of porosity of the fully carbonated phase, this does not prevent the material from cycling with good capacity retention. If the cracking seen in Figure 4.12 occurred during the carbonation, this would have exposed some core material to further reaction, explaining this good retention.

4.4 Discussion

It is important to understand the origins of the excellent CO$_2$ looping performance of Ba$_4$Sb$_2$O$_9$ as demonstrated by the TGA analysis, especially in comparison to the performance of pure CaO and BaO cycling [30, 208].

First, the reversible coupled Ba$_4$Sb$_2$O$_9$ reaction to form BaSb$_2$O$_6$ and the reaction of excess BaO with CO$_2$ to form BaCO$_3$ lowers the regeneration temperature of pure BaO from over 1500 K to 1223 K in 0.42 bar CO$_2$. The thermodynamics of the decomposition of BaO were studied previously by Basu and Searcy [208], and these are compared to data for the decomposition of CaO at 1000 K [202] and the thermodynamic parameters for Ba$_4$Sb$_2$O$_9$ calculated here (Table 4.2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_r$</th>
<th>$\Delta S_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>BaO[208]</td>
<td>252.1</td>
<td>146.6</td>
</tr>
<tr>
<td>CaO[202]</td>
<td>169(4)</td>
<td>151(4)</td>
</tr>
<tr>
<td>Ba$_4$Sb$_2$O$_9$</td>
<td>156(1)</td>
<td>131(1)</td>
</tr>
</tbody>
</table>

Table 4.2: Enthalpy and entropy values for the carbonation equilibria for BaO, CaO and Ba$_4$Sb$_2$O$_9$ respectively.

Since the decomposition reactions are all endothermic, compounds with a lower enthalpy of reaction will therefore decompose, i.e. regenerate at lower temperatures than those with greater enthalpies of reaction, for processes associated with similar entropies of reaction. In this case, there is a large decrease in $\Delta H_r$ for Ba$_4$Sb$_2$O$_9$ as compared to BaO, which explains the observed lower temperature of regeneration. It is interesting to note that
the reaction of the SbO$_x$ polyhedra (discussed in more detail below) coupled with the carbonation process leads to a significant shift in the reaction energy. A more detailed understanding of the energetics associated with the various phase transformations will require future theoretical studies to determine the ground state energies of the phases involved, and will give insight into the best strategy for altering the BaCO$_3$-BaO-CO$_2$ equilibrium, and indeed the equilibrium of other binary oxides.

Previous studies on other CO$_2$ capture materials have theorised that the carbonation reaction proceeds through a core-shell mechanism as, for example in Li$_2$ZrO$_3$, described by Ida et al. [139]. In this model, the rapid formation of a Li$_2$CO$_3$ and ZrO$_2$ shell around an unreacted core hinders the further reaction of Li$_2$ZrO$_3$ while simultaneously filling up any porosity of the original particle. Once the particle is covered in this product layer, further reaction can only occur through gas or ionic diffusion.

The SEM images of the fully carbonated particles of Ba$_4$Sb$_2$O$_9$ seem to suggest that the formation of BaCO$_3$ does indeed fill up any original porosity upon carbonation, producing a smooth and non-porous surface at the fully carbonated stage. However we still observe reversible carbonation occurring beyond the initial surface reaction, implying that either ionic or CO$_2$ diffusion allows the progression of the carbonation reaction. The presence of some poorly crystalline or amorphous material during the carbonation reaction, as seen in the in situ XRD may play a role in aiding the ionic conduction of both Ba and, or, O ions to the surface to allow the reaction to continue. Ba$_4$Sb$_2$O$_9$ was previously shown to be a moderately good oxygen ion conductor [205], and this could also facilitate the passage of ions from the core outwards towards the gas-solid reaction interface.

From the thermodynamic analysis above, it is seen that CaO and Ba$_4$Sb$_2$O$_9$ have similar carbonation equilibria, yet Ba$_4$Sb$_2$O$_9$ displays a far more stable cycling capacity in the long term. The origin of the excellent reversibility of the carbonation reaction could lie in the fact that Ba$_4$Sb$_2$O$_9$ reacts to form two phases, BaCO$_3$ and BaSb$_2$O$_6$, and in doing so extrudes BaO. For the CaCO$_3$-CaO-CO$_2$ system, CaCO$_3$ reconverts directly to CaO, and the fact there the reaction proceeds from one solid to another means there is nothing to prevent CaO from sintering. In this three component system, the BaSb$_2$O$_6$ particles appear to be completely coated by BaCO$_3$, as confirmed by the SEM images. The excellent mixing of these two product phases prevents the complete segregation of Ba and Sb in the carbonated particles, which in turn prevents the sintering of the Ba$_4$Sb$_2$O$_9$ particles. In this way, the Sb component acts more as an inert additive dispersed throughout the
BaCO$_3$ phase, analogous to the addition of mayenite to improve the cycling stability of CaO [37, 60, 61, 63, 213].

On an atomic level, the structures of both Ba$_4$Sb$_2$O$_9$ and BaSb$_2$O$_6$ are made up of SbO$_6$ octahedra and isolated Ba (Figure 4.1). Formally, Ba$_4$Sb$_2$O$_9$ is a 6H perovskite with formula Ba$_3$(BaSb$_2$)O$_9$, with the Ba and Sb octahedrally coordinated by oxygen. On transformation from Ba$_4$Sb$_2$O$_9$ to BaSb$_2$O$_6$, the connectivity of the Sb octahedra changes from isolated face-sharing dimers to sheets of edge-sharing octahedra, involving a condensation of the Sb$_2$O$_9$ dimers and the loss of oxygen ions (and by charge compensation, Ba$^{2+}$). This rearrangement can still proceed without any long-range migration of the Sb atoms, with the limited nature of the atomic rearrangement presumably aiding the transformation between the two structures during carbonation and regeneration. Furthermore, the ready transformation of SbO$_x$ units between the two phases must help prevent phase segregation and sintering. These reactions must, however, involve long-range migration of Ba$^{2+}$ and O$^{2-}$ ions. In both structures the Ba$^{2+}$ is free to move in the large spaces between the SbO$_6$ octahedra, either in channels in Ba$_4$Sb$_2$O$_9$ or along the ab-plane in BaSb$_2$O$_6$. The known oxygen transport in the Ba$_4$Sb$_2$O$_9$ material may also help this process [205]. The particle morphology in both the unreacted and fully regenerated samples seen in SEM (Figure 4.12) matches closely with the hexagonal symmetry of the high temperature Ba$_4$Sb$_2$O$_9$ phase, suggesting that the morphology of the Ba$_4$Sb$_2$O$_9$ particles is maintained during the reaction. Note that the development of more distinct Ba$_4$Sb$_2$O$_9$ and BaSb$_2$O$_6$ morphologies on cycling suggests that some long-range diffusion of Sb atoms does occur but that an optimum particle size/shape is achieved in the long-term.

The diffraction results from the decarbonation process at 1223 K, in which the Ba$_4$Sb$_2$O$_9$ phase is seen to reappear without a simultaneous decrease in the intensity of the crystalline decomposition products, indeed indicates that the material is not fully decarbonated over this time scale. It is likely that the short duration of the in situ experiment, as well as limitations in the gas flow cell arrangement such as poor gas mixing, lead to differences in CO$_2$ partial pressure in different parts of the capillary and inhomogeneity in the calcination reaction, explaining the failure to regenerate the Ba$_4$Sb$_2$O$_9$ fully, in contrast to the conditions and results of the TGA experiment. This inhomogeneity may also lead to a reaction front moving through the capillary, with areas that have begun the regeneration process existing at the same time as areas that are still fully carbonated. In this case, the diffraction experiment could be sampling both areas, leading
to the coexistence of strong diffraction peaks for both the carbonated and regenerated phases. Of note, the diffraction experiments also suggest that an amorphous component is involved in the transformation mechanism, at the temperatures investigated here.

4.5 Conclusions

The 6H-perovskite $\text{Ba}_4\text{Sb}_2\text{O}_9$ was found to react with $\text{CO}_2$ with an equilibrium constant similar to that of $\text{CaO}$ based sorbents. TGA cycling experiments showed that the material maintains a stable $\text{CO}_2$ uptake capacity up to 100 cycles, unlike CaO based materials whose capacity decays rapidly over cycles under similar operating conditions, making it an attractive alternative for a range of applications that require the separation of $\text{CO}_2$ from other gases, especially at high temperatures. Thermodynamic calculations indicated the reduction in the enthalpy of the $\text{Ba}_4\text{Sb}_2\text{O}_9$-$\text{BaCO}_3$-$\text{CO}_2$ equilibrium compared to the $\text{BaO}$-$\text{BaCO}_3$-$\text{CO}_2$ equilibrium is primarily responsible for the lower reaction temperatures below 1200 K.

In situ S-XRD studies were used to analyse the structural evolution of the material upon carbonation and regeneration. For the first time, the formation of the $\text{BaSb}_2\text{O}_6$ phase was observed in situ during the carbonation reaction. It was also possible to observe the relative amount of phases present in the reaction as a function of time, tracking the conversion of $\text{Ba}_4\text{Sb}_2\text{O}_9$ into $\text{BaCO}_3$ and $\text{BaSb}_2\text{O}_6$. A significant amount of $\text{Ba}_4\text{Sb}_2\text{O}_9$ was found to react to form poorly crystalline or amorphous phases in the initial stages of carbonation, which could aid ionic motion through the product layers to allow the reaction to continue.

SEM and EDX experiments confirmed the formation of $\text{BaCO}_3$ on the surface of the sorbent particles upon carbonation, and that partially regenerated samples still contain a significant amount of $\text{BaCO}_3$ while $\text{Ba}_4\text{Sb}_2\text{O}_9$ crystallites reappear across the surface. The regeneration of $\text{Ba}_4\text{Sb}_2\text{O}_9$ also leads to the recreation of the original particle morphology, accompanied by the regeneration of the porous structure from a dense shell of $\text{BaCO}_3$ in each cycle. This self-generating porosity is likely to be the key to the stable absorption capacity seen in TGA cycling studies, and is an important difference between $\text{Ba}_4\text{Sb}_2\text{O}_9$ and other deteriorating sorbents such as CaO.

Taken together, the TGA, XRD and SEM analysis suggest that the stability of $\text{Ba}_4\text{Sb}_2\text{O}_9$ upon $\text{CO}_2$ cycling comes from fact that Sb acts as a stable inert phase (as $\text{Ba}_4\text{Sb}_2\text{O}_9$ and $\text{BaSb}_2\text{O}_6$ respectively) that remains
well dispersed throughout the sorbent particles over the entire carbonation and regeneration processes, preventing the sintering of the particles.

Importantly, this study represents the first time a perovskite-type material has been shown to withstand 100 cycles of carbonation and decarbonation reactions, and the first demonstration of reversible carbon capture by a barium based sorbent. This work highlights the potential of using mixed metal oxides with stable and flexible chemical compositions and structures for this application. Further studies in this vein could lead to the rational design and development of new materials for looping applications with specific thermodynamic and chemical property requirements.
Chapter 5

Ion Dynamics in Li₂CO₃ Studied by Solid-State NMR and First-Principles Calculations

5.1 Introduction

Previously there have been few studies to understand how oxide-based materials function for CCS applications, especially to identify whether there is a link between temperature, structure and the kinetics of carbonation. Ida et al. previously proposed a double shell model for Li₂ZrO₃, a model compound for these carbonation reactions, in which the initial rapid reaction of CO₂ with Li₂ZrO₃ first forms an outer layer of Li₂CO₃ around a layer of ZrO₂ covering a core of unreacted Li₂ZrO₃ [139]. After this initial absorption process, carbonation can continue, but requires the motion of Li⁺ and O²⁻ ions through the ZrO₂ and Li₂CO₃ layers or through the grain boundaries. Across all of the different materials that have been considered for CCS applications, the formed carbonate remains a common phase through which the relevant ions need to be transported.

For a deeper insight into the structure, dynamics and mechanisms operating during carbonation in CCS materials, nuclear magnetic resonance (NMR) is well-placed as a complementary approach to more traditionally applied diffraction methods. The high sensitivity of NMR to the local chem-
Chapter 5. Ion Dynamics in Li$_2$CO$_3$ Studied by Solid-State NMR and First-Principles Calculations

ical environment means it can be applied to potentially dynamic and/or disordered systems that may be difficult to probe by other analytical methods. In particular, the modulation of quadrupolar interactions, which affect nuclei with spin $I > \frac{1}{2}$, can provide access to information about atomic and ionic motion on a range of timescales between $\sim 10^3 - 10^7$ s$^{-1}$. Furthermore, the recent development of density functional theory (DFT) codes that utilize periodic boundary conditions has enabled the calculation of NMR parameters in the solid state with very high accuracy [214, 215]. These codes have proven to be valuable complementary tools for gaining structural insight into a vast range of materials, and whilst they can only be applied straightforwardly to rigid crystalline model structures, a number of recent studies have shown how they may be used in conjunction with experimental NMR data to gain insight into dynamic systems [173, 174].

In this chapter, a detailed structural and dynamics study of Li$_2$CO$_3$ across the temperature range 293–973 K is presented. Using high-temperature XRD we found that while no significant long-range structural changes take place over this range, $^7$Li NMR reveals extensive Li ion dynamics. By combining the experimental NMR data with first-principles calculations and an appropriate dynamic model, it is possible to characterise and estimate an activation energy for the motion present. Using $^{17}$O MAS NMR, this motion at higher temperatures is found to be influenced by the dynamic rotation of the CO$_2^-$ anion groups. The dynamics observed in this work define the structural and dynamic characteristics of this common component in the Li-based systems proposed for CCS applications. Advances in understanding the temperature-dependent dynamics in Li$_2$CO$_3$ can be applied to the study of more complex systems in turn.

5.2 Experimental methods

Commercially available Li$_2$CO$_3$ (Sigma Aldrich, 99.997 %) and $^6$Li-enriched Li$_2$CO$_3$ (Cambridge Isotope Laboratories, 99.5 % $^6$Li) were used in the experiments. $^{17}$O-enriched Li$_2$CO$_3$ was made by placing $^{17}$O enriched LiOH in a tube furnace heated to 373 K under a flow of CO$_2$ gas (rate of 15 cm$^3$ min$^{-1}$) for 12 hours. $^{17}$O-enriched LiOH was synthesized following the procedure by Abys et al. [216] from the reaction between n-butyl lithium in hexane (52 ml) with 10 % $^{17}$O-enriched water (1.5 ml) in 100 ml of dry tetrahydrofuran resulting in 1.5 g of LiOH. To ensure sample purity, room-temperature X-ray powder diffraction (XRD) data were collected on
a Panalytical X’Pert Pro diffractometer using Cu Kα radiation. High temperature x-ray powder diffractograms were collected between room temperature and 973 K in the 2θ range 8–100° (step size: 0.02°; time/step: 3 seconds; delay time after reaching temperature: 10 minutes) and were collected under vacuum (pressure: \(5\times10^{-4}\) mbar) in Bragg-Brentano geometry on a Bruker D8-ADVANCE diffractometer equipped with an MRI high-temperature chamber using Cu Kα radiation, Göbel mirror for parallel primary beam, and a Vantec linear position sensitive detector.

\(^7\)Li NMR spectra were obtained both at 16.4 T on a Bruker Avance III 700 MHz spectrometer operating at a Larmor frequency of 272.05 MHz, and at 9.4 T on a Bruker Avance 400 MHz spectrometer operating at a Larmor frequency of 155.46 MHz. Variable temperature measurements from room temperature to 973 K were performed using Bruker laser probes on both spectrometers [217, 218]. Temperature calibration of the probe was carefully performed by using the \(^{79}\)Br resonance of KBr [219] over the whole temperature range. The temperatures given in the text correspond to actual sample temperatures with an estimated accuracy of ±10, 20 and 30 K in the 293–473 K, 473–673 K and 673–873 K temperature ranges. Samples were packed in 4 mm BN inserts within 7 mm zirconia rotors, which were subsequently spun at 4 kHz. One dimensional experiments were performed with a rotor-synchronised spin-echo pulse sequence. Relaxation experiments were performed with a saturation recovery pulse sequence. The \(^7\)Li chemical shifts were externally referenced to LiCl at 0 ppm. NMR data were processed with MatLab.

\(^{17}\)O NMR spectra were obtained at 16.4 T on a Bruker Avance III 700 MHz spectrometer operating at a Larmor frequency of 94.90 MHz. Variable temperature measurements from room temperature to 573 K were performed on a Bruker single channel WVT probe with a temperature booster unit. Temperature calibration of the probe was carefully performed by using the \(^{207}\)Pb resonance of Pb(NO\(_3\))\(_2\) [220, 221]. The temperatures given in the text correspond to actual sample temperatures with an estimated accuracy of ±5 K. Samples were packed in 4 mm zirconia rotors, which were subsequently spun at 12.5 kHz. One dimensional experiments were performed with a spin-echo pulse sequence with a 2.2 \(\mu\)s excitation pulse and a 30 \(\mu\)s central-transition selective 180° refocusing pulse. \(T_1\) relaxation measurements were carried out using a saturation-recovery pulse sequence. The \(^{17}\)O chemical shifts were externally referenced to H\(_2\)O at 0 ppm. Owing to the overlapped resonances in the \(^{17}\)O MAS NMR spectrum and the changes in lineshape with temperature, \(T_1\) values were not determined in-
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dependently for the two crystallographically-distinct oxygen sites. Instead, a single $T_1$ value was determined at each temperature by fitting the total integrated intensity of the unresolved lineshape. This gave a good fit to a single exponential, indicating that $T_1$ values for the two distinct oxygen sites are similar. Indeed, this is to be expected given the very similar quadrupolar parameters and dynamic exchange present in the system (see Table 1 in Leskes et al. [222]).

Calculations of NMR parameters were carried out using the CASTEP DFT code [223], employing the GIPAW algorithm [224] that allows reconstruction of the all-electron wave function in the presence of a magnetic field. The generalized gradient approximation (GGA) PBE functional [225] was employed and core-valence interactions were described by ultrasoft pseudopotentials [226, 227]. Total energies and NMR parameters were calculated using a planewave energy cut off of 50 Ry (680 eV) and a k-point spacing of 0.05 Å$^{-1}$. The quadrupolar coupling constant, $C_Q = eQV_{ZZ}/\hbar$ and asymmetry parameter, $\eta_Q = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$ are obtained directly from the principal components of the electric field gradient (EFG) tensor, which are ordered such that $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, where $Q$ is the nuclear quadrupole moment (for which experimentally determined values of -40.1 and -25.6 mb were used for $^7$Li and $^{17}$O, respectively [228]). Isotropic shielding reference values of 89.8 and 248.0 ppm were used for $^7$Li and $^{17}$O, respectively.

Initial atomic positions and unit cell parameters for Li$_2$CO$_3$ were taken from an experimental diffraction structure [229]. Prior to calculation of the NMR parameters, the structure was fully geometry-optimised with the unit cell parameters allowed to vary using a cut off energy of 50 Ry and k-point spacing of 0.05 Å$^{-1}$.

5.3 Results

5.3.1 Powder x-ray diffraction

The room-temperature crystal structure of Li$_2$CO$_3$ is well known, having a monoclinic $C2_1/c$ space group with lattice parameters $a = 8.3593$ Å, $b = 4.9725$ Å, $c = 6.1975$ Å and $\beta = 114.83^\circ$, as shown in Figure 5.1 [229, 230]. In order to determine if there were any structural changes over the temperature range of our study, in situ variable temperature XRD was performed from room temperature up to 973 K. Sequential Rietveld refinements on the data were carried out using GSAS with the graphical interface
EXPGUI [166, 167]. From these refinements lattice parameters as a function of temperature were extracted (Figure 5.2).

![Figure 5.1: Room-temperature crystal structure of Li$_2$CO$_3$ viewed down the (a) b axis and (b) c axis [229, 230]. Lithium atoms are shown in green, carbon atoms in black and oxygen atoms in red.](image)

Li$_2$CO$_3$ shows the expected lattice expansion behaviour consistent with increasing temperature, with some anisotropy, the $a$ and $c$ lattice parameters increasing steadily, $b$ remaining fairly constant over the same temperature range. At 873 K, a new phase appears which was identified as Li$_2$O, with both phases being present at this temperature. By 973 K all of the Li$_2$CO$_3$ had converted to Li$_2$O, as shown in Figure 5.3. This is unexpected, given that Li$_2$CO$_3$ should melt at $\sim$996 K before it is able to decompose to the oxide [231]. However, these measurements were performed under vacuum due to the nature of the XRD furnace, and it is likely that the atmospheric conditions lowered the decomposition temperature below the melting temperature. To confirm the retention of the Li$_2$CO$_3$ phase up to 973 K, a sample was heated under air in a muffle furnace, with subsequent XRD analysis confirming the sole presence of the Li$_2$CO$_3$ phase. The similar lattice parameters found at room temperature and 373 K are most likely due to larger temperature errors when the furnace is being used at such low temperatures.
Figure 5.2: Rietveld-refined lattice parameters for Li$_2$CO$_3$ heated under vacuum from room temperature to 873 K. The moderate anisotropic lattice expansion along the $a$ and $c$ axes can be clearly seen.
5.3. Results

Figure 5.3: X-ray diffractograms ($\lambda = 1.5418$ Å) of Li$_2$CO$_3$ under heating in vacuum to 973 K. The decomposition of Li$_2$CO$_3$ to Li$_2$O can clearly be seen in the patterns taken at 873 K and above, with the decomposition being complete by 973 K.

5.3.2 $^7$Li NMR

To gain further insight into the structure of Li$_2$CO$_3$, variable-temperature $^7$Li solid-state NMR experiments were carried out. Figure 5.4a shows $^7$Li MAS NMR spectra recorded in the temperature range 295–873 K. Considering first the room temperature spectrum, an intense central transition (CT) resonance is observed at around 0 ppm, together with a spinning sideband manifold associated with the first-order quadrupolar-broadened satellite transitions (STs) extending over the range $-200$ to $+200$ ppm. As the temperature is increased, the ST spinning sideband linewidth broadens, reaching a maximum at around 573 K, before abruptly narrowing upon further heating. Changes in ST spinning sideband linewidth can be a clear indication of ionic or molecular motion, as seen in other materials [173, 174]. However, it is difficult to quantify the motional broadening of the ST spinning sidebands accurately in the case of Li$_2$CO$_3$ as they are also expected to be significantly broadened by strong $^7$Li - $^7$Li homonuclear dipole-dipole interactions. To separate the motional contribution from the dipolar contribu-
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tion to the ST spinning sideband linewidth, variable-temperature $^7$Li MAS NMR experiments were repeated on 99 % $^6$Li-enriched Li$_2$CO$_3$ (hereafter referred to as $^6$Li$_2$CO$_3$). In this system, the residual dilute $^7$Li nuclei (1 %) in the sample are monitored, thus effectively removing the strong $^7$Li -$^7$Li dipolar interactions. The $^7$Li MAS NMR spectra, shown in Figure 5.4b still exhibit broadening of the ST spinning sidebands with increasing temperature, followed by abrupt narrowing at 673 K. At 873 K, the observation of similar linewidths in the central transition within the spectra for both the natural abundance (51 Hz) and $^6$Li-enriched (36 Hz) samples indicates the presence of a dynamic process which is fast enough to fully average the $^7$Li -$^7$Li dipolar couplings in the natural abundance sample. In addition to enabling the separation of purely dynamic effects in the $^7$Li MAS NMR spectra of Li$_2$CO$_3$, the comparison of the room-temperature $^7$Li MAS NMR spectra of natural abundance and $^6$Li-enriched Li$_2$CO$_3$ samples underlines the significant effect that the $^7$Li -$^7$Li dipolar coupling interaction can have on the linewidth and should be an important factor to consider in $^7$Li MAS NMR studies of other Li containing materials. More detailed NMR experiments carried out over finer temperature increments are planned to gain a more precise measurement of the changing CT and ST lineshape with increasing temperature and to improve upon these preliminary scans carried out at 100 K intervals.

To aid interpretation of the experimental $^7$Li MAS NMR spectra further, first-principles DFT calculations were carried out. Calculated $^7$Li NMR parameters and experimental NMR parameters obtained from fitting the room temperature $^7$Li MAS NMR spectrum of $^6$Li$_2$CO$_3$ are shown in Table 5.1. Good agreement is observed between the calculated and fitted NMR parameters, although the $^7$Li $C_Q$ is overestimated by approximately 20 %. Overestimation of $C_Q$ values by up to 12 % has been observed in studies of other oxide materials and may be an inherent error of the DFT method and/or pseudopotential used [174, 232]. The slightly larger overestimation would also be explained by the presence of significant Li thermal motion resulting in small amplitude bond librations even at room temperature, which could result in a reduction of the observed first-order quadrupolar broadening.

The results of the calculations, together with the symmetry of the structure, show that while there is only a single crystallographic Li site in the structure, there are two magnetically-inequivalent Li sites which have different relative orientations of the electric field gradient (EFG) tensor. Figure 5.6(a) and (b) show the crystal structure of Li$_2$CO$_3$ with magnetically-
5.3. Results

Figure 5.4: Comparison of $^7$Li MAS NMR spectra for (a) natural Li$_2$CO$_3$ and (b) $^6$Li-enriched Li$_2$CO$_3$ over the range 293–873 K, obtained at 9.4T and a MAS rate of 4 kHz.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (ppm)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>0.0</td>
<td>0.081</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>0.0(2)</td>
<td></td>
<td>0.80</td>
</tr>
<tr>
<td>O1</td>
<td>175.2</td>
<td>7.45</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>171.9(5)</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>O2</td>
<td>152.7</td>
<td>7.72</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>154.8(5)</td>
<td></td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 5.1: Calculated and experimental chemical shifts, $\delta_{iso}$, quadrupolar coupling constants, $C_Q$, and asymmetry parameters, $\eta_Q$, for $^7$Li and $^{17}$O in Li$_2$CO$_3$.

inequivalent sites denoted by light and dark blue colours. An expanded view of the structure in 5.6(c) shows the Li-Li proximities within a radius of 3.5 Å from a lithium ion in the structure. Five of the six closest Li-Li proximities are between magnetically-inequivalent Li ions.

The largest components ($V_{ZZ}$) of the EFG tensors are related by an angle of 89°. Fast exchange of Li ions between these sites will therefore result in partial averaging of the EFG tensor, leading to a change in the observed first-order quadrupolar broadening. Figure 5.5c shows a simulated $^7$Li MAS NMR spectrum based on the calculated NMR parameters assuming a fast two-site exchange process between the magnetically-inequivalent
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Figure 5.5: Comparison of experimental and simulated $^7$Li MAS NMR spectra for $^6$Li₂CO₃ at (a) and (b) ambient temperature and (c) and (d) 973 K. Simulations used the NMR parameters obtained from DFT calculations on the optimised room-temperature crystal structure [229, 230], and were produced using the software EXPRESS [233].

sites in the structure with a rate constant of $10^9$ Hz. The simulated spectrum shows excellent agreement with the experimental spectrum recorded at 973 K (Figure 5.5d). In comparison, there is a very poor fit at room temperature assuming zero motion (Figure 5.5a and Figure 5.5b). These results strongly suggest that even at room temperature, Li ions still display some residual ionic motion, while at high temperature Li ions undergo fast dynamic exchange between magnetically-inequivalent sites in the structure.

To interpret the data obtained in the intermediate temperature regime, consideration of precisely what effect Li ion dynamics should have on the $^7$Li ST spinning sideband linewidths is needed. It is possible to do this by considering the frequency change, $\Delta \nu$, in the $^7$Li first-order quadrupolar splitting that will result from the sudden exchange (hop) of a Li ion between two magnetically-inequivalent sites in the structure. This quantity is calculated using the magnitude and relative orientations of the $^7$Li EFG tensors that are determined by the DFT calculations on the optimised room temperature structure. In a powdered solid, there will be a distribution of $\Delta \nu$ values owing to the orientation dependence of the first-order quadrupolar splitting with respect to the magnetic field; therefore a root-mean square frequency change, $\Delta \nu_{\text{rms}}$, is considered as an appropriate mean
Figure 5.6: Crystal structure of Li$_2$CO$_3$ showing magnetically-equivalent and inequivalent sites. Li atoms are denoted by light and dark blue spheres, oxygen atoms as red spheres and carbon atoms as black spheres.
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of the powder distribution [173, 174, 234]. For Li$_2$CO$_3$, $\Delta \nu^{rms}$ was found to be 29.2 kHz; this value is relatively large, considering that the calculated quadrupolar splitting in the principal axis frame, $2\nu_Q^{PAS}$, is 40.4 kHz. Indeed, this reflects the fact that the angle relating the largest components of the EFG tensors for the two magnetically-inequivalent sites is close to 90°.

Previous work has shown that $\Delta \nu^{rms}$ values on the order of kHz or tens of kHz can result in significant broadening of ST spinning sidebands in MAS NMR spectra [173, 174]. To determine the expected broadening, a previously described analytical approach was used that models MAS as a train of spin echoes [234]. This method was used to predict the motional ST spinning sideband line broadening as a function of rate constant, $k$, for the exchange process, as plotted in Figure 5.7. An inherent line width of 36 Hz (based on the central transition line width measured experimentally for $^6$Li$_2$CO$_3$ at 973 K) was assumed in the simulation in order to account for any disorder or residual dipolar broadening. Figure 5.7 confirms that significant motional broadening of the ST spinning sidebands is expected across a wide range of rate constants. For values of $k$ between $\sim 10^4$ and $10^{3.5}$ s$^{-1}$, the ST spinning sideband line width is predicted to increase due to motional broadening. This is as observed experimentally between room temperature and 473 K. For values of $k$ greater than approximately $10^{3.5}$ s$^{-1}$, the motionally broadened linewidth is predicted to be above 1 kHz, meaning that the satellite transition spinning sidebands should be effectively unobservable in the $^7$Li MAS NMR spectrum. This explains the apparent loss of spinning sidebands around a temperature of 573 K. At rate constants greater than $10^5$ s$^{-1}$, motional narrowing is predicted. At a value of $k$ of $\sim 10^6$ s$^{-1}$, the predicted sideband line width is reduced back to approximately 1 kHz, where it should be observable once more in the spectrum. This is consistent with the reappearance of spinning sidebands at temperatures of 673 K and above. For rate constants greater than $10^6$ s$^{-1}$, further motional narrowing is predicted, until the inherent linewidth is approached around rates of $\sim 10^9$ s$^{-1}$.

While the use of this simple model is convenient for preliminary insights into the mechanism of ionic motion in Li$_2$CO$_3$, there are inherent limitations to its use. A possible difficulty is that only Li-ion hopping between magnetically inequivalent sites can be observed, and there may be hopping between equivalent sites that is unable to be seen in the NMR spectra. Investigation of the structure shows that while the closest Li-Li distance is between magnetically equivalent sites, the other 5 Li atoms within a 3.5 Å radius are all inequivalent (Figure 5.6). Therefore exchange between mag-
Figure 5.7: Log-log plot showing simulated ST spinning sideband linewidth as a function of rate constant for exchange of Li species between the two magnetically-inequivalent sites in Li$_2$CO$_3$. A MAS rate of 4 kHz and an inherent linewidth of 36 Hz is assumed in the simulation.

Figure 5.7: Log-log plot showing simulated ST spinning sideband linewidth as a function of rate constant for exchange of Li species between the two magnetically-inequivalent sites in Li$_2$CO$_3$. A MAS rate of 4 kHz and an inherent linewidth of 36 Hz is assumed in the simulation.

From the log$_{10}$-log$_{10}$ plot shown in Figure 5.7, it can be seen that the relationship between log$_{10}$($\Delta \nu^{ST}$/Hz) and log$_{10}$(k/s$^{-1}$) is approximately linear between calculated rate constants of $10^{2.5}$–$10^{4.5}$ and $10^{5.5}$–$10^{7}$ s$^{-1}$. It is therefore assumed that within these ranges, the motionally-broadened component of the experimental $^7$Li MAS NMR ST sideband linewidth, $\Delta \nu^{mot}$, will follow the Arrhenius law as a function of temperature, $T$, from which an activation energy, $E_a$, can be obtained via

$$\frac{d \ln(\Delta \nu^{mot})}{d(1/T)} = \pm \frac{E_a}{R}$$ (5.1)

where $R$ is the molar gas constant and $\Delta \nu^{mot}$ is obtained (in s$^{-1}$) by subtracting the estimated inherent linewidth of 36 s$^{-1}$ (36 Hz) from the measured $^7$Li MAS NMR ST sideband linewidth. The sign of Equation (5.1) is chosen to be negative or positive for values of $\Delta \nu^{mot}$ that correspond to points on the left and right, respectively, of the apex in Figure 5.7. A plot of ln($\Delta \nu^{mot}$/Hz) as a function of 1/T is shown in Figure 5.8. From the gradient of the line of best fit to the data between 577–672 K, a value for $E_a$ of 0.78 ± 0.05 eV is obtained. For the data between 826–921 K, a
significantly higher value for $E_a$ of $1.34 \pm 0.05$ eV is obtained, indicating that a second motional process may occur in the high temperature regime.

Figure 5.8: $^7$Li MAS NMR ST sideband linewidth, $\ln(\Delta \nu^{mot})$ plotted against inverse temperature for $^6\text{Li}_2\text{CO}_3$. Horizontal error bars correspond to temperature errors as outlined earlier, equal to $\pm 20$ K for temperatures between 473–673 K and $\pm 30$ K for temperatures between 673–873 K. These were interpolated from the measured linewidths of the ST sidebands in rotor-synchronized experiments, using the CASTEP model for Li ion exchange. Two different linear fits, for the low-temperature and high-temperature regimes respectively, were used in the Arrhenius analysis.

For natural abundance samples, analysis of the evolution of the $^7$Li central transition linewidth with temperature can also be used to probe ion dynamics [235, 236, 237]. In these cases, at some onset temperature, $T_C$, the linewidth (measured as full width at half maximum, FWHM) begins to narrow, as the onset of ionic motion starts to average the $^7$Li-$^7$Li homonuclear dipolar coupling interactions. Figure 5.9 shows linewidth as a function of temperature for natural abundance Li$_2$CO$_3$. In this case, $T_C = 461$ K; however, at lower temperatures a slight broadening of the central transition linewidth is observed before the onset of narrowing. The difference between these experiments and those of the previous studies is that these measurements were performed under MAS conditions, compared to static measurements previously. It is likely that the more complex evolution of the linewidth is due to interference effects between the modulating effects of both MAS and the ionic motion on the homonuclear dipolar interactions [172]. The linewidth reaches a plateau above $\sim 650$ K where dipolar cou-
plings are fully averaged, corresponding to the temperature range where sharp ST spinning sidebands begin to reappear in the NMR spectra.

Figure 5.9: $^7$Li NMR linewidths vs temperature for the central transition of Li$_2$CO$_3$.

### 5.3.3 $^{17}$O NMR

To investigate if there are any dynamic processes involving the carbonate ions, $^{17}$O NMR spectra were recorded at a range of temperatures from 307–484 K. The room-temperature spectrum for $^{17}$O-enriched Li$_2$CO$_3$ (Figure 5.10) agrees well with previously published studies [222]. As the temperature is increased, a narrowing of the CT linewidth is seen, a clear indication of some form of oxygen dynamics. Calculated $^{17}$O NMR parameters are summarised in Table 5.1. Good agreement is observed, although $^{17}$O $C_Q$ values are overestimated by up to 8%. This is within the range seen in other studies of inorganic oxides [174, 232]. In developing a model for oxygen exchange, it was assumed that oxygen ionic motion in Li$_2$CO$_3$ would be dominated by $C_3$ rotation of the CO$_3^{2-}$ units in the structure. Using the calculated NMR parameters the $^{17}$O spectra for Li$_2$CO$_3$ with varying rates of exchange between the three oxygens of the carbonate units were simulated using EXPRESS [233]. The comparison between the experimental spectra taken from room temperature up to 484 K, and those of the simulations is shown in Figure 5.10b. The simulated spectra show very good agreement with the experimental spectra, confirming that the rotation of the CO$_3^{2-}$ units is primarily responsible for the narrowing of the central transition. However, it was not possible to observe the spinning sidebands
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Figure 5.10: (a) Experimental and (b) simulated $^{17}$O MAS NMR spectra for $^{17}$O-enriched Li$_2$CO$_3$ at ambient temperature and up to 484 K. The rate of motion is given next to each simulated spectrum. Spinning sidebands are indicated with asterisks (*). The linear fit showing Arrhenius-like behaviour above 393 K is shown in (c).
in the experimental spectra for temperatures above \( \sim 400 \) K likely due to the decrease in resolution and poor signal to noise ratio in these spectra.

From these simulations hopping rate frequencies were extracted for the oxygen ion rotations, which are plotted as a function of \( 1/T \) in Figure 5.10c. Arrhenius-like behaviour is only observed at temperatures at which the frequency of ionic motion leads to visible changes in the central transition in the \(^{17}\text{O}\) spectra of \( \text{Li}_2\text{CO}_3 \).

5.3.4 \(^7\text{Li}\) and \(^{17}\text{O}\) \(T_1\) measurements

Another NMR technique that can be used to probe ionic motion is the measurement of spin-lattice relaxation rates \( T_1 \). The region of the \( T_1 \) temperature dependence corresponds to correlation rates on the order of the Larmor frequency, that is \( 10^8 \) Hz. Results for both \(^7\text{Li}\) and \(^{17}\text{O}\) at 16.4 T are shown in Figure 5.11. For \(^7\text{Li}\), a linear dependence between \( 1/T_1 \) and \( 1/T \) is observed at temperatures above \( \sim 650 \) K, indicating Arrhenius behaviour in this range. For \(^{17}\text{O}\), a similar linear dependence is seen above \( \sim 400 \) K. For both nuclei there is a weak dependence of \( T_1 \) on temperature at lower temperatures where the ionic motion is several orders of magnitude lower than that of the \( T_1 \) relaxation. At higher temperatures there is an approximate linear correlation for both ion types, indicating Arrhenius behaviour and that the change in \( T_1 \) with temperature is due to changes in the ionic motion in the material occurring on the MHz timescale.

Figure 5.11: \(^7\text{Li}\) and \(^{17}\text{O}\) relaxation rates \( T_1 \) measured through saturation recovery experiments at 16.4 T, plotted against inverse temperature for \(^6\text{Li}_2\text{CO}_3\) and \(^{17}\text{O}\)-enriched \( \text{Li}_2\text{CO}_3 \) respectively.
5.4 Discussion

In order to compare the results of the different experiments that are sensitive to motions over different frequency regimes, a correlation time $\tau_c$ was calculated at each of the different temperatures for the different NMR measurements. In the case of the $T_1$ measurements, a previously implemented relation shown in Equation (5.2) was used [238, 239]:

$$\frac{1}{T_1} = \frac{3}{200} \cdot \frac{2I + 3}{I^2(2I - 1)} \cdot C_Q^2 \cdot \left(1 + \frac{\eta_Q^2}{3}\right) \cdot \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2}\right]$$  \hspace{1cm} (5.2)

where $\omega_0$ is the $^7$Li or $^{17}$O Larmor frequency ($\frac{\omega_0}{2\pi}(^7\text{Li}) = 272.05$ MHz at 16.4 T, 155.46 MHz at 9.4 T and $\frac{\omega_0}{2\pi}(^{17}\text{O}) = 94.9$ MHz at 16.4 T) and $I$ is the nuclear spin ($I = 5/2$ and 3/2 for $^{17}$O and $^7$Li respectively). In extracting these values of $\tau_c$, the values of the quadrupole coupling constant $Q$ and asymmetry parameter $\eta_Q$ were derived from the experimental data shown in Table 5.1. For the linewidth analysis from which motional rates of lithium and oxygen ion hopping in Li$_2$CO$_3$ were derived, $\tau_c$ is simply the inverse of these frequencies.

If we take the $\tau_c^{-1}$ values to be equal to the average jump rates of their respective processes, $\tau_i^{-1}$, we can fit the linear parts of each curve to extract the activation energy $E_A$ and pre-exponential factor $\tau_i^{-1}$ for the ionic motion using the Arrhenius relationship shown in Equation (5.3) [236]:

$$\tau^{-1} = \tau_i^{-1} \cdot \exp\left(-\frac{E_A}{k_BT}\right)$$ \hspace{1cm} (5.3)

The results from this fitting are shown in Figure 5.12 and Table 5.2. They show reasonable agreement for the activation energy values obtained from the linewidth analysis as compared to the $T_1$ data, although there is a larger discrepancy between the two values obtained for the oxygen ionic motion of almost 0.4 eV. This is ascribed to the fact that the CT lineshape (Figure 5.10) shows the rate of rotation of the carbonate groups on the order of $\sim 10^4$ Hz, whereas $T_1$ indicates motional processes affecting $^{17}$O on the order of the Larmor frequency ($10^8$ Hz) at high temperatures (Figure 5.11).

While it was not possible to fit the central transition data in order to derive an activation energy as has been done elsewhere [236], various empirical formulas have used the relationship between linewidth and temperature to estimate $E_A$ of the motional process for other materials. In this work, the relation by Waugh and Fedin was used [240], which states $E_A = 0.156$
5.4. Discussion

\[ \ln(\tau^{-1}) \text{ (s}^{-1}) \]

\[ ^7\text{Li} \]

\[ ^{17}\text{O} \]

\[ \frac{1000}{(T / K)} \]

\[ 2.0 \ 3.0 \ 1.5 \ 2.5 \ 3.5 \ 1.0 \]

\[ L_\text{ithium} \]

\[ E_A (^7\text{Li}) = 0.74 \pm 0.05 \text{ eV} \]

\[ E_A (^{17}\text{O}) = 1.0 \pm 0.1 \text{ eV} \]

Figure 5.12: Arrhenius fitting of the inverse correlation times, \( \tau^{-1} \), derived from the measured \(^7\text{Li}\) and \(^{17}\text{O}\) relaxation rates \( T_1 \).

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>Method</th>
<th>Temperature Range</th>
<th>( E_A ) (eV)</th>
<th>( E_A ) (kJ mol(^{-1}))</th>
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<tr>
<td>Lithium</td>
<td>ST linewidth</td>
<td>577–672 K</td>
<td>0.78 ± 0.05</td>
<td>75 ± 5</td>
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<tr>
<td></td>
<td>ST linewidth</td>
<td>826–921 K</td>
<td>1.34 ± 0.05</td>
<td>129 ± 5</td>
</tr>
<tr>
<td></td>
<td>( T_1 )</td>
<td>294–875 K</td>
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<td>71 ± 5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>CT linewidth</td>
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<td>0.8 ± 0.1</td>
<td>77 ± 10</td>
</tr>
<tr>
<td></td>
<td>( T_1 )</td>
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<td>1.0 ± 0.1</td>
<td>96 ± 10</td>
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<tr>
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<td>CT linewidth</td>
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<td>1.39 ± 0.05</td>
<td>134 ± 5</td>
</tr>
</tbody>
</table>

Table 5.2: Activation energies \( E_A \) as determined from different NMR methods.

\( \times T_C \) (kJ mol\(^{-1}\) K\(^{-1}\)). Using the value for \( T_C \) obtained earlier, an estimate of \( E_A \sim 0.8 \text{ eV} \) was calculated, which is in fairly good agreement with the values for \( E_A \) from both the spinning sideband (in the lower temperature regime) and \( T_1 \) experimental analyses.

Reasonable agreement between the measured \( E_A \) of \(^7\text{Li}\) ionic motion obtained via both ST sideband analysis (obtained from using the Li hopping model described earlier) and \( T_1 \) analysis at low to intermediate temperatures, validates the hopping model used here as a reasonable estimation of the physical process occurring over this temperature range. The similarity in \( E_A \) values for the lithium ionic mobility at high temperatures and the rate of carbonate rotation possibly indicates that the actual Li ionic transport process at these high temperatures is assisted by cooperative rotation of the \( \text{CO}_3^{2-} \) ions, and is only activated once these rotations are activated.
Previous experimental studies using impedance spectroscopy found values for the activation energy of Li\(^+\) ionic motion in Li\(_2\)CO\(_3\) to be 0.77 eV between 348–553 K and 1.06 eV between 473–773 K respectively [241, 242]. These values agree well with those found in this study, and the trend of an increasing activation energy barrier with increasing temperature further supports our findings of a second motional regime at high temperature (albeit at higher temperatures than the previous studies). A recent theoretical study modelling ionic motion in Li\(_2\)CO\(_3\) under different voltage ranges also obtained a value for the activation energy of 0.78 eV at very low voltages (0.23 V), further supporting these findings [243].

Regardless of the physical transport mechanism, the fact that there appears to be a second, more rapid Li ionic transport that is activated at higher temperatures could explain the changes in absorption rates that are seen in Li-based materials at elevated temperatures once they are completely covered in a layer of Li\(_2\)CO\(_3\). For example, CO\(_2\) absorption curves seen in TGA experiments on Li\(_5\)AlO\(_4\) and Li\(_2\)CuO\(_2\) show clearly that there is a slower regime of CO\(_2\) absorption at lower temperatures, and at higher temperatures a more rapid absorption process dominates [114, 115, 117]. The experimental values for the activation energies required for lithium ionic motion through Li\(_2\)CO\(_3\) suggest that these different sorption regimes are directly related to the changing conduction mechanisms activated in the various reactant and product phases of the carbonation reaction.

In regards to the use of Li-based materials in CCS applications, Li\(_2\)CO\(_3\) is an important component of these promising systems. Once a layer of Li\(_2\)CO\(_3\) has formed on the surface of the original sorbent, continued reactivity of the material relies upon the transport of lithium and oxygen ions through the carbonate phase. Considering the usual temperature range at which these materials function (673–873 K), this study clearly shows that Li\(_2\)CO\(_3\) has significantly enhanced ionic mobility at these temperatures for lithium ions, enabled by cooperative CO\(_3^{2-}\) rotations, and that this mobility may very well be an important aspect of their function.

### 5.5 Conclusions

For Li\(_2\)CO\(_3\), an important material with applications in carbon capture and storage, we have observed dynamics of Li\(^+\) and CO\(_3^{2-}\) ions over the range of 10\(^3\)-10\(^9\) Hz. For these dynamic processes, the activation energies were determined to be 0.8 and 1.4 eV for the Li\(^+\) and CO\(_3^{2-}\) species, re-
5.5. Conclusions

respectively, with a higher activation energy of 1.3 eV observed for Li$^+$ over the temperature range 826–921 K. These results suggest that the dynamics in the structure play an important role in the mechanism of carbonation of Li-based materials, and that at higher temperatures these two dynamic processes are correlated, with cooperative rotation of the carbonate ions assisted the Li ionic transport. Considering the importance of ionic mobility in the function of Li-based materials in carbon capture, storage and separation processes, these results represent an important step forward towards a more complete understanding of the in situ function and dynamics of these materials. Li$_2$CO$_3$ is a common component in all of these systems, and these results clearly indicate that Li ion mobility is activated at the temperatures under which these materials are proposed to operate.

In particular, the approach demonstrated here provides quantitative information on two separate dynamic processes, namely exchange of the Li cations and rotation of the carbonate anions in the structure, with no requirement for a single crystal sample, as has been the case in other NMR studies of similar systems [236]. This approach therefore offers potential for the characterization of dynamics in other more complex systems of importance for CCS applications.
Chapter 6

Conclusions: Implications for CCS

This study has combined a thorough theoretical, experimental and analytical approach to further the understanding of materials used in CO$_2$ looping, and the underlying mechanisms that govern their performance. This interdisciplinary approach is unique in its scope, from in silico screening of novel materials, to the application of in situ experimental techniques to observe the function of these materials in real time. As such, there are many insights derived from this work that have important implications for future CCS research.

Through the development of a novel large scale screening process based on theoretical determination of gas-solid carbonation reactions, a number of promising candidate materials have been able to be suggested for use in high-temperature CO$_2$ looping CCS applications. Subsequent thermogravimetric and diffraction experimental studies have shown this screening methodology to be a valid approach to estimating carbonation equilibria and their associated heats of reaction, and pave the way for further studies into other gas-solid phase equilibria.

Importantly, the results from the screening have suggested that there are many materials that may show lower energy penalties and comparable capacities to existing materials, especially Mg based materials, and these should be the focus of further synthetic and experimental effort. Conversely, studies into Na-based materials may be less effective, considering their very high theoretical energy penalty. The screening also confirmed that ternary oxide materials generally have much lower energy penalties than their re-
lated binary oxides, and may be able to offer improved cycling capacities considering their much lower net volume changes upon carbonation.

An example of such a ternary oxide material that shows exemplary cycling stability is the novel 6H perovskite, \( \text{Ba}_4\text{Sb}_2\text{O}_9 \). These studies showed that not only did the addition of Sb into a BaO based material lead to a much lower carbonation enthalpy (and therefore lower energy penalty for use in CCS applications) compared to pure BaO, but the material also showed a remarkably stable cycling capacity over 100 cycles. This is the first perovskite material to be shown to be able to be cycled reversibly in this way, and suggests that further work into some of the many other perovskite-type materials may yield further materials with optimised properties and excellent cycling performance.

Furthermore, \textit{in situ} XRD and SEM studies of \( \text{Ba}_4\text{Sb}_2\text{O}_9 \) reveal some of the possible connections between the cycled structures and the overall performance of the material. The similarity of the local Sb environments in both the original oxide and the \( \text{BaSb}_2\text{O}_6 \) phase formed upon carbonation suggests that the Sb sublattice may act as a stable framework throughout the whole reaction, preventing sintering and loss of capacity as seen in CaO. This is also seen in the high level of retained surface area as seen in SEM, even after many cycles. This finding demonstrates that searching for materials with similar parent and carbonated structures may be a key predictor for cycling stability, and future work is planned to develop structure comparison algorithms to enhance the screening methodology. It also suggests that the current approach in CCS research, that of using additives to boost cycling stability, may be unnecessary, and that potentially better materials are ones that contain both the reactive material and the stable inert framework in a single phase.

Finally, this work sought to address a long postulated theory in CCS research that ionic mobility plays an important role in the carbonation reaction itself, especially in the second regime of slower absorption (after the initial rapid surface reaction). Through extensive variable temperature NMR experiments on a model compound \( \text{Li}_2\text{CO}_3 \), which is present in all of the Li-based materials during carbonation and is proposed to facilitate ionic transport to drive their continued carbonation, it was found at higher temperatures a more rapid Li ionic transport process is activated. This mechanism, which appears to be assisted by the rapid rotations of carbonate ions at higher temperatures, matches well with the observed changes in absorption rates for Li-based materials at these temperatures, and suggests that this high-temperature absorption is indeed facilitated through ionic
transport through a shell of Li$_2$CO$_3$.

This finding throws up a number of important questions for future research. Firstly, if ionic transport plays an important role in the high-temperature absorption of CCS materials, why do Ca-based materials show much faster rates of carbonation when Ca transport should be an order of magnitude lower than what is seen in the Li case? It also suggests that Mg-based materials, while having optimal thermodynamic properties, may suffer from slow kinetics which may limit their use. This study shows that further research is needed to better understand the link between structure, morphology and kinetics during carbonation, and the plan is to perform further experiments to explore this problem. One such study is using in situ x-ray tomography to observe morphological changes during the reaction, which should offer complementary insights to further NMR studies.

Another important conclusion is that finding materials that radically shift their relative carbonation equilibrium compared to their constituent binary oxides seems to influence the cycling performance of a material. In our studies, of the new materials tested, Ba$_4$Sb$_2$O$_9$ had a far superior cycling stability compared to Na$_3$SbO$_4$ and Ca$_3$V$_2$O$_8$. Comparing the carbonation thermodynamics of the three materials shows that Ba$_4$Sb$_2$O$_9$ was the only material to significantly alter its carbonation enthalpy compared to BaO, while the enthalpy change of Ca$_3$V$_2$O$_8$ and Na$_3$SbO$_4$ were very similar to that of CaO and Na$_2$O respectively. Taking into account the morphological changes of the materials upon cycling, it would appear that having a strong driving force for the original sorbent phase to reform with increasing temperature leads to stable capacities, as this reformation leads to the regeneration of the surface area and subsequent retention of the carbonation capacity. Materials whose formation energies do not differ greatly from their respective binary oxides most likely do not have the necessary driving force to reform, and therefore suffer from sintering and capacity fading. This is an important insight which should guide further efforts to find new CCS materials.

This study shows that a variety of new techniques can be applied to CCS research to derive novel materials and insights, and to suggest new directions for what is a very important problem. It also emphasises the importance of an interdisciplinary approach, and that considering the entire life cycle of a material, from theoretical prediction, to synthesis and thermogravimetric testing, to in situ analysis during its use, is necessary to gain the full picture of what is necessary to obtain an optimised CCS material.
Bibliography


