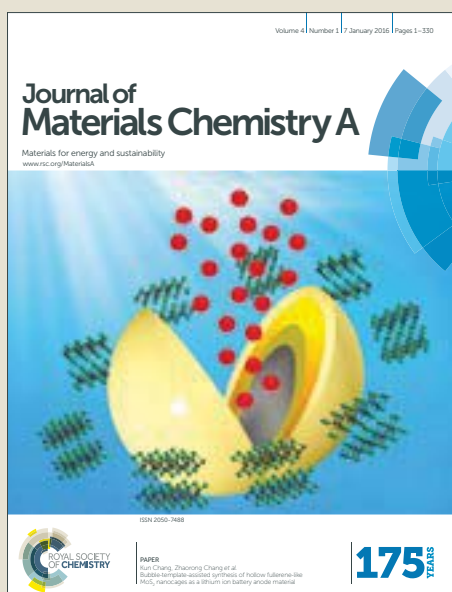


Journal of Materials Chemistry A

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: M. T. Izquierdo, A. Turan, S. García and M. Maroto-Valer, *J. Mater. Chem. A*, 2018, DOI: 10.1039/C7TA08738A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Optimization of Li₄SiO₄ synthesis conditions by solid state method for maximum CO₂ capture at high temperature

M.T. Izquierdo^{a,b,*}, A. Turan^{a,c}, S. García^a and M.M. Maroto-Valer^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

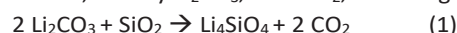
The aim of this research work is to optimize the synthesis of Li₄SiO₄ by solid state method to maximize CO₂ capture. This includes evaluating the main characteristics of the synthesised material which enhance CO₂ uptake performance. Starting from Li₂CO₃ and SiO₂ pure reagents, the effect of the sintering process conditions (heating rate, synthesis temperature and holding time) of the previously mixed powders has been studied. The samples were characterized by N₂ physisorption, particle size distribution and X-ray diffraction. The evaluation of the CO₂ uptake performance of the samples has been carried out at 600 °C in a thermobalance under a flow of almost pure CO₂. Unreacted Li₂CO₃ is present at low synthesis temperatures, and its content in the synthesised material decreases when higher temperatures are used, so complete conversion to Li₄SiO₄ is reached at 900°C. At this temperature, the maximum CO₂ uptake was found 20%, although it was yet far from the stoichiometric CO₂ uptake value of 36.7%. The holding time at a synthesis temperature of 900 °C was then varied and a maximum CO₂ uptake of 30.5% was obtained for a holding time of 2 h. Lastly, under optimised synthesis temperature and holding time conditions, the heating rate was varied. A value of 5 °C/min was found as the optimum one as the use of either lower or higher heating rates have a negative effect on CO₂ uptake performance. As crystalline phases, particle size and BET surface area were very similar among all prepared samples at 900 °C, crystal size was identified as the main physical property that could explain the CO₂ uptake performance of the samples, i.e., the lower crystal size, the higher CO₂ uptake.

1. Introduction

Lithium orthosilicate, Li₄SiO₄, is one of the lithium silicate ceramics studied for its wide range of applications such as those in secondary batteries, due to the ionic conductivity¹, Li-ion batteries, when doping with Co²⁺, and in future fusion reactors as a breeder blanket³. It has been also proposed as a solid sorbent for CO₂ capture⁴, because this ceramic shows immediate CO₂ absorption and desorption, which result in a theoretical weight change of up to 36.7%. In addition, CO₂ desorption is performed at lower temperature than that for CaO⁵, allowing its use in repeated cycles of absorption-desorption with lower energy demands. Its high stability under cyclic operation⁶ would also limit the need to add fresh sorbent to the absorbing bed.

The key of the success of this CO₂ sorbent-based capture process is the Li₄SiO₄ itself. The conventional solid-state synthesis method is the dominating protocol for ceramic synthesis due to its simplicity. It consists of a heat treatment, usually called sintering process, of a powder mixture of a Li-

source, usually Li₂CO₃, and SiO₂, following the reaction:



However, the heat treatment conditions during the production of ceramics strongly affect the material microstructure⁷, which can affect the sorbent performance. Although the sintering process for Li₄SiO₄ has already been studied (Table 1), a systematic study focused on the influence of the heat treatment parameters on the CO₂ uptake performance of the Li₄SiO₄ prepared is currently lacking. Additionally, in previous studies on solid state synthesis of Li₄SiO₄, no rationale behind the choice of synthesis conditions was given. Moreover, in most cases, authors do not present data for the heating rate used during the synthesis protocol, despite being one of the important variables that need to be considered in a sintering process⁷.

Furthermore, contradictory results in terms of CO₂ uptake for samples prepared under very similar conditions have been previously reported, as can be deduced from Table 1. For example, CO₂ uptake, some values reported in the literature are surprisingly high⁸, considering that the Si source come from a biomass ash with low Si content and the active mass for CO₂ capture is reduced by dilution effect (less than 50% Li₄SiO₄ content in all cases).

Likewise, the influence of CO₂ concentration on the Li₄SiO₄ sorbent performance has not been yet completely understood and it seems to be highly dependent on the sorbent

^a Research Centre for Carbon Solutions (RCCS), Institute of Mechanical, Process and Energy Engineering (IMPEE), School of Engineering and Physical Sciences, Heriot-Watt University, EH14 4AS, Edinburgh, United Kingdom.

^b Instituto de Carboquímica, ICB-CSIC. c/Miguel Luesma, 4.50018 Zaragoza, Spain. *e-mail: mizq@icb.csic.es

^c Chemical and Process Engineering Department, Faculty of Engineering, Yalova University, 77200, Yalova, Turkey.

characteristics, i.e. the preparation conditions, as can be deduced from Table 1. This is an important issue considering that CO₂ concentration in real CO₂ capture applications is in the range 4–20 %, under which theoretical CO₂ uptake will not be reached.

In this context, the main goal of this research work is to optimize Li₄SiO₄ preparation conditions by solid state method in order to maximize the CO₂ uptake (under an almost pure CO₂ flow) at high temperature, with a focus on identifying those sorbent characteristics that enhance CO₂ capture.

2. Experimental

2.1. Synthesis

The solid state method has been selected for the synthesis of lithium orthosilicate, Li₄SiO₄, using as starting materials Li₂CO₃ (Across Organics, purity 99%) and SiO₂ (Aldrich, purity 99.5%). Li source with a 10% of stoichiometric excess was added to prevent the sublimation of lithium at high temperature³.

Li₂CO₃ and SiO₂ powders were mixed in a planetary ball mill at 350 rpm during 30 min, changing stir direction each 5 min. The mixture was then placed in a crucible and it underwent isothermal sintering in a muffle furnace. During this heat thermal treatment, the temperature is increased monotonically to a synthesis temperature and lowered to room temperature afterwards. Accordingly, three variables were studied: heating rate, temperature and holding time. The samples were cooling down under the same conditions and they were removed from the furnace when the temperature was lower than 100 °C. After that, all the samples were grinded under the same procedure in a mechanical mortar by applying the same downforce and grinding time.

In order to optimize synthesis conditions to maximize CO₂ uptake, in a first set of experiments calcination temperature was varied in the range of 600–900 °C. Once selected the optimum calcination temperature, the holding time was varied in the range 1–10 h. Finally, once selected the holding time, the heating rate was varied in the range of 2–20 °C/min. In all cases, the amount of mixed powder was 5 g.

Samples were labelled as temperature-heating rate-holding time. For example, 900-5-4 refers to a sample prepared at 900 °C during 4 h at a heating rate of 5 °C/min.

2.2. Characterisation

Nitrogen physisorption at -196 °C in a Micromeritics Gemini VII was used to obtain BET surface area. The particle size distribution of the samples was measured by means of a laser diffraction technique according to ISO 13320 Standard with a LS 13320 Beckman Coulter equipment. Samples were examined by X-ray diffraction (XRD) in a Bruker D8 Advance X-ray powder diffractometer equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-dimensional detector. The diffraction pattern was obtained over the 2θ range of 10° to 80° with a step of 0.019°. The assignment of crystalline phases was performed using of Joint Committee on Powder Diffraction Standards and

DIFFRAC.EVA software; quantification of the crystal phase composition was performed by Rietveld refinement using TOPAS software.

2.3. CO₂ uptake experiments

A thermobalance Q500 from TA Instruments was used to obtain the CO₂ uptake capacity of the prepared sorbents. The performance of the sorbents was first tested under a flow of 65 ml/min containing 92.5% CO₂ (N₂ as balance).

The sample was in-situ pre-treated during 30 min at 110°C under N₂; after that, it was heated up to the carbonation temperature at a heating rate of 20 °C/min and equilibrated during 10 min under N₂. Then, the gas was switched to CO₂ and an isothermal period of 120 min at the carbonation temperature was maintained. Blank tests were performed for each carbonation temperature running condition to correct buoyancy.

3. Results and Discussion

The main variables determining the sinterability and the sintered microstructure of a powder may be divided into two categories: material variables and process variables⁷. The variables related to starting materials include not only chemical composition but also particle size and particle shape. In this work, well defined commercially available starting materials have been used and only a reproducible mixing process in a planetary ball mill was applied to the powders before they underwent heat treatment. On the other hand, process variables include temperature, time and heating rate⁷. In a first set of synthesis experiments, heating rate of 5 °C/min and holding time of 4 h were maintained constant and synthesis temperatures from 600 to 900 °C were selected. This range of temperatures was selected according to results obtained from a thermochemical model developed with the “Equilibrium Compositions Module” of HSC Chemistry 6.12 software (Fig. 1). This module utilizes the Gibbs energy minimization method and GIBBS solver was used for the calculations.

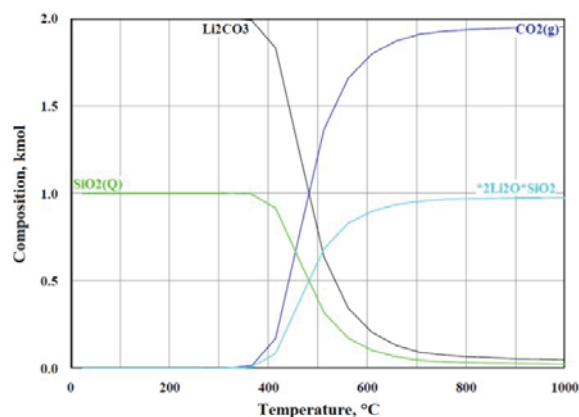


Fig. 1. Effect of synthesis temperature on the reaction products according to reaction (1).

Table 1. Heat treatment conditions for solid state preparation of Li_4SiO_4 in the literature and CO_2 uptake performance.

Ref.	Li source	Si source	Heat treatment conditions			Carbonation T(°C)/CO ₂ conc,%/CO ₂ uptake, %		
			T (°C)	rate (°C/min)	time (h)			
4	Li_2CO_3	SiO_2	1000	-	8	700/100/35	500/20/27	500/2/27
9	Li_2CO_3	SiO_2	950	-	2	-	-	-
10	Li_2CO_3	diatomite	700	-	4	620/50/24.5	-	-
11	Li_2CO_3	SiO_2	750	-	6	575/100/17	575/10/~7	700/10/0
12	Li_2CO_3	SiO_2	900	60	4	580/4/~1	-	-
13	Li_2CO_3	FA	950	-	8	500/100/4.7	-	-
14	Li_2CO_3	SiO_2	850	-	8	675/100/36.3	-	-
15	Li_2CO_3	SiO_2	800	-	4	500/100/~5	550/100/~12	600/100/~30
16*	Li_2CO_3	SiO_2	850	-	8	460/100/7.7	560/100/16.3	-
17**	Li_2O	SiO_2	800	-	8	-	-	-
18	Li_2CO_3	SiO_2	900/950	-	4	700/80/34.7	-	-
19	Li_2CO_3	SiO_2	800	6.7	6	-	-	-
20	LiOH	SiO_2	600/700/800	5	7	Porous 550/100/29.8	Non-porous 550/100/~8	-
8	Li_2CO_3	Ash	800	-	4	550/100/~7	680/100/31.6	-
21***	Li_2CO_3	SiO_2	720	5	6	Larger particles 668/100/19.2	Smaller particles 715/100/30.5	-
22	Li_2CO_3	H_2SiO_3	800	-	4	700/100/18	-	-
22	Li_2CO_3	H_2SiO_3	900	-	4	700/100/20.9	-	-
23	Li_2CO_3	SiO_2	700	-	20	600/100/~10	-	-
24	Commercial Li_4SiO_4	-	-	-	-	700/100/33.0	-	-
25	Li_2CO_3	SiO_2	750	-	6	515/10/1.1	565/10/2.1	590/10/0
26	Li_2CO_3	SiO_2	1000	-	10	700/100/32	-	-

* authors used different CO_2 flows. At increasing CO_2 flow, CO_2 uptake decreases with temperature.

** low temperature (<80°C) and humidity

*** prepared with different particle size

- Means not provided

Calculations show the change of predicted reaction products of reaction (1) at increasing synthesis temperature. $2\text{Li}_2\text{O}\cdot\text{SiO}_2$ in Fig. 1 is another chemical formula notation of Li_4SiO_4 (lithium orthosilicate)²⁷. The thermochemical data which was published by Barin et al.²⁷ were used for the thermodynamical calculations of Li_4SiO_4 formation by the software. It was predicted that the formation of Li_4SiO_4 starts at 446 °C and Li_4SiO_4 is the main component in solid reaction products by about 900 °C and at higher reaction temperatures.

If full conversion is achieved in reaction (1), the weight of Li_4SiO_4 obtained after heat treatment should be 2.688 g, based on starting weight of reactants, which was a total of 5 g (including the Li_2CO_3 molar excess) and the molar reaction 2:1. However, only that weight was observed under a heat treatment temperature of 900 °C, while higher weights were obtained for the other tested temperatures. Accordingly, it can be expected that unconverted Li_2CO_3 is present in those samples.

Fig. 2 shows the diffractograms of the samples obtained at 700, 800 and 900 °C with a heating rate of 5 °C/min and holding time of 4 h. As can be seen, Li_2CO_3 can be found as a crystalline phase in samples obtained at 700 and 800 °C, but at 900 °C reaction (1) has been completed and Li_4SiO_4 is the only present crystalline phase. The Li_4SiO_4 diffraction pattern was fitted to the JCPDS file 76–1085, corresponding to monoclinic system and P121/m1 space group, with reference cell parameters a: 5.147 Å, b: 6.094 Å, c: 5.293 Å and β : 90.33 °. Quantification of the crystalline phase accounts for 79.6, 92.5 and 100 % of Li_4SiO_4 for samples 700-5-4, 800-5-4 and 900-5-4, respectively. Accordingly, it was not necessary to use higher synthesis temperature than 900 °C.

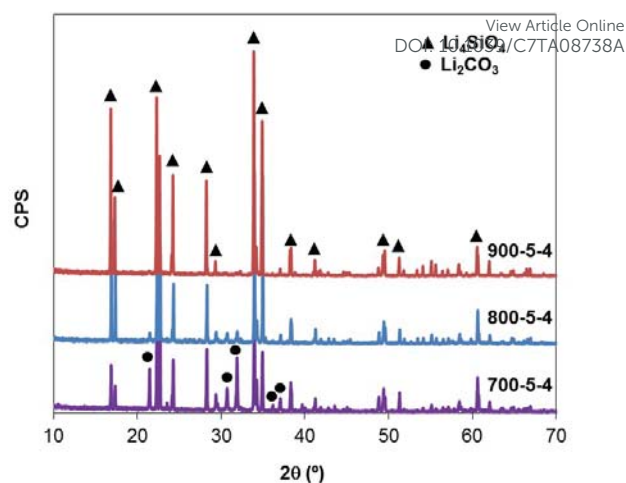


Fig. 2. XRD patterns of samples synthesised at a heating rate of 5 °C/min, at different temperatures during 4 h.

Fig. 3 a and b shows the CO_2 uptake for those samples under a flow containing 92.5 % CO_2 (N_2 balance) at isothermal carbonation temperatures of 600 and 700 °C, respectively. Except for sample 600-5-4, the CO_2 uptake is higher at a temperature of carbonation of 600 °C and, accordingly, this was the temperature selected for CO_2 uptake experiments. This is in agreement with inversion point temperatures reported for reaction (2) by using theoretical calculations²⁸.

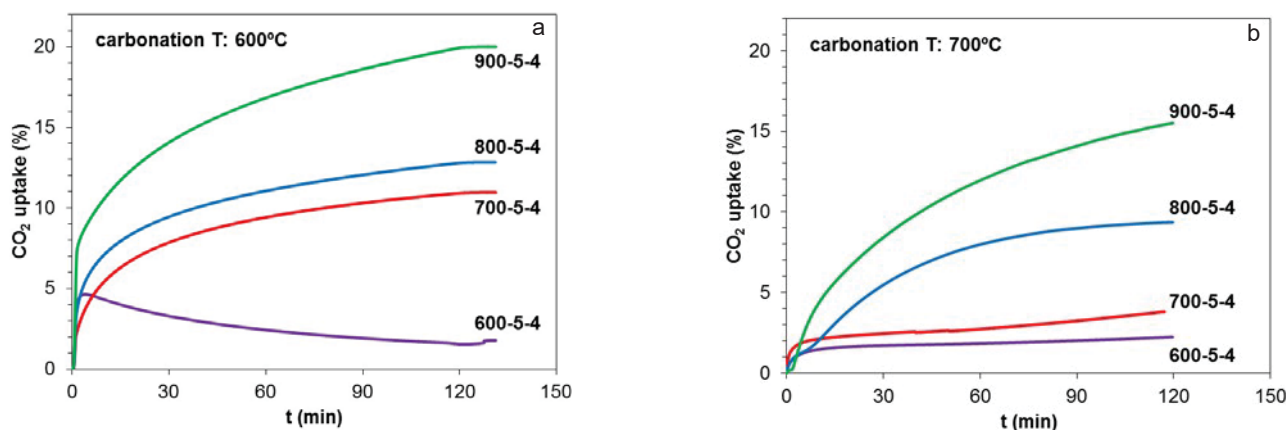
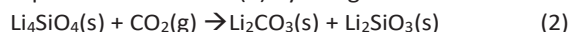


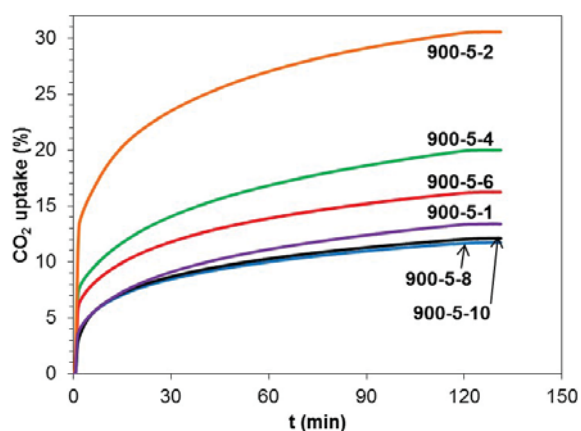
Fig. 3. CO_2 uptake (CO_2 conc. 92.5%) at 600 °C and 700 °C of samples synthesised at a heating rate of 5 °C/min and different temperatures during 4 h.

The inversion temperature separates CO_2 absorption from CO_2 desorption conditions. Depending on the CO_2 partial pressure, absorption will take place at different temperatures. For a given value of CO_2 partial pressure (0.92 in this case), conditions above the equilibrium line need to be met for the absorption process to take place. An optimum carbonation temperature between 550 and 600 °C was also found elsewhere²⁹.

Sample 700-5-4 exhibited a faster chemisorption at 600 °C; it should be taken into account that isotherm at 700 °C was performed over the chemisorption-desorption temperature limit²⁸, as the maxima CO_2 chemisorption temperature is about 600 °C. Then, at these specific conditions, Li_4SiO_4 is chemisorbing CO_2 , but at the same time, the Li_2CO_3 produced must decompose and desorbs CO_2 .

For sample 600-5-4, CO₂ uptake at 700 °C is significantly lower than that for other samples. This is probably due to: a) its pre-treatment at 700 °C under N₂ flow, which could have modified its composition because a 700 °C temperature is higher than that used for the synthesis of that sample, i.e., 600 °C; and b) lowest content of reactive phase, i.e., Li₄SiO₄. Also, for a carbonation temperature of 600 °C, CO₂ capture by sample 600-5-4 (Fig. 3a) is very limited, which corroborates its impure character and the need for a higher synthesis temperature to obtain pure Li₄SiO₄ sorbent materials.

The highest CO₂ uptake was obtained for sample synthesised at 900 °C, probably due to its 100% Li₄SiO₄ composition. However, the acquired uptake value of 20.0% is far from the theoretical one of 36.7 % (under pure CO₂). Thus, a synthesis temperature of 900 °C was selected to further investigate the influence of holding time and heating rate on the sintering process and on the CO₂ uptake.

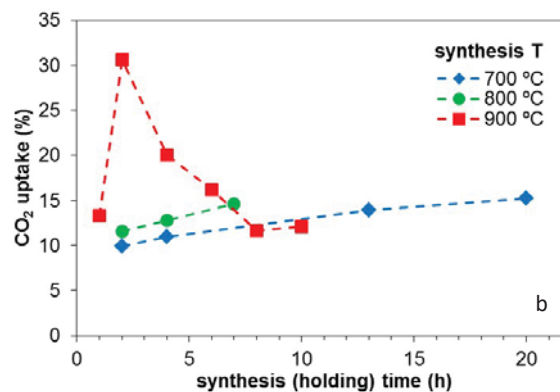


a

Fig. 4 (a) depicts the CO₂ uptake of samples synthesised at 900 °C, at different holding times and constant heating rate of 5 °C/min. As can be seen, the increase of the holding time reduces considerably the CO₂ uptake; this result cannot be compared with previously reported values for similar synthesis temperatures^{14, 16}, because as previously mentioned, the heating rate used in those studies is not provided. On the other hand, a decrease of the holding time increases the CO₂ uptake up to a maximum, obtained at a holding time of 2 h. A further decrease of the holding time dramatically decreases the CO₂ uptake.

In order to verify if this maximum of 2 h holding time was also an optimum value under different synthesis temperatures, shorter and larger holding times were used in experiments with synthesis temperatures of 700 °C and 800 °C (Fig. 4b). It is noteworthy that the observed trend for samples prepared at those synthesis temperatures differ from that observed at 900 °C (Fig. 4(b)), i.e. CO₂ uptake values increase steadily over the range of holding times studied. This fact could be explained in terms of increasing Li₄SiO₄ content with time, as it is shown below.

For the purpose of this study, a synthesis temperature of 900 °C and holding time of 2 h were therefore selected based on measured CO₂ uptake of the produced material. A last set of experiments was performed under the aforementioned synthesis conditions and heating rate values ranging from 2 to 20 °C/min. Fig. 5 shows the CO₂ uptake of samples synthesised at 900 °C during 2 h at different heating rates. Again, a maximum CO₂ uptake value was identified at 5 °C/min and, a very low or very high heating rate has a negative effect on the CO₂ capture performance of the sorbent (Fig. 5b).



b

Fig. 4. Effect of holding time during Li₄SiO₄ synthesis at 900 °C and a heating rate of 5 °C/min on CO₂ uptake at carbonation temperature of 600 °C: (a) CO₂ uptake curves; (b) CO₂ uptake trend with holding time.

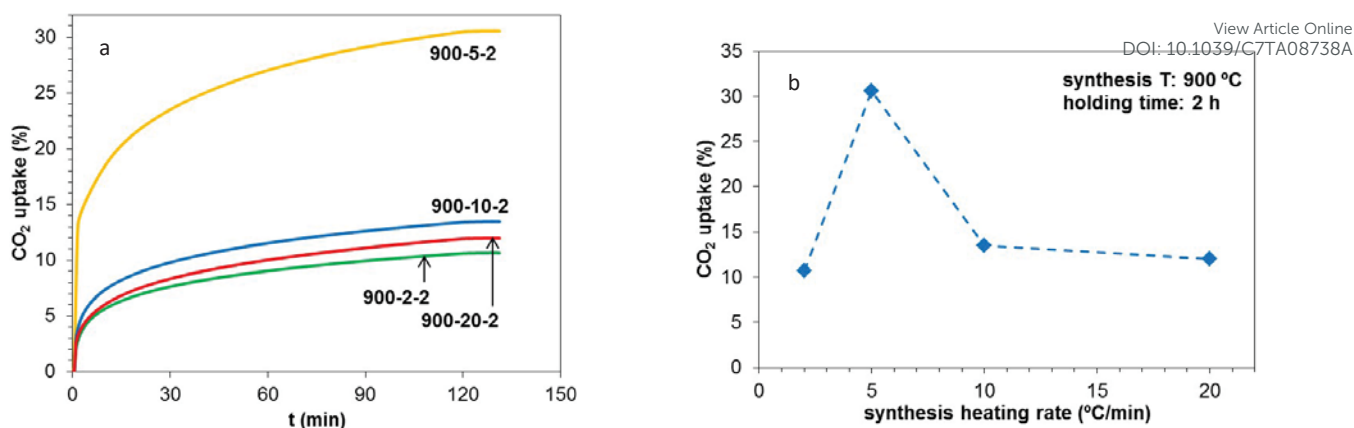


Fig. 5. Effect of heating rate (during synthesis at a temperature of 900 °C and holding time of 2 h) on CO₂ uptake at a carbonation temperature of 600 °C: (a) CO₂ uptake curves; (b) CO₂ uptake trend with heating rate.

Thus, results indicate that the optimum synthesis conditions to prepare Li₄SiO₄ by solid state method in order to maximize CO₂ uptake at high temperature (600 °C) are a heating rate of 5 °C/min, temperature of 900 °C and holding time of 2 h.

From these results it seems be clear that the synthesis of Li₄SiO₄ almost pure is not condition enough to reach high CO₂ uptake values: this material has to possess some characteristics which give it a CO₂ uptake performance near to the theoretical uptake value.

Particle size and surface area of synthetic ceramic materials have been previously investigated in the literature as the main characteristics that affect their CO₂ capture performance. For instance, Kanki et al.²³ reported that CO₂ capture capacities for Li₄SiO₄ varied after milling the sample. They observed a change of CO₂ uptake from 10% to approx. 30% for as-prepared Li₄SiO₄ and 120 min milled Li₄SiO₄, respectively, and they measured surface areas five times larger after 120 min ball milling. In the same way, Venegas et al.¹⁵ also reported enhanced CO₂ uptake when using very small ceramic particles (3 μm). In this work, samples were grinded under the same conditions in order to avoid the influence of particle size on CO₂ uptake results.

BET surface areas were measured for all synthesised samples and analysis of the particle size distribution of some randomly selected samples was also carried out (Table 2). As it can be seen, BET surface areas, mean particle size and particle size distribution of the samples are quite similar, which discard their effect on CO₂ uptake performance.

However, additional variables associated with particle size reduction need to be considered, as previously pointed out in the literature. Based on XRD patterns, Kanki et al.²³ reported not only the CO₂ uptake change after ball milling due to

modification of surface properties (surface area and particle size) but also a transition to amorphous Li₄SiO₄ with increasing ball milling times. The degree of amorphousness has been already claimed as a beneficial property that enables movement of ions among phases in looping processes for other solids³⁰; however, in this study, even though the amorphous content obtained from XRD (by S-Q method) for samples 700-5-4, 800-5-4, 900-5-4 and 900-5-2 is very similar (values of 11.8%, 13.1%, 11.1% and 10.2%, respectively), samples exhibited quite different CO₂ uptake capacities, ranging from 11% to 30.5%.

Venegas et al.¹⁵ attributed their enhanced CO₂ capture capacities when using very small particles (3 μm) to the presence of more Li atoms on the surface of the particles. This fact was in agreement with observations from Gauer and Heschel¹⁴, who claimed the introduction of vacancies into the crystal lattice of Li₄SiO₄ as the reason to improve Li⁺ mobility and to facilitate O²⁻ diffusion by offering more sites for ions hopping. These findings are in agreement with the mechanism proposed for the second stage of CO₂ uptake by López-Ortiz²⁸ for CO₂ uptake by Li₄SiO₄ sorbents. According to that study, CO₂ capture takes place in two stages; firstly, the Li₄SiO₄ particles react with CO₂ at the particle surface to form an external shell of lithium carbonate (Li₂CO₃) and a lithium secondary phase (Li₂SiO₃), and secondly, instead of a CO₂ diffusion process the authors reported a Li⁺ and O²⁻ ionic diffusion phenomena related with the introduction of vacancies in the crystal. These vacancies or “point defects”, as reported by Chang et al.³¹, allow fast Li-ion conduction, which could be the responsible for enhanced CO₂ uptake.

Table 2. Physical properties of some of the prepared samples.

View Article Online
DOI: 10.1039/C7TA08738A

Sample	surface area m ² /g	Particle size					
		Mean μm	<10% μm	<25% μm	<50% μm	<75% μm	<90% μm
700-5-4	1.5	21.3	2.7	8.0	18.9	34.2	44.9
700-5-20	1.7	19.9	1.6	7.1	17.3	33.3	40.2
800-5-4	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
800-5-7	1.4	27.7	7.5	12.6	20.8	34.2	55.4
900-5-1	1.2	19.2	2.2	6.1	15.2	32.2	44.0
900-5-2	1.2	23.2	3.6	9.3	20.5	36.7	46.6
900-5-4	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
900-5-8	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
900-5-10	1.0	24.6	4.5	9.1	23.8	38.2	43.9
900-20-2	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. not determined

It has been also stated previously that the smaller the crystal size the higher the abundance of point defects into metal crystals³². Thus, the importance of the crystal size of the samples prepared under different synthesis conditions cannot be disregarded.

The only crystal phase present in all the samples prepared at a synthesis temperature of 900 °C is Li₄SiO₄, except for sample 900-5-1, in which traces of Li₂CO₃ can be found (<1%, according to XRD quantification). However, for synthesis temperatures of 700 and 800 °C, Li₂CO₃ is present: 73.7%, 79.6% and 80.7% for samples 700-5-2, 700-5-4 and 700-5-20, respectively, and 89.9%, 92.5% and 93.1% for samples 800-5-2, 800-5-4 and 800-5-7, respectively.

In order to obtain Li₄SiO₄ phase crystallite size, a full pattern decomposition of XRD diffractograms was performed using the Pawley method with a pseudo-Voigt approach. The volume weighted column height (LVol-IB) was taken to obtain the average crystallite size.

Figure 6 shows the influence of Li₄SiO₄ crystal size on CO₂ capture exhibited by the different prepared samples. Strong evidence was found showing that the crystal size of metals has an effect on the adsorption properties of catalysts and this fact was related with the total number of surface atoms, which exponentially depends on crystal size³².

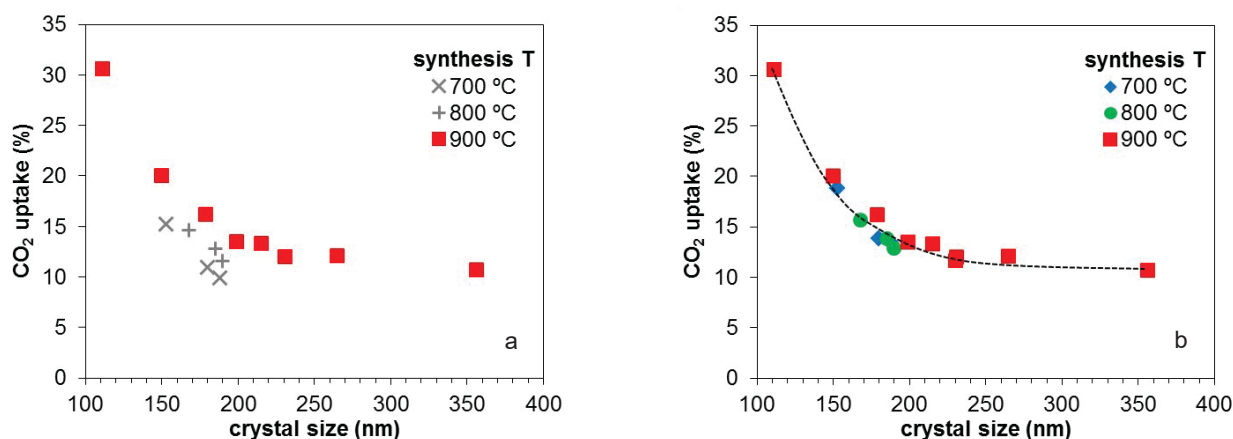


Fig 6. Influence of Li₄SiO₄ crystal size on CO₂ uptake. (a) CO₂ uptake referred to the total amount of sample; (b) CO₂ uptake normalised to the Li₄SiO₄ content of samples.

As can be seen in Fig. 6a, the general trend is that previously observed for metal crystals, i.e., lower crystal size enhanced catalytic and/or sorption properties. However, it seems that there is not a clear correlation between the crystal size in the range of 150-180 nm and the CO₂ uptake of samples prepared at the three studied temperatures. As the only compound that is able to adsorb CO₂ is Li₄SiO₄, the capture performance of those samples which contain unconverted Li₂CO₃ cannot be directly compared with those ones composed of almost pure

Li₄SiO₄. Accordingly, the CO₂ uptake was re-calculated by normalising the values with respect to the Li₄SiO₄ content of the samples. For samples synthesised at 900 °C the CO₂ uptake values are the same as those depicted in Figure 6a, and only the values corresponding to samples synthesised at 700 °C and 800 °C changed.

As can be seen in Fig. 6b, all data points are now under the same general trend, indicating that a lower crystal size uptake barely changes at crystal sizes larger than 200 nm. This

relationship between crystal size and catalysts^{33, 34} as well as sorbent's performance³⁴⁻³⁶ has already been observed.

The line depicted in Fig. 6b indicates only a trend. If a polynomial regression is obtained for data corresponding to samples synthesised at 900 °C, the regression coefficient obtained is 0.999. When the points corresponding to samples synthesised at 700 and 800 °C in Fig. 6a are included in the regression, the regression coefficient obtained is 0.952. But after the normalisation of those values, the regression in Fig. 6b gives a regression coefficient of 0.992. This fact indicates that the results of samples obtained at synthesis temperature of 900 °C are not the only responsible of the trend observed.

Under the studied conditions, the most important parameter affecting the crystal size has been the holding time. Long holding times allow the formation of large crystals. Very low holding time had a negative effect on CO₂ uptake, because the high crystal size obtained. In that case it is to say for the sample prepared at 900 °C the conversion to Li₄SiO₄ was not complete. For the same synthesis temperature and holding time, it seems that a very slow heating rate allows the formation of large crystals as reproducing a natural crystal formation; accordingly, that sample (900-2-2) exhibited the lowest CO₂ uptake performance.

It has been reported that the CO₂ chemisorption on Li₄SiO₄ fits to a double exponential model¹⁶ (eq. 3) assuming that there are two different processes during CO₂ absorption: chemisorption and lithium diffusion.

$$y = Ae^{-k_1t} + Be^{-k_2t} + C \quad (3)$$

In this equation, y represents the weight change of the sorbent, k_1 and k_2 are the rate constants for the CO₂ chemisorption on the sorbent surface and CO₂ chemisorption kinetically controlled by lithium diffusion, respectively, and t is the time.

As stated above, the crystal size controls the CO₂ capture under the studied conditions. Thus, it is supposed that the CO₂ absorption kinetic should change depending on the crystal size.

Table 3 reports the kinetic parameters obtained from the fitting of some isotherms (obtained at 600 °C), including R² values; as represented by the high R² values, the model accurately fitted CO₂ experimental absorption isotherms.

The values of k_1 were one order of magnitude larger than the k_2 values, indicating that the overall absorption CO₂ kinetics is controlled by the lithium diffusion rate; these values are in agreement with those found in the literature^{8, 16}. Sample 900-5-2 exhibited the highest k_1 value and this can be attributed to an increased number of sites for CO₂ chemisorption because its lower crystal size. Moreover, this sample also exhibited the highest k_2 value and this can be originated because the shorter diffusion path for lattice lithium as the lower crystal size.

Fig. 7 shows the relationship between the rate constants and the crystal size for samples in Table 3. Despite some dispersion of k_1 and k_2 values were observed, a trend is observed; in addition, it seems that at crystal sizes higher than 200 nm both rate constants are quite insensitive to a further increase of crystal size; this result is similar to that found in Fig. 6. This fact could be explained in terms of the intrinsic diffusion coefficient

for Li diffusion being the same for Li₄SiO₄, except when the diffusion is enhanced by shorter path length in smaller Li₄SiO₄ crystals. In addition, smaller crystal sizes lead to the introduction of vacancies into the crystal lattice of Li₄SiO₄ which improve Li mobility¹⁴.

These results seemed to confirm that for quite similar Li₄SiO₄ particle size and surface area, the crystal size was the materials characteristic to which CO₂ uptake performance of the samples is related.

Table 3. Kinetic parameters obtained from the experimental data fitted to a double exponential model (eq. 3)

sample	k_1 (s ⁻¹)	k_2 (s ⁻¹)	R ²
700-5-4	2.86 x10 ⁻³	2.60 x10 ⁻⁴	0.9998
800-5-4	3.01 x10 ⁻³	2.53 x10 ⁻⁴	0.9967
900-5-1	1.99 x10 ⁻³	2.10 x10 ⁻⁴	0.9998
900-5-2	3.36 x10 ⁻³	3.09 x10 ⁻⁴	0.9980
900-5-4	3.03 x10 ⁻³	2.62 x10 ⁻⁴	0.9991
900-5-8	2.18 x10 ⁻³	2.07 x10 ⁻⁴	0.9994
900-2-2	1.85 x10 ⁻³	2.07 x10 ⁻⁴	0.9995
900-10-2	2.90 x10 ⁻³	2.68 x10 ⁻⁴	0.9987

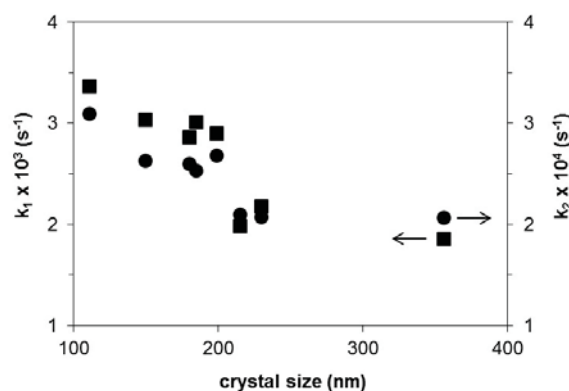


Fig. 7. Relationship between kinetic parameters obtained from the experimental data fitted to a double exponential model (eq. 3) and crystal size.

This work has been focused on optimize synthesis conditions to maximise CO₂ uptake. The high CO₂ absorption capacity should be maintained along several cycles of CO₂ absorption-desorption. Ongoing work on this topic will be further published, but previous results indicate that after 10 cycles the CO₂ uptake is maintained.

Conclusions

The effect of heating rate, synthesis temperature and holding time on prepared Li₄SiO₄ from Li₂CO₃ and SiO₂ by solid-state method and its influence on CO₂ uptake performance have been evaluated. Unconverted Li₂CO₃ is present in samples prepared at low synthesis temperatures under the same heating rate and holding time conditions. The content of

Li_2CO_3 in the synthesised materials decreases with increasing synthesis temperatures up to 900 °C, at which complete conversion to Li_4SiO_4 is reached. For this temperature, it was found that a synthesis process under a heating rate of 5 °C/min and holding time of 2 h produces the material exhibiting the maximum CO_2 uptake (30.5%) at 600 °C, among all samples prepared under a wide range of conditions. This sample also exhibited the highest rate constant values (k_1 and k_2).

The particle size and BET surface area are very similar for all prepared samples, and crystal size was found to be the only materials characteristic to which CO_2 uptake performance of the samples could be attributed, i.e., the lower the crystal size the higher CO_2 uptake. At crystal sizes over ca. 200 nm, increasing values of crystal size seem to have limited effect on CO_2 uptake. Samples with lower crystal size exhibit higher rate constant values, indicating an increased number of sites for CO_2 chemisorption because its lower crystal size. Moreover, smaller crystal sizes lead to the introduction of vacancies into the crystal lattice of Li_4SiO_4 which improve lithium mobility and facilitate ions hopping. At crystal sizes over ca. 200 nm both rate constants are quite insensitive to a further increase of crystal size because the reduction of vacancies in the crystal lattice at higher crystal sizes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The financial support of the Research Centre for Carbon Solutions (RCCS) at Heriot-Watt University is gratefully acknowledged.

M.T. Izquierdo thanks the Spanish Ministry of Education, Culture and Sports for the financial support under "Salvador Madariaga" programme for senior researchers (ref no. PRX17/00264).

A. Turan acknowledges the financial support for this research from The Scientific and Technological Research Council of Turkey (TÜBİTAK) under 2219 scholarship programme (application no: 1059B191600366 and 2016/1).

Notes and references

- 1 H. Kugai, N. Ota, S. Yamanaka, Y. Hisagai, Y. Ota, Negative electrode of lithium secondary battery, Patent n°. EP1174936-A2, Sumitomo Electric Ind Co; Kugai H; Ota N; Yamanaka S; Sumitomo Electric Ind Ltd.
- 2 Z. L. Gong, Y. X. Li and Y. Yang, *Journal of Power Sources*, 2007, **174**, 524-527.
- 3 Y. J. Feng, K. M. Feng, Q. X. Cao, J. Hu and H. Tang, *Fusion Engineering and Design*, 2012, **87**, 753-756.
- 4 M. Kato, K. Nakagawa, K. Essaki, Y. Maezawa, S. Takeda, R. Kogo and Y. Hagiwara, *International Journal of Applied Ceramic Technology*, 2005, **2**, 467-475.

- 5 J. C. Abanades, *Chemical Engineering Journal*, 2002, **90**, 303-306. DOI: 10.1039/C7TA08738A
- 6 K. Essaki and M. Kato, *Journal of Chemical Engineering of Japan*, 2006, **39**, 1161-1164.
- 7 S.-J. L. Kang, in *Sintering*, Butterworth-Heinemann, Oxford, 2005, pp. 3-8.
- 8 K. Wang, P. Zhao, X. Guo, D. Han and Y. Chao, *Environmental Progress & Sustainable Energy*, 2015, **34**, 526-532.
- 9 E. Carella and M. T. Hernandez, *Ceramics International*, 2014, **40**, 9499-9508.
- 10 S. Shan, Q. Jia, L. Jiang, Q. Li, Y. Wang and J. Peng, *Ceramics International*, 2013, **39**, 5437-5441.
- 11 S. Zhang, Q. Zhang, H. Wang, Y. Ni and Z. Zhu, *International Journal of Hydrogen Energy*, 2014, **39**, 17913-17920.
- 12 M. Seggiani, M. Puccini and S. Vitolo, *International Journal of Greenhouse Gas Control*, 2013, **17**, 25-31.
- 13 M. Olivares-Marin, T. C. Drage and M. M. Maroto-Valer, *International Journal of Greenhouse Gas Control*, 2010, **4**, 623-629.
- 14 C. Gauer and W. Heschel, *Journal of Materials Science*, 2006, **41**, 2405-2409.
- 15 M. J. Venegas, E. Fregoso-Israel, R. Escamilla and H. Pfeiffer, *Industrial & Engineering Chemistry Research*, 2007, **46**, 2407-2412.
- 16 R. Rodriguez-Mosqueda and H. Pfeiffer, *Journal of Physical Chemistry A*, 2010, **114**, 4535-4541.
- 17 B. Alcantar-Vazquez, P. R. D. Herrera, A. B. Gonzalez, Y. Duan and H. Pfeiffer, *Industrial & Engineering Chemistry Research*, 2015, **54**, 6884-6892.
- 18 M. E. Bretado, V. G. Velderrain, D. L. Gutierrez, V. Collins-Martinez and A. L. Ortiz, *Catalysis Today*, 2005, **107-08**, 863-867.
- 19 D. Mandal, M. C. Jadeja and B. K. Chougule, *Indian Chemical Engineer*, 2017, **59**, 21-30.
- 20 H. Kim, H. D. Jang and M. Choi, *Chemical Engineering Journal*, 2015, **280**, 132-137.
- 21 H. Xu, W. Cheng, X. Jin, G. Wang, H. Lu, H. Wang, D. Chen, B. Fan, T. Hou and R. Zhang, *Industrial & Engineering Chemistry Research*, 2013, **52**, 1886-1891.
- 22 G. J. Rao, R. Mazumder, S. Bhattacharyya and P. Chaudhuri, *Journal of Alloys and Compounds*, 2017, **725**, 461-471.
- 23 K. Kanki, H. Maki and M. Mizuhata, *International Journal of Hydrogen Energy*, 2016, **41**, 18893-18899.
- 24 S. M. Amorim, M. D. Domenico, T. L. P. Dantas, H. J. Jose and R. F. P. M. Moreira, *Chemical Engineering Journal*, 2016, **283**, 388-396.
- 25 S. Zhang, Q. Zhang, C. Shen, Y. Ni, Y. Wu, Q. Wu and Z. Zhu, *Industrial & Engineering Chemistry Research*, 2015, **54**, 7292-7300.
- 26 K. Yamauchi, N. Murayama and J. Shibata, *Materials Transactions*, 2007, **48**, 2739-2742.
- 27 I. K. Barin, O. Kubaschewski, O., *Thermochemical properties of inorganic substances. Supplement.*, Springer-Verlag Berlin Heidelberg, Düsseldorf, Germany, 1977.
- 28 A. Lopez Ortiz, M. A. Escobedo Bretado, V. Guzman Velderrain, M. Melendez Zaragoza, J. Salinas Gutierrez, D.

ARTICLE

Journal Name

- Lardizabal Gutierrez and V. Collins-Martinez, *International Journal of Hydrogen Energy*, 2014, **39**, 16656-16666.
- 29 K. Essaki, M. Kato and H. Uemoto, *Journal of Materials Science*, 2005, **40**, 5017-5019.
- 30 30. A. Cabello, P. Gayan, A. Abad, L. F. de Diego, F. Garcia-Labiano, M. T. Izquierdo, A. Scullard, G. Williams and J. Adanez, *International Journal of Greenhouse Gas Control*, 2016, **52**, 120-129.
- 31 C. C. Chang, C. C. Wang and P. N. Kumta, *Materials & Design*, 2001, **22**, 617-623.
- 32 R. Van Hardeveld and F. Hartog, *Surface Science*, 1969, **15**, 189-230.
- 33 D. Y. Murzin, *Journal of Molecular Catalysis a-Chemical*, 2010, **315**, 226-230.
- 34 34. V. N. Parmon, *Doklady Physical Chemistry*, 2007, **413**, 42-48.
- 35 C. Gómez-Giménez, D. Ballester, N. Ferrer, B. Rubio and M. T. Izquierdo, *Journal of Physics and Chemistry of Solids*, 2017, **110**, 173-179.
- 36 A. I. Rusanov, *Surface Science Reports*, 2005, **58**, 111-239.

View Article Online
DOI: 10.1039/C7TA08738A

Optimum Li_4SiO_4 synthesis conditions by SS method to enhance CO_2 uptake have been obtained: the lower crystal size the higher uptake.

