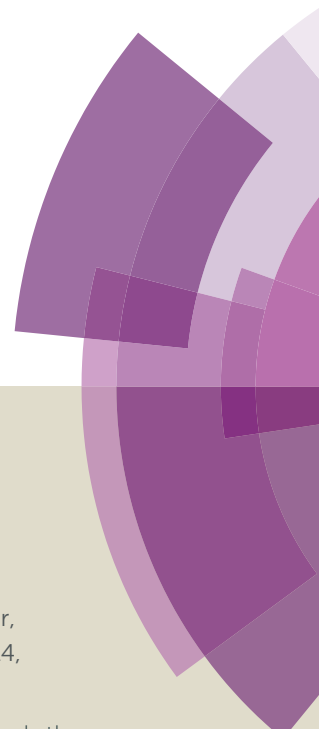


# Journal of Materials Chemistry A

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# Enhanced CO<sub>2</sub> absorption kinetics in lithium silicate platelets synthesized by a sol-gel approach

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Platelet shaped lithium orthosilicate particles synthesized by a sol gel approach employing the precursors lithium nitrate and colloidal silica displayed enhanced absorption kinetics for CO<sub>2</sub> compared to the powders prepared by a solid-state reaction process involving Li<sub>2</sub>CO<sub>3</sub> and silica. The sol-gel samples showed CO<sub>2</sub> absorption capacity of 350 mg/g at an absorption rate of 22.5 mg/g/min; a value 70% higher than the rate of 13.2 mg/g/min measured with the solid state samples under similar conditions. The higher sorption kinetics of CO<sub>2</sub> by the sol-gel derived lithium orthosilicate could be attributed to the unique platelet morphology of the particles with a very small thickness. A porous carbon mesh coated with the sol-gel based particles exhibited CO<sub>2</sub> absorption capacity of 150 mg/g at an absorption rate of 37.5 mg/g/min. This supported absorbent also showed stable absorption and desorption performance for the 8 cycles examined in this study. The excellent absorption characteristics of the sol-gel prepared powders, more specifically the coated strips provide a successful pathway for the commercialisation of these materials.

Keywords: lithium silicate; CO<sub>2</sub> absorption, sol gel synthesis, supported absorbents, cyclic stability

## 1. Introduction

Carbon dioxide emission to the atmosphere is an increasingly important concern owing to its perceived influence over the elevation in atmospheric temperature. Of the various approaches discussed to limit this threat, selective carbon dioxide capture by absorption followed by its sequestration is one of the most scrutinized strategies. Several research efforts are ongoing to design and develop new sorbents for selective CO<sub>2</sub> capture from power plant flue gases as well as other CO<sub>2</sub> discharging streams.<sup>1-10</sup> The development of advanced functional materials satisfying the essential requirements of faster sorption kinetics, higher sorption capacity, selectivity and durability is therefore of great significance.

Currently, there is significant interest in the development of regenerable sorbent materials for CO<sub>2</sub> absorption at high temperature.<sup>11-15</sup> Among the various carbon dioxide sorbents, lithium based ceramic absorbents are candidate materials for CO<sub>2</sub> capture at high temperatures (400-700°C).<sup>3,15-25</sup> In particular, lithium orthosilicate is considered to be the most promising material for designing efficient CO<sub>2</sub> separation systems by virtue of its large absorption capacity, faster kinetics and reasonable material costs.<sup>11,23,26-30</sup> Moreover lithium silicate shows excellent chemisorption properties wherein up to 8.3 mmol of CO<sub>2</sub> could be absorbed per gram of sorbent.<sup>22</sup> It also exhibits better thermal cyclability over a wide range of temperature.<sup>31</sup>

A number of strategies are reported in the literature for the synthesis of  $\text{Li}_4\text{SiO}_4$ , which include solid state mixing, sol-gel synthesis, combustion synthesis and ball milling techniques.<sup>2,32-</sup>

<sup>38</sup> Kato et al. (2002), the original inventors of lithium based  $\text{CO}_2$  absorbents, investigated  $\text{CO}_2$  absorption properties of  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{ZrO}_3$  in a wide range of temperature and  $\text{CO}_2$  concentrations. Their results showed that under similar sorption conditions, the absorption capacity of  $\text{Li}_4\text{SiO}_4$  is 30 times faster than that of the  $\text{Li}_2\text{ZrO}_3$ .<sup>7</sup> Lithium silicate is commonly synthesised by the reaction between silica and lithium carbonate powders, under dry or wet conditions in a ball mill followed by heat-treatment. Such solid state mixing processes are known to result in poor distribution of powder particles leading to inferior absorption properties. Numerous other issues such as contamination, volatilization as well as agglomeration of particles leading to inconsistency in structure and composition are also reported.<sup>20</sup> Wet chemical approaches are known to produce materials with controlled particles sizes, uniform size distribution, excellent homogeneity and large surface area. Such desirable powder attributes, help to realize high sorption capacity and faster kinetics in adsorbent materials. Our group was one of the first to report on the sol-gel synthesis of lithium zirconate based absorbents for the selective removal of  $\text{CO}_2$ .<sup>18,28</sup> Pfeiffer et al. have compared the influence of processing conditions such as solid state reaction, precipitation and sol-gel method on the composition and morphology of lithium meta silicate powders meant for breeder material applications.<sup>39</sup> The same authors have also reported on the wet chemical synthesis of lithium silicate based absorbents in their recent papers.<sup>30, 40</sup> The effect of particle size of the precursor materials on the mixing of the precursors, is reported recently by Lu et al.<sup>33</sup> Peng et al. have reported the effect of precursor silicon source (diatomite and pure silica) on carbon dioxide absorption capacities of the resulting powders and shown that  $\text{Li}_4\text{SiO}_4$  based sorbents developed from diatomite exhibited better absorption-desorption performance and absorption capacity.<sup>41</sup> Results discussed in the said papers point to the importance of precursor chemistry, their physical properties, and the processing conditions on the  $\text{CO}_2$  absorption performance of the resulting materials.

The present work reports on the synthesis of  $\text{Li}_4\text{SiO}_4$  platelet shaped particles by a wet chemical synthetic procedure involving colloidal silica and  $\text{LiNO}_3$  solutions. The sorption/desorption kinetics of  $\text{CO}_2$  and the cyclic stability of the synthesised particles are reported. The excellent  $\text{CO}_2$  absorption performance exhibited by supported lithium silicate absorbents, coated on a porous carbon strip, is also reported in this paper for the first time to the best of our knowledge.

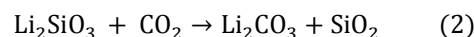
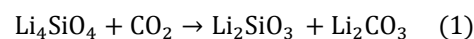
## 2. Experimental section

Lithium silicate was synthesised from lithium nitrate (Alfa Aesar, UK), and colloidal silica (Aldrich Chemicals, USA) as starting precursors. Initially, 15.4g of  $\text{LiNO}_3$  was dissolved in 225 ml of distilled water to prepare 1M aqueous lithium nitrate solution and was hydrolysed by the slow addition of

ammonium hydroxide (25%, S.D. FINE-CHEM Ltd., India) solution under constant stirring at room temperature, till the pH reached 8. Colloidal silica (3.3g, Aldrich Chemicals, USA) was added drop wise to this reaction mixture with constant stirring and kept at that condition for 1 h. The gel thus formed was aged further for 24 h at room temperature, dried at 110 °C and then heat-treated at 800°C (sample code - SG- $\text{LiSiO}_4$ ). Samples for comparison were prepared by the solid-state mixing and heat-treatment of silica and  $\text{Li}_2\text{CO}_3$  (Aldrich Chemicals, USA). Both the precursors were initially dried at 150 °C for 5 h and mixed mechanically in the molar ratio of 2.2:1. The mixture was dried at 100 °C/6h and calcined at 800 °C for 3 h. (sample code- SS- $\text{LiSiO}_4$ ). The crystalline phases of the powdered samples were analysed by X-ray diffraction (Philips X'pert Pro diffractometer) in the  $2\theta$  range 20–60° using Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). The morphological and micro structural analysis of the materials was carried out using a scanning electron microscope (SEM) operated at 20 kV. The BET surface area measurements were carried out by nitrogen adsorption using a Micromeritics Gemini 2375 surface area analyzer after degassing each sample at 200 °C for 2 h.  $\text{CO}_2$  absorption properties were measured using a TGA apparatus (Perkin Elmer STA 6000, Netherlands), in the temperature range of 150-750°C. In the set up used, actual temperatures close to sample were typically 5-10°C lower than the set temperatures that are mentioned throughout this paper.  $\text{CO}_2$ /Nitrogen flow rates through the sample chamber were ~50 ml/min unless otherwise mentioned. X-ray scattering set-up (Xeuss SAXS/WAXS system by Xenocs, France) was used to characterize the sample after  $\text{CO}_2$  absorption using Cu K $\alpha$  radiation ( $\lambda=0.154$  nm) generated at 0.60 mA and 50 kV in the  $2\theta$  range 4-36 °.

## 3. Results and discussion

The  $\text{CO}_2$  absorption mechanism of lithium orthosilicate involves the chemical conversion of lithium orthosilicate to lithium metasilicate or silica by the reaction with  $\text{CO}_2$  as in the following equations.<sup>30</sup>

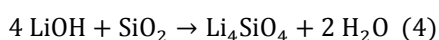
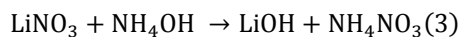


Based on the reaction (1) the theoretical absorption capacity of the  $\text{Li}_4\text{SiO}_4$  solid absorbent (MW=119.854) could be calculated as 36.7 wt% (8.3 mmol of  $\text{CO}_2$  per gram of  $\text{Li}_4\text{SiO}_4$ ). In practice, 30-35 wt% of  $\text{CO}_2$  could be absorbed at the temperature range of 400-700 °C followed by complete desorption at 600-800 °C depending upon the  $\text{CO}_2$  partial pressure, the exact stoichiometry and second phase/impurity present in the absorbent material.<sup>33</sup> Lithium rich phases like lithium orthosilicate and oxosilicate generally displays fast kinetics for  $\text{CO}_2$  absorption due to the extremely fast lithium ion hopping from core of the particle to the reaction interface. The completion of reaction forming silica as per equation (2) need absorption conditions favouring the take up of  $\text{CO}_2$  by the lithium metasilicate formed at the initial phase of the reaction

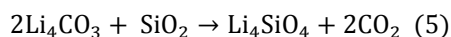
and is not typical of the absorption processes reported in literature.

It is reported that, for the wet chemical synthesis of lithium silicate, the preferred precursor is lithium nitrate for reasons that are yet to be fully understood.<sup>40</sup> Lithium nitrate solution when hydrolysed forms lithium hydroxide which undergoes poly condensation reactions with silica leading to the formation of a gel network.

This wet chemical synthesis reaction leading to the formation of lithium ortho silicate should be as follows:



The solid state reaction between lithium carbonate and silica should be as follows



Physical and structural characterisation as well as CO<sub>2</sub> absorption measurements were conducted on all the powder samples as reported below.

### 3.1. Phase characterization and morphological studies of Li<sub>4</sub>SiO<sub>4</sub>

The X-ray diffraction pattern of the SG-Li<sub>4</sub>SiO<sub>4</sub> powders synthesised through sol-gel route is shown in Fig.1 (a). The peak data confirmed the formation of Li<sub>4</sub>SiO<sub>4</sub> crystalline phase (JCPDS 37-1472) along with trace amounts of Li<sub>2</sub>SiO<sub>3</sub> phase (JCPDS 29-0828). The formation of Li<sub>2</sub>SiO<sub>3</sub> phase should be due to the reaction between SG-Li<sub>4</sub>SiO<sub>4</sub> and CO<sub>2</sub> from air.<sup>7</sup> Peaks corresponding to unreacted phases of lithium or silica were not observed and therefore it is safe to assume that the chemical reaction leading to the formation of lithium orthosilicate was complete under the synthesis conditions. The molar composition of Li:Si in the sample was determined as 4.12:1 by chemical analysis. The amount of lithium in the sample is slightly higher than the stoichiometric value of 4:1 of Li<sub>4</sub>SiO<sub>4</sub>, but remains well within in the range of values normally observed in these ceramics where excess lithium is added to usually balance any evaporation loss during use.

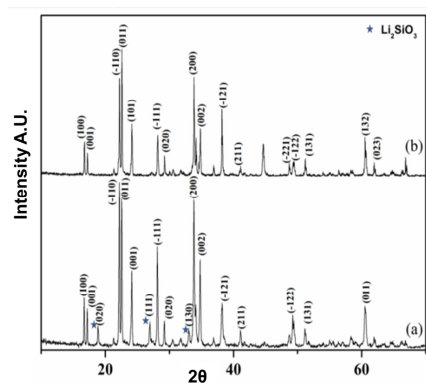


Fig. 1 XRD patterns of Li<sub>4</sub>SiO<sub>4</sub> synthesised by (a) Sol-gel method (b) Solid-state reaction. (Li<sub>4</sub>SiO<sub>4</sub>, JCPDS 37-1472), (Li<sub>2</sub>SiO<sub>3</sub>, JCPDS 29-0828).

XRD pattern of the SS-Li<sub>4</sub>SiO<sub>4</sub> sample synthesized through solid state mixing method as shown in Fig.1(b) also had all predominant peaks of lithium orthosilicate (JCPDS 37-1472). The crystallinity of the two samples seems to have some differences as indicated by the differences in heights of the peaks corresponding to [110] and [011] planes.

Morphological features of the powders were observed in SEM and are shown in Fig.2. SG-Li<sub>4</sub>SiO<sub>4</sub> appeared to have platelet morphology with length extending more than a micron and width of ~ 300nm. Powders made by solid state method were found to contain agglomerates with sizes larger than 10 microns and had a non-uniform particle size distribution.

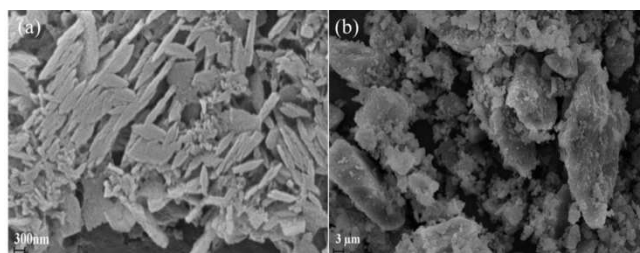


Fig. 2 SEM images of Li<sub>4</sub>SiO<sub>4</sub> synthesised by (a) Sol-gel method (b) Solid-state reaction.

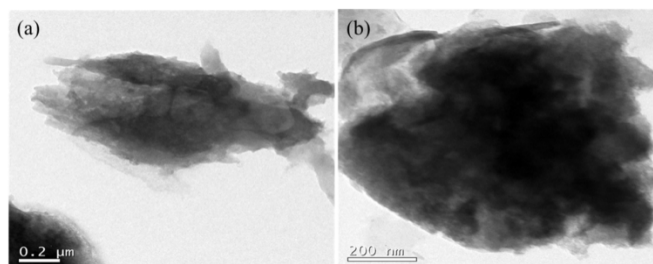


Fig. 3 TEM images of Li<sub>4</sub>SiO<sub>4</sub> synthesised by (a) Sol-gel method (b) Solid-state reaction.

The TEM pictures of the samples as shown in Fig. 3 clearly establish the identity of the constituent structures of the two types of powders. SS-Li<sub>4</sub>SiO<sub>4</sub> particles were observed as hard agglomerates with a size around 1 micrometer, whereas the SG-Li<sub>4</sub>SiO<sub>4</sub> particle seems to be an assembly of rod-like particles leading to platelet morphology.

### 3.2. CO<sub>2</sub> absorption studies

Fig. 4 represents the dynamic thermograms of the samples measured at 20°C/min using 100% CO<sub>2</sub>. Three different absorption steps were noticed. The absorption rate was found very small up to ~500°C. The increase in weight at such low temperatures could be attributed to the presence of absorption by lithium metasilicate which could be present in very small quantities as evidenced by the XRD results. Lithium orthosilicate is also known to absorb CO<sub>2</sub> slightly at this temperature range.<sup>7</sup> A sudden weight increase occurred after this temperature and was followed by a third step extending up to the end with more or less the same rate of weight increment. It is reported that CO<sub>2</sub> absorption process is limited to the



surface initially and only a superficial reaction occurs leading to the formation of an external lithium carbonate shell over the surface of the ceramic particles at this step. When the temperature is increased appropriately, the shell gets softened and the reaction extends to the bulk of the material. The second step should be due to the sudden formation of the shell of lithium carbonate around the particles and the third and final step should be determined by the diffusion of  $\text{CO}_2$  through the shell and  $\text{Li}^+$  through the skeleton thus extending the reaction to the bulk of the material. The second step was less obvious in the solid state sample, probably because of the lower surface area of the powder. As shown clearly in Fig.4, the kinetics of absorption was entirely different between the samples; sol-gel samples had higher absorption capacity at any given time compared to the solid state samples. At  $T > 720^\circ\text{C}$ ,  $\text{Li}_4\text{SiO}_4$  becomes the stable phase due to free energy considerations and a sudden weight loss owing to the full release of  $\text{CO}_2$  resulted in both samples, as shown in Fig. 4.

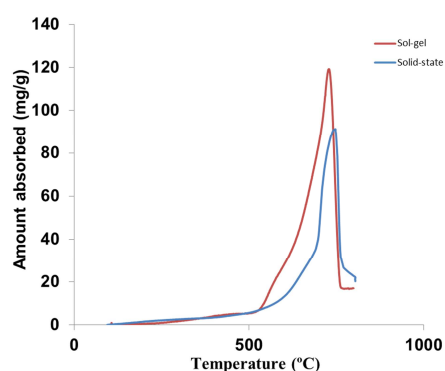


Fig. 4 Dynamic thermo gravimetric analysis of  $\text{Li}_4\text{SiO}_4$  samples measured at  $20^\circ\text{C}/\text{min}$  ( $100\% \text{CO}_2$ ) with respect to temperature.

Fig. 5 shows the XRD patterns of  $\text{SG-Li}_4\text{SiO}_4$  samples before and after  $\text{CO}_2$  absorption. The virgin samples predominantly contained  $\text{Li}_4\text{SiO}_4$  phase and the samples after  $\text{CO}_2$  absorption contained lithium metasilicate and  $\text{Li}_2\text{CO}_3$  phases. This XRD analysis confirmed the chemical conversion of lithium orthosilicate to lithium carbonate as per equation (1).

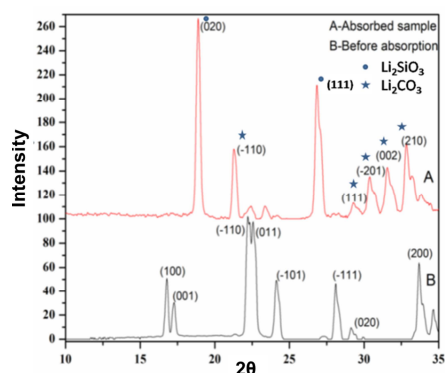


Fig. 5 XRD patterns of  $\text{Li}_4\text{SiO}_4$  (B) and the carbon dioxide absorbed sample (A) [ $\text{Li}_4\text{SiO}_4$  (JCPDS 37-1472),  $\text{Li}_2\text{SiO}_3$  (JCPDS 29-0828),  $\text{Li}_2\text{CO}_3$  (JCPDS 554-13-2)].

### 3.3. Kinetic analysis of $\text{Li}_4\text{SiO}_4$ absorbent performance

$\text{CO}_2$  absorption-desorption profile of materials synthesized from sol-gel route ( $\text{SG-Li}_4\text{SiO}_4$ ) and solid-state method ( $\text{SS-Li}_4\text{SiO}_4$ ) corresponding to different temperatures are shown in Figs. 6. As the dynamic absorption studies have shown that the absorption rate increased significantly above  $500^\circ\text{C}$ , we have studied the kinetics of  $\text{CO}_2$  absorption at temperatures above  $500^\circ\text{C}$  in detail. In this study, samples were heated to the absorption temperature at  $10^\circ\text{C}/\text{min}$  and held for 20 minutes under  $100\% \text{CO}_2$  gas flow to collect absorption data. Desorption was carried out at  $750^\circ\text{C}$  under the flow of  $\text{N}_2$  gas. Sample then was cooled to the subsequent absorption temperature. Absorption and desorption rates (calculated from the first 10 minutes) measured at the different temperatures studied are shown in Fig 7. The maximum absorption rate was obtained at  $700^\circ\text{C}$  and was found to be  $22.5 \text{ mg/g}/\text{min}$  for  $\text{SG-Li}_4\text{SiO}_4$  and  $13.2 \text{ mg/g}/\text{min}$  for  $\text{SS-Li}_4\text{SiO}_4$ .

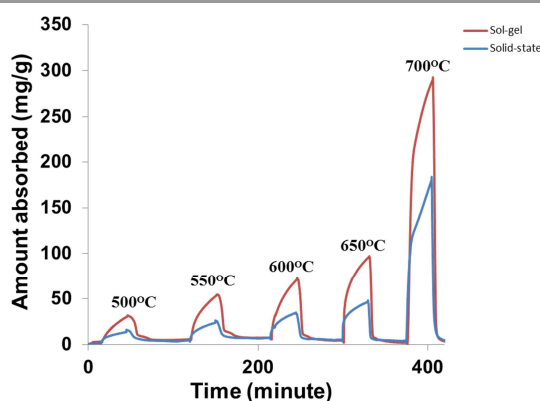


Fig. 6  $\text{CO}_2$  absorption kinetic analysis of lithium silicate synthesized by Sol-gel method and Solid-state reaction.

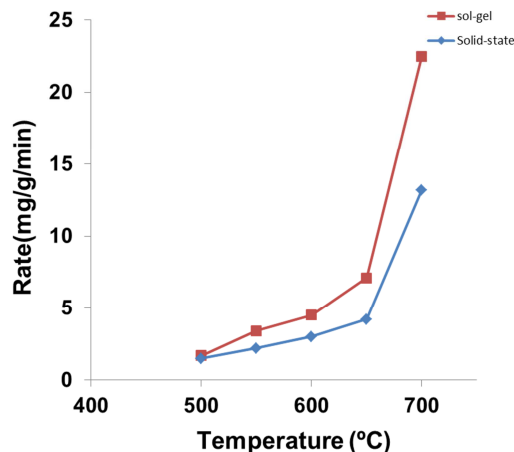


Fig.7 Absorption rates of  $\text{Li}_4\text{SiO}_4$  at different temperature (Rate values calculated from the first 10 minutes of absorption curve).

Desorption was carried out at  $750^\circ\text{C}$  in all the cases. Desorption rates measured with the sol-gel and solid state samples were more or less similar; sol-gel samples showed a desorption rate

of 25.7 mg/g/min whereas the solid state sample showed a slightly higher value of 26.1 mg/g/min. Desorption values normally has less dependence on powder uniformity as the shell of carbonate will be available around all the particles at the instant of the reverse reaction. However, during CO<sub>2</sub> up-take the structure of lithium silicate aggregates could determine the overall rate of the process. Comparison of data shown in Fig. 6 and Fig. 7 clearly indicate that the samples prepared by the sol-gel route are superior in terms of absorption capacity as well as kinetics. Furthermore, the absorption rate values are comparable to the values reported in recent literature.<sup>29</sup>

**Table 1.** Kinetic parameters obtained from the isotherms of Li<sub>4</sub>SiO<sub>4</sub> at different temperature fitted to a Double Exponential Model.

Temperature (°C)	Sol-gel method		
	k <sub>1</sub> (1/s)	k <sub>2</sub> (1/s)	R <sup>2</sup>
500	0.0043	0.0004	0.9987
550	0.0076	0.0005	0.9997
600	0.0007	0.0190	0.9997
650	0.0420	0.0010	0.9610

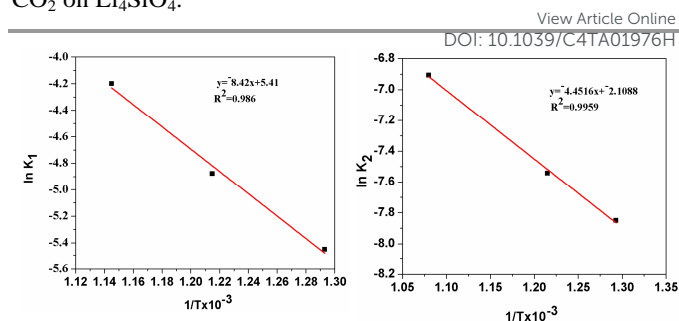
To clearly understand the rate determining steps during the absorption process, kinetic calculations were performed on the absorption isotherms of the sol-gel samples by fitting the curves with a double exponential model as reported by other authors.<sup>38</sup> The isotherm was fitted with

$$Y = A \cdot \text{Exp}^{-k_1 x} + B \cdot \text{Exp}^{-k_2 x} + C \quad (6)$$

In the above equation Y represents the amount of CO<sub>2</sub> absorbed at time "x". k<sub>1</sub> and k<sub>2</sub> are the exponential constants for the absorption of CO<sub>2</sub> on the surface of the particles and the part of absorption kinetically controlled by the diffusion processes on the bulk respectively. The k<sub>1</sub> and k<sub>2</sub> values calculated for the sample are listed in Table 1. Extremely good fitting could be obtained for all the isotherms as revealed by the very high R<sup>2</sup> values in the table. The reported values of k<sub>1</sub> are usually 10 times higher than that of k<sub>2</sub><sup>11</sup> and the same trend could be observed in the data in table 1 as well. However, there were some deviations in k<sub>1</sub> and k<sub>2</sub> values with respect to change in temperature; which could either be due to the nature of the measurement (we have used a continuous measurement mode in our study as in Fig. 6 or be due to the fact that the isotherms were incomplete in our study as absorption was limited to 20 minutes).

The kinetic constants were fitted against temperature, in the range 500-650°C where most of the published data are available, and shown as Arrhenius plots in Fig 8. The activation energy values for the sol-gel samples were calculated as 70 kJ/mol for the chemisorption of CO<sub>2</sub> on Li<sub>4</sub>SiO<sub>4</sub> and 37 kJ/mol for the diffusion ions. These calculated values are in line with other published reports.<sup>11</sup> and the higher activation energy

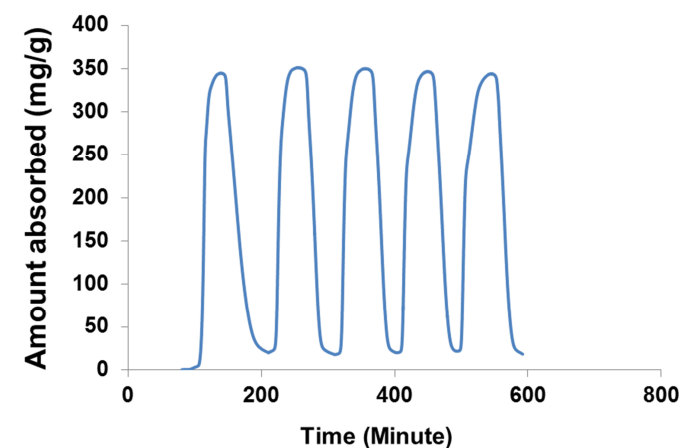
values for chemisorption are representative of the absorption of CO<sub>2</sub> on Li<sub>4</sub>SiO<sub>4</sub>.



**Fig. 8** Plots of ln k versus 1/T, for the two different processes chemisorption (k<sub>1</sub>) and diffusion (k<sub>2</sub>), observed on the SG sample (a,b).

### 3.5 Cyclic absorption-desorption performance

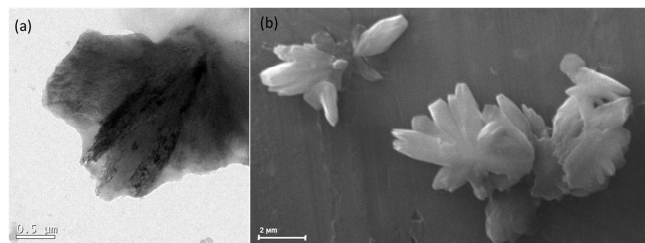
The stability and regenerability of synthesized Li<sub>4</sub>SiO<sub>4</sub> powders were investigated using cyclic absorption-desorption study at a fixed temperature by switching between 100% CO<sub>2</sub> and 100% N<sub>2</sub> gases. Measurement was performed at the maximum absorption temperature of 700°C in order to accelerate decay due to any durability issues. The cyclic CO<sub>2</sub> absorption capacities for 5 consecutive cycles are shown in Fig.9. Absorption was run at a CO<sub>2</sub> flow rate of 50 ml/min and desorption at a N<sub>2</sub> flow rate of 50ml/min. The switching was done manually; therefore absorption/desorption durations have slight variations between cycles. The purpose of the experiment was to see if absorption capacity decreased with cyclic loading due to material loss or segregation. More or less complete CO<sub>2</sub> absorption and release could be achieved in the measured 5 cycles and indicate the structural stability of the materials. However, further studies in 1000's of cycles are necessary for confirmation of this materials usage in any commercial CO<sub>2</sub> separation application.



**Fig. 9** Absorption-desorption performance of Li<sub>4</sub>SiO<sub>4</sub> based sorbent synthesized by sol-gel route (5 cycles at 700°C).

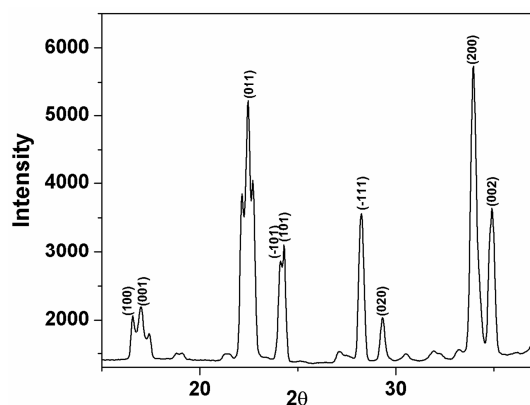
SEM, TEM and XRD studies were performed on the samples after cyclic study (5 cycles as in Fig. 9) to understand any

variations in morphology or crystal structure that might have occurred to the sample. The electron micrographs as shown in Figure 10 (a) and (b) did not however show any significant variation to the original samples (Fig.2 and Fig. 3). Powder particles retained their size and morphology to a reasonable extend, although minor changes are visible.



**Fig. 10** (a) TEM (b) SEM images of  $\text{Li}_4\text{SiO}_4$  after 5 cycles of absorption and desorption study.

XRD pattern of the samples as in Fig. 11 also resembled well with the pattern measured for the original sample (Fig. 5b). Nevertheless, peaks corresponding to [200] plane were found stronger in the samples after cyclic loading. It is clear that minor changes in crystal structure and probably morphology are happening in the sample during cyclic absorption and desorption. However, the changes have not been significant to influence the absorption performance of the samples at least till the 5 cycles we have followed in this study.

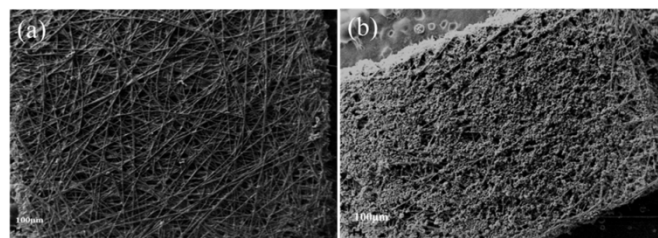


**Fig.11** XRD patterns of  $\text{Li}_4\text{SiO}_4$  5 cycles of absorption and desorption study. [( $\text{Li}_4\text{SiO}_4$  (JCPDS 37-1472))].

### 3.4. $\text{CO}_2$ absorption studies of $\text{Li}_4\text{SiO}_4$ coated over porous carbon mesh.

One of the main hurdles that limits the practical application of these kinds of absorbents is the difficulty in processing absorbent pellets for large scale applications. Water based ceramic extrusion processes have severe hurdles due to the corrosive nature of excess carbonates when dissolved in water. The near melt condition of the carbonate shell under the absorption/desorption conditions also could give rise to gravity driven shape deformation of the pellets with time. This could give rise to bulk flow limitations of gases within the absorption

column. Supported structures coated in mechanically strong shapes are one way to limit shape deformation. Slurry coating on the support substrate also is easier in terms of fabrication and handling as issues regarding the corrosive nature of the slurry could be better managed in any dip coating process. Hence, we tried to coat the sol-gel based powders on porous carbon sheets and tested the absorption behaviour of the resulting supported structures.



**Fig. 12** SEM micrographs of (a) Carbon support (b) Coated carbon support.

The surface microstructures of the uncoated and coated carbon sheet are shown in Fig.12(a) and (b). The slurry for dip coating was made by ball milling the sol-gel powder in isopropyl alcohol for 72 hours. From figure 10 (b), it is clear that the coating is uniform over the surface of the form. The absorbent powder weight was ~70% of the total weight of the coated structure.

Cyclic absorption and desorption of the supported sample was carried out at  $700^\circ\text{C}$  using 100%  $\text{CO}_2$  and  $\text{N}_2$  gases and the results are shown in Fig. 13. The absorption capacity was 150 mg/g for the coated sample (120 mg/g within the first 20 minutes as shown in Fig. 13) and the first 60% of absorption was completed at a rate of 37.5 mg/g/min. The measured absorption rate was considerably higher than the value of 22.5 mg/g/min measured for the powder samples. These results highlight the importance of macrostructure of the powders on absorption rate. Powder samples normally shape themselves into lump form during the pre-heating stage carried out at  $800^\circ\text{C}$  before the actual absorption measurements, thereby restricting the bulk  $\text{CO}_2$  gas flow through them. Coated samples, on the other hand, are capable of keeping the macrostructure intact and therefore could realise superior absorption rate during measurement. In addition, absorption capacity and rate of the coated sample remained same all through the 8 cycles measured in our study. It is clear that the samples with excellent absorption rate and cyclic stability could be obtained by this fabrication method. The durability of the carbon substrate for long-term use needs detailed verification and is in progress now. Further improvements, in terms of powder loading on the carbon substrates and therefore, on absorption capacity of the coated materials are also necessary for making the samples useful for any practical applications.

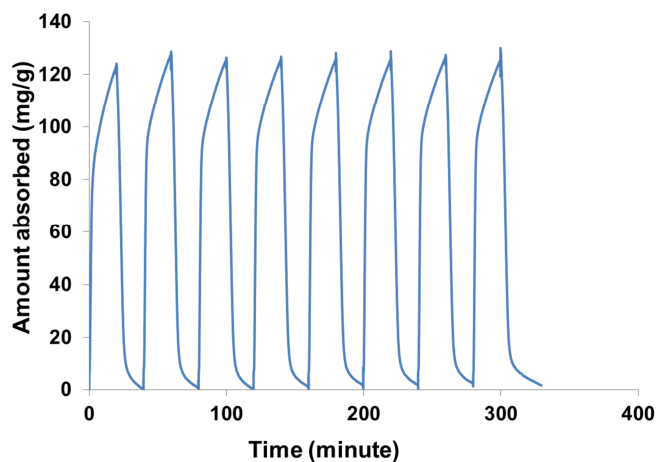


Fig. 13 Absorption-desorption performance of  $\text{Li}_4\text{SiO}_4$  based sorbent synthesized by sol-gel route coated over porous carbon support (8 cycles at  $700^\circ\text{C}$ ).

#### 4. Conclusion

$\text{Li}_4\text{SiO}_4$  sorbents for carbon dioxide absorption at elevated temperature were synthesized via, sol-gel as well as solid state method. Based on phase evolution studies as well as micro structural characteristics we concluded that the material developed by sol-gel technique is superior.  $\text{CO}_2$  up take and release studies performed on the samples clearly supported this; sol-gel samples showed an absorption capacity value of 350 mg/g and absorption rate of 22.5 mg/g/min. This absorption rate was considerably higher than the corresponding value of 13.2 mg/g/min measured on the solid state sample and should be due to the unique platelet morphology of the sol-gel samples. Absorption-desorption cyclic loading studies have shown that the sample remained durable for the 5 cycles studied. Supported absorbents on carbon mesh were developed and absorption rates as high as 37.5 mg/g/min were measured; the samples also showed excellent durability for the 8 cycles measured. Further improvements in terms of powder loading in the supports leading to higher absorption capacity of the supported structure may be required for making these supported structures candidates for any practical application.

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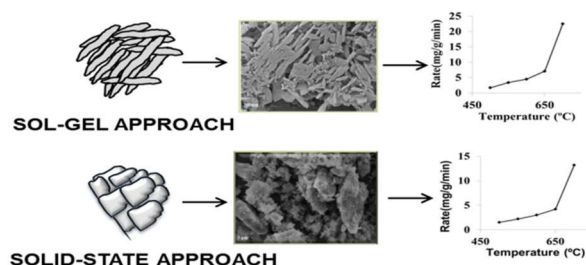
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## Enhanced CO<sub>2</sub> absorption kinetics in lithium silicate platelets synthesized by a sol-gel approach



Platelet shaped lithium orthosilicate particles synthesized by a sol gel approach showed CO<sub>2</sub> absorption capacity of 350 mg/g at an absorption rate of 22.5 mg/g/min; a value 70% higher than the rate of 13.2 mg/g/min measured with the solid state samples under similar conditions