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Research Article

Synthesis of Na-Doped Lithium Metatitanate and Its Absorption for Carbon Dioxide

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Na-doped lithium metatitanate (Na-doped Li_2TiO_3) absorbent was doped with Na_2CO_3 and lithium metatitanate (Li_2TiO_3) was prepared by a solid-state reaction method from mixture of TiO_2 and Li_2CO_3. The Na-doped lithium metatitanate was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and surface area. Carbon dioxide absorption on Na-doped lithium metatitanate was investigated using TG-DTA. The results reveal an increase of the CO_2 absorption capacity of the Na-doped materials with respect to pure Li_2TiO_3. XRD patterns of the doped samples suggest a limited substitution of Li by Na atoms within the Li_2TiO_3 structure. The results of experimental and modeling work were summarized to better understand the relationship between the sorbent microstructure and carbon dioxide absorption kinetics.

1. Introduction

Carbon dioxide is the largest contributor among greenhouse gases (GHS) in regard to its amount in the atmosphere. The explosive increase in energy consumption of fossil-fuels by the rapid increase of population resulted in an accumulation of anthropogenic carbon dioxide in the atmosphere. By the year 2100, the atmosphere may contain up around 570 ppmv carbon dioxide against 270 ppmv carbon dioxide before the industrial revolution. Carbon dioxide is causing a rise of mean global temperature of around 1.9°C and an increase of mean sea level of 38 m [1]. Fossil-fuel power plants are responsible for roughly 40 percent of total carbon dioxide emissions; hence it is important to capture carbon dioxide from coal-fired power plants in order to maintain the threshold value limit in the atmosphere and avoid any catastrophic effects.

Many researchers are working on the reduction of carbon dioxide emissions using various approaches since the Kyoto protocol was adopted at COP 3 in Japan [2–14]. Current technologies being considered for carbon dioxide capture include absorption, adsorption, membrane process, and disposal of carbon dioxide in deep oceans. If absorption is considered to be an economically viable technology for the carbonation reaction efficiency from combustion of flue gas, the solid absorbent properties are very important [2, 3]. Lithium salts have emerged as an excellent and regenerable absorbent for the capture of carbon dioxide. Lithium salts with higher capacity and selectivity for carbon dioxide were synthesized, characterized, and tested for capturing carbon dioxide either at postcombustion or precombustion temperature [4–10]. Nakagawa and Ohashi reported that the absorption reaction rate is accelerated when lithium zirconate is doped with sodium carbonate and/or potassium carbonate. The doping produces a eutectic of molten carbonate that reduces carbon dioxide diffusion resistance [11]. Xiong et al. have studied the absorption kinetics of carbon dioxide on K-doped Li_2ZrO_3 and found that the reaction rate accelerated as the absorbent particle size reduced. The temperature effect is complex, and the appropriate temperature is about 550–590°C [12]. Wang et al. employed Na-doped Li_4SiO_4, prepared by high-temperature solid-state reaction, as carbon dioxide absorbent from 500 to 750°C [6]. The influence of sodium doping on the absorption capacity and cycle performance was studied.

The results showed that sodium doping could improve the carbon dioxide absorption ability of lithium silicate [13–15]. Satisfactory heat tolerance, high carbon dioxide absorption capacity, and fast kinetics in multicycle operation are seldom provided with currently available absorbents.

Lithium plays an important role in capturing carbon dioxide by forming lithium carbonate. Lithium acts as promoter, titanium acts as stabilizer, and sodium acts as doping agent in the process of capturing carbon dioxide over absorbent. As carbon dioxide is acidic by nature, it is felt that incorporation of basicity in the parent matrix Li_2TiO_3 can increase the capacity and selectivity of absorbent to a higher value. Titanium dioxide has a synergy with parent matrix for higher carbon dioxide absorption capacity. Sodium doping causes an important increase of the absorption kinetic. In present study, Na-doped Li_2TiO_3 was introduced as a suitable absorbent for carbon dioxide, and the influence of various x values on the absorption capacity and cycle performance was discussed through different preliminary experiments.

2. Materials and Methods

2.1. Synthesis of Na-Doped Li_2TiO_3. The high temperature solid-phase process was used to prepare Na-doped Li_2TiO_3 in this work. Starting materials were Li_2CO_3 (AR, Sinopharm Chemical Reagent Co., Ltd), TiO_2 (AR, Sinopharm Chemical Reagent Co., Ltd), and Na_2CO_3 (AR, Sinopharm Chemical Reagent Co., Ltd). The molar ratio of the starting materials ($Li_2CO_3 : TiO_2 : Na_2CO_3$) was $1 - x : 1 : x$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.10$). In general, the composition of absorbent can be given as $Li_{2(1-x)}Na_{2x}TiO_3$. The $Li_{2(1-x)}$ and $Na_{(2x)}$ mole ratios were varied during the synthesis of these absorbents. The six samples were named LiNa-0, LiNa-1, LiNa-3, LiNa-5, LiNa-7, and LiNa-10, respectively, according to the following values of sodium content in % mole. TiO_2 were weighed, mixed with a suitable amount of ethanol, and dispersed 15 mins by the ultrasonic power. After Li_2CO_3 and Na_2CO_3 were added, the mixtures were stirred by magnetic stirrer for 2 h and dried at 80°C. The precursor was calcined at 800°C for 20 h. The calcined Na-doped Li_2TiO_3 was quenched in air and ground in an agate mortar before testing.

2.2. Characterization. The crystallinity of Na-doped Li_2TiO_3 was examined using X-ray powdered diffractometer ARL XTRA X-ray with Cu K_α radiation. The morphology of absorbent was observed by SEM (FEI Nano SEM430). The surface area of absorbent was measured by Micromeritics ASAP 2010 instrument. The N_2 BET surface area of the absorbent was observed to be 2.39 m^2/g. Since the capture of carbon dioxide over absorbent depends mainly on the chemical reactions, there is no direct correlation between the surface area and the capture of carbon dioxide.

2.3. Evaluation of Absorbents. Carbon dioxide absorption on the Na-doped Li_2TiO_3 was performed using a HCT-1 thermo gravimetric analyzer (Beijing Henven Scientific Instrument Factory). About 10 mg Na-doped Li_2TiO_3 powders were placed in the sample pan. The heating rate is 10°C/min, absorption temperature is 600°C, absorption time span is 180 min, and flow rate of pure carbon dioxide is 80 mL/min. Prior to absorption measurement, pure dried carbon dioxide was passed over the absorbent through thermo gravimetric analyzer in order to remove inner air.

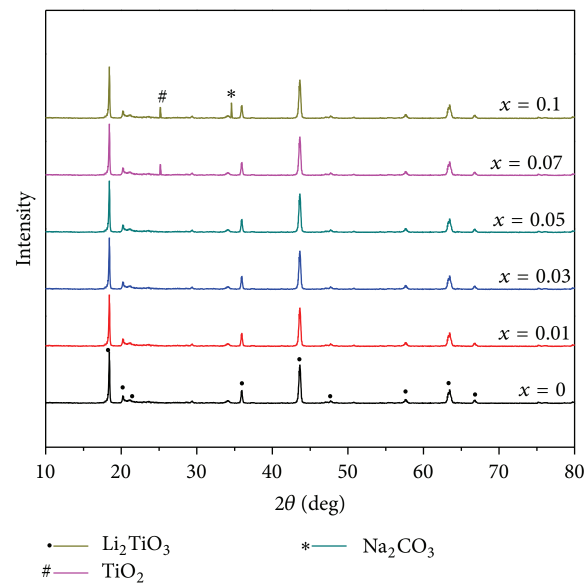


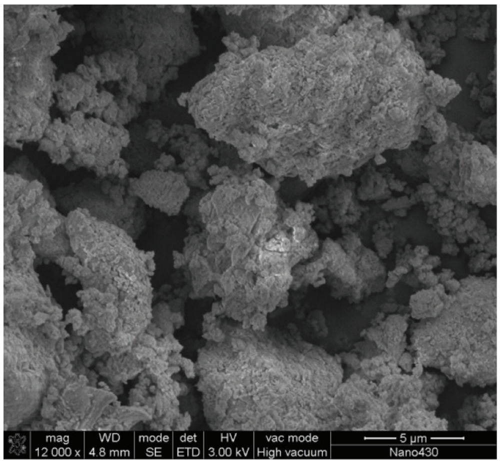
Figure 1: XRD patterns of Na-doped Li_2TiO_3 and Li_2TiO_3.

3. Results and Discussion

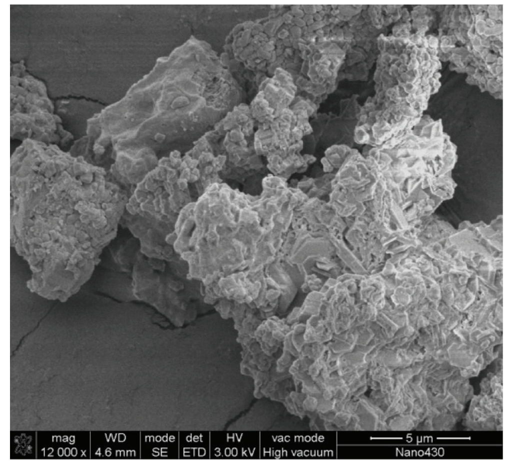
3.1. Characterization of Na-Doped Li_2TiO_3. The X-ray diffraction patterns of Na-doped Li_2TiO_3 and nondoped Li_2TiO_3 absorbents shown in Figure 1 reveal that Li_2TiO_3 is only monoclinic crystalline structure as the sodium doping is below 5% Na. However, the characteristic peaks of Na_2CO_3 and TiO_2 appear as the Na amounts are increased through Na doping from sample containing 5% up to 10% Na (samples LiNa-5, LiNa-7, and LiNa-10). XRD results did not show peaks associated with a Na_2TiO_3 structure clearly. It implies that a few Li are substituted by Na and a crystallographic phase is formed in Li_2TiO_3 crystals as the amount of Na is increased through doping. Furthermore, the crystal defects may increase absorption reactivity due to Na doping.

The SEM images of Na-doped Li_2TiO_3 at the magnification of 12000x are presented in Figure 2. It is observed that a greater degree of agglomeration with more irregular particle sizes appears as the Na amount is decreased from sample containing 10% to 1% Na. The morphology of sample LiNa-5 exhibits a more regular uniform crystalline solid material. Moreover, the performance improvement might be attributed to the creation of lattice defects in the Li_2TiO_3 crystals by Na doping. In addition, the grain growth of absorbent has been accelerated by Na doping.

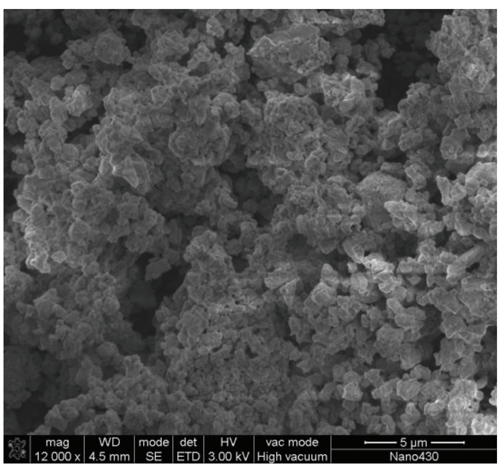
3.2. The Influence of Sodium Doping on CO_2 Absorption Capacity. CO_2 absorption on various Na-doped Li_2TiO_3 at 600°C is presented in Figure 3. It is found that sample LiNa-3



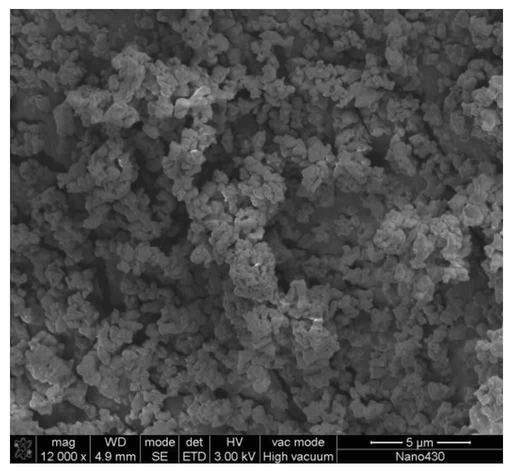
(a) $x = 0.01$.



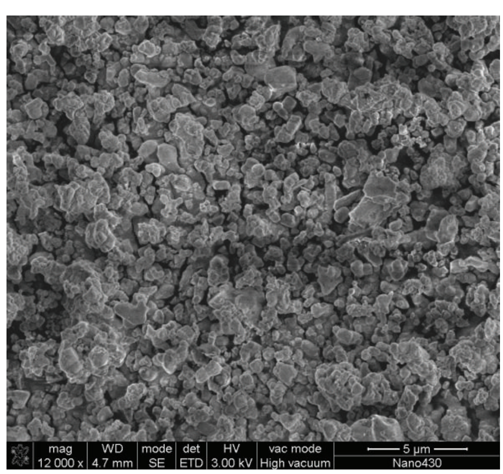
(b) $x= 0.03$.



(c) $x = 0.05$.



(d) $x = 0.07$.



(e) $x = 0.10$.

Figure 2: SEM images of Na-doped Li_2TiO_3.

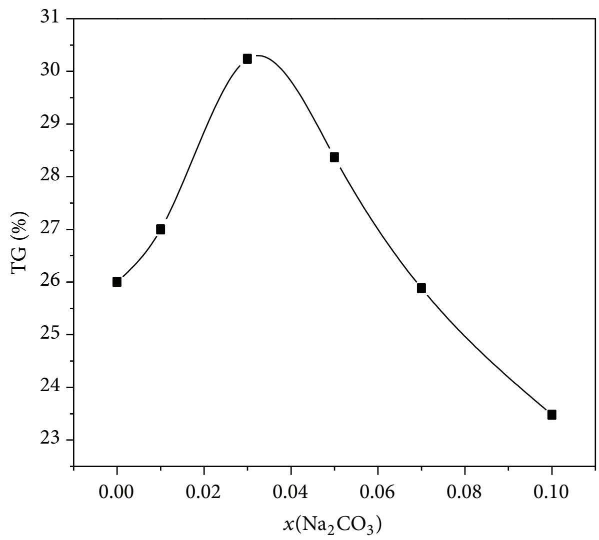


Figure 3: Impact of Na_2CO_3 doping on the CO_2 absorption capacity by Li_2TiO_3.

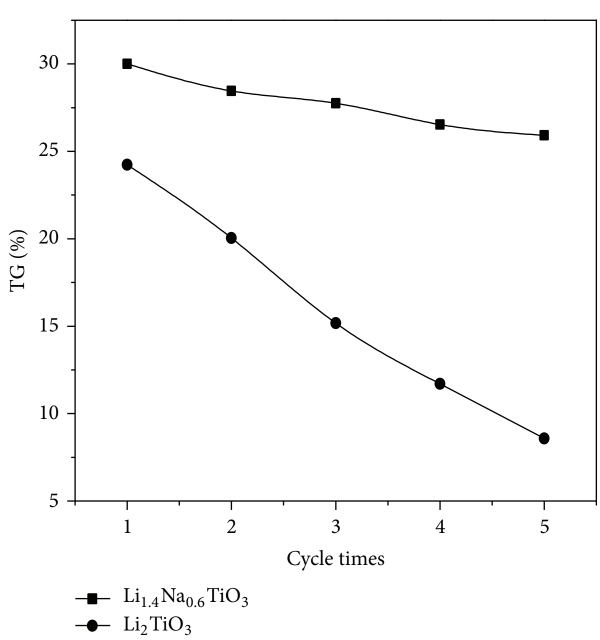


Figure 4: Effect of Na doping on cycle performance of CO_2 absorption on Li_2TiO_3.

possesses the best performance and absorbs as much as 30% (wt) of CO_2. Greater than or less than Na amount of sample LiNa-3 will consequently be traduced in a decrease of CO_2 absorption capacity. The capture of CO_2 over lithium silicate (Li/Si = 4) is 1.6 mmol/g at 525°C [16]. As much as (25 ± 0.6)% (wt) of CO_2 was absorbed by lithium zirconate [17].

3.3. The Influence of Sodium Doping on CO_2 Absorption Cycle Performance. CO_2 absorption cycle performances of pure nondoped Li_2TiO_3 and sample LiNa-3 are presented in Figure 4. As shown, CO_2 absorption capacity of two samples

Table 1: Relative permeability during absorption process at 500~600°C.

Item	Pure Li_2TiO_3	Na-doped Li_2TiO_3
TiO_2 layer state	Solid	Solid
O^{2-} permeability	~10^{-12} cm^2/m	~10^{-12} cm^2/m
Li_2CO_3 layer state	Solid	Liquid
CO_2 permeability	~10^{-14} cm^2/m	~10^{-8} cm^2/m
Rate-determining step	CO_2 diffusion	O^{2-} diffusion

both decrease, cycle performance of Na-doped Li_2TiO_3 falls 14.28% after 5 times cycle, but that of pure non doped Li_2TiO_3 falls 67.03% after the same times cycle. So the cycle performance increases obviously by Na doping. This behavior can be explained in terms of a newly formed structure after Na doping process [18].

3.4. The Double-Shell Mechanism of CO_2 Absorption on Na-Doped Li_2TiO_3. Xiao et al. investigated the double-shell mechanism of CO_2 absorption on Li_2ZrO_3 at high temperature [15]. The absorption process of CO_2 on Na-doped Li_2TiO_3 particles could properly be described by double-shell mechanism. Although eutectic molten carbonate composed of Li_2CO_3 and Na_2CO_3 on the outer layer cannot react with CO_2, molten carbonate facilitates the transfer of gaseous CO_2 into the inner unreacted layer. Meantime, O^{2-} and Li^+ released by Li_2TiO_3 reach inner layer through TiO_2 layer. Then O^{2-}, Li^+, and CO_2 encounter and react, forming Li_2CO_3 among inner layer. As this process proceeds, TiO_2 layer and molten salt layer are thickened, diffusion time of O^{2-}, Li^+, and CO_2 is lengthened, and absorption process is slowed down. The relative permeability of O^{2-} and CO_2 in absorption process at 500–600°C was listed in Table 1 [19].

From Table 1, the rate-determining steps of CO_2 absorption on pure Li_2TiO_3 and Na-doped Li_2TiO_3 are CO_2 diffusion rate and O^{2-} diffusion rate, respectively. O^{2-} diffusion rate is faster than CO_2. So absorption rate of CO_2 on Na-doped Li_2TiO_3 is faster. CO_2 absorption process on Na-doped Li_2TiO_3 was qualitatively described well by double-shell mechanism.

4. Conclusions

(1) CO_2 capacity on Na-doped Li_2TiO_3 can be improved by sodium doping. There is the maximum capacity when $n(TiO_2) : n(Li_2CO_3) : n(Na_2CO_3) = 1 : 0.97 : 0.03$.

(2) XRD patterns show that sodium doping led to crystal defect that could make absorption reactivity increase. From SEM images, it was speculated that sodium doping does not change morphology, but it makes particles looser and fracture phenomenon occurred.

(3) CO_2 absorption cycle performance decay dropped to 14.28%. Compared with the 67.03% of pure Li_2TiO_3, it has been greatly increased.

(4) The double-shell mechanism described CO_2 absorption process on Na-doped Li_2TiO_3; sodium presence changing rate-determining step of the process is the main reason of performance improved.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

Acknowledgments

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