Full Length Article

Experimental investigations on the combustion of lithium particles in CO_2 and CO_2-N_2 mixtures

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HIGHLIGHTS

- Lithium particles were burned in CO_2-containing atmospheres with nitrogen dilution.
- Optical and sampling methods were used to characterize combustion time scales.
- In nitrogen-diluted CO_2 atmospheres, the formation of Li_2CO_3 is retarded.
- Combustion temperature decreases with CO_2 partial pressure.

GRAPHICAL ABSTRACT
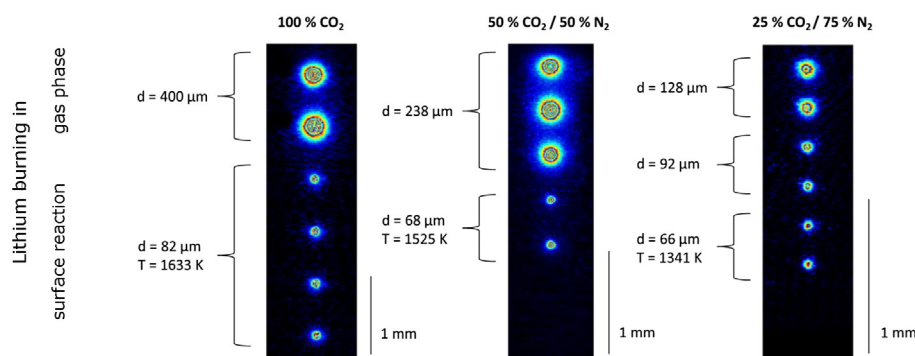
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ABSTRACT

Energy cycles based on lithium combustion have been proposed recently and provide an option to combine the benefits of high-density energy storage with carbon-free production of heat, power and chemicals. Knowledge on efficient combustion processes for lithium is limited. In the current work, combustion experiments for single lithium particles (d_p = 10–250 μm) burning in CO_2 and three different CO_2-N_2 mixtures are carried out using a laminar flow drop tube reactor. In order to determine combustion times, temperatures and burnout constituents, the burning particles are investigated using three different measurement techniques: a reflex camera, a high speed two-color pyrometer and a sampling probe to collect burnout samples. The results confirm the existence of two combustion stages, which have been observed before: gas-phase combustion and surface reaction. As detailed investigations show, the duration of the gas-phase combustion is approximately ten times shorter compared to the surface reaction. In addition, the burnout times of both combustion stages increase clearly for lower CO_2 partial pressures. The reduction of the CO_2 partial pressure leads to lower combustion temperatures as well as the production of less Li_2CO_3 and more Li_2O, while no nitrogen compounds are formed.

1. Introduction

Recently, the combustion of various metals has been investigated to develop a chemical energy carrier [1]. Renewable energy can be used to charge the energy carrier (i.e. splitting of metal salts). To discharge the stored energy, the metal is burned in pulverized or sprayed form to increase the surface-to-volume ratio and, therefore, the reaction rate. The heat produced during combustion can be used in internal combustion engines [2,3] or is converted to electricity using a water-steam cycle or Stirling engine [1]. In the past, aluminum and iron have been investigated regard-

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Table 1
Exothermic reactions of Li with exhaust gas components calculated with data from [26].

Reaction #	Chemical reaction	Reaction enthalpy [kJ/mol$_{Li}$] (298.15 K, 0.1 MPa)
1	$6\,Li + N_2 \rightarrow 2\,Li_3N$	−54
2	$Li_3N + 3\,H_2O \rightarrow 3\,LiOH + NH_3$	−145
3	$2\,Li + 2\,CO_2 \rightarrow Li_2CO_3 + CO$	−270
4	$2\,Li + 1\,CO_2 \rightarrow Li_2O + CO$	−157
5	$4\,Li + 1\,CO_2 \rightarrow 2\,Li_2O + C$	−201
6	$2\,Li + 2\,H_2O \rightarrow 2\,LiOH + H_2$	−202
7	$4\,Li + O_2 \rightarrow 2\,Li_2O$	−299

ing their potentials as chemical energy storage materials [4–11]. Another promising metal for a chemical energy carrier is lithium, as it reacts exothermally with various gases, including O_2, H_2O, N_2 and CO_2 [12–16]. Thus, lithium can be burned with the main components of fossil power plant exhaust gas, which enables the possibility to utilize the flue gas constituents. In addition, the reaction of lithium with N_2 [17] or CO_2 [18,19] produces valuable by-products such as Li_3N (reaction with N_2,) or CO (reaction with CO_2), which can be further converted to ammonia or synthetic hydrocarbon fuels. A good overview on the combustion of lithium is given in the reviews of Jeppson et al. [20], Rhein [21] and Schiemann et al. [22], who also sum up the combustion of lithium particles or droplets focusing on processes for energy utilization. The major chemical reactions for the different combustion processes are summarized in Table 1. Considering lithium as an energy carrier needs process schemes which go beyond the combustion process. The idea to use the metal as energy carrier and typical metal purification schemes lead to the idea of metal recycling. Focusing on lithium, it will be necessary to recycle the combustion products (Table 1: Li_3N (R1), Li_2CO_3 (R3), Li_2O (R4)) to reuse the lithium contained. The lithium carbonate price of ∼6400 US$ per metric ton

(2015, [23]) and the economic value of the chemical products (CO, (R3), NH_3 generated from Li_3N (R1, [17])) lead to an estimate for the allowed lithium loss per process cycle in the range of one percent [22]. However, there are even cheaper sources of lithium carbonate with prices below 1000 $/t$_{Li2CO3}$, such that the estimated loss rate can be higher by the corresponding factor. When NH_3 production is considered, the value of approx. 500 €/t$_{NH3}$ increases economic feasibility to a level which reduces the recycling efficiency demand drastically. The recycling step utilizing renewable energy is possible from lithium salts [24], which seems feasible for stationary plants. Lithium-based internal combustion engines would need a very efficient lithium capture, which might be more realizable when hydrogen production from lithium (Table 1, (R6)) is considered [25], but has not been investigated in depth yet.

In the past three years, the combustion of lithium particles in CO_2 has been investigated both experimentally and numerically [18,19]. For that purpose, a drop tube reactor was used to analyze the combustion behavior of single particles using a two-color pyrometer for the determination of combustion temperatures as well as particle sampling to analyze the burnout composition. It has been shown that, in pure CO_2, the combustion occurs in two different stages. After ignition, the particles start to burn in the gas phase with the flame detached from the particle surface. The gas-phase combustion (GPC) ends after a very short period of time (several ms) due to the accumulation of reaction products on the particle surface, which form a product layer. The layer hinders the diffusion of evaporated lithium from the particle surface to the detached flame and thus terminates the GPC and starts the second combustion stage. During the second stage, the reaction occurs at the particle surface. For the surface reaction (SR) in pure CO_2, reaction kinetics were derived from experimental data using a two-color pyrometer [18]. In addition, time-dependent particle sampling was conducted to determine the product constituents, which showed a nearly complete conversion to Li_2CO_3.
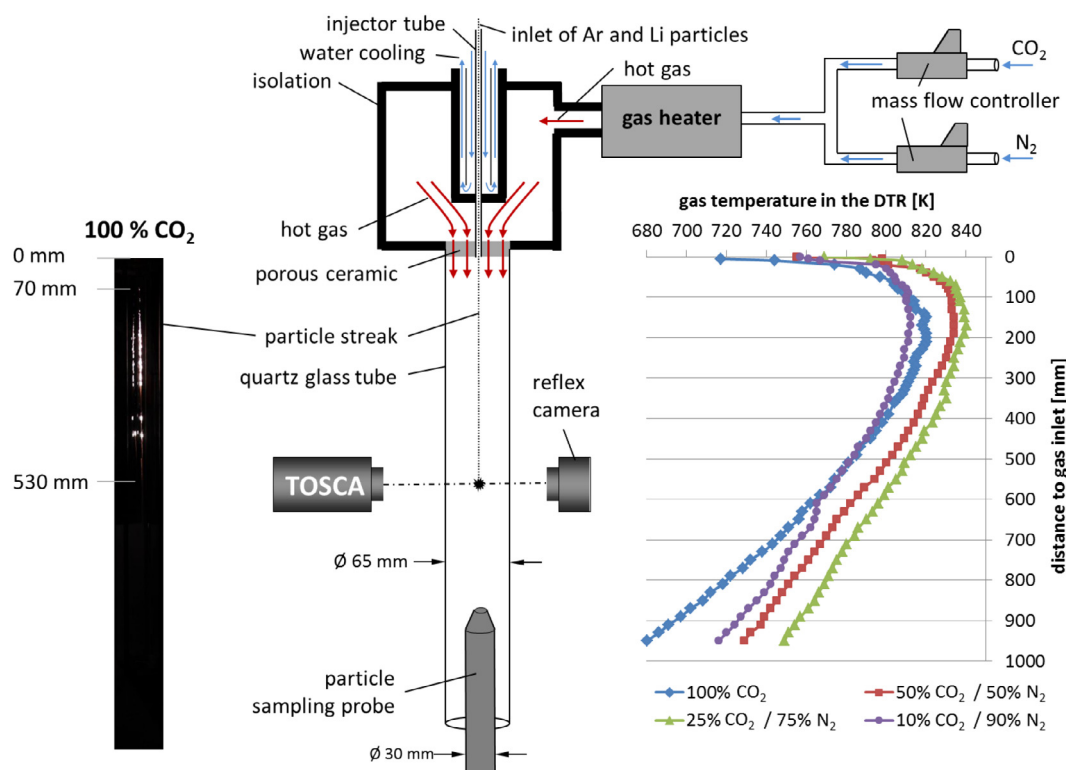
Fig. 1. Schematic drawing of the drop tube reactor (DTR) including gas temperature profiles along the reactor tube axis and a example of the particle streak for the combustion in 100% CO_2.