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A review of promising candidate reactions for chemical heat storage

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A B S T R A C T

Thermal energy storage is a necessary technology for the application of renewable energy and low-grade thermal energy. Chemical heat storage has been proved to be a feasible and promising method to store thermal energy. As compared to other thermal energy storage methods, chemical heat storage exhibits high energy storage density as well as feasibility for long-duration energy storage. In this paper, the basic principle of the chemical heat storage is firstly elaborated. Then the selection criteria of the chemical reaction are given. The aim of this review is to provide an insight into the promising candidate reactions for chemical heat storage application. The associated reversible chemical reactions available for thermal energy storage systems are summarized. Ongoing research and development studies illustrate that chemical heat storage is a very favorable option for the different application when diverse promising candidate reactions are selected. As working temperature is one of the key parameters for thermal energy storage systems, emphasis is given to the judgment of application temperature range for chemical heat storage. The determination of applicative temperature range of reversible chemical reactions is discussed. Besides, the challenge and prospect of the chemical heat storage technology are analyzed in the paper.

Contents

1. Introduction

Energy is an important element for the economic growth, social and environmental sustainable development. With the incremental depletion of conventional primary energy, the new alternative energy source becomes more and more important for the energy

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conservation. However, on the one hand, the renewable energy source, such as solar energy and wind energy, is intermittent and time dependent and thus restricts the large-scale utilization. On the other hand, more rational and efficient utilization of the energy is confronted with many technical difficulties. Energy storage provides a feasible solution due to improving the efficiency of the energy system and storing the surplus energy.

Energy storage is an indispensible technology for adjusting the instability and time-discrepancy between supply and demand of energy. It is mainly utilized for the intermittent occasion, such as solar energy, variable energy load, and excessive energy that would be wasted rather than effectively utilized if it cannot be stored. The energy that can be stored involves mechanical energy, electric energy, chemical energy and thermal energy. Thermal energy storage is capable of improving the efficiency of thermal energy systems. It can be used to alleviate the mismatch between energy supply and demand. Furthermore, thermal energy storage facilitates the solar thermal applications and other low grade heat recovery and utilization.

There are three thermal energy storage ways: sensible heat storage, latent heat storage and chemical heat storage. For sensible heat storage, thermal energy is stored or released accompanying with the temperature change of storage materials. Of all the ways, sensible heat storage is the simplest and the cheapest method, and thus it obtains the earliest practical application. This method, however, has low thermal capacity, making it necessary to use large sized storage device. Latent heat storage utilizes the enthalpy difference of the phase transitions of the phase change material (PCM), *i.e.* heat storage process is the phase change of the substance by either fusion or solidification. Compared to the sensible heat storage, latent heat storage has a distinct advantage of much higher storage density and the isothermal nature of storage process [1]. However, the properties of the phase change materials will degrade after the reduplicative cycling. Chemical heat storage relies on the reversible chemical reactions, during which the energy is absorbed or released by breaking or reforming chemical bonds. All the stored heat (or almost all) can be retrieved for later use, when synthesis reaction occurs.

Chemical heat storage has attracted considerable interest in recent years. Chemical heat storage has the capacity of high energy density and long-term storage duration at near ambient temperature among different thermal energy storage methods. The reactant undergoes the decomposition reaction with the aid of heat input, and therefore the thermal energy is converted into internal energy and simultaneously stored. The stored heat can be kept for a long time as long as the reaction products are separately stored. This makes this energy storage method a viable and effective technology for long-duration thermal energy storage and transport. This paper focused on the reversible chemical reactions available for chemical heat storage. A large number of promising candidate reactions for chemical heat storage are categorically summarized. In addition, the selection criteria of chemical reactions and the determination of applicative temperature range for chemical heat storage are addressed. Moreover, a more holistic view of the current state and the further direction and challenge of chemical heat storage are also presented and discussed.

2. Technology status

Chemical heat storage system stores thermal energy using stable chemical substances by converting heat energy into chemical potential energy. These chemical substances undergo reversible chemical reactions to store/release heat. Generally, the ideal chemical heat storage materials/reactions should have the following characteristics:

(1) Moderate reaction temperature and high reaction heat;
(2) Good reversibility without apparent secondary reaction;
(3) Fast enough forward and reverse reaction rate to facilitate the energy charging and discharging;
(4) Easily separated and stably stored reaction products;
(5) Non-toxic, non-corrosive, non-flammable and non-explosive reactants and products;
(6) Small volume variation during reaction;
(7) Large-scale availabilities and abundance, cheap price.

Chemical heat storage can be classified into two categories based on the reaction mechanism: chemical reaction heat storage (without sorption) and chemical sorption heat storage. Thermal energy can be stored through the reversible chemical reactions and sorption processes.

2.1. Chemical reaction heat storage

For chemical reaction heat storage, the heat storage and heat release process can typically be described as:

$$A + \text{heat} \Leftrightarrow B + C \tag{1}$$

The compound A is split into chemical substances B and C through an endothermic dissociation reaction. The produced chemical substances, B and C, stores thermal energy in the form of the chemical potential energy. The reaction products B and C are stored separately to achieve long period heat storage with little heat loss. When the reversible reaction occurs for the later heat utilization, compound A is regenerated resulting from the synthesis reaction between substances B and C. As a result, the stored thermal energy is retrieved.

2.1.1. Chemical reaction heat storage using gas–gas reaction

2.1.1.1. The $NH_3/N_2/H_2$ chemical reaction heat storage system. Ammonia-based chemical reaction heat storage system uses reversible dissociation of ammonia to store thermal energy. The chemical reaction is:

$$2NH_3(g) \Leftrightarrow N_2(g) + 3H_2(g) \tag{2}$$

The reaction enthalpy is 66.8 kJ/mol ammonia at 20 MPa and 300 K. This reaction can be faster by introduction of an appropriate catalyst. The application of ruthenium-on-carbon catalyst in place of the iron-based catalyst helps to lower the dissociation temperatures to 673 K and below. Carden [2,3] initially investigated the ammonia reversible reaction. The investigation work continued at the Australian National University (ANU). ANU devoted to ammonia dissociation and synthesis system for a period of approximately 40 years. They carried out a great deal of theoretical and experimental investigations on ammonia-based chemical reaction heat storage system [4–12]. Different studies that have been done reveal that the ammonia-based system for concentrating solar power is technically feasible. A 1500 t/day ammonia synthesis reactor can supply a 10-MW base-load plant with 400 large 400 m^2 dishes arranged in an array. The heat released by synthesis reaction is used to drive the power cycle to produce superheated steam at a temperature and pressure of up to 793 K and 10 MPa. Tower or dish solar collector systems enable the dissociation reaction to proceed more completely owing to the comparatively high temperature in the vicinity of 1273 K. In addition, the increase in the system pressure can greatly accelerate ammonia synthesis. This makes necessary for ammonia-based storage systems to operate at high pressures (10–30 MPa), although this will increase the costs due to material restriction on reactor and storage vessel. Ammonia dissociation and synthesis reaction has a number of obvious advantages [5,10]. One of the advantages is that it is easy to control the reactor since this reversible reaction is very simple with no unwanted side reactions.