Journal of Power Sources 286 (2015) 362–370

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Combined chemical looping for energy storage and conversion

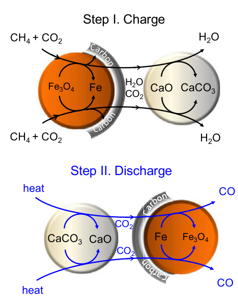
Vladimir V. Galvita*, Hilde Poelman, Guy B. Marin

Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Ghent, Belgium

HIGHLIGHTS

- Combined chemical looping as novel concept of energy storage: chemical looping combined with calcium looping.
- CH_4 induces metal reduction and surface carbon formation.
- $CaO-CaCO_3$ is used for storage-release of CO_2.
- CO_2 acts as mediation gas to oxidize metal and carbon deposits leading to CO production.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 February 2015
Received in revised form
27 March 2015
Accepted 30 March 2015
Available online 31 March 2015

Keywords:
Methane
Carbon dioxide
Iron oxide
Calcium oxide
Fuel
Carbon

ABSTRACT

Combined chemical looping was demonstrated as novel concept of energy storage in a laboratory scale test. The proposed technology is able to store and release energy from redox chemical looping reactions combined with calcium looping. This process uses Fe_3O_4 and CaO, two low cost and environmentally friendly materials, while $CH_4 + CO_2$ serve as feed. During the reduction of Fe_3O_4 by CH_4, both formation of carbon and metallic iron occur. CO_2 acts as mediation gas to facilitate the metal/metal oxide redox reaction and carbon gasification into CO. CaO, on the other hand, is used for storage of CO_2. Upon temperature rise, $CaCO_3$ releases CO_2, which re-oxidizes the carbon deposits and reduced Fe, thus producing carbon monoxide. The amount of produced CO is higher than the theoretical amount for Fe_3O_4, because carbon deposits from CH_4 equally contribute to the CO yield. After each redox cycle, the material is regenerated, so that it can be used repeatedly, providing a stable process.

1. Introduction

Energy is one of the most important topics in the 21st century as it is the foundation of today's society [1,2]. With the rapid depletion of fossil fuels and increasing environmental pollution caused by immense fossil fuel consumption, there is a high demand to make more efficient use of energy. Novel renewable and clean energy sources can substitute fossil fuels to enable the sustainable development of our society. On the pathway to improved energy efficiency, energy storage is an intermediate step [3–7]. Energy can be stored in different forms: as mechanical energy; in an electric or magnetic field; as chemical energy of reactants and fuels [6]. With the rapid development of industries and the increase of global population, the rate of electrical energy consumption has dramatically increased and its consumption manner is diversified. Hence, energy storage becomes even more complex and important, and high-performance energy storage techniques are required to enable efficient, versatile, and environmentally friendly use of energy including electricity [4,5]. In a typical energy storage process, one type of energy is converted into another form which can easily be stored and converted for use when needed [5]. Various energy

* Corresponding author.
E-mail address: vladimir.galvita@ugent.be (V.V. Galvita).

http://dx.doi.org/10.1016/j.jpowsour.2015.03.183
0378-7753/

storage systems are being developed aiming at proper utilization of different energy sources.

The metal–air battery is one such advanced energy storage and conversion technology [8]. It converts the chemical energy in lithium (anode) and oxygen (cathode) into electric energy during discharge, and stores electric energy by splitting Li–O_2 discharge products during charging using electricity (like an electrolysis device or a reversible fuel cell to generate hydrogen and oxygen by splitting water).

Recently, another type of metal–air battery was demonstrated combining a regenerative solid oxide fuel cell and a chemical looping redox cycle [9–11]. The air-electrode reactions in this battery involve only reduction and evolution of gaseous O_2, making clogging of the air-pathway no longer an issue. In addition, solid oxide-ion electrolytes are known to be stable in a broad range of gas mixtures and in contact with a variety of oxides [12–15]. In the new battery, the solid oxide electrochemical cell serves as the "electrical functioning unit" operating alternately between fuel cell and electrolyzer modes to realize the discharge/charge cycles. On the other hand, the redox cycle unit acts as the "energy storage system" to carry out reversible chemical–electrical energy conversion via H_2/H_2O-mediated metal/metal oxide (Me/MeO*x*) redox reactions. In this way, chemical energy is stored in redox couples that are physically separated from the electrodes of the solid oxide electrochemical cell. The distinct advantages of this battery over conventional metal–air batteries include O^{2-} transfer, state-of-charge independent electromotive force, high energy density and a design independent of power and energy [11,14,16].

The present novel energy storage unit proposes energy storage and conversion based on a combination of chemical looping and calcium looping processes. It uses a physical mixture of an oxygen storage material and a CO_2 sorbent material. CO_2 serves as mediation gas to facilitate metal oxidation and carbon gasification into CO by means of chemical looping [17–19], while the calcium looping process ensures storage and release of CO_2 [20–25].

Chemical looping combustion (CLC) is an emerging combustion technology [18,26,27]. In this process, fuel is oxidized by a reducible metal oxide, e.g. Fe_3O_4, and the reduced metal oxide is re-oxidized by air in a separate step. CLC hence produces a pure CO_2 stream, not diluted by N_2. By replacing air with H_2O or CO_2 as oxidizer, the chemical looping analogue to steam and dry reforming is proposed [17,19,28,29]. This process converts CO_2 to high-purity CO, providing an efficient path to CO_2 conversion [17]. The overall stoichiometry of the process indeed demonstrates that the oxidation step converts more CO_2 than was produced in the fuel combustion step.

The calcium looping technology is a promising new technique for high-temperature scrubbing of CO_2 from flue gas and syngas [30,31]. Calcium looping cycles have been intensively investigated in order to produce a concentrated CO_2 stream from the utilization of fossil fuels and biomass. Efficient CO_2 capture and storage using Ca-based sorbents can be achieved via the reversible reaction $CaO + CO_2 \rightleftharpoons CaCO_3$ ($\Delta H_{298\ K} = -178$ kJ mol^{-1}), the so-called Ca-looping cycle.

Combination of Fe_3O_4/Fe redox cycles with $CaO/CaCO_3$ looping provides a number of important advantages. Where chemical looping dry reforming immediately oxidizes fuel to CO_2, which is further converted to CO, the CO_2 mediation gas is now stored to be used at will. The $CaCO_3$ solid material acts both as CO_2 reservoir and supplier, by cyclic $CaO/CaCO_3$ calcination-carbonation. In addition, the adsorption of CO_2 gas from the stream during iron oxide reduction promotes faster material reduction and carbon formation [32].

The working principle of the "combined chemical looping" system is schematically shown in Fig. 1. The operation of the

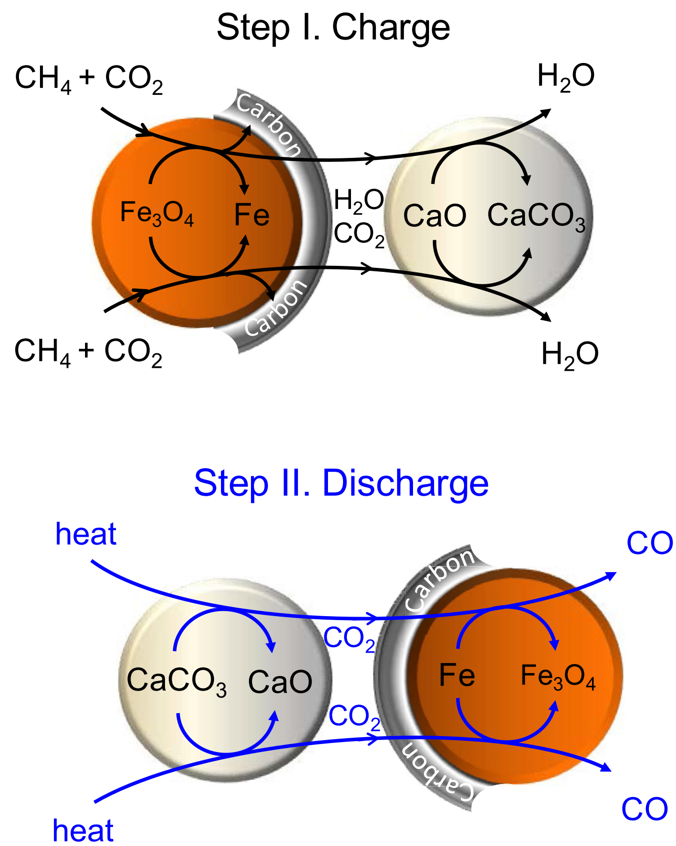


Fig. 1. Schematic working principle of the "combined chemical looping" for energy storage and conversion.

"chemical charge" and "discharge" cycles can be described as follows. During the reduction step ("charge process"), $CH_4 + CO_2$ is fed into a mechanical mixture of Fe_3O_4 and CaO. Interaction of methane with Fe_3O_4 leads to formation of metallic iron and surface carbon as well as CO_2, H_2O and H_2 (Eqs. (1) and (2)). The H_2 (Eq. (2)) obtained can be used for fuel cells. At the same time carbonation of calcium oxide occurs by interaction of CO_2 with CaO (Eq. (3)). CaO particles react with CO_2 with typical high temperatures (600–700 °C) to form $CaCO_3$ [20,23,24,33].

$$CH_4 + Fe_3O_4 \rightarrow 2H_2O + CO_2 + 3Fe \quad (1)$$

$$CH_4 \rightarrow C + 2H_2 \quad (2)$$

$$CaO + CO_2 \rightarrow CaCO_3 \quad (3)$$

The material can be kept in this "charged" condition if storage is required or be put to immediate use. For the oxidation step ("discharge"), the temperature of the sample is increased by 50–150 °C which leads to decomposition of calcium carbonate into CaO and CO_2 (Eq. (4)) [26,30,34].

$$CaCO_3 \rightarrow CaO + CO_2 \quad (4)$$

At the same time, the interaction of CO_2 with metallic iron as well as with carbon produces CO [17,35,36] via the following chemical reactions:

$$4CO_2 + 3Fe \rightarrow Fe_3O_4 + 4CO \quad (5)$$

$$C + CO_2 \rightarrow 2CO \quad (6)$$