

CHAPTER I

INTRODUCTION

1.1 Hydrogen energy

Alternative energies are of significant interest regarding the increase in global temperature, air pollution, and demand for fossil fuels with the depletion of crude oil resources. From Figure 1.1, the release of CO₂ per capita during 2001-2019 increases from 1.65 to 1.75 tCO₂/MWh in the afrika, whereas that in Europe decreases continuously to ~ 1.00 tCO₂/MWh (Dematteis et al., 2021). These trends are the implementation of greater uses of renewable energies in Europe that are beneficial in the reduction of CO₂ emissions.

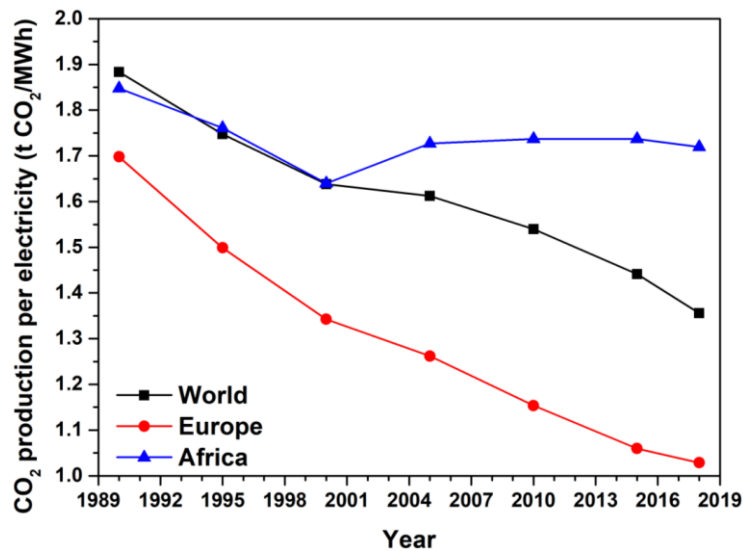


Figure 1.1 Global carbon dioxide (CO₂) production per electricity (Dematteis et al., 2021).

For Thailand, the government has drafted a plan to reduce greenhouse gas emissions, mostly from transportations and industries by aiming to increase the use of renewable.

energy up to 8-20% of the country's energy consumption within 2036(Thailand Power Development Plan, 2015). One of the most efficient renewable energies is hydrogen energy because of its high energy density (142 MJ kg^{-1}), great variety of sources (e.g., water, biomass, and organic matters), and low environmental impact (e.g., use in fuel cells) (Jain et al., 2010). Hydrogen is classified based on how the production process impacts the environment (Figure 1.2).

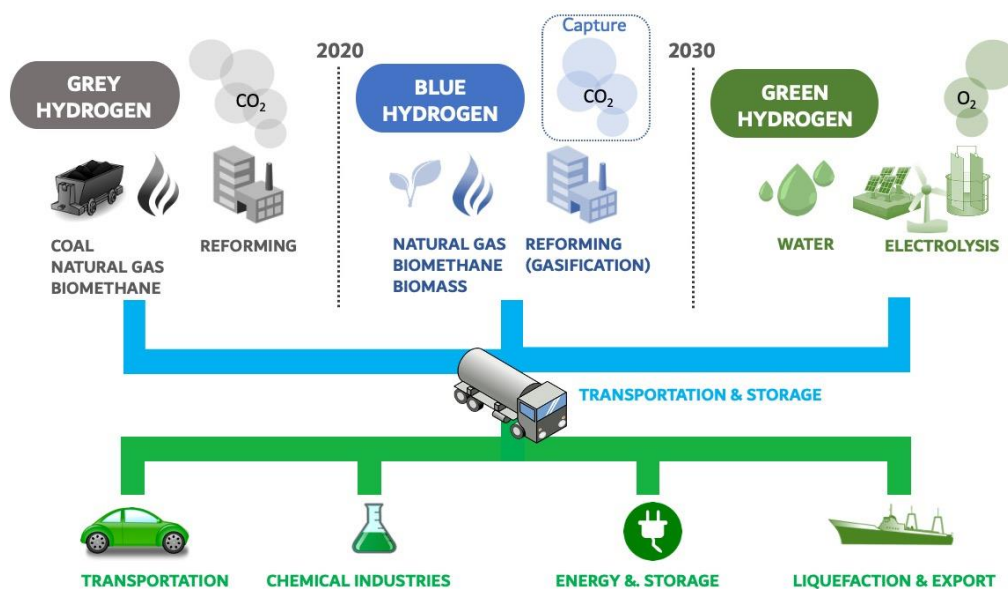


Figure 1.2 Visualization of the hydrogen production routes with a specific color. (<http://www.chem4us.be/blue-green-gray-the-colors-of-hydrogen/>).

Firstly, brown or gray hydrogen is produced by gasification or steam methane reforming (SMR) of hydrocarbon or fossil fuels. The products are a mixture of H_2 and CO_2 . Therefore, this method does not reduce carbon even though hydrogen gas is clean energy. Next, blue hydrogen uses hydrocarbon or fossil fuels as raw materials, while the obtained CO_2 is captured and used to produce other forms of renewable fuels. (Carbon Capture & Storage Technology). The last one is green hydrogen, which produced no CO_2 emissions using clean electricity from renewable energy sources, such as solar or wind power, to electrolyze water splitting. Among all hydrogen types,

green hydrogen is the most environmentally friendly (Hydrogen, 2021). Hydrogen energy is classified into two categories according to applications, i.e., (1) portable energy storage systems often used in applications requiring fast charging, such as mobile phones and electric vehicles and (2) stationary energy storage systems. Hydrogen energy in all sections consists of productions, storages, and utilizations in the fuel cell system (Jena et al., 2011). From Figure 1.3, hydrogen is produced from water splitting using renewable sources (e.g., sun and wind) through an electrolyzer, stored in the storage tank, and supplied to fuel cells to produce electricity. (Sharaf and Orhan et al., 2014). Our work has been focused on hydrogen storage materials and systems.

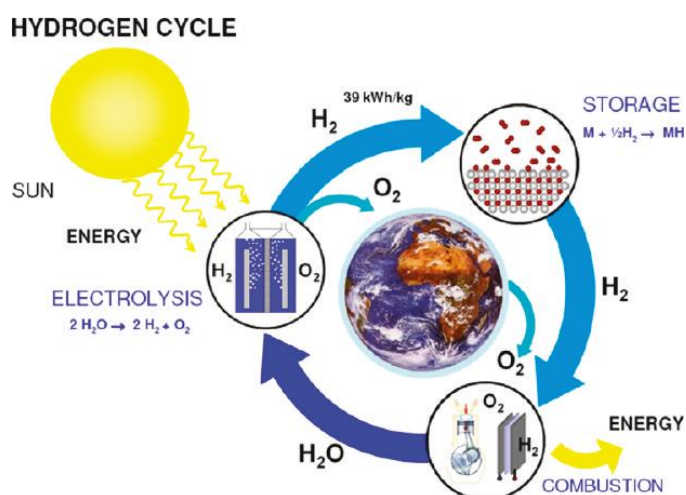


Figure 1.3 Hydrogen cycle (Jena, 2011).

2.2 Hydrogen storages methods and applications

Hydrogen can be stored by physical- and material-based methods (Figure 1.4) (Ren et al., 2017). For the physical-based method, the current technology practically used in the market is compressed hydrogen gas under 70 MPa with gravimetric and volumetric capacities of 5.7 wt. % H_2 and 40 gH_2/L , respectively. Although hydrogen capacities of the compressed gas is satisfied according to US-DOE targets (Table 2), its heavy and bulky tank as well as safety concerns due to high pressure still obstruct the practical uses. For cryogenic liquid, hydrogen is stored at low temperature ($\leq 20K$) to obtain higher volumetric hydrogen capacity ($70 \text{ kg}H_2m^{-3}$). However, large thermal losses

and the cost of insulation for storage tanks and hydrogen stations hinder its applications. Thus, physically and chemically material-based storage methods have been proposed. Hydrogen can be stored physically in microporous materials with high surface area through Van der Waals interaction and chemically in metal and complex hydrides (Ren et al., 2017).

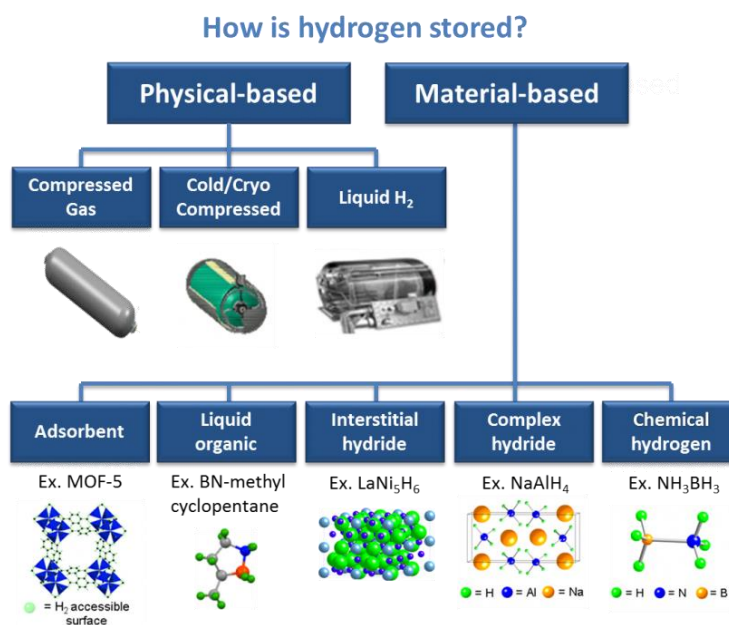


Figure 1.4 Hydrogen storage methods (Rambhujun et al., 2020).

Physisorption-based microporous materials include carbons, zeolites, and metal-organic frameworks (MOFs). They adsorb molecular hydrogen in their porous structures and hydrogen storage capacity depends on the specific surface area. In chemisorption, chemical reactions between metals or alloys with hydrogen provide high theoretical volumetric and gravimetric capacities of 40-120 kgH₂ m⁻³ and 5- 18 wt. % H₂, respectively. Nevertheless, high operating temperature and pressure conditions for de/rehydrogenation, for example, rehydrogenation of LiBH₄ at ~600 °C under 155 bar H₂ for >12 h (He et al., 2019), slow kinetics, and release of by-product gases poisoning fuel cell catalyst, and membranes (e.g., B₂H₆ from LiBH₄ and NH₃ from LiNH₂) (Yan et al., 2012) obstruct the application of hydrides as hydrogen storage materials.

Table 1.1 Targets of material-based automotive hydrogen storage systems set by the US-DOE. (<https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles>)

Storage System Targets	Gravimetric density (kg H ₂ /kg system)	Volumetric density (kg H ₂ /L system)	Temperature (°C)	Pressure (bar H ₂)
2025	0.055	0.040	-40-85	5-12
Ultimate	0.065	0.050	-40-85	5-12
Current Status	Gravimetric density (kg H ₂ /kg system)	Volumetric density (kg H ₂ /L system)	Temperature (°C)	Pressure (bar H ₂)
Metal Hydride (MH): NaAlH ₄	12	12	125	0.2-10
Sorbent: MOF-5	38	21	-193	100
Chemical hydrogen (CH) Storage: Off- Board Regenerable (AB)	46	40	-	-

In this work, we aim not only to improve kinetics and hydrogen capacities of hydrides approaching the 2020 US-DOE targets (Table 1.2) (Huang et al., 2021) but also upscaling to hydrogen storage tank. Among several solid-state hydrides, lithium amide (LiNH₂) is one of the most promising materials for reversible hydrogen storages because it contains high theoretical hydrogen content of 8.7 wt. % (Figure 1.5) (Miceli, 2010). However, ammonia (NH₃) released upon decomposition of LiNH₂ (equation (1.1)), toxic to fuel cell catalysts must be suppressed (Yao et al., 2007).



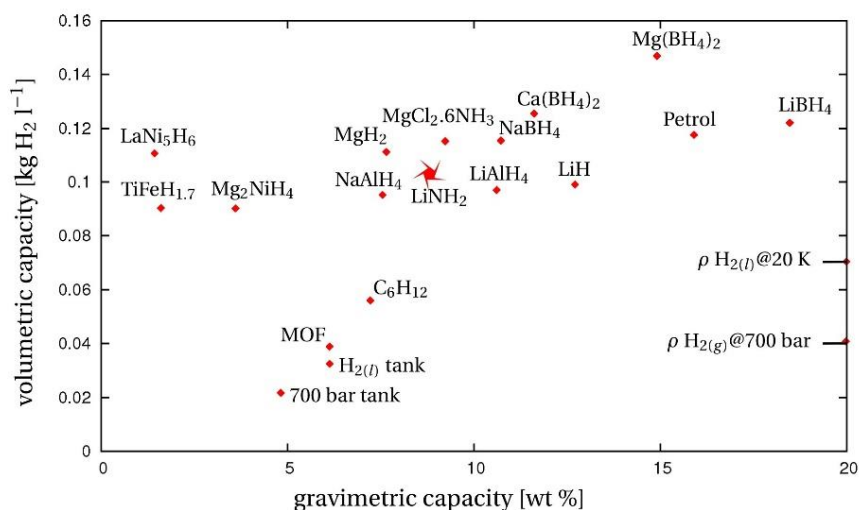


Figure 1.5 Theoretical hydrogen storage capacities of hydrogen storage materials (Miceli, G. (2010)).

To use LiNH₂ as hydrogen storage material, reactive hydride composites (RHCs) between LiNH₂ and other hydrides, such as LiNH₂-MgH₂ (Xilin et al., 2014), LiNH₂-LiAlH₄ (Dolotko et al., 2011), LiNH₂-LiBH₄ (Liu et al., 2009), LiNH₂-MgH₂-LiBH₄ (Wang et al., 2015), and LiNH₂-Ca(BH)₄ (Yua et al., 2011) have been proposed. Among all LiNH₂-based composites, LiNH₂-LiH is one of the best-performing materials for storing hydrogen due to its relatively low operating temperature, good reversibility, and low cost (Fernandez et al., 2013). Nevertheless, partial emission of NH₃ as well as poor kinetics, especially with the enhanced cycling numbers are observed. Thus, this work focuses on kinetic improvement and suppression of NH₃ release of LiNH₂-LiH composite by compaction into the pellets and sandwiching with LiH layer. Moreover, hydrogen storage performance in the small hydrogen storage tank is studied.

1.3 References

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