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Review on the thermal neutrality of application-oriented liquid organic hydrogen carrier for hydrogen energy storage and delivery

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ABSTRACT

The depletion and overuse of fossil fuels present formidable challenge to energy supply system and environment. The human society is in great need of clean, renewable and sustainable energy which can guarantee the long-term utilization without leading to escalation of greenhouse effect. Hydrogen, as an extraordinary secondary energy, is capable of realizing the target of environmental protection and transferring the intermittent primary energy to the application terminal, while its nature of low volumetric energy density and volatility need suitable storage method and proper carrier. In this context, liquid organic hydrogen carrier (LOHC), among a series of storage methods such as compressed and liquefied hydrogen, provokes a considerable amount of research interest, since it is proven to be a suitable carrier for hydrogen with safety and stability. However, the dehydrogenation of hydrogen-rich LOHC materials is an endothermic process and needs large energy consumption, which hampers the scale up of the LOHC system. The heat issue is thus essential to be addressed for fulfilling the potential of LOHC. In this work, several strategies of heat intensification and management for LOHC system, including the microwave irradiation, circulation of exhaust heat and direct LOHC fuel cell, are summarized and analyzed to provide suggestions and directions for future research.

1. Introduction

The overuse of fossil fuel has given rise to environmental issues like greenhouse effect and reduction of biodiversity both directly and indirectly [1,2]. To prevent further damage on our planet, the worldwide governments start to take joint actions to restrict the carbon emission and set a climate target of 2 °C [3,4]. The world is thus in great need of vicarious, non-hazardous and inexhaustible energy [5,6]. Therefore, the renewable and sustainable energy such as wind and solar energy draws plenty of attention [7,8]. Nonetheless, the intermittent nature of these primary energy hinders the efficient and scale-up utilization [9,10].

In this context, bonding the clean primary energy with the user terminal shows great prominence and elicits extensive study of the secondary energy which can carry the primary energy in abundance [11, 12]. During the process of seeking suitable energy form to bear the unsteady primary energy, hydrogen emerges from a series of energy carriers due to its properties of 33,000 Wh/kg gravimetric energy density and non-polluting oxidation [13,14]. It is then viewed as a splendid energy vector for the sustainable utilization in the current and future energy structure [15,16]. In the global perspective, the application of hydrogen energy consists of three major aspects: hydrogen production, hydrogen storage and delivery, and hydrogen utilization terminal (shown in Fig. 1). The production of hydrogen is almost well-developed and can be even realized with sustainable energy some day [17,18]. Meanwhile, The down-stream application of hydrogen to generate electricity through fuel cell or thermal engine has also gained high-level achievement [19,20]. It is the storage and delivery part of the hydrogen utilization chain that poses the challenge and haunts the scale up of hydrogen energy [21,22].

Nomenclature

Abbreviation

BPDM	Biphenyl and Diphenylmethane
DBT	Dibenzyltoluene
DIR	Dewar-like insulated reactor
FC	fuel cell
GT	gas turbine
ICE	internal combustion engine
LHV	lower heat value
LOHC	liquid organic hydrogen carrier
MHC	multiple hydrogen molecules carrier
MCH	Methylcyclohexane
NEC	N-ethylcarbazole
NPC	N-propylcarbazole
PEMFC	proton exchange membrane fuel cell
SHC	single hydrogen molecule carrier
SOFC	solid oxide fuel cell
TC	temperature cascade

The main issue of the chain midstream in Fig. 1 can be ascribed to the low density of 0.0899 kg/m^3 of its gaseous state. Meanwhile, the wide range of explosion concentration from 4.1% to 74.8% also consolidate the necessity of selecting a proper hydrogen carrier for storage and long-distance transportation. Currently, the storage methods can be divided into two types: physical storage and chemical storage. The former mainly consists of pressurized hydrogen of 35 MPa or higher and liquefied hydrogen of near zero degrees kelvin [23,24]. Although sophisticated technology has been developed, the energy consumption of pressurized and liquefied hydrogen storage still takes up 5–20% and 30–40% of the stored hydrogen's lower heating value severally as the inherent device requirement for high pressure or low temperature [23, 25]. The physical storage for hydrogen is thus confined to some particular fields like astronautics where the cost is outweighed by other factors. In the past few decades, chemical storage also received considerable progress and assorted compounds including metal hydride, salt hydride and liquid organic hydrogen carrier (LOHC) came into use successively. Among them, LOHC is viewed as one of the most promising materials due to its high capacity and stable liquid nature, which can not only meet the need of global transportation but also fit the existing petroleum fueling infrastructure [26,27]. In this case, the combination of hydrogen and LOHC exhibits great potential of prompting the application of renewable and sustainable energy [28,29]. Therefore, the annual LOHC-related articles gained increasing publishing tendency and the keywords concentrate on the energy storage, which is depicted in Fig. 2.

Despite of the great prospect of LOHC, the severe issue of extensive energy consumption resulting from the high dehydrogenation enthalpy of LOHC still remains, which significantly hampers the large scale utilization of LOHC in the mobile and onboard applications [30,31]. To illustrate, one of the intensively studied species Dibenzyltoluene (DBT), which owns the hydrogen capacity of 6.2 wt% and favors long distance transportation, has the dehydrogenation enthalpy as high as 65 kJ/mol H$_2$[32]. Even with the existence of hetero-atoms like nitrogen in N-ethylcarbazole (N addition helps to the drop of activation energy), the dehydrogenation still requires around 56 kJ/mol H$_2$ to proceed the conversion [33,34]. Basically, the dehydrogenation reactor of most
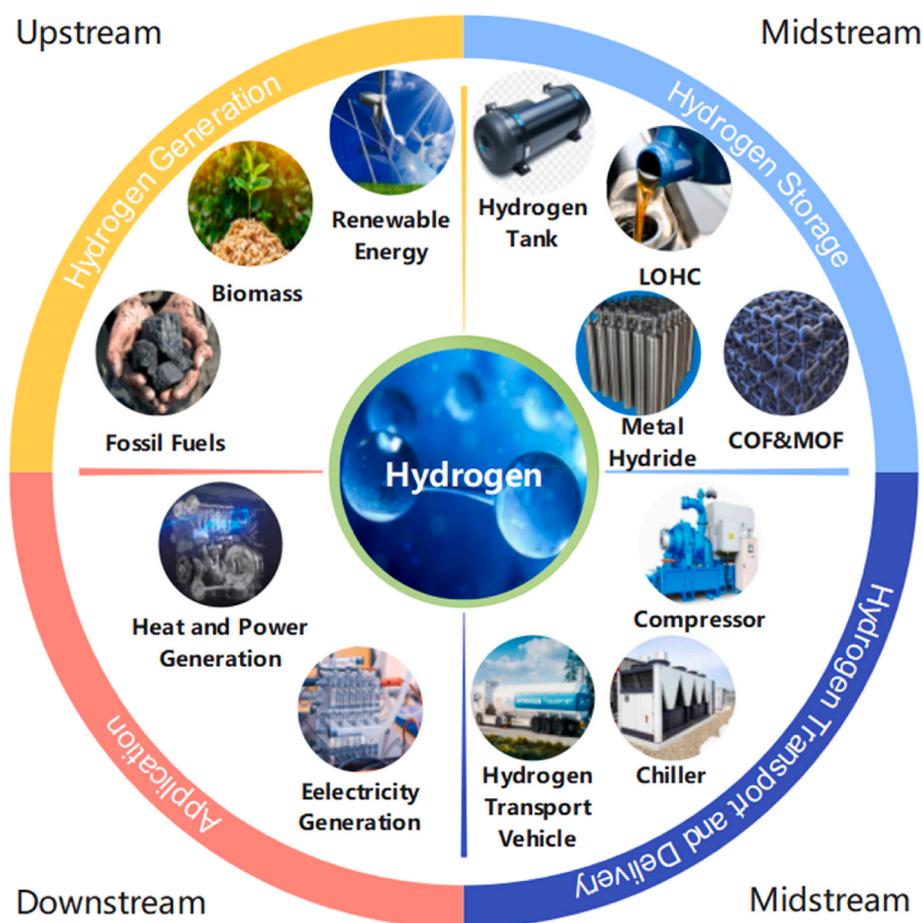
Fig. 1. The hydrogen application chain.

Fig. 2. Annual published LOHC-related articles and frequency statistics of keywords in the published literature from Web of Science Core Collection.

LOHC species requires the operating temperature of around 200–300 °C for activation energy of reactants and reaction enthalpy [32,35].

Therefore, to reduce the activation energy consumption is paramount to curtail the heat input. To optimize the dehydrogenation performance of LOHC reactor, the heat management draws considerable attention and has been intensively studied in recent years [36,37]. Among these researches, many strategies, for example, the reuse of exhaust heat, are proposed to address the problem of high energy consumption. Basically, these strategies consist of three characteristic patterns: heat intensification, heat management with and without integration. This review will summarize and analyze the previously reported studies concerning the heat issue within the LOHC contained systems. The article is developed with the following threads: Section 1 is the introduction of review background, Section 2 focuses on the most-studied species of LOHC with their individual properties, Section 3 and 4 review the already-published typical methods of heat intensification and management. After the above summary, a conclusion will be obtained to provide suggestions and directions for the future research.

2. LOHC species

The selection of LOHC species is tricky, because the carrier compound needs to primarily exhibit enough hydrogen capacity for meeting the economic demand. Moreover, the selected species ought to have abundant supply and accessible approach. From the perspective of safety, the target compound is required to remain stable and nontoxic during the process of transport and storage. In this section, a series of LOHC species is selected and briefly introduced for comparison. The selected species are divided into two categories based on their chemical properties due to different molecular structures: homocyclic compound and heterocyclic compound.

2.1. Homocyclic compound

2.1.1. Methylcyclohexane (MCH)

As a kind of primitive LOHC species, Methylcyclohexane (MCH) can date back to last century, since it is an accessible and cheap solvent in the organic synthesis [38]. The dehydrogenation process of MCH is shown in Fig. 3. Basically, MCH has a hydrogen capacity of 6.16 wt% and usually requires a dehydrogenation temperature of 300 °C or higher [39,40]. The MCH system is able to obtain both high conversion rate of 90% and almost pure hydrogen through the membrane-contained reactor [41,42]. The membrane within the reactor separates the released hydrogen as the reaction occurs, which thus promotes the conversion rate [43]. With the accumulation of long-term researches, the MCH membrane reactors gain great progress, and even achieve engineering scale [44]. For example, the commercialization of MCH is underway in Japan by the Chiyoda corporation [45].

2.1.2. Dibenzyltoluene (DBT)

Used to be a common thermal conduction oil, DBT enjoys the incomparably low cost and a hydrogen capacity of 6.2 wt% (a DBT molecule can carry 9 molecules of hydrogen as depicted in Fig. 4). In this case, DBT exhibits a complicated dehydrogenation mechanism [46].
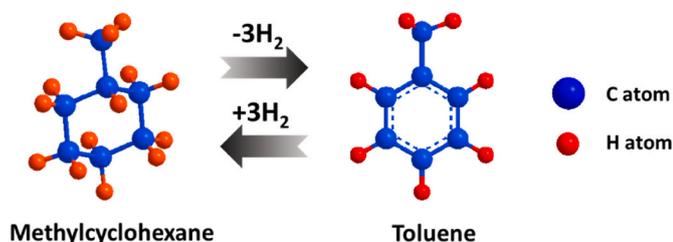
Fig. 3. Conversion between methylcyclohexane and toluene.

Besides, the average dehydrogenation enthalpy of DBT is reported to be 65 kJ/mol H_2, which requires the dehydrogenation reactor to be maintained at a temperature of over 200 °C [47,48]. Taking all these properties into consideration, DBT is reported to fit the demand of stationary hydrogen storage system with the pressure swing reactor, which allows long time for the hydrogen release and heat conservation [49, 50].

2.1.3. Naphthalene

Naphthalene is the simplest polycyclic aromatic hydrocarbon with its charged species of Decalin. As shown in Fig. 5, the maximum number of hydrogen molecules that a single Naphthalene can carry is 5 corresponding to a capacity of 7.23 wt%. It was reported that the hydrogen charging process occurs at 70 °C and is dominated by the second step of hydrogenation reaction [51,52]. The dehydrogenation of decalin is also highly endothermic, which draws about 59.46 kJ energy to release 1 mol hydrogen on average and thus results in an operating temperature of around 200 °C [53]. But high temperature is preferred for the *cis*-decalin, which has higher activity in dehydrogenation reaction than the *trans* isomer, tends to convert to *trans*-decalin at low temperature [54]. Both of the isomers share the same dielectric property as MCH and allow for the microwave-assisted heating which will be discussed in the next section.

2.1.4. Biphenyl and Diphenylmethane (BPDM)

BPDM is the eutectic mixture of Biphenyl and Diphenylmethane with a mass ratio of 35:65 (35 wt% Biphenyl, 65 wt% Diphenylmethane). Their feasibility of being LOHC with proper catalyst has already been verified by experiment severally [55,56]. The reason why Biphenyl and Diphenylmethane are mixed to be utilized is that the addition of Diphenylmethane can lower the melting point of mixture while guaranteeing a high hydrogen capacity of 6.9 wt% [57]. Mutual conversion between charged species and discharged species of BPDM is shown in Fig. 6. The dehydrogenation energy is reported as 70 kJ/mol H_2, which is corresponding to the operating temperature of 270~340 °C [58]. Meanwhile, the manifold intermediates appearing during reaction are not negligible since both of Biphenyl and Diphenylmethane undergo a multi-step dehydrogenation process.

2.2. Heterocyclic compound

2.2.1. N-ethylcarbazole (NEC)

With 6 molecules of hydrogen (shown in Fig. 7), NEC has a hydrogen capacity of 5.8 wt%. Unlike MCH and DBT, NEC molecule has a hetero atom of nitrogen on the ring, which cuts down the dehydrogenation enthalpy to around 50 kJ/mol H_2 [33,59]. In this case, the NEC system is permitted to operate under the temperature below 200 °C [60,61]. Besides, the activation energy is also reduced compared to Ethylcarbazole and the dehydrogenation kinetics enjoys an upgrade of triple fold [34]. Therefore, the NEC system is enabled to release all the carried hydrogen in 2 h [62]. Our previous research also demonstrated the NEC exhibits great potential in large scale application with proper optimization of reactor performance [36]. NEC is thus viewed as one of the most promising hydrogen carriers which can be applied in both mobile and stationary scenarios.

2.2.2. N-propylcarbazole (NPC)

Benefiting from the nitrogen atom, NPC also has a great kinetics as NEC, which makes it a potential LOHC candidate. The transformation between N-perhydro-propylcarbazole and NPC is depicted in Fig. 8. The dehydrogenation of charged NPC takes three steps with 2 molecules of hydrogen released at each step and can finish the process at the temperature as low as below 190 °C within 240 min [63]. The conversion rate is also as high as NEC, which is almost 100%. A recent study from Yang et al. even suggests that both hydrogenation and dehydrogenation can be further halved with the Pd/CeAl as the catalyst [64]. It is thus safe
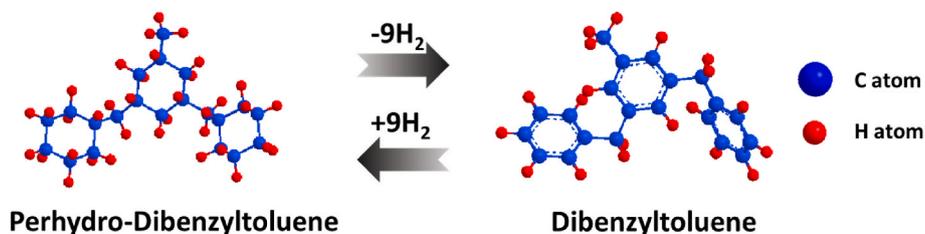
Fig. 4. Conversion between perhydro-dibenzyltoluene and dibenzyltoluene.
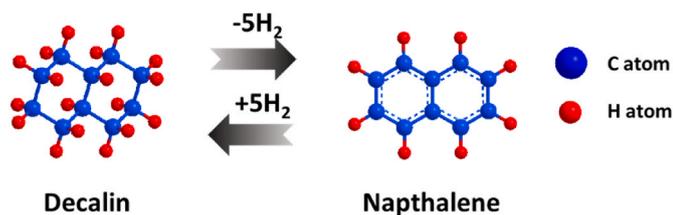
Fig. 5. Conversion between decalin and naphthalene.

to assert NPC has great kinetic performance under proper conditions. But the propyl group brings the capacity down to 5.4 wt%, which is a little lower than NEC.

2.3. Alcohol

Although a lot of alcohol species including methanol, ethanol and glycol are classified as LOHC, they usually undergo complete oxidation and thus produces CO_2 as the final product. Besides, their recharging process often engages steam reforming which differs from the reversible hydrogen charging process. Since this article concentrates on the application of hydrogen energy, this part will focus on the rechargeable alcohol species like isopropanol which is also further discussed in detail in chapter 4.

Isopropanol, as the simplest secondary alcohol, is able to discharge at the fuel cell and yield acetone as shown in Fig. 9. Since each isopropanol molecule can only release two protons at the anode, it has a relatively low hydrogen capacity of 3.3 wt% compared to NEC and DBT. The enthalpy of dehydrogenation from isopropanol to acetone is reported to be 100.4 kJ/mol H_2 [65]. However, this process is seldom performed during the utilization of isopropanol while direct LOHC fuel cell is more frequently adopted due to the high selectivity of electrochemical oxidation [66,67]. Besides, it is confirmed that direct isopropanol fuel cell exhibits higher real open circuit potential, less cross over through membrane and milder toxicological fuel profile compared to methanol fuel cell [68]. However, the utilization of isopropanol still faces the membrane dissolution issues [69].

2.4. Section summary

The representational LOHC species along with their advantages and disadvantages are summarized in Table 1 based on their individual characteristics. The power density of each species shown in Table 1 is calculated using Eq. (1).
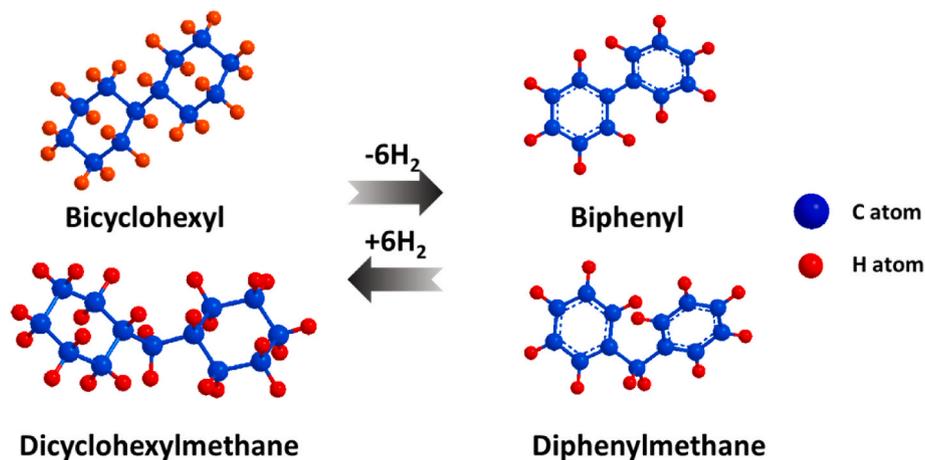
Fig. 6. Conversion between Biphenyl, Diphenylmethane and their charged species.
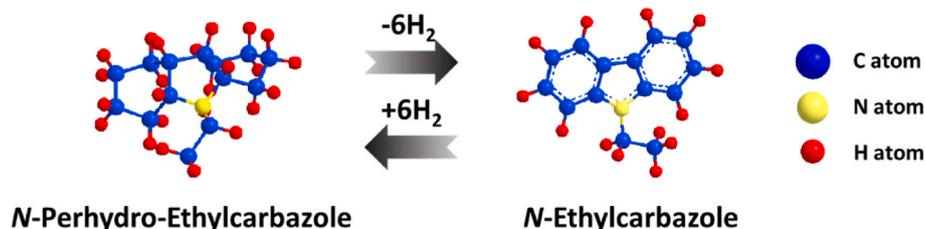
Fig. 7. Conversion between *N*-perhydro-ethylcarbazole to *N*-ethylcarbazole.
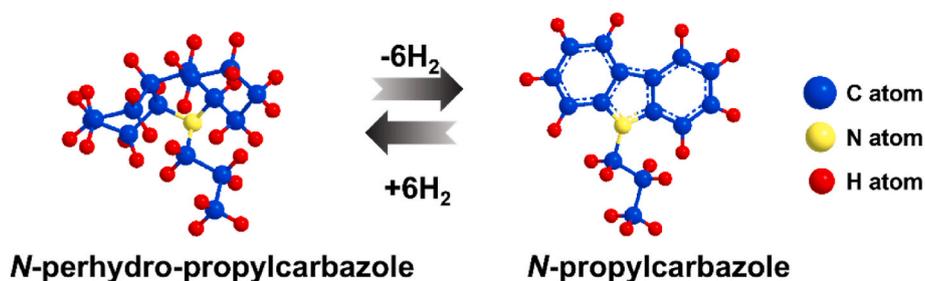
Fig. 8. Conversion between *N*-perhydro-propylcarbazole to *N*-propylcarbazole.
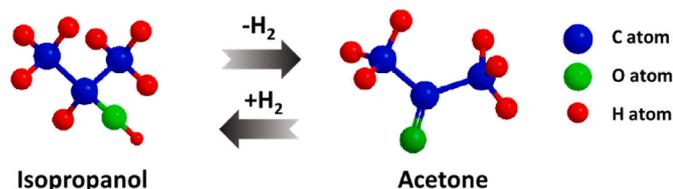
Fig. 9. Conversion between isopropanol and acetone.

Energy density = hydrogen capacity

$\times$ lower heating value of hydrogen $(120 kJ / kg)$ (1)

As can be seen in Table 1 and Fig. 10, all of the homocyclic species including MCH, DBT, Naphthalene and BPDM have high hydrogen capacity ranging from 6.16–7.30 wt% compared to NEC and NPC. Besides, they tend to have lower material cost in contrast to heterocyclic compounds. However, none of them exhibits the dehydrogenation temperature below 473 K, which demands for a large amount of heat consumption at the utilization stage. Even though the addition of nitrogen atom into the rings has already decreased the dehydrogenation enthalpies of NEC and NPC, their operating temperatures still stay close to 473 K. Meanwhile, the high value of the dehydrogenation enthalpy of Isopropanol necessitates the direct discharge process. It is thus not hard to conclude that effective method of heat management is in need to reduce or avoid the heat consumption when using the energy carried by LOHC. The following sections will focus on the heat management researches of LOHC, which will prompt its application.

3. Heat intensification through microwave irradiation

Amid multitude research fields, microwave technology, as a novel method, is universally applied in plenty of fields such as catalytic reaction and fuel processing [70,71]. Since the microwave technology can significantly intensify the heat transfer, it is thus introduced to the utilization of hydrogen energy to address the heat issue [72,73]. Generally, the improvement can be attributed to traits of microwave heat, including rapid heating rate, selective heating and high heating efficiency. By comparison, conventional heating mode requires the energy to transfer through multiple kinds of mediums to the target position. The whole process obeys the Fourier's law of heat conduction and Newton's law of cooling, during which the delivery rate of heat is dominated by the lowest heat conductivity of multiple mediums. The heat loss of mediums is considerable and unavoidable. In case of microwave heating, the energy is carried by the wave until meeting strong microwave-absorbent, where the energy is converted to thermal energy due to the dielectric loss. As the material of target positions exhibits extremely stronger absorbing ability of microwave than the intermediate medium, most of energy is delivered to the target position [74,75]. Thus, the energy loss in transfer can be significantly reduced or even avoided. In practice, the energy carried by microwave is usually absorbed by the carbon host of catalysts such as carbon nanotube and

active carbon, while the LOHC species like tetralin, decalin and methylcyclohexane consume almost no energy due to their non-polar molecular nature [76,77].

Benefiting from this extraordinary property, the reactor system which contains carbon-based catalysts can be heated swiftly and efficiently. Both the conversion rate and reaction rate are improved [78, 79]. For instance, a methylcyclohexane-toluene dehydrogenation reactor with microwave heating shows a rapid temperature rise from ambient temperature to 180 °C within 2 min, while it takes 35–40 min through a ceramic heater [80]. Moreover, the selective heating of microwave technology brings a large space for energy saving: 33 W of microwave heating in contrast to 139 W of conventional heating. Besides, the 2-min microwave heat is capable of obtaining a hydrogen yield of 94%, while the yield of ceramic heating reaches 60% only after 25 min.

This promotion of performance is ascribed to the intensification of species diffusion and fast microscopic kinetics resulting from the unique heat mechanism called "localized superheating" [80]. Generally, the reaction kinetics is determined by absorption of reactant to the active site, desorption of product from the active site and contacting reaction. The microwave irradiation facilitates the mass transfer step, since downward temperature gradient and desorption step share the same direction, which is a strong driving force [81]. As shown in Fig. 11, the active sites (metal particles) of catalyst are heated to a high temperature of over 550 °C, while the bulk has a low temperature of 340 °C [80]. In this case, the toluene desorbs rapidly after the occurrence of the contacting reaction on the active site, which spares active sites for the subsequent reactant to be absorbed.

In this heating mechanism, the trigger of improvement in the reactor performance is the superheating of catalyst and enhanced mass transfer. Superheating, usually relating to the formation of hot spot in the core of catalyst, can generate a temperature of 200 °C from the inside of catalyst to bulk solvent because of the selective heating. It is exactly these hot spots that exhibit advanced equilibrium and kinetics of reaction, thus resulting in high conversion rate. Without the formation of hot spots, the microwave irradiation can't promote the conversion rate [82]. In addition, the temperature gradient induced by the superheating shows the identical vector of product desorption, which enhances the mass transfer. There is also the evidence of non-thermal effect on the diffusion step which is confirmed by molecular simulation [83]. However, the enhancement of mass transfer only acts when the overall kinetics is controlled by the mass diffusion. In case of reaction control, this benefit is helpless, which is proven by the dehydrogenation of decalin in Horikoshi's study [84].

To further improve the system with microwave irradiation, heat management is also considered. Basically, three ways concerning the apparatus, additive and catalyst can be applied. The first one is heat insulation with the assistance of Dewar-like reactor capable of transmitting microwave without energy loss as shown in Fig. 12 [79,85]. The installment of Dewar-like reactor is demonstrated to save 40% of the energy of microwave irradiation to achieve a conversion rate of 56% for tetralin [79]. Secondly, the addition of ionic liquid into the reaction mixture is proven to be able to intensify the heat absorption of

Table 1
Summary of representative LOHC species for hydrogen storage.

LOHC species	Molar mass of charge species (g/mol)	Molar mass of discharged species (g/mol)	Hydrogen capacity (wt.%)	Energy density (kJ/g)	Dehydrogenation enthalpy (kJ/mol H₂)	Dehydrogenation temperature (K)	Advantages	Disadvantages	References
MCH	98.19	92.14	6.16	7.392	68.3	573	• High capacity • Low material cost • Engineering scale achieved	• Extremely high dehydrogenation temperature • Toxicity	[31,36]
DBT	290.54	272.39	6.25	7.5	65.4	Over 473	• High capacity • Safety • Low material cost	• High dehydrogenation temperature • Poor kinetics	[43,46]
Naphthalene	138.25	128.17	7.29	8.748	59.46	Around 473	• Extremely high capacity	• Incomplete hydrogenation and dehydrogenation • Isomeride issue • High dehydrogenation temperature	[46,47]
BPDM	166.31(Bicyclohexyl) 180.34 (Dicyclohexylmethane)	154.21(Biphenyl) 168.24 (Diphenylmethane)	7.30	8.76	70	543~613•		• Intermediates issue • High dehydrogenation temperature	[50,51]
NEC	207.36	195.27	5.83	6.996	50	Below 473	• Great kinetics	• High material cost	[53,55]
NPC	221.39	209.29	5.46	6.552	52.2	Below 473• •			[56,57]
Isopropanol	60.10	58.08	3.36	4.032	100.4	–	• Direct discharge of hydrogen-rich species at fuel cell	• Membrane dissolution	[58,62]
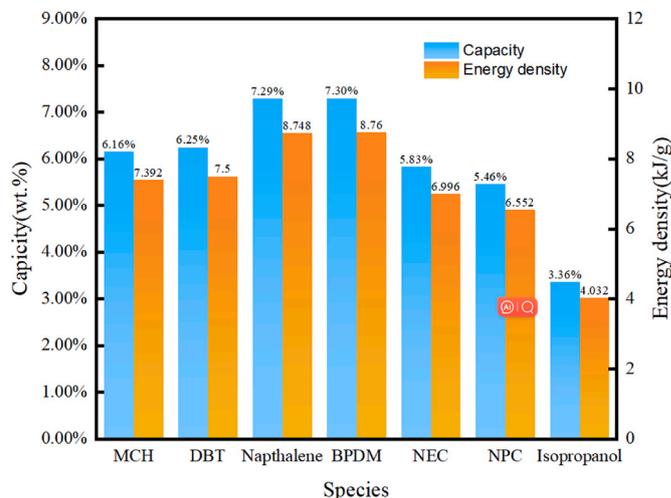
Fig. 10. Capacity and power density comparison among LOHC species.
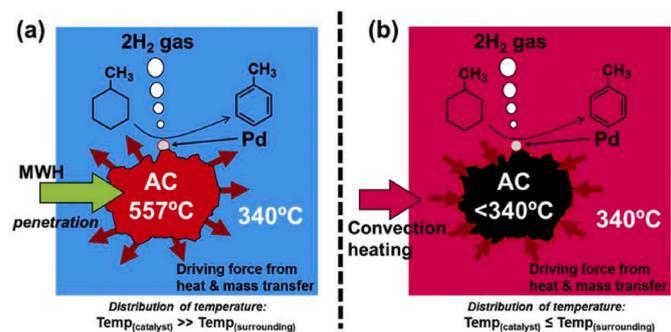
Fig. 11. Reaction process within the catalyst: (a) Microwave heating, (b) Conventional heating. Reprinted with permission from Ref. [80]Copyright 2016 Elsevier.

microwave irradiation [86]. With the heating power of microwave fixed at 190 W, the mixture with ionic liquid has a temperature ramp of 406 °C/min compared to those of 80 and 46 °C/min without ionic liquid [79]. Similarly, the carbon host, as the microwave absorbent, is studied to explore the influence of catalyst host on the thermal behavior of the reactor [76,87]. To select the best catalyst support, Zhou et al. tested the thermal behavior of five different carbon materials including carbon nanofiber, carbon black, graphite, activated carbon and carbon nanotube in the dehydrogenation reactor of decalin [88]. The carbon nanotube exhibits the best heating ability to raise the temperature of decalin mixture from ambient temperature to the boiling point of decalin (192.5 °C) within 4 min and to maintain at this point stably.

In summary, the microwave irradiation displays outstanding heating ability with a sharp reduction of energy consumption compared with the conventional heating. Due to its selective heating ability, the energy can be preferentially utilized at the active sites of catalyst instead of being dissipated on the way of heat conduction. Therefore, the non-polar LOHC species is required since microwave irradiation only affects the non-polar species positively [82,89]. Moreover, the mechanism of reactor enhancement is clarified that the microwave irradiation only takes action when the superheating and mass transfer control are met. Other improvements of heat intensification can be found at the insulation like Dewar-like reactor and strong microwave absorbent including ionic liquid and suitable carbon host of catalyst. Besides, more non-polar LOHC species along with the catalyst are suggested to be evaluated to provide more options. More importantly, engineering or amplification work should be done to achieve large scale utilization of microwave-assisted heating method instead of experiment-level trials.
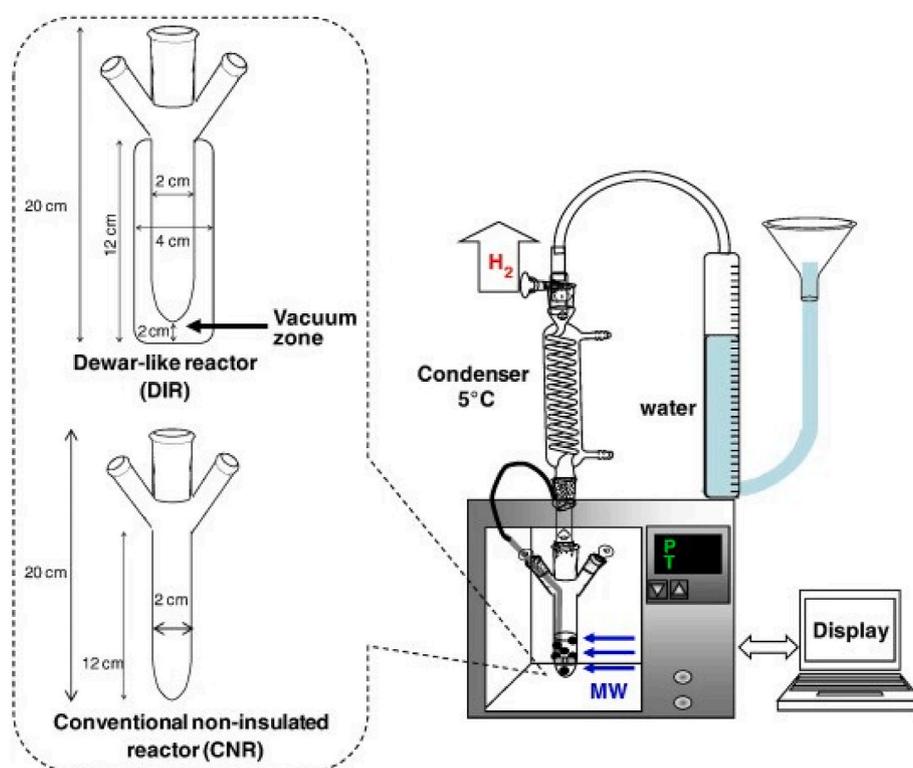
Fig. 12. Scheme of Dewar-like insulated reactor (DIR) and conventional non-insulated reactor configuration. Reprinted with permission from Ref. [79]Copyright 2012 Elsevier.

4. Heat management with integration

The above-mentioned methods like intensification of heat and mass transfer, rely on a negative way focusing on how to deliver energy both effectively and efficiently from heat source to application terminal. Besides, there are other options based on positive ways like increasing the efficiency of energy utilization and eliminating the dispensable energy consumption by system integration.

Utilization of LOHC-bound hydrogen with system integration depends on the integrated system design. For instance, the circulation of exhaust heat between different modules is a widely known concept, which has attracted plenty of researches and reports due to its high efficiency energy utilization. Another way is to eliminating dispensable energy, which can be exemplified with the fuel cell operating on the hydrogen carrier directly instead of hydrogen molecules. Such a strategy diminishes the energy input by leaving out the dehydrogenation step which consumes abundant energy as reaction enthalpy.

4.1. Integration through exhaust energy circulation

Exhaust heat is a wide range of unexploited energy usually carried by effluent fluid from factories, fuel cells and thermal engines due to the high operating temperature of these scenarios. Given the fluid nature, these types of heat can be effectively utilized through heat exchanger to cover the dehydrogenation enthalpy, which thus benefits the energy efficiency. In this section, heat issue of the LOHC dehydrogenation addressed by exhaust reuse will be discussed mainly through thermal engine and high temperature fuel cell.

4.1.1. Exhaust energy from gas turbine

Ever since thermal engines were invented centuries ago, they became the most universally used machines to generate power and brought efficiency to human society. Due to the long application and development history, thermal engines such as internal combustion engine (ICE) and gas turbine (GT) have already achieved sophisticated technology [90, 91]. In this case, they usually exhibit compact size, high reliability and flexibility for fuel species [92,93]. However, conventional GT along with other thermal engines often consumes carbonaceous fuels and has greenhouse emission issues. Under the circumstance of carbon neutralization and promotion of renewable energy, clean energy like hydrogen is introduced to GT combustion, which has been validated to be feasible and promising [94,95]. This can be partly attributed to the zero-CO_2 emission and high energy density of hydrogen characteristics [96]. Moreover, the detected and reported possible drawbacks including mixture issue of fuel feedstock and NO_x emission have already find their corresponding solutions, which further cleans up the halt of hydrogen application in GT [97,98]. Additionally, the heat recovery study suggests that the system efficiency could be promoted if the exhaust heat is properly utilized [99]. It is not hard to associate the high-quality exhaust heat of GT with the large dehydrogenation enthalpy of LOHC, which can cover plenty of energy investment [100,101]. Therefore, this section will focus on the combination of GT with LOHC based on the reported researches.

In 2015, Hampel et al. developed an integrated model to evaluate the feasibility of LOHC dehydrogenation with the exhaust heat from a micro gas turbine [102]. The dehydrogenation performance of hydrogen charged Dibenzyltoluene (DBT) and N-ethylcarbazole (NEC) under different temperatures and pressures were tested in the simulation work. Using the developed model, exhaust heat is re-utilized in two aspects: effluent dehydrogenated LOHC to preheat the input hydrogenated LOHC, and exhaust energy from GT to provide enthalpy for dehydrogenation reaction. As shown in Fig. 13, the required heat input is fully covered by the energy carried by the exhaust gas from GT. This chain is thus capable of realizing the thermal neutrality through the re-circulation of heat within the system.

Since the dehydrogenation of both NEC and DBT species is endothermic, it is as expected to observe higher mass flow rate of releasable hydrogen as the temperature of exhaust gas rises. The result suggests
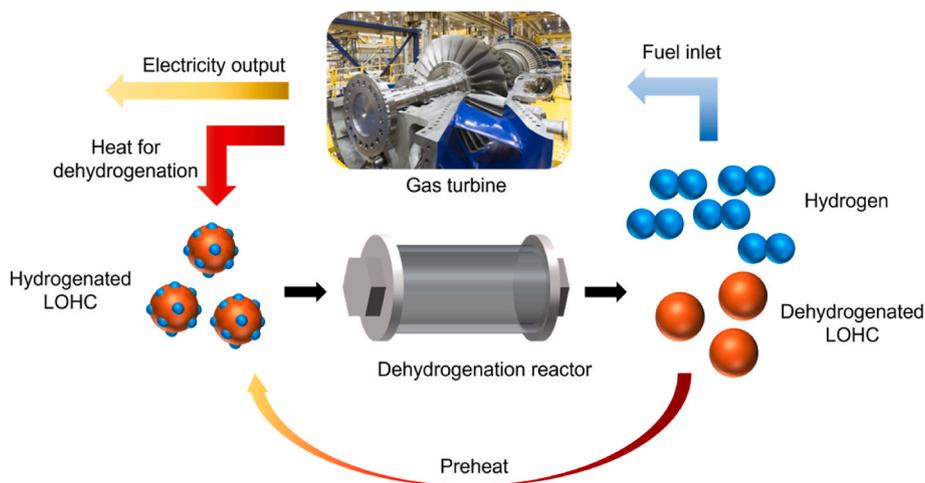
Fig. 13. Scheme of the heat circulation between the GT and reactor.

that NEC can release almost twice amount of hydrogen (14 g/s) as large as DBT under 542 K and 1 bar, which is attributed to the higher dehydrogenation enthalpy of DBT (65 kJ/mol H$_2$). Even though the temperature is raised to over 600 K, DBT (15 g/s H$_2$) still exhibits a lower releasable hydrogen flow than NEC (17.5 g/s H$_2$). What's more, DBT coupled with GT is not even capable of maintaining nominal power, once the pressure is fixed at 5 bar, which has adverse effect on dehydrogenation reaction. As a result, the max coupling efficiency (19%), which is defined as the electrical power output over the released hydrogen lower heat value (LHV), is achieved by NEC.

To further scale up the GT coupled with LOHC, Li et al. developed a steady-state model to study the heat integration of a DBT based LOHC dehydrogenation reactor and a 7.7 MW hydrogen-fueled GT [103]. Similar to Hampel's work, they use the dehydrogenated LOHC to preheat the input mass and GT exhaust heat to provide dehydrogenation enthalpy. The reactor consists of a catalyst bed and a plate heat exchanger with the length and width of 5 m and 350 mm, respectively. The scale up method is to form an array of 600 parallel reactors for dehydrogenation. With the assumed hydrogen yield of 79.29%, the system efficiency which takes the energy consumption of compression and pump into account, obtains its peak value of 22%.

The above researches evaluate and justify the feasibility and prominence of coupling GT with LOHC. However, the limit of the heat integration is also indicated. The GT engages the combustion process to transform chemical-fixed energy to thermal energy and electricity. Amid them, the thermal energy is carried by exhaust gas and is introduced to the heat exchanger to further provide energy for reaction. Based on the hypothesis that all the dehydrogenation enthalpy can be covered by exhaust heat, the corresponding profit of energy saving can be calculated with the LHV with different LOHC species as summarized in Table .2 and Fig. 14. On one hand, the cover rate of LHV signifies the potentiality of energy saving in coupled system. Higher cover rate equals more space for system optimization if the external energy input can be replaced by the internal exhaust heat circulation. On the other hand, high dehydrogenation enthalpy may affect the feasibility of the coupled system since the internal energy may not be balanced within the system. To illustrate this issue, the DBT based system under 5 bar is found to be not able to reach the nominal power of engaged GT over the entire range

of exhaust gas temperature [102].

4.1.2. Exhaust energy from solid oxide fuel cell

Owing to high efficiency and low pollution, fuel cell (FC) is a promising power device which has been successfully applied in many fields such as vehicles and buildings [104,105]. The FC acts like a combustion engine to output power via the oxidation of fuel. Instead of igniting the fuel, the cell releases the power contained in hydrocarbon molecules by electrochemical reactions, which emancipates them from the efficiency restriction of thermal engine cycle. Many fuel species have been applied in different types of fuel cells, among which hydrogen is one of the most promising energy carriers due to its high energy density and non-CO$_2$ emission [106,107]. Consequently, fuel cell is an ideal option for scenarios which require the transformation from hydrogen energy to electricity. Nevertheless, to provide the fuel cell with hydrogen also requires a dehydrogenation process from charged LOHC, which draws considerable heat. Herein, a possible solution is to combine the high-temperature FC like solid oxide fuel cell (SOFC) with the dehydrogenation reactor, fulfilling the heat of exhaust heat from SOFC.

Among multiple power devices, SOFC is viewed as reliable and promising due to its electrical efficiency of around 80% [108,109], flexibility for both carbonaceous and non-carbonaceous fuels [110,111], wide range magnitude of output power level from watt to megawatts [112,113], and high quality of applicable heat (600–1000 °C operating temperature) [114,115]. All these properties make SOFC suitable for the combination with LOHC application. Therefore, numerous researches have been developed to integrate the application of LOHC with SOFC through the heat circulation between these two modules.

Generally, the combined LOHC and SOFC systems have these main elements: a SOFC stack which oxidizes fuel to generate electricity, a dehydrogenation unit that provides hydrogen as fuel, a combustor or burner which utilizes the effluent gas from SOFC stack to generate heat for dehydrogenation demand and some other supporting modules. The main theme of heat integration is to make full use of the generated heat within the system to avoid extra energy input from outside.

Preuster et al. established a model to bind a 5 kW SOFC with a DBT-based dehydrogenation unit to test feasibility of match up and proposed an optimized layout to further improve the heat circulation within

Table 2
Summary of LOHC coupled GT system.

Scale	Species	Reactor type	Hydrogen yield	Performance	Reference
100 kW GT	NEC	–	–	System efficiency of 19% at 1 bar and 14% at 5 bar	[102]
	DBT	–	–	System efficiency of 9% at 1 bar	
7.7 MW GT, 600 parallel reactors	DBT	Horizontal tube reactor	79.29%	System efficiency of 22% at about 1 bar	[103]
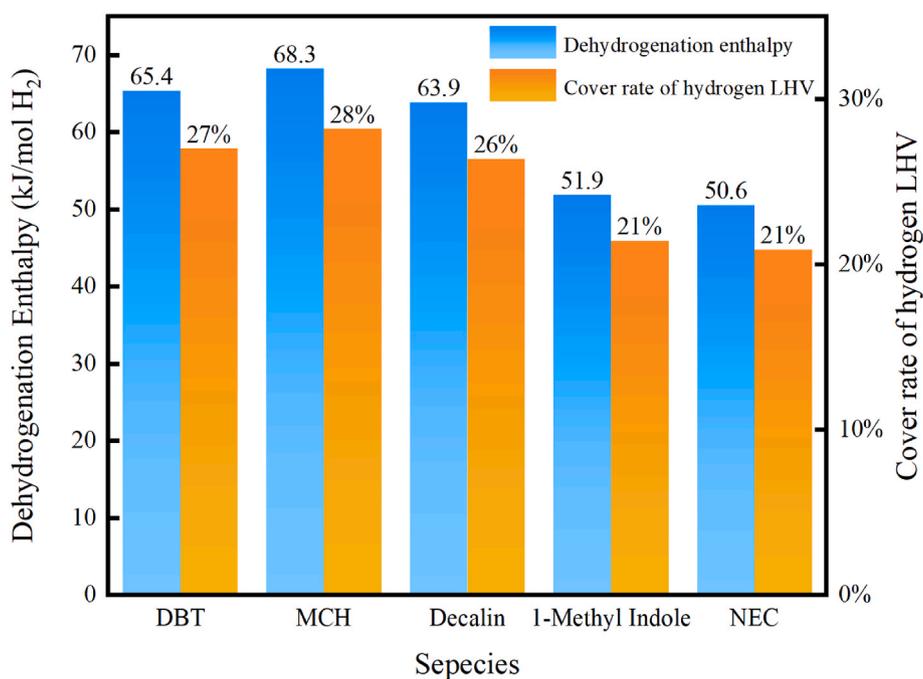
Fig. 14. Comparison of dehydrogenation enthalpy and hydrogen LHV cover rate of LOHC molecules [32].

system [116]. They started with a less complicated configuration which only reuses the heat of effluent fluid from anode, cathode and reactor to preheat the inlet fuels as shown in Fig. 15. In addition to the preheating energy, another part of dehydrogenation enthalpy is supplied by a catalytic burner which combusts the untapped hydrogen and air from SOFC. In this situation, the fuel utilization is limited to be under 67%, since higher value may lead to insufficient heat for dehydrogenation demand. To optimize the system, the exhaust heat from reactor is recirculated to the air heater of anode and catalyst burner (Fig. 15). With this change, the heat demand of reactor becomes proportional to the extractable heat carried by exhaust gas, which raises the fuel utilization rate and electrical efficiency to 80% and 45%, respectively. The results were also validated in other report with the similar system layout [117].

To further exploit the heat in the system, a concept of temperature cascade (TC) dehydrogenation unit coupled with SOFC was proposed by Lim [118]. The concept aims to fulfill the utilization of flue gas energy from SOFC stack by four different LOHC species (ammonia, BPDM, N-phenylcarbazole, and NEC) with gradient dehydrogenation temperatures in a single unit as depicted in Fig. 16 (a). With the temperature cascade design, each species can obtain necessary dehydrogenation heat and avoid unexpected decomposition of molecules due to extremely high temperature. The hybrid TC system is competent of generating 1.06 kWh energy with 1 kg input LOHC, which outperforms all the other single LOHC systems except ammonia as shown in Fig. 16 (b). Besides, the scale up is also achievable and can finally have a yield of 18.04 kW of total energy for an hour to output 1 kg hydrogen, corresponding to an energy efficiency of 53.67%.

In general, the main theme of exhaust heat utilization is to reintroduce the unused heat to system to cover dehydrogenation enthalpy. Although the GT and SOFC share the similar characteristics of fixed fuel-to-energy efficiency, high operating temperature and large amount of flue gas, SOFC combined with LOHC exhibits higher efficiency as shown in Table 3. This is mainly ascribed to the nature of fuel cell overcoming the cycle efficiency restriction of thermal engine. Additionally, the difference between GT and SOFC in LOHC system lies on the supply of dehydrogenation enthalpy. With GT, the flue gas is fuel-less and provides the heat directly. In case of SOFC, it may need an extra combustor to oxidize the fuel in flue gas to provide heat for dehydrogenation. Meanwhile, the degradation of energy conversion in SOFC should also

be taken into consideration, since the stability is of great significance [119,120].

To further improve the energy efficiency, the combined heat and power system with the LOHC storage is suggested, which has high self-consumption rate and self-sufficiency [121,122]. Future work should pay more attention on such energy system, since it possesses great potentiality to prompt the application of LOHC in fields like residential unit. In addition, more practical efforts need to be done to verify the feasibility and prominence of LOHC-based GT and SOFC system from the perspective of experiment.

4.2. Integration through direct LOHC fuel cell

As stated before, the utilization of LOHC-bound hydrogen usually draws an immense amount of heat to maintain high temperature for necessary conversion rate and kinetics. Apart from strategy like reuse of the exhaust heat, there is another option to address the heat consumption issue with low-temperature fuel cell capable of skipping dehydrogenation step. Namely, fuel cell directly operates on LOHC molecules, which attracts a lot of attention because the high-energy-consuming step can be eliminated. As depicted in Fig. 17, direct LOHC fuel cell can avoid the tremendous heat input of activation energy by directly oxidizing the LOHC molecules instead of hydrogen. In this section, rechargeable LOHC species like isopropanol will be discussed while non-recyclable materials like methanol and ethanol, undergoing complete oxidation to form CO_2, will not be included.

Among plenty of alcohols, short chain species such as methanol, ethanol and propanol are intensively tested on fuel cells since they are common industrial products and can be manufactured in large scale [123,124]. Furthermore, alcohol fuel cells exhibit great performance with high open circuit voltage of 250 mV and power density of 302 mW/cm^2 [125,126]. Their universality for both acidic and alkaline environment allows for varieties of design scenarios [127,128]. For most, their low operating temperature of below 100 °C saves a lot of energy [129,130]. Based on these superior properties, alcohols are considered as ideal liquid organic hydrogen carriers. Amid them, isopropanol, different from others, is able to achieve incomplete oxidation, which signifies that fuel cells only utilize the hydrogen of the carrier [127,131].
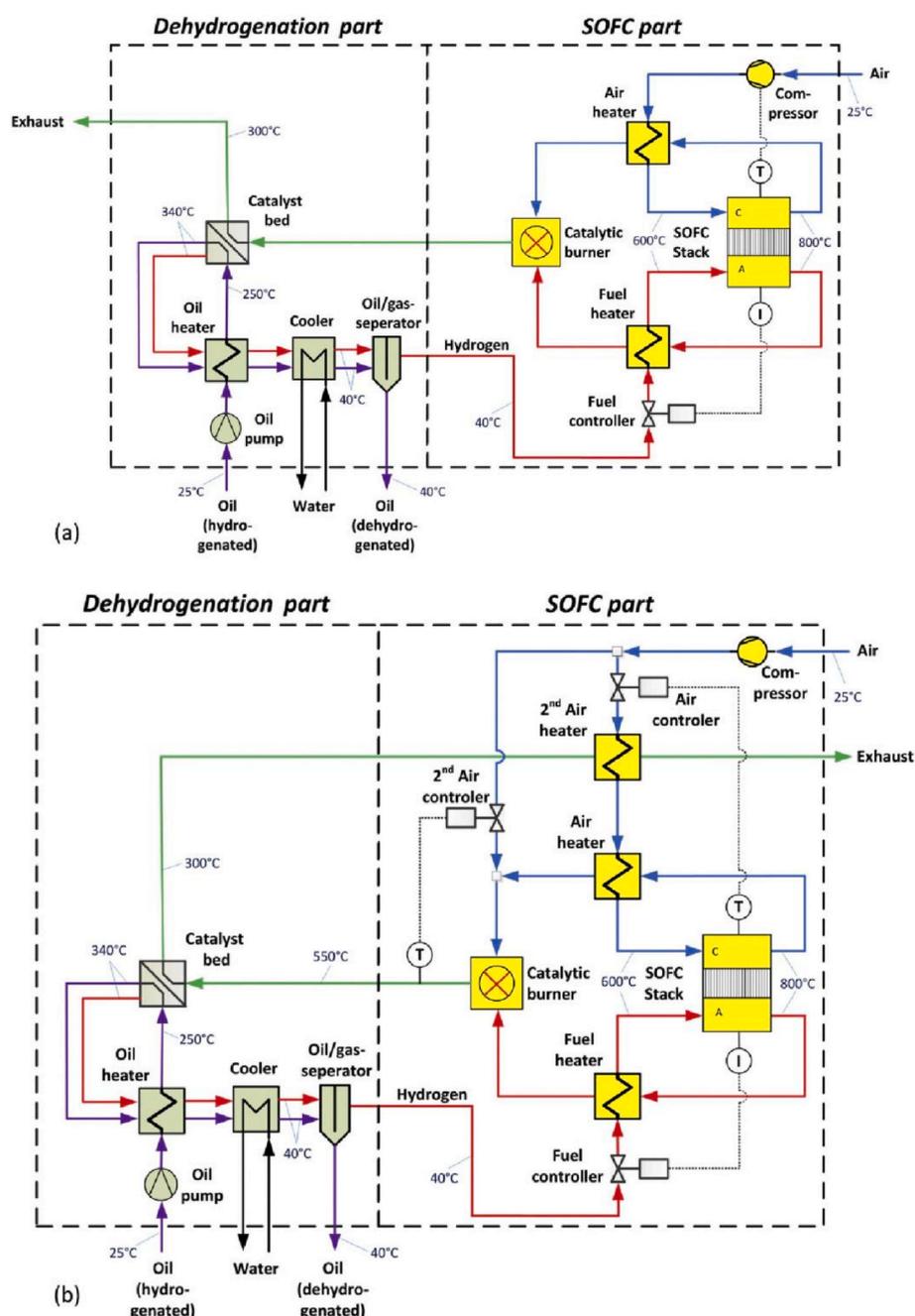
Fig. 15. Process layout of LOHC-based SOFC system – a) least complicated layout; b) optimized layout. Reprinted from [116]Copyright 2018 Elsevier.

In addition, alcohols fuel cell is also able to support continuous operation. An experiment conducted by Nobuko et al. suggests the feasibility of "rechargeable fuel cell" [132]. In their study, several LOHC materials including isopropanol and cyclohexanol were tested using proton exchange membrane fuel cell (PEMFC). The results indicated that isopropanol PEMFC has the highest maximum power density of 70 mW/cm^2 and the highest stability in galvanostatic operation. Aside from power density and stability, another extraordinary point is that the cell operated below 100 °C, which is much lower than the required dehydrogenation temperature (200–300 °C) of the isopropanol. In this case, the direct LOHC fuel cell can not only save dehydrogenation activation energy, but also eliminate the dehydrogenation process which may require extra reactor module. After the cell test, the electrolysis of oxidation product acetone was successfully carried out, which proves the possibility of circulation of isopropanol/acetone as rechargeable

hydrogen carrier. The feasibility of charging ketones is also verified by Christoph's study [133].

However, another factor, the capacity should be taken into consideration when selecting proper LOHC. From this perspective, LOHC species can be further divided into two types based on the number of hydrogen molecule they carry: single hydrogen molecule carrier (SHC) and multiple hydrogen molecules carrier (MHC). For instance, alcohols like ethanol and methanol are viewed as MHC carrier, since they typically carry 2 and 3 molecules of hydrogen. In another case, the carriers like isopropanol and cyclohexanol, which only carry one molecule of hydrogen, are classified as SHC. In addition to alcohol species, other hetero-aromatic compounds such as Indole and *N*-benzyldeneaniline also the examples of SHC [134]. As shown in Table 4, isopropanol has relatively low hydrogen capacity compared to other LOHCs since isopropanol is a typical SHC. Aside from capacity issue, transportation
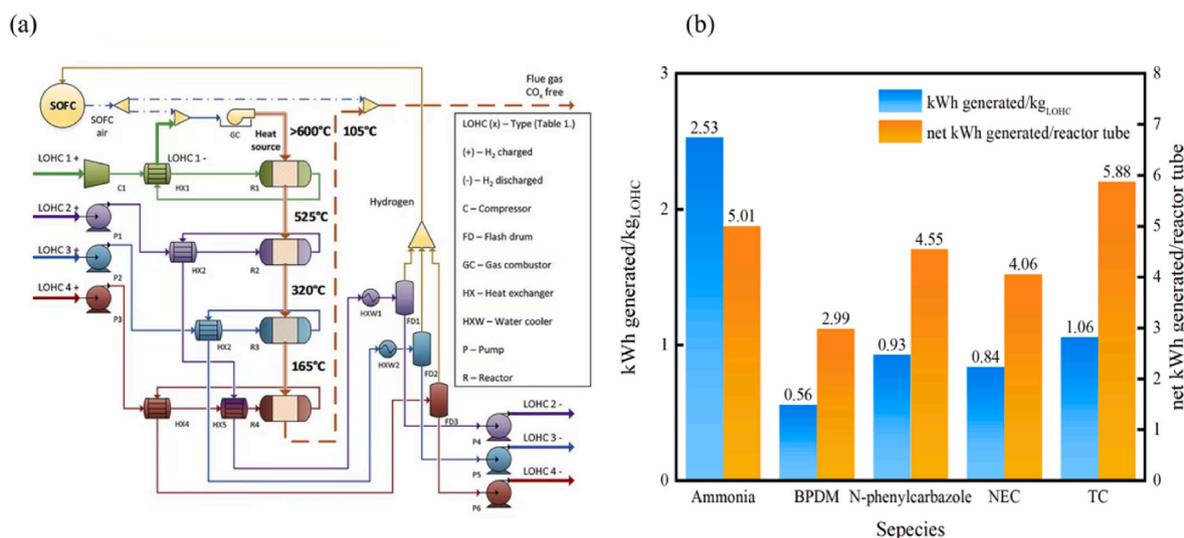
Fig. 16. Heat utilization cascade scheme (a) and power generation of different species (b). Reproduced from Ref. [118]Copyright 2020 Elsevier.

Table 3
Summary of LOHC coupled SOFC system.

Scale	species	Reactor type	Hydrogen yield	Performance	Reference
5260 W	DBT	Tubular reactor	≥90%	Hydrogen-bound LOHC to electricity efficiency of 45% under steady state	[117]
18040 W	Ammonia, BPDM, NPC, NEC	Tubular reactor	Almost 100%	System overall efficiency of 54.1%	[118]

safety also needs to be paid attention. The isopropanol and acetone have relatively low evaporation point of 82.5 °C and 56.5 °C, respectively, which may foster the fire hazard. From the perspective of safety and economy for long distance hydrogen transportation, MHCs like DBT or NEC are preferable.

As shown in section 2, the dehydrogenation of hydrogen charged DBT and NEC usually requires high temperature around 200–300 °C [138,139]. It is definitely an energy-consuming process to extract the hydrogen from the carrier at such high temperatures. Inspired by the direct isopropanol fuel cell, Sievi et al. proposed a novel concept to utilize DBT with the help of isopropanol/acetone66. The notion is to cover the high energy demand of perhydro-DBT dehydrogenation with the exothermic hydrogenation of acetone whose product will be direct consumed in fuel cell. Under 190 °C, the acetone is able to achieve a conversion rate of over 40% which is corresponding to a power density of 20 mW/cm^2. Besides, the separation of DBT and isopropanol/acetone mixture can be simply achieved due to their different evaporation points. More importantly, the concurrent hydrogenation and dehydrogenation reactions taking place in the reactor are able to achieve heat neutralization. To emphasize, the dehydrogenation enthalpy (+65 kJ/mol H$_2$) of DBT almost coincides with hydrogenation enthalpy (−70 kJ/mol H$_2$) of acetone. That is to say, the heat required by DBT can be completely covered by the released heat from acetone hydrogenation.

The isopropanol yield in Sievi's study leaves large space for optimization [66]. Based on this concept, a theoretical evaluation was carried out by Karsten et al. [140]. In their study, a 10 kW$_{el}$-sized integrated power system was applied with the conversion rate at 80% from perhydro-DBT to DBT and fuel utilization efficiency of 98%. It was reported that the heat of coupled dehydrogenation and hydrogenation reactions are reduced to +10.3 ± 3.1 kJ/mol H$_2$, which saves almost

85% of the dehydrogenation enthalpy (+65.4 ± 2.3 kJ/mol H$_2$) of perhydro-DBT. In this case, the energy efficiency from hydrogen to electric energy can achieve 36.5 ± 9.7%.

From these experiments, the energy saving can be attributed to the counterbalance of heat absorption and release between two different LOHC species' dehydrogenation and hydrogenation, which is called hydrogen transfer. Thus, a successive hydrogen delivery prospect aiming to address the heat issues during the hydrogen application process can be derived. As shown in Fig. 18, primary hydrogen resource like green hydrogen can be transported with MHC over long distance [141]. The transported MHC acts as the secondary hydrogen resource which proceeds the hydrogen transfer with SHC. The hydrogen can be further utilized after shifting the carrier to SHC such as isopropanol which has already achieved sophisticated technology [67,142]. Amid several stages, the hydrogen transfer is the most vital and tricky part since it can guarantee the power density, heat consumption and fuel utilization feasibility simultaneously. On one hand, SHCs such as isopropanol usually have relatively lower hydrogen capacity and power density in contrast to the large capacity and power density of MHC as shown in Fig. 10. On the other hand, MHC species usually engage in multi-stage and time-consuming dehydrogenation process to achieve large conversion [143,144]. Besides, the fuel cell operating directly on MHC is incapable of attaining large conversion rate of fuel [137]. In this case, hydrogen transfer is necessary because it can circumvent the disadvantages and fulfill the advantages of MHC and SHC. Simultaneously, the reaction heat demand can be hugely covered.

In short, the successive hydrogen delivery mainly relies on three aspects: transport of MHCs, hydrogen transfer between MHC and SHC, and direct use of SHC on fuel cell. Thus, future research can be carried out with a view to intensify the "hydrogen transfer process" to pursue high conversion rate. Additionally, system research should be developed on the integration of hydrogen transfer reactor and power device for different scenarios. To sum up, direct LOHC fuel cell can be viewed as a promising way to save the energy consumption under varieties of application contexts [140].

5. Challenges and directions

Several reports and researches of LOHC heat management bring about strategies to address issues existing in application scenarios. However, challenges still need to be attached great importance as the scale up of LOHC is not realized practically. Table 5 summarizes the methods mentioned in this article with their future directions.

In brief, microwave irradiation mainly focuses on species like decalin
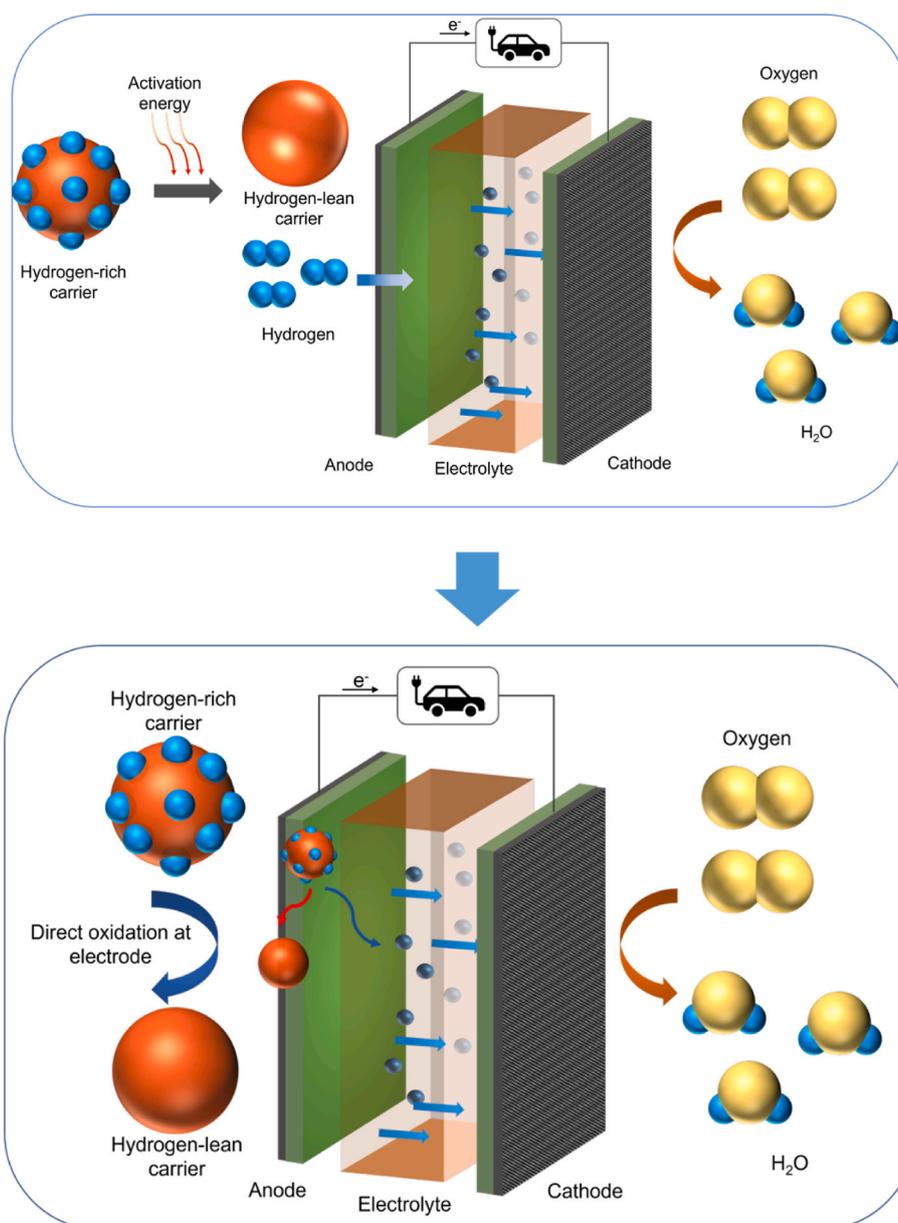
Fig. 17. Comparison of fuel cell operating on hydrogen and directly on LOHC molecules.

Table 4
Comparison of capacity of different liquid organic hydrogen carrier.

Species	H_2/molecule carried	Capacity wt.%	OCV E^0(V)	CO_2 emission	Reference
Isopropanol	1	3.3	1.1	No	[135]
Cyclohexanol	1	2.0	1.04	No	[132]
Methanol	2	12.5	1.19	Yes	[132]
Ethanol	3	13.0	1.14	Yes	[136]
Methylcyclohexane	3	6.2	1.068	No	[135]
N-ethylcarbazole	6	5.8	1.319	No	[137]
Dibenzyltoluene	9	6.2	–	No	[32]

and lacks scale up test. Thus, more dielectric LOHC materials are suggested to be added in the test list. The scale up is also indispensable. The researches of heat recirculation depend significantly on model establishment, where experiment should be emphasized during the future work to further verify the feasibility and detect more underlying problems during the operation. The system efficiency can be solved by heat exchange intensification or system design. For the concept of hydrogen transfer, in addition to DBT, more species such as NEC, NPC, Naphthalene or BPDM should be tested with isopropanol. The molar ratio and reactor structure need to be considered to gain more progress. Besides, the decomposition of isopropanol caused by superheating during hydrogenation of acetone is also a great problem. Thus, the reactor design plays an extremely important role in the realization of hydrogen transfer.

6. Conclusion

Heat is always a crucial factor that not only influences the performance but also determines large scale application of LOHC system as heat supply directly affects the dehydrogenation extent and the efficiency of energy system. Strategies for heat issue mainly concentrate on three perspectives: heat intensification through microwave intensification, heat circulation with exhaust energy and direct LOHC fuel cell.
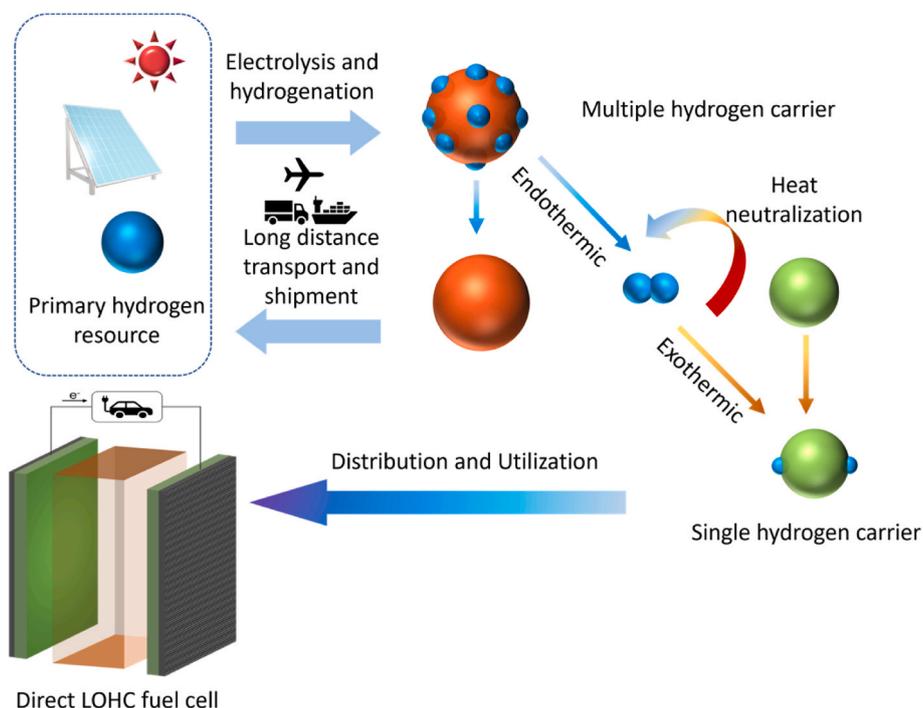
Fig. 18. Diagram of hydrogen transfer concept.

Table 5
Challenges and directions of LOHC heat management.

Methods	Challenges	Directions
• Heat intensification through microwave irradiation • Recirculation of exhaust heat from gas turbine • Recirculation of exhaust heat from SOFC • Direct utilization of LOHC in fuel cell	• Scale up issue • Limited species • Equipment cost • Restricted system efficiency • Absence of experiment • Absence of experiment	• Reactor scale up • More tests for other species • Novel recirculation design • Heat exchange intensification • Experiment verification
	• Unconsidered economy • Absence of verification of more species • Membrane dissolution issue of isopropanol fuel cell	• Global economy analysis • Introduction of more species and reactor improvement • Membrane development • Fuel cell design

1) Microwave irradiation is a mighty and novel method of heat supply which can selectively heat the target position in the reaction mixture due to microwave absorption disparity of different materials. With this property, a carbon-based catalyst, as the absorbent, is heated up without the energy loss resulting from the heat conduction and convection compared to the conventional heating. But it should be emphasized that microwave irradiations do have restrictions for the application scenarios. i) Hot spot with a temperature difference of about 200 °C higher than the bulk must be formed to enhance the mass diffusion, otherwise the kinetics won't be improved greatly. ii) The reaction kinetics is required to be controlled by mass transfer. In case of decalin which is not controlled by mass transfer, microwave assistance can't promote the reaction kinetics. iii) The reactant should be chosen from non-polar species which absorbs almost no energy from microwave irradiation. To further intensify the system, Dewar-like reactor and ionic liquid can be deployed. Future research should introduce and evaluate more LOHC species into the

microwave dehydrogenation system so that microwave irradiation will gain more possibility of being used universally.

2) Exhaust heat is abundant in the industrial production, which leaves capacious space for the reuse in the application of LOHC dehydrogenation. Thermal engines like gas turbine generate stupendous amount of heat carried by the effluent gas at high temperatures. Thus, the dehydrogenation temperature of LOHC species can be satisfied once the reactor is combined with a gas turbine. DBT and MCH are suggested to be utilized with thermal engines since the stationary scenarios such as gas turbine provide long time and high temperature for them to release the hydrogen thoroughly. Similarly, SOFC is able to generate high-quality heat which can be exerted in the dehydrogenation of high-enthalpy including DBT. Besides, SOFC has great prospect in the civil application field like the combined heat and power system. The research on exhaust heat is suggested to further raise the energy efficiency through gradient utilization or heat intensification based on different scenarios.

3) Direct LOHC fuel cells bring another option that the high energy demand of dehydrogenation can be omitted with the specific LOHC which can directly discharge at the electrode. Isopropanol is viewed as one of the most promising species since its corresponding fuel has already been frequently studied. Due to its simple molecular structure, the hydrogenation and dehydrogenation both exhibit splendid feasibility with almost no byproduct. As a regular alcohol species, isopropanol can be abundantly produced with the current technology. More importantly, a novel notion is proposed that the system is able to achieve thermal neutrality by covering dehydrogenation enthalpy of LOHC like DBT with the hydrogenation enthalpy of acetone. On one hand, LOHC species such as DBT which is capable of carrying enormous amount of hydrogen to meet the demand of economy but consumes dehydrogenation energy. On the other hand, LOCH species like isopropanol, which is feasible for direct fuel cell, can be hydrogenated by the hydrogen from the DBT and supply the dehydrogenation energy. With this cycle, the renewable and sustainable energy generated from the remote region can be transferred to the civil utilization terminal without the energy wastage of dehydrogenation. Other LOHC species including NEC and MCH are suggested to be combined with isopropanol to save the energy

consumption of dehydrogenation. Besides, the reaction unit or even factory of the hydrogen transfer ought to be developed, evaluated and optimized.

Credit author statement

Yikun Yang: Conceptualization, Methodology, Investigation, Formal Analysis, Writing-Original Draft, Visualization. **Zhen Wu**: Conceptualization, Writing-Review & Editing, Supervision. **Ruiqing Li**: Data Curation, Formal Analysis. **Huan Wang**: Data Curation, Visualization. **Jianwei Ren**: Investigation, Methodology. **Bo Li**: Software, Investigation. **Fusheng Yang**: Supervision, Investigation. **Zaoxiao Zhang**: Supervision.

Declaration of competing interest

1. This manuscript is the authors' original work and has not been published previously, and not under consideration for publication elsewhere, in part or in whole.

2. No conflict of interest exits in the submission of this manuscript, and the manuscript is approved by all authors for possible publication.

Data availability

Data will be made available on request.

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References

[1] N.J. Azhari, et al., Results in Eng. 16 (2022), 100711.
[2] Q. Hassan, et al., Results in Eng. 18 (2023), 101165.
[3] K. Solaun, E. Cerdá, Renew. Sustain. Energy Rev. 116 (2019), 109415.
[4] H. Zhang, X. Zhang, Yuan, J. Renew.Sustain. Energy Rev. 132 (2020), 110102.
[5] P. Liu, X. Han, Int. J. Hydrogen Energy 47 (2022) 9485–9503.
[6] M. Santhosh, C. Venkaiah, D. Kumar, Eng. Rep. 2 (2020), e12178.
[7] C. Li, et al., Renew. Sustain. Energy Rev. 164 (2022), 112603.
[8] R. Li, X. Liu, Chen, J. Exploration 20220027 (2022) 1–13.
[9] O. Ellabban, H. Abu-Rub, F. Blaabjerg, Renew. Sustain. Snergy Rev. 39 (2014) 748–764.
[10] P. Marocco, D. Ferrero, A. Lanzini, M. Santarelli, J. Energy Storage 46 (2022), 103893.
[11] M. Aziz, A. Darmawan, F.B. Juangsa, Int. J. Hydrogen Energy 46 (2021) 33756–33781.
[12] M.Y. Suberu, M.W. Mustafa, N. Bashir, Renew. Sustain. Energy Rev. 35 (2014) 499–514.
[13] P. Preuster, A. Alekseev, P. Wasserscheid, Annu. Rev. Chem. Biomol. Eng. 8 (2017) 445–471.
[14] K. Martins, J.G. Carton, Results in Eng. 18 (2023), 101030.
[15] Z. Abdin, et al., Renew. Sustain. Energy Rev. 120 (2020), 109620.
[16] J.D. Fonseca, M. Camargo, J.-M. Commenge, L. Falk, I.D. Gil, Int. J. Hydrogen Energy 44 (2019) 9486–9504.
[17] F. Dawood, M. Anda, G. Shafiullah, Int. J. Hydrogen Energy 45 (2020) 3847–3869.
[18] C.B. Agaton, K.I.T. Batac, E.M. Reyes Jr., Int. J. Hydrogen Energy 45 (2022) 17859–17870.
[19] U.R. Singh, A.S. Kaushik, S.S. Bhogilla, Sustain. Energy Technol. Assessments 51 (2022), 101978.
[20] T. Tsujimura, Y. Suzuki, Int. J. Hydrogen Energy 44 (2019) 11355–11369.
[21] R.R. Ratnakar, et al., Int. J. Hydrogen Energy 46 (2021) 24149–24168.
[22] M. Niermann, A. Beckendorff, M. Kaltschmitt, K. Bonhoff, Int. J. Hydrogen Energy 44 (2019) 6631–6654.
[23] J. Zheng, et al., Int. J. Hydrogen Energy 37 (2012) 1048–1057.
[24] G. Valenti, Comp. Hydrogen Energy 2 (2016) 27–51.
[25] S.M. Aceves, et al., Int. J. Hydrogen Energy 35 (2010) 1219–1226.
[26] M. Hurskainen, J. Ihonen, Int. J. Hydrogen Energy 45 (2020) 32098–32112.
[27] M. Niermann, S. Timmerberg, S. Drünert, M. Kaltschmitt, Renew. Sustain. Energy Rev. 135 (2021), 110171.
[28] Y. Song, K. Ji, H. Duan, M. Shao, Explorations 1 (2021), 20210050.
[29] P.M. Modisha, C.N.M. Ouma, R. Garidzirai, P. Wasserscheid, D. Bessarabov, Energy Fuel. 33 (2019) 2778–2796.
[30] V.N. Emel'yanenko, et al., J. Phys. Chem. C 119 (2015) 26381–26389.
[31] D. Teichmann, W. Arlt, P. Wasserscheid, R. Freymann, Energy Environ. Sci. 4 (2011) 2767–2773.
[32] P.C. Rao, M. Yoon, Energies 13 (2020) 6040.
[33] F. Sotoodeh, B. Huber, K.J. Smith, Appl. Catal. A Gen. 419–420 (2012) 67–72.
[34] F. Sotoodeh, K.J. Smith, Can. J. Chem. Eng. 91 (2013) 1477–1490.
[35] M. Geißelbrecht, et al., Energy Environ. Sci. 13 (2020) 3119–3128.
[36] Y.K. Yang, et al., Fuel 321 (2022), 124095.
[37] V. Yadav, G. Sivakumar, V. Gupta, E. Balaraman, ACS Catal. 11 (2021) 14712–14726.
[38] J.K. Ali, A. Baiker, Appl. Catal. Gen. 155 (1997) 41–57.
[39] M.H. Hamayun, M. Hussain, I.M. Maafa, R. Aslam, Int. J. Hydrogen Energy 44 (2019) 20213–20222.
[40] M.I. Hatim, M.U. Fazara, A.M. Syarhabil, F. Riduwan, Procedia Eng. 53 (2013) 71–80.
[41] M. Cholewa, B. Zehner, H. Kreuder, P. Pfeifer, Chem. Eng. Process 125 (2017) 325–333.
[42] Y.-R. Chen, T. Tsuru, D.-Y. Kang, Int. J. Hydrogen Energy 42 (2017) 26296–26307.
[43] M.D.I. Hatim, M.A.U. Fazara, A.M. Syarhabil, F. Riduwan, Malaysian technical universities conference on engineering & technology, 2012 (Mucet 2012) 53 (2013) 71–80.
[44] F. Gallucci, E. Fernandez, P. Corengia, M.V. Annaland, Chem. Eng. Sci. 92 (2013) 40–66.
[45] D. Acharya, D. Ng, Z. Xie, Membranes 11 (2021) 955.
[46] S. Dürr, et al., Int. J. Hydrogen Energy 46 (2021) 32583–32594.
[47] S. Lee, et al., Int. J. Hydrogen Energy 46 (2021) 5520–5529.
[48] L. Shi, et al., Int. J. Hydrogen Energy 44 (2019) 5345–5354.
[49] H. Jorschick, et al., Energy Environ. Sci. 10 (2017) 1652–1659.
[50] H. Jorschick, S. Dürr, P. Preuster, A. Bösmann, P. Wasserscheid, Energy Technol. 7 (2019) 146–152.
[51] Z.A. Tong, et al., J. Fuel Chem. Technol. 49 (2021) 1181–1189.
[52] J. Ma, et al., Fuel 333 (2023), 126307.
[53] S. Hodoshima, H. Arai, S. Takaiwa, Y. Saito, Int. J. Hydrogen Energy 28 (2003) 1255–1262.
[54] E.A. Martynenko, S.V. Vostrikov, A.A. Pimerzin, React. Kinet. Mech. Catal. 133 (2021) 713–728.
[55] C. Gleichweit, et al., J. Phys. Chem. C 119 (2015) 20299–20311.
[56] A.N. Kalenchuk, V.I. Bogdan, S.F. Dunaev, L.M. Kustov, Int. J. Hydrogen Energy 43 (2018) 6191–6196.
[57] D.J. Han, et al., Energy Technol. 7 (2019) 113–121.
[58] Y. Kwak, et al., Fuel 284 (2021), 119285.
[59] S.P. Verevkin, V.N. Emel'yanenko, A. Heintz, K. Stark, W. Arlt, Ind. Eng. Chem. Res. 51 (2012) 12150–12153.
[60] M.Y. Zhu, L.X. Xu, L. Du, Y. An, C. Wan, Catalysts 8 (2018) 638.
[61] B. Wang, et al., Int. J. Hydrogen Energy 43 (2018) 7317–7325.
[62] Y. Ming, C. Han, N. Gang, J. Wu, H. Cheng, Int. J. Hydrogen Energy 37 (2012) 12839–12845.
[63] C. Ding, et al., Int. J. Hydrogen Energy 45 (2020) 16144–16152.
[64] C. Li, et al., Int. J. Hydrogen Energy 48 (2023) 90–100.
[65] Y. Saito, H. Kameyama, K. Yoshida, Int. J. Energy Res. 11 (1987) 549–558.
[66] G. Sievi, et al., Energy Environ. Sci. 12 (2019) 2305–2314.
[67] P. Hauenstein, D. Seeberger, P. Wasserscheid, S. Thiele, Electrochem. Commun. 118 (2020), 106786.
[68] B. Matthew, et al., Energy Technol. 9 (2021), 2100164.
[69] K. Braun, et al., Energy Technol. 10 (2022), 2200343.
[70] S. Mutyala, et al., Fuel Process. Technol. 91 (2010) 127–135.
[71] L. Bazzi, I. Ayouch, H. Tachallait, S. El Hankari, Results in Eng. 13 (2022), 100378.
[72] H. Zhang, H. Geerlings, J. Lin, W.S. Chin, Int. J. Hydrogen Energy 36 (2011) 7580–7586.
[73] S. Gonzalez-Cortes, et al., Sci. Rep. 6 (2016) 1–11.
[74] J. Menéndez, et al., Fuel Process. Technol. 91 (2010) 1–8.
[75] Y. Tsukahara, et al., J. Phys. Chem. C 114 (2010) 8965–8970.
[76] L.J. Shi, et al., Int. J. Hydrogen Energy 42 (2017) 17403–17413.
[77] L.J. Shi, et al., Catal. Today 276 (2016) 121–127.
[78] Y. Suttisawat, S. Horikoshi, H. Sakai, M. Abe, Int. J. Hydrogen Energy 35 (2010) 6179–6183.
[79] Y. Suttisawat, S. Horikoshi, H. Sakai, P. Rangsunvigit, M. Abe, Fuel Process. Technol. 95 (2012) 27–32.
[80] S. Horikoshi, M. Kamata, T. Sumi, N. Serpone, Int. J. Hydrogen Energy 41 (2016) 12029–12037.
[81] X.L. Zhang, D.O. Hayward, C. Lee, D.M.P. Mingos, Appl. Catal. B Environ. 33 (2001) 137–148.
[82] B. Nigrovski, et al., Carbon 46 (2008) 1678–1686.
[83] C. Antonio, R.T. Deam, Phys. Chem. Chem. Phys. 9 (2007) 2976–2982.
[84] Y. Suttisawat, H. Sakai, M. Abe, P. Rangsunvigit, S. Horikoshi, Int. J. Hydrogen Energy 37 (2012) 3242–3250.
[85] S. Horikoshi, A. Osawa, Y. Suttisawat, M. Abe, N. Serpone, Org. Process Res. Dev. 14 (2010) 1453–1456.
[86] A. de la Hoz, A. Diaz-Ortiz, A. Moreno, Chem. Soc. Rev. 34 (2005) 164–178.
[87] L. Shi, et al., Catal. Today 276 (2016) 121–127.
[88] X. Li, et al., Carbon 67 (2014) 775–783.
[89] J.S. Sung, et al., Int. J. Hydrogen Energy 33 (2008) 4116–4121.

[90] A. Taylor, Energy Pol. 36 (2008) 4657–4667.
[91] T. Heppenstall, Appl. Therm. Eng. 18 (1998) 837–846.
[92] Y. Najjar, Appl. Therm. Eng. 20 (2000) 179–197.
[93] R. Agbadede, B. Kainga, I. Allison, Results in Eng. 17 (2023), 100865.
[94] P. Chiesa, G. Lozza, L.J. Mazzocchi, Eng. Gas Turbines Power 127 (2005) 73–80.
[95] P. Gobbato, M. Masi, A. Toffolo, A. Lazzaretto, Int. J. Hydrogen Energy 36 (2011) 7993–8002.
[96] J. Beita, M. Talibi, S. Sadasivuni, R. Balachandran, Hydrogen 2 (2021) 33–57.
[97] A. Cappelletti, F. Martelli, Int. J. Hydrogen Energy 42 (2017) 10513–10523.
[98] F. Reale, R. Sannino, Int. J. Hydrogen Energy 46 (2021) 24366–24381.
[99] A. Görgülü, H. Yağlı, Y. Koç, A. Koç, Int. J. Hydrogen Energy 45 (2020) 34254–34267.
[100] M. Schumacher, T. Mederer, M. Wensing, SAE Technical Paper 1 (2013) 2525.
[101] M. Eypasch, et al., Appl. Energy 185 (2017) 320–330.
[102] B. Hampel, S. Bauer, N. Heublein, C. Hirsch, T. Sattelmayer, Turbo Expo: Power for Land, Sea, and Air. V008T023A016, American Society of Mechanical Engineers, 2015, 43168.
[103] J. Dennis, T. Bexten, N. Petersen, M. Wirsum, P. Preuster, J. Eng. Gas Turbines and Power-Trans. Asme 143 (2021).
[104] G. Wang, et al., Fuel Process. Technol. 179 (2018) 203–228.
[105] L. Tan, X. Dong, C. Chen, Z. Gong, M. Wang, Energy Convers. Manag. 245 (2021), 114539.
[106] R.-A. Felseghi, E. Carcadea, M.S. Raboaca, C.N. Trufin, C. Filote, Energies 12 (2019) 4593.
[107] M. Zunita, A. Raizki, R. Aditya, I.G. Wenten, Results in Eng. 16 (2022), 100653.
[108] N. Kamalimeera, V. Kirubakaran, Renew. Sustain. Energy Rev. 143 (2021), 110914.
[109] C. Berges, J. Hidalgo, R. Andújar, R. Campana, G. Herranz, Results in Eng. 11 (2021), 100268.
[110] A.S. Mehr, A. Lanzini, M. Santarelli, M.A. Rosen, Energy 228 (2021), 120613.
[111] A. Weber, Fuel Cell. 21 (2021) 440–452.
[112] S. Lee, et al., Int. J. Hydrogen Energy 45 (2020) 13398–13405.
[113] J. Padulles, G.W. Ault, J.R. McDonald, J. Power Sources 86 (2000) 495–500.
[114] B. Nastasi, L.G. Basso, Energy 110 (2016) 5–22.
[115] P. Kazempoor, V. Dorer, A. Weber, Int. J. Hydrogen Energy 36 (2011) 13241–13249.
[116] P. Preuster, et al., Int. J. Hydrogen Energy 43 (2018) 1758–1768.
[117] R. Peters, et al., Int. J. Hydrogen Energy 44 (2019) 13794–13806.
[118] B. Brigljević, et al., Cell Rep. Phys. Sci. 1 (2020), 100032.
[119] K. Knosala, et al., Int. J. Hydrogen Energy 46 (2021) 21748–21763.
[120] D. Yan, et al., Appl. Energy 175 (2016) 414–420.
[121] A. Haupt, K. Muller, Energy 118 (2017) 1123–1130.
[122] V. Palomba, et al., Appl. Energy 216 (2018) 620–633.
[123] S.S. Gupta, J. Datta, J. Chem. Sci. 117 (2005) 337–344.
[124] Q. Yi, Q. Chen, Z. Yang, J. Power Sources 298 (2015) 171–176.
[125] K. Tran, T. Nguyen, A. Bartrom, A. Sadiki, Haan, J. Fuel Cells 14 (2014) 834–841.
[126] M.L. Perry, Z. Yang, J. Electrochem. Soc. 166 (2019) F3268.
[127] X. Yu, L. Cheng, Y. Liu, A. Manthiram, J. Phys. Chem. C 122 (2018) 13558–13563.
[128] Z. Qi, A. Kaufman, J. Power Sources 112 (2002) 121–129.
[129] Y. Dong, et al., ACS Appl. Energy Mater. 1 (2018) 4285–4292.
[130] H. Pourrahmani, A. Yavarinasab, M. Siavashi, M. Matian, Van herle, J. Energy Reviews 1 (2022), 100002.
[131] M.C. Figueiredo, et al., J. Power Sources 275 (2015) 341–350.
[132] N. Kariya, Phys. Chem. Chem. Phys. 8 (2006) 1724–1730.
[133] C.J. Bondue, F. Calle-Vallejo, M.C. Figueiredo, M.T. Koper, Nat. Catal. 2 (2019) 243–250.
[134] P. Driscoll, et al., ECS Trans. 35 (2011) 3.
[135] C.M. Araujo, et al., Energy Environ. Sci. 5 (2012) 9534–9542.
[136] J. Mann, N. Yao, A.B. Bocarsly, Langmuir 22 (2006) 10432–10436.
[137] J.R. Ferrell III, et al., J. Electrochem. Soc. 159 (2012) B371.
[138] F. Auer, et al., Catal. Sci. Technol. 9 (2019) 3537–3547.
[139] N. Heublein, M. Stelzner, T. Sattelmayer, Int. J. Hydrogen Energy 45 (2020) 24902–24916.
[140] K. Müller, S. Thiele, P. Wasserscheid, Energy Fuel. 33 (2019) 10324–10330.
[141] M. Niermann, S. Drünert, M. Kaltschmitt, K. Bonhoff, Energy Environ. Sci. 12 (2019) 290–307.
[142] S. Auffarth, et al., J. Mater. Chem. A 10 (2022) 17208–17216.
[143] A. Wunsch, M. Mohr, P. Pfeifer, Membranes 8 (2018) 112.
[144] L.B. Shi, et al., Int. J. Hydrogen Energy 44 (2019) 5345–5354.

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