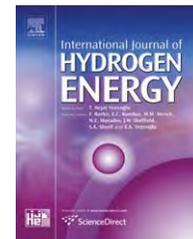


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Review

Renewable carbohydrates are a potential high-density hydrogen carrier

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ABSTRACT

The possibility of using renewable biomass carbohydrates as a potential high-density hydrogen carrier is discussed here. Gravimetric density of polysaccharides is 14.8 H₂ mass% where water can be recycled from PEM fuel cells or 8.33% H₂ mass% without water recycling; volumetric densities of polysaccharides are >100 kg of H₂/m³. Renewable carbohydrates (e.g., cellulosic materials and starch) are less expensive based on GJ than are other hydrogen carriers, such as hydrocarbons, biodiesel, methanol, ethanol, and ammonia. Biotransformation of carbohydrates to hydrogen by cell-free synthetic (enzymatic) pathway biotransformation (SyPaB) has numerous advantages, such as high product yield (12 H₂/glucose unit), 100% selectivity, high energy conversion efficiency (122%, based on combustion energy), high-purity hydrogen generated, mild reaction conditions, low-cost of bioreactor, few safety concerns, and nearly no toxicity hazards. Although SyPaB may suffer from current low reaction rates, numerous approaches for accelerating hydrogen production rates are proposed and discussed. Potential applications of carbohydrate-based hydrogen/electricity generation would include hydrogen bioreactors, home-size electricity generators, sugar batteries for portable electronics, sugar-powered passenger vehicles, and so on. Developments in thermostable enzymes as standardized building blocks for cell-free SyPaB projects, use of stable and low-cost biomimetic NAD cofactors, and accelerating reaction rates are among the top research & development priorities. International collaborations are urgently needed to solve the above obstacles within a short time.

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1. Introduction

The hydrogen economy will be a linked network of chemical processes that produces hydrogen, stores hydrogen chemically

or physically, and converts the stored hydrogen to electrical energy at the point of use. Its most important application is transportation, especially for light-duty passenger vehicles, because hydrogen/polymer electrolyte membrane (PEM) fuel

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cell systems have much higher energy conversion efficiencies and produce fewer pollutants than do internal combustion engines. In the future, transportation fuels might mainly consist of hydrogen for light-duty vehicles, electricity for short-distance vehicles, and high-energy density liquid biofuels for heavy-duty vehicles and jet planes.

Large-scale implementation of the hydrogen economy has several obstacles: sustainable hydrogen production, high-density hydrogen storage, hydrogen distribution infrastructure, fuel cell cost and lifetime, and safety concerns [1]. Central to the development of the hydrogen economy is the safe, efficient, and viable storage of hydrogen [2]. Hydrogen can be stored (i) in high-pressure gas cylinders; (ii) as liquid hydrogen in cryogenic tanks at 21 K; and (iii) in solid forms (e.g., adsorption on large specific surface area solid materials or hydrides or by the reaction of light metals and water [2–4]). Now most research on hydrogen storage is focused on storing hydrogen as a lightweight, compact energy carrier for mobile applications. An optimum hydrogen storage material is required to have the following properties: high hydrogen capacity per unit mass and unit volume, low dissociation temperature, moderate dissociation pressure, low heat of formation in order to minimize the energy necessary for hydrogen release, low heat dissipation during exothermic hydride formation, reversibility, limited energy loss during charge and discharge of hydrogen, fast kinetics, high stability against O₂ and moisture to allow a long cycle life, cyclability, a low cost of recycling and charging infrastructures, and a high level of safety [5]. The search for ultra-high capacity materials has led to the synthesis and characterization of more and more exotic and reactive compounds: complex metal hydrides, such as NaAlH₄, LiAlH₄ and AlH₃; metal organic frameworks (MOFs); borohydrides, such as LiBH₄ and Mg(BH₄)₂, destabilized borohydrides, ammonia borane; and amide/imide systems.

In order to dramatize and incentivize hydrogen research, the H-Prize has been established to competitively award cash prizes that will advance the commercial application of hydrogen energy technologies [6]. The 2009–11 H-prize will be awarded in the area of storage materials in mobile systems for light-duty vehicles. The basic requirements are (i) 7.5% reversible H₂ mass at conditions between –40 and +85 °C and between 1.5 and 150 bar of H₂ pressure; (ii) 70 kg of total releasable hydrogen/m³; (iii) charging kinetics – greater than or equal to 0.0004 g of hydrogen per gram of material per second between –40 and +85 °C and between 1.5 and 150 bar of H₂ pressure, (iv) discharge kinetics – greater than or equal to 0.00002 g of hydrogen per gram of material per second at conditions between –40 and +80 °C and an outlet hydrogen

pressure of ≥ 1.5 bar; and (v) a cycle life of 100 without a significant loss of capacity [6].

Cellulosic biomass is the most abundant renewable biological resource (ca. 1×10^{11} tons/year) [7–9]. Biomass is produced locally, and is more evenly distributed than are fossil fuels. Each year, the overall chemical energy stored in biomass by plants is approximately 6–7 times of the total human energy consumption [4]. The use of a small fraction of low-cost renewable biomass for producing transportation fuels (e.g., cellulosic ethanol and hydrogen) provides benefits to the environment, economy, and national security [7,8,10]. At the dawn of the 21st century, a combination of economic, technological, resource, and political developments is driving the emergence of a renewable carbohydrate economy [7].

In this paper, I compare different means for hydrogen production from biomass sugars, propose the use of renewable carbohydrates as a high-density hydrogen carrier, discussed potential applications, and highlight future R&D priorities.

2. Production of hydrogen from biomass sugars

The production of hydrogen from low-cost renewable biomass (\$60 per dry ton or \$3.60 per GJ) is appealing [4] because biomass is an enriched, collectable chemical energy source. Most times, solar energy is not really free because of the high hidden costs for its scale-up and storage [11].

Table 1 shows a number of biomass-to-hydrogen production approaches. In principle, up to 12 mol of hydrogen can be produced per mole of glucose and water. But natural microorganisms might produce as much as 4 mol of hydrogen per mole of glucose along with 2 mol of acetate, called the Thauer limit [12]. In practice, much lower hydrogen yields (e.g., 1–3.2 mol of hydrogen per mole of glucose) are obtained for dark anaerobic fermentation [13–15]. In order to increase overall hydrogen yields, a bioelectrochemically-assisted microbial fuel cell reactor has been shown to convert 2 mol of acetate to up to 8 mol of hydrogen with the help of a little electricity [16]. Considering electricity input and conversion loss, the overall hydrogen yields by this combination are approximately 9 mol per mole of glucose. Another combinatorial biological and chemical catalysis is ethanol microbial fermentation followed by ethanol partial oxidation reforming [17,18], resulting in an overall yield of ~9 mol of hydrogen per mole of glucose.

Chemical catalysis for the production of hydrogen includes pyrolysis, gasification, and aqueous phase reforming (APR). Pyrolysis is the chemical decomposition of a condensed

Table 1 – Comparison of converting carbohydrates to hydrogen.

Method	Theoretical yield	Practical yield	Energy efficiency	Ref
Dark fermentation (DF)	4	1–3.2	10–30%	[13–15,33]
DF + electricity-assisted microbial fuel cell	12	9	~75%	[34,80]
Ethanol fermentation/partial oxidation reforming	10	9	~60%	[7,17,18]
Gasification	12	2–8	35–50%	[81,82]
Pyrolysis	12	2.5–8	30–50%	[21,83–86]
Hydrolysis + aqueous phase reforming	12	6–8	30–50%	[22,23,87–89]
Synthetic pathway biotransformation	12	~12	~122%	[26,27]

Since most of the reactions catalyzed by the enzymes are reversible, the removal of gaseous products – H₂ and CO₂ from the aqueous phase under mild reaction conditions (<100 °C and ~1 atm) favors the unidirectional reaction for the desired products. Thermodynamic analysis suggests that the overall reactions from starch or cellulosic materials and water are spontaneous and endothermic (i.e., $\Delta G^\circ = -49.8$ kJ/mol and $\Delta H^\circ = +598$ kJ/mol) [26,27]. Such reactions are driven by entropy gain rather than enthalpy loss. These entropy-driven chemical reactions can generate more output of chemical energy in the form of hydrogen than input of chemical energy in polysaccharides by adsorbing ambient-temperature thermal energy [26,27]. For example, there are two entropy-driven reactions of N₂O₅ (s) → 2NO₂ (g) + ½O₂ (g) and Ba(OH)₂·8H₂O (s) + 2NH₄SCN (s) → Ba(SCN)₂ (aq) + 2NH₃ (aq) + 10H₂O (l), both of which involve phase changes from more orderly to less orderly.

When a low concentration cellobiose (2 mM) is used as the substrate, the overall yields of H₂ and CO₂ are 11.2 mol of H₂ and 5.64 mol of CO₂ per mole of anhydroglucose unit of cellobiose, corresponding to 93% and 94% of the theoretical yields, respectively [26]. The slightly less than theoretical value is readily explained by accumulated equilibrium intermediates (e.g., G-1-P, G-6-P, NADPH) in a batch reaction. The theoretical yield (12H₂ per glucose unit) is expected to be obtained when a continuous reactor is run. By using SyPaB, a ~20-fold enhancement in hydrogen production rates from 0.21 to 3.92 mmol/L/h has been achieved by increasing the rate-limiting hydrogenase concentration, increasing the substrate concentration, and elevating the reaction temperature slightly from 30 to 32 °C [26]. So far the production rate of H₂ is higher than those of photobiological systems and comparable to those reported for dark fermentations and electrohydrogenesis [33,34].

The opinions that SyPaBs are too costly for the production of low-value biofuels are mainly attributed to costly unstable purified enzymes and labile cofactors [e.g., NAD(P)H]. With regard to unstable enzymes, a number of (hyper)-thermostable enzymes have been cloned and expressed in *Escherichia coli* [35,36], for example, *Clostridium thermocellum* phosphoglucomutase (CthPGM) [30], *Thermotoga maritima* 6PGDH (Tm6PGDH) [37], and fructose biphosphatase (TmFBPase) [38]. A combination of enzyme immobilization and thermostable enzymes can further increase the lifetime of enzymes [4,24]. For example, in the food industry, immobilized thermostable glucose isomerase can work at 60 °C for more than two years before it must be replaced [39]. In order to decrease enzyme purification costs, simple scalable protein purification approaches by adsorption/desorption [37,40,41] or heat precipitation for thermostable enzymes [37,42] have been developed. Now several industrial (recombinant) enzymes production costs (e.g., cellulases) have been decreased to as low as tens of dollars per kg of dry protein weight [8]. With regard to costly labile cofactors, efficient NAD(P)H recycling through immobilization of the cofactor linked to polymers has been developed [43]. The highest turn-over number (TTN) of NAD reported in the literature is ~1,000,000 [44]. As a result, the pharmaceutical industry has no motivation to increase the TTN of NAD for synthesis of high-value chiral drugs [45,46]. It is expected that the high-cost of cofactors will be solved by using less costly biomimetic NAD analogues [47–49].

The ultimate hydrogen production cost is expected to be as low as \$1.50 per kg [24,50], based on three inputs: (i) sugar prices of \$0.18/kg of carbohydrates [4], (ii) all the enzymes with a weight-based total turn-over number (TTN_w) of >100,000, and (iii) coenzymes or biomimic coenzymes with a TTN of ~1,000,000. In this case, carbohydrate accounts for 80% of the final product price, a typical value for the production of bio-commodities [50,51]. With regard to the 1st input requirement, \$0.18 per kg of carbohydrates is a very conservative estimate, comparable or even higher than an ultimate goal of sugars isolated from biomass predicted by the DOE. With regard to the 2nd input requirement, developing thermostable enzymes with TTN_w of >100,000 is highly operative. For example, three recombinant thermophilic building blocks – *Clostridium thermocellum* phosphoglucomutase [30], *Thermotoga maritima* 6-phosphogluconate dehydrogenase [37], and *T. maritima* fructose biphosphatase [38] – are stable with TTN_w of >200,000 at ~60 °C. The above results suggest that discovery and utilization of highly stable thermophilic enzymes from extremophiles that have known genomic sequences are highly doable [25]. When all enzymes have met the TTN_w requirement of >100,000, the enzyme costs are less than \$0.01 per kg of hydrogen produced. With regard to the 3rd input requirement, NAD with a TTN of ~1,000,000 has been reported previously [44]. Furthermore, the use of low-cost and more stable biomimetic NAD coenzymes is even more economically promising [49,52]. Based on the above analysis, hydrogen production from biomass carbohydrates would be very economically viable if all of the thermostable enzymes are available and biomimic cofactors can be used by the enzymes.

3. Carbohydrates as a H₂ carrier

Use of hydrogen carriers, such as hydrocarbons, biodiesel, methanol, ethanol, and ammonia, is another alternative to solve the hydrogen storage challenge. But end users must have a converter that can convert hydrogen carriers to hydrogen. When hydrogen stream contains impurities (e.g., CO), it must pass through a hydrogen purifier before entering PEM fuel cells. The risk of explosion is an essential safety concern in the transportation sector, which can block the potential use of any energy carrier [53].

Thanks to the 100% chemical selectivity of enzymes in SyPaB, mild reaction conditions, and high-purity hydrogen (CO₂ is not a toxic compound for PEMFC), I propose the use of renewable carbohydrates as a high-density hydrogen carrier. Polysaccharides have the chemical formula C₆H₁₀O₅ with a reaction of C₆H₁₀O₅ (aq) + 7H₂O (l) → 12H₂ (g) + 6CO₂ (g). As a result, hydrogen storage density in polysaccharides is 24/162 = 14.8 H₂ mass%, where water can be recycled from PEM fuel cells. Dry starch and amorphous cellulose have specific densities of 0.7 and 1.4 kg/m³, respectively [9]. Even without water recycling from fuel cells, the sugar/water slurry would have a hydrogen density of 24/(162 + 18 × 7) = 8.33% H₂ mass%. Obviously, carbohydrates as a hydrogen carrier (8.33 or 14.8 H₂ mass% and >100 kg of H₂/m³) can meet the goals of the DOE's gravimetric density and volumetric density for hydrogen storage.

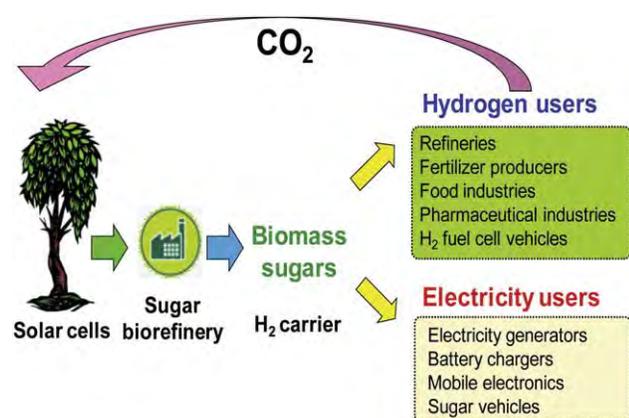


Fig. 2 – The scheme of the hydrogen economy based on renewable carbohydrates.

Fig. 2 shows the scheme of the future hydrogen economy based on renewable carbohydrates. Terrestrial plants work like solar cells that can fix atmospheric CO₂ and convert solar energy to lignocellulosic biomass; local sugar biorefineries would pretreat biomass for producing solid sugar powders; trucks would deliver solid sugars to end users. For hydrogen users, sugars plus water can be used to produce hydrogen for oil refineries, fertilizer producers, industrial food usage, pharmaceutical industries, or hydrogen fuel cell vehicles. For electricity users, a combination of hydrogen generation with fuel cells can produce electricity for remote areas, or provide an auxiliary power source, or work as a battery charger [4]. Carbohydrates can also power enzymatic fuel cells for portable electronics [54,55]. The most ambitious goal is to develop a sugar-powered vehicle that includes a sugar tank, an on-board bioreformer, PEM fuel cells, rechargeable batteries, and a motor [4,56]. This hypothetical power train system, called the sugar car, would have high energy storage densities of ~10 MJ electricity output/kg carbohydrate, high power density, high biomass-to-wheel efficiency, and low fuel costs [4,56].

Table 2 presents a comparison of several hydrogen carriers based on their prices, catalysis temperature, reactor cost, product purification, and safety/toxicity. Hydrocarbons can be converted to hydrogen and CO₂ via catalytic steam reforming (CSR) and partial oxidation [57]. Since a small amount of CO can poison the catalysts of PEM fuel cells [17], extra steps are required to remove CO before entering the PEMFC. Carbon

monoxide clean-up can be done in several ways – water-gas shifting, selective CO removal, methanation, and using a Pd alloy membrane. These reformers have been shown to be highly complicated, difficult to operate, bulky, and expensive [58]. Ethanol can be converted to hydrogen and CO₂ via autothermal reforming [17], but a small amount of CO requires further purification before the hydrogen stream enters the PEM fuel cells.

Methanol can be converted to hydrogen easily via reforming, or can be converted to electricity through a direct methanol fuel cell (DMFC). Therefore, George A. Olah, Nobel Prize Winner, advocates the use of methanol as a hydrogen carrier [59]. Since the DMFC has a relatively low power density and low energy conversion efficiency [60,61], it may work well as a power source for portable electronics but not for vehicles [62].

Ammonia, an easily-liquefied, carbon-free gas, has been suggested as a hydrogen carrier [53]. Ammonia production is a well-established industry based on the Haber–Bosch process with an overall efficiency of about 60–65% based on methane input. Since it seemed impossible to mate ammonia-as-fuel with PEM fuel cells, the USA DOE did not plan to fund any study pertaining to ammonia as a hydrogen carrier [63].

Carbohydrates have prices of \$~0.18/kg (i.e., 10.6/GJ), much less costly than other carriers. Hydrogen generation from carbohydrates mediated by SyPaB can be implemented at mild conditions of ~30–80 °C and ~1 atm, the process does not need any costly high-pressure reactor, and high-purity hydrogen mixed with CO₂ is generated, making extra product purification unnecessary. Under these mild reaction conditions, separation of the gaseous products and the aqueous reaction is easy and nearly no cost. Also, renewable carbohydrates are nearly inflammable and not toxic at all. Obviously, renewable carbohydrates may be an appealing hydrogen carrier (Table 2).

4. Reaction rates and potential applications

Practical applications of biohydrogen systems must be coupled with hydrogen fuel cell technologies (and vice versa) [64]. Whether carbohydrates work as a hydrogen carrier or not is closely correlated with hydrogen production rates and applications. The current hydrogen production rate of SyPaB is 3.92 mmol per liter of reactor per hour, where the substrate concentration is 8 mM (~1.4 g/L) and the temperature is 32 °C [26].

Table 2 – Comparison of hydrogen carriers.

Compound	Carrier costs ^a	Catalysis temp	Reactor cost	Purification needed	Safety/Toxicity
Hydrocarbons	Modest	\$17.8/GJ	High	High	Modest
Biodiesel	Very high	\$31.3/GJ	High	High	Modest
Ethanol	High	\$27.5/GJ	Modest	High	Low
Methanol	Modest	\$16.8/GJ	Low	Modest	Modest
Ammonia	Modest	\$19.1/GJ	Low	Modest	Modest
Carbohydrates	Very low	\$12.9/GJ	Very low	No need	Very low

^a based on the end users' prices: hydrocarbons (gasoline): \$2.50 per gallon; biodiesel, \$4.00 per gallon; methanol, \$1.00/gallon; ethanol, \$2.50 per gallon; ammonia, \$355/ton; and delivered carbohydrates, \$0.22/kg.

Table 3 – Analysis of potential hydrogen rate increases for SyPaB.

Technology	Potential fold	Ref.	Predicted fold
Increasing reaction temperatures from 30 to 80 °C	32	Q10 effect [26,37,65]	20
Increasing the use of enzymes responsible for rate-limited reactions	10	[26]	5
Increasing overall enzyme concentration	10	[74]	5
Increasing substrate concentration by 50-fold	10	[26]	3
Creating metabolite channeling among enzymes	~2–100	[38,66,67]	2
Increase catalytic efficiency of enzymes	~10		
Overall accelerating rates	640,000–32000,000		3,000

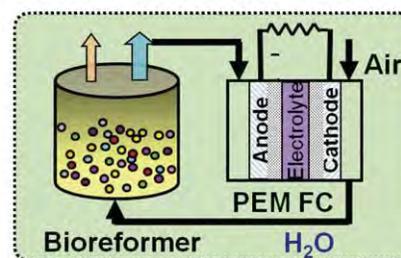
Table 3 shows an analysis of the methods for increasing hydrogen generation rates by SyPaB. They are:

1. Increasing reaction temperatures from 30 to 80 °C or higher. The rule of thumb of enzyme kinetics suggests that most enzymatic reaction rates double every 10 °C increase (i.e., the Q_{10} effect). Therefore, an increase in the reaction temperature from 30 °C to 80 °C may result in ~32-fold higher reaction rates. For example, the hyperthermophilic *P. furious* hydrogenase at 32 °C exhibits <1% of its maximum activity [65].
2. Increasing the use of enzymes responsible for rate-limited reactions. By applying metabolic control analysis, the model suggests another at least 5-fold increase in reaction rates by increasing the key enzyme loadings [26].
3. Increasing substrate concentrations by 50-fold or higher. In the proof-of-concept experiments, the substrate concentrations are very low (e.g., 2–8 mM) [26,27]. Practical hydrogen generation at high substrate concentrations (for example, 400 mM = 72 g/L) would result in another 3-fold increase in the reaction rates.
4. Increasing overall enzyme concentrations by 10-fold or higher. Since cell-free SyPaB systems do not contain other macromolecules (such as protein, RNA, DNA, membrane) that are responsible for cell duplication and basic metabolism maintenance, it is feasible to increase reaction rates 5-fold by adding more enzymes.
5. Accelerating the reaction rates by metabolite (product) channeling, in which one product of the first enzyme is transferred to the second enzyme without complete equilibrium with the bulk phase. When the overall enzyme concentration is high, macromolecular crowding effects could lead to metabolite channeling between the cascade enzymes, which could be attributed to another reaction rate enhancement by ~2–100 fold [66]. In addition, use of scaffoldin to link two cascade enzymes has been shown to greatly accelerate reaction rates through metabolite channeling [67–71]. The hydrolysis product channeling among a cellulolytic microbe and cellulose has been reported to increase the overall reaction rates by several folds [72].
6. Increasing the catalytic efficiency of enzymes. There are great enhancement potentials for increasing the catalytic efficiency of currently-used enzymes by several orders of magnitude, because most of their catalytic efficiencies are still much lower than those of catalytically-perfect enzymes [73] and most of the current enzymes used [26,27] are far less active than the highest values reported in the BRENDA database.

The above analysis may result in increasing rate potentials from 640,000- to 32,000,000-fold. In practice, the conservative estimation is that hydrogen production rates would increase 3000-fold to 23.52 g H₂/L/h. In support of the feasibility of this estimate, the highest biological hydrogen production rate (i.e., 23.6 g H₂/L/h) has been reported by high-cell density (i.e., more biocatalyst) microbial fermentation [74]. Since enzymatic reactions are usually faster than microbial fermentations [24,75], increasing reaction rates by three or four orders of magnitude would be highly achievable. The current bio-hydrogen production experiments are conducted using off-the-shelf enzymes with little optimization. With more collaboration and optimization, the reaction rates could be accelerated greatly through intensive R&D efforts. For example, the power density of microbial fuel cells has been improved by greater than 100,000–10,000,000 fold during the past 10 plus years [76].

One potential application is a 1-kW home-size electricity generator, as shown in Fig. 3A. Assuming the efficiency of PEM fuel cells = 50% and a 5-fold increase in the hydrogen production rate (i.e., 0.0392 g H₂/L/h), the bioreformer tank size would be 1280 L, which is acceptable in the basement of a home. In the New England area, tanks of heating oil are approximately this size. Producing hydrogen for 1-kW electricity generator (24 kWh per day) would consume 8.2 kg of

A High-power electricity generator



B Low-power sugar battery

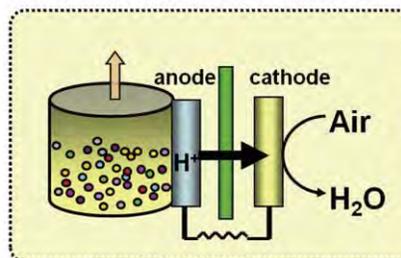


Fig. 3 – Two different electricity generation systems based on carbohydrates.

sugar per day or 245 kg of sugar per month. Giving the delivered sugar prices of \$0.22/kg (based on selling prices of \$0.18/kg from local sugar refineries), the sugar costs for electricity would be \$644 per year. Assuming 80% of hydrogen costs from carbohydrates, electricity costs generated from this system would be \$0.13 per kWh, which is comparable to current prices of delivered electricity. But the above sugar-hydrogen systems would have four other benefits: (1) ability to co-generate hot water for home users, (2) nearly zero net carbon emissions based on the whole life cycle, (3) creation of local jobs (e.g., biomass planting, collection, biorefinery and sugar delivery), and (4) promotion of the rural economy.

The most ambitious application is sugar-powered vehicles. A typical compact 5-person vehicle requires ~20-kW for constant-speed running on highways. Giving the efficiencies of PEM fuel cells of 50%, the sugar car would consume ca. 1 kg of hydrogen per hour. Assuming that the on-board bioreformer has a hydrogen generation rate of 23.52 g H₂/L/h, similar to the highest biological hydrogen production rate [74], the bioreformer tank size could be 42.8 L, which is possible to put in a small car. In order to meet requirements such as accelerating and start-up, rechargeable batteries are needed and the maximum output of the motor could be approximately 80 kW [4]. In order to have long driving distance for sugar fuel cell vehicles, the sugar car need store ca. 5 h of fuel, i.e., ca. 5 kg of hydrogen or 33.8 kg of sugar. Such an amount of sugar occupies a tank of ~48 L or 12.8 gallons, which is comparable to current gas tank size in a compact car. Current gasoline/internal combustion cars require maintenance every 3000 miles (e.g., 4800 kilometers) or 3 months, i.e., 50–100 driving hours. Obtaining thermophilic enzymes that are stable at 80 °C for more than 100 h is also operative, for example, *T. maritima* 6-phosphogluconate dehydrogenase [37]. It is expected that enzyme deactivation in the bioreactor could be solved through frequent maintenance, similar to the oil/air filter change for gasoline cars. Dry sugar powder from local sugar stations may be added into sugar vehicles by nitrogen blowing with fast refilling rates.

Fig. 3 shows two electricity generation pathways from carbohydrates: (1) hydrogen generated through SyPaB followed by PEMFC, which can produce high power by using small-sized PEM fuel cells with power densities of ~500–800 mW/cm² of anode area [62], and (2) enzymatic fuel cells with power densities of ~1–10 mW/cm² of anode area [54,55,77,78]. PEM fuel cells have such a high power density that their use would be good for the transportation sector and for home-size electricity generation, and the bioreforming tank sizes would depend on the hydrogen production rates. The enzymatic fuel cells have much lower power densities [54,55], making this use good for portable electronics, competing with DMFC or rechargeable batteries in the future [79].

5. Concluding remarks

Use of carbohydrates as a hydrogen carrier is a new concept. As compared to other sugar-to-hydrogen production methods, SyPaB may be the best mean for low-cost hydrogen production if thermostable enzymes are available and oxidoreductases can be engineered for utilizing low-cost

biomimic cofactors. Compared to other hydrogen carriers, carbohydrates are very appealing due to their low cost, renewable source, high-purity hydrogen generated, and so on. Now the developments of thermostable enzymes as building blocks, stable and low-cost biomimetic NAD cofactors, and accelerated reaction rates are urgently needed [4,24,25]. Obviously, such efforts cannot be finished by a single laboratory. Similarly, modern computers cannot be made by a single company anymore. International collaborations will be vital to the success of the carbohydrate hydrogen economy.

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