

Investigation of hydrogen production from boron compounds for pem fuel cells

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Received 27 May 2005; received in revised form 20 July 2005; accepted 22 July 2005

Available online 19 October 2005

Abstract

This paper presents a comprehensive study of hydrogen production from sodium borohydride (NaBH_4), which is synthesized from sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) decomposition, for proton exchange membrane (PEM) fuel cells. For this purpose, $\text{Na}_2\text{B}_4\text{O}_7$ decomposition reaction at 450–500 °C under hydrogen atmosphere and NaBH_4 decomposition reaction at 25–40 °C under atmospheric pressure are selected as a common temperature range in practice, and the inlet molar quantities of $\text{Na}_2\text{B}_4\text{O}_7$ are chosen from 1 to 6 mol with 0.5 mol interval as well. In order to form NaBH_4 solution with 7.5 wt.% NaBH_4 , 1 wt.% NaOH , 91.5 wt.% H_2O , the molar quantities of NaBH_4 are determined. For a PEM fuel cell operation, the required hydrogen production rates are estimated depending on 60, 65, 70 and 75 g of catalyst used in the NaBH_4 solution at 25, 32.5 and 40 °C, respectively. It is concluded that the highest rate of hydrogen production per unit area from NaBH_4 solution at 40 °C is found to be $3.834 \times 10^{-5} \text{ g H}_2 \text{ s}^{-1} \text{ cm}^{-2}$ for 75 g catalyst. Utilizing 80% of this hydrogen production, the maximum amounts of power generation from a PEM fuel cell per unit area at 80 °C under 5 atm are estimated as 1.121 W cm^{-2} for 0.016 cm by utilizing hydrogen from 75 g catalyst assisted NaBH_4 solution at 40 °C.

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Keywords: Sodium tetraborate; Sodium borohydride; Hydrogen gas; PEM fuel cell; Power generation

1. Introduction

Energy is a key element of the interactions between nature and society and is considered a key input for economic development and sustainable future. Environmental issues span a continuously growing range of pollutants, hazards and ecosystem degradation factors that affect areas ranging from local through regional to global. Some of these concerns arise from observable, chronic effects on, for instance, human health, while others stem from actual or perceived environmental risks such as possible accidental releases of hazardous materials. Many environmental issues are caused by or relate to the production, transformation and use of energy, for example, acid rain, strato-

spheric ozone depletion and global climate change. It is crystal clear that such serious adverse environmental impacts arise from the emission of greenhouse gases when fossil fuels are burned and that these contribute to global increases in temperature and sea-level, with resulting shifts in food-producing areas and patterns of disease, and species extinction. These changes, and the migration of people as a result of this cause, could affect peace and international security. Furthermore, the major effects of acid precipitation, arising from the SO_2 and NO_x emissions, are the increasing incidence of asthma and other respiratory diseases, the acidification of lakes, streams and ground waters, deterioration of buildings and metal structures, and damage to forests and agricultural crops.

In order to overcome the above said problems, hydrogen appears to be an excellent energy carrier and can be produced from any source by using solar, hydro, biomass, wind, geothermal, etc. One of the potential ways of producing hydrogen could be through sodium borohydride. It is important to note

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Nomenclature

F	Faraday's constant ($96,485 \text{ C}(\text{mol})^{-1}$)
i	current density for PEMFC (A cm^{-2})
i_0	exchange current density (A cm^{-2})
i_{max}	limiting current density ($=2 \text{ A cm}^{-2}$)
m_{catalyst}	catalyst quantity (g)
n	number of electron involved in PEMFC (2.0)
$\dot{n}_{\text{H}_2, \text{pro}}$	hydrogen production rate from NaBH_4 solution ($(\text{mol}) \text{ s}^{-1} \text{ cm}^{-2}$)
$\dot{n}_{\text{H}_2, \text{r}}$	reacted hydrogen molar rate in PEMFC ($(\text{mol}) \text{ s}^{-1} \text{ cm}^{-2}$)
P_{H_2}	hydrogen partial pressures (atm)
P_{O_2}	oxygen partial pressures (atm)
R	universal gas constant ($8.314 \text{ J}(\text{mol}\cdot\text{K})^{-1}$)
r_{H_2}	hydrogen production rate per catalyst ($\text{g H}_2(\text{s}\cdot\text{g catalyst})^{-1}$)
T_{FC}	PEM fuel cell reaction temperature (K)
t_{mem}	membrane thickness of cell (cm)
x_i	molar quantity of i th component (mol)
$V(i)$	net output cell voltage (V)
V_{rev}	reversible cell voltage (V)
\dot{W}_{FC}	electrical power generation in PEMFC (W cm^{-2})

Greek letters

α_{A}	anode transfer coefficients (0.5)
α_{C}	cathode transfer coefficients (1.0)
β_1, β_2	constants of concentration overpotential
λ_{mem}	membrane humidity
ν_{act}	activation overpotential (V)
ν_{conc}	concentration overpotential (V)
ν_{ohm}	ohmic overpotential (V)

here that hydrogen is produced from the boron compound but before that happens the boron compound needs to be “charged” with hydrogen that is produced some other way (reformation, electrolysis, etc.). Sodium borohydride can be synthesized from boron compounds such as $\text{Na}_2\text{B}_4\text{O}_7$, called sodium tetra borate. Borohydrides are important as potential fuels for fuel cells [1]. Stabilized NaBH_4 solutions have been demonstrated to be an effective source for hydrogen production. Due to system simplicity (NaBH_4 solution simply contacts ruthenium to produce H_2); it can be used in applications where H_2 gas is used, e.g., PEM fuel cells [2]. Fuel cells are considered electrochemical energy conversion devices that convert chemical energy of fuel, typical hydrogen, directly into electrical energy. One of the most important fuel cell types is a PEM fuel cell. A typical PEM fuel cell has efficiency much higher than the ones of conventional combustion engines, and hence a fuel cell vehicle would have higher efficiency [3].

In the open literature, very few studies are found on boron–hydrogen–fuel cell integration. For example, Kaufman and Sen [4] and Levy et al. [5] investigated cobalt and nickel borides as catalysts for practical, controlled generation of H_2 from NaBH_4 solutions. Brown and Brown [6] investigated a

series of metal salts and found that ruthenium (Ru) and rhodium (Rh) salts liberated H_2 most rapidly from borohydride solutions. Also, they found that Ru had a lower cost and generates H_2 at faster rates than metallic Rh. Aiello et al. [7] synthesized and tested various chemical hydrides for use hydrogen storage for portable fuel cell applications. Aiello et al. [8] developed a method producing H_2 from hydrolysis of chemical hydrides for use in hand-portable fuel cells. Two type of the direct borohydride fuel cell (DBFC) has reported by Amendola et al. [9]. Kong et al. [10] investigated the feasibility of a hydrogen storage system for alkaline fuel cells using decomposable hydrides. Amendola et al. [2,11] reported the application of Ru-catalyzed hydrolysis of aqueous NaBH_4 solution as hydrogen. Kojima and Haga [12] demonstrated that NaBO_2 can be recycled back to NaBH_4 using coke of methane. Kojima et al. [3] discussed the performance testing of the hydrogen generator using Pt-LiCoO₂-coated honeycomb monolith. Li et al. [13] investigated a fuel cell was assembled using alkaline borohydride solutions as the fuel. Krishnan et al. [14] studied on an efficient catalyst (PtRu-LiCoO₂) for hydrogen generation from sodium borohydride solutions.

The primary purpose of this paper is to develop a new methodology to investigate the hydrogen production through NaBH_4 , synthesized from $\text{Na}_2\text{B}_4\text{O}_7$ decomposition, for PEM fuel cell. This system combines boron–hydrogen production and a PEM fuel cell–power generation, basically from boron compounds to the electricity production from PEM fuel cells. We also model the power production to study the effects of the key parameters considered such as sodium tetra borate quantity, hydrogen production rates from NaBH_4 solution, reaction temperatures of NaBH_4 decomposition, catalyst quantities in NaBH_4 solution, and the operating temperature and pressure, and membrane thickness of PEM fuel cell.

2. Analysis

In this analysis section we consider the following subsections: general assumptions, process descriptions, and calculation procedures.

2.1. General assumptions

In order to theoretically investigate hydrogen production from sodium borohydride (NaBH_4), which is synthesized from sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) decomposition, for proton exchange membrane fuel cell, the following general assumptions are considered.

- In Fig. 1, the reactions in chambers 1 and 2 are reversible and adiabatic, referring to the 100% conversion efficiency.
- Sodium tetra borate ($\text{Na}_2\text{B}_4\text{O}_7$) quantities are chosen from 1 to 6 mol on a 0.5 mol interval for sodium tetra borate ($\text{Na}_2\text{B}_4\text{O}_7$) decomposition reaction in chamber 1.
- The sodium borohydride quantities produced from the $\text{Na}_2\text{B}_4\text{O}_7$ decomposition reaction are directly used in the NaBH_4 decomposition reaction to produce H_2 .

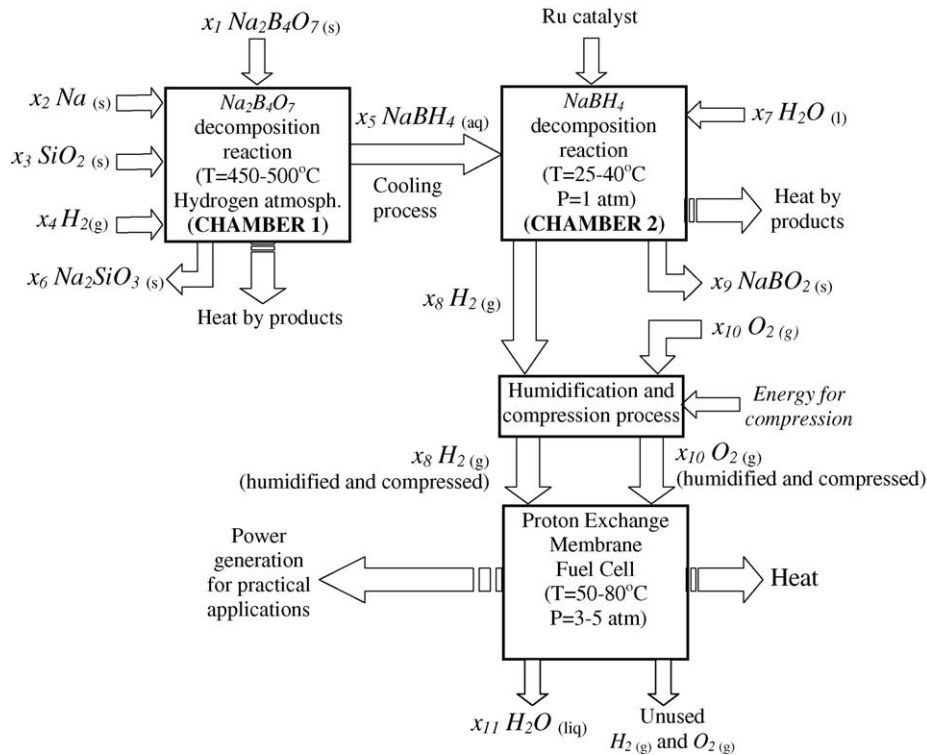
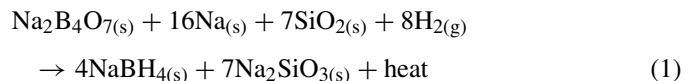


Fig. 1. Process flow diagram for power generation from PEM fuel cell using hydrogen from NaBH_4 synthesized from $\text{Na}_2\text{B}_4\text{O}_7$ decomposition.

- The reactant temperatures are equal to the product temperatures in the first reaction because $\text{Na}_2\text{B}_4\text{O}_7$ decomposition reaction is reversibly conducted at 450–500 °C.
- Hydrogen production rates per catalyst at different temperatures of NaBH_4 decomposition reaction are taken from literature [11].
- The compressing hydrogen in the cell operating pressures is used in PEM fuel cell.
- The reactant temperatures are equal to the product temperatures because NaBH_4 decomposition reaction under atmospheric pressure is reversibly conducted at 25–40 °C.
- NaBH_4 solution is catalyzed by 5% Ru supported on IRA-400 resin [11]. The catalyst quantities used in sodium borohydride decomposition reaction are chosen as 60, 65, 70 and 75 g, respectively.
- The temperatures of NaBH_4 decomposition reaction for hydrogen production are chosen as 25, 32.5, and 40 °C from the literature [11].
- The utilization ratios of hydrogen and oxygen in PEM fuel cell are taken to be 80 and 50%, respectively, because they are commonly used in literature [15].
- The PEM fuel cell is run under steady-state conditions.
- The cell pressures considered are 3, 4, and 5 atm, respectively.
- The cell operating temperatures are 50, 60, 70, and 80 °C, and membrane thicknesses are 0.016, 0.018, and 0.020 cm, respectively.
- The mass flow rate of the water used to humidify the oxygen and hydrogen streams is negligible because the flow rate of humidification water is small and it is at near-environmental conditions [16,17].

2.2. Process description

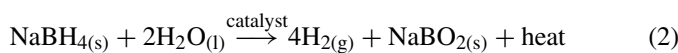
Considering the above-listed assumptions, the process diagram of hydrogen production from sodium borohydride (NaBH_4), which is synthesized from sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) decomposition, for PEM fuel cell is developed as shown in Fig. 1. Here, sodium borohydride (NaBH_4) in chamber 1 is synthesized from the mixture of sodium tetra borate ($\text{Na}_2\text{B}_4\text{O}_7$), quartz (SiO_2) and sodium metal (Na) at 450–500 °C under hydrogen atmosphere. Thus, the following reaction takes place [1,18]:



In this reaction, it should be explained how the chemicals involved by the process are produced, and how can be reused or recycled. $\text{Na}_2\text{B}_4\text{O}_7$ is a boron compound called sodium tetraborate and is abundantly found in Turkey. Na, metallic sodium, can be abundantly found in the nature and also produced from the chemical reaction of NaCl and H_2O by using electrolysis technique. SiO_2 can be abundantly found all over the world, and used as a solid base in this reaction. H_2 can be produced from non-fossil fuels such as water, biomass, etc., by using renewable energy sources. Na_2SiO_3 from this reaction can be reused as a raw material in glass industry.

For the NaBH_4 solution in chamber 2, the NaBH_4 that is synthesized from $\text{Na}_2\text{B}_4\text{O}_7$ decomposition is mixed with water. After NaBH_4 solution is catalyzed at 25–40 °C, H_2 gas and

sodium metaborate, NaBO_2 , are produced [2,11,12,19]:



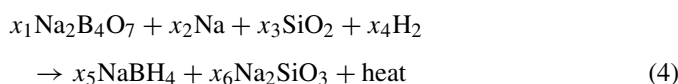
In this reaction, NaBO_2 product from this reaction can be recycled to produce NaBH_4 using hydrogen from non-fossil fuels such as water, biomass, etc.

This reaction can occur without a catalyst if the solution $\text{pH} < 9$. However, to increase the shelf life of NaBH_4 solution (and to prevent hydrogen gas from being slowly produced upon standing), NaBH_4 solution is typically maintained as strongly alkaline solution by adding NaOH [11]. The key feature of using a catalyzed reaction to produce hydrogen is that hydrogen generation in alkaline ($\text{pH} > 14$) NaBH_4 solution can occur only when this solution contacts the selected heterogeneous catalyst. Without catalyst, strongly alkaline NaBH_4 solution does not produce appreciable hydrogen.

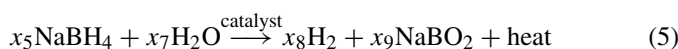
In PEM fuel cell, the following reaction occurs for power generation:



Taking into consideration the conversion ratios in Eqs. (1)–(3), we can write the model reactions as given in Eqs. (4)–(6) using different unknown coefficients for the parametric investigation. In the model reactions, the values of x_i , molar quantity of i th component ($i = 1 \dots 11$), can be estimated depending on the inlet molar quantities of $\text{Na}_2\text{B}_4\text{O}_7$ in chamber 1 in accordance with the main conversion ratios in Eqs. (1)–(3). Thus, with the above description and Fig. 1, the following model reaction is conducted in chamber 1 at 450–500 °C for NaBH_4 in solid phase:



For decomposition of $\text{Na}_2\text{B}_4\text{O}_7$, x_1 mole of $\text{Na}_2\text{B}_4\text{O}_7$, x_2 mole of Na , and x_3 mole of SiO_2 are entered to the chamber 1. In order to generate a hydrogen atmosphere in chamber 1, x_4 mole of hydrogen gas that is supplied from the renewable energy sources should be inserted in chamber 1. After that, a strong exothermic decomposition reaction of $\text{Na}_2\text{B}_4\text{O}_7$ occurs at about 450–500 °C under hydrogen atmosphere in chamber 1. High amount of heat by products is released from the reaction tanks to the exothermic chemical process. At the end of $\text{Na}_2\text{B}_4\text{O}_7$ decomposition in chamber 1, x_5 mole of $\text{NaBH}_4(\text{s})$, and x_6 mole of $\text{Na}_2\text{SiO}_3(\text{s})$ are produced. Actually, the products of the $\text{Na}_2\text{B}_4\text{O}_7$ decomposition reaction should be cooled to prevent their decomposition under high temperature. Then, for NaBH_4 decomposition that is the main process for hydrogen production, x_7 mole H_2O should be entered in chamber 2. $\text{NaBH}_4(\text{s})$ decomposition occurs at 25–40 °C under atmospheric pressure in chamber 2 for hydrogen synthesis. Based on the model reaction in Eq. (5), some heat is then released, and x_9 mole of NaBO_2 , and x_8 mole of H_2 are obtained as products:



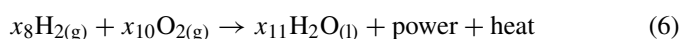
We note that hydrogen production rate from NaBH_4 solution is directly proportional to the amount of catalyst. One clear

advantage of this method is that rapid (but controlled) hydrogen generation can be achieved at the ambient temperature without mechanical compression, addition of water, acid or heat. In this condition, little hydrogen can be produced from the stabilized NaBH_4 solution without catalyst. Also, the catalytically production of hydrogen gas from NaBH_4 solution has the following advantages [11]:

- Method of H_2 generation from NaBH_4 solution is considerably safer, more efficient, and controllable than other chemical methods.
- NaBH_4 solutions are non-flammable.
- NaBH_4 solution is stable in air for months.
- H_2 generation only occurs in the presence of selected catalysts.
- The only other product in the gas stream is water vapor.
- Reaction products are environmentally safe.
- H_2 generation rates are easily controlled.
- Volumetric and gravimetric H_2 storage efficiencies are high.
- The reaction products can be recycled.
- H_2 can be generated even at 0 °C.

As a comparison with other means of producing hydrogen cleanly, it can be said that hydrogen production from boron compounds such as sodium borohydride is more suitable process than the hydrogen production from fossil-based energy sources. Why? If hydrogen is produced from fossil fuels such as oil, natural gas, coal, etc., the emissions can include some amount of harmful gases such as dioxides throughout the chemical reactions in pyrolysis, gasification and reforming processes. In order to remove or partially reduce the harmful emissions of hydrogen production from fossil fuels, a non-fossil fuel sources such as water, biomass, sodium borohydride, etc., should be taken into consideration. In this regard, NaBH_4 that is synthesized from boron compounds such as $\text{Na}_2\text{B}_4\text{O}_7$ is considered to produce hydrogen for power generation via PEM fuel cell. As understood from the reactions in this manuscript, it can be said that the emissions of NaBH_4 decomposition reaction would include only hydrogen and NaBO_2 that do not have harmful effects to the environment.

In order to increase the hydrogen production rate, Ru catalyst, which is supported on anion exchange resin beads, is used. The hydrogen gas, produced in chamber 2 is transported to PEM fuel cell after humidification process. Thus, PEM fuel cell generates power according to the following model reaction:



2.3. Calculation procedure

The theoretical molar values in these model reactions form a base for the investigation of hydrogen production from sodium borohydride (NaBH_4), which is synthesized from sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) decomposition, and the power generation through PEM fuel cell. For this purpose, the calculation procedure can be summarized as follows in Fig. 2.

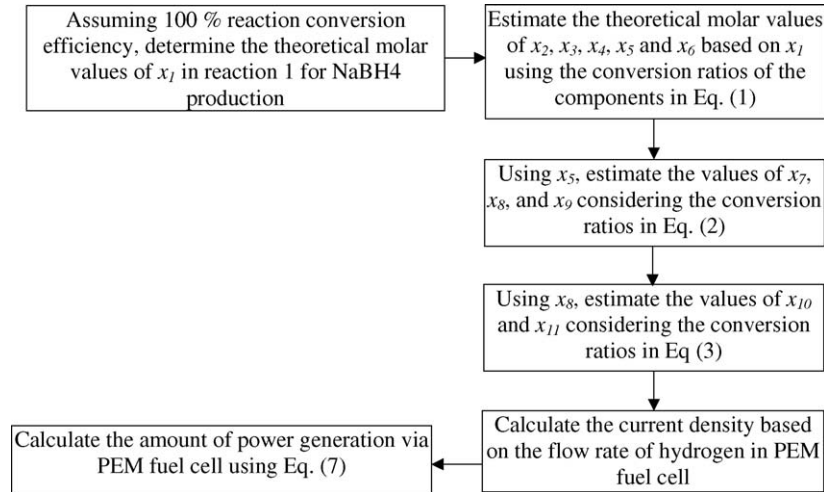


Fig. 2. Calculation procedure of power generation via PEM fuel cell using hydrogen from NaBH₄ that is synthesized from Na₂B₄O₇ decomposition reaction.

Thus, the power generated by PEM fuel cell can be calculated using the following equation:

$$\begin{aligned} \dot{W}_{FC} &= V(i) \times i = i \times [V_{\text{rev}} - v_{\text{act}} - v_{\text{ohm}} - v_{\text{conc}}] \\ &= i \times \left\{ 1.229 - 8.5 \times 10^{-4} (T_{\text{FC}} - 298.15) + 4.3085 \times 10^{-5} \times T_{\text{FC}} \left[\ln(P_{\text{H}_2}) + \left(\frac{1}{2}\right) \ln(P_{\text{O}_2}) \right] \right\} - i \\ &\quad \times \left\{ \left(\frac{\alpha_A + \alpha_C}{\alpha_A \alpha_C} \right) \left(\frac{RT_{\text{FC}}}{nF} \right) \ln \left(\frac{i}{i_0} \right) \right\} - i \times \left\{ i \times t_{\text{mem}} \times \left[(0.005139 \lambda_{\text{mem}} - 0.00326) \exp \left[1268 \left(\frac{1/303 - 1}{T_{\text{FC}}} \right) \right] \right]^{-1} \right\} \\ &\quad - i \times \left\{ i \left(\beta_1 \left(\frac{i}{i_{\text{max}}} \right) \right)^{\beta_2} \right\} \end{aligned} \quad (7)$$

where $V(i)$ is net output cell voltage; $V_{\text{rev}} = E$ reversible cell voltage [20,21]; v_{act} , v_{ohm} , and v_{conc} , the activation [22], ohmic [22], and concentration [23] overpotentials, respectively. Furthermore, T_{FC} is PEM fuel cell reaction temperature; t_{mem} , membrane thickness; R , universal gas constant; F , Faraday's constant; n , number of electron involved [22]; i_0 , exchange current density [24]; i_{max} , limiting current density (2 A cm^{-2}); λ_{mem} , membrane water content [25]; p_{H_2} and p_{O_2} , hydrogen and oxygen partial pressures; α_A and α_C , anode and cathode transfer coefficients [26], respectively; β_1 and β_2 , constants of concentration overpotential [23]. β_2 is equal to 2 and the detailed information on β_1 constant is presented in literature [23].

Here, the current density (i) can be estimated as

$$i = 2\dot{n}_{\text{H}_2, \text{r}} \times F \quad (8)$$

where, $\dot{n}_{\text{H}_2, \text{r}}$, molar utilization ratio of hydrogen reacted in fuel cell, F Faraday's constant. In this study, it is considered that PEM fuel cell is directly fed with hydrogen from NaBH₄ solution, and 80% of hydrogen is utilized in the cell [15].

Thus, the molar utilization ratio of hydrogen reacted in the fuel cell can be estimated as

$$\dot{n}_{\text{H}_2, \text{r}} = 0.8 \times \dot{n}_{\text{H}_2, \text{pro}} \quad (9)$$

where $\dot{n}_{\text{H}_2, \text{pro}}$ defines molar hydrogen production ratio from NaBH₄ solution and can be defined as

$$\dot{n}_{\text{H}_2, \text{pro}} = r_{\text{H}_2} \times m_{\text{catalyst}} \quad (10)$$

where r_{H_2} explains hydrogen production ratio per catalyst at different reaction temperatures; m_{catalyst} catalyst quantity. The values of r_{H_2} based on the reaction temperatures of NaBH₄ solution are taken from the literature [11], which are $5.28 \times 10^{-4} \text{ g H}_2 \text{ (s-g catalyst)}^{-1}$ for 25 °C; $8.46 \times 10^{-4} \text{ g H}_2 \text{ (s-g catalyst)}^{-1}$ for 32.5 °C, and $15.34 \times 10^{-4} \text{ g H}_2 \text{ (s-g catalyst)}^{-1}$ for 40 °C, respectively.

For parametric investigation, the foremost values in Table 1 are taken into account.

3. Results and discussion

In this paper, a study is conducted to investigate hydrogen production from sodium borohydride (NaBH₄), which is synthesized from sodium tetraborate (Na₂B₄O₇) decomposition, for PEM fuel cell. Assuming 100% conversion efficiency of the reactions, the variations in Figs. 3–8 are analyzed and discussed in detail.

Fig. 3 illustrates the variations of the required reactant quantities in chamber 1 for NaBH₄ production from Na₂B₄O₇ decomposition reaction. The required reactant quantities for NaBH₄ production in chamber 1, Eqs. (1) and (4), are taken into consideration. As shown in Fig. 3, assuming 100% conversion

Table 1
Theoretical values of the coefficients in the model reactions

x_1 (mol)	x_2 (mol)	x_3 (mol)	x_4 (mol)	x_5 (mol)	x_6 (mol)	x_7 (mol)	x_8 (mol)	x_9 (mol)	x_{10} (mol)	x_{11} (mol)
1	16	7	8	4	7	8	16	4	8	16
1.5	24	10.5	12	6	10.5	12	24	6	12	24
2	32	14	16	8	14	16	32	8	16	32
2.5	40	17.5	20	10	17.5	20	40	10	20	40
3.0	48	21	24	12	21	24	48	12	24	48
3.5	56	24.5	28	14	24.5	28	56	14	28	56
4.0	64	28	32	16	28	32	64	16	32	64
4.5	72	31.5	36	18	31.5	36	72	18	36	72
5.0	80	35	40	20	35	40	80	20	40	80
5.5	88	38.5	44	22	38.5	44	88	22	44	88
6.0	96	42	48	24	42	48	96	24	48	96

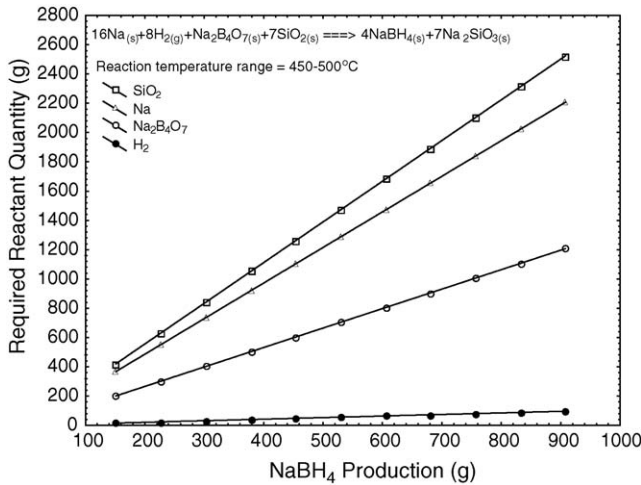


Fig. 3. Variations of the required reactant quantity for NaBH₄ production from Na₂B₄O₇ decomposition reaction.

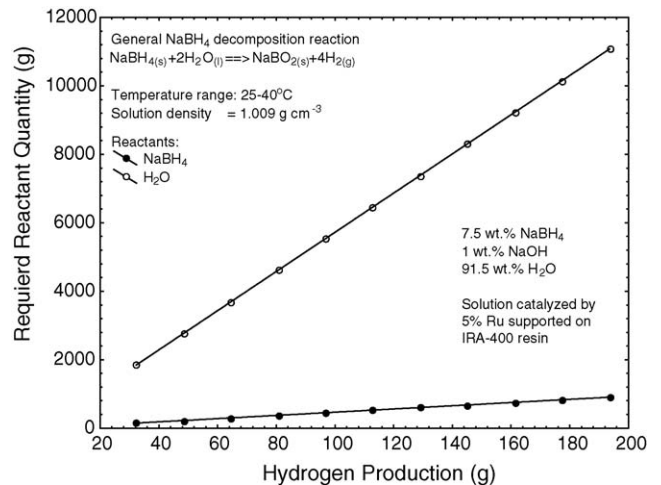


Fig. 4. Variations of the required reactant quantity for hydrogen production from NaBH₄ decomposition reaction.

efficiency and considering the Na₂B₄O₇ mole quantities changing from 1 to 6 mol, 201.22 g Na₂B₄O₇ (1 mol), 367.84 g Na, 420.63 SiO₂, and 16.128 g H₂ are needed for 151.328 g NaBH₄ production. Similarly, 1207.32 g Na₂B₄O₇ (6 mol), 2207.04 g Na, 2523.78 SiO₂, and 96.768 g H₂ are required for 907.968 g

NaBH₄ production. Thus, the theoretical production ratio of NaBH₄ is estimated as 15.045%.

Fig. 4 shows the variations of the required reactant quantities in chamber 2 for hydrogen production from NaBH₄ decomposition. We basically employ Eqs. (2) and (5) to estimate the

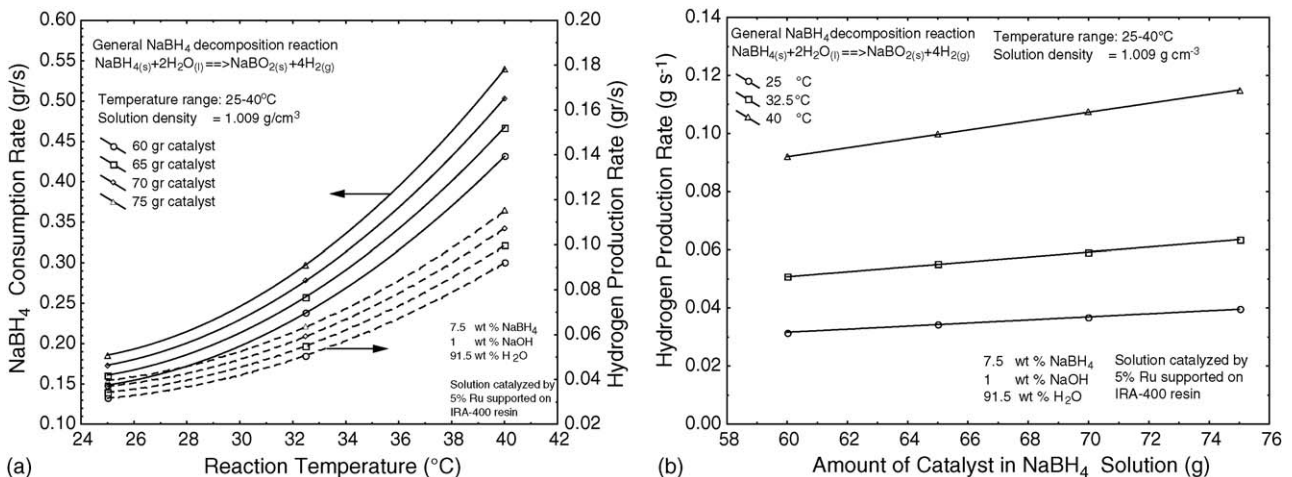


Fig. 5. (a) Variations of NaBH₄ consumption and H₂ production rates as a function of reaction temperatures based on different amounts of catalyst. (b) Variations of H₂ production rates as a function of the amount of catalyst in NaBH₄ solution based on reaction temperatures.

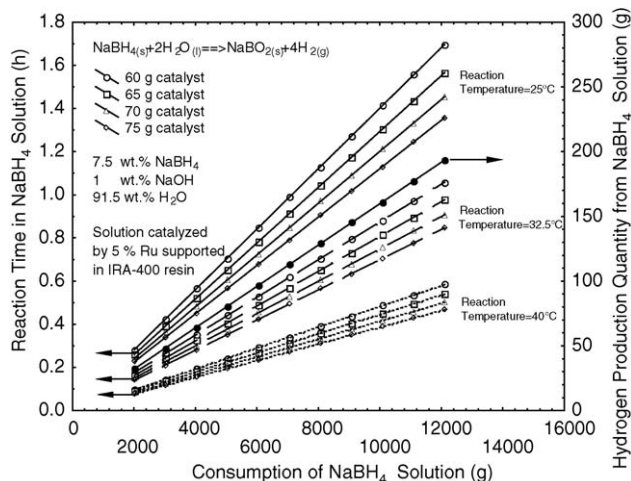


Fig. 6. Variations of the reaction time in NaBH_4 solution and hydrogen production as a function of NaBH_4 solution consumption.

required reactant quantities for hydrogen production in chamber 2. We note that the NaBH_4 mole quantities vary from 4 to 24 mol, depending on the mole quantities of $\text{Na}_2\text{B}_4\text{O}_7$ from 1 to 6 mol. Assuming a conversion efficiency of 100%, 151.328 g NaBH_4 (4 mol from Eq. (1)) and 1846.201 g H_2O are required for 32.256 g H_2 production through Eqs. (2) and (5). Similarly, 907.968 g NaBH_4 (24 mol) and 11,077.21 g H_2O are needed for 193.536 g H_2 production. Thus, the production ratio of H_2 from NaBH_4 solution under atmospheric pressure at 25–40 °C is estimated as 1.615%.

Fig. 5a presents the variation of NaBH_4 consumption rate and H_2 production rate as a function of reaction temperature depending on the amounts of catalyst while Fig. 5b exhibits the variation of hydrogen production rates with the amounts of catalyst based on the reaction temperatures of NaBH_4 decomposition reaction. In order to calculate the hydrogen production and NaBH_4 consumption rates based on the amounts of catalyst, the reference values of hydrogen production rate per g catalyst at different temperatures of NaBH_4 decomposition reaction were taken from literature [11]. As shown in these figures, the NaBH_4 consumption rate and H_2 production rate increase with a rise of reaction temperature and the amount of catalyst used in the NaBH_4 solution under atmospheric pressure. For example, if assuming 100% conversion efficiency, it is estimated that the theoretical H_2 production rate and NaBH_4 consumption rate are, respectively, 0.040 g $\text{H}_2 \text{ s}^{-1}$ and 0.186 g $\text{NaBH}_4 \text{ s}^{-1}$ for 75 g catalyst at 25 °C. However, H_2 production rate and NaBH_4 consumption rate are, respectively, found to be 0.115 g $\text{H}_2 \text{ s}^{-1}$ and 0.540 g $\text{NaBH}_4 \text{ s}^{-1}$ for 75 g catalyst at 40 °C.

Fig. 6 presents the variations of the reaction time in NaBH_4 solution and hydrogen production quantity as a function of NaBH_4 solution consumption. In this figure, the reaction time of NaBH_4 decomposition is calculated depending on the reaction temperatures and the amounts of catalyst in NaBH_4 solution. It is considered that the reaction temperature of NaBH_4 decomposition and the amount of catalyst in NaBH_4 solution do not affect the hydrogen production quantity but they influence the hydrogen production time from NaBH_4 solution. In order to reduce the

hydrogen production time from NaBH_4 solution, it is considered that different amounts of catalyst are used in NaBH_4 solution that is catalyzed with 5% Ru supported in IRA-400 resin. In this case, it was determined that 32.256 g of hydrogen would be theoretically produced in 0.226 h at 25 °C and in 0.0779 h at 40 °C of NaBH_4 decomposition reaction using 75 g catalyst, respectively. In addition, 193.536 g of hydrogen would be theoretically obtained in 1.358 h at 25 °C and in 0.467 h at 40 °C of NaBH_4 decomposition reaction using 75 g catalyst, respectively. Thus, the maximum hydrogen production from NaBH_4 solution at least time should be main goal in practical applications. Therefore, it is suggested that, in order to produce 193.536 g of hydrogen from NaBH_4 solution in 0.467 h, NaBH_4 decomposition reaction should be conducted at 40 °C using 75 g catalyst.

Fig. 7(a and b) illustrate the variations of power generation per area from a PEM fuel cell (under 3 atm and 80 °C) and current density as a function of hydrogen production rate per area from NaBH_4 solution depending on the different membrane thicknesses. According to Fig. 7(a and b), the maximum power can be generated from a PEM fuel cell with 0.016 cm under constant operating conditions (3 atm and 80 °C) by using hydrogen quantities from 75 g catalyst assisted NaBH_4 solution at 40 °C. Assuming 100% conversion efficiency, we obtained the hydrogen production rate per area from NaBH_4 solution at 40 °C under atmospheric pressure to be $3.834 \times 10^{-5} \text{ g H}_2 \text{ s}^{-1} \text{ cm}^{-2}$ for 75 g catalyst. Utilizing 80% of this hydrogen rate in a PEM fuel cell, the maximum power generation is estimated to be 1.079 W cm^{-2} . The value of current density is found to be 1.835 A cm^{-2} .

Fig. 7(c and d) present the variations of power generation per area from a PEM fuel cell (under 3 atm and 0.018 cm) and current density as a function of hydrogen production rate per area from NaBH_4 solution depending on the different cell operating temperatures. In this situation, we note that the values of current densities are same as those given earlier. So, such outcomes will not be repeated for Fig. 7(c–f). Considering Fig. 7(c and d), the maximum power generation can be conducted from a PEM fuel cell that is operated at 80 °C under constant operating pressure and membrane thickness (3 atm and 0.018 cm) by using hydrogen quantities from 75 g catalyst assisted NaBH_4 solution at 40 °C. Assuming 100% conversion efficiency, if 80% of $3.834 \times 10^{-5} \text{ g H}_2 \text{ s}^{-1} \text{ cm}^{-2}$ for 75 g catalyst of hydrogen production rate from NaBH_4 solution at 40 °C is used by the PEM fuel cell, then the maximum power generation per area will be estimated to be 1.024 W cm^{-2} at a cell temperature of 80 °C.

Fig. 7(e and f) show the variations of power generation per area from a PEM fuel cell (under 80 °C and 0.018 membrane thickness) and current density as a function of hydrogen production rate per area from NaBH_4 solution depending on different cell operating pressure. In these figures, the maximum power generation can be obtained from a PEM fuel cell that is operated at 5 atm under constant operating temperature and membrane thickness (80 °C and 0.018 cm) by using hydrogen quantities from 75 g catalyst assisted NaBH_4 solution at 40 °C. Assuming 100% conversion efficiency, if 80% of $3.834 \times 10^{-5} \text{ g H}_2 \text{ s}^{-1} \text{ cm}^{-2}$ for 75 g catalyst of hydrogen production rates per area from NaBH_4 solution at 40 °C is used by

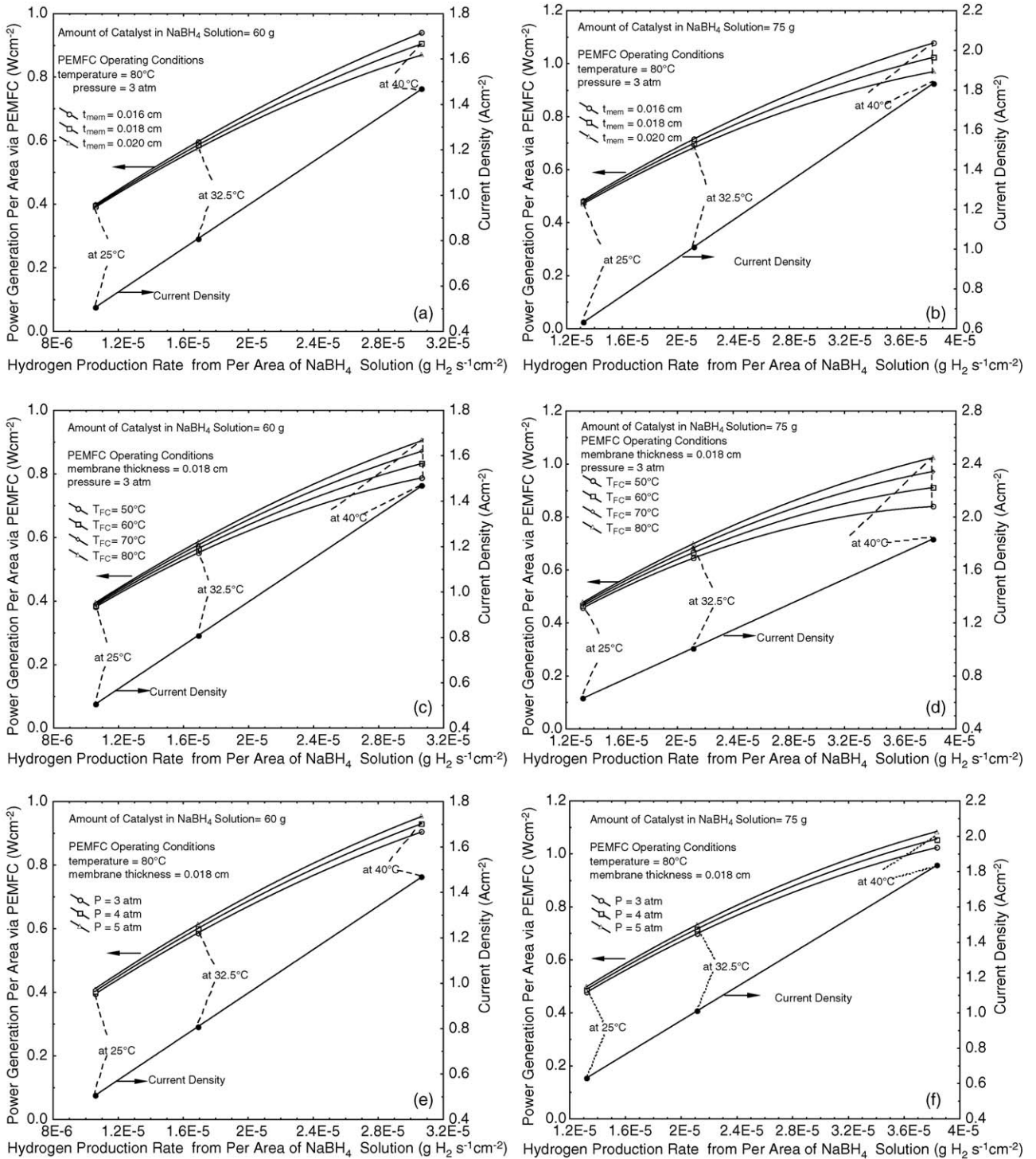


Fig. 7. (a) Variations of power generation per area from PEM fuel cell under 3 atm at 80 °C and current density as a function of hydrogen production rate per area from 60 g catalyst assisted NaBH₄ solution. (b) Variations of power generation per area from PEM fuel cell under 3 atm at 80 °C and current density as a function of hydrogen production rate per area from 75 g catalyst assisted NaBH₄ solution. (c) Variations of power generation per area from PEM fuel cell operating under 3 atm at different cell temperatures, and current density as a function of hydrogen production rate per area from 60 g catalyst assisted NaBH₄ solution. (d) Variations of power generation per area from PEM fuel cell operating under 3 atm at different cell temperatures, and current density as a function of hydrogen production rate per area from 75 g catalyst assisted NaBH₄ solution. (e) Variations of power generation per area from PEM fuel cell operating at 80 °C under different cell pressures, and current density as a function of hydrogen production rate per area from 60 g catalyst assisted NaBH₄ solution. (f) Variations of power generation per area from PEM fuel cell operating at 80 °C under different cell pressures, and current density as a function of hydrogen production rate per area from 75 g catalyst assisted NaBH₄ solution.

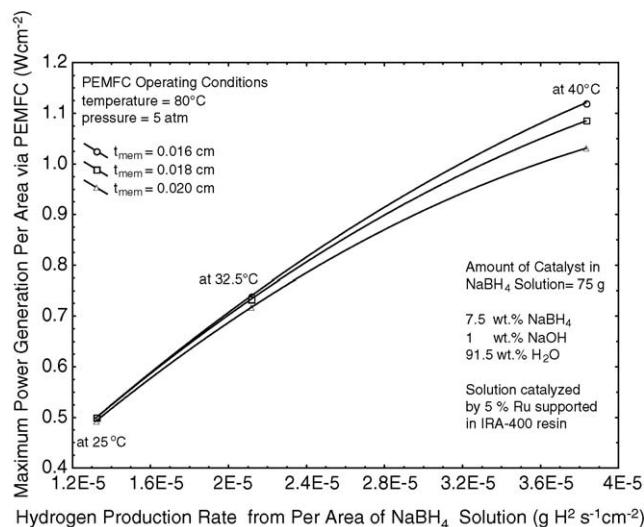


Fig. 8. Maximum power generation per area from a PEM fuel cell at 5 atm and 80 °C operating conditions by using hydrogen production rate per area from 75 g catalyst assisted NaBH₄ solution.

a PEM fuel cell under a cell pressure of 5 atm, the maximum power generation per area is obtained to be 1.085 W cm⁻².

In light of the above discussion, it is possible to determine the best conditions at which the maximum hydrogen production rate per area from NaBH₄ solution and the maximum power generation per area from a PEM fuel cell are estimated depending on the temperatures of NaBH₄ decomposition reaction. In this regard, Fig. 8 is presented to illustrate the maximum power generation per area as a function of hydrogen production rate per area from NaBH₄ solution depending on the temperature of NaBH₄ solution and membrane thickness of PEM fuel cell at 5 atm and 80 °C. As shown in Fig. 8, the maximum power generation per area from PEM fuel cell is estimated for different membrane thicknesses, such as 0.016, 0.018, and 0.02 cm at a constant pressure of 5 atm and a temperature of 80 °C of a PEM fuel cell using hydrogen production rates per area from 75 g catalyst assisted NaBH₄ solution. If we assume 100% reaction conversion efficiency, we will estimate the hydrogen production rate per area from 75 g catalyst assisted NaBH₄ solution at 40 °C under atmospheric pressure to be 3.834×10^{-5} g H₂ s⁻¹ cm⁻². Utilizing 80% of this hydrogen rates, the maximum amounts of power generation per area from PEM fuel cell at 80 °C under 5 atm will be estimated as 1.121 W cm⁻² for 0.016 cm, 1.085 W cm⁻² for 0.018 cm, and 1.031 W cm⁻², respectively, for a membrane thickness of 0.020 cm.

4. Conclusion

This paper presents a methodology to investigate the possibility of hydrogen production from sodium borohydride (NaBH₄), which is synthesized from sodium tetraborate (Na₂B₄O₇) decomposition, for power generation via a PEM fuel cell. It is concluded that, in order to obtain the maximum power generation per unit area from a PEM fuel cell, the cell should possess a membrane thickness of 0.016 cm, and be fed with hydrogen

from 75 g catalyst assisted NaBH₄ solution under atmospheric pressure at 40 °C, and operated at 80 °C under 5 atm. In addition, the formation of hydrogen atmosphere throughout sodium tetraborate decomposition, the utilization of a well catalyzed sodium borohydride solution and the reduction of the cell losses will increase the power generation from a boron–hydrogen-PEM fuel cell integration system. Therefore, it is suggested that, the required hydrogen quantity to create a hydrogen atmosphere for sodium tetraborate decomposition should be supplied from non-fossil sources such as solar, hydraulic, biomass, etc. Also, the catalyst quantity and reaction temperature in and of NaBH₄ solution under atmospheric pressure should be chosen depending on the hydrogen quantity required for a PEM fuel cell under optimum operating conditions. Accordingly, it is expected that this study will contribute the scientists and researchers to develop a methodology to produce hydrogen from boron compounds for practical clean power generation, and also to encourage particularly use of the boron–hydrogen-PEM fuel cell integration systems for future applications, and finally to increase the motivation on boron compounds and PEM fuel cells for clean energy supply and progress all over the world.

Acknowledgements

The authors acknowledge the support provided by Nigde University in Turkey, and University of Ontario Institute of Technology and the Natural Sciences and Engineering Research Council of Canada in Canada. The authors also appreciate the efforts of the editor, Dr. Bruno Scrosati for getting the paper reviewed by the expert referees and the constructive comments of the referees which help improve the paper considerably.

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