

Integrated One-Step PEMFC-Grade Hydrogen Production From Liquid Hydrocarbons Using Pd Membrane Reactor

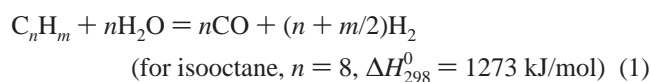
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A process of hydrogen production for application to proton exchange membrane fuel cells (PEMFC), a kind of efficient and almost zero-emission power-generation device, was developed by integrating the reactions during the steam reforming of multicomponent liquid hydrocarbon fuels and hydrogen enrichment in a Pd membrane reactor. A highly hydrogen permeable, permselective Pd composite membrane, and an active catalyst for steam reforming of not only higher hydrocarbons but also of methane at temperatures lower than 823 K, made one-step hydrogen production from steam reforming of liquid hydrocarbons in a membrane reactor feasible near practical working conditions. Furthermore, a theoretical energy balance calculation showed that the membrane not only separated hydrogen but also adjusted the selectivities of products, which could be applied to achieve autothermal operation, e.g., catalytic combustion of the reformat from the retentate side of the Pd membrane could provide the energy for the endothermic steam reforming reactions in such a fuel processor system.

1. Introduction

There is continued interest in H₂ production from fossil fuels, particularly biomass-derived fuels, in view of the sustainable development requirement.^{1,2} H₂ production from the steam reforming of naphtha on large scales has been well-established in the chemical industry;³ it is a multistep process, including prereforming, high-temperature (over 1 123 K) reforming, two-stage water gas shift (WGS), and H₂ enrichment by pressure-swing adsorption or cryogenic purification. However, for small-scale H₂ production or fuel processors able to be coupled with fuel cell application, the traditional naphtha steam reforming process is very complicated and uneconomical. Thus, much investigation work has been performed worldwide, aiming to develop suitable processes for economically producing H₂ on smaller scales to meet the specific requirement of proton exchange membrane fuel cells (PEMFC). Usually, the steam reforming of higher hydrocarbons could be represented by reactions 1–3.⁴



The concept of multifunctional catalytic reactors integrating reaction and separation in the same unit is attracting more and more interest, because of the enormous advantages such a method could provide: i.e., attainment of higher conversion and product yield, simplified separation of products, and reduced costs for plant equipment and maintenance. Thus, reactions such

as dehydrogenation of higher hydrocarbons and methane steam reforming in Pd based membrane reactors have been extensively investigated in the past decade.^{5–7} In comparison with natural gas, the advantages of liquid hydrocarbons as a fuel source for H₂ production over natural gas lie in the fact that the distribution infrastructure can be readily adapted from the existing gasoline system worldwide. However, there has been little experimental investigation on H₂ production from steam reforming of liquid hydrocarbons in a membrane reactor. Only very recently, Chen and Elnashaie^{8,9} simulated the *n*-heptane steam reforming in a circulating fluidized-bed membrane reformer (CFBMR). They found that yield of H₂ (Y_{H_2}) could be efficiently enhanced, while the yield of methane (Y_{CH_4}) could be significantly reduced. However, the process was still very complicated and unsuitable for small-scale H₂ production for PEMFC application, in that it was carried out using a fluidized-bed reformer, including operations such as reforming, regeneration of coked catalyst, gas–solid separation, hot catalyst circulation, and external H₂ separation.

To achieve efficient H₂ production from the steam reforming of liquid hydrocarbons in a membrane reactor, a high-performance membrane and a highly active catalyst are the two key factors. In this paper, an improved electroless method for preparation of Pd composite membrane, and H₂ production from steam reforming of a mixture of liquid hydrocarbons (carbon numbers in the range of 4–8, with an average formula of C_{6.43}H_{14.84}, light distillate of Daqing Fisher–Tropsch synthesis products, simplified as “fuel” in the following text, with the concrete composition of fuel given in ref 10), in a membrane reactor was reported.

2. Experimental Section

2.1. Pd Membrane Preparation and Characterization. The Pd composite membrane was prepared according to procedures described in Scheme 1, and the details were given in ref 11. Commercial α -Al₂O₃ membrane support (i.d. = 6.2 mm and o.d. = 10.2 mm) was supplied by the Membrane Science Research Center of Nanjing University of Technology. Accord-

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Scheme 1. Procedures for Preparing Pd Composite Membrane

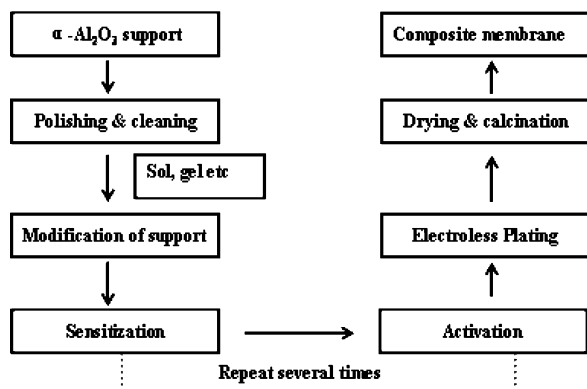
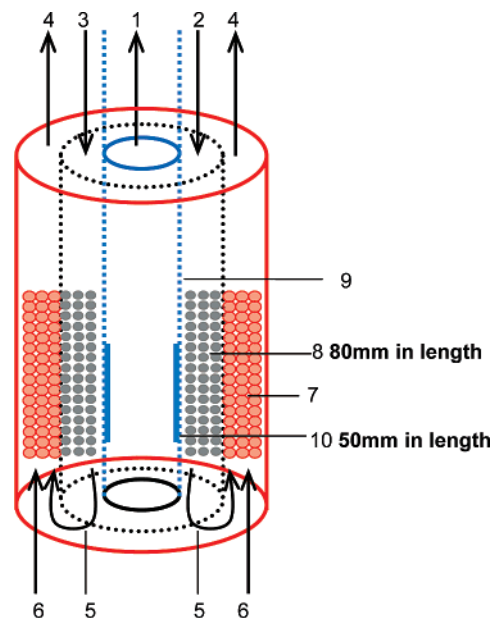


Table 1. Typical Chemical Component in the Plating Solution and Its Property

chemical component or property	values and unit
PdCl ₂	1–4 (g/dm ³)
EDTA·2Na	65–80 (g/dm ³)
N ₂ H ₄	0.3–1.0 (g/dm ³)
NH ₃ ·H ₂ O (28.0%)	300–400 (mL/dm ³)
pH value	~10.0
temperature	313–343 K

ing to the manufacturer's specification, the total length of the support was 300 mm with 250 mm covered by glaze, and the rest was the porous part with an average pore size of 500 nm. As indicated in Scheme 1, the support was washed with dilute hydrochloride solution, NaOH solution, and then petroleum ether. After cleaning, the porous part of the membrane support was modified using a sol–gel method.¹¹ The modified support was then dipped in an activation/sensitization solution OPC-50 inducer C and then in the OPC-150 cryster MU (Okuno Chemical Industries Co. Ltd., Japan), which was repeated several times to deposit a suitable amount of Pd⁰ crystallite on the support. After that, the porous part of the membrane was placed in the plating bath (typical composition and characteristics of the plating bath were shown in Table 1, Okuno Chemical Industries Co. Ltd., Japan) for about 30 min; the plating process may repeat several times to get a thin, dense Pd composite membrane. The permeation properties of the Pd composite membrane were evaluated for H₂ and N₂ at several temperatures between 623–823 K and pressure drop of 100–300 kPa. The apparatuses for the gas permeation test, reaction, and analysis were the same as those described in ref 12. The dependence of H₂ permeation flux versus transmembrane H₂ partial pressure was determined at 773 K, and dependence of H₂ permeation flux versus operation temperature was determined at 100 kPa transmembrane H₂ partial pressure at several temperatures between 623 and 823 K. The permeation flux of N₂ across the membrane was also measured at 773 K and a transmembrane pressure of 100–300 kPa. The thickness of the Pd layer was estimated by weight increment of the membrane module, as well as scanning electron microscopy (SEM) (JSM-6360SA) characterization.

2.2. Catalyst Preparation and Performance in a Conventional Fixed-Bed Reactor. The catalyst preparation and pretreatment was described in a previous report.^{12,13} The composition of the catalyst was 50.0 wt % NiO, 10.0 wt % La₂O₃, and balance alumina. The catalyst amount was 1.0 g, used as a granule with the size in the range 420–630 μm, diluted with 5.0 g silica of the same size. The catalytic performance for steam reforming of fuel was investigated on a continuous-flow, fixed-bed stainless steel reactor (i.d. = 16 mm) under working

Scheme 2. Illustration of the Reactor for Realizing the One-Step Pure Hydrogen Production from the Steam Reforming of Liquid Hydrocarbons with Autothermal Operation (1, Hydrogen; 2, Liquid Hydrocarbons; 3, Steam; 4, CO₂ + H₂O + N₂ (Air as Oxidant); 5, Retentate Gas; 6, Oxygen/Air; 7, Catalytic Combustion Catalyst; 8, Steam Reforming Catalyst; 9, Pd Composite Membrane; 10, Pd Membrane)

conditions of $T = 763$ K, $P = 500$ kPa, and $S/C = 2.7$. The catalytic activity for the steam reforming of methane was also investigated using the same reactor under various working conditions, and the results were compared with literature data.

2.3. Membrane Reactor Configuration and Conceptual Autothermal Operation. The illustration of a self-made setup for reaction and products analysis has also been described in ref 12. Except the membrane, the procedures for performing the steam reforming of liquid hydrocarbons in a membrane reactor and the terminology used were the same, partly to test the repeatability of the results. In this work, a conceptual autothermal operation mode and the structure of the reactor are shown in Scheme 2 in detail. First, an extended catalyst bed was applied, e.g., the length of the catalyst bed was 80 mm, while the length of the Pd membrane was only 50 mm; thus, the catalyst bed was extended 30 mm above the membrane. Second, catalytic combustion of reformat from the reaction side (or the retentate side of the membrane) in another outside chamber at around 873 K was supposed to supply the necessary heat for the steam reforming reactions. The reactions were performed under previously optimized working conditions of $T = 823$ K, gas hourly space velocity (GHSV) of 7 500 or 15 000 mL g⁻¹ h⁻¹, reaction pressure in the range of 200–900 kPa, $S/C = 2.7$, and sweep ratio (I) in the range of 0–4.0 using argon gas.

3. Results and Discussion

3.1. Property of Pd Composite Membrane. Figure 1 shows the SEM pictures of the surface and fractured cross section of the Pd composite membrane. The deposited layer was defect-free and estimated to be about 4.0 μm in thickness, which was consistent with the result deduced from the weight increment after the electroless plating process. Figure 2 shows the dependence of hydrogen flux on transmembrane H₂ partial

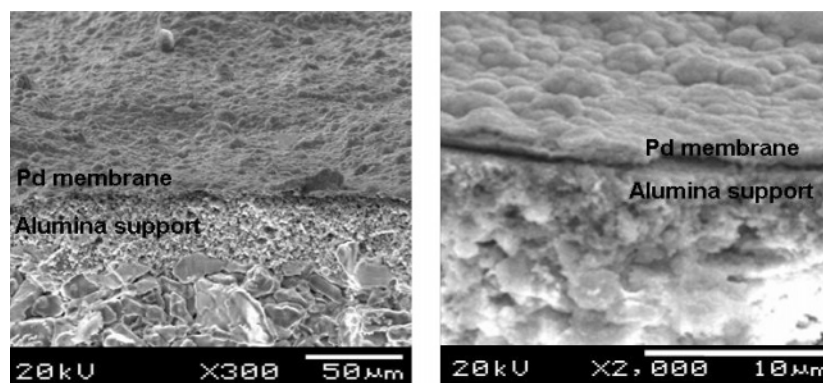


Figure 1. SEM morphology of the prepared thin Pd membrane.

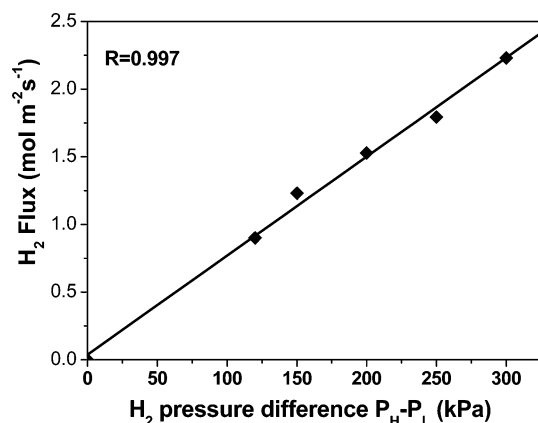


Figure 2. H_2 flux versus H_2 pressure difference across the Pd membrane at operation temperature $T = 773$ K.

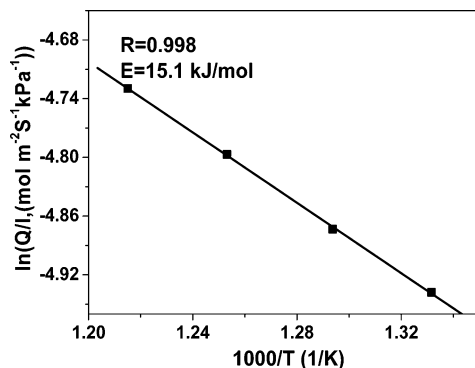


Figure 3. Arrhenius plot for the Pd/ Al_2O_3 composite membrane at H_2 partial pressure difference of 100 kPa within 723–823 K.

pressure difference for the composite membrane. The hydrogen flux was not proportional to the difference of the square root of hydrogen partial pressure but rather to the difference of partial pressure itself, suggesting that the dissociative adsorption of hydrogen on the Pd surface dominates in hydrogen transport through the ultrathin metallic films while the transport resistance from the porous support could be neglected. Figure 3 shows the hydrogen permeation flux versus operation temperature in the range of 623–823 K, from which an apparent activation energy of 15.1 kJ/mol for H_2 transport through the Pd membrane was obtained, which was consistent with previously reported results, e.g., usually the apparent activation energy was 10–20 kJ/mol.

3.2. Catalytic Performance in Conventional Fixed-Bed Reactor. The direct contact of higher hydrocarbons with the Pd membrane has always been a problem associated with coke deposition on the Pd membrane surface, which would degrade the Pd based membrane or the applied catalyst quickly.^{14–17}

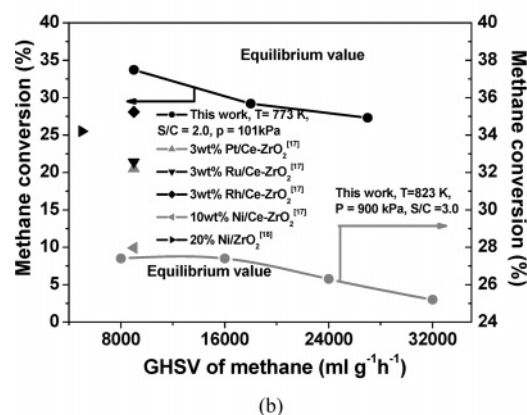
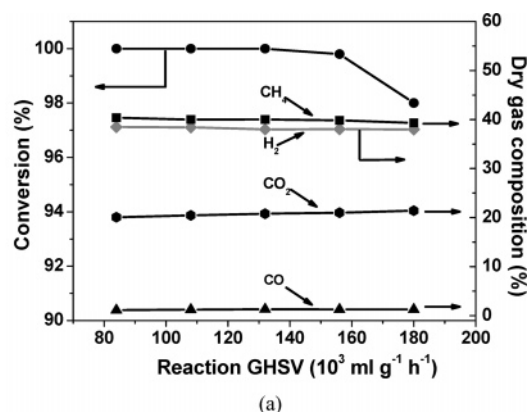


Figure 4. Catalytic performance of the catalyst for steam reforming of fuel (a) under working conditions of $T = 763$ K, $P = 500$ kPa, $S/C = 2.7$, for steam reforming of methane and comparison with literature results (b).

For example, reactions such as dehydrogenation of higher hydrocarbons have never been performed steadily without the input of steam. Thus, in this work, in order to avoid the direct contact of higher hydrocarbons, particularly alkenes or aromatics with high adsorption ability on the metallic surface, with the Pd metallic surface, an extended catalytic bed was applied. As we know, the two key factors to achieve efficient hydrogen production using membrane reactors are a high-performance membrane and a highly active catalyst. The high-performance membrane separates H_2 efficiently, while the highly active catalyst increases H_2 partial pressure promptly along the axis of the reactor and benefits H_2 separation. In order to estimate the required catalytic bed length to completely avoid the direct contact, the catalytic performance for the steam reforming of liquid hydrocarbons and methane was determined, and the results are shown in Figure 4. The catalyst showed high catalytic performance for the steam reforming of liquid hydrocarbons,

Table 2. Performance of Pd Membrane Reactor Under Various Working Conditions ($T = 823$ K, $S/C = 2.7$, and $H_2/C = 0.1$)

GHSV ($\text{mL g}^{-1} \text{h}^{-1}$)	P , kPa	I	with membrane (yield, R_{H_2} , & S_{H_2}) ^a				equilibrium yield	
			Y_{CH_4}	Y_{H_2}	R_{H_2} %	S_{H_2} %	CH_4	H_2
15 000	500	0	2.30	10.6	41.0	69.5	3.8	6.6
15 000	500	1.0	1.69	13.3	65.6	79.7		
15 000	700	0	1.93	12.3	62.6	76.2	4.0	5.7
15 000	700	1.0	1.47	14.4	69.0	83.0		
15 000	900	0	1.74	13.1	73.0	79.1	4.1	5.1
15 000	900	1.0	1.41	14.0	78.0	83.2		
7 500	500	0	2.11	11.4	49.4	73.0	3.8	6.6
7 500	500	1.8	0.91	16.5	84.7	90.0		
7 500	700	0	1.44	14.5	70.8	83.0	4.0	5.7
7 500	700	1.8	0.69	17.6	90.2	92.6		
7 500	900	0	0.99	16.5	81.3	88.9	4.1	5.1
7 500	900	1.8	0.30	19.4	95.2	97.0		

^a I = sweep ratio, R_{H_2} = recovery rate of hydrogen, S_{H_2} = selectivity to hydrogen.

as seen in Figure 4a. Under working conditions of $T = 763$ K, $P = 500$ kPa, $S/C = 2.7$, and $H_2/C = 0.1$, the conversion of fuel was almost complete within the GHSV of $130\,000 \text{ mL g}^{-1} \text{h}^{-1}$. An even further increase of GHSV to $168\,000 \text{ mL g}^{-1} \text{h}^{-1}$ only resulted in a conversion decrease to 94.5%. Thus, in the membrane reactor, an extended catalyst bed of about 10.0 mm was enough to avoid the direct contact of higher hydrocarbons with the Pd metallic surface. What's more, the catalyst also showed high catalytic performance for methane steam reforming in comparison with recent literature results. For instance, at $T = 773$ K, $P = 101$ kPa, $S/C = 2.0$, and $\text{GHSV}_{\text{methane}} = 9\,000 \text{ mL g}^{-1} \text{h}^{-1}$, the highest methane conversion was 28.1% among the three precious-metal catalysts, while over our catalyst, it equaled the thermodynamic control one of 33.7%. Even under working conditions of $\text{GHSV}_{\text{methane}} = 27\,000 \text{ mL g}^{-1} \text{h}^{-1}$, conversion was still around 27.3%. To the best of our knowledge, the catalyst showed better catalytic performance for the steam reforming of methane at 773 K than previous results.^{18,19} The catalyst also showed good performance for methane steam reforming at higher reaction pressures, as seen in Figure 4b. The good performance of the catalyst may be related with the coprecipitation process and nanosized Ni^0 after reduction at around 823 K.²⁰

3.3. Performance of Membrane Reactor. Table 2 lists the performance of the Pd membrane reactor in terms of Y_{CH_4} , selectivity to hydrogen (S_{H_2}), and R_{H_2} along with the corresponding thermodynamic control values. It can be seen that H_2 yields increased by 18–290% compared with thermodynamic control values, depending on working conditions. In the membrane reactor, first, at a lower reaction pressure, R_{H_2} was small and Y_{H_2} increase in the membrane reactor was also small. For example, R_{H_2} was only 11.2% and Y_{H_2} increase was only 18% at 300 kPa, which suggested that, under working conditions without sweep gas, Y_{H_2} could not be efficiently promoted because of the limited H_2 permeation driving force and membrane separation efficiency. Higher reaction pressure increased the driving force for H_2 permeation, and Y_{H_2} could be efficiently enhanced. At 823 K, within 500–900 kPa, a higher reaction pressure provided a higher driving force for H_2 permeation; thus, higher Y_{H_2} , R_{H_2} , and lower Y_{CH_4} were observed. For example, at $P = 900$ kPa, $\text{GHSV} = 15\,000 \text{ mL g}^{-1} \text{h}^{-1}$, and $I = 1.0$, R_{H_2} was 78% and Y_{H_2} was increased by 185% compared with the equilibrium values. Second, the presence of the sweep gas favored the R_{H_2} , and it became more distinct at a lower reaction pressure. For instance, R_{H_2} increased by 25.6% at $I = 1.0$ compared to the one at $I = 0$ when the reaction was performed at 500 kPa, while it only increased by 6.0% at 900 kPa. A sweep gas flux decreased the H_2 partial pressures in the permeate side,

which drove more H_2 transport across the membrane. Thus, more hydrogen was removed from the reaction zone and Y_{H_2} was increased. Third, a lower GHSV meant a longer contact time for the reactions and a longer time for the generated hydrogen to diffuse from the reaction zone to the Pd membrane interface, which resulted in a higher R_{H_2} and Y_{H_2} , as seen in Table 1. The H_2 production capacity of the membrane reactor was $19.8 \text{ m}^3 \text{ m}^{-2} \text{h}^{-1}$ at $T = 823$ K, $P = 900$ kPa, $\text{GHSV} = 7\,500 \text{ mL g}^{-1} \text{h}^{-1}$, $H_2/C = 0.1$, and $I = 1.8$.

For coupling to small-scale fuel cell application to an auxiliary power unit, or as a portable H_2 source, an autothermal operation mode of a fuel processor would make this technology more appealing. Therefore, we carried out the feasibility study of autothermal operation, by designing the membrane reformer in such a way that the stream on the retentate side was directly delivered into a catalytic combustion chamber, operated slightly higher than that the steam reforming reactions while sufficiently lower than the upper temperature limit for keeping the Pd membrane stable, generally in the range of 723–873 K, which was located outside of the stainless tube, as shown in Scheme 2. The reactions in the catalytic combustion chamber could be described using eqs 4–6.



The heat generated (Q_g) by these reactions maintained the endothermic steam reforming reactions. Autothermal operation can be realized if Q_g multiplied by heat exchange efficiency (λ) equaled the sum of the heat consumed (Q_c) by the reforming reactions and those needed to vaporize and preheat the feedstocks, as shown in eq 7.

$$Q_g \times \lambda = Q_c \quad (7)$$

For the calculation, the following assumptions were made:

- reaction conditions of $T = 823$ K, $P = 900$ kPa, $S/C = 2.7$;
 - $\lambda = 50$ –70%;
 - fast establishment of the thermodynamic equilibrium for reaction 2;
 - isothermal and isobaric conditions on the reforming side;
 - ideal gas heat capacity and temperature coefficients.²¹
- If 1 mol of isooctane and 21.6 mol of water were fed to the reactor; taking the value for S_{CH_4} as x and the selectivity to CO_2

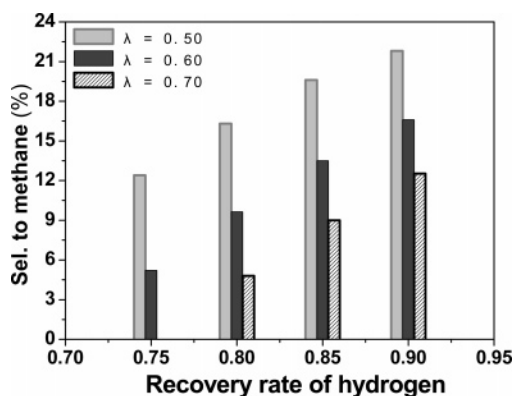


Figure 5. Dependence of theoretical selectivity to methane (S_{CH_4}) on recovery rate of hydrogen (R_{H_2}) and heat exchange efficiency to achieve autothermal operation.

as y , then the heat balance equation can be established, as described in eq 8

$$\lambda[(6418.4x + 242(1 - R_{H_2})(17 - 24x - 8y) + 2264(1 - x - y)] = (1273.2 - 1649.6x - 328.8y) - Q_a(1 - \lambda)(13.84 + 8x - 8y) \quad (8)$$

where Q_a was the energy needed to heat 1 mol of water from 298 to 823 K. And the R_{H_2} value in the range of 70–95% was assumed, which can be readily achieved in this Pd membrane reactor, as displayed in Table 1. Thus, a relationship between x and y can be obtained by solving the heat balance equation. By using the relationship between x and y and solving the equilibrium equation for reaction 2, one obtained x values, which were compared to the experimentally obtained values.

The results are presented in Figure 5. The S_{CH_4} required to achieve autothermal operation was found in the range of 5.0–25.0%, which lies in the experimental data range, as implicated in Table 2. The higher the λ , the lower is the S_{CH_4} to achieve autothermal operation. For instance, at $\lambda = 50\%$ and $R_{H_2} = 80\%$, the autothermal operation could be achieved at $S_{CH_4} = 16.3\%$; while at $\lambda = 70\%$ and $R_{H_2} = 80\%$, the S_{CH_4} was about 5.0%. Second, the lower the R_{H_2} , the lower the S_{CH_4} to maintain autothermal operation. For example, at $\lambda = 50\%$ and $R_{H_2} = 75\%$, the S_{CH_4} was 12.4%; while at $\lambda = 50\%$ and $R_{H_2} = 90\%$, the S_{CH_4} was 21.8%. The calculation of the energy balance suggested that the membrane reactor could achieve autothermal operation under high H_2 production capacity conditions, though further experimental verification of the autothermal operation is required, which is our work under way now.

In addition to the feasible autothermal operation, in such a membrane reactor configuration, it was also convenient for further CO_2 utilization or sequestration that almost pure CO_2 was produced in the catalytic chamber, when oxygen was fed to the catalytic combustion chamber. Moreover, this membrane reactor presented good stability under the steam reforming reaction conditions. During a 48 h continuous operation at 823 K, no degradation of the Pd composite membrane was observed. Further experiments are under way to study the long-term stability between 723–873 K, for the reason that, generally, the Pd membrane could not tolerate temperatures over 873 K, while for the steam reforming of higher hydrocarbons and steam reforming of methane, temperatures higher than 723 K are necessary to totally convert higher hydrocarbons, avoiding the direct contact of higher hydrocarbons with the Pd membrane. For the stable operation of the Pd membrane reactor, the thermal cycling process should be slow enough to avoid large stress in

the metallic film, generally a heating rate lower than 5 K/min. Thus, the fuel processor may be unsuitable for the on-board hydrogen production for PEMFC.

4. Conclusions

A Pd composite membrane with high performance for hydrogen permeation was successfully developed via an improved electroless plating method. The membrane was applied to construct a membrane reactor to investigate the hydrogen production from the steam reforming of multicomponent liquid hydrocarbon fuels. The results suggested that one-step production of hydrogen from the steam reforming of liquid hydrocarbons could be realized using such a membrane reformer. The membrane in situ separated hydrogen from the reaction zone, simultaneously adjusting the selectivities of products. Thus, the yield of hydrogen was significantly enhanced while the yield of methane was reduced in membrane reactor. By designing a catalytic combustion chamber outside the membrane reformer, it was feasible to realize autothermal operation in such a fuel processor system, by using the heat released from the catalytic combustion of retentate gas for the endothermic steam reforming reactions. The high performance of the membrane, combined with an active catalyst for the steam reforming not only of liquid hydrocarbons but also of methane, guaranteed a high yield of hydrogen and recovery rate, even when the reaction was carried out near practical working conditions.

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List of Nomenclature and Abbreviations

PEMFC = proton exchange membrane fuel cell

WGS = water gas shift

CFBMR = circulating fluidized-bed membrane reformer

GHSV = gas hourly space velocity

SEM = scanning electron microscopy

i.d. = inner diameter

o.d. = outer diameter

S/C = steam-to-carbon feed ratio

λ = heat exchange efficiency

S_{H_2} = selectivity of hydrogen, the percentage of hydrogen atoms distributed in H_2 among the total hydrogen atoms in products

Y_{H_2} = yield of hydrogen, defined as the ratio between the moles of hydrogen produced and the moles of fuel fed to the reactor

Y_{CH_4} = yield of methane, defined as the ratio between the moles of methane produced and the moles of fuel fed to the reactor

S_{CH_4} = selectivity of methane, defined as $[CH_4]/([CH_4] + [CO] + [CO_2]) \times 100\%$ according to the concentration of products

I = sweep ratio, defined as the ratio between the fluxes of argon sweep gas to the input flux of carbon; for a specific higher hydrocarbon, the flux of hydrocarbon in the gas phase was converted to flux of carbon by simply multiplying the carbon numbers in its molecule

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