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Article

Bifunctional palladium composite membrane for hydrogen separation and catalytic CO methanation

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ABSTRACT

NiO was introduced into the porous Al_2O_3 substrate by impregnation, and the resulting $\text{NiO}/\text{Al}_2\text{O}_3$ was coated with the lead of a 2B pencil to modify its surface. A palladium layer with a thickness of 5 μm was deposited by electroless plating on the Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ substrate, and a Pd/Pencil/ $\text{Ni}/\text{Al}_2\text{O}_3$ membrane was obtained after reduction with hydrogen. For reference, a Ni-free Pd/Pencil/ Al_2O_3 membrane was also fabricated. The surface and cross-sectional morphologies of the membranes were studied by scanning electron microscopy and metallographic microscopy. The hydrogen permeation kinetics was investigated by single gas tests, and the hydrogen separation performances of the Pd/Pencil/ Al_2O_3 and Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ membranes were tested with a hydrogen feed composed of H_2 77.8%, CO 5.2%, CO_2 13.5%, and CH_4 3.5%. The Ni-free Pd/Pencil/ Al_2O_3 membrane only shows function of hydrogen separation, while the Pd/Pencil/ $\text{Ni}/\text{Al}_2\text{O}_3$ is also catalytically effective for methanation of CO and CO_2 in hydrogen, forming a bifunctional palladium membrane concept. Since the amount of CO and CO_2 in the hydrogen after membrane separation is very low, the consumption of hydrogen by the methanation reactions is negligible. The bifunctional membrane is promising for proton exchange membrane fuel cells because the catalytic methanation treatment solves the CO poisoning problem of the fuel cell electrodes and consequently allows the palladium membrane to tolerate more membrane defects and to achieve longer life.

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1. Introduction

Being different from the hydrogen production for industrial applications, that for hydrogen energy utilizations places a high demand on the miniaturization and portability of the hydrogen generation system, and a key unit of which is the hydrogen separator. Among various hydrogen separation processes, the membrane technology is of great advantage. Proton exchange membrane (PEM) fuel cells are the most common hydrogen-fueled ones [1,2]. Their anode contains a platinum catalyst, which is able to oxidize hydrogen to water at room tempera-

ture and release the electric power, but this catalyst requires a very high purity of hydrogen. Currently, most of the hydrogen is produced by steam reforming of fossil fuels, and it unavoidably contains a small amount of CO . Since CO can easily poison the platinum catalyst of the PEM fuel cell anode, the CO content in the hydrogen fuel has to be controlled to below 0.001% [3,4], and this is highly challenging for the membrane selectivity. A number of hydrogen separation membranes have been reported, but palladium and palladium-alloy membranes are preferred because they have high hydrogen permeability and the best permselectivity and can reject any other gas. On the

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other hand, it is of great interest to eliminate the CO in the hydrogen fuel. Apart from the membrane technology [5,6], catalytic oxidation [7,8] or methanation of CO [9,10] can be an alternative. The catalytic oxidation route needs the introduction of appropriate amount of oxygen and should convert CO to CO₂ without the oxidation of hydrogen, and the catalyst selectivity is of key importance. Catalytic methanation converts CO into CH₄ through catalytic hydrogenation. In addition to CO, the industrial hydrogen often contains CO₂, which can also be converted during methanation. Since the methanation of each mole of CO or CO₂ will need 3 or 4 mol hydrogen, this process is not applicable for the hydrogen feed with a high amount of CO and CO₂.

Commercial palladium alloy membranes are fabricated by cold rolling, and their thickness can be as thick as 50 μm or higher. Their disadvantages such as high cost, low hydrogen permeance, and poor mechanical strength greatly limited their applications. A significant improvement can be achieved by the use of composite membranes, i.e., very thin membranes supported on porous materials, and they can be one order of magnitude thinner than the conventional ones. However, the stability of composite Pd membranes is the key factor that limits their industrial applications. During long term membrane operation, pinholes will gradually appear and lead to a decrease in hydrogen purity. Once the CO concentration exceeds the level acceptable for the PEM fuel cells, the life of the Pd membranes is over. Since the PEM fuel cells are so sensitive to CO, the lifetime of the composite Pd membranes eventually becomes a key problem. Based on the characteristics of the methanation and membrane separation approaches, we invented a kind of bifunctional membranes [11], i.e., the Pd membranes with a Ni catalyst supported on their porous substrate material, so that both functions of hydrogen separation and CO methanation are integrated. On one hand, the catalytic methanation eases the strict requirement on the CO leakage through the Pd membranes and equivalently prolongs the membrane life. On the other hand, the contents of CO and CO₂ in the hydrogen after membrane separation are extremely low, and the hydrogen consumption will be negligible if the methanation is conducted thereafter.

In this work, a bifunctional Pd/Pencil/Ni/Al₂O₃ membrane with the functions of hydrogen separation and CO methanation was prepared, and its hydrogen separation performance was compared with that of the Ni-free Pd/Pencil/Al₂O₃ membrane.

2. Experimental

2.1. Membrane preparation

2.1.1. NiO deposition on Al₂O₃ substrate

Conventional porous Al₂O₃ ceramic tubes (o.d., 13 mm; i.d., 8 mm; length, 75 mm) with a symmetric structure were employed as the substrate material. They were cleaned with a hot solution of a commercial detergent, rinsed repeatedly with deionized water, and finally dried at 120 °C overnight.

NiO/Al₂O₃ was prepared by impregnation. The Al₂O₃ substrate was immersed in a Ni(NO₃)₂ solution (0.25 mol/L) for 10

h, then dried at 120 °C for 12 h, and finally calcined at 450 °C for 3 h. The NiO content as measured by weight gain was 3.6%, which amounts to a nickel content of 2.8%.

2.1.2. Substrate surface modification

The Al₂O₃ and NiO/Al₂O₃ surfaces were modified by means of pencil coating [12,13], which was carried out by scraping with a conventional 2B pencil so that a uniform and continuous coating layer can be created. The modified substrates were calcined at 450 °C for 3 h to burn off oil contaminants, resulting Pencil/Al₂O₃ and Pencil/NiO/Al₂O₃.

2.1.3. Electroless plating [14]

Before plating, the Pencil/Al₂O₃ and Pencil/NiO/Al₂O₃ were activated with the SnCl₂/PdCl₂ method. The sensitization and activation reagents were composed of 5 g/L SnCl₂ and 0.2 g/L PdCl₂, respectively, and both of reagents also contain 1 ml/L concentrated HCl. The electroless plating was carried out at 30 °C. The plating bath was composed of 5 g/L PdCl₂, 70 g/L Na₂EDTA, and 250 mL/L NH₃·H₂O (28%), and the reducing agent was a hydrazine solution (0.2 mol/L). The thickness of the Pd membranes was controlled by the volume of the plating bath, and it would be 5 μm if there was no loss of palladium.

2.2. Characterization and permeation tests

The pore size of the Al₂O₃ substrate was measured with a porometer (GaoQ PSDA-20) through a bubble-point (also known as gas-liquid displacement or capillary flow) method [15]. The surface morphology was studied by scanning electron microscopy (SEM, FEI Quanta-200). The cross-section of the Pd membranes was observed with a metallographic microscope (Leica DM-4000M), but the specimen were encapsulated with epoxy resin and pretreated on a grinder-polisher (Buehler Phenix Beta) before analysis.

The palladium membrane was assembled in a module (GaoQ PM-201S). The permeation kinetics was studied by the single gas method, and the practical hydrogen separation performance was tested with a gas mixture (H₂ 77.8%, CO 5.2%, CO₂ 13.5%, and CH₄ 3.5%). The pressure at the shell side of the membrane was controllable, while the pressure at the tube side of the membrane was always ambient. During testing, the NiO supported on the Al₂O₃ substrate was reduced in situ into the metallic nickel catalyst. The permeated hydrogen was analyzed with an online gas chromatograph (Shimadzu-2014).

3. Results and discussion

3.1. Membrane morphology

Porous Al₂O₃ is the most common substrate material for palladium membranes, but in this work it was also used as a support of the methanation catalyst. The porometry results indicate that the largest and the average pore sizes of the porous Al₂O₃ substrate are 1.5 and 3.7 μm, respectively. As reported in the literature, the substrate materials for Pd membranes often have an average pore size below 0.2 μm, and they

Fig. 1. Photos of the fresh porous Al_2O_3 substrate (a), $\text{NiO}/\text{Al}_2\text{O}_3$ (b), $\text{Pencil}/\text{Al}_2\text{O}_3$ (c), $\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ (d), $\text{Pd}/\text{Pencil}/\text{Al}_2\text{O}_3$ (e), and $\text{Pd}/\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ (f).

have an asymmetric structure in order to control the pore size and the diffusion resistance, leading to a very high cost. This work chose a low-cost macroporous Al_2O_3 as the substrate material so as to reduce the whole membrane cost and promote the membrane commercialization. The photos of the substrate materials and membranes are displayed in Fig. 1. The Al_2O_3 substrate surface was rough, and the $\text{NiO}/\text{Al}_2\text{O}_3$ surface is black and uniform. The $\text{Pencil}/\text{Al}_2\text{O}_3$ and $\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ are lustrous and show typical graphite color. In fact, the pencil coating process has been developed specially by our group for the surface modification of the macroporous substrate materials. It is simple, low cost, and environmental benign. The $\text{Pd}/\text{Pencil}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ membranes prepared in this work look lustrous and homogeneous.

The surface views are demonstrated in Fig. 2. The Al_2O_3 substrate is composed of the sintered irregular ceramic particles, while the $\text{NiO}/\text{Al}_2\text{O}_3$ surface shows a very different morphology because a layer of fine particles appears, and this is obviously caused by the deposition of NiO . The $\text{Pencil}/\text{Al}_2\text{O}_3$ and $\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ have low surface roughness and almost the same morphology, and so do the $\text{Pd}/\text{Pencil}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ membranes, indicating no significant influence of the NiO deposition on the membrane preparation. The cross-sectional metallographic photomicrographs of the $\text{Pd}/\text{Pencil}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ membranes are shown in Fig. 3. After grinding and polishing, the Pd layer became highly bright and can be clearly observed with microscope. The cross-sectional morphologies of the two palladium membranes are similar, and the Pd layers are uniform and bonded well onto the substrates. During membrane preparation, the membrane thickness has been controlled to be $5\text{ }\mu\text{m}$ through the volume of the plating bath. As confirmed by Fig. 3, the thicknesses of the two membranes are indeed close to $5\text{ }\mu\text{m}$, indicating that the palladium ions in the plating bath have been sufficiently transferred. During electroless plating, excess hydrazine has been added before every plating bath renewing so that the remnant palladium ions can be fully reduced and the loss of the precious palladium can be avoided.

3.2. Hydrogen permeation kinetics

The permeation kinetics of the Pd membranes was analyzed with the H_2/N_2 single gas method [14], and the testing temper-

Fig. 2. SEM micrographs of the fresh Al_2O_3 substrate (a), $\text{NiO}/\text{Al}_2\text{O}_3$ (b), $\text{Pencil}/\text{Al}_2\text{O}_3$ (c), $\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ (d), $\text{Pd}/\text{Pencil}/\text{Al}_2\text{O}_3$ (e), and $\text{Pd}/\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ (f).

atures were 350, 400, and 450 °C. The hydrogen permeation follows a solution-diffusion mechanism, and the hydrogen flux can be universally described as $J = F(p_r^n - p_p^n)$, where J is the hydrogen flux ($\text{m}^3/(\text{m}^2 \cdot \text{h})$), F is the hydrogen permeance ($\text{m}^3/(\text{m}^2 \cdot \text{h} \cdot \text{MPa}^n)$), p_r and p_p are the pressures (MPa) at the retentate and permeate sides, and n is the pressure exponent ($0.5 \leq n \leq 1$). In general, the hydrogen diffusion in the bulk of the Pd layer is the rate determining step, and the hydrogen permeation kinetics obeys the Sievert's Law [16,17], i.e., $n = 0.5$.

The testing results are shown in Fig. 4, where the membrane selectivity is defined as the ratio of H_2 flux to N_2 flux under the same temperature and pressure. The higher the selectivity, the fewer the membrane defects are. During testing, the NiO in the

Fig. 3. Metallographic micrographs of the cross-sections of $\text{Pd}/\text{Pencil}/\text{Al}_2\text{O}_3$ (a) and $\text{Pd}/\text{Pencil}/\text{NiO}/\text{Al}_2\text{O}_3$ (b) membranes.

Fig. 4. Permeation performance of Pd/Pencil/Al₂O₃ and Pd/Pencil/Ni/Al₂O₃ membranes.

Pd/Pencil/NiO/Al₂O₃ was reduced in situ by hydrogen, and a Pd/Pencil/Ni/Al₂O₃ membrane was obtained.

It has been already found in our previous work that the pencil coating can effectively avoid the problem of the substrate surface defects and consequently facilitate the membrane preparation [12]. However, the original intention of this work is to investigate the effects of the nickel catalyst on the methanation of CO leaked through membrane defects, and therefore a Pd/Pencil/Ni/Al₂O₃ membrane with a lower H₂/N₂ selectivity was selected. The permeation results are shown in Fig. 4. The H₂/N₂ selectivities of the Pd/Pencil/Al₂O₃ and Pd/Pencil/Ni/Al₂O₃ membranes were >5000 and <1000, respectively. The best linear correlation between the hydrogen flux and the pressure can be established when $n = 0.5$, indicating that the hydrogen permeation kinetics obeys the Sievert's Law. At 350, 400, and 450 °C, the hydrogen permeabilities of the Pd/Pencil/Al₂O₃ membrane were 110, 126, and 144 m³/(m²·h·MPa^{0.5}), while those of the Pd/Pencil/Ni/Al₂O₃ membrane were 120, 133, and 150 m³/(m²·h·MPa^{0.5}), respectively. It can be concluded that the permeabilities of the two membranes are quite close.

The results in Fig. 4 reveal that the deposition of the nickel catalyst has little influence on the permeation performance of the palladium membrane. At first, the nickel catalyst has been deposited into the pores of the Al₂O₃ substrate, and it does not contact with the palladium layer because of the pencil coating layer on Al₂O₃ so that it will not contaminate the palladium membrane or hamper the membrane preparation. Secondly, the amount of the nickel deposition is too low to cause significant resistance for gas diffusion. Thirdly, the hydrogen diffusion resistance of the substrate is much lower than that of the

palladium layer, the hydrogen atom diffusion in palladium bulk remains to be the rate determining step, and this is consistent with the kinetic results in Fig. 4. For each of the two membranes, both the hydrogen permeability and the H₂/N₂ selectivity increase with increasing temperature, and this is a typical feature of a palladium membrane. The leakage of nitrogen through the defects of a palladium membrane often follows Knudsen and Poiseuille diffusions, and the N₂ flux is proportional to the $T^{-0.5}$ and T^{-1} , that is, it decreases with increasing temperature.

3.3. Hydrogen separation and CO methanation performance

Under the practical conditions, the impurities in the feed hydrogen will decrease the permeability of the Pd membranes [18–20]. Apart from the pressure, temperature, and feed gas composition, the expected hydrogen recovery will also influence the capacity and the hydrogen output of the palladium membranes. When the hydrogen feed flows at the retentate side of a palladium membrane, the hydrogen concentration and partial pressure gradually decrease because of the hydrogen separation, and the corresponding local hydrogen flux also decreases. For a given palladium membrane, an increase in the hydrogen feed rate will lead to a decrease in the hydrogen recovery (because of the insufficient hydrogen separation) and an increase in the purified hydrogen producibility (because of the high hydrogen partial pressure). Therefore, a higher hydrogen recovery means a lower producibility of the purified hydrogen. Once the hydrogen partial pressure of the membrane retentate offgas equals to the pressure of the membrane permeate hydrogen, the hydrogen recovery reaches a maxi-

Fig. 5. Hydrogen producibility as a function of feed pressure (hydrogen recovery, 70%).

mum. Both the increase in the membrane retentate pressure and the decrease in membrane permeate pressure are effective in improving the membrane producibility and the hydrogen recovery.

In this work, the membrane producibility as a function of the feed pressure was tested with a feed gas, whose composition is H₂ 77.8%, CO 5.2%, CO₂ 13.5%, and CH₄ 3.5%, and the hydrogen recovery was maintained at 70%. The results are exhibited in Fig. 5. No significant difference between the hydrogen producibilities of the Pd/Pencil/Al₂O₃ and Pd/Pencil/Ni/Al₂O₃ membranes can be observed at the same temperature and feed pressure. For example, the hydrogen producibilities of the Pd/Pencil/Al₂O₃ membrane under a feed pressure of 0.25 MPa at 350, 400, and 450 °C are 11.8, 14.5, and 17.0 m³/(m²·h), while corresponding those of the Pd/Pencil/Ni/Al₂O₃ membrane are 12.7, 14.1, and 16.8 m³/(m²·h), respectively.

The purity of the hydrogen after membrane separation depends on the feed gas composition, the membrane operating conditions, and the membrane integrity. During membrane preparation and the long-term operation, pinholes may appear on the membrane and cause a decrease in hydrogen purity. It was well known that the PEM fuel cells are extremely sensitive to CO. Aiming at this characteristic, this work introduced a nickel catalyst into the pores of the Al₂O₃ substrate so that the CO leaked through membrane defects can be methanized. Under the action of the methanation catalyst, both CO and CO₂ can be hydrogenated according to the following reactions:

Eventually, the Pd/Pencil/Ni/Al₂O₃ membrane possessed both functions of hydrogen separation and CO methanation, and the principle is shown in Fig. 6. Despite that 1 mol CO and

CO₂ will consume 3 and 4 mol H₂ and produce 2 and 3 moles of new impurities, respectively, the produced small amount of CH₄ and H₂O will be of no poisoning or side effect for PEM fuel cells. Since the concentrations of the leaked CO and CO₂ through the palladium membrane are so low, the consumed hydrogen during the methanation reactions is negligible.

The concentrations of CO, CO₂ and CH₄ in the hydrogen permeated through the Pd/Pencil/Al₂O₃ and Pd/Pencil/Ni/Al₂O₃ membranes at a feed pressure of 0.25 MPa and a hydrogen recovery of 70% are listed in Table 1. After separation by the Pd/Pencil/Al₂O₃ membrane, the concentrations of CO, CO₂, and CH₄ are three orders of magnitude lower than those in the feed gas, indicating the excellent membrane separation effect. Compared with those for the Pd/Pencil/Al₂O₃ membrane, the concentrations of CO and CO₂ after separation by the Pd/Pencil/Ni/Al₂O₃ membrane are at least one order of magnitude lower, but the concentration of CH₄ is two orders of magnitude higher. Obviously, these results are due to the catalytic methanation effect by the Pd/Pencil/Ni/Al₂O₃ membrane. As already proved by the results in Fig. 4, the Pd/Pencil/Ni/Al₂O₃ has more defects than the Pd/Pencil/Al₂O₃, but the concentrations of CO and CO₂ for the Pd/Pencil/Ni/Al₂O₃ are significantly lower than those for the Pd/Pencil/Al₂O₃, indicating that the CO

Fig. 6. Mechanism of the bifunctional Pd/Pencil/Ni/Al₂O₃ membrane.

Table 1

Concentrations of CO, CO₂, and CH₄ in the hydrogen permeated from the Pd membranes at different temperatures under a feed pressure of 0.25 MPa and a hydrogen recovery of 70%.

Impurity	Feed	Concentration (%)					
		Pd/Pencil/Al ₂ O ₃			Pd/Pencil/Ni/Al ₂ O ₃		
		350 °C	400 °C	450 °C	350 °C	400 °C	450 °C
CH ₄	3.5	5.4×10 ⁻³	3.9×10 ⁻³	2.8×10 ⁻³	0.36	0.35	0.22
CO	5.2	5.6×10 ⁻³	4.5×10 ⁻³	3.6×10 ⁻³	1.0×10 ⁻⁴	— ^a	— ^a
CO ₂	13.5	1.8×10 ⁻²	1.5×10 ⁻²	1.0×10 ⁻²	5.4×10 ⁻³	2.9×10 ⁻⁴	1.0×10 ⁻⁴

^a Below 5×10⁻⁵ %.

Graphical Abstract

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Bifunctional palladium composite membrane for hydrogen separation and catalytic CO methanation

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Aiming at the hydrogen purification for proton exchange membrane fuel cells, a bifunctional Pd/Pencil/Ni/Al₂O₃ membrane that is capable of hydrogen separation and catalytic CO methanation was developed. It was compared with the Pd/Pencil/Al₂O₃ membrane without the nickel methanation catalyst.

and CO₂ has been converted or eliminated by the Pd/Pencil/Ni/Al₂O₃. Moreover, the ratios among the concentrations of CO, CO₂, and CH₄ in the hydrogen from the Pd/Pencil/Al₂O₃ were close to those in the feed gas, while the concentration of CH₄ in the hydrogen from the Pd/Pencil/Ni/Al₂O₃ membrane was greatly higher than those of CO and CO₂, indicating that the Pd/Pencil/Ni/Al₂O₃ membrane is effective in methanation of CO and CO₂. Since the concentration of CO in hydrogen from the Pd/Pencil/Ni/Al₂O₃ membrane is below 0.0001%, the requirement of the PEM fuel cells can be fully satisfied. The results in Table 1 also reveal that an increase in temperature tends to cause a decrease in the concentrations of CO, CO₂, and CH₄, and this coincides with the results in Fig. 4, i.e., the membrane selectivity increases with increasing temperature.

Like nickel, the palladium is also a well known methanation catalyst [21], but the palladium particle size of conventional palladium catalysts is in nanometer scale, and the palladium membrane will not generate significant methanation activity because of the small surface area. Moreover, the Pd layer is very thin and distributed only on the substrate surface, and the contact time of the CO and CO₂ leaked through membrane defects is extremely short. Therefore, significant methanation effect will not occur on the conventional palladium membranes (such as Pd/Pencil/Al₂O₃), and that on the Pd/Pencil/Ni/Al₂O₃ membrane is obviously ascribed to the introduced nickel catalyst. Such a bifunctional membrane is particularly suitable for the hydrogen separation for PEM fuel cells. On one hand, it solved the problem that the PEM fuel cells are extremely sensitive to the CO in hydrogen; on the other hand, it increased the tolerance against the appearance of membrane defects, and this is equivalent to prolong the life of the palladium membrane.

4. Conclusions

A bifunctional palladium membrane Pd/Pencil/Ni/Al₂O₃ with capacities of both hydrogen separation and catalytic CO methanation was successfully developed by introduction of Ni catalyst into the porous Al₂O₃ substrate. It not only solves the problem that the PEM fuel cells are extremely sensitive to the CO in hydrogen but also prolongs the life of the palladium membrane. Moreover, the hydrogen that is consumed during methanation reactions is negligible because the amount of the CO and CO₂ leaked through membrane defects is very low.

Therefore, the bifunctional Pd/Pencil/Ni/Al₂O₃ membrane is particularly ideal for hydrogen separation for PEM fuel cells. According to the preparation process of the bifunctional membrane in this work, the introduction of nickel catalyst almost has no influence on the preparation and performance of the palladium membrane itself, and the pencil coating not only modified the Al₂O₃ substrate surface but also avoided the direct contact between nickel catalyst and palladium membrane. The nickel-free palladium membrane Pd/Pencil/Al₂O₃ showed no significant activity on catalytic CO methanation.

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氢分离与CO催化甲烷化双功能型钯复合膜

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摘要: 以多孔 Al_2O_3 陶瓷为基体材料, 采用浸渍法负载NiO后用2B铅笔修饰NiO/ Al_2O_3 表面, 通过化学镀法沉积约5 μm 厚的金属钯, 还原后成功制得Pd/Pencil/Ni/ Al_2O_3 膜. 为进行对比, 还制备了未负载镍的Pd/Pencil/ Al_2O_3 膜. 膜的表面和断面形貌分别采用扫描电镜和金相显微镜观测, 膜的透氢动力学通过 H_2/N_2 单气体法测试, 并以成分为 H_2 77.8%, CO 5.2%, CO_2 13.5%和 CH_4 3.5%的原料氢测定了膜的氢分离效果. 结果表明, 未载镍的Pd/Pencil/ Al_2O_3 膜只具有氢分离作用, 而Pd/Pencil/Ni/ Al_2O_3 膜还可以有效地将钯膜泄漏的CO和 CO_2 转化为甲烷, 因而成为双功能型钯膜. 这种双功能膜尤其适用于面向质子交换膜燃料电池(PEMFC)的氢气分离, 既有效解决了PEMFC对氢燃料中CO格外敏感的难题, 又提高了对钯膜缺陷的容忍度, 因而延长了钯膜的使用寿命.

关键词: 钯膜; 氢分离; 一氧化碳甲烷化; 双功能; 镍催化剂; 质子交换膜燃料电池

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1. 前言

与氢气的工业化生产不同, 面向氢能的产氢系统对小型化和便携性都提出了很高要求. 氢分离是产氢系统的关键单元, 在各种氢分离工艺中, 膜分离法具有突出的优势. 质子交换膜燃料电池(PEMFC)是最为成熟的氢能电源^[1,2], 它的阳极含有Pt催化剂, 能在室温下将氢气催化氧化为水并产生电能, 但对氢气纯度要求较高. 目前, PEMFC所用的氢燃料主要来源于化石原料的水蒸气重整反应, 难免含有少量CO杂质. 由于CO极容易毒化Pt催化剂, 燃料氢中的CO含量一般必须控制在0.001%以下^[3,4], 这就对膜分离选择性提出了极为苛刻的要求. 在各种氢气分离膜中, 性能最为突出的当属钯和钯合金膜, 该膜不仅透氢性好, 而且具有无与伦比的渗透选择性, 能阻挡其它任何气体. 另一方面, 有针对性地消除氢中的CO则能够起到事半功倍的效果. 除膜分离法^[5,6]之外, 氢中少量CO的消除主要有选择氧化^[7,8]和甲烷化^[9,10]法. 选择氧化法是在避免 H_2 氧化的情况下将CO催化氧化为 CO_2 , 但该方法需通入适量 O_2 且对催化剂选择性要求较高. 甲烷化法是在催化剂的作用下将CO与 H_2 反应生成 CH_4 . 除CO外, 工业氢气中往往还含有 CO_2 , 在甲烷化过程中也会被转化. 每1 mol的CO和 CO_2 分别要消耗3和4 mol的 H_2 , 因此当原料氢中CO和 CO_2 的量较多时不宜直接采用甲烷化法.

商业化的钯合金膜通常采用冷轧法制备, 厚度多在50 μm 以上, 存在机械强度差、透氢率低、成本高等缺点,

因此膜分离法也受到巨大限制. 为此, 将钯膜负载于多孔基体材料形成的钯复合膜则成为人们关注的焦点, 其膜厚一般仅为传统钯合金膜的1/10. 然而, 钯复合膜的稳定性是限制其工业化应用的关键因素, 因为在长期运行过程中, 钯复合膜会逐渐产生针孔, 导致氢纯度逐渐下降, 一旦CO浓度超出燃料电池的容忍限度, 则意味着钯复合膜的使用寿命结束. 鉴于PEMFC对CO极其敏感, 则钯复合膜的使用寿命势必成为关键问题. 针对甲烷化法和膜分离法的特点, 本课题组发明了一种双功能膜^[11], 即在钯复合膜的多孔基体材料中负载甲烷化催化剂, 从而实现了膜分离与甲烷化过程的耦合. 一方面, 甲烷化过程降低了对钯复合膜CO泄漏量的苛刻要求, 相当于直接延长了钯复合膜的使用寿命; 另一方面, 经过钯复合膜的分离, 氢气中的CO和 CO_2 浓度已处于极低水平, 此时进行甲烷化处理则耗氢量完全可以忽略不计.

本工作制备了具有氢分离和CO甲烷化双功能的钯复合膜Pd/Pencil/Ni/ Al_2O_3 , 并对比了其与不含镍催化剂的Pd/Pencil/ Al_2O_3 膜的氢分离性能.

2. 实验部分

2.1. 膜的制备

2.1.1. 在 Al_2O_3 基体上负载NiO

所用基体材料为普通多孔 Al_2O_3 陶瓷管, 长75 mm, 外径13 mm, 内径8 mm. 先用市售洗洁精溶液煮洗, 然后用去离子水反复漂洗, 最后置于烘箱中120 $^{\circ}\text{C}$ 干燥.

采用浸渍法制备NiO/ Al_2O_3 . 将 Al_2O_3 基体在

$\text{Ni}(\text{NO}_3)_2$ 溶液(0.25 mol/L)中浸泡10 h, 在120 °C干燥12 h 后再在450 °C下焙烧3 h. 通过称重法算得基体中的NiO含量为3.6%, 折合金属镍含量为2.8%.

2.1.2. 表面修饰

Al_2O_3 基体和 $\text{NiO}/\text{Al}_2\text{O}_3$ 的表面采用石墨涂层法修饰^[12,13], 用市售2B铅笔在基体表面涂划以产生均匀、连续的修饰层, 在450 °C下焙烧3 h以除去油污, 得到Pencil/ Al_2O_3 和Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$.

2.1.3. 化学镀^[14]

将Pencil/ Al_2O_3 和Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 预先采用 $\text{SnCl}_2/\text{PdCl}_2$ 法活化. 其中, 敏化液含 SnCl_2 5 g/L和浓盐酸1 ml/L, 活化液含 PdCl_2 0.2 g/L和浓盐酸1 ml/L. 化学镀操作温度为30 °C, 镀液组成为 PdCl_2 5 g/L, Na_2EDTA 70 g/L和浓氨水(28%) 250 mL/L. 还原剂为0.2 mol/L的 N_2H_4 溶液. 钯膜的厚度通过镀液用量控制, 若没有钯的损失, 膜厚将为5 μm .

2.2. 膜的表征与氢分离性能测试

多孔陶瓷基体的孔径采用孔径分析仪(GaoQ PSDA-20)通过泡点法(又称气液排出法、毛细流动法)测量^[15]. 样品的表面形貌分析采用扫描电镜(FEI Quanta-200)进行. 钯膜的断面结构采用金相显微镜(Leica DM-4000M)观测, 但预先将样品用环氧树脂镶嵌并用磨抛机(Buehler Phenix Beta)打磨、抛光.

将所制钯复合膜安装于膜组件(GaoQ PM-201S). 膜的透氢动力学采用 H_2/N_2 单气体法表征, 并以混合气(H_2 77.8%, CO 5.2%, CO_2 13.5%和 CH_4 3.5%)为原料气测试膜的实际氢分离性能. 膜管外侧为滞留侧, 压力可调; 膜管内侧为渗透侧, 压力为常压. 测试过程中, 钯膜基体材料中的NiO在氢气通入后被原位还原为金属镍催化剂. 渗透侧气体成分采用气相色谱仪(岛津GC-2014)在线分析.

3. 结果与讨论

3.1. 膜的形貌

多孔 Al_2O_3 陶瓷是最常见的钯膜基体材料, 而在本工作中它还被用作甲烷化催化剂的载体. 孔径分析结果表明, 其最大孔径和平均孔径分别为1.5和3.7 μm . 文献报道的钯膜基体材料平均孔径多在0.2 μm 以下, 需做成非对称结构以控制孔径并降低扩散阻力, 价格较为昂贵. 本工作选用普通大孔陶瓷为基体材料, 有利于降低钯膜成本并实现产业化. 图1示出了 Al_2O_3 基体, $\text{NiO}/\text{Al}_2\text{O}_3$, Pencil/ Al_2O_3 , Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$, Pd/Pencil/ Al_2O_3 膜和Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 膜的照片. Al_2O_3 基体材料表面较为粗糙.

$\text{NiO}/\text{Al}_2\text{O}_3$ 呈黑色且颜色分布均匀. Pencil/ Al_2O_3 和Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 表面均呈石墨颜色且十分光滑. 实际上, 石墨铅笔修饰工艺是我们课题组专门为修饰大孔基体而开发的^[12,13], 不仅操作简便, 成本低廉, 而且几乎没有污染. 本工作制得的钯膜Pd/Pencil/ Al_2O_3 和Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 表面光亮且外观均匀.

图2示出了上述6种材料的表面微观形貌. Al_2O_3 基体材料由不规则的陶瓷颗粒烧结而成. $\text{NiO}/\text{Al}_2\text{O}_3$ 与 Al_2O_3 基体表面显著不同, 出现了一层细小颗粒, 这显然是由于NiO的担载所致. 经铅笔涂层修饰之后, 所得Pencil/ Al_2O_3 与Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 表面形貌几乎完全相同, 都变得更加平滑. Pd/Pencil/ Al_2O_3 与Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 膜的表面形貌也几乎完全相同, 膜面均十分平整, 未见明显缺陷, 表明NiO的担载对膜的制备没有显著影响. 两种钯膜的断面微观结构如图3所示. 样品断面经打磨和抛光后, 钯金属层变得极为光亮, 因此可通过光学显微镜清楚观察. Pd/Pencil/ Al_2O_3 与Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 膜的断面形貌十分相似, 钯金属层厚度均匀且与基体结合良好. 如前所述, 我们在制膜过程中通过改变镀液用量控制膜厚为5 μm , 而图3表明这与膜的实际厚度非常接近, 说明本工作所采用的化学镀工艺能够充分转化镀液中的钯离子并沉积成膜. 例如, 在每次更新镀液前均向镀液中添加了过量联胺, 从而使镀液中残留的钯离子充分还原, 避免了贵金属钯的损失.

3.2. 膜的透氢性能

钯膜的透氢性能采用 H_2/N_2 单气体法测试^[14], 温度为350, 400和450 °C. 钯膜的透氢过程遵循溶解-扩散机制, 氢通量 J 可用下式计算: $J = F(p_r^n - p_p^n)$. 式中, F 为膜的渗透率, p_r 和 p_p 分别为膜滞留侧和渗透侧的氢气压力, n 为压力指数, $0.5 \leq n \leq 1$. 通常, 氢在钯膜体相中的扩散为速率控制步骤, 符合Sievert定律, 则 $n = 0.5$ ^[16,17].

测试结果如图4所示. 其中, 膜的选择性定义为同等条件下氢气和氮气通量之比, 选择性越高则说明膜的缺陷越少. 在测试条件下, Pd/Pencil/ $\text{NiO}/\text{Al}_2\text{O}_3$ 中的NiO将被氢气还原, 从而原位得到Pd/Pencil/ $\text{Ni}/\text{Al}_2\text{O}_3$ 膜.

我们前期研究发现, 铅笔修饰技术能有效避免基体表面缺陷对制膜造成的不利影响, 即使在普通大孔基体上也可以制得高选择性钯膜, 从而使钯膜的制备变得更加容易^[12]. 但是由于本工作的初衷是为了研究镍催化剂对膜泄漏CO的转化效果, 因此特意选择了一个 H_2/N_2 选择性较低、膜缺陷较多的Pd/Pencil/ $\text{Ni}/\text{Al}_2\text{O}_3$ 膜进行透氢和催化性能研究. 单气体渗透测试结果如图4所示. Pd/Pencil/

Al_2O_3 和Pd/Pencil/Ni/ Al_2O_3 膜的 H_2/N_2 选择性分别在5000以上和1000以下. 当压力指数 $n = 0.5$ 时, 两膜的氢通量与膜两侧氢气压力的关系曲线均呈良好的线性关系, 说明氢原子体相扩散是速率控制步骤. 在350, 400和450 °C下, Pd/Pencil/ Al_2O_3 膜的氢气渗透率 F 分别为110, 126和144 $\text{m}^3/(\text{m}^2 \cdot \text{h} \cdot \text{MPa}^{0.5})$, 而Pd/Pencil/Ni/ Al_2O_3 膜的氢气渗透率 F 分别为120, 133和150 $\text{m}^3/(\text{m}^2 \cdot \text{h} \cdot \text{MPa}^{0.5})$. 可见, 在同样条件下两膜的氢气渗透率相近.

图4的结果表明Ni的担载对钯膜的氢渗透性能几乎没有影响. 首先, 镍催化剂位于 Al_2O_3 基体孔道内, 与钯膜之间相隔一层石墨修饰材料, 不会污染钯膜或妨碍钯膜的制备; 其次, 镍的担载量少, 并不会显著提高 Al_2O_3 基体的气体渗透阻力; 再次, 基体材料的氢气渗透阻力远小于氢原子在金属钯体相中的扩散阻力, 氢原子体相扩散仍是透氢速率控制步骤, 这也与图4的动力学分析结果相吻合. 膜的氢通量与 H_2/N_2 透氢选择性随温度的升高而升高, 这是钯膜的典型特征. 氮气从钯膜缺陷处的泄漏方式一般是Knudsen或Poiseuille扩散, N_2 通量分别与 $T^{-0.5}$ 或 T^{-1} 成正比, 亦即随温度的升高而降低.

3.3. 膜的氢分离与CO甲烷化性能

在实际工作条件下, 原料氢中的杂质气体会降低钯膜的透氢量^[18–20]. 除与压力、温度及原料气组成有关外, 钯膜的原料气处理能力和氢气产出量还与氢气回收率密切相关. 当原料氢从钯膜滞留侧流过时, 随着氢气不断被分离, 氢气浓度或氢分压不断下降, 钯膜的局部氢通量也随之下降. 对任何一个特定的钯膜而言, 进料越快, 则原料中的氢越来不及分离, 从而氢气回收率越低, 但钯膜滞留侧的氢分压损失越小, 因而产氢量越高. 由此可见, 氢气回收率越高则产氢量越低, 当钯膜滞留侧的尾气氢气分压与渗透侧的氢气压力相等时, 氢气的回收率将达到极限. 提高膜滞留侧压力和降低膜渗透侧压力是实现高产氢量和高氢气回收率的有效手段.

本工作采用组成为 H_2 77.8%, CO 5.2%, CO_2 13.5%和 CH_4 3.5%的原料气, 测试了氢回收率为70%时进料压力与钯膜产氢量的关系, 结果如图5所示. 对比而言, Pd/Pencil/ Al_2O_3 和Pd/Pencil/Ni/ Al_2O_3 膜在同样温度和进料压力下的产氢量并没有明显的差别. 例如, 在350, 400和450 °C下, Pd/Pencil/ Al_2O_3 膜在进料压力为0.25 MPa时的产氢量分别为11.8, 14.5和17.0 $\text{m}^3/(\text{m}^2 \cdot \text{h})$, 而Pd/Pencil/Ni/ Al_2O_3 膜的相应产氢量分别为12.7, 14.1和16.8 $\text{m}^3/(\text{m}^2 \cdot \text{h})$.

钯膜的产氢纯度取决于原料氢浓度、膜的操作条件

和膜的完整性. 在膜的制备和长期运行过程中, 钯膜上会出现针孔, 导致氢纯度下降. 本工作主要针对氢燃料电池PEMFC对CO特别敏感的特点, 在 Al_2O_3 基体材料孔道内引入Ni催化剂, 从而可将膜泄漏的CO进行甲烷化. 在Ni催化剂的作用下, CO和 CO_2 可与 H_2 发生如下反应:

这样, Pd/Pencil/Ni/ Al_2O_3 膜就同时具备了氢气分离和CO催化甲烷化两种功能, 其工作原理如图6所示. 尽管每1 mol的CO和 CO_2 分别要消耗3和4 mol氢气并产生2和3 mol的新杂质, 但少量的 CH_4 和 H_2O 杂质对PEMFC没有毒副作用. 由于钯膜泄漏的CO和 CO_2 浓度极低, 甲烷化过程中所消耗的氢气完全可以忽略不计.

在进料压力0.25 MPa及氢回收率70%的条件下, Pd/Pencil/ Al_2O_3 和Pd/Pencil/Ni/ Al_2O_3 膜产出氢中CO, CO_2 和 CH_4 的浓度见表1. 与原料气相比, Pd/Pencil/ Al_2O_3 膜产出氢中CO, CO_2 和 CH_4 的浓度均下降了3个数量级, 证明该膜具有良好的氢分离作用. 与Pd/Pencil/ Al_2O_3 相比, Pd/Pencil/Ni/ Al_2O_3 膜产出氢中CO和 CO_2 的浓度均至少低了1个数量级, 但 CH_4 浓度却高了约2个数量级, 这显然是Pd/Pencil/Ni/ Al_2O_3 膜通过催化甲烷化所造成的. 一方面, 图4结果已表明, Pd/Pencil/Ni/ Al_2O_3 膜比Pd/Pencil/ Al_2O_3 膜拥有更多缺陷, 但前者产出氢中CO和 CO_2 的浓度却显著低于后者, 说明CO和 CO_2 已被额外转化或消除. 另一方面, Pd/Pencil/ Al_2O_3 膜产出氢中CO, CO_2 和 CH_4 的浓度之比与原料气较为相近, 但Pd/Pencil/ Al_2O_3 膜产出氢中 CH_4 浓度大大高于CO和 CO_2 , 说明Pd/Pencil/Ni/ Al_2O_3 膜具有良好的甲烷化作用. 其产出氢中CO的浓度不超过0.0001%, 完全能够满足PEMFC的要求. 表1的结果还表明, 随着温度的升高, Pd/Pencil/ Al_2O_3 和Pd/Pencil/Ni/ Al_2O_3 膜产出氢中CO, CO_2 和 CH_4 的浓度均呈下降趋势, 这与图4结果相吻合, 亦即膜的透氢选择性随温度的升高而升高.

众所周知, 金属钯也是甲烷化催化剂^[21], 但通常催化剂中的钯金属颗粒直径都在纳米级, 而钯膜的表面积非常小, 因此不会引起显著的甲烷化作用. 另外, 钯膜厚度只有5 μm 且钯金属只是分布在基体表面, 导致钯膜泄漏的CO和 CO_2 与金属钯的接触时间极短, 一般的钯膜(如Pd/Pencil/ Al_2O_3)并不会产生明显的甲烷化作用, 因此Pd/Pencil/Ni/ Al_2O_3 膜的甲烷化功能显然只能归功于所引入的镍催化剂. 这种双功能膜尤其适用于面向PEMFC的氢气分离, 既有效解决了PEMFC对氢燃料中CO格外敏感的问题, 又提高了对钯膜缺陷的容忍度, 因而相当

于延长了钯膜的使用寿命.

4. 结论

通过向多孔 Al_2O_3 基体材料中引入镍催化剂, 成功制备了同时具有氢分离和一氧化碳催化甲烷化功能的钯复合膜Pd/Pencil/Ni/ Al_2O_3 , 既有效解决了质子交换膜燃料电池(PEMFC)对氢燃料中CO格外敏感的问题, 又延长了钯膜的使用寿命, 而且由于钯膜所泄漏的CO和

CO_2 量极少, 甲烷化反应所消耗的氢气也可忽略不计. 因此, 这种双功能膜Pd/Pencil/Ni/ Al_2O_3 尤其适合于面向PEMFC的氢分离用途. 本工作所提供的双功能膜制备工艺中, 镍催化剂的引入对钯膜本身的制备和透氢性能几乎没有影响, 铅笔涂层不仅起到修饰 Al_2O_3 基体的作用, 而且避免了镍催化剂与钯膜的直接接触. 未引入镍催化剂的钯膜Pd/Pencil/ Al_2O_3 对CO甲烷化几乎没有催化作用.