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Research Paper

Novel Electroless Plating of Ruthenium for Fabrication of Palladium-Ruthenium Composite Membrane on PSS Substrate and Its Characterization

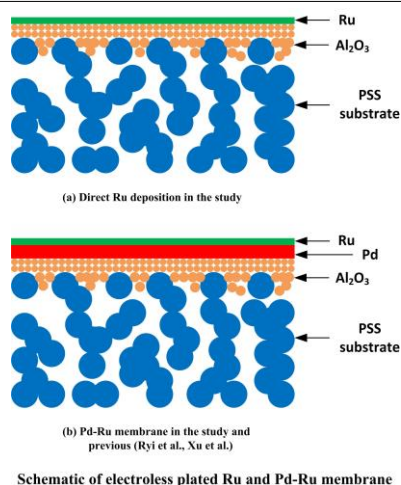Nong Xu[1], Sung Su Kim[1], Anwu Li[*1,2], John R. Grace[1], C. Jim Lim[1], Tony Boyd[2]

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HIGHLIGHTS

> This paper presents a novel method of electroless plating ruthenium (Ru) on solid or porous substrates.
> The electroless plating rate of Ru is greatly improved.
> The working conditions of electroless plating bath of Ru are moderated for industrial application.
> Based on the new electroless plating method, palladium-ruthenium (Pd-Ru) composite membrane was fabricated.

GRAPHICAL ABSTRACT

(a) Direct Ru deposition in the study

(b) Pd-Ru membrane in the study and previous (Ryi et al., Xu et al.)

Schematic of electroless plated Ru and Pd-Ru membrane

ARTICLE INFO

ABSTRACT

This paper focused on a novel method of electroless plating ruthenium (Ru) on solid or porous substrates like porous stainless steel (PSS) discs or ceramic tubes. A novel complexing plating bath of Ru was developed. It is proven that Ru can be deposited directly on these substrates by the bath at a temperature of 328 K and strong alkaline environment. TGA, SEM, EDX and XRD confirmed the successful deposition of Ru. Relationships among plating rate, plating time, plating bath temperature and concentrations were also investigated. The Ru plating procedure was optimized. Based on the optimized procedure, a Ru layer was deposited by electroless plating of Ru onto the surface of pretreated aluminum-oxide modified PSS substrate. A 7.6 µm thick Pd-Ru membrane could be fabricated by electroless plating with a palladium (Pd) layer overlying the PSS substrate and a Ru layer overlying the Pd layer. Helium leakage and hydrogen permeation tests confirmed that the membrane was free of defects. Hydrogen diffusion through the Pd-Ru membrane was found to be the rate-controlling step in permeation. A new Pd-Ru composite membrane had the same features and permeation behavior as a previous one, indicating that electroless plating of both Ru and Pd is reliable and repeatable.

1. Introduction

Production, separation, and purification of hydrogen can be achieved by a number of technologies. Dense Pd-based membrane and membrane reactor technology are among the most promising methods for production of high-purity hydrogen. Palladium (Pd) dense membrane and Pd-based composite membranes command particular attention [1,2] in this regard. Pd-based composite membranes are the most common membranes for hydrogen

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separation due to their high resistance to hydrogen embrittlement and oxidation, good thermal stability, favorable catalytic activity for hydrogen dissociation and recombination, as well as appropriate hydrogen permeability. The most commonly studied thin Pd-based composite membranes are Palladium-Silver (Pd-Ag) and Palladium-Copper (Pd-Cu) [3,4].

Ru, with a silvery white colour, atomic number 44, atomic weight 101.07, and density 12.41 g/cm^3, belongs to the precious metals [5,6]. Its properties make it an alternative to well-known platinum or rhodium, but its cost is only 15% of that of platinum or rhodium. Due to this, Ru plays an important role in relevant applications. Ru electroplating processes have been developed rapidly for more than ten years in the finishing industry and chemical engineering [7]. Several kinds of non-aqueous (aqueous) electrolytes and fused salt baths have been built for the electrodeposition of Ru. Typical Ru plating electrolytes can be found in several references [7,8]. Compared with electroplating, electroless plating (or chemical plating) has many advantages. It does not require an external Direct Current (DC) power supply. It is available on a variety of different substrates, such as metals, non-metallic, semiconductor and other materials. For fabrication of Pd-based membranes, it is a plating method for dense film with less pin-holes and cracks. What is more, the technology is controllable for uniform membrane coating on large-scale supports with different industrial geometries. Little information is available on electroless plating of thin dense Palladium-Ruthenium (Pd-Ru) membranes [5,6], especially on the electroless deposition of Ruthenium (Ru).

Here we are concerned with the electroless plating of Ru for preparation of pilot-scale or commercial-scale Pd-Ru membranes. Valsiuniene and Norgalaite [9] described the deposition of Ru from RuNO(OH)$_3$ complex, using NaBH$_4$ as the reductant. The deposition rate increased with increasing temperature and Ru concentration. Hyland [10] reported that sodium oxalate could be a stabilized complexant for RuCl$_3$•xH$_2$O reduction under alkaline conditions. The reductant was hydrazine at a temperature of 50 °C. Chang and Chou [11] developed hypophosphite in RuCl$_3$•xH$_2$O solution with pH>9 to deposit Ru. Note tha their products were surface-modified Silicon-Ruthenium (Si-Ru) wafers for special semiconductors. Thus the average plating rate was too low and the plating temperature was relatively high. The process time was about 20 h for only 1.8 µm deposition of Ru at 85 °C. Researchers from Japan and United States [12-16] have published several patents that featured electroless plating of Ru from the 1980s to 1990s. Though some details of the Ru complex introduced were omitted in these sources, one can reasonably speculate that the reaction solutions included ruthenium nitrosylamine complex, sodium hydroxide and/or ammonia to adjust the pH, and hydrazine as the reducing agent. Plating parameters of pH and temperature covered a wide range, from 10 to 13 and from 35 to 60 °C, respectively. It is clear that over the past few decades, a number of attempts have been conducted on this field. But there is little agreement on these electroless plating methods. What seems to be lacking are details of the operating parameters, due to protection of intellectual property. Although several studies [12,15,16] have claimed their successful deposition of Ru with electroless methods, the validity and reproducibility of these plating recipes need to be confirmed.

A previous short communication [17] provides the composition of an electroless plating bath for deposition of Ru. The recipe is simple and easy to practice compared with the procedure for electroless plating of Ru in the previous study [9-12]. Besides using RuCl$_3$•xH$_2$O as the raw material and hydrazine as the reducing agent, it employs only ammonia to adjust the pH. The electroless plating procedure of Ru was fully presented, leading to further demonstration of the capability of Pd-Ru composite membranes [18]. But, the plating of Ru was slow. The plating rate is dependent on temperature and on the concentrations of the reactants. The temperature of the plating bath reached 85 °C, and the concentration of the reactant, hydrazine, increased from 1% to 5%. However, a plating time of about 12-15 h was still required for less than 0.4 µm deposition of Ru, a rate that is too low for lab-scale and large-scale Pd-Ru membrane preparation and for industrial applications. Furthermore, higher plating temperatures and greater chemical concentrations imply higher capital and operating costs in practice.

This paper presents a fully novel electroless plating method which greatly improves the plating rate of Ru. The working conditions for electroless plating bath are moderated. For example, plating temperature is decreased to 55 °C to accommodate large-scale plating. On the basis of more than 150 lab-scale experimental selections of the conditions for electroless plating of Ru, we screened parameters and procedures for the reaction. Furthermore, Ru can be deposited singly by electroless plating with a Ru layer overlying the Pd layer [19,18] based on the novel technology. Based on the new method, Pd-Ru composite membranes were successfully fabricated and the Ru plating rate was investigated. Finally, individually-plated Ru membranes and successfully prepared Pd-Ru membranes were confirmed and characterized by advanced instrumental analysis.

The proposed Ru deposition method is promising not only for Pd-based membrane fabrication, but also for other applications. Since Ru and Ru-doped electrodes have very strong resistance against attack by acid and brine (or seawater) corrosion, the method has a variety of applications.

2. Experimental and methods

2.1. Pretreatment of alumina modified PSS substrate

Porous Stainless Steel (PSS) 316 substrates of 50.8 mm diameter and 1.37 mm thickness from Mott Corporation, with Media Grade 0.2 and a porosity of 35%, served as substrates. Pretreatment steps for these porous stainless steel substrates included washing, polishing, etching, diffusion barrier coating with aluminum oxides (Al$_2$O$_3$), calcination and a repair cycle. For the detailed procedure, refer to references [20,21].

2.2. Electroless plating of palladium

Palladium films were deposited on pretreated porous stainless steel substrates by electroless plating. Prior to plating, the substrates were impregnated with a solution of PdCl$_2$ (0.01 M), followed by drying and reduction in hydrogen at 723 K for 2 hours. We previously provided the composition of the bath [19] for preparing palladium composite membranes. The plating temperature was controlled at 333 K. For the detailed procedure, see references [20,22].

2.3. Electroless plating of Ru

Table 1 lists the operating parameters and the composition of the Ru electroless plating bath. Ru should be controlled between 1 to 10 wt% in the Pd-Ru membrane. After completing the Ru plating, the fresh Pd-Ru membrane was cleaned several times with deionized water and dried overnight in an oven at 393 K. The thickness of Pd-Ru membrane was determined by both weight gain and cross-sectional Scanning Electron Microscopy (SEM) observation. Helium leakage was tested with a pressure difference of 100 kPa at room temperature to ensure the integrity of the dense Pd-Ru composite membrane.

Table 1
Operating parameters and composition for electroless plating of Ru.

Components and parameters	Electroless plating of Ru	Chemical name or value
Material of Ru	Ru plating solution prepared from U.S. patent*	2.89 ml/cm^2 substrate
Reductant	Hydrazine, prepared 1 M N$_2$H$_4$·H$_2$O solution	0.0744 ml/cm^2 substrate
pH control	Yes	NaOH and NH$_3$•H$_2$O, >11
Temperature of plating bath	-	328 K
Additional agents	Yes	Sodium nitrite
Electroless plating rate	moderate	0.43 µm/h
Electroless plating time	controllable	15 ~ 60 min

* Boyd et al., Electroless plating Ru and Ru-plated products, U. S. patent Pub. No.: US2014/0170328 A1, Pub. Date: Jun. 19, 2014

2.4. Characterization

A Thermo Gravimetric Analyser (TGA Thermax 500) from Thermo Scientific was employed to determine the high-temperature weight gain of Ru foil. The surfaces of Ru and Pd-Ru membrane were characterized by a SEM (Hitachi S-3100), Energy Dispersive X-ray spectroscopy (EDX). The crystal structure of the fabricated membranes was examined by X-ray Diffraction (XRD) by means of a Shimadzu instrument, at a current of 20 mA and a voltage of 40 kV, using a copper target (λ = 0.1540 nm). An X-ray Photoelectron Spectrometer (XPS, Omicron & Leybold MAX 200) determined the surface composition of the prepared samples.

3. Results and Discussion

3.1. Electroless plating of Ru

Table 2 lists previous methods for electroless plating of Ru. Most researches in Table 2 employed chemical compounds containing Ru^{+3}. According to Seddon and Seddon [6], the striking chemical features of Ru^{+3} are twice as many as the combined features of Ru^{+4}, Ru^{+5}, Ru^{+6}, Ru^{+7} and

Ru^{+8}. Ru^{+3} can form many stable or unstable cationic, neutral and anionic complexes, which are kinetically active or inert. Among these complexes, ruthenium nitrosyl are the most complex, but also most useful for electroless plating. Only recently have studies on the interactions between Ru^{+3} and nitrite in aqueous solution been reported [6,8].

This reveals that in the alkaline environment of ammonia, $[Ru(NO)(NH_3)_5]OH_3$ and $[Ru(NO)(OH)(NH_3)_4]OH_2$ complexes are stable in solution. Thus addition of sodium nitrite to $RuCl_3 \cdot xH_2O$ before the electroless plating was our first choice. Note that other researchers have also employed ammonium oxalate, sodium oxalate and ammonium citrate instead of sodium nitrite [11,13,16]. Generally speaking, they play the same role as sodium nitrite in the Ru stock solution, so similar electroless plating results should be expected. But we found that sodium nitrite was better in practice. The possible reason is that complicated derivatives from ruthenium-ammine complexes increase the stability during electroless plating.

Table 2
Details of previous investigations of electroless deposition of Ru.

Items	Surface plating on Ni*	Surface plating on Si*	Pore-free plating of Ru	Surface plating of Ru
References	[12,14]	[8,11,7]	[9,8]	[10,8]
Chemical combination of Ru	Ru**	$RuCl_3 \cdot xH_2O$	$RuNO(OH)_3$	$RuCl_3 \cdot xH_2O$
Reductant	Hydrazine	Hypophosphite	$NaBH_4$	Hydrazine
pH	≤ 13	> 9	10-13	13
Temperature of the plating bath (K)	328-338	358	293-323	323
Additional agents	Yes, unknown	Yes, unknown	$(NH_2OH)_2 H_2SO_4$	$Na_2C_2O_4$
Electroless plating rate (µm/h)	1.7	0.11	< 0.9	< 1.0

* Ni as nickel and Si as silica. ** Unknown chemical compound of Ru.

Given hydrazine as the reductant, the choice and control of pH is the key parameter for electroless plating of Ru. Previous researchers [6,8] observed that hydrazine was not a controllable reductant with $RuCl_3 \cdot xH_2O$. For example, at pH 11, the strong reducing agent (hydrazine) seems to lose its reductive performance, or the performance is weakened. In another case at 85℃, the pH of the solution decreased with continuous evaporation of ammonia from the plating bath. This caused precipitation of ruthenium oxide instead of Ru. Based on our investigation, the pH should be >11 during the entire electroless plating process. Here sodium hydroxide is introduced to maintain the strong alkaline condition. It is also noted that sodium hydroxide easily absorbs carbon dioxide from the air, so that it is easily neutralized. But the electroless plating reaction is very sensitive to pH. Hence it is prudent to prepare the sodium hydroxide solution immediately before the Ru plating. It should never be stored for a long time.

3.2. Carbon-free Ru deposition

Most electroless plating studies have used organic compounds to increase the stability of the bath, assisting in controlling the process at appropriate pH and temperatures [8,10,11,13]. We used EDTA salt for the Pd plating process in our previous study [22]. However, organic complex compounds like oxalate or EDTA salt result in low purity of the metallic layer owing to incorporation of complexes within the metal deposit [23]. Moreover, they are a source of carbon, which degrades the performance of the deposited metal [24]. Therefore, many electroless plating methods have been developed [25,26] which avoid organic complex compounds when preparing thin, dense and high-performance metallic foil, film or membranes. We present such a technique here. To further confirm that the Ru sample is carbolic contaminant-free, TGA was carried out with CO_2 as the carrier gas. A pure Ru sample for TGA analysis was made by peeling the Ru film from a porous ceramic substrate, and additional plating was carried out to gain enough Ru for TGA analysis. The 35.93 mg sample was ramped to 973 K at 1 K/min, held at 973 K for 6 h, and then cooled at 1 K/min to room temperature. Roa and Way [27] reported a 6.5 wt% proportion of carbon from the EDTA salt in electroless-plated Pd-based membrane by TGA analysis. Carbon removal started when the sample reached about 433 K, and proceeded rapidly from there until the temperature reached 673 K. Less than 0.2% (wt%) weight difference is observed in Figure 1, indicating that no carbon contaminant was present in the Ru sample.

3.3. Electroless plating rate of Ru

The rate of Ru deposition on the PSS substrate was determined for a series of plating solutions. Ru deposition increased as a function of plating time, as shown in Figure 2. About 73% Ru was utilized in about 3 h. It is difficult to compare Figure 2 with other studies because of the lack of related reports, but the deposition rate was faster than those of our previous studies

[17,18]. Table 3 summarizes our previous parameters for electroless plating of Ru. The plating rate in Table 3 is below 0.10 µm/h. However, it reaches 0.43 µm/h with the new bath in Table 1. An appropriate choice of sodium nitrite as additional agent, and careful control of pH during the plating contributed to this. Ru deposition achieved a maximum deposition rate of 0.05 µm/min during the first 10 minutes and an average rate of 0.0038 µm/min for 3 h of plating at a temperature of 328 K with 2.89 ml Ru and 0.0744 ml hydrazine per cm^2. Higher electroless plating bath temperature and higher Ru or hydrazine concentrations resulted in more rapid growth of Ru deposition. Figure 3 depicts the relationship between bath temperature and plating time needed to provide a 0.5 µm deposition thickness of Ru. A higher electroless plating temperature led to shorter plating time for a fixed thickness of Ru. When the temperature reached 358K, it only required about 12 min to reach a thickness of 0.5 µm, implying very strong correlation between the two parameters. We chose 328 K for the lab-scale case. But when scaled-up, the temperature could be between 313 K and 333 K, considering key industrial aspects such as operating cost, control of plating rate, and equipment cost.
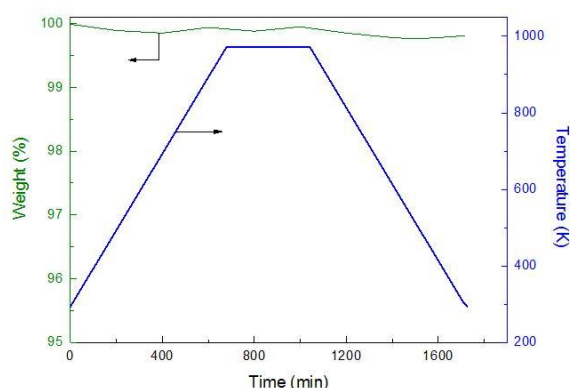

Fig. 1. Weight fluctuation and temperature profiles carried out with TGA under flowing CO2 for electroless plated Ru.
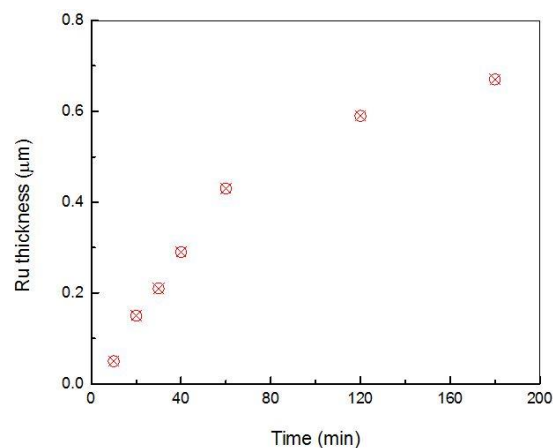

Fig. 2. Ru electroless plating rate and thickness as a function of plating time at 328 K.

The study also investigated the influence of Ru^{+3} and hydrazine concentrations on the electroless plating rate. Higher concentrations of Ru^{+3} or hydrazine caused earlier onset of bath decomposition, i.e. bulk precipitation. In particular, increasing the hydrazine concentration led to failure of the deposition, as indicated by murkiness of the plating solution and generation of large bubbles [28]. Catalytic decomposition of hydrazine due to Ru may be one factor [13]. In our case, 1 M hydrazine was prepared for plating at 358 K. Over the temperature range of 313 to 333 K for other applications, it is better to maintain the hydrazine concentration below 2 M. Otherwise, our observations suggest that it would be extremely difficult to control the plating rate.

3.4. Characterization of Ru

It is very important to confirm the electroless plating of Ru and to compare the surface morphology of pure Ru and a Pd-Ru membrane. Direct deposition of Ru was carried out on the surface of PSS substrate. Figure 4 illustrates schematically the cross-section of directly deposited Ru. Compared

with Figure 1 of Ryi et al. [17], Figure 4 shows a schematic of the direct Ru plating. The total cross-section has two layers, i.e. porous metal support pre-treated by aluminum oxide and a thin ruthenium layer. However, three layers appear in Ryi et al. [17]. Hence, "direct" here means omission of the Pd middle layer in Figure 1 of Ryi et al. [17]. So a comparative study could be performed comparing the two schematic layers. Figure 5 shows the lab-scale sample with direct Ru plating on the surface. The substrate at the centre of the plastic dish is a 1 inch (25.4 mm) diameter PSS disc modified with aluminum oxide with a 0.5 μm thickness of Ru deposited on its surface.
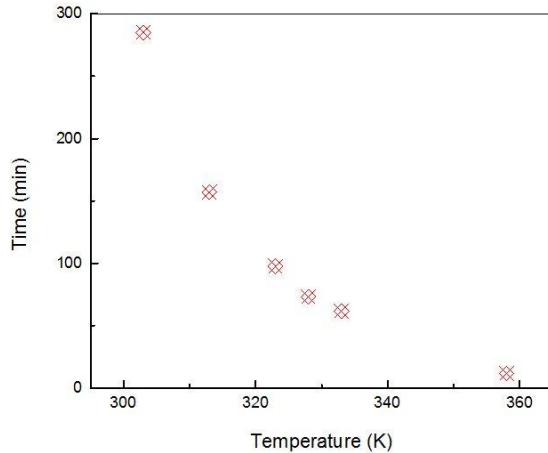
Fig. 3. Influence of temperature of electroless plating bath on plating time when 0.5 μm deposition thickness of Ru is reached.

Table 3
Previous parameters and composition for electroless plating of Ru.

Components	Electroless plating of Ru on Pd	Value
Chemical combination of Ru	$RuCl_3 \cdot xH_2O$	0.32 g/1 bath
Reductant	Hydrazine, from 1 to 5 %	50 ml/1 bath
pH control	Yes	28% $NH_3 \cdot H_2O$ 32 ml/1 bath
Temperature of plating bath	-	358 K
Additional agents	None	-
Electroless plating rate	Low	< 0.10 μm/h
References	[17,18]	-

Figure 6 shows an SEM image of the deposited microstructure of Ru. The morphology of the pure Ru layer in the SEM image of Figure 6 is compared with the Pd-Ru (Ru 5 wt%) membrane image of Figure 1(b) of Xu et al [18]. 1000-fold magnifications show that there are both similarities and differences between the topography of pure Ru and Pd-Ru. The pure Ru layer is similar to the Pd-Ru membrane that covered the PSS substrate continuously. But the pure Ru layer is more irregular and coarser than the Pd-Ru. Figure 7 shows an EDX profile of the disc surface. The peaks observed on the surface were 100% Ru, indicating that the Ru layer was successfully plated on the outermost top of the disc. Figure 8 displays the colourful EDX surface mapping of the disc in Figure 5. Blackish green (Ru) covered the entire picture, without differences in colour depth and brightness. This is also powerful evidence that Ru fully covered the PSS substrate, though its morphology is rougher than that of pure Pd or Pd-Ru [18]. The Ru layer was also analyzed by X-ray spectroscopy. The XRD results are shown in Figure 9. The diffraction peaks of Ru appeared in the XRD patterns of the analyzed sample. It shows only distinct phases of crystal Ru when cross-checked by professional software MDI jade 7.0. This also suggests very satisfactory plating of Ru.

3.5. Hydrogen permeation behaviour of Pd-Ru membrane

Although this research emphasizes the novel method of Ru plating, the ultimate goal is fabrication of thin, dense and pin-hole free Pd-Ru membranes for hydrogen separation, purification and reactor technology. The hydrogen permeability is commonly expressed in terms of a permeation equation,

$$J = \frac{Q}{D}\left(P_r^{\,n} - P_p^{\,n} \right)$$

(1)

where J is the hydrogen permeation flux (m^3/m^2.h), Q is the permeability constant of hydrogen through the membrane (m^3/m.h.Pa), D is the thickness of the membrane, P_r and P_p are the hydrogen partial pressures on the retentate side and permeation side, respectively, and n is a constant exponent indicating the pressure dependency. The permeability constant Q is dependent on temperature and can be expressed in the form of an Arrhenius expression,

$$Q = Q_0 \exp\left(-\frac{\Delta E}{RT} \right)$$

(2)

where Q_0 is the pre-exponential factor, ΔE is the apparent activation energy for hydrogen permeation, R is the gas constant, and T is the absolute temperature [2,4].

(a) Direct Ru deposition on aluminum oxide modified PSS substrate.

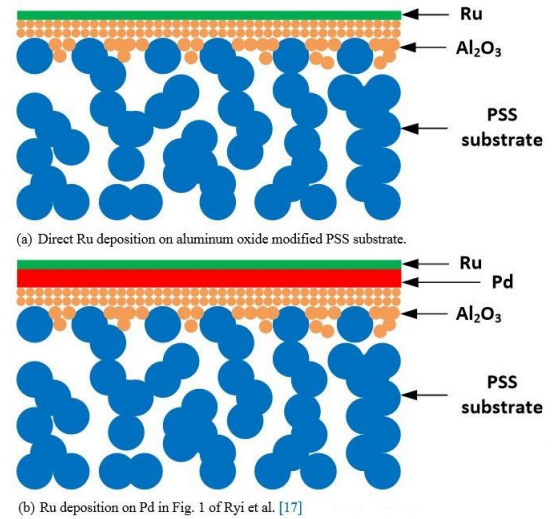(b) Ru deposition on Pd in Fig. 1 of Ryi et al. [17]

Fig. 4. Schematic of electroless plating of Ru on aluminum oxide modified PSS substrate.
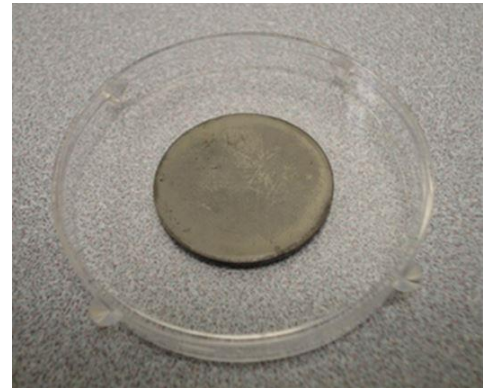

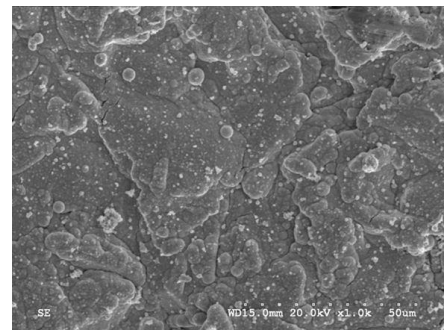**Fig. 5.** Direct Ru plating on surface of lab-scale PSS disc of 25.4 mm diameter.

Fig. 6. Surface microstructure of Ru deposition by electroless plating at 328 K.
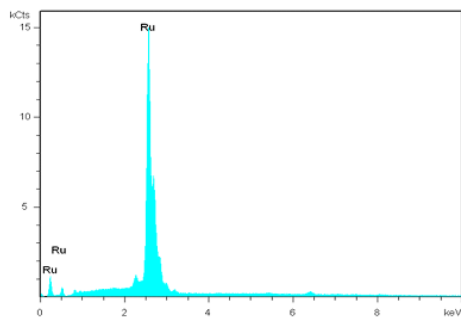
Fig. 7. 100% of Ru peaks observed at top surface with EDX scan.

The prepared Pd-Ru membranes were mounted in stainless steel permeation cells with graphite gaskets. The thickness of the fresh Pd layer was 7.0 µm. Helium leak tests were first conducted at a pressure difference of 100 kPa and at room temperature before hydrogen permeation. Next the membranes were heated slowly under helium until the temperature exceeded 573 K to prevent membrane fracture due to phase transition. Permeation tests were then conducted with hydrogen at temperatures of 623-823 K and absolute pressures of 120-290 kPa, while permeate side was maintained atmosphere. The permeation rate of hydrogen was measured by a soap-bubble flow meter or monitored by a mass flow meter (MFM). The hydrogen permeation fluxes were calculated from Eq. (1). The profiles of hydrogen permeation fluxes at different temperatures are plotted in Figure 10. The value of n was 0.50, determined by least squares fitting. Based on Eq. (2), the logarithms of Q are plotted against reciprocal temperature in Figure 11, giving an apparent activation energy of 24.37 kJ/mol, which compares well with values suggested by Ryi et al [17]. It is clear that different methods for electroless plating of Ru lead to very little change in the hydrogen permeation behaviour of Pd-Ru membranes.
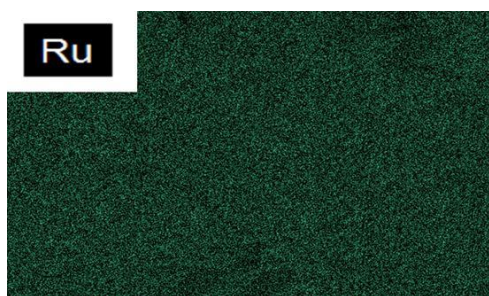

Fig. 8. Colourful EDX surface mapping showing that blackish green (Ru) covered the entire sample.
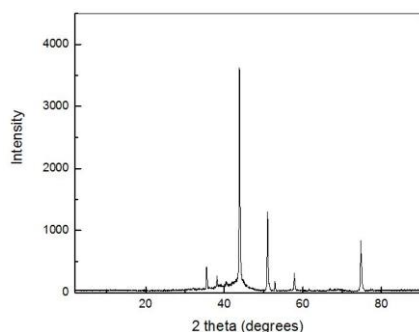

Fig. 9. Crystal structure of electroless plated metal examined by X-ray Diffraction (XRD).

Wang et al. [29] reported hydrogen permeability of their Pd-Ag (Ag 30 wt%) membrane was 2.0×10^{-8} mol•m^{-1}•s^{-1}•Pa$^{-0.5}$. It was 2 times larger than the Pd membrane (1.0×10^{-8} mol•m^{-1}•s^{-1}•Pa$^{-0.5}$). The ternary alloy composite membrane of Pd-Ag-Ru (69, 30, 1 wt%) exhibited unique high hydrogen permeability in comparison with Pd membrane or with Pd-Ag binary alloy membrane. The hydrogen permeability of Pd-Ag-Ru (69, 30, 1 wt%) membrane was about three to four times higher than that of pure Pd membrane at 773 K. We also noticed the hydrogen permeability of the 7.6 µm Pd-Ru membrane was about 1.4-1.5 times as large as that of pure Pd membrane. Alloyed (or partially alloyed) Pd-Ru phase in the composite

membrane may contribute more to the increase. However, Gade et al. [30] tested the hydrogen permeability of the electroless co-deposition Pd-Ru (Ru 5 wt%) membrane at 773 K as 1.4×10^{-8} mol•m^{-1}•s^{-1}•Pa$^{-0.5}$, which was between the pure Pd membrane results of Li et al. [22] (1.2×10^{-8} mol•m^{-1}•s^{-1}•Pa$^{-0.5}$) and Ryi et al. [19] (1.6×10^{-8} mol•m^{-1}•s^{-1}•Pa$^{-0.5}$). Hence, reports from different studies are not the same. Further in-depth research and mechanism study on the binary alloy (or ternary alloy) are needed.
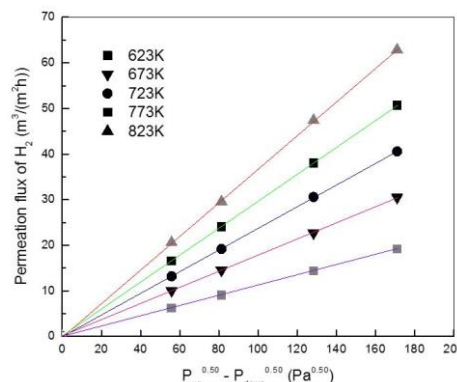

Fig. 10. Hydrogen permeation flux as a function of pressure difference at various temperatures.

3.6. Characterization of Pd-Ru membrane

Another concern of the research was to characterize the properties of the plated Pd-Ru membrane. The final results from surface SEM image, cross-sectional EDX line scanning, XRD profile and XPS scanning are similar to those reported by Xu et al. [18]. All of these indicate integrity of the Pd-Ru membrane, confirming the Ru/Pd/Al$_2$O$_3$ three-layer structure on the PSS substrate and demonstrating the effectiveness of the membrane preparation.
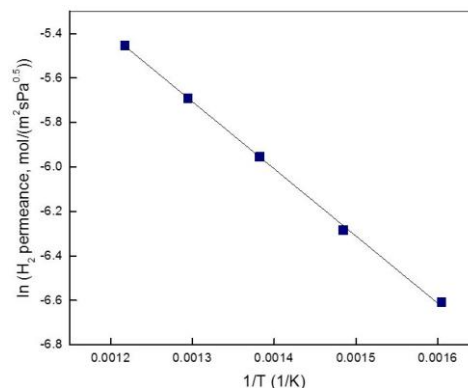

Fig. 11. Arrhenius plot to determine apparent activation energy of new Pd-Ru membrane.

4. Conclusions

A new method for electroless plating of Ru, with two innovative features, is presented on solid or porous inorganic substrates. One feature is the addition of sodium nitrite to form stable Ru complexes before plating. The other is providing a strong alkaline environment by using sodium hydroxide. The plated materials were investigated by TGA, SEM, EDX and XRD, confirming the deposition of a carbon-free Ru layer. The relationship among plating rate, plating time, Ru deposition thickness, plating bath temperature and concentrations are determined. Optimized steps for the plating of Ru are outlined. 1 M hydrazine was chosen at pH >11 and 328 K for reduction of Ru in several hours. Based on the novel method, a Ru layer was deposited by electroless plating of Ru on the surface of pretreated aluminum-oxide-modified porous stainless steel substrate.

Following Ru deposition, Pd-Ru composite membranes were prepared in the Ru/Pd/Al$_2$O$_3$/PSS structure and again investigated by SEM, EDX, XRD and XPS. The new Ru plating method does not appreciably change the performance of the plated Pd-Ru membrane. Hydrogen diffusion through the Pd-Ru membrane was the rate-controlling step for permeation. The method is promising for the development of new electrodes or to protect against acidic corrosion.

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