

## Effects of Synthesis Conditions on the PdCu Membrane Structure

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### Abstract

In this study, it was aimed to plate PdCu alloy layer on porous glass supports by using electroless plating technique. It was also aimed to achieve coexistence of fcc (face-centered cubic) and bcc (body-centered cubic) phases on the alloy membrane layer. The fcc and bcc phases were seen together in the structures of the membranes synthesized at all three bath temperatures (30 °C, 40 °C and 50 °C), but, it was shown that the most suitable coating rate was achieved when the coating bath temperature was 40 °C. The appropriate composition of PdCu (74% Pd, 26% Cu) was achieved by following a synthesis procedure as follows: Coating in Pd bath three times for 60 minutes each followed by coating in Cu bath at the low formaldehyde concentration (5 mL/L) for 15 minutes. Hydrogen flux in the membrane was measured as  $1.9 \times 10^{-6}$  mol/cm<sup>2</sup>s. After flux measurements, it was determined that the membrane structure changed and the fcc (200) structure, which did not previously exist in the structure, was formed.

### Keywords

Electroless plating, PdCu, Composite membrane, Characterization.

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## 1. INTRODUCTION

Having been observed around the world in recent years, climate change has led to the development of technologies to reduce carbon emissions. Membrane and hydrogen separation technologies have come into prominence at this point. Exhibiting high hydrogen selectivity, palladium-based membranes are widely used in hydrogen separation processes. However, membrane fragility together with hydrogen permeability in pure Pd membranes is an important problem. Since hydrogen does not dissolve under low temperatures, it is impossible to work below 300 °C in purification processes. The use of Pd alloys instead of pure Pd membrane is suggested to overcome membrane rupture problems. As well as helping to overcome rupture problems, the use of alloy membranes also ensures significant improvements in permeability values. It is also reported that membrane poisoning caused by sulphur and carbon compounds can be overcome by using Pd alloy membranes [1-5]. Studies in the literature show that many different types of Pd alloys (PdAu, PdPt, PdAuPt, PdNi, PdAg, PdRu, VPd and PdCu) are used in hydrogen separation processes. The two of the most commonly used methods in the synthesis of alloyed membranes are sputtering coating and electroless plating (EP). Lee et al. prepared PdAu membranes using the sputtering method. The results showed that covering the membrane surface with a layer of Pt-ZrO<sub>2</sub> did not affect hydrogen permeability and selectivity, and also protected the membrane from H<sub>2</sub>S poisoning [6]. Kim et al. obtained a very thin (6 µm) PdAu membrane layer using the sputtering technique. As expected, a very high hydrogen permeability was observed in the membrane [7]. Patki et al. subsequently plated PdAu alloy thin-film membranes using the electroless and displacement plating techniques. Homogenization was achieved by annealing the composite membranes at 550 °C in 3 MPa H<sub>2</sub> for up to 120 h [8]. Mardilovich et al. determined that the transport rate of hydrogen in the synthesis gas in PdAu, PdPt and PdAuPt membranes was higher than that in the pure Pd membrane. While dilatations were observed in the pure Pd membrane after hydrogen permeability, hydrogen permeability values in PdAuPt membranes did not vary even after 4275 hours of test [9]. Lu et al. covered alumina supports with a PdNi membrane layer using the electroless plating technique. While permeability and selectivity values were close to those in the pure Pd membrane in the synthesized membrane, the durability of the membrane was better at the end of 100 hours of test at 300 °C [10]. Abu El Hawa et al. synthesized PdRu and PdPt membranes using the electroless plating method. While no effect of adding Ru on membrane stability was observed, PdPt membranes were quite stable [11]. Hydrogen permeability was examined in commercially supplied VPd membranes by Alimov et al. They reported higher hydrogen permeability values compared to pure Pd in all membranes containing Pd in different amounts (5% -18.8% by mass)

[12]. Alimov et al., electrolessly plated V-κPd tubular membranes with a layer of Pd and the thickness of the coating was from 1 to 2 μm. The synthesized membrane was designed for feeding 1 kW PEMFC and demonstrated a highly productive extraction of ultrapure hydrogen from WGS mixture [13]. Flanagan and Wang prepared Pd-Al alloys by arc melting the pure elements under argon. From the equilibrium isotherms, thermodynamic properties have been determined (423-523 K) for a series of Pd-Al alloys [14]. Yan et.al investigated that the effect of Pd overlayer and mixed gases on hydrogen permeation of Pd/Nb<sub>30</sub>Hf<sub>35</sub>Co<sub>35</sub>/Pd composite membranes. Nb<sub>30</sub>Hf<sub>35</sub>Co<sub>35</sub> alloy (mol %) were prepared by arc melting method using Nb, Hf and Co (99.99 mass % purity for all) under argon atmosphere. It was demonstrated that Nb-based hydrogen permeable alloy improved permeability and selectivity [15]. The number of studies on PdAg and PdCu alloys is considerable. It is known that PdAg membranes have a higher hydrogen permeability than PdCu membranes. However, the synthesis cost of PdCu membranes is quite lower than that of PdAg membranes. Lee et al. showed that PdAg membranes prepared using the sputtering method maintained their stability even after long test periods (>2000 hours) [16]. Peters et al. reported that H<sub>2</sub>S in the environment reduced hydrogen permeability when adsorbed on the surface of PdAg membrane, however, coke formation was prevented as the adsorption made the surface adhesion of the hydrocarbons in the reaction environment harder [17]. Not only are PdCu membranes more cost-effective but also more durable towards membrane poisoning caused by sulphur compounds than PdAg membranes. Some studies show the positive effects on hydrogen permeability and sulphur resistance of the co-existence of fcc (face-centered-cubic) and bcc (body-centered-cubic) phases in the structure of membranes with PdCu alloy prepared using the sputtering method [18, 19]. Nayebossari et al. examined the effects on permeability of adding low amount of Ag to the structure of PdCu membrane. They observed no change in permeability values when the bcc phase was dominant in the membrane structure containing 2.3% of Ag by mass. In addition to the bcc phase, an fcc phase was formed and the permeability value increased when Ag was added to the membrane structure at the amount of 3.9% [20]. Using the electroless plating method, Islam et al. synthesized PdCu membranes. Different from the traditional electroless plating method, DTAB was used in Pd and Cu plating baths during the synthesis. The results showed that the membrane layer obtained with the use of this surfactant was thinner and that the coating process accelerated [21]. In the study carried out by Gao et al., membranes with different Pd/Cu ratios were synthesized using the electroless plating method. Porous stainless steel supports were modified using ZrO<sub>2</sub> prior to the coating process. Only a bcc phase was observed in the structure of the alloy membrane with low Pd content, and low hydrogen permeability was determined in

this membrane. The alloy consisted of bcc and fcc phases mixture with an increase in Pd concentration, and the permeability values increased consequently [22]. Numerous studies have pointed out that the modification of porous supports with an oxide layer before their use in membrane preparation has advantages over other methods in forming a thin membrane layer on the support surface and increasing the dependence between the support and the membrane [22, 23]. Yuan et al. prepared PdCu membranes at a thickness of 3-7  $\mu\text{m}$  on ceramic supports using the electroless plating technique. They reported that the synthesized alloy membrane structure was in the fcc phase, and that its permeability activation energy decreased with an increase in Pd concentration [24]. Having synthesized PdCu membranes using the electroless plating technique, Pomerantz and Ma determined that the fcc phase was at the top layer while the bcc phase was at the bottom layer in low annealing temperatures, indicating that obtaining membranes with a high sulphur resistance and high permeability values is possible. In this study, Pd layer was also covered on PdCu membranes using the galvanic displacement method. The results show that despite having a high sulphur resistance, PdCuPd membranes had significantly lower permeability values than PdCu membrane [1]. On the basis of the studies mentioned above, it is suggested that the mass ratio of Pd metal in the structure of the alloy is between 60 and 70%. The results of these studies on PdCu membranes point out that the phase structure of the alloy layer is an important parameter in the membranes in the transportation of hydrogen and that the co-existence of fcc and bcc phases in the structure increases hydrogen permeability values. In this study, commercially provided porous glass supports were modified using alumina, and then PdCu composite membranes were prepared using the electroless plating technique. The initial experiments addressed how the membrane structure would be affected by plating bath temperature. Afterwards, membrane preparation experiments were carried out to obtain the appropriate composition (approximately 70% Pd by mass and 30% Cu by mass) and phase structure was analyzed after determining the suitable bath temperature for the coating studies. Measurement of hydrogen flux was conducted in the PdCu composite membrane using pure hydrogen. The morphology and composition of the membranes were analyzed using SEM/EDS, and the phase formation and structure were analyzed using XPS and XRD.

## **2. MATERIALS AND METHODS**

### **2.1. Synthesis Experiments**

#### **2.1.1. Pre-treatments applied on the support**

Porous glasses with a thickness of 3 mm and diameter of 3 cm supplied from Robu Glasfilter Company were used as support in the synthesis of PdCu composite membrane. The cleaning

process was performed on the porous supports by boiling them in 0.1 N NaOH, 0.1 N HCl and pure water for 30 min, respectively. The cleaned supports were modified by alumina in order to increase the attachment between the membrane and the support material, to eliminate the expansion differences that may occur in the membrane as a result of thermal processes, and to provide the membrane with a better selective permeability. 100 mL 0.4 M  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 650 mL 1 M  $\text{CO}(\text{NH}_2)_2$  solutions were mixed for modification, and glass supports were immersed into this mixture by covering one side with teflon tape. The supports were removed from  $\text{Al}(\text{OH})_3$  gel formed after being kept at 90 °C for 20 h and then subjected to heat treatment at 600 °C for 18 h. This process was repeated once again. Activation process was carried out on modified supports for the purpose of seeding the Pd, which initiates the autocatalytic coating, to the surface. In the activation process, the supports were first kept in HCl solution of 0.2 N, 1 L of which contains 2.0 g  $\text{SnCl}_2$ , and then in HCl solution of 0.2 N, 1 L of which contains 0.15 g  $\text{PdCl}_2$ , and lastly in pure water for 10 min. This process was repeated 10 times. The loading amount of the solutions was kept at 0.17 mL/mm<sup>2</sup>.

### 2.1.2. Synthesis of PdCu composite membrane at different coating bath temperatures

Activated supports were subjected to coating process at three different temperatures, 30 °C, 40 °C and 50 °C to determine the effect of coating temperature on membrane structure. Table 1 presents the coating bath compositions and conditions used in these experiments.

Table 1. Coating bath compositions and conditions.

	Pd-based bath	Cu-based bath
$\text{PdCl}_2$	5 g/L	-
$\text{CuCl}_2$	-	5 g/L
$\text{Na}_2\text{EDTA}$	10 g/L	10 g/L
$\text{NH}_4\text{OH}$ (25%)	650 mL/L	-
NaOH	-	5 g/L
$\text{N}_2\text{H}_4$ (1M)	20 mL/L	-
Formaldehyde (37%)	-	25 mL/L
pH	10-11	12-13

The simple experimental setup consisted of beaker, burette, pH meter and an ultrasonic water bath with mixing and temperature setting. The coating experiments were performed as two coating steps in Pd bath for 60 min, followed by two coating steps in Cu bath for 30 min at each temperature. The bath loading was kept at 0.2 mL/1mm<sup>2</sup> in each coating. The reducing agents were added to the coating bath step by step to prevent bulk phase accumulation. Annealing treatment was performed at 500 °C for 8 h.

### 2.1.3. Membrane preparation studies for the appropriate composition

40 °C was determined to be a suitable bath temperature in the experiments in which the temperature of the coating bath was examined as a parameter. Three experiments were performed to prepare the membrane layer matching the appropriate composition (Table 2).

**Table 2.** Experimental sets on the membrane preparation studies for the appropriate composition.

Set #	Coating time (minutes)		Number of coating step	Formaldehyde concentration (mL/L)	
	Pd-based bath	Cu-based bath		Pd-based bath	Cu-based bath
1	60	15	1	1	25
2	60	15	3	1	15
3	60	15	3	1	5

The amount of Cu was much higher than the appropriate value on the membrane surface even in the synthesis where the suitable bath temperature was defined to be 40 °C. For this reason, the coating process was performed once in each bath by reducing coating time in Cu bath (15 min). After determining the high amount of Cu on the surface again, the formaldehyde concentration was reduced to 15 mL/L (set 2) and 5 mL/L (set 3), and two different PdCu composite membrane synthesis were performed. In these experiments, firstly the supports were subjected to coating process in Pd bath for 60 min three times and then in Cu bath containing formaldehyde at the relevant amount for 15 min once. After all experimental sets, the supports were washed in pure water and dried at room temperature for a week, and then subjected to annealing process at 500 °C for 8 h.

## 2.2. Characterization Experiments

A SEM/EDS (FEI/Nova Nanosem 430) device was used in the structural evolution of the synthesized membrane. XRD (Rigaku, D/MAX 2200) and XPS (SPECS) were used for the analysis of the alloy phase structure.

## 2.3. Determination of the Hydrogen Flux

The membrane in the appropriate composition was obtained in the experiments carried out in the coating bath with 5 mL/L formaldehyde concentration. The experiments were conducted to determine the flux of pure hydrogen through this synthesized membrane. The pressure was increased by sending hydrogen gas to the upper part of the cell and analyzed under the atmospheric pressure in the lower part. The difference in pressure between the two faces of the membrane was adjusted at 8 kPa with the help of a valve placed at upper exit. Flux measurements were performed at room temperature. The hydrogen flow passing from the upper region to the lower region of the membrane was determined using a soap flowmeter.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Characterization Experiments

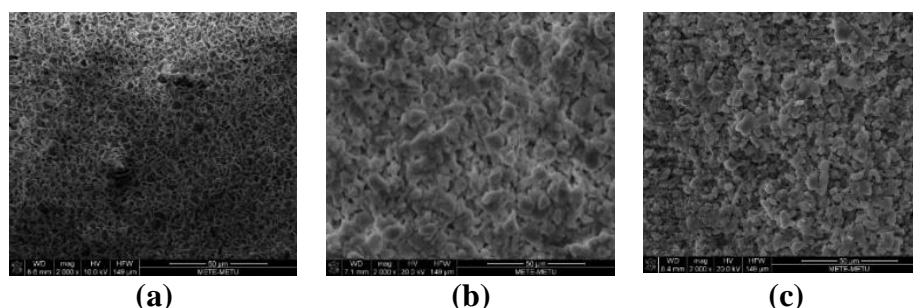
##### 3.1.1. Pre-treatments effects on support structure

Porous glass supports (average pore radius:  $1.3 \times 10^3$  nm, porosity: 0.46) supplied from Robu Glasfilter company were used in PdCu composite membrane synthesis experiments. Before the onset of membrane coating experiments, the porous supports were first subjected to pre-treatments of cleaning, modification with alumina and activation. The aim of modification with alumina was to increase the adherence between the coating and support material, eliminate the expansion differences in thermal processes and provide the membrane with a better selective permeability. The activation process was performed on the modified supports to initiate the EP coating process based on the autocatalytic reduction principle. Table 3 shows the surface compositions of the support, modified support and activated support determined using EDS analyses. As a result of modification with alumina, the Al/Si ratio on the support surface was 0.14 and this ratio increased more than 4 times compared to that prior to modification. After the activation process, it was shown that Pd could be loaded on the support surface.

**Table 3.** The surface compositions of the support, modified support and activated support (EDS analyses).

Compound	O	Na	Al	Si	Cl	Fe	Pd
Support	55.11	2.24	1.17	41.32	0.03	0.13	0.00
Modified support	61.45	1.90	4.56	31.87	0.20	0.02	0.00
Activated support	52.49	1.45	4.53	37.08	2.24	0.00	2.21

The surface SEM photographs of the support, modified support and activated support are presented in Figure 1, indicating that the support surface that was not subjected to any treatment had a fine-grained cavity structure. As for the modified support structure, it was observed that alumina grains formed a surface on top of each other fused at the surface. After the activation process, a less-small grained structure caused by Pd grains was observed to be loaded on the surface.



**Figure 1.** Surface SEM photographs (a): support (b): modified support (c): activated support.

### 3.1.2. Effects of the coating bath temperature on PdCu composite membrane structure

Coating experiments were initiated using the EP technique after pre-treatments were applied on the support. The coating experiments were performed at three different temperatures, 30, 40 and 50 °C, in order to analyze the effect of temperature on membrane structure. The coating experiments consisted of two coating stages each lasting 60 min in the Pd-based coating bath, followed by two coating stages each lasting 30 min in the Cu-based coating bath. PdCu composite structures synthesized were subjected to annealing process at 500 °C for 8 h in order to make the formation of the alloy possible. The surface compositions of PdCu composite membranes obtained at different temperatures using the EDS analyses are shown in Table 4, indicating that the lowest Pd ratio was in the membrane structure obtained in the coating bath at 30 °C. This was due to the low coating rate at 30 °C. Pd coating rate increased in the coating bath at 40 °C.

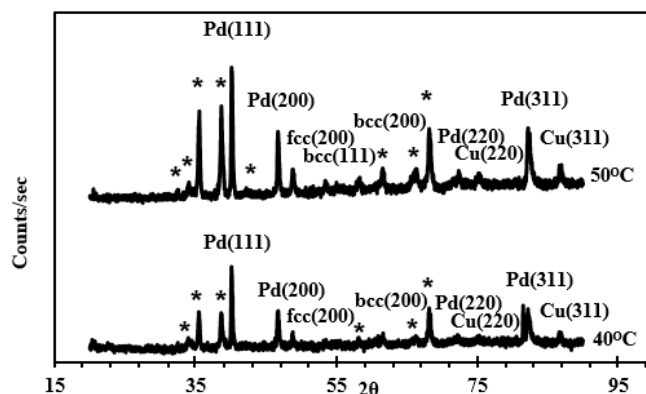
**Table 4.** The surface compositions of PdCu composite membrane synthesised at different temperatures (EDS analyses).

Compound	30 °C	40 °C	50 °C
O	9.23	7.64	18.48
Na	2.14	0.55	3.64
Mg	0.00	0.00	0.00
Al	0.21	0.06	0.23
Si	1.56	1.24	3.02
Cl	0.09	0.23	0.03
Ca	0.02	0.00	0.01
Fe	0.02	0.00	0.00
Cu	86.27	75.97	70.19
Zr	0.01	0.00	0.06
Pd	0.45	15.31	4.34

Pd was approximately 35 times more in the membrane synthesized in the bath at 40 °C than at 30 °C. Coating rate is known to increase with an increase in temperature, however, Pd was much lower in the membrane structure synthesized in the coating bath at 50 °C than at 40 °C, which was accounted for by the rapid accumulation at high temperature in the bulk phase rather than the support. The experimental observations indicate that there was a significant accumulation in vessel walls at 50 °C. The experiments show that the bath at 40 °C in the synthesis of the composite membrane using the EP technique is suitable. Figure 2 demonstrates XRD diffraction patterns of the membranes prepared at 40 °C and 50 °C at which Pd coatings were successful. Pd and Cu metal peaks in addition to PdCu alloy phase peaks (fcc and bcc phases) were observed in the membranes synthesized at both bath temperatures (Figure 2). The



bcc phase decreased in the membrane synthesized at 40 °C. The peak intensity of Pd and Cu metals at (111), (200), (220) planes was lower in the membrane structure synthesized at 40 °C than at 50 °C, indicating that the amount of alloy formation was high at 40 °C [21]. The decrease in the alumina peak intensities in the membrane synthesized at 40 °C shows that the coating was more successful at 40 °C than at 50 °C.



**Figure 2.** XRD diffraction patterns of PdCu composite membranes synthesized at 40 °C and 50 °C (\*:alumina).

### 3.1.3. Membrane layer preparation experiments at the appropriate composition

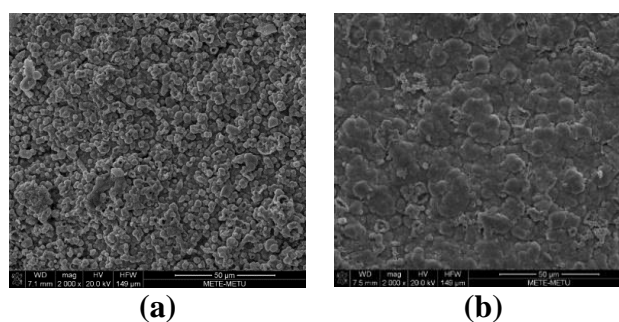
Based on the coating experiments performed at different coating bath temperatures, 40 °C was determined to be the most suitable bath temperature for PdCu composite membrane synthesis. Experiments were performed to prepare the membrane layer at the appropriate composition (70% Pd and 30% Cu by mass). For this purpose, the activated support was first coated in the Pd-based coating bath for 60 min once, and then in Cu-based coating bath for 15 min once. Annealing process was conducted to examine the effect of bath temperature under the same conditions (500 °C, 8 h). In the EDS analyses, the surface composition of the synthesized composite membrane was determined as 23% Pd and 77% Cu by mass. This result showed that the surface was coated with Pd and Cu at a significant amount. However, there was still much more Cu on the surface than the appropriate composition. Since high Cu content on the surface would negatively affect hydrogen transport, following experiments were performed to decrease its amount. For this purpose, the concentration of formaldehyde used as a reducing agent in Cu-based coating bath was reduced to 15 mL/L and 5 mL/L, and two different PdCu composite membrane synthesis experiments were performed. In these experiments, the supports were first subjected to Pd-based coating bath for 60 min three times, and then to Cu-based coating bath for 15 min once. The results of EDS analyses after annealing process (Table 5) indicate that the compositions consisted of 12% Pd and 88% Cu by mass on the composite membrane surface obtained in the coating bath containing 15 mL/L formaldehyde when the compounds except for

Pd and Cu were removed. 74% Pd and 26% Cu by mass were determined on the composite membrane surface obtained in the coating bath containing 5 mL/L formaldehyde. The composite membrane matching the appropriate composition was achieved with a decrease in the formaldehyde concentration to 5 mL/L.

**Table 5.** The surface compositions of PdCu composite membranes synthesized in different formaldehyde concentrations (EDS analyses).

Compound	Mass % (formaldehyde: 15mL/L)	Mass % (formaldehyde: 5mL/L)
O	8.66	23.79
Na	0.84	2.13
Mg	0.13	0.65
Al	0.37	2.03
Si	1.87	4.04
Cl	0.20	0.66
Ca	0.08	0.09
Fe	0.27	0.27
Cu	76.61	16.94
Zr	0.51	0.88
Pd	10.46	48.52

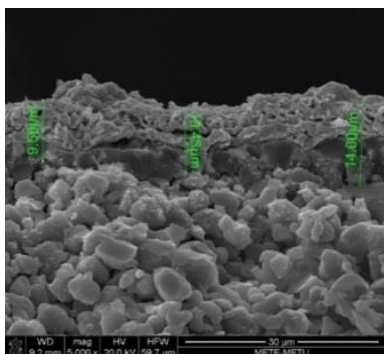
The surface SEM photographs of PdCu composite membranes synthesized at different formaldehyde concentrations are shown in Figure 3. With the synthesis of the membrane structure at the formaldehyde concentration of 15 mL/L, the surface displayed a granular structure while no integration and fusion was observed between the grains. When the membrane structure was prepared at the formaldehyde concentration of 5 mL/L, the surface grains merged and created a firm layer.



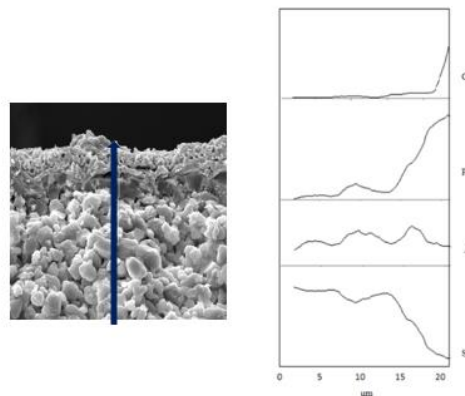
**Figure 3.** Surface SEM photographs of PdCu composite membranes synthesized at different formaldehyde concentrations (a):15mL/L (b): 5mL/L.

Figure 4 presents the cross-sectional SEM photograph of PdCu composite membrane prepared at the formaldehyde concentration of 5 mL/L. The thickness of the upper layer covered was approximately 11  $\mu\text{m}$ . The tighter structure with bigger grains under the tight and small-grained structure on the surface was the alumina layer. Figure 5 shows Si, Al, Pd and Cu spectra of the membrane cross-section. Si peak intensities gradually decreased and this decrease was sharp at

the coating thickness of 11  $\mu\text{m}$ . Al spectrum started at a particular level as it was also present in the support structure. Pd peak intensities started to increase in activated support region and reached the highest value in the coating thickness. Cu co-existed with Pd metal along the coating thickness. The decrease in the Pd peak intensities was explained by the dilution that resulted from the formation of the alloy.

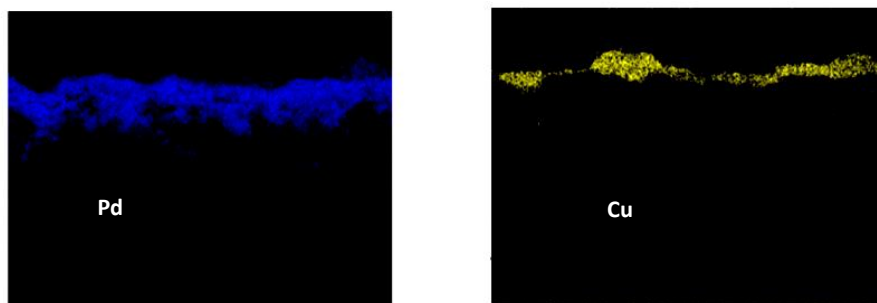


**Figure 4.** The cross-sectional SEM photograph of the PdCu composite membrane synthesized at formaldehyde concentration of 5 mL/L.



**Figure 5.** Metal spectra in the PdCu composite membrane cross-section synthesized at formaldehyde concentration of 5 mL/L.

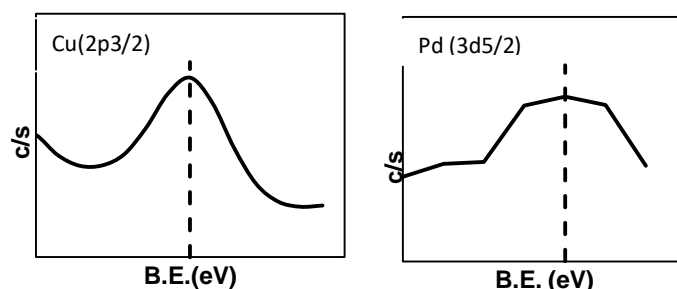
The distribution of Pd and Cu metals in the cross-section of the synthesized PdCu membrane was determined using EDS analyses (Figure 6). Figure 6 indicates that there was a Cu layer that did not exhibit regular distribution on the dense Pd layer. The alloy structure where Pd and Cu grains co-existed was observed under this layer.



**Figure 6.** The mapping on the cross-section of PdCu composite membrane synthesized in the bath with 5 mL/L formaldehyde concentration (EDS analyses).

XPS curve of the PdCu composite membrane obtained from the synthesis experiments carried out with 5 mL/L formaldehyde concentration is given in Figure 7. The expected Cu ( $2p_{3/2}$ ) peak at 932.7 eV for pure Cu metal was predicted at 931.0 eV with a 1.7 eV shift. Similarly, a shift of 0.81 eV was detected for Pd ( $3d_{5/2}$ ) peak expected at 335 eV for pure Pd metal. The shifts observed for both metals supported the formation of the alloy shown by XRD results. The formation of metallic bonds for the alloy caused the redistribution of the electrons between sp and d levels of Cu. The empty orbital of the original Cu became partially full with the formation

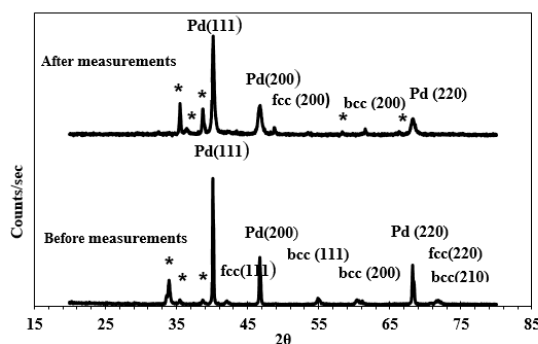
of the alloy. Having been stored on Pd surface during annealing processing, Cu diffused on the Pd layer, and PdCu alloy structure was formed.



**Figure 7.** XPS curve of PdCu composite membrane synthesized at formaldehyde concentration of 5 mL/L.

### 3.2. Determination of the Hydrogen Flux Value in the Synthesized Membrane

The appropriate membrane composition was achieved by working in the Cu bath with 5 mL/L formaldehyde concentration. Hydrogen flux measurements were carried out on the membrane synthesized under these conditions. The measurements were performed at room temperature by creating a pressure difference of 8 kPa between the two sides of the membrane. Cracks occurred in the structure of the membrane after determining a flux value of  $1.9 \times 10^{-6}$  mol/cm<sup>2</sup>s for the transport of pure hydrogen through the membrane. XRD analyses were performed before and after flux measurements in order to determine the reason for deformation (Figure 8). An fcc (200) structure was formed after the flux measurements. The peaks signifying the fcc (111), bcc (210) and fcc (220) structures were lost after the measurement. It was concluded that these lost structures formed the fcc(200) structure by transforming. Significant decreases occurred in the peak intensity of Pd(111), Pd(200) and Pd(220) after the flux measurements. Pd metal peaks also contributed to the formation of fcc(200) structure. Crack formation was explained by the changes in the membrane structure.



**Figure 8.** XRD diffraction patterns of PdCu composite membrane before and after the hydrogen flux measurements (\*: alumina).

#### 4. CONCLUSION

The use of pure Pd membranes with high hydrogen selectivity is limited due to their fragility and poisoning problems. Studies on eliminating these problems by using the alloy of palladium with different metals (Ag, Cu, Au, Ni, etc.) have gained importance. In this study, porous glass supports were coated with PdCu alloy layer using the EP technique after being modified with alumina. Minor changes made in coating bath temperature significantly affected the membrane structure. While very low coating rate was observed at 30 °C, coating occurred in vessel walls and in bulk phase rather than the support with high coating rate observed at 50 °C. The most suitable coating rate value was determined in the coating bath of 40 °C. Membrane layer matching the appropriate phase structure (fcc+bcc) and composition was obtained. Deformation was observed in the membrane layer after hydrogen flux measurements. XRD diffraction patterns of the membrane before and after the flux measurements were compared in order to determine the reason for deformation. The structures of the fcc (111), bcc (210) and fcc (220) planes that existed in the membrane structure before made the formation of fcc (200) phase structure possible. The structures of Pd (111), Pd (200) and Pd (220) planes contributed to the formation of fcc (200) structure. It is suggested that the synthesized membrane contact hydrogen during synthesis before being used in hydrogen flux measurements. In this way, deformation caused by phase transformation can be prevented.

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