

Effect of anode electrocatalyst for direct hydrazine fuel cell using proton exchange membrane

Koji Yamada ^{a,1}, Kazuaki Yasuda ^{b,*}, Hirohisa Tanaka ^a,
Yoshinori Miyazaki ^b, Tetsuhiko Kobayashi ^b

^a Department of Materials R&D, Materials Engineering Division, Daihatsu Motor Co. Ltd., 3000 Yamanoue, Ryuo-cho, Gamo-gun, Shiga 520-2593, Japan

^b Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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Abstract

Hydrazine was examined as a fuel in a direct-liquid-fueled fuel cell that uses proton exchange membrane (PEM) such as Nafion®. Different kinds of noble metals were examined as anode electrocatalysts for direct hydrazine fuel cells (DHFCs). In DHFC using platinum or palladium as the anode electrocatalyst, more than 1 V of cell voltage was obtained in the low-current density region. The *I*–*V* characteristics changed drastically depending on the kind of anode electrocatalyst used. Compositions of the exhaust materials from each electrode were analyzed to investigate the reaction occurring at the electrodes. The analysis revealed that the catalytic decomposition reaction of hydrazine proceeded further than the electro-oxidation reaction on the anode side using rhodium or ruthenium.

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1. Introduction

Fuel cells are attracting increasing interest as the most promising clean power source because the theoretical energy efficiency of fuel cells is higher than internal combustion engines. In particular, proton exchange membrane fuel cells (PEMFCs) using an ionomeric membrane for the electrolyte are suitable as a power source for vehicles and mobile electric appliances because of their high power density at low operating temperatures. Although pure hydrogen is an ideal fuel for PEMFC from the viewpoint of cell performance, high-density storage and handling of hydrogen are problems when using pure hydrogen as a fuel. Direct-fueled fuel cell systems, where a liquid fuel with high energy density and ease of handling is directly supplied to the fuel cell without reforming to hydrogen, have been proposed and studied using methanol as a fuel. However, the efficiency and power output of direct methanol fuel cells (DMFCs) are low because of severe poisoning of the anode catalyst by reaction

intermediates such as CO and methanol crossover through the electrolyte membrane [1].

Hydrazine (N₂H₄) is an ideal fuel for a direct fuel cell system because it does not exhaust environmentally loading materials such as CO₂ and the thermodynamic reversible potential for the direct hydrazine fuel cell (DHFC) is 1.56 V [2]. In addition, studies have shown that the hydrazine electro-oxidation process does not suffer from any poisoning effect [3,4]. Hydrazine FC was investigated intensively in the 1960s–1970s, as an alkaline fuel cell (AFC) using liquid alkaline electrolyte [5–7]. The Governmental Industrial Research Institute, Osaka (GIRIO, now known as the National Institute of Advanced Industrial Science and Technology, Kansai), and Daihatsu Motor Co. Ltd., produced a hydrazine–air fuel cell vehicle experimentally in 1972, and driving experiments were carried out [8]. The recent progress of PEMFC using perfluorosulfonic acid membranes has been remarkable. To our knowledge, however, no study of DHFC using current PEMFC technology has been reported. In the previous paper, we reported that DHFC using a proton exchange membrane (PEM) showed much higher cell voltage than DMFC especially in the low-current density region, and noted that the development of a more effective anode catalysts was an important task

* Corresponding author. Tel.: +81-72-751-9653; fax: +81-72-751-9629.

E-mail addresses: k-yasuda@aist.go.jp (K. Yasuda),

koji_yamada@mail.daihatsu.co.jp (K. Yamada).

¹ Tel.: +81-748-57-1685; fax: +81-748-57-1064.

[9]. In order to design a suitable anode, this report concentrates on the characteristics of various noble metals as anode electrocatalysts for PEM type DHFC.

As for anodes of hydrazine fuel cells using an alkaline electrolyte, Raney nickel [8], nickel boride [6] and silver [7] were reported as the electrocatalyst. Since PEM such as Nafion[®] has a highly acidic character, stable noble metals are the preferred catalyst for PEMFC electrodes. This study focused on four kinds of noble metals, namely, platinum (Pt), palladium (Pd), ruthenium (Ru) and rhodium (Rh). Pt and Pd have often been studied to determine the anodic oxidation of hydrazine and were used as the anode catalyst in previous prototypes of direct hydrazine AFCs [2,7]. Electroless deposition of Ru was also used as the anode activation in the report of Shell Research Ltd. [8]. Higher electrocatalytic activity of Rh for hydrazine oxidation was seen in a study using single-crystal electrodes [10].

2. Experimental

2.1. Anode electrocatalysts

Four kinds of unsupported powder catalyst, platinum (purity: 99%, specific surface area: 35 m²/g), rhodium (purity: 86.6%, specific surface area: 123.8 m²/g), palladium (purity: 96.5%, specific surface area: 34.1 m²/g) and ruthenium oxide (purity as ruthenium: 64.9%, specific surface area: 140 m²/g), were purchased from Tanaka K.K. In order to avoid the effects of difference in specific surface area, these catalysts were heat treated in an oven under a nitrogen atmosphere. The specific surface areas of all catalysts were adjusted to about 7 m²/g (Pt: 6.3 m²/g, Pd: 5.9 m²/g, Ru: 8.3 m²/g, Rh: 10.2 m²/g). The specific surface areas were determined by the BET method using nitrogen as the adsorbate.

To examine the effect of the specific surface area of a catalyst, anode Pt catalysts with various specific surface areas, from 24.5 to 1.3 m²/g, were prepared with heat treatment as described above. Samples were abbreviated to Pt(1.3), Pt(6.3), Pt(12.4), Pt(24.5), and Pt(35), respectively, expressing their values of specific surface areas.

2.2. Membrane electrode assembly (MEA) preparation

The catalyst was mixed with 5 wt.% Nafion[®] solution (Aldrich) at the fixed ratio. The mixture was stirred for over 2 h, and then it was thoroughly dispersed in an ultrasonic bath to make the catalyst ink. For the preparation of MEA, the prepared ink was directly sprayed onto a Nafion[®] 117 (E.I. Du Pont de Nemours and Company) electrolyte membrane, after the viscosity had been moderately adjusted in ethanol. Carbon black supported 60 wt.% platinum catalyst (Tanaka K.K.) was applied to the cathode, and formed into an electrode using a similar method to that for the anode. Both electrodes were fixed to the membrane by applying the

electrode to both sides of the membrane and leaving at room temperature for 30 min, and then, hot-pressing for 5 min at 120 °C. A sintered titanium fiber was used as the current collector on the anode side. A carbon cloth having a thin gas diffusion layer was used on the cathode side.

2.3. The measurement of cell performance

The experimental details involved in this measurement have already been reported [9]. A prepared MEA, with a round shaped working electrode area of 10 cm², was inserted in a single cell to measure the cell performance. An aqueous solution of hydrazine hydrate (N₂H₄·H₂O) of 10 wt.% was supplied to the anode at the flow rate of 2 ml/min, and oxygen gas humidified at 80 °C was supplied to the cathode at the flow rate of 400 ml/min. Fuel utilization ratio was low in order to supply enough amount of hydrazine to the anode. The applied shape of the flow-fields was serpentine for the anode and comb-shaped for the cathode. Before measuring DHFC performance, the cell was operated for 1 h with pure hydrogen fuel, following 1-h operation by 10 wt.% N₂H₄·H₂O as fuel. The cell temperature was controlled at 80 °C. The operating pressures on the anode and cathode side were 0.1 and 0.15 MPa, respectively.

2.4. The composition analysis of the exhaust materials

To investigate the reaction during cell operation, compositions of the exhaust from both electrodes were analyzed in various conditions. The gas composition (hydrogen, oxygen, nitrogen) was measured by gas chromatography. The water-soluble components (ammonia and hydrazine) were measured by ion chromatography and absorption spectrophotometry, respectively. Results are given in 10⁻⁶ mol/min units.

3. Results and discussion

Fig. 1 compares the current–voltage (*I*–*V*) characteristics of DHFCs employing four kinds of anode made of different electrocatalysts. These electrodes include the same loading amount of noble metal catalyst with almost the same specific surface area. This figure shows the different *I*–*V* characteristics when using different kinds of catalyst metal. The high open-circuit voltages over 1 V were observed for DHFC using Pt and Pd. The Pd electrode was found to have a similar trend to the Pt electrode in the dependence of cell voltage on current density. Using Pd, the cell voltage was lower than using Pt and decreased more rapidly with increasing the current density in the low-current density region below 40 mA/cm². The open-circuit voltage of the cell using Rh was 0.8 V, the lowest value of all four electrodes. However, the cell using Rh gave the lowest cell-voltage loss with increase of current density and the highest cell voltage at current densities over 70 mA/cm². The poorest performance was obtained in

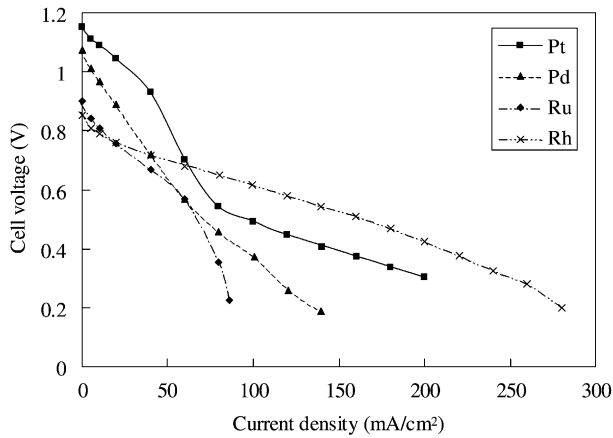


Fig. 1. Effect of the anode noble catalyst in a direct hydrazine fuel cell. Loading of anode/cathode catalysts = 2/3 mg/cm².

the cell using Ru electrocatalyst. The open-circuit voltage was low and the cell voltage showed the lowest value at almost all current densities. This difference in the shape of I - V curve with the kind of anode metal is a unique character of PEM type DHFC in comparison with other PEMFC.

To examine the reactions in DHFC with different anode catalyst metals, the composition of the exhaust from both electrodes under DHFC operation was analyzed. Fig. 2 shows anode exhaust composition from each cell under operation at the current density of 20 mA/cm². Evolution of hydrogen and ammonia other than nitrogen were observed. This fact indicates that the supplied hydrazine was catalytically decomposed on the anode. As described in the previous paper, hydrazine is not only electrochemically oxidized but also catalytically decomposes into nitrogen on the anode

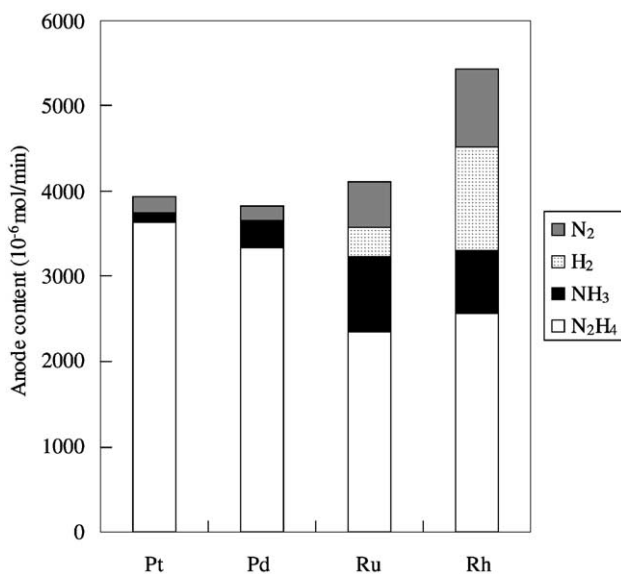


Fig. 2. The content of exhaust materials from the anode electrode with different anode catalysts. Current density = 20 mA/cm², anode/cathode pressures = 0.1/0.1 MPa.

by side reactions as shown in Eqs. (1) and (2) at the anode of DHFC.



This catalytic decomposition not only decreases the fuel utilization but also seems to lower the cell voltage because the hydrogen that was generated by decomposition reaction contributed to the anode reaction. From analysis of the anode exhaust composition of the cells using Pt or Pd, it was found that a large amount of unreacted hydrazine was exhausted and a small amount of nitrogen, ammonia and almost no hydrogen was detected. These results clearly show that electro-oxidation of hydrazine was dominant in the cells using Pt or Pd. On the other hand when Rh or Ru were used, the ratio of unreacted hydrazine decreased and the ratio of the products by catalytic decomposition increased. From these results it was found that the rate of catalytic decomposition of hydrazine is much less on Pt or Pd than on Rh or Ru. The ratio of unreacted hydrazine in anode exhaust was in the order of Pt > Pd \gg Rh > Ru. Although the trend of Pd is similar to Pt, a larger amount of ammonia was evident in anode exhaust, which indicates that the catalytic decomposition rate of Pd is larger than that of Pt. Using Rh or Ru, a large amount of catalytically decomposed product was evident, which suggests catalytic decomposition was dominant. The decrease of hydrazine concentration by decomposition and the electro-oxidation of the evolved molecular hydrogen at the anode reduce the cell voltage of the cells using Rh or Ru in the low-current density region. It was also found that the rate of hydrogen evolution reaction (1) was larger than ammonia evolution reaction (2) in the cell using Rh. On the other hand, the rate of reaction (2) was larger than reaction (1) in the cell using Ru. So, the order of the amount of reaction products in anode exhaust was Rh > Ru \gg Pd > Pt. The generated ammonia is considered not to react at the anode because of fairly low electroactivity at the operating temperature of PEMFCs [2].

Fig. 3 shows cathode exhaust composition from each cell under operation at the same current density in Fig. 2. A large amount of unreacted oxygen was omitted in this figure. Nitrogen and ammonia were also detected from the exhaust on the cathode side. Concerning the results of the anode exhaust measurement and the previous paper [9], it seems that nitrogen was produced at the cathode by oxidation of the hydrazine that permeated through the membrane to the cathode, and the ammonia is regarded as being formed in the anode and having permeated through the membrane. The permeated hydrazine is easily oxidized into nitrogen and water at the cathode. On the other hand, the permeated ammonia seems not to be reactive at the cathode and can be exhausted without decomposition because the oxidation rate of the ammonia is low at this cell temperature. At the cathode of DHFC, the hydrazine that permeated through the membrane reacts on the cathode catalyst and reduces the cath-

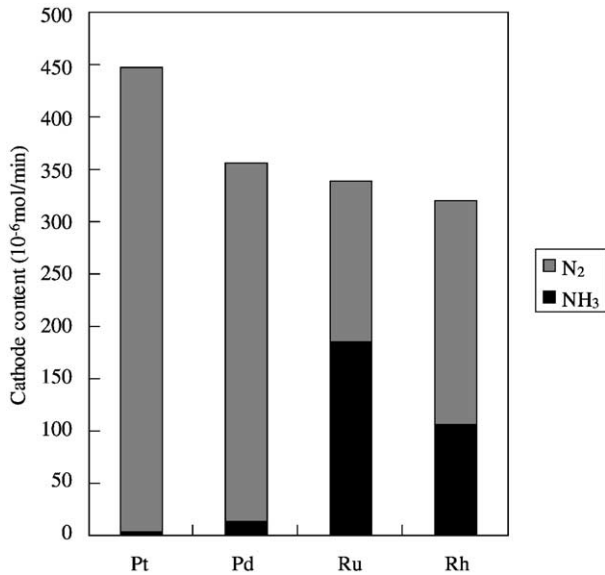


Fig. 3. The content of exhaust materials from the cathode electrode with different anode catalysts. Conditions as in Fig. 2.

ode potential. The loss of cell voltage by the formation of mixed potential at the cathode due to the fuel permeation is a significant problem in direct-fueled fuel cells using PEM. Especially for DHFC using PEM such as Nafion[®], hydrazine permeation increases with increase of current density as shown in the previous results [9]. The order of the nitrogen amount in cathode exhaust was Pt > Pd > Rh > Ru, which is the same order of the ratio of hydrazine in anode exhaust. This fact also suggests that the amount of nitrogen in cathode exhaust relates to the crossover rate of hydrazine.

Fig. 4 shows the dependence of I - V characteristics of the cell using Pt on the flow rate of oxygen at the cathode. Fig. 5

shows the dependence of the cell using Rh. The voltage of the cell using Pt remarkably depended on the flow rate of oxygen. The increasing flow rate reduced the voltage loss. On the other hand, the cell voltage did not depend on the flow rate using Rh. This fact also shows that the effect of crossover is much greater on the cathode of the cell using Pt than that using Rh.

From the results in Figs. 2–5, the crossover rate of hydrazine was low in Rh or Ru anode because of hydrazine decomposition on the anode catalyst. Since the hydrazine crossover rate in the cells using Rh or Ru is lower than that using Pt or Pd, the lower voltage of the cells using Rh or Ru in the low-current density region can be attributed not to the cathode but to the anode reaction. These results indicate that Pt is the most effective anode catalyst for operation at high efficiency in DHFC of all these electrocatalysts. However, reduction of the crossover effect is important in the operation of the cell using Pt. In particular, the phenomena of the cell voltage loss with increase of current density using the Pt electrode may relate to the increase of hydrazine crossover [9] and this problem should be overcome.

Fig. 6 shows the dependence of the cell performance on the specific surface area of the Pt anode electrocatalyst in DHFC. The high open-circuit voltage, over 1.1 V, was obtained on the samples of Pt(12.4) and Pt(6.3). Pt(1.3), having a minimum surface area of 1.3 m²/g in this study, showed deterioration of cell performance and decrease in open-circuit voltage to 0.88 V. Only Pt(6.3) showed high cell voltage in the low-current density region. Fig. 7 shows the dependence of the cell voltage at each current density on the specific surface area of Pt. In the low-current density region (~40 mA/cm²), there is a peak of cell voltage at the specific surface area, 7 m²/g. At the specific surface area below this

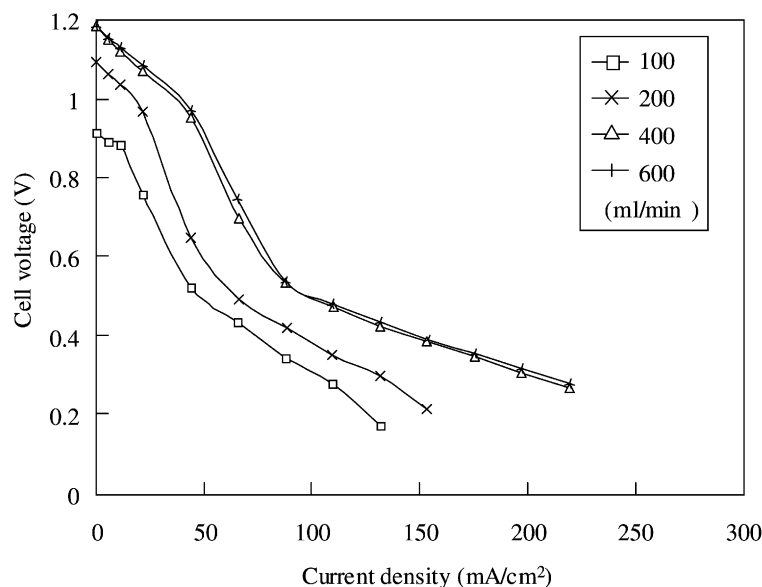


Fig. 4. Dependence of the cell voltage of the direct hydrazine fuel cell using Pt anode on the cathode flow rate of oxygen.

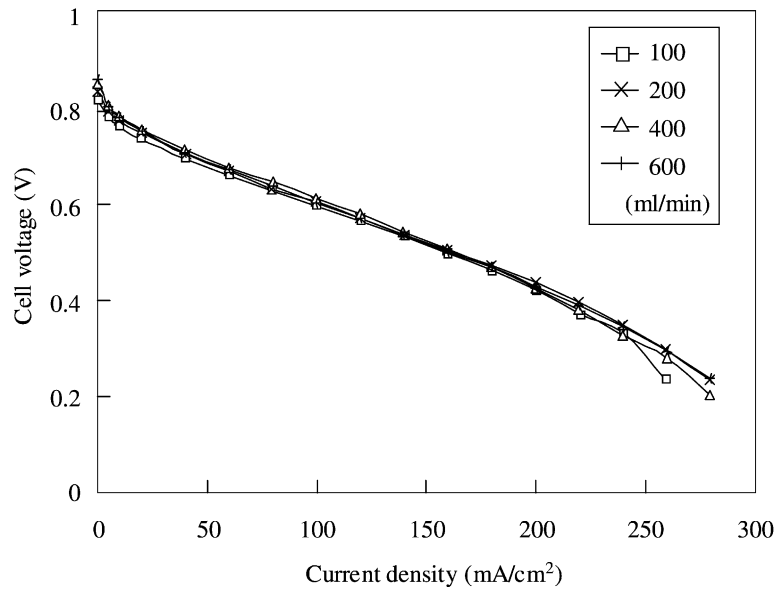


Fig. 5. Dependence of the cell voltage of the direct hydrazine fuel cell using Rh anode on the cathode flow rate of oxygen.

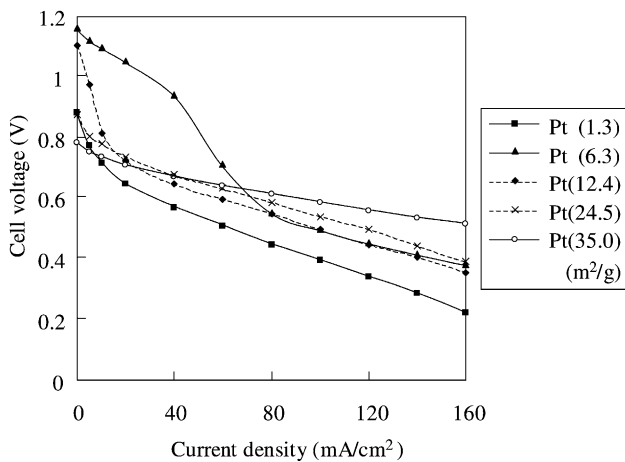


Fig. 6. Dependence of the cell performances on the specific surface area of Pt anode catalyst in direct hydrazine fuel cell.

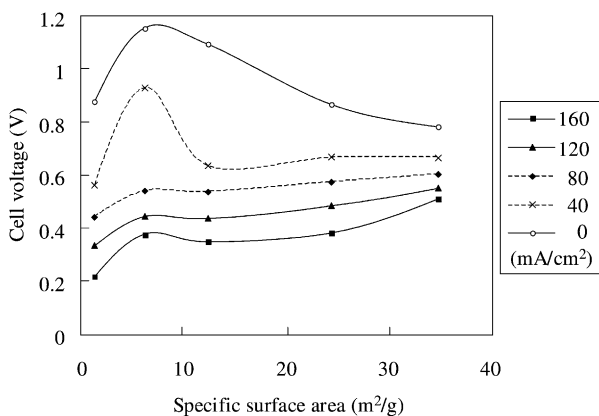


Fig. 7. Dependence of the cell voltage at each current density on the specific surface area of Pt anode catalyst in direct hydrazine fuel cell.

value, electrocatalytic activity is considered insufficient because of low surface area. At the specific surface area over this value, the catalytic decomposition rate increases and the cell voltage decreases like the cells using Rh or Ru. This was supported by comparison between the results of anode exhaust analysis of the cell using high surface area ($35 \text{ m}^2/\text{g}$) Pt and that using low surface area ($7 \text{ m}^2/\text{g}$) Pt electrocatalyst. As is seen in Fig. 7, even Pt which is the most effective anode catalyst for generation of high cell voltage over 1 V, the specific surface area of the catalyst has to be controlled. Further study is needed to determine the reason for such change of reaction selectivity.

4. Conclusions

This study compared four kinds of noble metals as anode electrocatalysts in DHFC using a Nafion[®] membrane.

- The trend of the cell voltage in the low-current density region was $\text{Pt} > \text{Pd} > \text{Rh} \approx \text{Ru}$ and high voltage over 1 V was obtained when using Pt or Pd as the anode electrocatalyst.
- The order of catalytic decomposition rate was $\text{Ru} > \text{Rh} \gg \text{Pd} > \text{Pt}$. It is considered that the dominant catalytic decomposition of hydrazine affects the anode reaction and reduces the cell voltage in the cell using Rh or Ru.
- Judging from the high electrochemical reactivity and lower decomposition rate, Pt was the most effective anode catalyst for operation at high efficiency in DHFC of all the electrocatalysts studied in this report.
- There was a peak cell voltage at the specific surface area of the Pt electrocatalyst, $7 \text{ m}^2/\text{g}$.

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