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Effect of hydrogen partial pressure on a polymer electrolyte fuel cell performance

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Abstract−We first investigated the effect of partial pressure of hydrogen (H_2) on the performance of polymer electrolyte fuel cells (PEFCs) by controlling the ratio of hydrogen and nitrogen (N_2). The cell performance with Pt/C anode was significantly decreased with reduction of the partial pressure of H_2 in the presence of carbon monoxide (CO), while the performance variation was negligible in the absence of CO. Severe CO poisoning on Pt/C electrode at low partial pressure of H_2 might be attributed to the hindering effect by N_2 and CO. On the other hand, PtRu/C anode showed consistent power performance even at low partial pressure of H_2.

Key words: PEM Fuel Cells, Reforming Gas, H_2/N_2 Ratio, CO, Recovery Test

INTRODUCTION

There have been several alternative portable energy systems of thin film battery, supercapacitors, solar cells and fuel cells for the operation of mobile devices such as cellular phones, lap-top computers, wheelchairs, robots and electric scooters [1-10]. Among the fuel cells, we could develop the following four types; 1) polymer electrolyte fuel cells with a micro reformer of hydrocarbons (micro-PEFCs), 2) PEFCs applying hydrogen from chemical hydride (e.g., $NaBH_4$), 3) direct liquid fuel cells (formic acid, L-ascorbic acid, methanol, ethanol), and 4) micro solid oxide and carbon fuel cells. In micro-PEFCs, hydrogen containing low concentrated CO produced *via* steam reforming or partial oxidation of methanol/methane or other hydrocarbons (C_nH_m) requires noble metals and metal alloys as anode catalysts, since CO even below 10 ppm could cause severe energy dissipation and very low catalytic utilization [11-18]. Note that the product from micro reformer of hydrocarbons (C_nH_m) is composed of CO, N_2, H_2, H_2O among others. As noted above, in addition to the presence of CO in the reformed product, another important factor would be the partial pressure of H_2 and N_2 in the gaseous mixture, as these may significantly affect the performance of the PEFCs. Also, we should consider another important factor of partial pressure of hydrogen and nitrogen in the presence of CO.

In this work, we describe the comparative power performance in relation to various H_2/N_2 ratios in PEFCs experiments using both Pt/C and PtRu/C anode.

EXPERIMENTAL

Two anodes of Pt/C and PtRu/C were prepared by spraying the catalyst slurry of 0.3 mg/cm^2 (40% Pt/C, Tanaka), 0.6 mg/ cm^2 (40% PtRu/C, E-tek), respectively. Pt/C of 0.3 mg/cm^2 (40% Pt/C, Tanaka) was used as cathode. SGL 10BC was adopted as diffusion media of anode and cathode which have 5% Teflonized carbon microporous layer for easier access of oxygen and easy removal of produced water. Then, additional ionomer solution was sprayed onto the catalyst layer of each electrode in order to decrease the contact resistance with the polymer electrolyte membrane (Nafion 212, Dupont). Membrane-electrode assemblies (MEAs) of 9 cm^2 were prepared by hot pressing with Nafion 212 at a temperature of 140 °C and a pressure of 30 kg$_f$/cm^2 for 5 min.

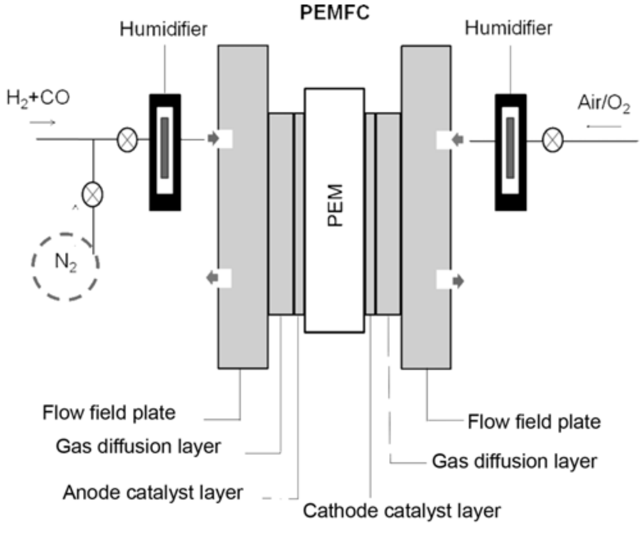

Fig. 1. Schematic of fuel cell setup with H_2/N_2 ratio (0.35-1.0) and N_2 gas supplied into the anode inlet. (a) H_2/N_2 ratio=1.0, (b) H_2/N_2 ratio=0.6, (c) H_2/N_2 ratio=0.35. Cell temperature and relative humidity were at 70 °C and RH 100%, respectively. The reaction gases were supplied through a humidifier and a mass flow controller from H_2/N_2 mixture and air tanks. The reactant gases flowed in accordance with stoichiometry value (1.1-1.5 and 2.5 stoics for H_2/N_2 and air).

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As shown in Fig. 1, hydrogen with nitrogen gas was supplied into the anode inlet by mass flow controller. Cell temperature and relative humidity were fixed at 70 °C and RH 100%, respectively. The reactant gases of H_2/N_2 and air flowed in accordance with stoichiometry value of (1.2/2.5 stoics for H_2/N_2 and air) loaded current.

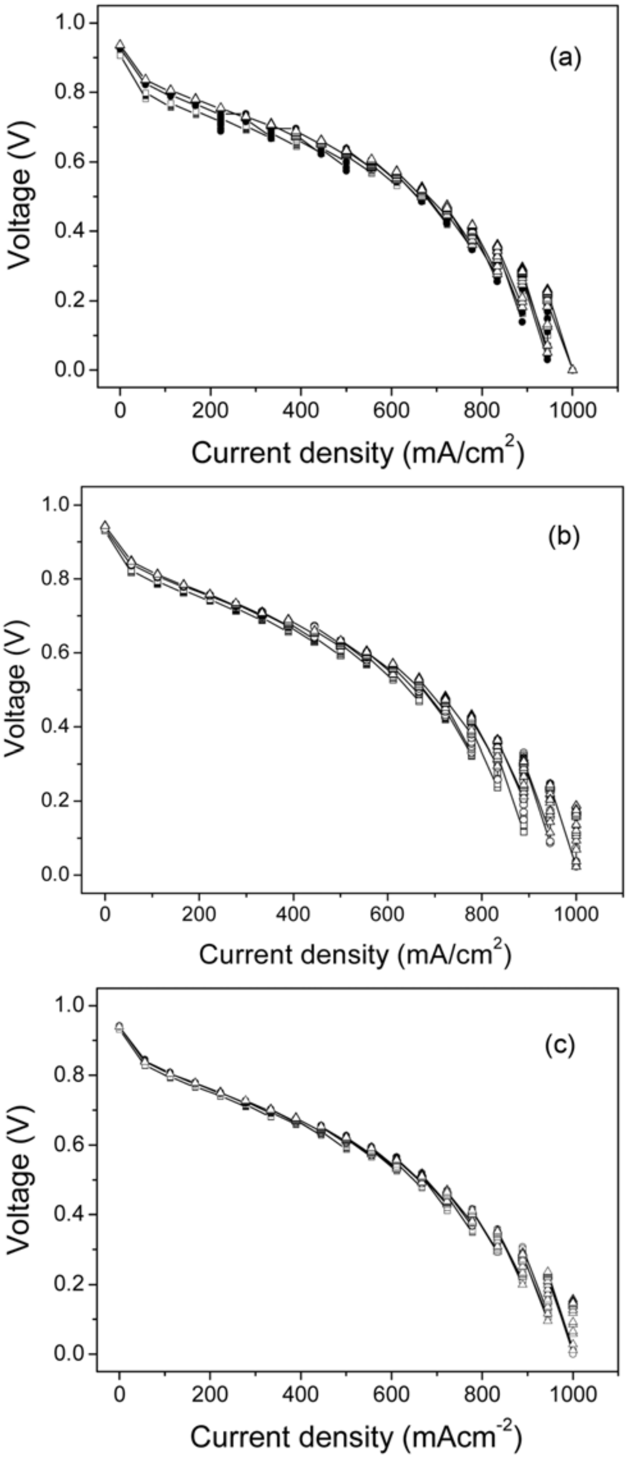

Fig. 2. Polarization curves of Pt/C of various H_2/N_2 ratio with N_2 gas supplied into the anode inlet. (a) H_2/N_2 ratio=1.0, (b) H_2/N_2 ratio=0.6, (c) H_2/N_2 ratio=0.35. Stoichiometry value of H_2/N_2 (■)=1.1 , (●)=1.2 and (▼)=1.5.

Current-voltage polarization curves were galvanostatically measured by using a fuel cell test station (Scitech Korea Inc). Both consecutive CO recovery test and durability test were performed and polarization curves were obtained at various H_2/N_2 partial pressures.

RESULTS AND DISCUSSION

Fig. 2 shows the polarization curves of Pt/C anode and Pt/C cathode under different H_2/N_2 ratios and stoichiometric values (based on H_2) in the absence of CO. The cell performance does not show any significant difference with changes in H_2/N_2 ratio and stoichiometric values of hydrogen to 1.1 (■), 1.2 (●) and 1.5 (▼). This result indicates that the performance is not significantly affected by pure H_2/N_2 ratio as well as stoichiometry value.

The effect of CO on the performance of Pt/C anode catalysts was tested with a gas mixture of H_2 and N_2 as shown in Fig. 3. The cell performance in Fig. 3(a) exhibited less activity than that of 10 ppm CO (see Fig. 3(b)) in all partial pressure of hydrogen, which might

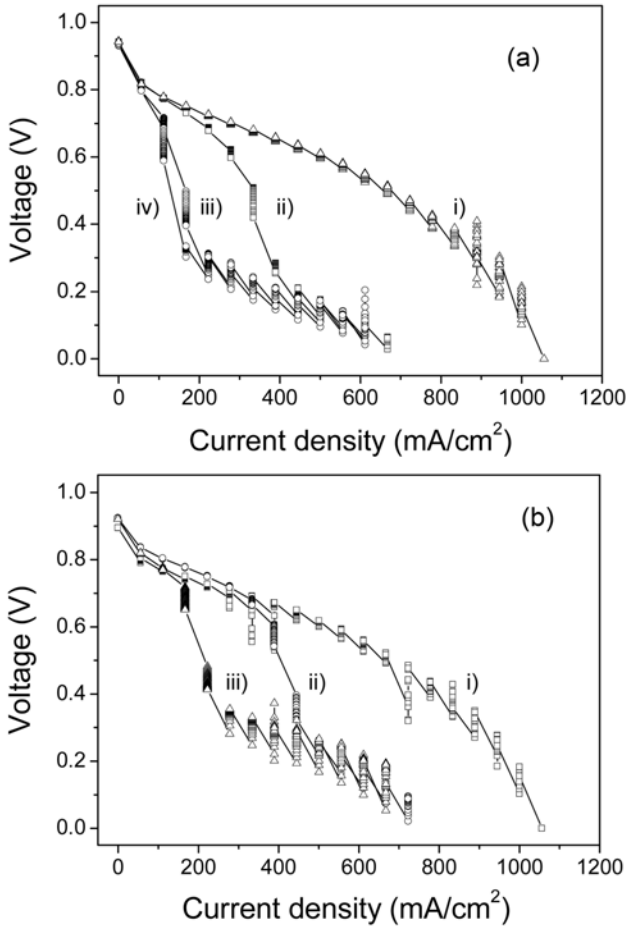

Fig. 3. Polarization curves of Pt/C various H_2/N_2 ratio with (a) 100 ppm CO concentrations and (b) 10 ppm CO concentrations. (a) 100 ppm CO concentrations; i) H_2/N_2 without CO concentration ii) H_2/N_2=1.0, iii) H_2/N_2=0.6, iv) H_2/N_2=0.35. (b) 10 ppm CO concentrations; i) H_2/N_2=1.0, ii) H_2/N_2=0.6, iii) H_2/N_2=0.35. The measurement is conducted at 70 °C. Both anode and cathode=100% humidification. Flow rate of H_2/N_2=1.2 and air=2.5, respectively (stoich).

have resulted from severe poisoning of Pt surface. The performance of a single cell was significantly decreased when H_2/N_2 ratio was decreased in the presence of CO. As shown in Fig. 3(a), the power performance of the H_2/N_2 ratio (iv) of 0.35 was lower than the H_2/N_2 ratio (iii) of 0.6 at 0.4 V, and we observed similar results in Figs. 3(b)-(ii) and 3(b)-(iii), as also shown in Table 1. It indicates that this performance was more critically affected by CO poisoning itself at high saturated CO. Fig. 3(a)-(ii) shows that even if the ratio of 1.0 is applied, the energy dissipation is already 60% compared to the performance obtained by applying pure hydrogen gas. It indicates that the performance was more affected by blocking Pt active surface area unlike the results shown in Fig. 3(b), which was caused by N_2 hindering effect at low saturated CO. An increase of moles of N_2 plays a role in increasing its partial pressure according to the kinetic theory (1) [19].

Table 1. Current density of Pt/C with various H_2/N_2 ratio with two concentrations of 10 ppm and 100 ppm CO at 0.4 V, which are reproduced from Fig. 3. The measurement is conducted at 70 °C. Both anode and cathode=100% humidification. Flow rate of H_2/N_2=1.2 and air=2.5 (stoich)

H_2/N_2 ratio	10 ppm CO	100 ppm CO
1.0	800 mA/cm^2	333 mA/cm^2
0.6	445 mA/cm^{-2}	167 mA/cm^2
0.35	230 mA/cm^2	160 mA/cm^2

$$P=nMc^2/3V \quad (1)$$

where n is the mole, M is the molecular weight, c is the root mean square velocity and V is the volume.

The internal total pressure of a H_2/N_2 ratio with 0.35 is relatively higher (Fig. 3(b)-iii) than others (Fig. 3(b)-i and 3(b)-ii), which could result in more decreased cell performance. As expected, Fig. 3(b) shows that the current density was decreased with the reduced H_2/N_2 ratio in the operating potential of 0.4V. This means the current density increased with the increase in the H_2/N_2 ratios. In the operating potential of 0.4 V, a 71% and 51% reduction of current density was observed with a gas mixture of H_2/N_2 ratio from 1.0 to 0.35 in the presence of CO concentration of 10 and 100 ppm, respectively.

Another interesting phenomenon, which is practically undesirable, is the saw-tooth shape behavior shown in all of the polarization curves. The oscillation seems to have something to do with inhomogeneous distribution of reactant through the catalyst layer, partially because it appears at lower cell voltage when we applied H_2/CO mixture or at high current density where we may be able to observe mass transfer limitation of reactant.

To support the evidence of N_2 convection effect with H_2/N_2 ratio, recovery experiments of Pt anode catalyst were performed after polarization measurements by applying 100 ppm of CO. Fig. 4 shows a series of CO recovery polarization curves in fuel cell operation in a way that repeated polarization measurements were carried out at a regular time interval. It was found that CO molecules become more strongly adsorbed on the surface of the catalyst as the H_2/N_2 ratio becomes lower. In other words, the CO hindering effect markedly

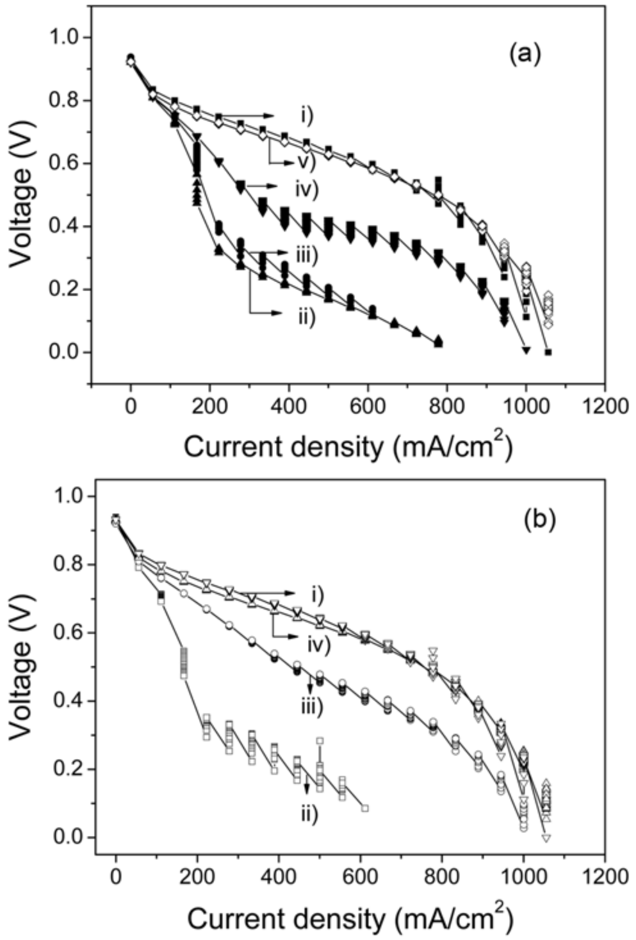

Fig. 4. Polarization curves obtained for (a) H_2/N_2 ratio=1.0 and (b) H_2/N_2 ratio=0.35 after 100 ppm CO adsorption. The consecutive stripping tests were performed with different current steps. (a) H_2/N_2 ratio=1.0; i) H_2, ii) CO 100 ppm, iii) 30 s, iv) 90 s and v) 180 s. (b) H_2/N_2 ratio=0.35; i) H_2, ii) CO 100 ppm, iii) 90 s, iv) 180 s. The measurement is conducted at 70 °C. Both anode and cathode=100% humidification. Flow rate of H_2/N_2=1.2 and air=2.5, respectively (stoich).

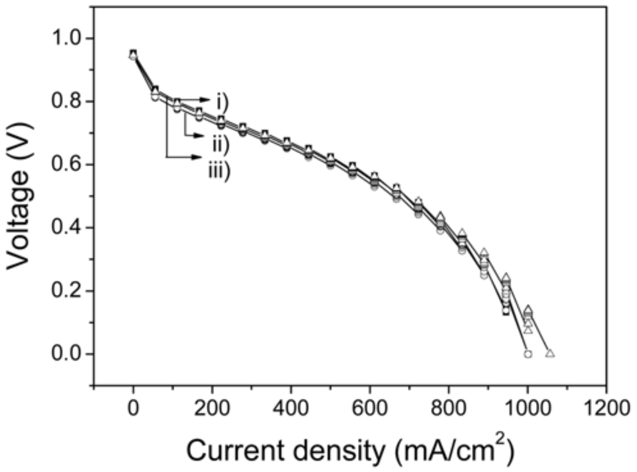

Fig. 5. Polarization curves of PtRu/C anode applying various H_2/N_2 ratio with CO of 10 ppm. i) H_2/N_2=1.0, ii) H_2/N_2=0.6, iii) H_2/N_2=0.35. The measurement is conducted at 70 °C. Both anode and cathode=100% humidification. Flow rate of H_2/N_2=1.2 and air=2.5, respectively (stoich).

increased the CO poisoning on Pt surfaces as the ratio of H_2/N_2 decreased. After consecutive current-voltage polarization measurements were conducted through a step-wise increment current for 30 s, 90 s and 180 s by applying pure hydrogen, both the H_2/N_2 ratio of 1.0 and H_2/N_2 ratio of 0.35 reach almost the initial value of current density. Interestingly, initial cell performance was lower with H_2/N_2 ratio of 0.35 (see Fig. 4(b)) than that of 1.0 (see Fig. 4(a)), whereas the recovery of low H_2/N_2 ratio shows a higher performance. It might be expected that the slightly larger performance of the H_2/N_2 ratio of 0.35 than that of 1.0 was due to the forced convection effect of N_2 gas.

Based on above experimental observations, it is likely that Pt/C anode is not efficient for CO tolerance, especially with lower hydrogen partial pressure. Fig. 5 shows the current-voltage curves of PtRu/C with different partial pressure of H_2 and N_2 gas. As shown in Fig. 5, the cell performance was not decreased with the 10 ppm CO. The PtRu/C anode had better performance than that of Pt/C catalyst as expected. The better activity would be explained as that CO is weakly adsorbed on the PtRu/C surface and the CO_{ads} can be easily removed at lower potential than that of the Pt/C by way of bifunctional mechanism. The Pt-Ru alloy catalyst with a 50% Ru atomic composition has been a well-known electrocatalyst with CO-tolerance [20,21].

We also investigated the effects of N_2 gas with two anode catalysts of Pt/C and PtRu/C via a durability test by measuring the voltage variation as a function of time with respect to the H_2/N_2 ratios from 1.0, 0.6 and 0.35. As shown in Fig. 6, it was observed that the voltage drop increased with a decrease of H_2/N_2 ratio. In addition, the voltage profile was stabilized and slightly dropped for three times longer in the use of PtRu/C anode, especially in 1.0 of H_2/N_2 ratio. The cell voltage drop rates for the Pt/C with a gas mixture of H_2/N_2 ratio from 1.0 to 0.35 showed 0.13 mV/s, 0.27 mV/s and 0.42 mV/s, respectively, while the cell voltage drop rates for the PtRu/C of the same partial pressures were 0.046 mV/s, 0.14 mV/s and 0.12 mV/s, respectively. These results clearly support that PtRu/C and/or Pt-alloy/C anode catalyst in PEFCs are still clearly inevitable in terms of the performance and durability if one insists on using a reformate gas as a fuel.

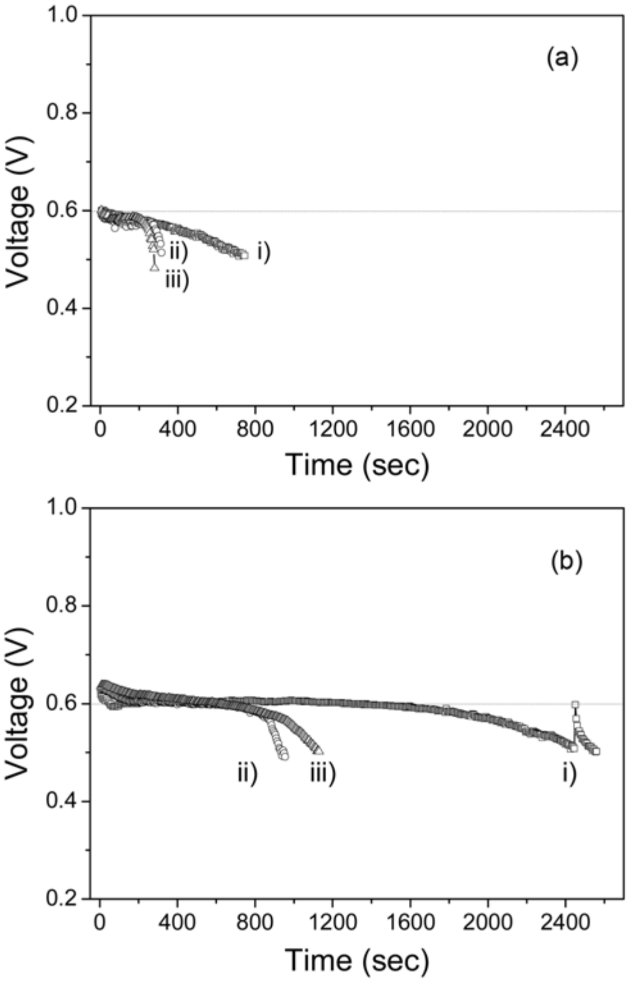

Fig. 6. Durability results in presence of 100 ppm CO applying 555 mA/cm^2. (a) 55 wt% Pt/C i) H_2/N_2 ratio=1.0 ii) H_2/N_2 ratio=0.6 iii) H_2/N_2 ratio=0.35. (b) 40 wt% PtRu/C i) H_2/N_2 ratio=1.0 ii) H_2/N_2 ratio=0.6 iii) H_2/N_2 ratio=0.35. The measurement is conducted at 70 °C. Both anode and cathode=100% humidification. Flow rate of H_2/N_2=1.2 and air=2.5, respectively (stoich).

CONCLUSIONS

The cell performance was significantly affected by the ratio of the H_2/N_2 in the presence of carbon monoxide (CO). The CO poisoning in addition to the blanket effect of N_2 as a carrier gas impedes the favorable access of hydrogen fuel into the active surface area of the catalyst. In the operating potential of 0.4 V with Pt/C, a 71% and 51% reduction of current density was observed with a gas mixture of H_2/N_2 ratio from 1.0 to 0.35 in the presence of CO concentration of 10 and 100 ppm, respectively. For a more practical application of the reformate system to fuel cell unit, in-depth research regarding the effect of impurity in a fuel should be accompanied with the development of robust anode catalyst possessing high selectivity and tolerance.

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