

Preparation of highly dispersed Pt catalyst using sodium alkoxide as a reducing agent and its application to the methanol electro-oxidation

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Abstract

A platinum precursor (H_2PtCl_6) was reduced to platinum nanoparticles using sodium alkoxide in the presence of a carbon support. Various electrolytes such as H_2O , HCl , and NaCl were used in order to deposit platinum nanoparticles on the carbon support. In the case of H_2O and NaCl , Pt nanoparticles were not successfully supported on the carbon. However, HCl was found to be efficient for the deposition of Pt nanoparticles on the carbon support. The supported Pt catalysts with various Pt loadings (40–80 wt.%) were prepared and characterized by comparison with commercially available carbon-supported Pt catalysts. It was revealed that the prepared Pt catalysts showed a better catalytic performance than the commercial catalysts in the electro-oxidation of methanol, due to the enhanced active metal surface areas of the prepared Pt catalysts.

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1. Introduction

Carbon-supported Pt catalysts have attracted considerable attention as electro-catalysts in the polymer electrolyte fuel cell [1–3]. Carbon-supported catalysts with high Pt loadings (in excess of 20 wt.%) are typically used in the fabrication of membrane-electrolyte assembly (MEA) because of their many advantages over the carbon-supported catalysts with low Pt loadings [4]. Due to the limited surface area of carbon supports, however, the preparation of carbon-supported Pt catalysts with both a high Pt loading and a fine dispersion would be highly desirable.

Several methods such as impregnation [5], chemical reduction [6], and electrodeposition [7] have been used for the deposition of Pt nanoparticles on the carbon support. Among these methods, the chemical reduction method, which involves the reduction of metal ion by a chemical reducing agent, has been widely used due to the relative simplicity for obtaining a carbon-supported Pt catalyst with high metal loading [8,9]. The reduction of metal ion has been occasionally carried out in the

presence of stabilizer. For example, polyvinylpyrrolidone has been used for the preparation of a carbon-supported Pt catalyst with both high metal loading and narrow particle size distribution [10,11]. However, this method has been recognized as rather a laborious way because an additional process to remove the stabilizer is required. On the other hand, it was reported that a partially oxidized species, which was believed to originate from the reducing agent such as ethylene glycol, has served as an efficient stabilizer in forming finely dispersed Pt/C catalyst with narrow particle size distribution [12–14]. Therefore, this method has been accepted as a more attractive way in a sense that an additional stabilizer is not necessary to prevent the metal growth for the fine dispersion of reduced metal particles. In the meanwhile, considerable attention has also been paid to control the synthesis parameters such as homogeneous heating of reaction mixture [14,15].

Reported in this work is the preparation of carbon-supported Pt catalysts with high metal loading and narrow particle size distribution, which was achieved using sodium alkoxide as a reducing agent for platinum ions. The prepared carbon-supported Pt catalysts were tested as electro-catalysts in the methanol electro-oxidation. Since the whole preparation process was carried out at low temperatures with a broad temperature window (room

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temperature $\sim 80^\circ\text{C}$), it is expected that one can prepare the carbon-supported Pt catalysts with reproducibility.

2. Experimental

2.1. Preparation of carbon-supported Pt catalyst

Vulcan XC-72 (Cabot, BET surface area of $230\text{ m}^2/\text{g}$) and hexachloroplatinic acid (Arcos, H_2PtCl_6) were used as a carbon support and a platinum precursor, respectively. Carbon support (100 mg) was added into a mixed ethanol solution of H_2PtCl_6 and sodium ethoxide (Aldrich, $\text{NaOCH}_2\text{CH}_3$) (or sodium methoxide (Aldrich, NaOCH_3)) with a molar ratio of 1:8. The mixture was sonicated for 30 min, followed by complete reduction of metal ions at 65°C for 3 h. After complete reduction of Pt ions, an aqueous solution of HCl was added into the mixture for the deposition of reduced Pt nanoparticles on the carbon support. The resulting black precipitate was filtered and washed with large amounts of water, and then it was dried overnight at 120°C . H_2O and an aqueous solution of NaOH were also tested for the deposition of Pt nanoparticles on the carbon support.

2.2. Characterization and methanol electro-oxidation

X-ray diffraction (XRD, MAC/Science M18XHF-SRA) measurements were carried out in order to investigate the crystalline phases of prepared catalysts and to determine the crystallite size of Pt particles on the carbon support. The size and location of Pt particles on the carbon surface were confirmed by transmission electron microscopy (TEM, Joel JXA-8900R and HR-TEM, Jeol JEM-3010) using an ultrasonically dispersed catalyst sample (in a mixed solution of ethanol and distilled water) deposited on a carbon grid. Average Pt particle sizes were determined by the equation, $d = (\sum n_i d_i) / n_i$. The chemical state of Pt on the carbon support was investigated by X-ray photoelectron spectroscopy (XPS, ThermoVG SIGMA PROBE). The Pt loadings in the prepared catalysts were measured using FE-SEM-EDX (JSM-6700F).

Methanol electro-oxidation was carried out in a conventional three-electrode system with saturated calomel and platinum gauge as a reference and a counter electrode, respectively. The

working electrode was prepared by coating a small amount of catalyst ink on a disk-type graphite. Prior to the coating with catalyst ink, the graphite surface was polished by alumina paste and washed with de-ionized water. Cyclic voltammograms and galvanostatic polarization curves were obtained at room temperature in $0.5\text{ M H}_2\text{SO}_4$ solution containing $2\text{ M CH}_3\text{OH}$ (EG & G 263A potentiostat/galvanostat).

3. Results and discussion

3.1. Pt nanoparticles on the carbon support

Sodium alkoxide has been used for the preparation of unsupported metal or metal oxide nanoparticles [16,17]. It was reported that the reduction of Pt precursor (hexachloroplatinic acid) by sodium ethoxide in ethanol solution produced various species such as suspended Pt nanoparticles, soluble Pt species, acetaldehyde, and NaCl [17]. Among the chemical species produced, the soluble Pt(II) that was identified as a sodium-type analogue of Zeise's salt was believed to serve as a stabilizer for the Pt nanoparticles. Although such species is obviously efficient for the formation of small sized Pt sols, it is rather problematic to deposit Pt sols onto the carbon support because of their strong stability in ethanol or air [17]. In this research, several electrolytes such as H_2O , HCl, and NaOH were tested for the supporting of Pt nanoparticles onto the carbon support.

Fig. 1 shows the pictures of solution mixture taken after reduction of Pt ions using sodium ethoxide (a) followed by the addition of H_2O , (b) followed by the addition of aqueous HCl, and (c) followed by the addition of aqueous NaOH. Same result was observed with NaOH and H_2O . As shown in Fig. 1, no precipitate was formed by the addition of aqueous NaOH. It is expected that Pt nanoparticles reduced by sodium ethoxide are dispersed in the ethanol solution. Due to the limited solubility of NaOH in the ethanol solution, it is likely that NaOH could not serve as a sedimentation promoter for Pt nanoparticles. The solubility of electrolyte in ethanol is a very important factor for the deposition of Pt nanoparticles on the carbon support. Because both Pt sols and sodium-type Zeise's salts were dispersed in ethanol, it was observed that the electrolytes such as NaOH and NaNO_3 with low solubility in ethanol was ineffective to decompose a sodium-type Zeise's salt, and consequently,

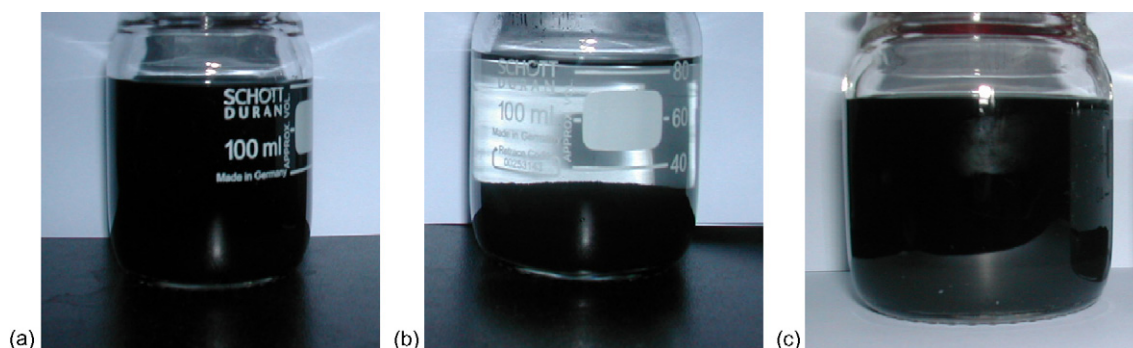


Fig. 1. Pictures of solution mixture taken after reduction of Pt ions using sodium ethoxide (a) followed by the addition of H_2O , (b) followed by the addition of aqueous HCl, and (c) followed by the addition of aqueous NaOH.

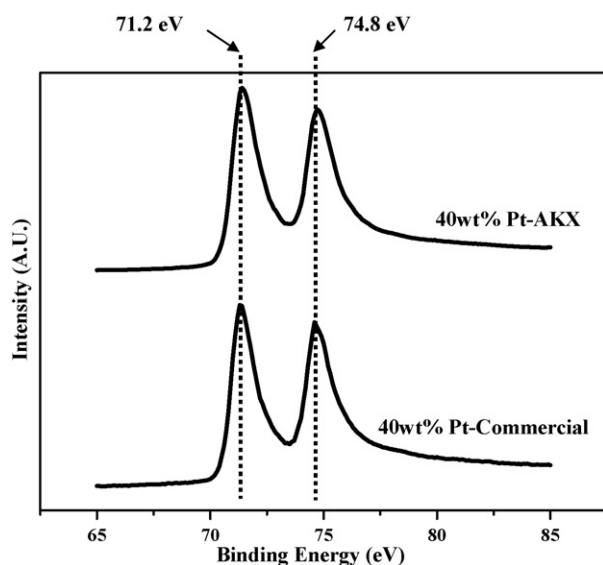


Fig. 2. X-ray photoelectron spectra of Pt 4f for 40 wt.% Pt-AKX catalyst and 40 wt.% commercial Pt catalyst.

was ineffective to deposit Pt sols onto the carbon support. On the other hand, HCl has high solubility in ethanol. Therefore, it is believed that a sodium-type Zeise's salt rapidly reacted with HCl and was decomposed to form black precipitate, indicating that the suspended Pt nanoparticles were completely supported on the carbon support. ICP-AES results revealed that the filtrate from HCl-treated mixture contained no Pt components. FE-SEM-EDX analyses also showed that there were no impurities such as chlorine and sodium compounds in the prepared carbon-supported Pt catalysts (the carbon-supported Pt catalyst prepared using sodium ethoxide followed by the addition of HCl was denoted as Pt-AKX hereafter).

Fig. 2 shows the XPS spectra of Pt 4f for 40 wt.% Pt-AKX catalyst and 40 wt.% commercial Pt catalyst (E-TEK). It was observed that both catalysts showed distinct two peaks at 71.2 and 74.8 eV, corresponding to Pt 4f_{7/2} and Pt 4f_{5/2} of metallic Pt, respectively. It should be noted that XPS peaks for the oxidized Pt(II) compound, which were reported to appear at 72.8 and 75.9 eV [16], were not observed in the Pt-AKX catalyst. From these results, it is believed that the structure of soluble Pt(II) species (sodium-type analogue of Zeise's salt) was destroyed after the addition of aqueous HCl, and at the same time, leading to the reduction of Pt(II) species by a by-product such as acetaldehyde. In addition, no peaks related to Cl and Na species were found in the XPS spectra of Pt-AKX (although the spectra were not shown here), indicating the successful deposition of metallic Pt on the carbon support.

Fig. 3 shows the X-ray diffraction patterns of Pt-AKX and commercial Pt catalysts with variation of Pt loading. The characteristic diffraction peaks for face centered cubic phase of Pt were observed in all catalysts. By applying Scherrer equation to the (2 2 0) diffraction, the average size of Pt crystallite was calculated as listed in Table 1. On the whole, the size of Pt crystallite increased with increasing Pt loading. However, such a trend was less sensitive in the Pt-AKX catalyst than in the commercial catalyst, indicating that the method suggested in this work was very

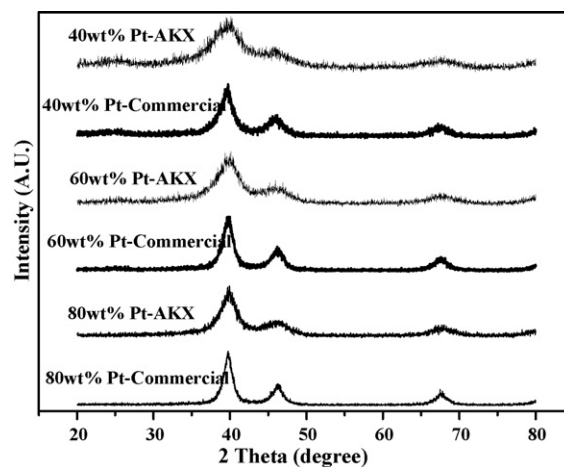


Fig. 3. X-ray diffraction patterns of Pt-AKX and commercial Pt catalysts with variation of Pt loading.

efficient for the preparation of Pt catalyst with high loading. The metal surface area was calculated using the following equations: $S = 6000/\rho d$, where d is average crystallite size (nm), S the surface area (m^2/g), and ρ represents Pt density ($21.4 \text{ g}/\text{cm}^3$). As listed in Table 1, the Pt-AKX catalyst was found to have higher metal surface area than the corresponding commercial catalyst.

Surface morphology and dispersion of Pt particles on the carbon support were confirmed by TEM images. TEM images for selected samples (40 wt.% Pt/C) are shown in Fig. 4. It was observed that the Pt-AKX catalyst (Fig. 4(a) and (b)) showed uniform particle size distribution with an average Pt size of 2.3 nm without agglomerates of Pt particles, while a broad particle size distribution and some agglomerates of Pt particles (average Pt size was 3.9 nm) were observed in the commercial catalyst (Fig. 4(c)).

3.2. Electrochemical performance and methanol electro-oxidation

In order to measure the electrochemical surface area (EAS), the cyclic voltammograms (CVs) were obtained in a solution of 0.5 M H_2SO_4 . To minimize the effect of dissolved oxygen on the current of hydrogen adsorption–desorption region, the

Table 1
Pt particle size and Pt surface area

Sample	Particle size (nm) ^a	Pt surface area (m^2/g) ^b
40 wt.% Pt-AKX	2.1	132
40 wt.% Pt-commercial	3.6	77
60 wt.% Pt-AKX	2.4	116
60 wt.% Pt-commercial	4.6	61
80 wt.% Pt-AKX	3.0	92
80 wt.% Pt-commercial	6.7	54

^a $D = 0.9\lambda/B \cos \theta_B$, where D is average crystallite size, λ the X-ray wavelength, θ_B the (2 2 0) peak position, and B represents FWHM value (radian scale).

^b $S = 6000/\rho d$, where d is average crystallite size (nm), S the surface area (m^2/g), and ρ represents Pt density ($21.4 \text{ g}/\text{cm}^3$).

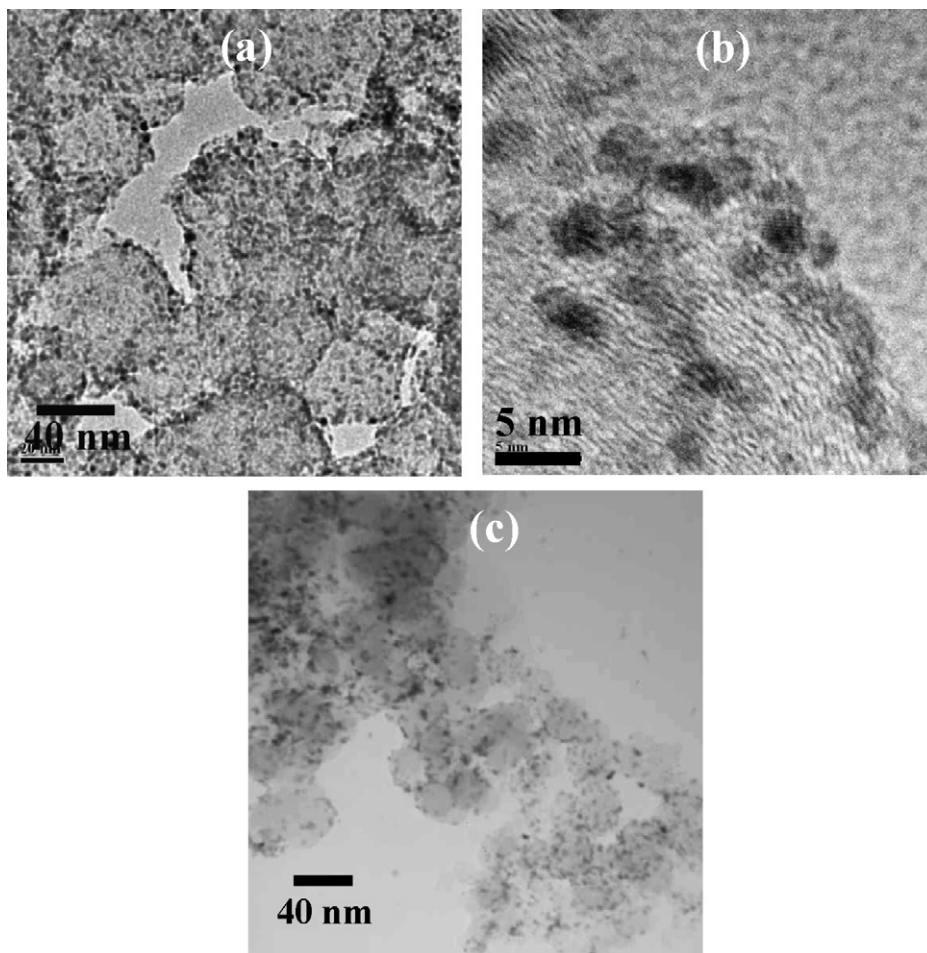


Fig. 4. TEM images of (a) 40 wt.% Pt-AKX (low magnification), (b) 40 wt.% Pt-AKX (high magnification), and (c) 40 wt.% commercial Pt catalyst.

electrolyte solution was purged with nitrogen to remove any dissolved oxygen prior to the measurements of cyclic voltammograms. In addition, all of the voltammograms obtained in this work were measured at the same conditions. As shown in Fig. 5,

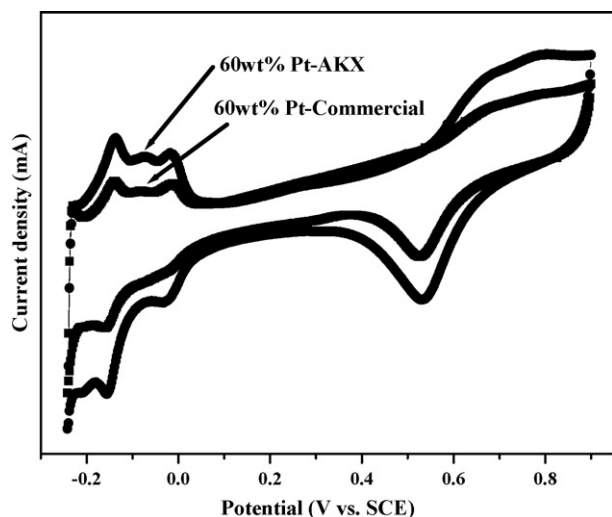


Fig. 5. Cyclic voltammograms on 60 wt.% Pt-AKX catalyst and 60 wt.% commercial Pt catalyst in 0.5 M H_2SO_4 .

the slopes in the electric double layer regions were almost the same in both catalysts. This indicates that the effect of slope on the calculation of EAS would be negligible. The base line for the calculation of EAS was taken horizontally in the region of hydrogen adsorption–desorption after the correction of electric double layer charging current. As shown in Fig. 5, the CVs on selected samples (60 wt.% Pt/C) exhibited typical patterns of electro-adsorption and desorption of hydrogen on the Pt sites. The electrochemical active surface areas (EAS) were calculated from the mean value of Coulombic charges exchanged during the electro-adsorption and desorption of hydrogen. The result showed that the Pt-AKX catalyst ($105 \text{ m}^2/\text{g}$) retained 2.3 times higher EAS than the commercial catalyst ($45 \text{ m}^2/\text{g}$).

Fig. 6 shows the cyclic voltammograms for methanol electro-oxidation on selected catalyst samples (60 wt.% Pt/C) in electrolyte of 0.5 M H_2SO_4 containing 2 M CH_3OH at room temperature. Both catalysts showed a similar CV pattern, where the current peak at 0–0.7 V in the forward scan was observed because of the electro-oxidation of methanol. It should be noted that the Pt-AKX catalyst exhibited higher peak current than the commercial catalyst, indicating better electro-catalytic performance of the Pt-AKX catalyst.

The galvanostatic polarization in methanol solution has been frequently used to investigate the catalytic performance in the

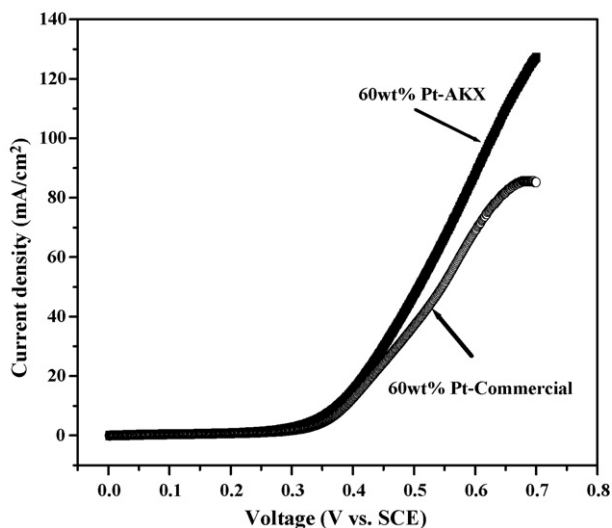


Fig. 6. Cyclic voltammograms on 60 wt.% Pt-AKX catalyst and 60 wt.% commercial Pt catalyst in 0.5 M H_2SO_4 containing 2 M CH_3OH with a scan rate of 5 mV/s. The current density represents the current that was divided by the area of electrode.

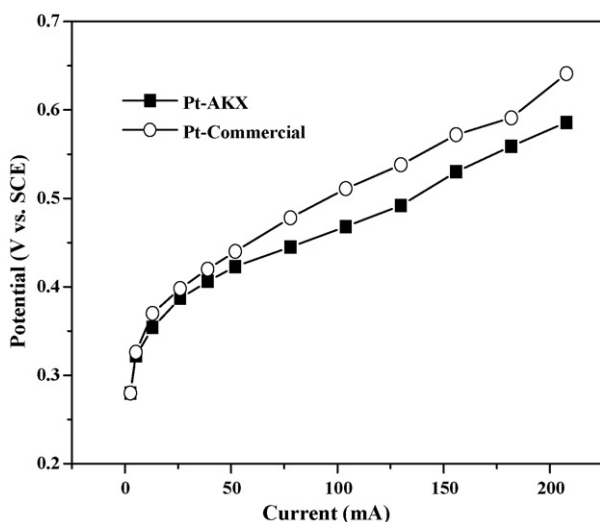


Fig. 7. Galvanostatic polarization curves on 60 wt.% Pt/C catalysts in the methanol electro-oxidation in 0.5 M H_2SO_4 containing 2 M CH_3OH .

methanol electro-oxidation [1, 18]. To compare the catalytic performance, the galvanostatic polarization curves were obtained on the 60 wt.% Pt/C catalysts as shown in Fig. 7. Both catalysts showed a similar polarization behavior, where the large increase of over-potential was followed by the small increase of over-potential. However, the Pt-AKX catalyst showed lower polarization performance within entire range of current density, indicating higher catalytic performance of Pt-AKX in the methanol electro-oxidation than the commercial Pt catalyst. It

is believed that the enhanced catalytic performance of Pt-AKX catalyst was attributed to its high EAS.

4. Conclusions

In order to prepare the carbon-supported Pt catalyst, the reduction of Pt precursor was conducted using sodium alkoxide in a mixed solution of ethanol and carbon support. It was found that the structure of soluble Pt(II) species was destroyed by the reaction with aqueous HCl, resulting in the deposition of Pt nanoparticles on the carbon support. The prepared Pt-AKX catalysts showed higher metal dispersion (active metal surface area) and narrow particle size distribution than the commercial Pt catalysts. In the methanol electro-oxidation, the Pt-AKX catalysts exhibited better catalytic performance than the commercial catalysts, due to the enhanced electrochemical active surface area of the Pt-AKX catalyst.

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