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Effect of silver catalyst on the activity and mechanism of a gas diffusion type oxygen cathode for chlor-alkali electrolysis

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Abstract

Application of a gas-diffusion type oxygen cathode will contribute to energy saving in chlor-alkali electrolysis. For this purpose the development of gas-diffusion electrodes with high performance and durability is essential. We have investigated the performance for oxygen reduction and the mechanism of its on gas-diffusion electrodes with and without Ag catalyst in order to develop such oxygen cathodes with high performance and durability. It has been found that an electrode with no catalyst, that is, carbon support only in the reaction layer, shows electrochemical activity for oxygen reduction in 32 wt % NaOH at 80 °C and 1 atm O_2, but loading of 2 mg cm^{-2} Ag of particle size 300 nm, not only improves the activity by about 100 mV but promotes the four-electron reduction to produce OH^-, while H_2O_2 is the predominant reaction intermediate in the absence of the Ag catalyst. The production of H_2O_2 has been demonstrated by conducting CV measurements to detect H_2O_2 in the anodic scan after a cathodic sweep up to 0.3 V vs RHE. It has been shown that the gas-diffusion type oxygen cathode with Ag catalyst has the high performance and durability necessary for chlor-alkali electrolysis.

1. Introduction

In Japan, the chlor-alkali industry has been producing 4.4 million tons per year caustic soda and over 4.2 million tons per year chlorine by the membrane cell process. Although the electrical power consumption of this process is smaller than for the diaphragm and mercury processes, it is as high as 100 billion kW per year. It is necessary, therefore, to reduce the power consumption in view of cost reduction, as well as reduction of CO_2 emission for improving the global environment.

Application of gas-diffusion type oxygen cathodes to the chlor-alkali process has been discussed in view of energy saving [1–3]. The cathode reaction of the usual chlor-alkali process using an ion exchange membrane is hydrogen evolution as given by Equation 1, while that of the process utilizing a gas diffusion electrode cathode is oxygen reduction as shown by Equation 2:

$$2H_2O + 2e^- = 2OH^- + H_2 \quad E = -0.82\,\text{V vs NHE} \qquad (1)$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad E = +0.40\,\text{V vs NHE} \qquad (2)$$

It is theoretically possible, therefore, to reduce the cell voltage by 1.2 V by using a gas-diffusion type oxygen cathode. In fact, reduction of cell voltage by as much as 1.0 V has been achieved by using the oxygen cathode for the chlor-alkali process [3].

In previous work we studied the catalytic activities of Pt and Ag catalysts for O_2 electroreduction in 32% NaOH at 80 °C and showed that both Pt and Ag catalysts showed stable performance over three years [4, 5] for the optimum catalyst particle size and loading, which were 0.3 μm and 2 mg cm^{-2}, respectively, for Ag.

During previous studies, we also found that even a gas diffusion electrode with no supported catalyst on the reaction layer showed activity for oxygen reduction, although the activity was lower than that with Ag or Pt catalyst by about 100 mV in terms of the electrode potential. However, no mechanistic studies on the gas diffusion cathodes with and without loaded catalyst were conducted in the former reports to investigate the role of the catalyst.

The purpose of the present report is to describe comparative mechanistic studies of oxygen reduction on gas diffusion cathodes with and without Ag catalyst in order to elucidate the role of the catalyst in the oxygen reduction reaction.

2. Experimental details

2.1. *Preparation of the gas diffusion electrode*

The reaction layer (RL) was made from a hydrophilic carbon black (AB-12, Denki Kagaku Kogyo) and a

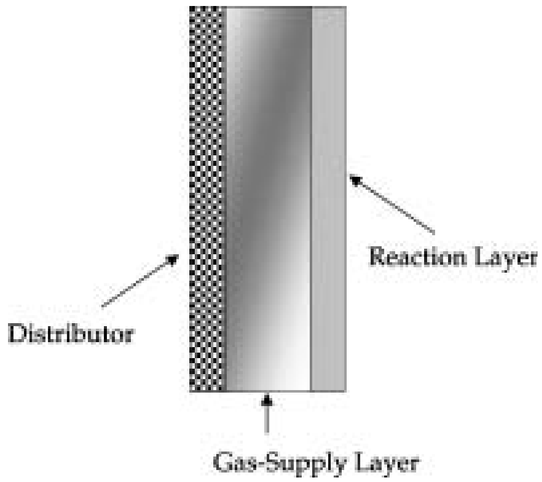


Fig. 1. Illustration of a gas diffusion electrode.

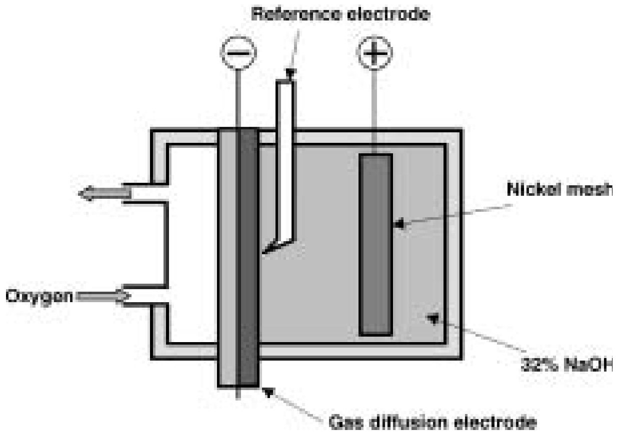


Fig. 2. Experimental system used to measure cathode *I–V* performance for oxygen reduction.

hydrophobic carbon black (No. 6, Denki Kagaku Kogyo) and polytetrafluoroethylene (D-1, Daikin Kogyo), and Ag catalyst powder of 0.3 μm particle size. The gas diffusion electrodes with and without the loaded Ag catalyst on the reaction layer will be termed the 'Ag–C-electrode' and 'C-electrode', respectively. The gas-supplying layer (GSL) was made from a hydrophobic carbon black and polytetrafluoroethylene. A silver net with 1 mm mesh and 0.1 mm thick was integrated in the gas-supplying layer and used as a current collector (Figure 1). The gas supply layer thus prepared is hydrophobic, while the reaction layer is hydrophilic and is wetted by aqueous electrolytes [6].

To prepare the RL and GSL the constituent materials were first dispersed in aqueous solutions with a surfactant. Then, the solutions were filtered to separate the aggregates of the constituent materials which were then rolled into sheets of RL and GSL, respectively. The surfactant was removed from the sheets by ethanol extraction. A gas diffusion electrode was made by hot pressing the sheets of RL and GSL with the silver mesh at 380 °C and 4.9 MPa for 1 min.

2.2. *Measurement of the electrode I–V performance*

Figure 2 illustrates the experimental system for the measurements of electrode *I–V* performance. The potential of the gas diffusion electrode was measured for different applied current densities in 32 wt % sodium hydroxide solution at 60 °C or 80 °C while supplying pure oxygen gas, as indicated in Figure 2. A reversible hydrogen electrode in the same solution (RHE) at the same temperature was used as reference. The electrochemically active area of the electrodes was 12.56 cm^2 (geometrical).

2.3. *SEM observation*

The surfaces of the Ag–C and C-electrodes were observed by SEM before and after electrolysis to observe the effects, if any, of operation in the strongly alkaline solution at the elevated temperatures on the surface morphology.

2.4. *Determination of the number of electrons involved in the oxygen reduction process*

While measuring the *I–V* performance, oxygen consumption at the gas diffusion electrode was measured at 0.3 A cm^{-2} by using two mass flow meters placed at the inlet and outlet of the oxygen flow for determination of the number of electrons involved in the oxygen reduction process.

2.5. *Cyclic voltammetry*

Cyclic voltammograms (CV) of the Ag–C and the C-electrodes were measured in 32 wt % NaOH at 80 °C under nitrogen or oxygen atmosphere. The CV measurements were conducted in the potential range between 0.4 and 1.5 V at 0.1 to 1.0 V s^{-1}.

3. Results and discussions

3.1. *I–V Oxygen reduction characteristics*

I–V performances of oxygen reduction at the Ag–C and the C-electrodes are shown in Figure 3. It can be seen that the C-electrode with no Ag catalyst shows reasonable activity for oxygen reduction, although its potential is lower than the Ag–C-electrode by about 100 mV in the entire region of current density studied. Therefore, we can conclude that oxygen reduction proceeds not only on the Ag catalyst but also on the carbon support.

3.2. *Number of electrons and oxygen reaction mechanisms*

Figure 4 shows the rate of oxygen consumption observed on the gas diffusion electrodes at 0.3 A cm^{-2}. The rate at the C-electrode was 0.020 $\text{cm}^3\ \text{s}^{-1}\ \text{cm}^{-2}$ which is slightly higher than that at the Ag–C-electrode, which

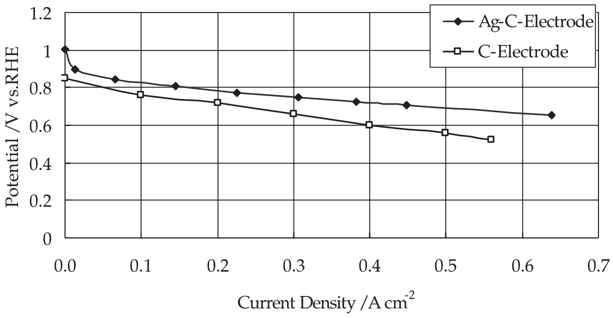


Fig. 3. Dependence of current density on oxygen reduction potential of Ag–C and C-electrodes.

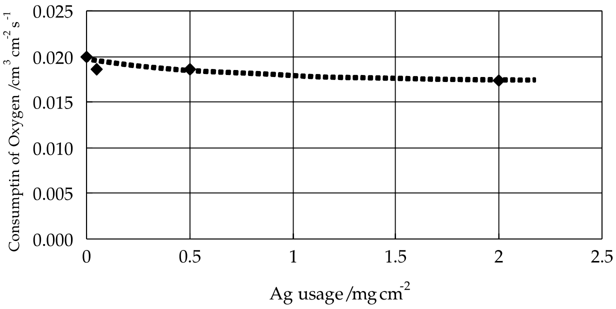


Fig. 4. Dependence on Ag usage of oxygen consumption during electrolysis at 0.3 A cm^{-2} in 32% NaOH at 80 °C.

tends to decrease from 0.018 to 0.017 cm^3 s^{-1} cm^{-2} with increase in Ag catalyst concentration. The number of electrons for oxygen reduction was calculated from the data shown in Figure 4 and the results are plotted in Figure 5 as a function of Ag catalyst loading. The number of electrons is almost 4 with Ag catalyst, which is the value expected for four electron O_2 reduction to produce OH^- as shown in Equation 2.

The number of electrons is 3.5 on the C-electrode, as shown in Figure 5. This lower number of electrons suggests a side reaction to form a reaction intermediate such as $H_2O_2^-$ which requires two electrons as shown by Equation 3:

$$O_2 + 2H_2O + 2e^- = 2H_2O_2^- \qquad (3)$$

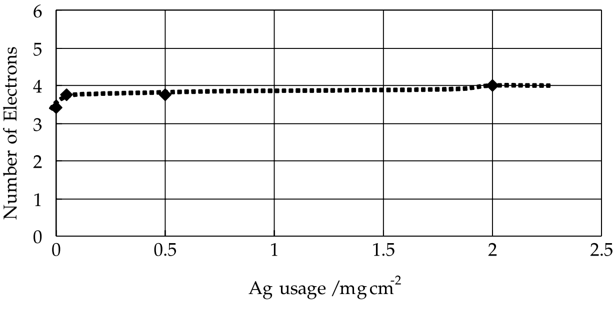
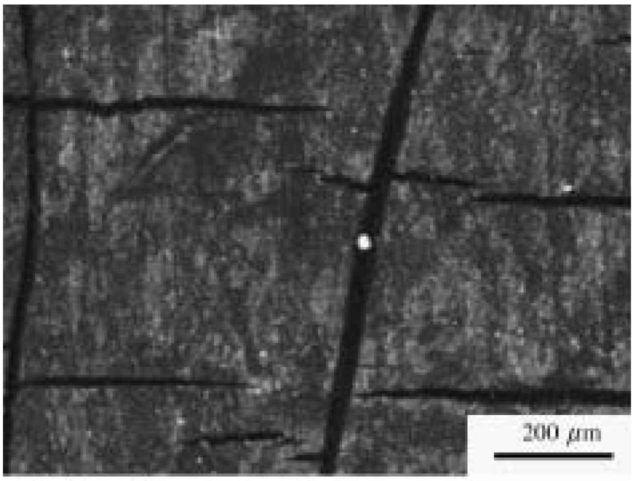


Fig. 5. Dependence on Ag usage of number of electrons of the oxygen reduction reaction determined from data in Figure 4.

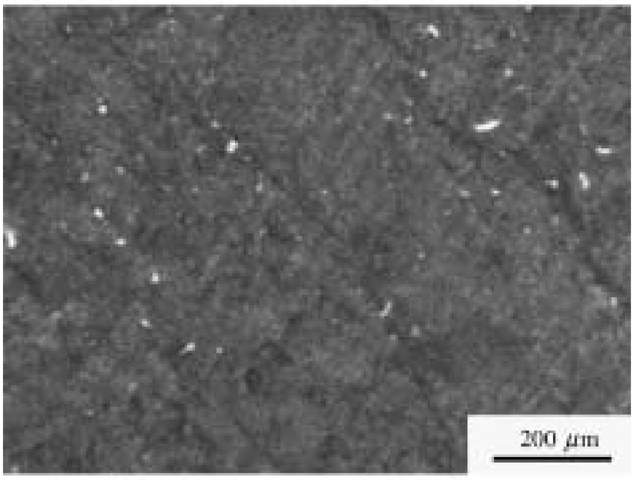
3.3. *Surface condition of the Ag–C and C-electrodes after electrolysis*

The SEM images of the surfaces of the respective electrodes after electrolysis at 60 °C are shown in Figure 6. There are some cracks on the C-electrode, most likely produced during the electrolysis, while no such cracks are seen on the Ag–C-electrode. No cracks were detected, however, on either electrode after electrolysis at 80 °C.

Formation of cracks on the C-electrode may be explained tentatively based on the reaction mechanism discussed above. Production of $H_2O_2^-$ by the Reaction 3 may lead to formation of NaOOH, which then deposits in the reaction layer [7, 8]. Accumulation of the insoluble deposit in the reaction layer may cause crack formation as shown in Figure 6. At 80 °C, however, the solubility of NaOOH is higher and much less NaOOH deposits in the reaction layer, which prevents crack formation as observed at 80 °C.



(a) C-Electrode



(b) Ag-C-Electrode

Fig. 6. SEM images of Ag–C and C-electrode surfaces after the electrolysis in 32% NaOH at 60 °C.

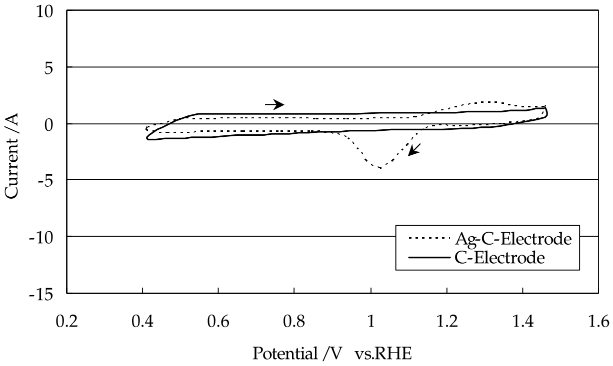


Fig. 7. Cyclic voltammograms of Ag–C and C-electrodes obtained in nitrogen atmosphere in 32% NaOH at 80 °C between 0.4 and 1.5 V with sweep rate of 1.0 V s^{-1}.

3.4. *CV of Ag–C and C-electrodes in nitrogen atmosphere*

Figure 7 shows the cyclic voltammograms of the Ag–C and C-electrodes in nitrogen atmosphere. The CV of the Ag–C-electrode has a feature common to metal electrodes in having an anodic wave above about 1.15 V in the positive potential sweep due to surface oxidation of the Ag catalyst and the corresponding cathodic current peak around 1.02 V due to reduction of the surface oxide in the negative potential sweep. On the other hand, the CV of the C-electrode shows no characteristic feature due to oxidation/reduction of the carbon support, but only a broad current component due to charging/discharging of the electric double layer at the carbon–electrolyte interface.

3.5. *CV of Ag–C and C-electrodes in oxygen atmosphere*

Figure 8 shows the cyclic voltammograms of the Ag–C and the C-electrodes observed in oxygen atmosphere. The cathodic currents observed on both electrodes below about 0.8 V are due to oxygen reduction, while the voltammetric feature observed above 0.8 V is specific to each electrode. The Ag–C-electrode shows similar features to that observed in nitrogen corresponding to oxidation/reduction of the Ag surface as shown in Figure 7, while there is a broad anodic current peak around 1.2 V for the C-electrode which is absent in nitrogen. In view of the mechanism of oxygen reduction on the C-electrode discussed earlier, the origin of the anodic current peak observed on the C-electrode is most likely oxidation of H_2O_2 produced during the negative potential sweep. Production of H_2O_2 during oxygen reduction on the C-electrode was suggested based on the number of electrons determined from the rate of oxygen consumption. The CV measurements shown in Figure 8 give further support for H_2O_2 formation during oxygen reduction on the C-electrode.

Oxidation/reduction of the Ag catalyst clearly observed by the CV measurements may play an important role in protecting oxidation of the carbon support when the power is interrupted unexpectedly and the current flow is reversed during chlor-alkali electrolysis.

3.6. *Dependence of CV on sweep rate*

Figure 9 shows the effect of sweep rate on the cyclic voltammogram of the Ag–C electrode observed under oxygen atmosphere. The sweep rate was increased between 0.2 and 1.0 V s^{-1}, but the oxygen reduction region below 0.8 V exhibits little dependence on sweep rate, while the surface oxidation/reduction current increases with increase in sweep rate. The charge under the cathodic peak due to reduction of the Ag surface should be constant when the sweep rate is increased, if the oxidation/reduction processes are reversible. However, determination of the charge under the cathodic peaks for the three sweep rates has shown that the charge actually decreases with increase in sweep rate; 0.74 C at 0.2 V s^{-1} to 0.54 C at 1 V s^{-1}. This suggests that the oxidation/reduction processes of the Ag catalyst supported on carbon is not completely reversible.

Figure 10 shows the cyclic voltammograms of the C-electrode observed between 0.2 and 1.0 V s^{-1} under oxygen atmosphere. The broad current peak above 0.8 V, which was assigned to oxidation of H_2O_2 in the forgoing part, increases for the higher sweep rates, while

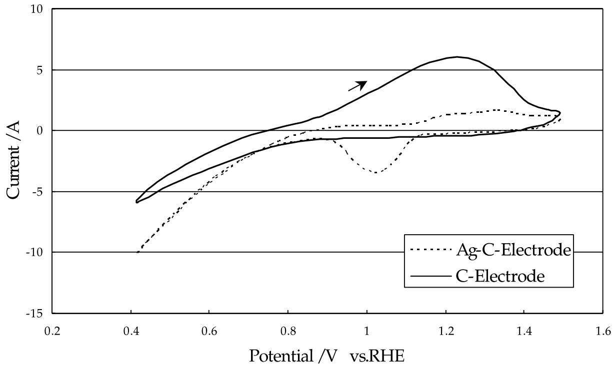


Fig. 8. Cyclic voltammograms of Ag–C and C-electrodes obtained in oxygen atmosphere in 32% NaOH at 80 °C between 0.4 and 1.5 V with sweep rate of 1.0 V s^{-1}.

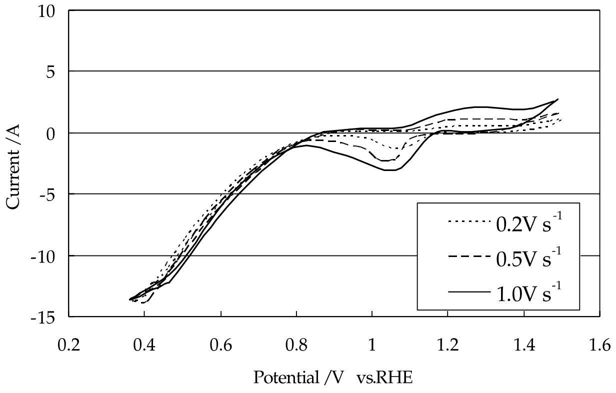


Fig. 9. Cyclic voltammograms of Ag–C-electrode obtained in oxygen atmosphere in 32% NaOH at 80 °C between 0.3 and 1.5 V with sweep rates between 0.2 and 1.0 V s^{-1}.

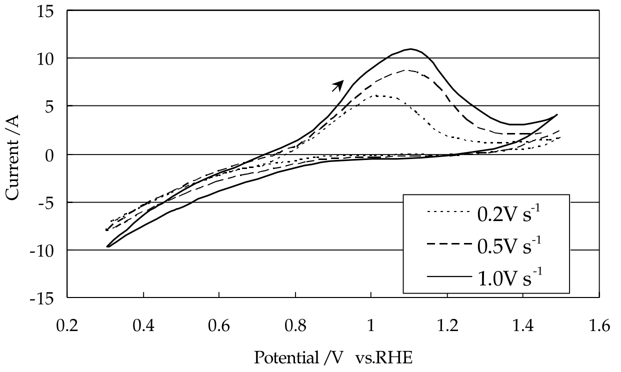


Fig. 10. Cyclic voltammograms of C-electrode obtained in oxygen atmosphere in 32% NaOH at 80 °C between 0.3 and 1.5 V with sweep rates between 0.2 and 1.0 V s^{-1}.

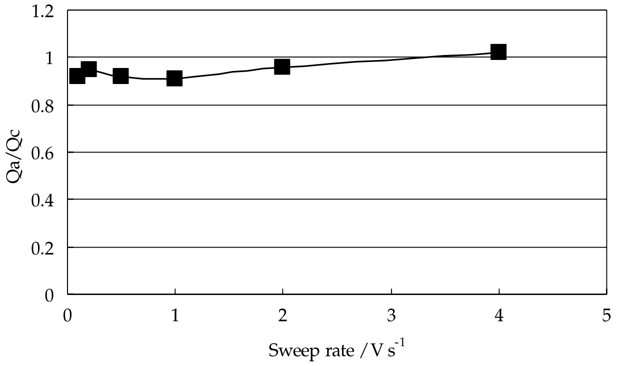


Fig. 11. Dependence of charge ratio, Q_a/Q_c, calculated from Figure 10, on sweep rate determined on the C-electrode in 32% NaOH at 80 °C.

the dependence of the *I–V* profile below 0.8 V on sweep rate is much smaller.

From the CVs in Figure 10 the ratio of the charges Q_a/Q_c were calculated and are plotted in Figure 11. Here Q_a is the cathodic charge used for oxygen reduction and Q_c is the anodic charge generated during H_2O_2 oxidation.

The charge ratio is around 0.9 at the lower sweep rates but tends to increase at the higher sweep rates, finally reaching 1.0 at 4 V s^{-1}. The charge ratio of 1.0 implies that all the H_2O_2 molecules are oxidized on the reverse anodic scan. In other words the collection efficiency of H_2O_2 was 100% as expected at the higher sweep rates and confirmed in Figure 11. The high collection efficiency is most likely specific to the structure of a gas diffusion electrode having a network of fine pores in the reaction layer in which the H_2O_2 produced during oxygen reduction is trapped and is not lost by diffusion into the solution bulk.

The CV measurements suggest, as discussed above, that the major reaction product is H_2O_2 and not OH^-. This is in apparent contradiction with the number of electrons, 3.5, as determined on the C-electrode, but this may be explained by the nature of the respective measurements. The determination of the number of electrons was conducted under steady state conditions at 0.3 A cm^{-2} at which continuous reduction of H_2O_2 to H_2O takes place. This gives rise to a number of electrons close to 4.0. The loss of H_2O_2 by diffusion into the solution bulk and decomposition in the reaction layer would naturally lead to a smaller number of electrons than 4, as observed in Figure 5. On the other hand, it is reasonable to expect that nearly all the H_2O_2 molecules produced by oxygen reduction during the cathodic sweep are oxidized in the anodic scan before they are further reduced to H_2O.

4. Conclusion

Comparative studies of oxygen reduction on gas diffusion electrodes with and without Ag catalyst in the reaction layer has shown that addition of silver not only enhances oxygen reduction but also affects the reaction mechanism and promotes the four-electron reduction of oxygen to produce OH^-.

Without the Ag catalyst production of H_2O_2, as the major reaction intermediate, predominates on the carbon support, as demonstrated by the CV measurements.

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