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The Catalytic Electroreduction of Oxygen in an Aqueous Solution on Glassy Carbon Electrodes Covalently Modified with [5,10,15,20-Tetrakis(4-carboxyphenyl)porphinato]iron(III)

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The catalytic electroreduction of an oxygen molecule on a glassy carbon electrode covalently modified with [5,10,15,20-tetrakis(4-carboxyphenyl)porphinato]iron(III) (abbreviated as GC-O-Fe(III)TCPP) was investigated in an aqueous solution. The reduction of oxygen on the GC-O-Fe(III)TCPP electrode occurs at a more anodic potential than on the glassy carbon electrode adsorbing Fe(III)TCPP. This anodic shift of the oxygen reduction potential may be closely related to the number of bonds between a metalloporphyrin molecule and the electrode material. The oxygen molecule is reduced via the one-step reduction accompanying four-electron and four-proton transfer at pH 7—11 and via two successive reductions accompanying two-electron transfer and subsequently two-electron and four-proton transfer at pH>11.5. At pH<6, the number of transferred electron could not be reproducibly determined because of the cleavage of several ester linkages.

A number of studies of the application of transition metal complexes with such macrocyclic compounds as porphyrins and phthalocyanines to the electrocatalytic reduction of molecular oxygen have been reported.[1,2] Recently, Kobayashi and Osa reported a study of the catalytic electroreduction of molecular oxygen using 5,10,15,20-tetrakis(4-carboxyphenyl)porphinato iron in aqueous solutions.[3] In their study, molecular oxygen was reduced on either a polished solid electrode in a metalloporphyrin complex solution or a metalloporphyrin-adsorbed electrode in a supporting electrolyte solution. They suggested the mechanism of the catalytic reduction to be an electrochemical (EC) catalytic regeneration.

We have been interested in preparing covalently modified electrodes with iron porphyrin complexes and studying the electrochemical behavior of the modified electrodes.[4] Although solid electrodes have previously been modified by fixing porphyrins through amide[5-9] or ester[4,10] linkage, the reduction of oxygen using these modified electrodes has been rarely studied.[11]

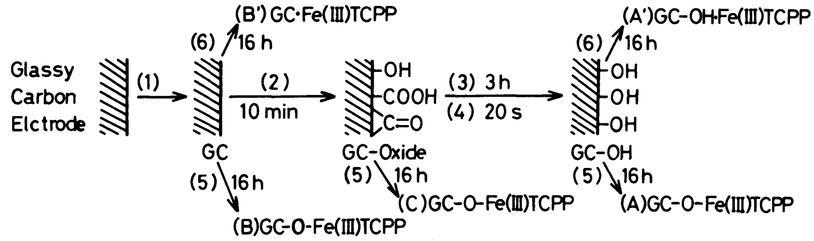
In the present paper, we will report on an electrochemical study of catalytic oxygen reduction on glassy carbon electrodes covalently modified with [5,10,15,20-tetrakis(4-carboxyphenyl)porphinato]iron(III) (represented by Fe(III)TCPP) and will report our finding that the oxygen reduction proceeds with an EC mechanism which changes with the pH-range.

Experimental

Materials. The Fe(III)TCPP was prepared by the metal insertion of 5,10,15,20-tetrakis(4-carboxyphenyl)porphine (Porphyrin Products Inc.) with $FeCl_2$.[12] The purification of Fe(III)TCPP was carried out several times by adding an HCl solution to the crude Fe(III)TCPP alkaline solution until the pH became ca. 5. The precipitated product was dried over phosphorus pentoxide at a reduced pressure for 20 h and identified by means of elemental analysis. Found: C, 65.88; H, 3.46; N, 6.55%. Calcd for Fe(III)TCPP(H_2O)(OH): C, 65.54; H, 3.55; N, 6.37%.

The water-soluble carbodiimide hydrochloride (WSCD·HCl, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride) used for dehydration was obtained from the Peptide Institute, Inc. (Osaka). All the other chemicals of a guaranteed reagent grade (Wako Pure Chemical Industries) were used without further purification.

Modification of Glassy Carbon Electrodes. A glassy carbon rod (GC-30, 5.4 mmϕ, Tokai Carbon, Ltd.) was inserted into a Teflon tube to give an exposed disc of area of ca. 0.23 cm^2; this rod then served as a working electrode. The mechanical and chemical treatments in the preparation procedure of each modified electrode are shown in Scheme 1. The numbers, (1) to (6), in Scheme 1 represent the following treatment steps, (1) *Mechanical polishing*: The exposed disc surface of the GC-30 electrode was polished with abrasive paper, followed by suspensions of alumina powders (Marumoto, Ltd.) of decreasing size, down to 0.06 μm, until a mirror-like finish was obtained. (2) *Oxidation*: The polished electrodes were immersed in a 0.4 mol dm^{-3}



Scheme 1. Modification procedures of GC electrode.

$Na_2Cr_2O_7$ acidic (H_2SO_4) solution and then refluxed at ca. 100 °C. (3) *Reduction*: The oxidized electrodes were immersed in a refluxed 0.1 mol dm^{-3} $LiAlH_4$ diethyl ether solution. (4) *Cleaning*: The $Al(OH)_3$ precipitated on the surface during the (3) treatment was removed by ultrasonic cleaning in a 0.05 mol dm^{-3} H_2SO_4 solution. (5) *Dehydration condensation*: Fe(III)TCPP was linked to the electrode surface covered with a hydroxyl group by dehydration condensation in dichloromethane saturated with Fe(III)TCPP and WSCD·HCl. (6) *Adsorption*: Fe(III)TCPP was adsorbed on the electrodes by immersing the elerctrodes for 16 h in dichloromethane saturated with Fe(III)TCPP.

Each time of treatment is also presented in Scheme 1. The electrodes prepared are identified by abbreviations, such as GC-OH or (A)GC-O-Fe(III)TCPP.

Electrochemical Measurements. The cyclic voltammetric measurement was performed using a Nikko Keisoku NPGFZ-2501-A potentiogalvanostat. For rotating disc voltammetry, a Nikko Keisoku DPGS-1 potentiogalvanostat, an NPS-2 potential sweeper, an RRDE-1 rotator, and an SC-5 speed controller were also used.

In the oxygen-free experiment, the solutions were deaerated by passing nitrogen gas through them for 20 min prior to the electrochemical measurement and by then keeping them blanketed during the measurement, though the reduction experiments of oxygen were carried out in air-saturated solutions. The potentials were referred to a saturated calomel electrode (SCE).

The buffer solutions, which also served as supporting electrolytes, were prepared from acetate, phosphate, borate, and carbonate. The adjustment of the pH was done using H_2SO_4 and/or NaOH, and the ionic strength was adjusted at 0.1 mol dm^{-3} with Na_2SO_4. The pH values were measured with a Toa-5B pH meter. All the measurements were performed at 25 °C.

Results and Discussion

The cyclic voltammetric current-potential (I–E) curves obtained on the (A)GC-O-Fe(III)TCPP and (B)GC-O-Fe(III)TCPP electrodes in oxygen-free electrolytic solutions at pH 7 are shown in Fig. 1. The hatched area for each curve corresponds to the charges consumed during the reduction of modified Fe(III)-TCPP to Fe(II)TCPP. The close potentials of the cathodic and anodic peaks indicate that the corresponding redox process is a surface one.[13,14] The peak current values were so small that we can not examine the dependence of the peak current on the potential sweep rate. In spite of the large difference in residual currents observed on the (A) and (B) electrodes, the same amount of attached Fe(III)TCPP was determined by integrating the cathodic peak current of the wave. The details of these results will be discussed below (see Table 1).

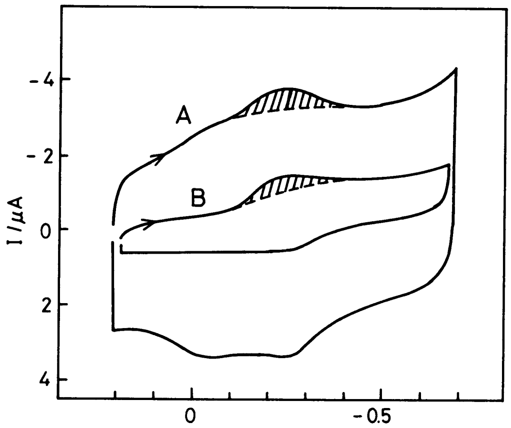


Fig. 1. Cyclic voltammetric I–E curves on the Fe(III)TCPP modified electrodes (A) and (B) obtained in pH 7 solutions in the absence of O_2. Scan rate=0.05 V s^{-1}.

Figure 2 shows the reduction waves of oxygen

Table 1. The Peak Potential of Oxygen Reduction and the Surface Concentration of Fe(III)TCPP Attached to the Electrodes

Electrode	E_p/V	10^6[Quantity of electricity]/C	10^{11}[Surface concentration]/mol cm^{-2}
A	−0.207	1.30	5.9
B	−0.286	1.60	7.2
C	−0.270	0.60	2.7
A′	−0.300	—	—
B′	−0.350	—	—

Scan rate: 0.05 V s^{-1}.

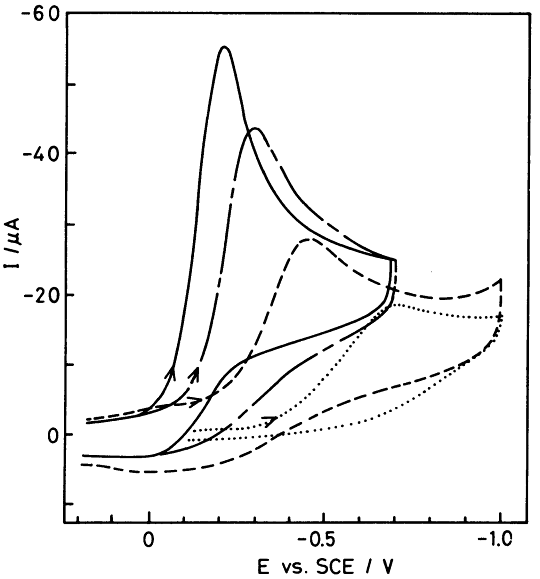


Fig. 2. Cyclic voltammograms for the reduction of O_2 on a glassy carbon and the chemically modified glassy carbon electrodes in the air saturated electrolyte solutions of pH 7. —— (A)GC-O-Fe(III)TCPP, —·— (A′)GC-OH·Fe(III)TCPP, ------ GC-OH, and ······ GC. Scan rates: 0.05 V s^{-1}.

observed on the four kinds of electrodes in air-saturated electrolytic solutions at pH 7. The anodic shift of the peak potential attributable to the Fe(III)TCPP modification is considerably greater on the (A)GC-O-Fe(III)TCPP electrode than on the (A′)GC-OH·Fe(III)TCPP-adsorbed electrode (see also Fig. 3).

The peak potentials of oxygen reduction in aqueous solutions of pH 7 and the quantities of Fe(III)TCPP molecules on the modified electrodes (A, B, and C), obtained from the quantity of the charge in the reduction of Fe(III)TCPP, are listed in Table 1, together with the values on the Fe(III)TCPP-adsorbed electrodes. In order to exclude the reduction current attributable to the residual oxygen in the solution, the peak potentials were measured after consecutive scans, in which no variation in the current had been observed. The amounts of Fe(III)TCPP covalently attached to the (A) and (B) electrodes were almost the same, while the amount attached on the (C) electrode was about a half of that value. On the 1st scan in the cyclic voltammogram, the (C) electrode gave almost the same area of the reduction peak as those of the (A) and (B) electrodes. In the case of the (C) electrode, however, the consecutive scans caused an abrupt decrease in the area of the reduction peak with a slight decrease in the residual current. This observation suggests that the Fe(III)TCPP attached on the GC-Oxide partially peeled off during the consecutive potential scans.

The amounts of the hydroxyl group on the (A) and (B) electrodes, which was calculated from the quantity of the charge in the reduction of the 3,5-dinitrobenzoyl chloride covalently attached to the OH group of the GC and GC-OH electrodes,[4,15,16] were 1.9×10^{14} and 0.53×10^{14} molecules respectively. In spite of the large difference (ca. 4 times) in the amount of hydroxyl group on the surfaces, the amount of Fe(III)TCPP on the (A) electrode was nearly equal to that on the (B) electrode. This indicates that a large portion of the hydroxyl groups introduced on the (A) electrode is covered with the attached large molecule of Fe(III)-TCPP and is not utilized effectively for the modification. This interpretation is supported by the fact that the redox peak couple at −0.05 V, probably attributable to groups introduced by the oxidation, observed on the (A) electrode was not noticeable on the (B) electrode, as is shown in Fig. 1.[4]

Table 1 shows that the reduction of oxygen on the covalently attached (A)GC-O-Fe(III)TCPP electrode occurs at the most anodic potential among the series of Fe(III)TCPP modified GC electrodes: The peak potential of oxygen reduction on the (A) electrode shifted ca. 80, 90, and 140 mV toward the positive direction compared to those on the (B), (A′), and (B′) electrodes respectively.

Figure 3 shows the peak potential of oxygen reduction on the (A)GC-O-Fe(III)TCPP electrode as a function of the condensation time with WSCD·HCl. The complete potential shift, ca. 100 mV, is obtained within 10 min of the condensation. Because of the previously mentioned existence of the excess hydroxyl group on the (A)GC-O-Fe(III)TCPP electrode, all the four carboxyl groups of Fe(III)TCPP may link with the electrode. A preliminary experiment on the modified GC electrode with hemin, which has two carboxyl groups, showed an anodic potential shift of ca. 30—40 mV for oxygen reduction. A similar anodic shift upon the oxygen reduction was reported by Kobayashi et at.[11] on the electrode modified with the metalloporphyrin through amide linkages. Consequently, it can be speculated that this anodic shift of

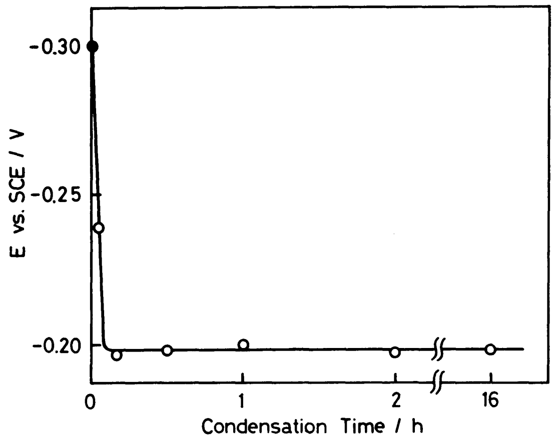


Fig. 3. Plots of the peak potential of oxygen reduction vs. condensation time. ○: (A)GC-O-Fe(III)TCPP, ●: (A′)GC-OH·Fe(III)TCPP.

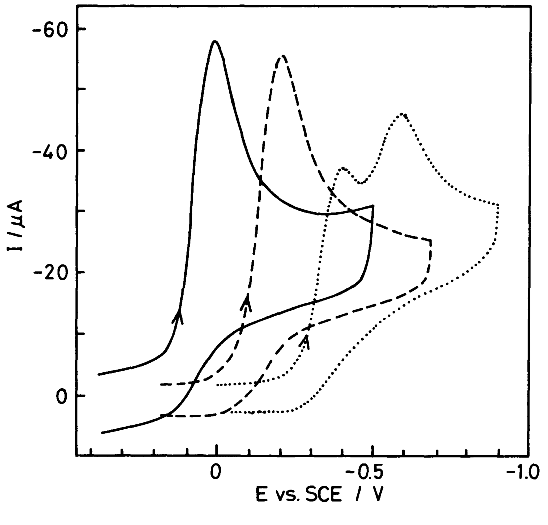


Fig. 4. Cyclic voltammograms for oxygen reduction on the (A)GC-O-Fe(III)TCPP electrode in the air saturated electrolyte solution of pH 1.3 (——), 7.0 (-----), and 12.4 (······).

the oxygen-reduction potential on the covalently modified electrodes is closely related to the number of bonds between a metalloporphyrin and an electrode material. The more cathodic potential of oxygen reduction on the (B) electrode compared to that on the (A) electrode is probably attributable to the smaller number of covalent bonds per metalloporphyrin molecule on the electrode.

Figure 4 shows some typical cyclic voltammograms obtained on the (A)GC-O-Fe(III)TCPP electrode in air-saturated aqueous solutions of various pHs. The peak potential of oxygen reduction is shifted cathodically with an increase in the pH of the solution. In a high-pH solution, a discrete and successive two-step reduction was observed. The dependence of the peak potential on the pH of the solutions is represented in Fig. 5. Three different potential shifts per unit of pH were observed according as the pH range was pH<5, pH 6—11, or pH>11. The peak-potential shifts with slopes of ca. −55 mV/pH at pH 6—11; that is, the reduction of the oxygen molecule is accompanied by the addition of one electron per one-proton addtition. At pH>11, two successive reduction waves are observed. They shift with slopes of 0 mV/pH and ca. −110 mV/pH; that is, one oxygen molecule is reduced by the electron addition followed by a one-electron addition per two-proton addition. At pH<5, on the other hand, the slope of the peak potential shift is reduced with a decrease in the pH.

In Fig. 5, the dashed line represents the data for oxygen reduction on the GC-20 electrode in Fe(III)TCPP aqueous solutions, while the open triangle is the peak potential on the Fe(III)TCPP-adsorbed GC-20 electrode in the porphyrin-free solution, as reported by Kobayashi and Osa.[3] Though the peak potential on the adsorbed electrode is almost the same as on the naked electrode in the porphyrin solution, the oxygen reduction potential on our covalently modified electrode shifts anodically by ca. 175 mV in the range of pH 6—11.

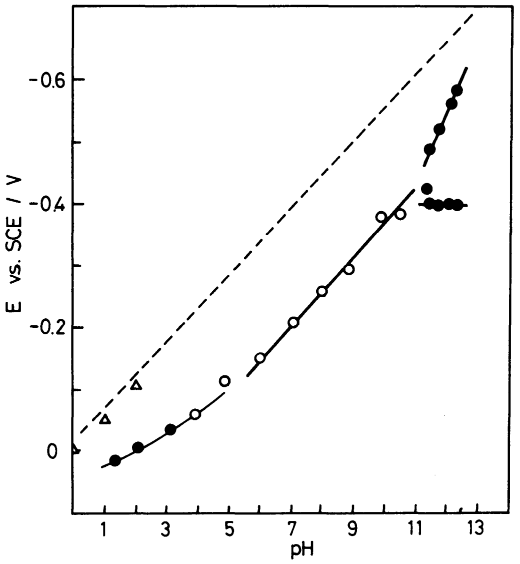


Fig. 5. The peak potentials of oxygen reduction on the (A)GC-O-Fe(III)TCPP electrodes as a function of the pH. ○: in buffered solutions, ●: in non-buffered solutions, △ and dashed line: replotted from Ref. 3.

In order to estimate the number of transferred electrons in the oxygen reduction, current-potential curves were obtained using an (A)GC-O-Fe(III)TCPP rotating electrode. Figure 6 shows some typical current-potential curves obtained in air-saturated solutions at the pHs corresponding to the ranges in Fig. 5. Because of the lower stability of the modified electrodes at low pHs, the current increased slowly with an increase in the potential, and the reproducibility of the values of limiting current was poor. This behavior suggests the presence of complicating electrode processes, including the cleavage of some ester linkages and the release of Fe(III)TCPP molecules from the surface. Except for the acidic solution, the Levich plots (the limiting current vs. (the rotating rate)$^{1/2}$)[8] showed good straight lines through the point of origin. The number of transferred electrons in the oxygen reduction was calculated by the use of the Levich equation from the limiting current at each rotation rate (250, 500, 750, 1000, and 1250 rpm). In the calculation, the following values were used for the variables in the equation: $2.1\times10^{-5}\,\mathrm{cm^2\,s^{-1}}$ and $2.4\times10^{-4}\,\mathrm{mol\,dm^{-3}}$[1] for the diffusion coefficient and the concentration of oxygen in air-saturated solutions respectively, $8.9\times10^{-3}\,\mathrm{cm^2\,s^{-1}}$ for the kinetic viscosity of aqueous solutins, and $0.23\,\mathrm{cm^2}$ for the surface area of modified electrodes.

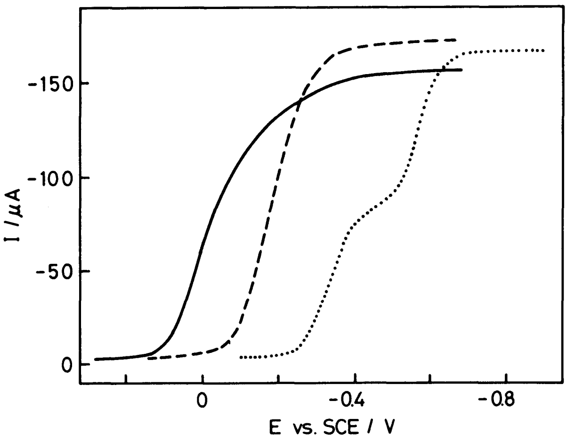


Fig. 6. Current-potential curves of the reduction of oxygen at the rotating disc modified (A) Electrodes. The electrode was rotated at 500 rpm. The potential was scanned at 50 mV s^{-1}. —— pH 3.1, ----- pH 7.1, ······pH 12.0

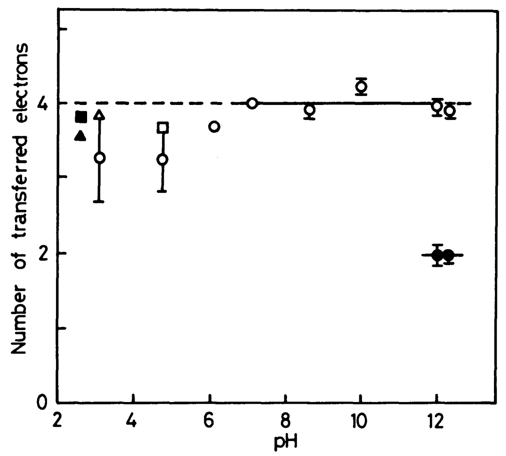


Fig. 7. Number of transferred electrons for the oxygen reduction at the rotating disc modified (A) electrodes as a function of the pH. ○: average overall number of transferred electrons. ●: average number of transferred electrons at the first wave at pH>11.5. Rotation rate (rpm): △250, ▲500, □1000, and ■1250.

Figure 7 shows the relationship between the number of transferred electrons measured on the (A) GC-O-Fe(III)TCPP rotating electrode and the pH of the solutions. At pH>11.5, the solid circle and the open circle indicate the number of transferred electrons in the 1st reduction wave and in the overall reduction respectively. Figure 7 indicates that the oxygen molecule is reduced via a one-step reaction with four-electron transfer at pH 7—11 and via two successive reactions, each with a two-electron transfer, at pH>11.5.

The numbers of transferred electrons and protons in the oxygen reduction suggest that the reduction of the oxygen molecules in the solutions on the (A)GC-O-Fe(III)TCPP electrode proceeds via the following EC catalytic regeneration mechanisms. At pH 7—11, the linked Fe(III)TCPP molecules are reduced to Fe(II)-TCPP by Eq. 1 (E step) and reproduced by Eq. 2 (C step), reducing an oxygen molecule to H_2O:

$$\mathrm{Fe(III)TCPP} + e^- \longrightarrow \mathrm{Fe(II)TCPP} \qquad (1)$$

$$4\mathrm{Fe(II)TCPP} + O_2 + 4H^+ \longrightarrow 4\mathrm{Fe(III)TCPP} + 2H_2O \qquad (2)$$

At pH>11.5, however, the Fe(II)TCPP molecules, which are produced by Eq. 1 (E step), reduce an oxygen molecule to the O_2^{2-} ion by Eq. 3 (C step) at the first peak potential; then they reduce O_2^{2-} by Eq. 4 (C step) at the more cathodic potential:

$$2\mathrm{Fe(II)TCPP} + O_2 \longrightarrow 2\mathrm{Fe(III)TCPP} + O_2^{2-} \qquad (3)$$

$$2\mathrm{Fe(II)TCPP} + O_2^{2-} + 2H_2O \longrightarrow 2\mathrm{Fe(III)TCPP} + 4OH^- \qquad (4)$$

In the solution at pH<6, there was some scatter in the limiting current of oxygen reduction. However, the largest number of transferred electron determined was nearly equal to four. Therefore, the reduction of oxygen in the solution at pH<6 probably proceed via essentially the same mechanism as that observed in the solution at pH 7—11.

Though the transient formation of an intermediate such as hydrogen peroxide during the reduction of oxygen could be considered, we did not detect the formation of any intermediates by the use of the RDE apparatus.

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