

A potential anode material for the direct alcohol fuel cell

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Abstract

One of the key points to develop a cost-effective direct alcohol fuel cell (DAFC) is to investigate cheaper electrocatalysts for the oxidation of alcohol at the anode, allowing an increase in the current density and a decrease in the anodic overvoltage. In this respect, polycrystalline deposits of platinum and platinum–ruthenium on a CuNi (70:30) alloy support are investigated here. Electro-oxidation of ethanol in 0.5 M NaOH is studied over these electrodes. Cyclic voltammetry, steady state polarization and electrochemical impedance spectroscopy are used to investigate the kinetics and mechanism of ethanol electro-oxidation. Efforts are also made to correlate the catalytic activity of such electrodes with their surface morphology.

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1. Introduction

To date, the best performing fuel cell electrodes are either platinum or platinum-based materials, including the anode in a direct alcohol fuel cell (DAFC) [1]. Platinum metal has been one of the most expensive materials in the fabrication of components for these fuel cells. Still if a pure platinum catalyst is used for alcohol electro-oxidation, the anode surface is poisoned and the reactivity is reduced or even stopped entirely [2]. Notable enhancement of the electrocatalytic activity of platinum has been observed by introducing a second metal: Pt–Ru [3–5], Pt–Sn [6–8], Pt–Pd [9], Pt–Rh [10], Pt–Mo [11]. The best of these has been found to be a codeposit of platinum and ruthenium. For sufficiently active catalyst for DAFC anode at least a few mg/cm² of precious metals is still required. It is, therefore, necessary to develop more active anode catalysts for DAFC to be economically viable.

There are several solutions that can be adopted to achieve this goal namely, (i) synthesis of finely dispersed catalyst layers on conducting surfaces; (ii) reduction of relative loading of Pt metal on the catalyst surface; and (iii) use of substrate that not only offers enhanced surface area but also assist in the catalytic activity of the noble metal deposits during electro-oxidation of the fuel.

In recent years, most of the studies related to DMFCs have involved carbon supports for preparation of the electro-

catalysts [12–16]. In this paper, we have selected the 70:30 copper–nickel alloy as the potential substrate for fabricating the anode component of a DAFC. CuNi alloy substrate can change the density of states of the d-band and hence the local electronic character of the active sites. Such changes in the local electronic structure may influence the electron transfer between the adsorbate molecule and the catalyst layers.

We describe results with CuNi alloy based catalysts for direct oxidation of ethanol in alkaline medium. Use of ethanol as fuel in DAFCs has been widely advocated because it enjoys distinct advantages over other alcohols [2]. Its mass production from agricultural products may decrease its price so that it may compete economically with methanol. Moreover ethanol is relatively nontoxic and possesses good energy density (8.00 kWh/kg) compared to that of hydrocarbon and gasoline (e.g. 10–11 kWh/kg).

2. Experimental

2.1. Preparation of electrocatalysts

A commercially available 70:30 CuNi alloy was used as substrate for noble metal deposits. The CuNi material comprised plate of 1.0 mm thickness from which specimens of size 1.3 cm × 0.5 cm was cut. The specimens were ground and polished to a 0.3 mm finish, washed and degreased.

Pt and PtRu codeposition on CuNi alloy substrate was achieved under galvanostatic condition (5 mA/cm²) from

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0.5 M HCl solutions containing 5×10^{-2} M of the respective metal chlorides ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ from Arora Matthey Ltd.). A current density of 20 mA/cm^2 was used for deposition from a dilute suspension (2% (w/w)) of polytetrafluoroethylene (PTFE) emulsion containing a similar concentration of noble metal salts. The electrodes prepared via electrodeposition from PTFE emulsion are hereafter referred to as CuNi/Pt (PTFE) and CuNi/PtRu (PTFE) while those prepared from HCl solution without PTFE are designated as CuNi/Pt and CuNi/PtRu. All electrodepositions were carried out at room temperature. The electrodes were rinsed with triple distilled water and dried. The catalyst loading ($\sim 2 \text{ mg/cm}^2$) on the alloy substrate was determined by the mass difference of the substrate before and after deposition.

The surface morphology of the electrocatalysts was investigated with a LEO S 430i scanning electron microscope at an accelerating potential of 20 kV. The chemical composition of the catalyst layers was determined by energy dispersive X-ray (EDX) using Link ISIS EDX detector (Oxford Instruments, UK) coupled with the scanning electron microscope.

2.2. Electrochemical measurements

All electrochemical measurements were conducted using a computer controlled potentiostat/galvanostat with PG STAT 12 and FRA modules (Ecochemie B.V., The Netherlands). Experiments were carried out in a glass cell using a conventional three-electrode set up incorporating a mercury–mercuric oxide reference electrode (0.14 V versus SHE) and a bright Pt-foil (10 mm \times 10 mm) counter electrode. Nitrogen gas (XL grade from BOC India Ltd.) was bubbled in the 0.5 M NaOH supporting electrolyte for 15 min before starting each electrochemical experiments. All test solutions were prepared using triple distilled water.

To assess the stability of the CuNi alloy and the supported catalyst layers in the alkaline electrolyte, potentiodynamic polarisation studies were performed in both aerated and deaerated solution containing 0.5 M NaOH (LR grade, Merck) at a scan rate of 0.5 mV/s.

Ethanol (AR grade, Merck) was added to the nitrogen saturated 0.5 M NaOH electrolyte to give 0.5 M EtOH concentration. Cyclic voltammograms (CV) of ethanol electro-oxidation were recorded in this solution between -1.0 and 0.5 V at a sweep rate of 50 mV/s. Steady state potentiostatic data were recorded after polarisation for 5 min in the same solution. Electrochemical impedance measurements were performed with amplitude of 5 mV in the frequency range 65 kHz to 5 mHz at a potential of 0.5 V.

Open circuit potential (OCP) measurements at different temperatures were carried out in a two-compartment cell with an asbestos separator. The cell anode was fed with 1 M EtOH/0.5 M NaOH solution while the cathode chamber was continuously purged with oxygen (XL grade from BOC

India Ltd.) at a flow rate of 140 ml/min. A platinised Pt electrode (1 cm^2) was used as the cathode.

3. Results and discussion

3.1. Surface characterization

SEM image (Fig. 1a) of the CuNi/Pt catalyst prepared by electrodeposition from chloroplatinic acid solution reveals a homogeneous platinum layer on the surface with some prominent ring-like growths. While there are platinum deposits within the comparatively larger rings, the dark regions of the smaller rings are indicative of the exposed alloy substrate as determined by EDX analysis. In contrast, platinum electrodeposited from PTFE suspension shows a uniform distribution of spherical platinum particles (Fig. 1b). Besides, the close packing of the platinum particles ensures high roughness factor of the catalyst layer. For the CuNi/PtRu (PTFE) electrocatalyst, the SEM image (Fig. 1c) shows homogeneously distributed small dark particles of about 50 nm in diameter which we attribute to Ru deposits on the platinum layers as confirmed by EDX.

3.2. Corrosion studies

Fig. 2 shows the potentiodynamic polarisation plots in 0.5 M NaOH of the CuNi alloy substrate as well as the supported catalyst layers prepared from PTFE suspension. Evaluation of the corrosion parameters shows that the corrosion current density is of the order of 10^{-5} A/cm^2 for almost all the electrodes under study. This may in part be attributed to an oxide/hydroxide film formed on the alloy substrate in alkaline medium. Further retention of chloride ions on the catalyst layers from the deposition bath may account for the slight increase in the corrosion rate of the prepared electrocatalysts as compared to the CuNi alloy itself. Notably, the positive shift in E_{cor} values for the PTFE-modified electrocatalysts as compared to the bare alloy is indicative of the nobler behavior of the former in alkaline medium.

3.3. Ethanol oxidation in alkaline solution

3.3.1. Cyclic voltammetry and steady state polarisation studies

The CVs in Fig. 3 illustrate the ethanol oxidation behavior on CuNi alloy based electrocatalysts in 0.5 M NaOH solution at room temperature. As is evident from Fig. 3a, in the course of multiple scanning there is a steady rise of the anodic peak current for the CuNi/Pt (PTFE) electrocatalyst. The peak current increases substantially from the 1st to the 50th scan. This enhancement may be attributed to an increased rate of adsorption of oxidative species during potential cycling until a steady state is attained. Fig. 3b highlights a clear kinetic enhancement for ethanol electro-oxidation on CuNi/PtRu (PTFE) over the

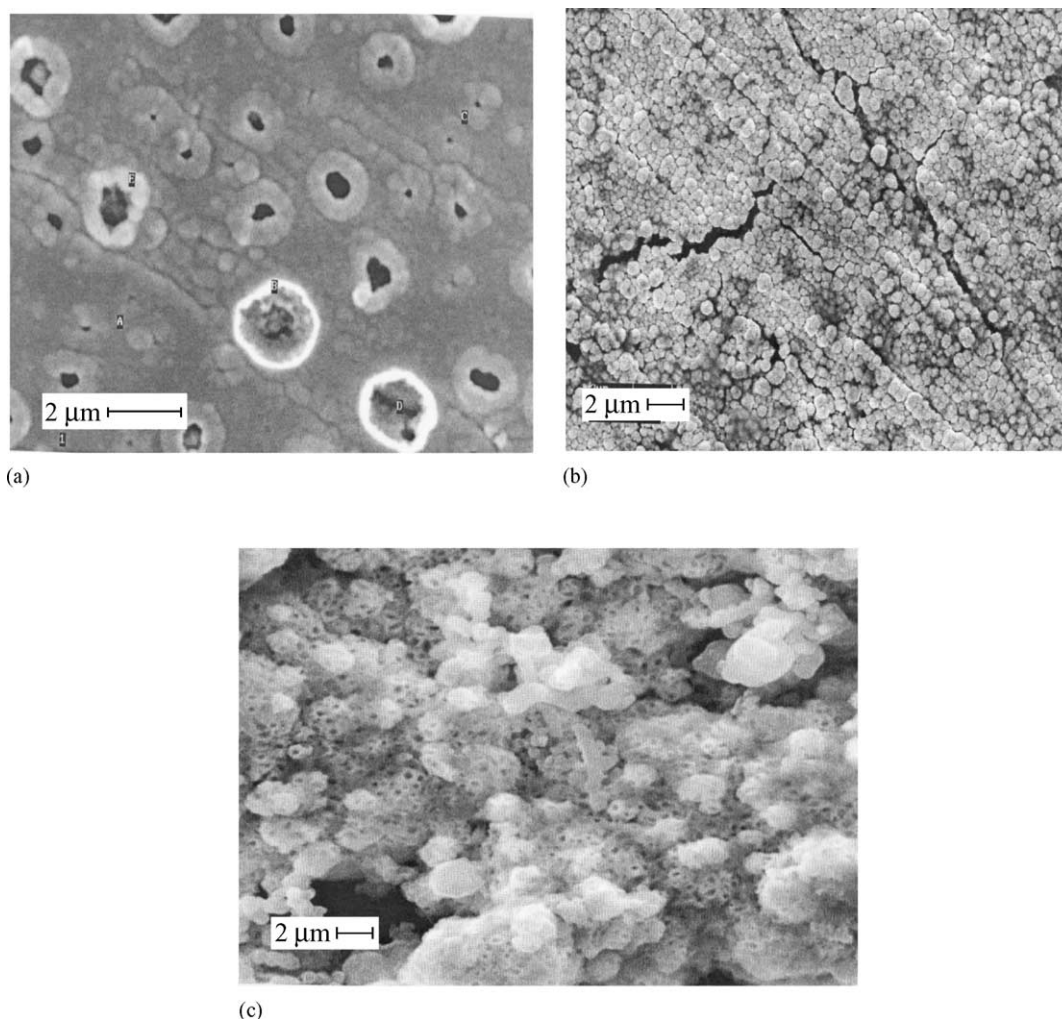


Fig. 1. SEM images of: (a) CuNi/Pt; (b) CuNi/Pt (PTFE); (c) CuNi/PtRu (PTFE).

CuNi/Pt (PTFE) electrode. For the different electrodes used in this study, the shapes of the voltammograms were similar indicating that the mechanism of ethanol oxidation is identical.

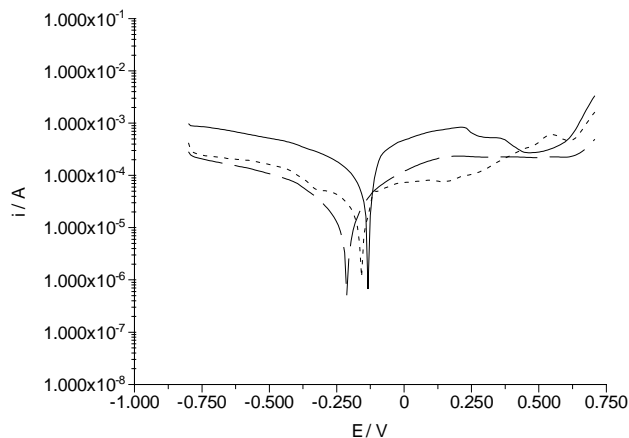


Fig. 2. Potentiodynamic polarisation plots in deaerated 0.5 M NaOH at a scan rate of 0.5 mV/s; (---) CuNi, (· · ·) CuNi/PtRu (PTFE), (—) CuNi/Pt (PTFE).

Fig. 4 shows the anodic polarisation curves for ethanol oxidation at room temperature. It is evident that the polarisation curves have linear Tafel portions in the potential range of approximately -0.6 to -0.4 V. As is evident, there is a significant enhancement in the activity of ethanol oxidation for the catalyst layers electro-deposited from PTFE suspension as compared to those prepared from HCl medium. This may in part be attributed to the better dispersion of the catalyst particles for the preparation technique involving PTFE as revealed in the SEM images. The higher electrocatalytic activity for the binary PtRu deposits is easily explained on the basis of the promoting effect of Ru for the electro-oxidation of alcohols [3].

It is expected that ethanol oxidation in alkaline medium undergoes parallel pathways leading to different soluble products. In this connection, the electrocatalysis of the C–C bond cleavage is a topic of interest. Studies undertaken on the electro-oxidation of ethanol in acid medium [17,18] have shown that the presence of Ru in the catalyst layers facilitates the cleavage of the C–C bond in the ethanol molecule upon adsorption. The present investigation, made in alkaline ethanol solution after prolonged continuous run

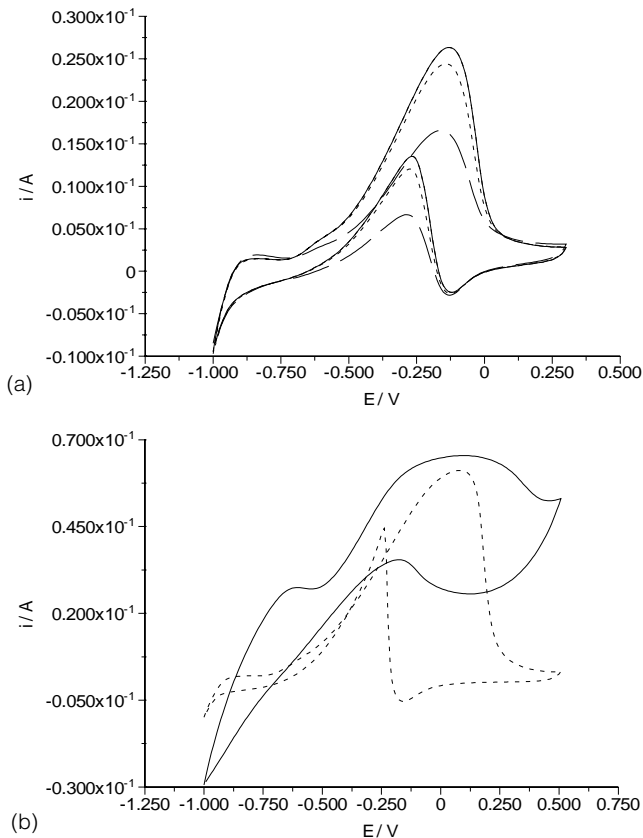


Fig. 3. Cyclic voltammograms for ethanol (1.0 M) oxidation in 0.5 M NaOH at a scan rate of 50 mV/s on (a) CuNi/Pt, (-----) 1st scan, (· · · · ·) 25th scan, (—) 50th scan; (b) (· · ·) CuNi/Pt (PTFE) and (—) CuNi/PtRu (PTFE).

of the cell, showed the presence of acetaldehyde and CO₂ (as carbonate) with the CuNi/PtRu (PTFE) anode. Anodic stripping voltammetry was performed for the determination of acetaldehyde [19] using a VA Trace Analyser (Metrohm

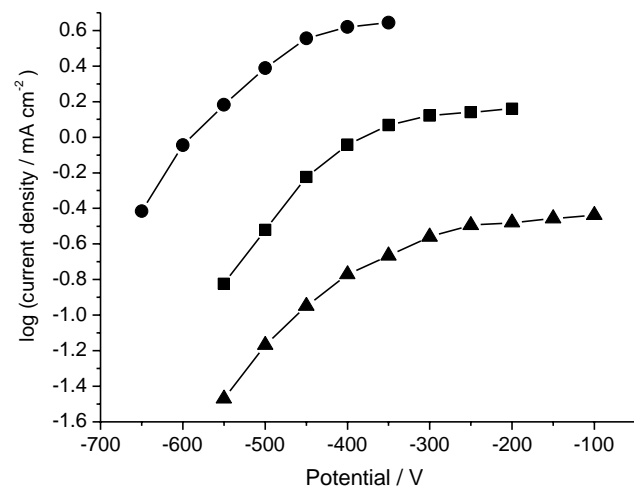


Fig. 4. Potentiostatic polarisation curves for ethanol oxidation in 0.5 M NaOH on different electrodes: (●) CuNi/PtRu (PTFE); (■) CuNi/Pt (PTFE); and (▲) CuNi/Pt.

Table 1

Charge transfer resistance for the oxidation of 1 M ethanol in 0.5 M NaOH

Electrode	Charge transfer resistance, R_{ct} (Ω)
CuNi/PtRu	22
CuNi/Pt	99
CuNi/PtRu (PTFE)	15.9
CuNi/Pt (PTFE)	217.5

Electrode potential: 0.5 V vs. Hg/HgO, frequency range: 65 kHz to 5 mHz.

Ltd., Switzerland). During oxidation of ethanol the CO₂ evolved was absorbed in the electrolyte and this was then determined by potentiometric titration with HCl [20] using the combined glass electrode and 702 SM Titrino (Metrohm Ltd., Switzerland). The presence of CO₂ in the product mixture is indicative of the fact that C–C bond cleavage does indeed occur in the electro-oxidation of ethanol in alkaline medium. In view of this observation, detailed studies will be performed in the future using spectrochemical techniques with the aim of attaining a better understanding of the mechanism involved in the oxidation of ethanol.

3.4. EIS studies

Nyquist plots for the electro-oxidation of ethanol in 0.5 M NaOH are summarised in Fig. 5 and Table 1. The charge transfer resistance R_{ct} , as measured by the diameter of the semi-circle in the plot, is related to the charge transfer reaction kinetics according to the following equation [21]:

$$R_{ct} = \frac{RT}{nFi_0} \quad (1)$$

where

$$i_0 = nFAk_0C_0^{*(1-\alpha)}C_R^{*\alpha} \quad (2)$$

R is the molar gas constant (J/(mol K)); T is the temperature (K); n is the number of electrons transferred; F is the Faraday constant (C); i_0 is the exchange current (A); A is the reaction area (cm²); k_0 is the standard heterogeneous rate constant (cm/s); C_0^* , C_R^* are the bulk concentration of oxidation and reduction species (mol/l); and α is the transfer coefficient.

Examination of Fig. 5 shows a significant decrease in the magnitude of R_{ct} for PtRu codeposited surfaces indicating an increase in reaction kinetics [22], as would be expected from the analysis of the cyclic voltammograms. Identical nature of the impedance spectra that the mechanism of electro-oxidation on different CuNi based electrodes is similar. The highest charge transfer resistance was observed for the Pt deposited electrodes indicating the greater poisoning effect on such surfaces.

3.5. Variation of OCP with temperature

Fig. 6 shows the variation of OCP with temperature. Except for the CuNi/Pt, OCP generally increases with the rise in temperature indicating an increase in reaction kinetics.

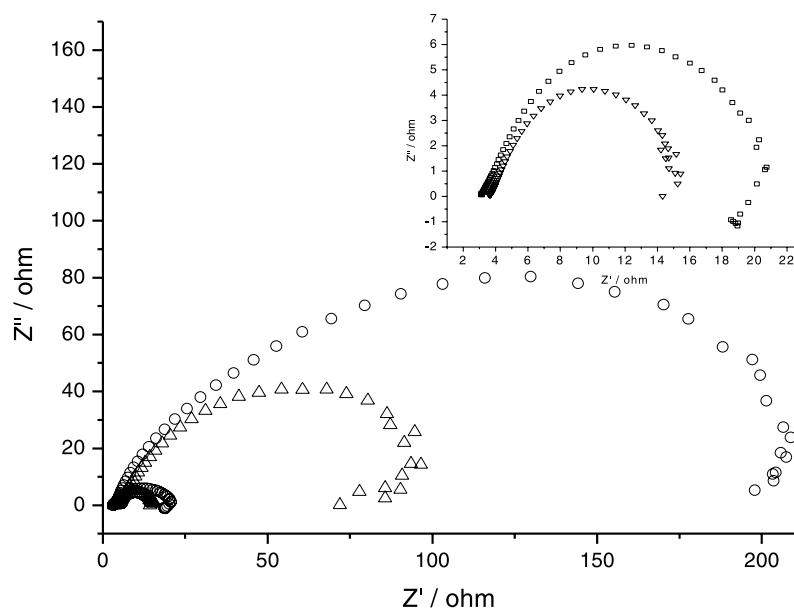


Fig. 5. Electrochemical impedance spectra in 0.5 M NaOH + 1.0 M EtOH at 0.5 V of (∇) CuNi/PtRu (PTFE), (\circ) CuNi/Pt (PTFE), (\square) CuNi/PtRu, and (\triangle) CuNi/Pt.

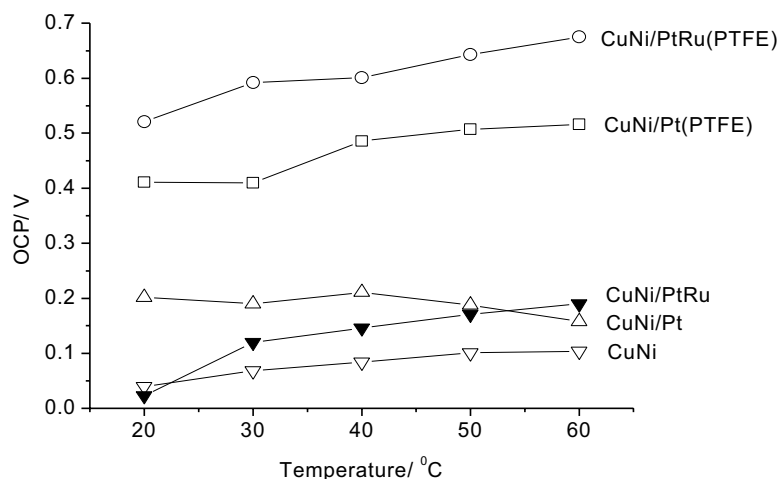


Fig. 6. Variation of open circuit potential with temperature for different electrodes.

The best performing electrodes are those prepared via electrodeposition from PTFE suspension as would be expected from the results of polarisation and EIS measurements.

4. Conclusions

From the analysis of the experimental data obtained from EIS, SEM, CV and polarisation studies, the following important conclusions can be drawn: (i) The resistance to charge transfer, R_{ct} is greatly reduced in the PtRu-modified CuNi electrodes, probably reflecting an interfacial structure change after the deposition of catalyst particles; (ii) Both CV and polarisation studies reveal a higher electrocatalytic activity towards ethanol oxidation for catalyst layers prepared from PTFE suspension of noble metal salts. This may

be attributed to the better dispersion of catalyst particles from PTFE, as revealed by SEM images; (iii) In the present study, the best performing electrode for alkaline DAFC is CuNi/PtRu (PTFE). Its enhanced electrocatalytic activity over other electrodes may be explained on the basis of the bifunctional mechanism proposed by Watanabe and Motoo.

Novel CuNi alloy supported electrocatalyst synthesised from PTFE suspension of noble metal salts can be an alternative anode material for DAFC.

Acknowledgements

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