ORIGINAL PAPER

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Catalyst preparation by combustion synthesis for electrochemical hydrocarbon devices

Abstract Metals and ceramics can behave as active electrocatalyst materials, particularly in hydrocarbon oxidation in anodic reaction fuel cells. Combustion synthesis is a very reliable, fruitful and rapid synthesis method to produce metals, ceramics and cermets with low particle size and high specific surface area. This work describes the preparation of nanoparticle Pt/Ru alloys, ceramic perovskites such as $Sm_{0.95}CoO_{3-\delta}$, and $Sm_{0.95}CoO_{3-\delta}$/Pt cermets, and shows how promising these materials can be in the role of electrochemically active materials.

Keywords Anode materials · Combustion synthesis · Electrocatalysts

Introduction

Hydrocarbons such as methanol can be electrochemically oxidized at a fuel cell anode either directly, which provides a compact electrical energy power source with particularly high energy densities compared to alternative electrochemical energy conversion systems, or indirectly, whereby hydrocarbons are initially reformed to give hydrogen in a high-temperature step [1].

However, fuel cells, such as hydrogen protonic exchange membrane fuel cells (PEMFCs) and direct

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methanol fuel cells (DMFCs), have been beset with difficulties as a result of performance losses mainly due to Pt poisoning of the anode [2].

The use of bimetallic (Pt/Ru) electrocatalytic sites [3] is an alternative strategy for creating regions on the surface able to adsorb reactive oxygen in the proximity of the adsorbed poisoning intermediates. Another alternative is the use of suitable active metal mixed oxides, such as perovskites with high specific surface area, to partially substitute the Pt metal and create surface regions that promote O^{2-} ion transport close to the reaction sites with adsorbed poisoning intermediates [3].

Ceramic perovskite oxides have attracted much attention in the last two decades in the field of catalysis, and are currently used as substitutes for noble metals in electrocatalysis. The perovskite structure can be tailored to have many desirable properties [1] by varying the valence state of transition metal ions, the binding energy and diffusion of O in the lattice, the distance between active sites, and the electrical conduction properties of the solid. Lago et al. [2] studied the partial oxidation of methane to synthesis gas using $LnCoO_3$ perovskites (where Ln = La, Pr, Nd, Sm and Gd) as catalyst precursors. Perovskite material can, therefore, be used in the partial oxidation of hydrocarbons alone or with appropriate Pt additions. In this respect, it is easy to recognize the possibility for the use of a Pt-perovskite cermet in the direct reforming of hydrocarbons in intermediate temperature solid oxide fuel cells (IT SOFCs). According to White and Sammells [3], the $SmCoO_{3-\delta}$ perovskite might be a promising cermet material as an anode in IT SOFCs [4].

Preparing high specific surface area electrocatalyst powders is a rather problematic work. Many powder synthesis techniques have been used and wet chemical methods (sol-gel, coprecipitation, impregnation, etc.) provide the best results, since they produce single or multiphase oxide powders with high surface area and well-defined compositions. However, in spite of the quality of the resultant powders, many solution

processes are complicated and time consuming, which limits their applicability.

However, combustion synthesis of multicomponent oxides has been gaining reputation as a simple preparation process to produce homogeneous, very fine and crystalline powders, without the need for intermediate decomposition and/or calcining steps [5, 6]. The basis of the combustion synthesis technique comes from the thermochemical concepts used in the field of propellants and explosives. Briefly, to produce a mixed oxide by combustion, a saturated aqueous solution containing the desired metal ions in the correct stoichiometry and a suitable organic fuel is brought to boil until the mixture ignites and a self-sustaining and extremely fast combustion reaction takes place, leaving a dry foamy powder in the combustion vessel. Redox reactions such as this are exothermic in nature and ignite at temperatures much lower than the oxide phase-formation temperature.

The aim of this work is the preparation, by combustion synthesis, of various catalysts, namely $Sm_{0.95}CoO_{3-\delta}$, $(Sm_{0.95}CoO_{3-\delta})_{0.4}Pt_{0.6}$ (to produce a dispersion of small Pt particles in the $Sm_{0.95}CoO_{3-\delta}$, resulting in a typical cermet), and of a composite material containing Pt/Ru alloy nanoparticles.

To this aim, the powder combustion synthesis was investigated, the characterization of the resultant powders was carried out, and the catalytic activities of the $SmCoO_{3-\delta}$/Pt cermet and $SrCO_3$-Pt/Ru composites, as anodes in a PEMFC, were measured. Small single-cell PEMFCs were fabricated and their characteristic polarization curves were obtained.

Experimental

The compositions prepared by combustion were $Sm_{0.95}CoO_{3-\delta}$ and $(Sm_{0.95}CoO_{3-\delta})_{0.4}Pt_{0.6}$ perovskites and $SrCO_3$-Pt/Ru composites. The precursors for the combustion synthesis were: $Sm(NO_3)_3.6H_2O$ (Aldrich), $Co(NO_3)_2.6H_2O$ (Merck), $Sr(NO_3)_2$ (Merck), $[CH_3COCH=C(O)CH_3]_2Pt$ (Aldrich), $[CH_3COCH=C(O)CH_3]_3Ru$ (Aldrich); urea $[CO(NH_2)_2]$ (Aldrich) was used as fuel. Homogenization and melting were achieved at 150 °C. Ignition took place at 300 °C. Figure 1 shows schematically the main stages of the process. The perovskite powders were calcined at 800 °C for 12 h in air.
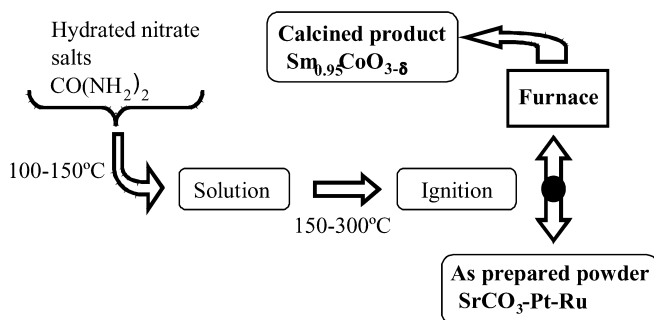
Fig. 1 Schematic view of the combustion synthesis technique used to prepare the powders

The powders were characterized by X-ray diffraction (XRD, Siemens D5000-Kristalloflex 710 diffractometer, using Cu Kα radiation at 40 kV and 20 mA, with a scanning rate of 2° 2θ/min), BET (Quantachrome MS-13, Monosorb surface area analyser), scanning electron microscopy (SEM, Zeiss-DSM 950 at 30 kV) and transmission electron microscopy (TEM, JEOL 2010 microscope at 200 kV). For electrical measurements, undoped and Pt-$SmCoO_{3-\delta}$ powders were pressed into pellets at 200 MPa and then sintered in air, in the temperature range 1200–1300 °C. Four-point electrical conductivity measurements were conducted in air using the pellets.

The $Sm_{0.95}CoO_{3-\delta}$ perovskite, with and without Pt, and the Pt/Ru composite as-prepared powders were used, together with Vulcan C (high specific surface area ∼600 m²/g), to fabricate the anode in a small (5 cm² electrode active area) single-cell membrane electrode assembly (MEA); a Nafion 117 membrane was used as the electrolyte and commercial Pt-C (40% Pt) as the cathode. The complete apparatus for electrochemical polarization measurements was used to obtain polarization curves of the single PEMFC [7].

Results and discussion

Figure 2 shows the XRD patterns of the various as-prepared powders. It can be seen that the samarium cobaltite has low crystallinity and the perovskite peaks do not appear in the powder. On the other hand, broad XRD peaks can undoubtedly be assigned to Pt metal, indicating a small Pt crystallite size (< 10 nm). A high specific surface area of 25 m²/g was determined for the undoped samarium cobaltite.

In the case of the $SrCO_3$-Pt/Ru material (Fig. 2), the Pt peaks present are shifted towards higher 2θ angles and no ruthenium peaks were observed. This suggests the presence of a Pt-Ru alloy. A specific surface area of 12 m²/g was obtained for this powder.

After a calcination step at 800 °C, the undoped samarium cobaltite powders developed the perovskite phase and presented a 9 m²/g specific surface area. Although lower than that of the as-prepared powder, this is still high for a calcined powder. Figure 3 shows the XRD patterns of sintered $Sm_{0.95}CoO_{3-\delta}$ and $Sm_{0.95}CoO_{3-\delta}$-Pt. In both cases, the samarium cobaltite remains a single perovskite phase, as in the calcined powders. However, the crystallinity of Pt is sharply increased, as compared with the as-prepared powders. This is due to the expected sharp Pt crystal growth with temperature.

Figure 4a is a SEM micrograph of the calcined undoped samarium cobaltite powders. These powders consist of big agglomerates of interconnecting rounded grains (ca. 180 nm), with a very uniform porosity (ca. 250 nm pore size). This skeleton morphology is appropriate for use as an electrode.

Figure 4b is a TEM micrograph of the $SrCO_3$-Pt/Ru as-prepared powders, showing very small (< 10 nm) Pt metal particles (black points located on the clearer part of the micrograph). Although the particles are nanocrystalline, the electron diffraction pattern shows rings characteristic of amorphous powders.

The microstructure of the sintered Pt-modified samarium cobaltite is shown in Fig. 5. Pt is homogeneously dispersed throughout the samarium cobaltite,

Fig. 2 X-ray diffraction patterns of the as-prepared combustion powders
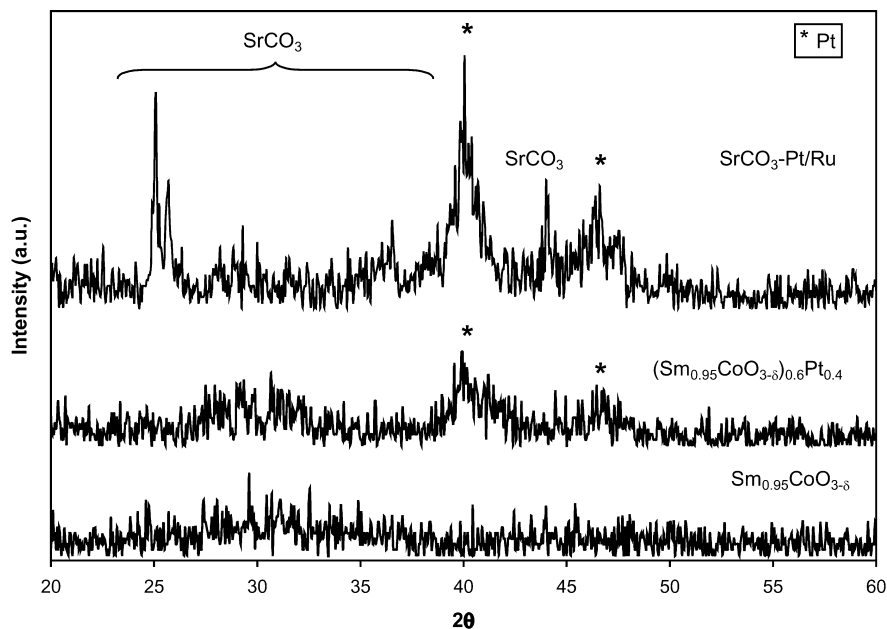
**Fig. 3** X-ray diffraction patterns of the sintered perovskites
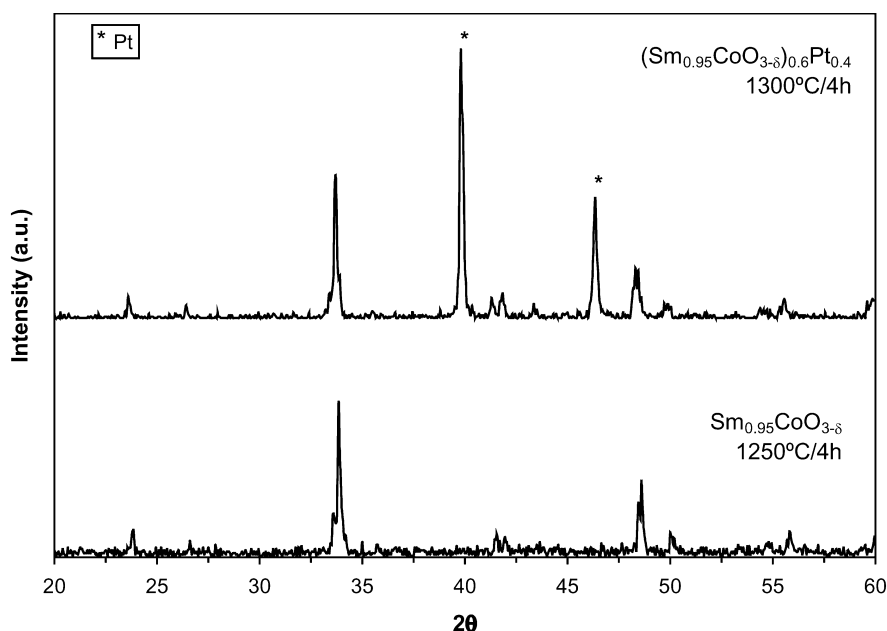
producing a cermet in which Pt particles are not percolated. These features are well suited to the application in IT SOFCs, using this material both as anode and catalyst to obtain hydrogen from hydrocarbons.

The four-point electrical conductivity behaviour of the sintered samarium cobaltite, presented as resistivity versus temperature in Fig. 6, shows a significant change at 475 K, which could be assigned to a semiconductor–metal transition (it could be regarded as either a typical Mott transition or narrow band semiconductor behaviour). Studies carried out with single-crystal cobaltites [8] showed similar activation energy. The conductivity of the $Sm_{0.95}CoO_{3-\delta}$-Pt samples is two orders of magnitude higher than that of the undoped $Sm_{0.95}CoO_{3-\delta}$, which is

due to the fact that the Pt particles present are not percolated. The conduction process can be ascribed to an electronic tunnel mechanism, rather than typical metallic conduction through interconnected Pt particles, since the Pt amount is not enough to percolate. Given that the composition $Sm_{0.95}CoO_{3-\delta}$ is Sm-deficient and so is likely to contain a small amount of Co^{4+}, the reduction in conductivity with increasing temperature could also be due to a loss of oxygen, reducing the number of charge carriers (Co^{4+}). However, in temperature programmed reduction (TPR) experiments [7], only Co^{3+} and Co^{2+} were detected.
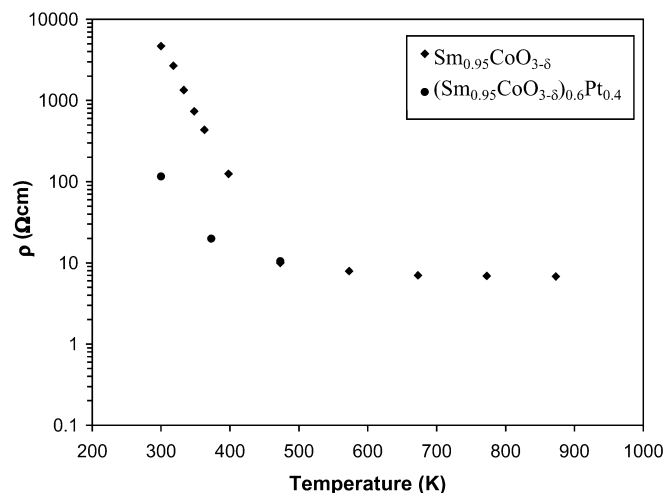
To produce the anode electrocatalyst in the single PEMFC, Pt-modified samarium cobaltite and $SrCO_3$-

Fig. 4 (**a**) SEM micrograph of $Sm_{0.95}CoO_{3-\delta}$ calcined at 800 °C in air; (**b**) TEM micrograph of $SrCO_3$-Pt/Ru composite as-prepared powder and its electron diffraction pattern
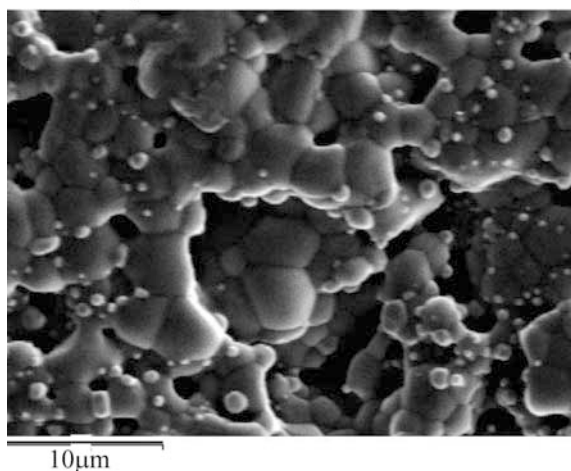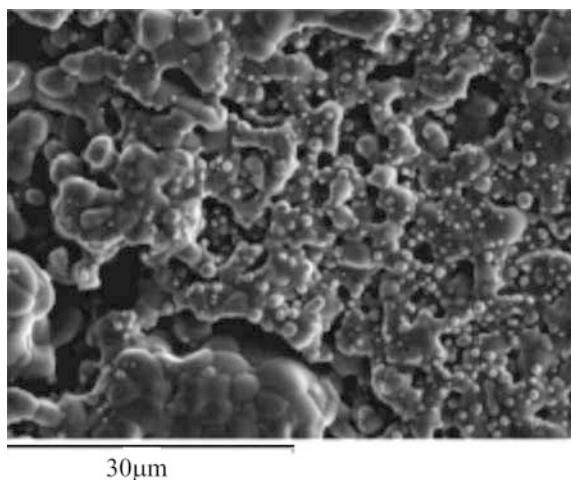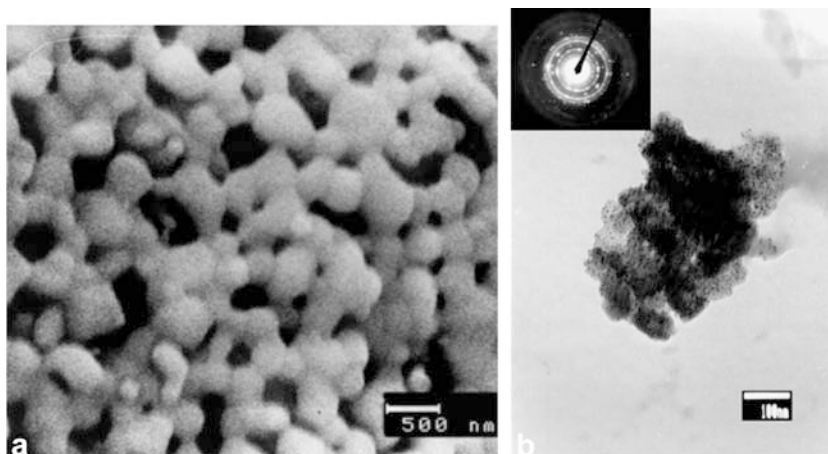
Fig. 5 SEM micrographs of $(Sm_{0.95}CoO_{3-\delta})_{0.4}Pt_{0.6}$ sintered at 1300 °C for 4 h in air

Fig. 6 Four-point d.c. resistivity vs. temperature curves for the $SmCoO_{3-\delta}$ and $(Sm_{0.95}CoO_{3-\delta})_{0.4}Pt_{0.6}$ sintered samples

Pt/Ru powders were used in the as-prepared form. Figure 7 compares the polarization curves of a commercial PEM fuel cell with those with anodes prepared from the powders. Figure 7a shows that the current density with a $SmCoO_{3-\delta}$-Pt anode is three times lower than that of the typical commercial PEMFC. Figure 7b shows that the $SrCO_3$-Pt/Ru anode result is very promising, since the current density is only slightly lower than that of the commercial PEMFC. This could be due to the high specific surface area of the Pt/Ru small particles.

Figure 8 shows the results of preliminary methanol conversion tests and indicates a significant conversion of 45% at a temperature as low as 345 °C when undoped samarium cobaltite is used as catalyst. In the case of Pt-modified $Sm_{0.95}CoO_{3-\delta}$, a 65% methanol conversion was attained.

Figure 8 also shows that the initial methanol conversion temperature (225 °C) is very close to the temperature (205 °C) at which the electronic semiconductor–metal transition takes place (Fig. 6). This suggests that at this transition temperature the electron transfer $Co^{3+} \rightarrow Co^{2+}$ could have an itinerating feature instead of a polaron/localized state character.

Conclusions

1. The combustion as-prepared powders show a small particle size ($\sim$10 nm) and low crystallinity.

a

b
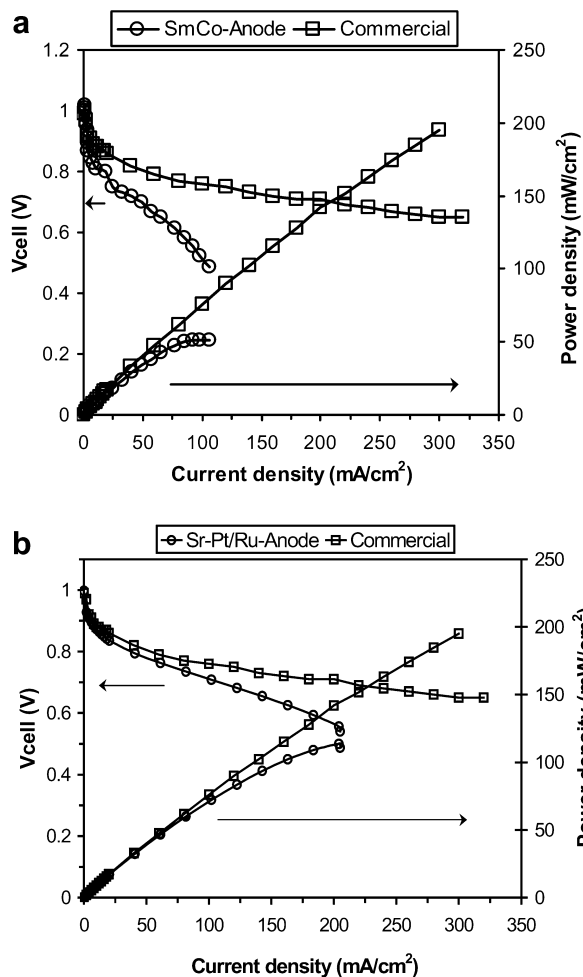
Fig. 7 MEA polarization curves, measured at 60 °C cell temperature and 2 bar pressure on the electrodes, as a function of the electrocatalyst used in the anode: (**a**) $(Sm_{0.95}CoO_{3-\delta})_{0.4}Pt_{0.6}$ and (**b**) $SrCO_3$-Pt/Ru

2. An alloy of Pt-Ru with a small particle size (13 nm) was produced.
3. After calcination at 800 °C, a single-phase perovskite with an agglomerate size of $\sim$150 nm and high specific surface area (5–9 m^2/g) was obtained.
4. The presence of small Pt particles produces an increase in the conductivity of two orders of magnitude, when compared with that of the undoped sample. That material also has a semiconductor behaviour.
5. $Sm_{0.95}CoO_{3-\delta}$ and $(Sm_{0.95}CoO_{3-\delta})_{0.6}Pt_{0.4}$ show a semiconductor–metal transition.
6. The samarium cobaltite perovskite could be used as a catalyst in methanol conversion and in PEMFCs and DMFCs.
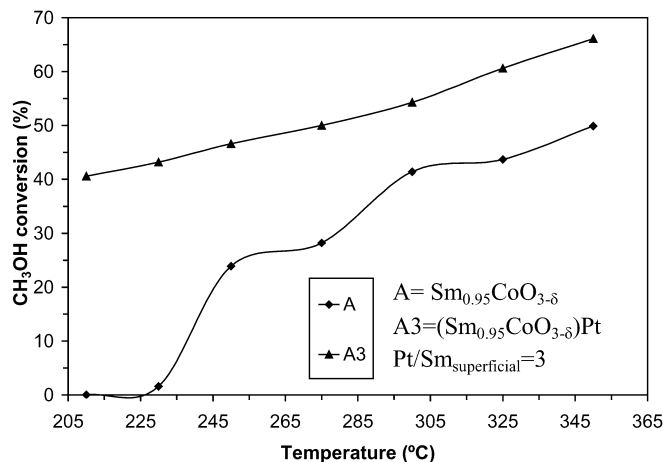
Fig. 8 Methanol conversion vs. temperature for $Sm_{0.95}CoO_{3-\delta}$ and $Sm_{0.95}CoO_{3-\delta}$-Pt

7. $SrCO_3$-Pt/Ru shows good anodic behaviour in PEMFCs.

Possible applications of these catalysts could be: partial methanol oxidation and hydrogen production from hydrocarbons; catalyst for anodes in PEMFCs and DMFCs for high temperatures (100–200 °C); anodes in IT SOFCs ($SmCoO_{3-\delta}$/Pt 40%); and anodes in gas separation membranes.

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