A-SITE DEFICIENT LANTHANUM FERRITES AS CATHODE MATERIALS FOR SOFCs

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ABSTRACT

Several \((\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_3\) perovskites were evaluated for their use as SOFC cathodes. Emphasis was placed on the effect of a small A-site deficiency on the properties of these perovskites. It was found that the A-site deficient compositions possess an increased sintering activity. This was more pronounced for the cobalt-containing perovskites than for pure ferrites. The perovskites were also used as cathodes of SOFC single cells to determine the electrochemical properties. The performance of the perovskites with a small A-site deficiency was significantly increased in comparison to the stoichiometric composition. This effect was stronger for the cobalt-containing materials. Increased Sr-substitution on the A-site and the addition of cobalt on the B-site also led to an enhanced performance. The composition with the highest electrochemical activity was \(\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3\). SOFCs with these cathodes achieved power densities of up to 1.0 W/cm² at 0.7 V and 750°C with hydrogen as the fuel.

INTRODUCTION

Aiming at a reduction of the cost of power systems based on SOFCs, the power densities of SOFCs have to be increased, while the operating temperatures have to be reduced. One way to achieve these goals is to use mixed conducting iron- and cobalt-based perovskites (e.g. \((\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_3\), LSCF) as the cathode material instead of the state-of-the-art cathode material \((\text{La}, \text{Sr})\text{MnO}_3\)\(^{1}\). The LSCF perovskites exhibit an enhanced catalytic activity for the cathode reactions and significant oxygen ion conductivity, enlarging the active surface area, which also makes them more tolerant to chromium-poisoning. Earlier measurements \(^{1}\) indicated a strong influence of the A-site deficiency on the performance of these perovskites, when used as SOFC cathode materials. Therefore, the effect of the A-site deficiency on the properties of LSCF was evaluated in more detail.

EXPERIMENTAL

Sample Preparation and Characterisation

All examined cathode powders were synthesized by spray-drying followed by calcination at 900°C. The powders were then ground by ball milling for several hours until a mean particle size (d₅₀) of approx. 0.8 µm was achieved.
The powders' stoichiometry was controlled by optical emission spectroscopy (ICP-OES). The phase composition was evaluated after an additional calcination at 1100°C (similar to the cathode sintering temperature) by X-ray diffraction using a Siemens D500 equipped with a monochromated Cu Kα radiation source. Characterisation of the microstructures was performed using scanning electron microscopes (Jeol T300 and LEO 1530 (Gemini)).

The electrochemical tests were carried out on anode-supported SOFCs (50 x 50 mm²). These consisted of an anode substrate (Ni/8YSZ, thickness ~ 1.5 mm) coated with an anode functional layer (Ni/8YSZ, ~ 10 μm) and an electrolyte (8YSZ, ~ 10 μm) which were co-fired at 1400°C. All of the samples were additionally coated by screen-printing with a 40 x 40 mm² Ce₀.₅Gd₀.₂O₂₋₃ interlayer (CGO, from Treibacher Auermet, Austria). This layer was used to prevent chemical reactions between the cathode and the 8YSZ electrolyte and was sintered at 1300°C (resulting thickness ~ 7 μm).

From the ground perovskite powders, screen-printing pastes were prepared by mixing the powders with an ethyl cellulose binder and a terpineol-based solvent. These were screen-printed on top of the CGO-layers followed by sintering for 3 h, resulting in 40 x 40 mm² cathodes with a thickness of approx. 45 μm. Different sintering temperatures were chosen for each material due to their different sintering activities (see below). More details on the manufacturing procedures can be found elsewhere (1).

**Electrochemical Measurements**

Electrochemical measurements of the SOFCs were performed in an alumina test housing. On the anode side a Ni mesh and on the cathode side a Pt mesh was used as contacts. Sealing of the gas compartment was obtained by a gold seal. All measurements shown in this paper were done with hydrogen containing 3 vol.% of water vapour as the fuel gas and air on the cathode side. Both gas flows were set at 1000 ml/min (STP) using mass flow controllers. The measurements were performed from 650 to 800°C. More details of measurement procedures can also be found in (1).

**RESULTS AND DISCUSSION**

**Element Composition and Crystal Structure**

In Table I the compositions of the used materials are listed together with the results obtained by ICP-OES and XRD and the abbreviations used in this paper. The given error margins are the errors of the individual measurements resulting from the evaluation of 3 samples and at least 3 spectral lines per element. The stoichiometries were calculated from the measured weight ratios by setting the sum of A- and B-site occupancy to the sum of the desired composition (i.e. 2, 1.98 or 1.95). The analysed compositions matched the desired ones well. The analysed A/B-ratios were also in accordance with the desired ratios, with a tendency to increased B-site occupancies, meaning that a desired A-site deficiency of 2% corresponds to an analysed deficiency of 1% and that stoichiometric (A/B = 1) compositions have been analysed as rather being B-site deficient.
Table I. Compositions of the powders according to ICP-OES and XRD-analyses.

| Desired composition (abbreviation) | Analysed composition | Crystalline phases* | Ratio A/B |
|-----------------------------------|----------------------|---------------------|-----------|
| La_{0.8}Sr_{0.2}FeO_{3-δ} (L80SF) | La_{0.799±0.023}Sr_{0.203±0.021}Fe_{0.998±0.003}O_{3-δ} | oP, (L) | 1.004 ± 0.039 |
| La_{0.7}Sr_{0.3}FeO_{3-δ} (L78SF) | La_{0.788±0.007}Sr_{0.198±0.001}Fe_{0.995±0.004}O_{3-δ} | oP, (L) | 0.990 ± 0.011 |
| La_{0.6}Sr_{0.4}FeO_{3-δ} (L60SF) | La_{0.616±0.005}Sr_{0.397±0.009}Fe_{0.998±0.017}O_{3-δ} | rP, (K2) | 1.020 ± 0.016 |
| La_{0.5}Sr_{0.5}FeO_{3-δ} (L58SF) | La_{0.598±0.011}Sr_{0.388±0.019}Fe_{0.994±0.008}O_{3-δ} | rP | 0.992 ± 0.017 |
| La_{0.4}Sr_{0.6}Co_{0.2}FeO_{3-δ} (L80SCF) | La_{0.810±0.012}Sr_{0.201±0.013}Co_{0.184±0.004}Fe_{0.809±0.012}O_{3-δ} | rP | 1.022 ± 0.018 |
| La_{0.4}Sr_{0.5}Co_{0.2}FeO_{3-δ} (L78SCF) | La_{0.785±0.005}Sr_{0.201±0.001}Co_{0.194±0.002}Fe_{0.806±0.006}O_{3-δ} | rP | 0.990 ± 0.008 |
| La_{0.3}Sr_{0.5}Co_{0.2}FeO_{3-δ} (L60SCF) | La_{0.681±0.006}Sr_{0.405±0.006}Co_{0.194±0.002}Fe_{0.809±0.002}O_{3-δ} | rP | 1.044 ± 0.007 |
| La_{0.3}Sr_{0.4}Co_{0.2}FeO_{3-δ} (L58SCF) | La_{0.587±0.007}Sr_{0.398±0.008}Co_{0.192±0.002}Fe_{0.803±0.010}O_{3-δ} | rP | 0.991 ± 0.015 |
| La_{0.3}Sr_{0.4}Co_{0.2}FeO_{3-δ} (L55SCF) | La_{0.550±0.006}Sr_{0.391±0.010}Co_{0.207±0.004}Fe_{0.801±0.018}O_{3-δ} | rP, (S) | 0.934 ± 0.021 |

*formed after calcination at 1100 °C: rP = rhombohedral perovskite, oP = orthorhombic perovskite, (S) = traces of spinel, (L) = traces of La_{2}O_{3}, (K2) = traces of a K_{2}NiF_{4}-type phase.

In the X-Ray diffractograms, only traces of secondary phases were visible, which were not considered detrimental for use as an SOFC cathode. These secondary phases were more prominent when analysing powders calcined at 900°C, while they were undetectable after calcination at 1100°C for most of the powders (see also Table I). The stoichiometric compositions tended to contain La_{2}O_{3} as a second phase, while the A-site deficient LSCFs (after calcination at 1100°C only detected for La_{0.55}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}) tended to contain (CoFe)_{3}O_{4} spinel phases. In the diffractograms, a transition from an orthorhombic to a rhombohedral perovskite structure with increasing Sr- and Co-content could be seen, which has already been reported by other authors (2-4): La_{0.8}Sr_{0.2}FeO_{3-δ} and La_{0.7}Sr_{0.3}FeO_{3-δ} display an orthorhombic distorted perovskite structure, while La_{0.6}Sr_{0.4}FeO_{3-δ} and La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ} crystallised in a rhombohedral distorted perovskite structure. It was found, that the size of the crystals’ unit cell of La_{1-x-y}Sr_{x}Co_{y}Fe_{1-y}O_{3-δ} is smaller for y = 0.2 than for y = 0 and for x = 0.4 in comparison to x = 0.2. This had also been reported by the authors mentioned above. An A-site deficiency (z > 0) also led to a slightly decreased size of the unit cell.

Sintering Characteristics and Microstructures

The sintering temperature influences the microstructure of the cathodes and therefore it influences the electrochemical performance of the SOFCs (5). The ionic and electronic conductivity and the gas permeability of the cathode are improved by a coarser structure, while a finer structure increases the number of catalytic active sites. When comparing different cathode materials, the sintering temperature is often optimised beforehand for one of the materials under investigation (6-8) and all of the various compositions are sub-

Electrochemical Society Proceedings Volume 2005-07 1629

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sequently sintered at that temperature. As a consequence, the pure influence of the materials characteristics on the electrochemical performance can not be easily determined.

Figure 1 and 2 show the influence of the A-site deficiency on the sintering activity for the cobalt-containing LSCFs. As expected, the pictures show the coarsening of the microstructure with increasing sintering temperature. The sintering activity is significantly increased for the A-site deficient LSCF materials. While the microstructure of the La_{0.8}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode is still very fine after sintering at 1080°C (Figure 2a) with hardly any sintering necks between the powder grains, the La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode is already sintered to a coarser microstructure at that temperature (Figure 1b). Similar microstructures for the L58SCF and the L60SCF cathode were obtained when sintering the first at 1080°C and the latter at 1200°C, both for 3 h (see Figures 1b and 2c).

For the materials without cobalt on the B-site, the sintering activity was nearly independent of the A-site deficiency (see Figure 3). The La_{0.6}Sr_{0.4}FeO_{3-δ} and the La_{0.58}Sr_{0.4}FeO_{3-δ} cathode have a similar microstructure after sintering at 1150°C for 3 h (Figures 3b and c), with the grains looking slightly coarser for the La_{0.58}Sr_{0.4}FeO_{3-δ}. While cobalt on the B-site is obviously increasing, the sintering activity for the powders with A-site deficiency (compare the microstructures of La_{0.58}Sr_{0.4}FeO_{3-δ} (Figure 3c) and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (Figure 1c)), it seems to have the opposite effect for the stoichiometric powders La_{0.6}Sr_{0.4}FeO_{3-δ} and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (compare Figure 2 and Figure 3, left and middle pictures, respectively). The described trends were also observed for the other materials. The sintering activity of the material with an A-site deficiency of 5% (La_{0.55}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}) was not further enhanced, when compared to the La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} perovskite.

Figure 1. La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathodes sintered at 1040, 1080 and 1120°C for 3 h.

Figure 2. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathodes sintered at 1080, 1150 and 1200°C for 3 h.
For possible explanations for the enhanced sintering behaviour of the A-site deficient LSCF compositions, two effects of the A-site deficiency are of particular interest. Firstly, the A-site deficient LSCFs have an enhanced tendency to form oxygen vacancies at higher temperatures (9). This tendency was also concluded by Kostogloudis and Frikos (10) from the enhanced decrease of the electrical conductivity with increasing temperature for A-site deficient LSCFs. A higher oxygen vacancy concentration could lead to an enhanced sintering activity of the material, due to a higher ion mobility. Secondly, the predominant secondary phase for the A-site deficient LSCFs was a (Co,Fe)$_3$O$_4$-spinel, which was detected in La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$. This might also be a secondary phase with a fraction undetectable by XRD (less than approx. 3 %) in the other A-site deficient materials. Cobalt oxide is known as a sintering aid for (Ce,Gd)O$_{2-δ}$ (11), so it might also act as a sintering aid for the LSCF.

It is unclear, how far these two effects also count for the cobalt-free LSF perovskites, for which the sintering activity was only slightly influenced by the A-site deficiency. The oxygen vacancy concentration of the A-site deficient LSF powders has not yet been measured, and the effect of iron oxide as a sintering aid for (Ce,Gd)O$_{2-δ}$ was reported to be smaller than for cobalt oxide (11). However, Simner et al. (8) have reported an increased sintering activity for A-site deficient (La$_{0.8}$Sr$_{0.2}$)$_{1-δ}$Fe$_{0.3}$O$_{3-δ}$ materials when compared to the stoichiometric and B-site deficient compositions.

**Electrochemical Characterisation**

**Effect of the Sintering Temperature.** SOFCs with La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ and La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ cathodes were sintered each at three different sintering temperatures to determine the effects of the resulting microstructures on the electrochemical properties. The cells with Lao.58Sr0.4Fe0.8O3.5 cathodes were sintered at 1040°C, 1080°C and 1120°C. Figure 4 and Table II show, that for the cathodes sintered at the highest temperature (1120°C), the lowest current densities were measured. The current densities of the cathodes that were sintered at 1040°C and 1080°C were similar, with the cathode sintered at 1080°C having a slightly higher performance at higher temperatures. For the cells with the Lao.6Sr0.4Co0.2Fe0.8O3.5-based cathodes, significantly lower current densities were measured (see Figure 5 and Table II). Here, the cathodes sintered at 1150°C showed the highest performance, while the cathodes sintered at 1080 and 1200°C resulted in slightly lower current densities.
Figure 4. I-V-curves at 750°C of L58SCF-based SOFCs sintered at various temperatures.

Figure 5. I-V-curves at 750°C of L60SCF-based SOFCs sintered at various temperatures.

Table II. Current densities (A/cm²) at 0.7 V of SOFCs with L58SCF and L60SCF cathodes as a function of the sintering temperature Tₛ of the cathode.

| Temperature (°C) | La₀.₅₈Sr₀.₄Co₀.₂Fe₀.₈O₃₋₅ cathodes | La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋₅ cathodes |
|-----------------|-------------------------------------|-----------------------------------|
|                 | Tₛ: 1040°C 1080°C 1120°C            | Tₛ: 1080°C 1150 °C 1200 °C       |
| 800             | 1.51 ± 0.12 1.60 ± 0.08 1.00 ± 0.10 | 0.95 ± 0.02 1.05 ± 0.09 0.90 ± 0.04 |
| 750             | 1.26 ± 0.10 1.31 ± 0.04 0.79 ± 0.09 | 0.78 ± 0.08 0.87 ± 0.04 0.77 ± 0.02 |
| 700             | 0.93 ± 0.04 0.92 ± 0.01 0.52 ± 0.05 | 0.57 ± 0.05 0.65 ± 0.03 0.54 ± 0.02 |
| 650             | 0.60 ± 0.01 0.55 ± 0.01 0.29 ± 0.01 | 0.38 ± 0.01 0.42 ± 0.03 0.34 ± 0.01 |

The given values are the averages from measurements on two identical cells, the error margins being the differences between the two measurements. For cells with L58SCF cathodes, a slightly different CGO interlayer was used, resulting in an approx. 10% lower performance (see also Table III).

The higher performance of the A-site deficient composition (La₀.₅₈Sr₀.₄Co₀.₂Fe₀.₈O₃₋₅) can be explained by a higher oxygen vacancy concentration (9), leading to a higher catalytic activity for that material. It has also been mentioned above, that the sintering activity is higher for the A-site deficient La₀.₅₈Sr₀.₄Co₀.₂Fe₀.₈O₃₋₅. High sintering temperatures can lead to the formation of insulating SrZrO₃ segregations between the CGO buffer layer and the 8YSZ electrolyte via Sr diffusion through that buffer layer, which is detrimental for the performance of the SOFC. This also explains the drastically lower performance of the Lao.58Sr0.4Co0.2Fe0.8O3-s cathode sintered at 1120°C, because the SrZrO₃ formation is aggravated by the increased sintering temperature. The better performance of the A-site deficient material has therefore two likely causes: a higher catalytic activity (due to a higher vacancy concentration) and a higher sintering activity (allowing lower sintering temperatures, which leads to less SrZrO₃ formation).

**Influence of the Composition on the Electrochemical Performance.** To compare the performance of the different cathode materials, all of the cathodes were sintered at temperatures that resulted in similar microstructures. The sintering temperatures were adapted for each material until a microstructure similar to that of the La₀.₅₈Sr₀.₄Co₀.₂Fe₀.₈O₃₋₅ cathode sintered at 1080°C (Figure 1b) was achieved. The
resulting sintering temperatures are tabulated in Table III, together with the current densities measured at various temperatures at 0.7 V.

Table III. Current densities for cells with various cathode materials.

| Material   | Sintering temperature (°C) | Current density (A/cm², 700 mV) |
|------------|----------------------------|----------------------------------|
|            | 800°C | 1080 | 1080 | 1200 | 1060 | 1150 | 1150 | 1150 | 1150 |
| L55SCF     | 1.23  | 1.76 | 0.90 | 1.20 | 0.68 | 0.82 | 0.81 | 0.68 | 0.51 |
| L58SCF     | 1.04  | 1.43 | 0.77 | 0.96 | 0.56 | 0.79 | 0.69 | 0.57 | 0.47 |
| L60SCF     | 0.74  | 0.99 | 0.54 | 0.63 | 0.42 | 0.61 | 0.55 | 0.36 | 0.36 |
| L78SCF     | 0.46  | 0.58 | 0.34 | 0.36 | 0.24 | 0.43 | 0.39 | 0.26 | 0.24 |
| L80SCF     |       |      |      |      |      |      |      |      |      |
| L58SF      |       |      |      |      |      |      |      |      |      |
| L60SF      |       |      |      |      |      |      |      |      |      |
| L78SF      |       |      |      |      |      |      |      |      |      |
| L80SF      |       |      |      |      |      |      |      |      |      |

"*Difference to the values in Table II is due the use of a different CGO interlayer. *Values from Table II. All measurements with H₂ + 3% H₂O as fuel gas and air on the cathode side, both with a flow of 1000 sccm.

From these results, a few general trends can be concluded: An A-site deficiency of 2% is beneficial for all of the materials. This trend is stronger for the cobalt-containing LSCF perovskites, which might be partly due to the different sintering activities. In contrast to these results, Simner et al. (8) reported a lower electrochemical performance for A-site deficient (La₀.₈Str₀.₂Fe₀.₈O₃₋₄) compositions in comparison to the stoichiometric compositions. However, they also state that an equal sintering temperature was taken for all of the compositions, while that temperature was optimised beforehand for the stoichiometric composition (x = 0). Together with the different sintering activities they observed, this led to over-sintered or poorly adhered cathodes for the x > 0 and x < 0 compositions, respectively.

A higher amount of strontium substitution also leads to a higher electrochemical performance. The reason for this is probably the increased amount of oxygen vacancies and electron holes due to a larger amount of the bivalent strontium (12, 13). A substitution of 20% of the iron on the B-site by cobalt is also increasing the electrochemical performance. Cobalt substitution also leads to an increased formation of oxygen vacancies, enhancing the electrochemical properties (12). The beneficial effects of cobalt on the B-site for oxidation reactions are also well known (14).

From these trends, it seems likely that a higher A-site deficiency would lead to even higher performances. However, a deficiency of 5% led to a reduced electrochemical performance of La₀.₅Sr₀.₄Co₀.₂Fe₀.₈O₃₋₄ when compared to La₀.₅Sr₀.₄Co₀.₂Fe₀.₈O₃₋₄. Higher amounts of strontium or cobalt substitutions are also likely to increase the performance. However, this both leads to higher thermal expansion coefficients (13), which may result in a mechanical failure of the cathode. For example, the La₀.₅Sr₀.₄Co₀.₂Fe₀.₈O₃₋₄ cathode sintered at 1200°C showed cracks and a spalling of parts of the cathode, which is probably due to a higher thermal expansion mismatch. A higher amount of Sr-substitution will also lead to an increased tendency to form SrZrO₃ segregations.

Cells with cathodes based on La₀.₅Sr₀.₄Co₀.₂Fe₀.₈O₃₋₄ showed the best performance of the examined compositions. The measured power densities of up to 1.0 W/cm² at 0.7 V and 750°C are significantly higher than values measured for SOFCs with LSM/YSZ-based cathodes (15).
CONCLUSIONS

The characteristics of several lanthanum ferrite-based perovskites were evaluated for the use as SOFC cathodes. Hereby, the emphasis was placed on the influence of the A-site deficiency on sintering and electrochemical characteristics. It was shown that a small A-site deficiency strongly enhances the sintering activity of the cobalt-containing LSCF perovskites, while this influence was only slightly visible for the pure lanthanum ferrites. This enhancement might be due to the higher amount of oxygen vacancies for the A-site deficient materials but might also be due to traces of secondary phases like cobalt oxide.

The electrochemical tests showed that the optimum sintering temperature for $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3.5}$ is 1080°C, while it is 1150°C for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{O}_{3.5}$. The strong decrease in performance of the $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3.5}$ cathodes with increased sintering temperatures is probably not only originated by the changes in its microstructures, but also by the tendency to form the insulating SrZrO$_3$ with the YSZ electrolyte despite the presence of a CGO interlayer. The electrochemical performance of the materials was increased by a small (2 %) A-site deficiency, a large amount (40 %) of Sr-substitution on the A-site and the addition of 20 % cobalt on the B-site. The highest performances were achieved with $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3.5}$ cathodes. SOFCs with these cathodes delivered power densities of up to 1.0 W/cm$^2$ at 750°C and 0.7 V.

ACKNOWLEDGMENTS

The authors wish to thank the staff of the FZJ-IWV-department, for processing the anode substrates and electrolyte layers, namely Mr. M. Kampel, Mr. St. Heinz and Mr. Blaß, as well as for spray drying of the powders, especially Ms. M. Andreas, and for performing the electrochemical measurements, in particular Ms. C. Tropartz, Ms. B. Röwekamp and Mr. H. Wesemeyer. Thanks go also to Dr. S. Uhlenbruck for providing pictures of L58SCF cells sintered at 1040 and 1120°C. Financial support from the Bundesministerium für Bildung und Forschung (BMBF), Verbundprojekt Erneuerbare Energien under contract no. 01SF0039 is gratefully acknowledged.

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