

Synthesis of carbon nanotubes on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ as substrate

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A carbon nanotube/perovskite composite material was developed as material for air electrodes in fuel cells or zinc-air batteries. For this purpose, carbon nanotubes were directly grown on the perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ impregnated with Fe solution which acted as substrate. The synthesis was carried out in a fluidised bed reactor. The carbon source was acetylene. The influence of the temperature on the growth of carbon nanotubes and on the stability of the perovskite was investigated. All samples contained multi-wall carbon nanotubes; however, at a temperature above 675 °C the perovskite was reduced by hydrogen originating from acetylene. The samples with the intact perovskite were further processed to air electrodes to catalyze the oxygen reduction reaction. These electrodes showed an improved performance compared to electrodes made of acetylene black and perovskites.

1. Introduction

In the past carbon nanotubes (CNTs) were considered for electrochemical applications like actuators [1], supercapacitors [2,3] or as support material in gas diffusion electrodes [4–7]. In gas diffusion electrodes for fuel cells or zinc-air batteries, the oxygen reduction reaction takes place at the three phase boundary (catalyst, gas, and electrolyte). For high reaction rates it is important that the catalyst is effectively dispersed on the support material in order to form many of such three phase boundary sites. Furthermore, it is essential that the support material has certain porosity. That way the gas can diffuse fast enough to the catalyst sites to maintain the reaction [8].

The electrode material in fuel cells commonly used today is platinum on carbon. In several works [4–7], carbon black was replaced by carbon nanotubes and it was shown that the Pt particles are much more homogeneously dispersed on carbon nanotubes than on carbon black, which leads to the better performance of these electrodes. Furthermore, it was demonstrated that defect sites on carbon nanotubes are essential for their catalytic activity [9–11]. Britto et al. [9] showed with ab initio density-functional-theory calculations and molecular dynamics simulations that the oxygen reduction reaction takes place with a larger charge transfer at defect sites (pentagons and heptagons) compared to the hexagonal sites. The defect sites act as electrophilic reaction sites due to their higher density of states. Maldonado and Stevenson [10] referred to

the importance of nitrogen doping of the CNTs to increase their catalytic activity. It was stated that the substitution of N atoms into the graphene structure leads to the formation of pentagonal defects and is most likely responsible for the compartmentalized-like morphology. Esplandiu et al. [11] found as well that bamboo-like CNTs are most suitable for electrochemical applications in sensors.

Platinum as catalyst has some drawbacks: it causes a high activation polarisation at low overvoltages leading to an efficiency loss, it gets easily poisoned and due to its limited reserves it is extremely expensive [8]. A promising substitute might be perovskites. Already in 1970, Meadowcroft [12] suggested the use of LaCoO_3 as catalyst material in zinc-air batteries. Many works on perovskites followed, either without [13–16] or with carbon blacks as support material [17–20]. But only few works [21] exist with perovskites and carbon nanotubes. Weidenkaff et al. [21] used $\text{La}_{1-x}(\text{Ca}, \text{Sr})_x\text{CoO}_3$ to grow CNTs. It was reported that although the perovskite structure was partially destroyed during the CNT synthesis, the catalytic activity of the produced CNT/metal oxide composite was comparable with a graphite/perovskite composite electrode. The catalytic activity for CNTs grown on an intact perovskite is expected to be much higher as compared to the CNT/metal oxide composite.

In this paper we demonstrate that multi-wall carbon nanotubes (MWCNTs) can be grown on perovskites without major damage of the oxide, leading to a CNT/perovskite composite applicable in air electrodes for the oxygen reduction reaction. The perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ was used as substrate powder impregnated with a Fe solution as catalyst for the CNT synthesis in a fluidised bed chemical vapour deposition (CVD) system. The influence of the synthesis temperature and the Fe concentration on the structure and morphology of the produced material was investigated by X-ray diffraction (XRD) and transmission

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electron microscopy (TEM). Furthermore, electrodes were produced on the basis of the carbon nanotube/La_{0.6}Sr_{0.4}CoO₃ composite material and characterised by steady-state current-potential curves.

2. Experimental

2.1. Synthesis of the carbon nanotube/La_{0.6}Sr_{0.4}CoO₃ composite and characterisation

Carbon nanotubes were synthesised in a fluidised bed reactor [22]. The apparatus consists of a vertical furnace with a quartz glass tube, 40 cm in length and 3 cm in diameter. In the middle of the tube a quartz filter (pore size: 20–40 μm) is mounted. The substrate powder is filled in the tube on the quartz filter and fluidised by the gas flow.

The substrate powder La_{0.6}Sr_{0.4}CoO₃ (supplied from Empa, Laboratory for High Performance Ceramics, Überlandstrasse 129, CH-8600 Dübendorf) impregnated with a Fe nitrate solution was prepared by the following procedure: A 30 mmol (type 30) respectively 15 mmol (type 15) Fe nitrate solution was added to 1 g of perovskite, sonicated for 20 min and dried in air. The flaky product was milled by hand. After placing the catalyst onto the quartz filter, the atmosphere in the tube was purged with an Ar flow of 410 scm³/min (standard cm³/min) for 5 min. The furnace was then heated to the desired temperature. Synthesis runs between 600 and 800 °C were carried out. The synthesis was started by the introduction of 42 scm³/min acetylene mixed with 368 scm³/min argon for 20 min. 0.3 g of the “as-produced” product was immersed in 30 ml 30% HCl at 50 °C for 16 h in order to remove all by-products. The nanotube suspension was filtered and the nanotubes were washed with distilled water until pH neutrality was reached and dried in air. To isolate the influence of Fe, one experiment with the pure perovskite (without any Fe) was carried out at 750 °C.

The crystal chemical evolution of the perovskite was investigated by X-ray diffraction (Kristalloflex D500, Siemens) and the morphology of the CNTs was analysed by transmission electron microscopy (Philips CM 200). The diffraction pattern of graphite was simulated by using the program Powder Cell [23]. Specific surface areas were determined by the BET method (Belsorp-Max, Bel Japan).

2.2. Synthesis of the electrodes and characterisation

Electrodes were produced from the unpurified samples, synthesised below 700 °C. CNTs/La_{0.6}Sr_{0.4}CoO₃ composite material, PTFE dispersion and distilled water were mixed ultrasonically for 1 h. The mixture was dried for 18 h at 60 °C under air and then heated to 350 °C for 2 h to fix the PTFE onto the carbon surface. 0.04 g of the resulting powder was mixed with 0.16 g petroleum (Petroleum special, bp 180–220 °C, Fluka) to make a paste, which was spread onto a round piece (24 mm in diameter) of teflonized Toray Carbon Paper TP-090T (QuinTech), serving as gas diffusion layer. The two layers, catalytic active layer and gas diffusion layer, were pressed together and heated to 320 °C for 1 h. And the electrode is finished.

For comparison one electrode was manufactured with acetylene black (Alfa Aesar) instead of CNTs and another electrode consisted only of CNTs. The detailed composition of these electrodes is listed in Table 1.

The electrochemical measurements were conducted with a ZAHNER IM6eX electrochemical work station. A three electrode arrangement was

Table 1
Composition of different electrodes

Electrode	Composition	
1	80 wt.% CNTs/La _{0.6} Sr _{0.4} CoO ₃	20 wt.% PTFE
2	40 wt.% AB ^a 40 wt.% La _{0.6} Sr _{0.4} CoO ₃	20 wt.% PTFE
3	80 wt.% CNTs	20 wt.% PTFE

^a Acetylene black.

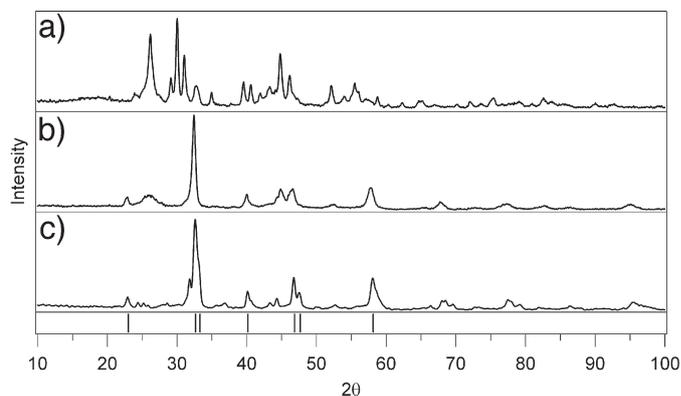


Fig. 1. XRD spectra of the “as-produced” material, produced with type 30 catalyst at a) 800 °C and b) 600 °C, c) XRD spectrum of the perovskite La_{0.6}Sr_{0.4}CoO₃.

chosen: The electrode foil under investigation was pressed against the contact plate in the holder and served as working electrode. The geometrical active area of the electrode was 0.785 cm². The back side (Toray Carbon Paper) was purged with air and the catalytic active side was in contact with the electrolyte. The reference electrode was a Hg/HgO electrode (Radiometer Analytical) in a Haber-Luggin capillary and the counter electrode was a Pt disk (Radiometer Analytical). All measurements were carried out in 6 M KOH (Aldrich) at room temperature. Steady-state current-potential curves were measured from –0.4 V to 0.8 V vs. Hg/HgO.

3. Results

3.1. Influence of the temperature and Fe concentration on the stability of the perovskite

In the X-ray spectra of the “as-produced” samples, synthesised at temperatures of 600 °C (Fig. 1b) to 675 °C, perovskite peaks predominate; while they almost disappear in the “as-produced” samples, which were synthesised at temperatures of 700 °C to 800 °C (Fig. 1a). From that we conclude that the perovskite decomposes between 675 °C and 700 °C under reducing conditions. The perovskite peaks of the “as-produced” samples, synthesised below this temperature of 700 °C (further referred to as decomposition temperature of the perovskite), are slightly shifted by about 0.1 to 0.2° to smaller angles compared to the untreated perovskite (Fig. 1c). The perovskite peaks are not present in the purified samples (Fig. 2a and b), which indicate that the perovskite was completely dissolved during the HCl treatment. This also signifies that the perovskite is not incorporated into CNTs. The main products in the purified samples, synthesised below the decomposition temperature of the perovskite, are CNTs and Fe.

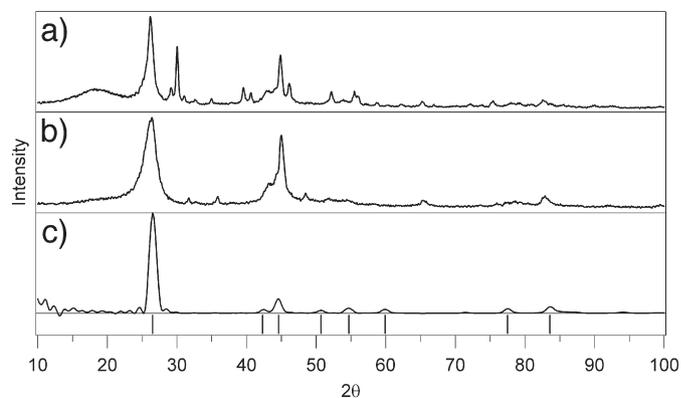


Fig. 2. XRD spectra of purified CNTs, produced with type 30 catalyst at a) 800 °C and b) 600 °C, c) simulated XRD spectrum of graphite.

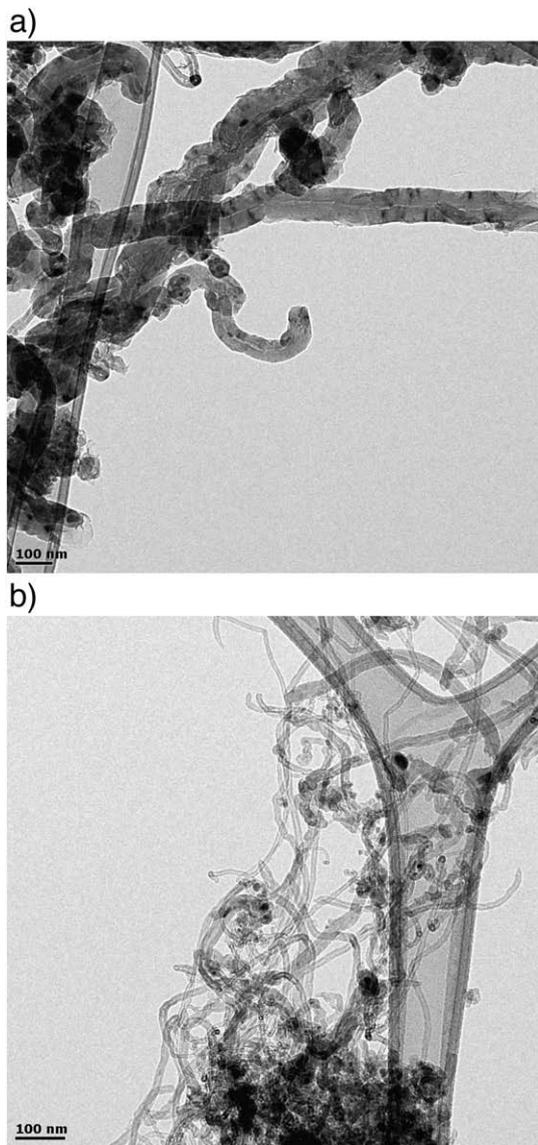


Fig. 3. TEM images of CNTs, produced with type 30 catalyst at a) 800 °C and b) 600 °C.

Above the decomposition temperature, the perovskite decomposes into Co, La_2O_3 and other unidentified products (Fig. 1a). The pattern contains also a strong CNT peak at 26.2° and Fe and/or Fe_3C peaks. In the purified sample synthesised at 800 °C (Fig. 2a) La_2O_3 and Co peaks are still visible indicating that not all of the perovskite break-down products were dissolved during the purification step.

With type 30 as well as with type 15 catalyst, the perovskite decomposes at the same temperature. No influence of the Fe concentration on the stability of the perovskite is observed. The main difference between the samples produced with type 15 and type 30 catalyst is that the intensity ratio of Co to Fe peaks changes.

In the “as-produced” sample, which was synthesised with the pure perovskite at 750 °C, the peaks of the decomposition products of the perovskite are similar to those of the samples synthesised with the perovskite impregnated with Fe. The main difference is that in the sample without Fe, the CNT peaks have only little intensity. The addition of Fe in our CNT synthesis process is thus necessary to gain a high yield of CNTs.

3.2. Influence of the temperature and Fe concentration on the CNT growth

The morphology of the multi-wall carbon nanotubes (MWCNTs) was investigated by transmission electron microscopy. Diameter and

morphology of the tubes change with temperature. For the 600 °C sample the diameter ranges between 5 and 30 nm (Fig. 3a) for type 15 and type 30 catalyst, while for the 800 °C sample the diameter ranges between 16 and 116 nm (Fig. 3b) for type 30 catalyst and between 12 and 75 nm for type 15 catalyst. The decrease of the full width of half maximum (FWHM) of the CNT peak at 26.2° in the XRD spectra with increasing synthesis temperature confirms the microscopic observations. The FWHM is inversely correlated with the CNT diameter; the smaller the FWHM is, the larger the CNT diameter becomes. In the low temperature samples the majority of MWCNTs are several μm long, almost no fibers were found. The high temperature samples contain MWCNTs, bamboo-like CNTs and fibers with diameters up to 150 nm and up to 110 nm for type 30 catalyst and for type 15 catalyst, respectively. There are short CNTs with a big diameter and fibers of less than 1 μm up to 3 μm long, as well as very long, thin CNTs up to 20 μm . Here, the term CNT refers to a carbon filament with tubular graphene walls parallel to the axis, whereas the term fiber is used for a carbon filament with graphene layers at other angles. The graphitization level is higher in the high temperature samples than in the low temperature samples. Small round and larger elongated particles with a length of up to 40 nm are incorporated in the CNTs and fibers. The number of such inclusions increases with increasing temperature. Some of the individual segments of the bamboo-like CNTs carry a particle. The number of open ended CNTs decreases with increasing temperature. Samples produced with type 15 catalyst have a more uniform tube morphology; the deviation from the average diameter is much smaller than with type 30 catalyst.

The CNT diameter of the sample synthesised with the pure perovskite ranges between 10 and 40 nm. Bamboo-like CNTs, fibers and onion structures with diameters of up to 160 nm are also present.

3.3. Further characterisation of the carbon nanotube/ $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ composite

The unpurified samples synthesised below 700 °C are interesting for further electrochemical characterisations. Fig. 4 shows the steady-state current-potential curves of the electrodes listed in Table 1. In the region of low overvoltages, the electrodes containing perovskites show a significant lower activation polarisation than the electrode only made of carbon nanotubes. This indicates that the perovskite has a catalytic activity for the oxygen reduction reaction. In the region of high overvoltages, the electrodes containing carbon nanotubes show a remarkable lower concentration polarisation than the electrode

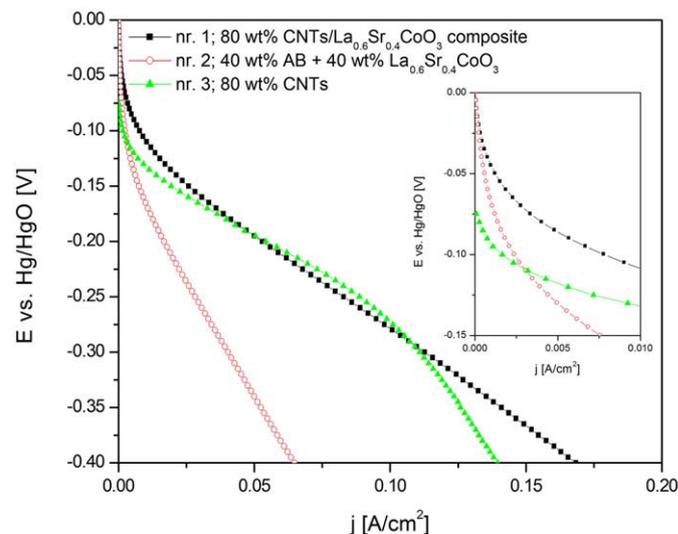


Fig. 4. Steady-state current-potential curves of the electrodes, summarized in Table 1.

containing acetylene black instead of carbon nanotubes. This proves that the carbon nanotubes lead to an improved electrode morphology. In total, the electrode made of the carbon nanotube/La_{0.6}Sr_{0.4}CoO₃ composite shows the best performance.

In different works it was shown that the specific surface area of the perovskite [19] as well as of the support material [20] plays a crucial role for a catalytic active electrode. Therefore, specific surface areas were determined. The pure perovskite had a BET surface area of 9.9 m²/g. The unpurified carbon nanotube/perovskite composites synthesised between 600 and 675 °C with type 15 catalyst had a BET surface between 60 and 40 m²/g, while those produced with type 30 catalyst had a BET surface between 80 and 60 m²/g. Acetylene black used in electrode 2 and the carbon nanotubes used in electrode 3 had specific surface areas of 60 and 440 m²/g, respectively.

4. Discussion

4.1. Influence of the temperature and Fe concentration on the stability of the perovskite

La-Co based perovskites are not stable under reducing conditions. In M²⁺-substituted perovskites, such as La_{1-x}(Ca, Sr)_xCoO₃ the octahedrally coordinated Co cations are partially oxidized from the trivalent state to the quadrivalent state. Under reducing conditions, the quadrivalent Co⁴⁺ is reduced back under release of oxygen. The loss of oxygen leads to an increase of the unit cell volume, which is responsible for the observed X-ray peak shifts found in the treated samples [24].

Impregnation of the perovskite may protect the perovskite from reduction and final break-down as shown by Weidenkaff et al. [21] who impregnated La_{1-x}(Ca, Sr)_xCoO₃ with Co solution and grew CNTs on the surface of the intact perovskite at elevated temperatures at which the non-impregnated perovskite was decomposed. The impregnation leads to a smaller surface-to-bulk ratio, which prevents the perovskite from decomposing. In our case the perovskite is not completely covered by the Fe. Therefore, the perovskite still decomposes at temperatures above 675 °C. However, in the temperature range from 600 to 675 °C carbon nanotubes are successfully grown on the surface of the intact perovskite. This perovskite is still catalytically active because not the whole surface is covered with Fe and CNTs.

At 750 °C, CNTs were grown on the pure perovskite as catalyst precursor. At this temperature the perovskite was destroyed and Co acted as a catalyst particle or nucleation centre. This is in good agreement with the findings of Weidenkaff et al. [21].

4.2. Influence of the temperature and Fe concentration on the CNT growth

We found that the diameter of the carbon nanotubes increases with increasing process temperature which is in good agreement with literature [25,26]. The diameter of the carbon nanotubes depends mainly on the size of the catalyst particle. With increasing synthesis temperature small catalyst particles on the perovskite coalesce, and form larger particles, leading to CNTs with larger diameters. Also, the higher carbon supply at high temperature contributes to the growth of CNTs with large diameters. Due to higher dissolution and diffusion rates of carbon in the catalyst particle at high temperatures, it is more likely that bulk diffusion takes place. This implies that carbon precipitates on the back of the catalyst particle and forms a graphitic shell which is then lifted. If this happens regularly, a bamboo-like CNT is formed. Kim et al. [27] synthesised CNTs on silicon oxide substrates by pyrolyzing metal phthalocyanine in the temperature range 700–1000 °C. He found as well bamboo-like CNTs with a larger diameter at the higher temperature with frequently encapsulated nanoparticles. According to the theory of Kim et al. [27], sometimes the strain between graphitic shell and catalyst particle is so high that the catalyst particle can be split and is lifted off

with the graphitic shell to explain why the compartment layers of the bamboo-like CNTs carry catalyst particles. The occurrence of bamboo-like CNTs is more likely on larger catalyst particles, because the graphitic shell needs to be less bended which results in a lower energy demand compared to high curvature on small catalyst particles [28]. For this reason, we observe many thin CNTs with open ends in the low temperature samples, in which the catalyst particles are small.

Li et al. [29] investigated the structure of the CNTs in dependence from synthesis temperature and gas pressure. At low gas pressures (0.6 Torr), hollow CNTs were synthesised at low temperatures and bamboo-like CNTs at high temperatures, while at high gas pressures (760 Torr) bamboo-like CNTs were synthesised irrespectively from the temperature. This is in contradiction with our findings because in our high pressure system bamboo-like CNTs were synthesised only at high temperatures.

4.3. Electrochemical characterisation

The goal of this work was to produce carbon nanotubes on an intact perovskite. We succeeded, when the growth temperature was below 700 °C. In literature [9–11] it is described that carbon nanotubes with many defect sites and especially bamboo-like CNTs have an increased catalytic activity. But bamboo-like CNTs were mainly produced at higher temperatures at which the perovskite is destroyed. However, the material with the intact perovskite was further processed to electrodes. These electrodes showed a better performance than electrodes composed of the perovskite and acetylene black, because of the better distribution of the perovskite on the carbon nanotubes. This result is in agreement with several works [4–7] where platinum and carbon nanotubes were combined and compared with platinum on carbon.

Arai et al. [20] showed that the carbon support with the higher specific surface area leads to the better performance of the electrode because of the larger reaction area. The CNT/La_{0.6}Sr_{0.4}CoO₃ composite had about the same specific surface area as acetylene black (60 m²/g), but showed a significant better performance. This is attributed to the better dispersion of the perovskite on the carbon nanotubes and due to the higher porosity of the carbon nanotubes. Acetylene black consists of spherical particles, which form larger dense aggregates. In contrast, the CNTs create a conductive network connecting the perovskite particles effectively.

5. Conclusions

Multi-wall carbon nanotubes (MWCNTs) are successfully grown on the intact perovskite La_{0.6}Sr_{0.4}CoO₃ by fluidised bed CVD, as long as the synthesis temperature is below 700 °C. At synthesis temperatures of 700 °C and higher the perovskite is reduced by the hydrogen originating from the acetylene and especially, bamboo-like CNTs are obtained. Electrodes prepared from the intact perovskite/carbon nanotube composite catalyze the oxygen reduction reaction significantly better than electrodes made of La_{0.6}Sr_{0.4}CoO₃ and acetylene black due to a superior electrode morphology.

Future work will be to improve the composite material further by a gentle purification process which leaves the perovskite intact and removes the by-products of the carbon nanotubes synthesis which do not contribute to a catalytic active electrode. Another approach will be to modify the synthesis process that way that bamboo-like CNTs on the intact perovskite are obtained because the bamboo-like CNTs are more catalytic active themselves.

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