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REVIEW PAPER

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TUNABLE SYNTHETIC APPROACHES FOR THE OPTIMIZATION OF NANOSTRUCTURED FUEL CELL CATALYSTS: AN OVERVIEW

Highly active nanostructured pluri-metal catalysts for fuel cell applications can be obtained by designing synthetic protocol where the particle size, metal composition and morphology can be readily tailored. Tunable synthesis relates to combining the various synthetic methodologies available for generating nanostructured metal catalysts with desired catalytic properties. Herein, we discuss some of these synthetic methodologies which were developed to combine the advantages of each pathway in generating efficient fuel cell catalysts and to learn how the composition and morphology of the metals be fine tuned.

Nanostructured metal particles are of great importance in catalysis due to the enhanced catalytic activity owing to large active surface areas they possess. Bottom-up synthesis has been conveniently used for generating colloidal nanoparticles. Right from its inception as early as in 1857 by Faraday [1], there has been an enormous growth in the synthetic strategies for the preparation of nanoparticles using this technique. The greatest advantage resides in the finding that, depending on the method used, uniform particle size distribution can be achieved and size control is possible. A number of useful contributions aiming at the understanding of colloidal particle behaviour has been put forward by leading scientists in the field [2–14].

The general understanding of nanoparticle formation during bottom up synthesis is (shown in Fig. 1) either via agglomeration of zero-valent metal atoms or by an autocatalytic pathway. Metal salts are reduced to give irreversibly a "seed" of zerovalent metal nuclei. The embryonic stage of nucleation has recently been studied in the case of the aluminumorganic synthesis of Pt nanoparticles [15,16]. Various contributions including differences in re-dox potentials of the metal salt and the reducing agent, the strength of the metal-metal bonds formed, and surface tension parameters determine the diameter of the "seed" nuclei. The size of the resulting metal particle is determined by the colloidal protective shells which control the relative rates of nucleation and particle growth [2,17–26].

Various synthetic methodologies have been used making use of a plethora of protecting agents in conjunction with various reducing agents to generate colloidal nanoparticles e.g., polyols, hydrides, aluminumorganic reagents etc. Protecting agents play a crucial role in shielding the particles against oxidation

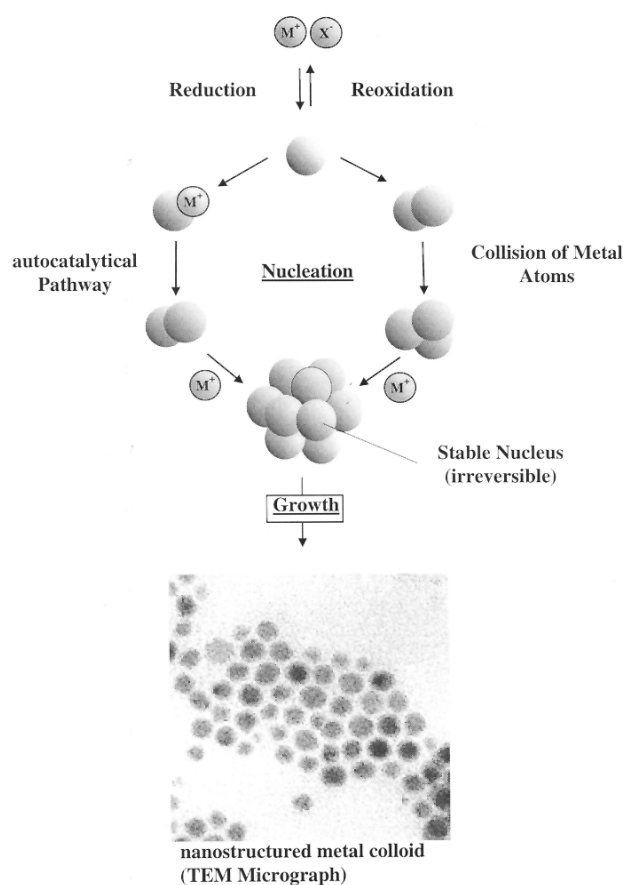


Figure 1. Formation of nanostructured metal colloids via the "salt reduction" method [adapted from (26)]

and agglomeration. In addition, their interaction with the metal surface controls the size and shape of the particles. Relatively higher ratio of surface free energy to lattice energy of smaller particles induces their growth to form thermodynamically more stable agglomerated particles. In order to prevent unwanted agglomeration during synthesis, suitable protecting agents have to be selected. In order to generate active catalysts from colloidal precursors, an additional step of protecting

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shell removal (e.g., "reactive annealing") has to follow. For this purpose we have designed a process to retain the advantageous size of < 3 nm.

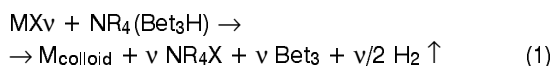
Electrostatic stabilization relies on the electrical double layer formed by ions adsorbed at the particle surface and the corresponding counter ions, causing a coulombic repulsion between particles. Reduction of $[\text{AuCl}_4]^-$ with sodium citrate to produce gold sols is a famous example for this [2–4].

Two basic modes of steric particle stabilization have been distinguished [27,28] where the use of solvents or ligands for stabilization is finely distinguished. Sterically bulky organic molecules on the metal surface act as powerful protective shields. Many protective groups have been studied including polymers and block copolymers. Further, P, N, S– donors (e.g. phosphines, amines, thioethers), solvents such as THF, THF/MeOH or propylene carbonate, long chain alcohols, surfactants and organometallics have been conveniently used [see reviews 8,10,14,29].

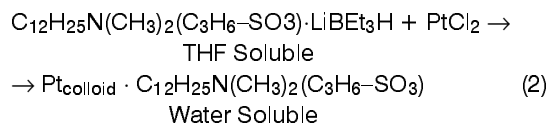
Depending on the nature of these protecting shells, the resulting metal colloid may be dispersed in either organic (organosols) or aqueous (hydrosols) medium. Lipophilic surfactants generate organosols while the use of hydrophilic surfactants generate hydrosols.

SALT REDUCTION METHOD FOR COLLOIDAL NANOPARTICLE SYNTHESIS

Salt reduction is one of the most used wet chemical methods for colloidal nanoparticle synthesis. The major advantages of the salt reduction method are that it allows colloidal nanoparticles to be prepared with good reproducibility in multi-gram amounts having narrow size distribution. A number of strong reducing agents including e.g., diboranes [30,31], hydrogen in conjunction with polyoxoanion [32–36], tetraalkylammoniumtriorganoborates [7,8,10,14,29,37], borates, silanes [38,39], aluminumalkyls [14,15,16,29] electrons trapped in $\text{K}^+[(\text{crown})_2\text{K}]^-$ [40] have been used successfully. Apart from these, alcohols containing α -hydrogens [41–44], tetrakis(hydroxymethyl)-phosphoniumchloride (THPC) [45,46], polyols, CO [47], formic acid or sodium formate, aldehydes [48], hydrazine, hydroxylamine are also regularly used [see 8,10,14,29]. In hydrotriorganoborates having tetraalkylammonium cations, hydride as the reducing agent is used in combination with NR_4^+ as the stabilizing agent [7,8,10,37,49–51]. This method offers a wide range of applications in the wet chemical reduction of transition metal salts (Eq. 1 and 2). The production of organosols (1) and hydrosols (2) [37] by this method has been extensively reviewed [12,28,37,52].



M = metals of the groups 6–11; X = Cl, Br; v = 1,2,3; and R = alkyl, $\text{C}_6 - \text{C}_{20}$



The formation of surface active NR_4^+ salts right at the reduction center in high local concentration prevents particle agglomeration. The resulting colloids can be purified and isolated in solid form by suitable treatment of the colloid with solvents having different polarity. The other advantage is that the isolated particles can be re-dissolved in various solvents in high concentration of the metal (upto 1 molar solutions). Additionally, trialkylboron can be recovered unchanged from the reaction and thus no borides contaminate the products. A pictorial representation of the interaction between tetraalkylammonium and the metallic particle is shown in Figure 2 [53].

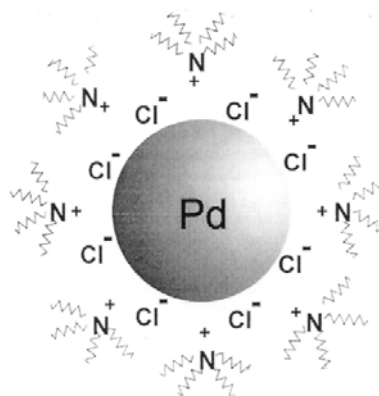


Figure 2. Model of NR_4Cl stabilized metal core. [(53) adapted with permission from Elsevier Science].

It is also possible to mix the protecting group with the metal salt which is to be reduced and then treat this adduct with the reducing agent. This "double salt pathway" gives an option of using different reducing agents to generate colloidal nanoparticles [7,37,54].

Fig. 3 highlights the $[\text{BEt}_3\text{H}]^-$ method along with typical particle sizes obtained. The advantages of the method may be summarized as follows:

1. It is generally applicable to salts of metals in groups 4–11 of the periodic table,
2. It yields extraordinary stable metal colloids dispersible in high metal concentration in a number of organic solvents,
3. They are easy to isolate as dry, re-dispersible powders, and
4. The particle size distribution is nearly monodisperse.

Further, bi- and pluri-metallic colloids are easily accessible via co-reduction. By consecutive (stepwise) reduction of different metal salts, core-shell colloids are

It was experimentally proved that the resulting colloids are dispersible in a wide range of lipophilic and hydrophilic solvents including water (the solubility exceeding 100 mg of metal per liter). The catalyst precursors obtained by "reductive stabilization" not only give particles in a ultra fine powder form having solubility properties to be tailored at will, there is also ample room for fine tuning the catalyst systems to obtain superior performances.

Nanopowders can be generated by carefully removing the protecting shell. The method chosen for protecting shell removal, however, depends on the nature of the protecting shell used and varies greatly.

APPLICATION IN FUEL CELL CATALYSIS

While preparation of colloidal catalyst precursors of controlled particle size, shape and structure can be achieved in our laboratory, the colloidal catalyst preparation in addition offers ways to fine tune the

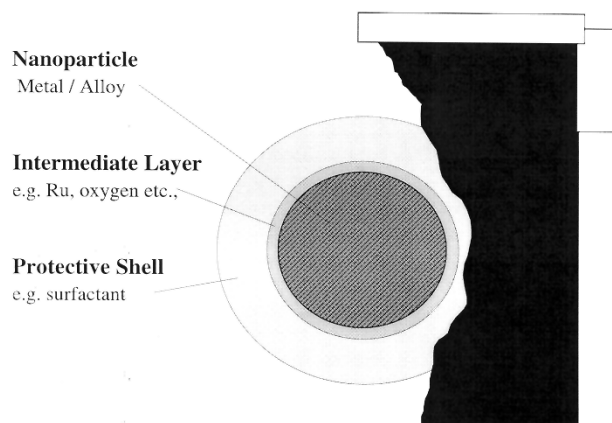


Figure 5. The precursor concept [(8) adapted with permission from Elsevier Science]

electrocatalyst properties during deposition of nanoparticles on supports [Precursor Concept]. A thin uniform carpet of the colloidal precursor on the support can be achieved by simply dipping the support in an appropriate solution of the pre-prepared particles yielding an egg-shell type catalyst. Typical supports are conductive carbon (e.g. Vulcan), various oxidic support materials, and even low-surface materials such as quartz, sapphire, and highly oriented pyrolytic graphite (HOPG) (see Fig. 5) [7,8,10,37,49-51].

In the case of tetraalkylammonium protected colloidal nanometals, depending on the alkyl group, the active catalysts are generated from the supported precursors via reactive annealing at a pre-determined temperature (called 'conditioning') [78]. During "conditioning", despite of an inevitable sintering, no drastic changes in either the size or the morphology of the metal particles on the support is observed. For example, a Pt-Ru (1.5–3.0 nm) organosol obtained by the tetraoctylammonium triorganohydroborate method was treated at 300°C with a stream of gases i.e., first argon, then oxygen/argon (3 vol% oxygen) to be followed by hydrogen. This procedure removes most of the protecting shell and leaves an active nanometal surface on the support (size 2.5–3.0 nm). The intermediate oxidation step is done in order to oxidize the organic residues at the particle surface and also to surface oxidize the metals which will be re-reduced in the subsequent reduction step. The XPS spectra of Pt-Ru organosol in Figure 6 give a clear view of the step by step removal of the protecting shell during "conditioning" [79]. The "conditioning" by reactive annealing can be performed for all precursor type catalysts. The individual treatment has to be suitably optimized to get the most active and long term stable electrocatalysts.

There has been a number of reviews elaborating the importance of the colloidal catalysts being used in

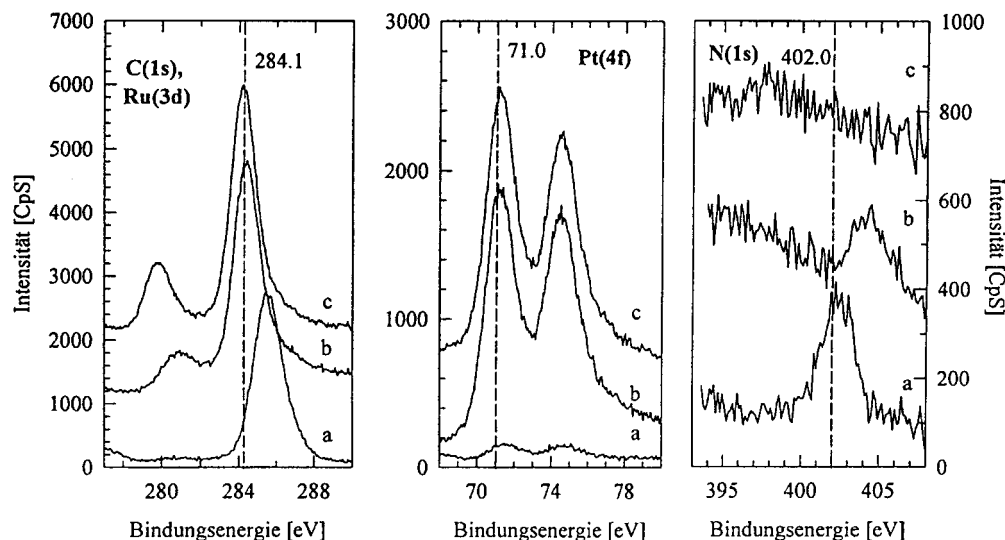


Figure 6. XPS study on the precursor catalyst [(79) adapted with permission from ECS]

chemical catalysis [8,37,52]. Here, the emphasis lies on the importance of such catalysts in fuel cell applications.

Use of fuel cells can be seen in low-emission transport systems, stationary power stations, and combined heat and power sources for small devices. In order to convert chemical energy into electrical energy in fuel cells besides the membranes, catalyst system forms an important component [80,81]. For pure hydrogen feed, metallic Pt is good enough as a catalyst but for reformer gas or methanol feeds Pt-alloy particles (e.g., Pt-Ru) of 1–3 nm size are needed as catalyst components since they offer CO tolerance in the anode [82–87]. Bimetallic colloids whose catalytic aspects and structural information has been reviewed [11] are readily accessible by the controlled co-reduction or stepwise reduction of two different metal ions [7,8,37,41–44,88–98].

Three main types of fuel cells, PAFC (phosphoric acid fuel cell), PEMFC (polymer electrolyte fuel cell) and DMFC (direct methanol fuel cell) have gained prominence in recent years. A PAFC operating between 160–220°C, uses orthophosphoric acid as the electrolyte; the anode catalyst is Pt and the cathode can be a bi- or a pluri metallic composite, e.g. Pt/Cr/Co [99–103]. Tri-metallic colloidal precursor of the composition Pt₅₀Co₃₀Cr₂₀ (size 3.8 nm) were prepared for this purpose by the co-reduction of corresponding metal salts [104–106]. A comparison of the electrocatalytic performance of colloidal tri-metallic system with an industrial catalyst (tri-metallic crystallite, size 6.0 nm) showed a good activity combined with an improved durability, favorable for PAFC applications. As low as 10 mV potential decay was found after 22h fuel cell operation [107].

PEM (polymer electrolyte membrane) fuel cells use a solid proton conducting polymer as the electrolyte between 50–125°C. The cathode catalysts are based on Pt alone but a combination of Pt and Ru is preferred for the anode because of the required tolerance to CO [82–87]. For low-temperature (80°C) polymer electrolyte membrane fuel cells (PEMFC) which are fed with CO-contaminated hydrogen produced in on-board methanol reformers, colloidal Pt/Ru catalysts are currently under investigation. These are also proposed for the use in DMFC. The ultimate dispersion state of the metals is essential for CO-tolerant PEMFC, and truly alloyed Pt/Ru colloid particles of less than 2 nm size seem to best fit these requirements [82,84,108–114]. Using the colloid synthesis, three PtRu samples consisting of alloyed PtRu/C, co-deposited Pt+Ru/C, and mixed Pt/C+Ru/C were compared. They were characterized by CO stripping and continuous oxidation of simulated reformat with respect to their performances as PEMFC anode materials. According to the bi-functional mechanism the sample with the highest number of Pt–Ru contacts, that is alloyed PtRu/C exhibited the best activity towards CO oxidation.

However, the other two samples also showed good CO tolerance. Mechanistic implications for the CO tolerance on these samples are discussed in [115].

In DMFC catalysts, in contrast, unsupported Pt/Ru nanopowders of 3–5 nm size or thin films are used [85–87]. For the electrocatalytic methanol oxidation, a Pt metal or a Pt metal alloy catalyst has been developed where a Ru phthalocyanine complex is added as a dopant [106]. Using CO and a CO/H₂ gas mixture (simulated reformer gas) as the feed, the electrocatalytic activity of a standard catalyst was compared with that of a bimetallic Pt₅₀/Ru₅₀-N(Oct₄)Cl colloid (1.7 nm) prepared by the borate co-reduction [7,49–51,108]. Preparation and characterization of new Pt–Ru alloy colloids which are suitable as precursors for advantageous fuel cell catalysts has been reported [116] and their structures examined by X-ray absorption near edge structure spectroscopy (XANES) [116,117].

Pt₅₀/Ru₅₀-N(Oct₄)Cl colloids on glassy carbon substrate were examined by CO-stripping voltammetry. In a rotating disk electrode set-up, the activity of the colloid toward the continuous oxidation of 2% CO in H₂ was determined at 25°C in 0.5 M H₂SO₄, and the results led to the conclusion that these Pt/Ru colloids are very suitable precursors for high-surface-area fuel cell catalysts [110]. Their structural features were reported in some detail [117]. A comparison of the electrocatalyst developed from the organosol method (organoborate reduction) was made recently with the industrial sample under identical conditions. Their electrochemical properties are as shown in Figure 7. From the onset potential for CO oxidation and the active surface area measurements, it can be concluded that the colloidal precursor method is really advantageous.

This demonstrates the potential for further developments of colloid precursors for bimetallic and pluri-metallic fuel cell catalysts especially when considering the ease of manipulating surface composition using this approach. Scanning probe microscopy (SPM) has also been applied in order to

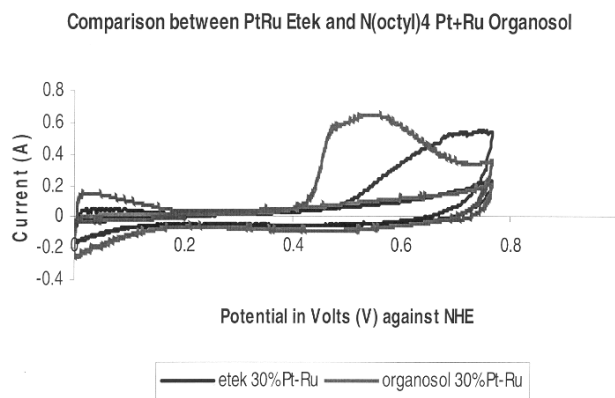
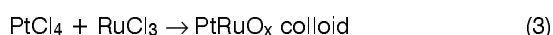


Figure 7. Comparison of electrochemical activity of catalyst obtained from organoborate method and the commercial ETEK sample (both 30% Pt–Ru on Vulcan).

characterize the real-space morphology of the electrode surfaces of supported nanostructured metal colloids on the nanometer scale [118]. From the results, it can be concluded that colloidal Pt₅₀/Ru₅₀ precursors (<2 nm) raise the tolerance to CO, allowing higher CO concentrations in the H₂-feed of a reformat PEMFC without a significant drop in performance [109,110]. Similarly, a catalyst for the oxidation of H₂ in the presence of CO in fuel cells comprising of Pt_xMo_y particles where x is 0.5–0.9 and y is 0.5–0.1 was patented [119]. Generally speaking, the colloid method was found to be a highly suitable exploratory approach to finding improved formulations for binary and ternary Pt-based anode electrocatalysts. The other metals used include Ru, W, Mo, and Sn [120]. The combinatorial screening method has successfully been applied to electrocatalysts [121], and it is an obvious step to include tunable colloid synthesis in these experiments.

Results of electrochemical measurements have demonstrated that for methanol oxidation, the introduction of a transition metal oxide (WO_x, MoO_x, VO_x) leads to an improvement of catalytic activity [122]. As an alternative to the reductive metal colloid synthesis, the so-called "metal oxide concept" was developed which allows the fabrication of binary and ternary colloidal metal oxides as electrocatalyst precursors (Eq. 3) [123–125].



Colloidal Pt/RuO_x (1.5 ± 0.4 nm) stabilized by a surfactant was prepared by co-hydrolysis of PtCl₄ and RuCl₃ under basic conditions. These oxides are reduced to metals by the application of H₂ (optionally in the immobilized form). Additional metals which can bring beneficial effects are also incorporated in "metal oxide concept" (Eq. 3) in order to get access binary and ternary mixed metal oxides in colloidal form. For example, WO_x with Pt–Ru is regarded as a good pre-catalyst especially for the application in DMFCs. Main group elements such as Al have been included in multi-metallic alloy systems in order to improve the durability of fuel cell catalysts. Pt₃AlCo_{0.5} alloyed with Cr, Mo, or W particles of 4–7 nm size has been prepared by sequential precipitation on conductive carbon supports like Vulcan XC72[®] [126]. Alternatively, colloidal precursors composed of Pt/Ru/Al were used for the manufacture of multi-metallic fuel cell catalysts (1–2 nm) having a metal loading of >20% [127]. The colloidal Pt/Ru/Al precursor is pre-prepared via the organoaluminum route (Eq.2) [16,111,128,129]. In the absence of surfactants, the co-reduction of organic Pt and Ru salts using Al(CH₃)₃ gives halogen-free, multi-metallic Pt colloids, e.g. Pt₅₀Ru₅₀/Al (size 1.2±0.3 nm) [127]. By changing the stoichiometric ratio of the metal salts the ratio of Pt to the second metal in the colloidal precursor can easily be adjusted and the addition of alcohols or suitable surfactants to the

organoaluminum precursor allows the dispersion to be tailored without affecting the particle size (Eq. 2). In the second step the Pt/Ru/Al colloid is adsorbed on high surface area carbon by treatment at 40°C for 24h. In the third conditioning step the dried Pt/Ru/Al Vulcan catalyst powders are exposed to O₂ and H₂ for 30 minutes each at 250–300°C to remove the organic residues completely from the metal particle surface. The particle size of the Pt/Ru/Al colloid adsorbed on the support did not change much (<2 nm) after the thermal treatment. This size-stabilization observed for these supported Pt/Ru particles and the improved catalyst durability was attributed to residues of aluminumoxide on the particle surface after the conditioning. Better performing catalyst in terms of their CO tolerance and its long time durability under the fuel cell conditions were the objectives of this exercise.

CONCLUSION

Though a thorough evaluation of the colloidal precursor method as tunable tool for combinatorial fuel cell catalyst research has not been performed so far, it is obvious today that high performance fuel cell catalyst in terms of CO tolerance and long term durability under the fuel cell conditions will emerge in the near future. Tailoring colloidal precursors for effective fuel cell catalysts both in PEMFC and DMFC applications is certainly a worthwhile exercise.

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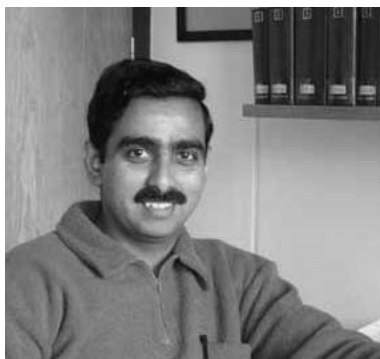
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