

Hybrid proton-conducting membranes for polymer electrolyte fuel cells Phosphomolybdic acid doped poly(2,5-benzimidazole)—(ABPBI-H₃PMo₁₂O₄₀)

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Abstract

The synthesis and characterization of a novel hybrid organic–inorganic material formed by phosphomolybdic acid H₃PMo₁₂O₄₀ (PMo₁₂) and poly(2,5-benzimidazole) (ABPBI) is reported. This material, composed of two proton-conducting components, can be cast in the form of membranes from methanesulfonic acid (MSA) solutions. Upon impregnation with phosphoric acid, the hybrid membranes present higher conductivity than the best ABPBI polymer membranes impregnated in the same conditions. These electrolyte membranes are stable up to 200 °C, and have a proton conductivity of $3 \times 10^{-2} \text{ S cm}^{-1}$ at 185 °C without humidification. These properties make them very good candidates as membranes for polymer electrolyte membrane fuel cells (PEMFC) at temperatures of 100–200 °C.

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1. Introduction

The membrane is one of the key components in the design of improved polymer electrolyte membrane fuel cells (PEMFCs). Current technologies are based on sulfonated membranes, with Nafion® as a foremost example. Such membranes have to be highly hydrated to be effective proton conductors, and when the temperature rises above 100 °C, their conductivity drops dramatically. Furthermore, the Pt/C electrodes used in PEMFCs are very sensitive to traces of CO present in the reactant gases (normally H₂ and O₂), since CO is absorbed by Pt producing the poisoning of the electrodes, whereas CO desorbs easily from Pt at temperatures above 150 °C. With these considerations in mind, it is easy to understand why the most promising trends in the development of PEM fuel cells involve the development of novel membranes for cells working at increased temperatures (150–200 °C).

In order to achieve higher working temperatures and conductivities, many new materials have been studied in recent years, and exhaustive reviews can be found in the literature [1–3]. Among them, polybenzimidazoles (PBI, Fig. 1) have stood up as specially sturdy materials with a high thermal stability and good membrane-forming properties. PBI membranes can be impregnated with variable amounts of phosphoric acid to yield proton-conducting membranes that can work at temperatures up to 200 °C. Both the polymers and their acid-loaded membranes have been studied by several research groups [4–9]. Phosphoric acid doped PBI has been used successfully at temperatures up to 200 °C using hydrogen [6,7,10], methanol [9], and even propane [8] as fuel. Benzimidazole polymers have also been used successfully as solid electrolytes in sensors [11] and electrochemical supercapacitors [12].

Yet, the family of polybenzimidazoles is not limited to commercial PBI. Poly(2,5-benzimidazole) (ABPBI, Fig. 1), among others [13–15] (as well as its sulfonated derivatives [15c]) is an alternative benzimidazole type polymer with

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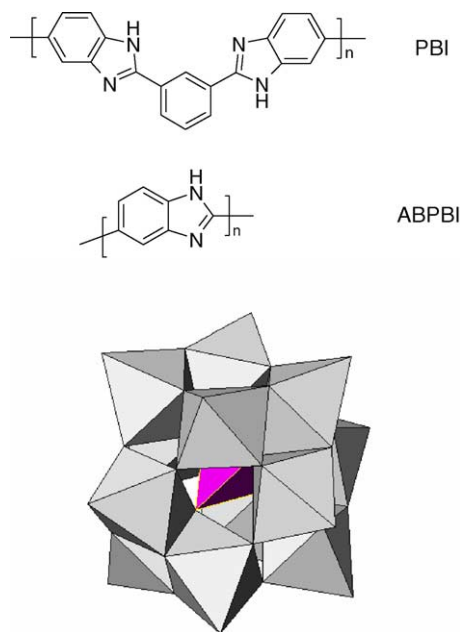


Fig. 1. ABPBI and PBI repeating units and the molecular structure of the phosphomolybdic acid (Keggin type heteropolyacid), a cluster with a diameter of 10 Å.

thermal stability and conducting properties as good as those of PBI, with comparable performance in high-temperatures PEM fuel cells, but with added advantages from the point of view of their synthesis [15a,b].

Finally, in addition to proton-conducting organic polymers, there are a good number of inorganic phases with well-known proton conductivity [16]. Heteropolyacids (HPAs) in general and the phosphomolybdic acid in particular ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, denoted here as PMo_{12}) have been long characterized as solid acids with high proton conductivity thanks to their dense, hydrogen-bonded hydration water network [17]. Yet, the molecular nature of these cluster species makes them soluble in many common solvents, including water, which prevents their use as membrane materials.

We have recently shown how these soluble cluster species can be effectively anchored within the framework of conducting polymers, such as polyaniline or polypyrrole to yield hybrid electrodes and functional materials [18].

This same hybrid approach could be used to develop solid electrolyte membranes when the polymer used is not a conductive polymer but a proton-conducting material, and this is precisely the approach we have followed for the development of the novel hybrids described here.

Doping of PBI with heteropoly acids has been attempted, but the conductivity of these materials was not high enough to be used in PEM fuel cells [19–21]. Li et al. have reported that the addition of heteropoly acids to phosphoric acid membranes reduce the conductivity for the same PBI:phosphoric acid ratio [22].

Recently, we have communicated preliminary results on the enhancement of conductivity in phosphoric acid doped ABPBI membranes by PMo_{12} and other polyanions [23]

Here, we present a more exhaustive report on the synthesis, physicochemical characterization and properties of these hybrid proton-conducting materials.

2. Experimental

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) powder was purchased from Aldrich. 3,4-Diaminobenzoic acid (DABA) 97% and methanesulfonic acid (MSA) 99% were obtained from Across Organics and used without further purification. Polyphosphoric acid (PPA) 85% P_2O_5 and phosphoric acid 85% were purchased from Panreac.

Chemical analyses of elemental C, N, H and S, using a Carlo Erba Instruments EA1108 Elemental Analyzer, were systematically performed for the materials in their different forms, from the as-prepared polymer powders to the final doped membranes. A Canon-Fenske 300 viscosimeter was used for the measurement of viscosities of polymer solutions in H_2SO_4 96%.

All membranes were studied by FTIR spectroscopy. FTIR spectra of the membranes were recorded on a Shimadzu FTIR-8300 spectrophotometer.

TGA analyses were performed in a Mettler-Toledo TG50, under N_2 or air at $10^\circ\text{C min}^{-1}$. X-ray diffraction patterns were collected with a rotating anode Rigaku Rotaflex Ru-200B diffractometer ($\lambda = 1.5418 \text{ \AA}$, Cu $K\alpha$) 2θ between 5° and 60° (0.02° step, 4° min^{-1}).

Conductivity of acid-impregnated ABPBI- PMo_{12} and ABPBI membranes has been determined by a 4 probe AC impedance method at $100\text{--}185^\circ\text{C}$ at room humidity. Thus, according to a conventional procedure, samples were cut as strips of $3 \text{ cm} \times 0.6 \text{ cm}$, AC current was applied between the ends of the sample, and the voltage drop was measured by two silver wires placed in the middle and separated 1 cm. A more complete description of the method can be found in the literature [24].

2.1. Polymer synthesis

Poly(2,5-benzimidazole) was polymerized by condensation of 3,4-diaminobenzoic acid in polyphosphoric acid (85% P_2O_5 content) following a procedure based in a synthesis described earlier [25]. ABPBI used in this work has an inherent viscosity of $2.3\text{--}2.4 \text{ dl g}^{-1}$ (0.5 g dl^{-1} measured in concentrated sulfuric acid at 30°C).

3. Results and discussion

3.1. Membrane casting

The large molecular size of PMo_{12} prevents the diffusion of the cluster into membranes of PBI polymers. This anticipated result was confirmed by preliminary tests in which a PBI membrane was immersed into a 20% PMo_{12} solution,

Table 1
ABPBI/PMO₁₂/MSA mixtures for the preparation of ABPBI–PMO₁₂ membranes

Membrane	ABPBI (mg)	PMO ₁₂ (mg)	MSA (ml)	Stirring time (h)	PMO ₁₂ /nominal (%)	PMO ₁₂ /experimental (%)
Mo #1	200	36	3	24	13.6	6
Mo #2	200	184	3	24	45	41
Mo #5	200	350	4	48	60	54
Mo #7	200	556	4	48	70	50
Mo #8	200	556	4.5	48	70	56
Mo #9	200	952	5	72	80	36
Mo #10	400	700	8	72	60	–
Mo #11	400	368	6	72	45	–

with no weight increase. Similar results were observed by Xing and Savadogo, who found that H₃PW₁₂O₄₀ (PW₁₂) did not increase the PBI conductivity when a membrane was soaked in PW₁₂ solutions (up to 60%) [26]. Thus, for the isolation of our hybrid materials, we used a direct acid casting technique for the preparation of a PMO₁₂ benzimidazole polymer. The polymer selected was poly(2,5-benzimidazole).

Polybenzimidazoles are soluble in a very limited number of solvents. ABPBI membranes can be cast from methanesulfonic acid solutions as described earlier [15,27]. For casting ABPBI–PMO₁₂ hybrid membranes, we followed a similar procedure, dissolving a given amount of ABPBI in MSA stirring at room temperature, adding variable amounts of the PMO₁₂ acid to the solution and stirring further until a homogeneous viscous solution was obtained. The specific amounts used for a series of hybrid materials are detailed in Table 1. As during the casting of the membrane, the PMO₁₂ is completely dissolved, no differences are observed for different stirring times.

These solutions were spread on a glass surface and heated in the hood until complete evaporation of MSA. While heating, the mixture turned into a homogeneous transparent solution. Membranes were peeled off by immersion into a water bath. Elemental analyses showed the presence in these crude membranes of residual MSA, which could be completely removed by washing in boiling water for at least 24 h. The contents of PMO₁₂ in the hybrid membranes once washed and dried were estimated from thermogravimetric analyses as described below. Hybrid membranes with up to 60% PMO₁₂ by weight could be prepared with a minimal loss of PMO₁₂ during the washing as showed in Fig. 2. Below 60% PMO₁₂ percentage is close to nominal, but a small amount of PMO₁₂ possibly superficial is always lost.

3.2. Phosphoric acid uptake

In order to reach high conductivity values, the hybrid ABPBI–PMO₁₂ membranes prepared as described above had to be impregnated with phosphoric acid, just as their polymeric counterparts. Staiti et al. [19–21,28] also found relatively low conductivity values of 10^{−8} S cm^{−1} [20] for a PBI–H₃SiW₁₂O₄₀ adduct (50:50 in weight). That is why our approach relies on the combination of both heteropolyacid

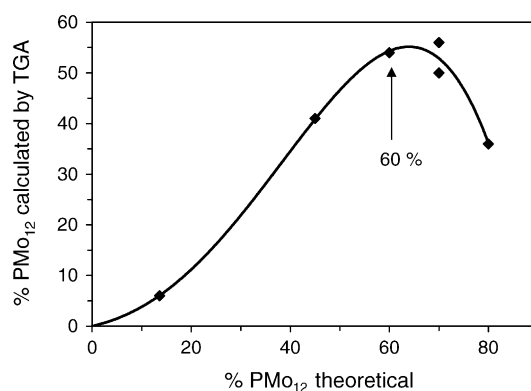


Fig. 2. Composition of the ABPBI–PMO₁₂ calculated by TGA as a function of the nominal composition.

and phosphoric acid in a single polymer membrane, in an attempt to improve conductivity and increase the stability of the resulting hybrid membrane. In the best case, the heteropolyacid could also help prevent the loss of phosphoric acid detected by several laboratories working with PBI membranes.

Phosphoric acid impregnation of ABPBI–PMO₁₂ hybrid membranes was carried out by soaking a 60% PMO₁₂ membrane (20 μm thickness) in H₃PO₄ (85%)/H₂O baths of different concentrations as summarized in Table 2. This ABPBI–PMO₁₂ (60%) membrane can be doped in a bath concentration up to approximately 68% H₃PO₄. When increasing the bath concentration, the membrane is broken up or even dissolved into the bath. The thickness of membranes can be controlled during the tape casting procedure, but we have typically prepared membranes of 20 μm.

Table 2
H₃PO₄ doping of samples of the membrane Mo #10 (nominal composition 60% PMO₁₂) into different acid concentrations

Membrane	H ₃ PO ₄ 85%/ H ₂ O (v/v)	Concentration H ₃ PO ₄ (%)	Doped membrane characteristics
Mo #10 AP1	50:50	53.5	Flexible
Mo #10 AP2	70:30	67.9	Flexible
Mo #10 AP6	70:30	67.9	Flexible
Mo #10 AP5	80:20	74.1	Broken in the bath
Mo #10 AP4	90:10	79.8	Broken in the bath
Mo #10 AP3	100:0	85.0	Soluble in the acid

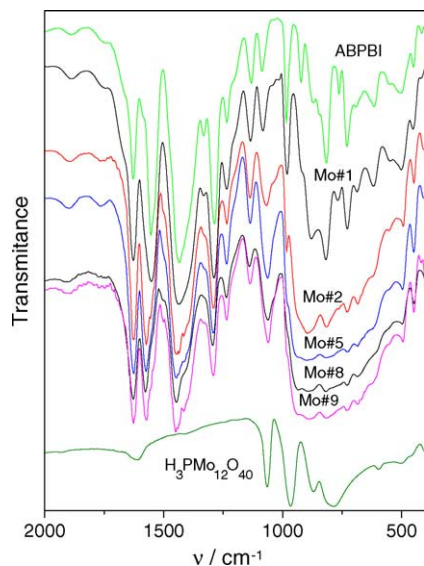


Fig. 3. FT-IR spectra of the ABPBI-PMO₁₂ hybrid membranes of different compositions listed on Table 1.

3.3. FT-IR spectroscopy

Hybrid membranes 20 μm in thickness have proved adequate for measurement of their FT-IR spectra directly in the film form, without further sample preparation. Fig. 3 shows the spectra of ABPBI-PMO₁₂ hybrid membranes of different compositions (as listed on Table 1), showing increasing intensities for the peaks assigned to PMO₁₂ as the nominal amount of the heteropolyacid increases. On the other hand, Fig. 4 compares the FT-IR spectra of ABPBI-PMO₁₂ (60%) before and after H₃PO₄ impregnation. In the latter case, PMO₁₂ bands do not disappear, while bands assigned to H₃PO₄ in-

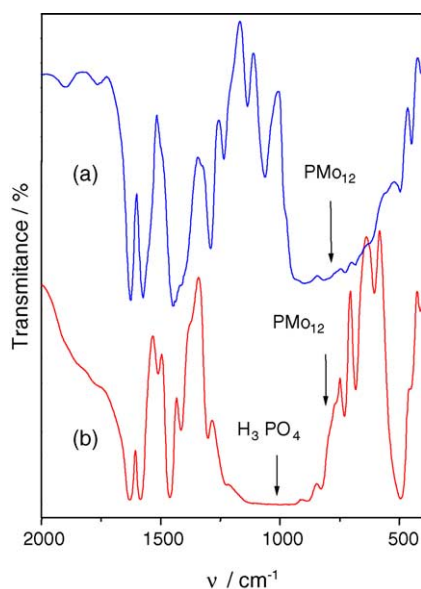


Fig. 4. FT-IR of ABPBI-60% PMO₁₂ (a) before and (b) after doping in a H₃PO₄ 85%/H₂O bath (50:50, v/v).

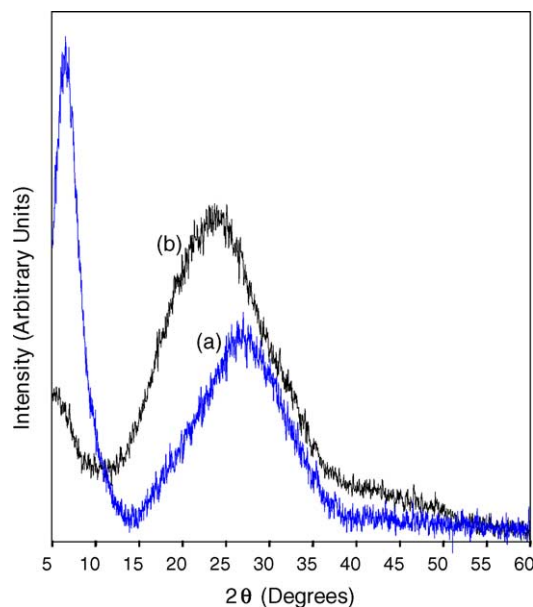


Fig. 5. X Ray diffraction of an ABPBI-60% PMO₁₂ membrane (a) before, and (b) after impregnation in a phosphoric acid bath (H₃PO₄ 85%/H₂O 70:30, v/v).

crease, showing that the membrane can be effectively loaded with phosphoric acid with no loss of the PMO₁₂ cluster.

3.4. X-ray diffraction

The X-ray diffraction pattern of ABPBI-PMO₁₂ membranes (Fig. 5) shows two very broad peaks, indicating a quasi-amorphous structure. The first peak is centered at about 26–28° and corresponds to a d spacing of 3.3 Å, characteristic of the stacking of ABPBI chains [27]. The second, appears at lower angles about 6.4–6.9° (spacing ca. 13.5 Å), is characteristic of the present hybrid membranes, increases in intensity as the contents of PMO₁₂ increase, and can therefore be assigned to an expanded stacking spacing due to the presence of PMO₁₂ clusters. The lower angle peak almost disappears after impregnation with phosphoric acid (Fig. 5b), indicating the loss of the expanded long-range order associated to that process.

3.5. Thermal stability

Thermogravimetric analyses (Fig. 6) have been applied with a two-fold purpose. First, they have allowed to quantitatively determine the actual composition of ABPBI-MO₁₂ hybrid membranes as well as their water contents. But of course, TGA analyses are also most useful to determine the range of stability and operativity of the electrolyte membranes (Fig. 7).

From Fig. 6, we can see how loosely bound water is lost from the beginning of the TGA run up to about 200 °C. ABPBI is decomposed at about 450–600 °C, and the remaining weight is attributed to PMO₁₂. The resulting compositions are consistent and confirm the nominal compositions of the

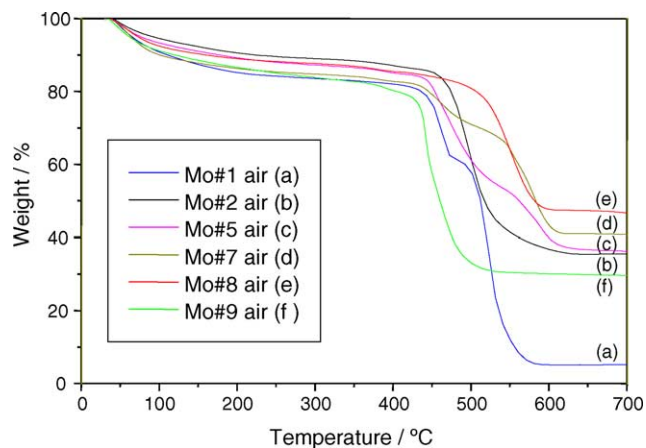


Fig. 6. TGA of the ABPBI-PMO₁₂ membranes listed on Table 2 at 10 °C min⁻¹ in air.

membranes up to 60% PMO₁₂. At higher PMO₁₂ contents, the TGA shows an inorganic percentage lower than the expected one, indicating that probably some PMO₁₂ is lost during the water washing for compositions with PMO₁₂ contents higher than 60%, but not for lower amounts.

Fig. 7 shows the TGA of an acid doped ABPBI-PMO₁₂ hybrid membrane. Similarly to what is found for the corresponding PBI and ABPBI membranes loaded with phosphoric acid, the absorbed water is lost below 100 °C, and the phosphoric acid dehydration starts near 150 °C, and is centered at 200 °C so, as in the case of ABPBI and PBI, 200 °C is again the maximal operation temperature for the phosphoric acid doped hybrid membranes.

3.6. Conductivity

Fig. 8 shows the conductivity of an ABPBI-PMO₁₂ (45%) membrane and an ABPBI membrane, both doped in the same phosphoric acid bath under the same conditions (H₃PO₄ 85%/H₂O 70:30, v/v) for comparison. Experimental phosphoric acid absorption was studied using ca 60% PMO₁₂ be-

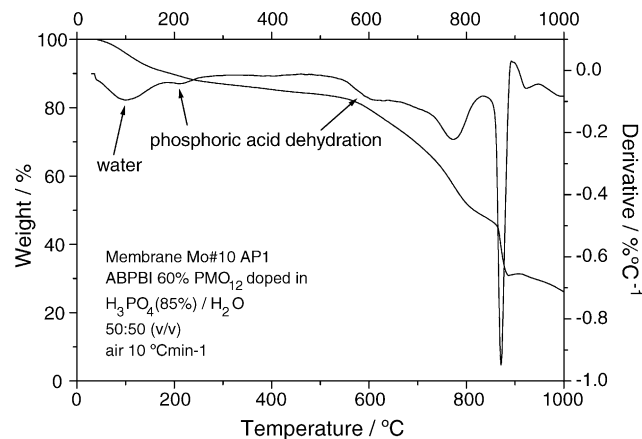


Fig. 7. TGA in air at 10 °C min⁻¹ of ABPBI-60% PMO₁₂ doped in H₃PO₄ 85%/H₂O (50:50, v/v).

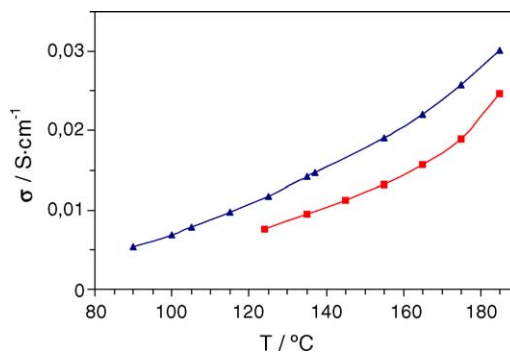


Fig. 8. AC conductivity AC of ABPBI 2.7 H₃PO₄ (■) and ABPBI 45% PMO₁₂ × H₃PO₄ (▲), both doped in H₃PO₄ 85%/H₂O 70:30 (v/v). Conductivity was measured on dry membranes. In order to dry the membrane before measuring, the sample was heated in the sample holder up to 180–185 °C and once the conductivity was stabilized, the conductivity was measured as a function of temperature while cooling.

cause this was the higher PMO₁₂ amount achieved, but as acid absorption was so high, the mechanical stability was lower as happens for ABPBI and PBI. Thus, 45% that also absorbed a high amount of acid and had better mechanical properties was selected for conductivity measurements. It is clear that the hybrid membrane presents a higher conductivity, which can be due to the combination of the conductivities of both the phosphomolybdic and phosphoric acid, or to an increased uptake of phosphoric acid induced by the presence of the heteropolyacid. We continue to study this and related hybrid membranes in order to clarify this point, but in any event, our results show that the PMO₁₂ containing hybrid membrane is superior to the corresponding polymer membrane in this respect.

It has recently been reported [28] that the addition of PW₁₂ or SiW₁₂ to phosphoric acid doped PBI, having all the samples the same number of phosphoric acid molecules per PBI repeating unit, leads to a decrease in conductivity. From our point of view, the addition of a high amount of HPA results in a lower H₃PO₄ percentage. Thus, as the conductivity is mainly correlated to the phosphoric acid percentage in the sample, the reported decrease of proton conductivity can be understood in that particular case.

4. Conclusions

Sturdy ABPBI-PMO₁₂ hybrid membranes have been prepared by casting of solutions of the organic polymer and the inorganic cluster in MSA, achieving compositions of up to 60% in PMO₁₂. These hybrid membranes can be impregnated with phosphoric acid in a similar way to the parent polymeric membranes in order to achieve higher proton conductivities and are stable at temperatures higher than 400 °C (before phosphoric acid impregnation) and, as electrolytes, up to 200 °C (after phosphoric acid impregnation), similarly to the corresponding PBI and ABPBI membranes. On the other hand, the impregnated ABPBI-PMO₁₂ hybrid mem-

branes show better conductivities than their parent polymer membranes (an ABPBI–45% PMo₁₂ membrane impregnated in a 68% phosphoric acid solution reaches $3 \times 10^{-2} \text{ S cm}^{-1}$ at 185 °C in dry conditions). These results improve upon earlier reports of materials and membranes with poorer conductivities and allow us to conclude that the methods and the hybrid membranes based on polybenzimidazoles and heteropolyacids reported here represent a step forward in the development of improved membranes and are promising systems for the development of higher temperature PEM fuel cells.

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