Stability of a carbon gel electrode when used for the electro-assisted removal of ions from brackish water

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Abstract

A porous carbon gel obtained from the poly-condensation of resorcinol and formaldehyde was synthesized and used as an electrode material for the capacitive deionization (CDI) of synthetic brackish water. The desalting capacity of this material was evaluated in terms of applied voltage and zero-voltage regeneration over a number of cycles, and compared to that of commercially available carbon materials (powdered activated carbon and activated carbon cloth). Due to an adequate combination of chemical and porous features, the deionization capacity of the carbon gel electrode exceeded that of the electrodes based on conventional microporous carbons over a larger number of adsorption/regeneration cycles. An almost fully reversible ionic removal (ca. 90 % recovery) was obtained for this electrode material when regeneration was carried out at zero-voltage conditions. Characterization of the cycled electrodes showed that the carbon gel was resistant to electrochemical anodic oxidation under the polarization conditions used (applied voltage of up to 1.2 V), whereas the electrodes produced from the two commercial carbon materials undergo severe modifications (oxidation and a decrease in surface area) when the applied voltage was maintained for several cycles.

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1. Introduction

Capacitive deionization (CDI) is an electrochemical water treatment process employed to remove ionic materials (or charged species). In the CDI process, a brackish water stream flows between pairs of high surface area electrodes that are held at a potential difference. Due to the electrostatic interactions that appear at the electrode/electrolyte interface during the polarization of the electrodes, the charged species in the solution move to and are held on the opposite-charged electrode surface. Based on this mechanism, large surface area electrodes are required for achieving high desalting capacities. Moreover, the regeneration of the electrodes can be easily performed by either discharging the electrodes (removing the applied potential) or reversing the polarization between both electrodes under controlled conditions [1, 2].

Although pioneering studies on CDI date from early 1960's, advances on this technology have remained somewhat behind due to the lack of adequate electrode materials. For their versatility of forms and structures, the use of carbonaceous materials as electrodes in CDI technology is currently considered a promising alternative that could compete with conventional technologies for desalination of water -such as ion-exchange, reverse osmosis, electro-dialysis and evaporation-, overcoming their current practical limitations [2-5]. Particularly those associated with the energy consumption, if the capacitive energy that is stored during the electro-adsorption of ions were efficiently recovered [5]. Consequently, a number of studies have been reported on the electrochemical performance of a wide variety of carbon materials as electrodes in CDI (nanotubes, aerogels, activated carbons, graphene-like nanoflakes and so-forth) [6-14]. At converse, scarce studies have focused on the modifications that occur on the carbon electrodes as a

result of the imposed electric field during long times, nor the consequences on the life-time span of the electrodes and their cycle-ability. On the other hand, extensive work has been done on the synthesis, characterization and applications of carbon gels. Due to a unique combination of physicochemical and structural properties, that may be conveniently adapted during the synthesis and processing [15-17], carbon gels possess great potential and versatility in numerous fields [14, 18-21].

The objective of this work was to investigate the electrochemical behaviour of a porous carbon gel obtained from the poly-condensation of resorcinol and formaldehyde as electrode for CDI of synthetic brackish water. The desalting capacity of the carbon gel was compared to that of an activated carbon and a carbon cloth, and discussed in terms of applied voltage, zero-voltage regeneration, as well as the chemical stability of the electrodes upon cycling.

2. Experimental Methods

2.1 Materials

The carbon xerogel was synthesized by the sol-gel polymerization of resorcinol (R) and formaldehyde (F) in water (W), using sodium carbonate (C) as catalyst and following the procedure described by Pekala and co-workers [17]. The reactant to catalyst (R/C) ratio was kept at 100, the molar ratio R/F was fixed at 0.5, and the R/W at 0.06. Briefly, the precursors were mixed in sealed glass moulds under magnetic stirring, and placed in an oven at 70 °C for 150 h to undergo gelation and aging. The cross-linked gel was dried by evaporation of the solvent at atmospheric pressure and 150 °C for 24 hours. After drying, the organic gel was pyrolysed at 800 °C under nitrogen flow in a horizontal tube reactor

under a controlled heating programme (i.e., heating rate $2\text{ }^{\circ}\text{C min}^{-1}$ up to $400\text{ }^{\circ}\text{C}$ and hold for 60 min followed by heating up to $800\text{ }^{\circ}\text{C}$ and hold for 60 min). The carbon xerogel was designated as XG. For comparison purposes, an activated carbon cloth (CC, supplied by Actitex) and a powdered activated carbon (AC, supplied by Agrovin) were also used for manufacturing the electrodes.

2.2 Electrochemical characterization

The electrochemical performance of the carbon materials was studied in a three-electrode configuration. The electrodes are in the form of 1 cm^2 self-standing cloth disks or pellets obtained by pressing a mixture of carbon material (85 wt. %), percolator (5 wt. % Pure Black, Superior Graphite) and polyvinylidene fluoride (PVDF, 10 wt. %) as binder. Teflon Swagelock® cells were constituted of the working carbon electrode (mass about 10 to 15 mg) electrically isolated by a glassy fibrous separator from the counter electrode (graphite rod), and the corresponding reference electrode upon the nature of the electrolyte (ca. $\text{Hg/Hg}_2\text{SO}_4$ and $\text{Hg}_2\text{Cl}_2/\text{Hg}$ [SCE] for the electrolytes 1 M H_2SO_4 and 1 M NaCl , respectively). All the potentials have been normalized versus the Normal Hydrogen Electrode (NHE). Electrochemical characteristics were determined at room temperature by cyclic voltammetry using a VMP (Biologic) potentiostat.

2.3 Chemical and textural characterization of the carbon materials

The nanotexture of the electrodes (i.e., cloth disks or composites built using 85 wt.% carbon material, 10 wt.% binder and 5 wt.% percolator), was characterized by N_2 adsorption-desorption isotherms at $-196\text{ }^{\circ}\text{C}$ (ASAP 2010, Micromeritics). Before the experiments, the electrodes were outgased under primary vacuum at $120\text{ }^{\circ}\text{C}$ overnight.

The isotherms were used to calculate the specific surface area, S_{BET} , total pore volume, V_{T} , and pore size distributions using the density functional theory (DFT) approach [22]. Elemental analysis was carried out in LECO automatic analyzers (LECO CHNS-932 and LECO VTF-900). The materials were further characterized by temperature-programmed desorption (TPD) coupled to a mass spectrometer. The amounts of CO and CO₂ evolved during the TPD experiments were quantified.

2.4 Capacitive Deionization measurements

For the capacitive deionization measurements the electrode materials were deposited on graphite foil current collectors. Two electrodes were placed face to face, separated by a glass paper and sandwiched between two Teflon plates. The assembly was immersed in a batch reactor (ca. 100 mL) containing the ionic solution and kept under continuous stirring to avoid mass transfer restrictions from the bulk solution. Deionization cycles were performed by polarization of the electrodes by applying a constant voltage (between 0.6 and 1.2 V). The change in the ionic concentration during the experiments was monitored using an ion conductivity meter. After deionization, regeneration cycles were immediately performed by reversing the polarization between the electrodes. Physically adsorbed amount of ions at open circuit conditions (OC) was also measured without applying polarization between the electrodes. The desalting capacity was calculated as the ionic removal efficiency -defined as the percentage of ions removed versus the amount initially present in the solution- under two conditions, considering the amount of ions removed by i) physical adsorption plus electro-sorption (OC+pol series) and ii) only when polarization is applied (pol series).

3. Results and discussion

3.1 Nanotextural and chemical characterization of the electrodes

The N₂ adsorption isotherms of the carbon electrodes are shown in Figure 1 A, along with the main textural parameters summarized in Table 1. The textural characterization of the electrodes (cloth disks and the carbon composites) rather than that of the carbon materials themselves was carried out in order to counterbalance any modification in the porosity of the carbon materials that might arise from the addition of binder and percolator during the manufacture of the electrodes.

Figure 1. N₂ adsorption isotherms at 196 °C of the electrodes (A) and pore size distribution evaluated from the DFT method (B).

It can be observed in Figure 1 A that the three materials exhibit very different porous features. The carbon gel displays a combination of type I and type IV isotherm

(according to the BDDT classification) characteristic of mesoporous materials, with a prominent hysteresis loop (type H2) at relative pressures above 0.8 that indicates the presence of large mesopores. This is clearly seen in Figure 1B, which depicts the incremental pore volume *vs* pore width (*w*); the mesopore volume of carbon XG accounts for almost three quarters of the total pore volume, but the contribution of microporosity cannot be neglected (i.e., $V_{\text{MICRO}} 0.23 \text{ cm}^3 \text{ g}^{-1}$). In contrast, samples CC and AC exhibit type I isotherms which are characteristics of microporous materials; the analysis of the distribution of pore sizes revealed that sample AC presents the typical broad distribution of activated carbons in the microporous region with small contribution of small mesopores, whereas sample CC exhibits a sharp pore size distribution centred at about 0.7 nm (Figure 1B).

Table 1. Main physicochemical and textural parameters of the studied samples.

	XG	AC	CC
S_{BET} [$\text{m}^2 \text{ g}^{-1}$]	753	1048	1018
$V_{\text{TOTAL}}^{\S}$ [$\text{cm}^3 \text{ g}^{-1}$]	0.89	0.57	0.43
$V_{\text{MICRO}}^{\dagger}$ [$\text{cm}^3 \text{ g}^{-1}$]	0.23	0.32	0.38
$V_{\text{MESO}}^{\dagger}$ [$\text{cm}^3 \text{ g}^{-1}$]	0.61	0.13	0.02
$V_{\text{MESO}}/V_{\text{MICRO}}$	2.7	0.4	0.05
	XG	AC	CC
CO evolved [$\mu\text{mol/g}$]	515	450	1115
CO₂ evolved [$\mu\text{mol/g}$]	80	170	390
Oxygen content [%]	3.6	1.9	5.5
<i>§ evaluated at $p/p_0 \sim 0.99$</i>			
<i>† evaluated from DFT applied to N_2 adsorption data</i>			

The elemental analysis data of the studied carbon materials indicated that they consist

mainly of carbon and small quantities of oxygen varying between 5-2 wt.% (Table 1), which suggests a low population of oxygen containing surface groups. This is also in good agreement with the quantification of CO and CO₂ detected by TPD-MS (Table 1).

3.2 Electrochemical characterization of the electrodes

The electrochemical characterization of the carbon electrodes was carried out in a three-electrode cell configuration in acidic (1M H₂SO₄) and neutral (1M NaCl) electrolytes. Figure 2 shows the corresponding cyclic voltammograms (CV) of the electrodes in both electrolytes recorded at a scan rate of 5 mV s⁻¹. The potential cut-off was initially hold between +50 and +850 mV vs NHE in both sulphuric and NaCl electrolytes, to prevent the anodic and cathodic currents related with the decomposition of water and the oxidation of the electrodes [23].

In acidic medium, when the electrodes were exposed to polarization between +50 and +850 mV vs NHE (Figure 2 A), the voltammograms slightly deviated from the ideal rectangular shape, showing the wide and reversible humps due to redox transfer reactions likely involving the oxygen-containing functionalities present in the carbon matrix. The position of the cathodic and anodic peaks (reduction potential close to +500 mV vs. NHE) is in agreement with the values reported for the quinone/hydroquinone pair in carbon materials in various environments or pyrone-like structures [23]. The presence of oxygen-containing functional groups on these materials was corroborated by elemental analysis and TPD-MS (Table 1) as above-mentioned. When the potential cut-off was extended down to more negative values, the electrochemical response changed (Figure 2 B). Below -350 mV vs NHE, a fast cathodic current leap related with proton reduction

and formation of nascent hydrogen starts to be observed, along with the hump during the anodic sweep (ca., +250 mV vs NHE) corresponding to the electro-oxidation of the hydrogen stored in the porosity of the carbon electrode. For the anodic sweep, the oxidation of the carbon materials started to be observed at potentials above +1050 mV vs NHE.

Figure 2. Cyclic voltammograms (5mV/s) showing the potential stability window of the investigated electrodes in 1M H_2SO_4 (A and B) and 1M NaCl (C and D) at different potential ranges.

Contrary to acidic medium, in 1M NaCl all the materials showed a pure capacitive behavior (charge/discharge of the electric double layer) with nearly rectangular shaped voltammograms (Figure 2 C). This is reasonable, since the amount of protons available for the quinone/hydroquinone redox reaction is largely reduced in the neutral electrolyte,

and thus the contribution of current arising from the pseudo-faradaic redox reactions involving the protonation of functional groups is reduced [23, 24]. It should also be highlighted that the stability potential window in NaCl electrolyte was enlarged compared to acidic medium (ca. almost 2 V) due to the high over-potential for hydrogen evolution. This is clearly illustrated in Figure 2 D for the carbon gel electrode as an example (a similar trend was obtained for AC and CC). Similar stability windows in neutral electrolytes have been reported for carbon materials with varied surface chemistry and porous structure [24]. This behaviour is of paramount importance as it might allow the application of high voltage to the carbon electrodes during the CDI experiments, while suppressing the water electrochemical breakdown.

3.3 Capacitive deionization performance of the electrodes

After the electrochemical characterization of the electrodes, their performance on the electro-assisted removal of ions was explored by application of a constant voltage between two adjacent electrodes. The dependence of the salt removal efficiency (deionization capacity) on the applied voltage was initially evaluated by polarization of the electrodes at different voltage values ranging from 0.6 to 1.2 V. As expected, the desalting capacity of a given electrode increased with the applied voltage; ionic removal efficiencies below 10 % were obtained for all the studied materials after 60 min of polarization at 0.6 and 0.8 V (data not shown), thus subsequent CDI experiments were carried out at 1 and 1.2 V.

Figure 3 shows the capacitive deionization performance of the studied electrodes immersed in a NaCl solution containing 1500 mg L⁻¹ TDS (total dissolved solids) with an

initial conductivity of 2600 $\mu\text{S cm}^{-1}$ (simulating the concentration of brackish water). Due to the porosity of the electrodes, the amount of ions physically adsorbed on the electrode surface cannot be neglected in the absence of polarization (open circuit conditions, OC). To counterbalance this contribution, the systems were allowed to rest at OC conditions for 30 minutes before polarizing the electrodes. The arrow in Figure 3 indicates when the voltage started to be applied. Upon immersion of the electrodes, a decrease in the solution conductivity was observed -due to physical adsorption-. Although this trend was similar for all the tested materials, a somewhat better performance was observed for sample CC at long times (in OC conditions), which could be attributed to the larger microporosity of this material compared to AC and XG electrodes (Figure 1). This observation seems reasonable as physical adsorption would only be expected to depend on the porous features of the electrodes, and thus could (should) be modulated by an adequate choice of the electrode material.

It can be observed in Figure 3 that polarization of the electrodes caused a fast drop in the solution salinity due to the ion electro-sorption in the electric double layer created at the electrode/electrolyte interface. The corresponding ionic removal efficiencies evaluated by applied voltages of 1 and 1.2 V are shown in Figure 3 B. The obtained values for CC and AC are similar to those reported for microporous carbons in the literature [7, 8, 13, 25]. If the ionic removal efficiency is calculated during the polarization of the electrodes (series *pol* in Figure 3 B), disregarding the amount of ions removed at OC conditions, the best performance was obtained for the carbon gel. For this material, the decrease in the solution conductivity was fast during the first 30-40 minutes of the polarization, and it gradually approached a plateau after 80 minutes when the change in the conductivity

became less evident (slow). The CDI performance for AC and CC electrodes were similar between them and in any case smaller than the ionic removal observed for sample XG.

Figure 3. A) Physical adsorption (OC conditions) and electro-assisted adsorption at applied voltage of 1 V on the xerogel, activated carbon and carbon cloth. Solution initial concentration: 1500 mg L^{-1} TDS. Arrows indicate the starting and final point of polarization, and the star indicates the overall process including physical adsorption. B) Amount of ions removed when voltages of 1 and 1.2 V are applied (pol series) and considering physical adsorption followed by polarization (OC+pol series).

These differences were noticed from the early CDI stage suggesting a faster ionic electro-sorption kinetic for electrode XG. Taking into account that XG is characterized by a large mesopore volume (Figure 1), it seemed that the accessibility of the ions to the polarized electrode surface (guaranteed by the adequate and interconnected network of

transport pores of the carbon gel) is an important factor to be considered in CDI systems. The almost negligible mesopore volume of CC could explain why the saturation plateau is reached at shorter times for this material (Figure 3 A). When the ionic removal is evaluated from the starting point of the CDI experiment (series *overall* in Figure 3 B) the differences in the performance of the three investigated electrodes became smaller. In this case, both the ions physically and electrically adsorbed were considered in the count and the results show that XG still outperforms AC and CC electrodes.

The physical adsorption has an important implication during the regeneration of the electrodes. In this view, a large ionic removal efficiency is required for an effective CDI performance, as it would assure a good reversibility during the discharge process. However, physical adsorption might affect the amount of ions released from the electrode surface during the regeneration step, particularly if this is intended to be carried out at zero voltage to minimize the energy consumption penalty.

Compared to previous studies from the literature, the XG electrode shows better performance than other carbonaceous materials used as electrodes [7-9, 26-29]. This behavior could be attributed to the micro/mesoporous structure of the XG electrode. However, it should be mentioned that comparison with data from the literature is not always straightforward due to the variation in the CDI systems (concerning mass and dimension of the electrodes, configuration of the CDI system, and concentration of the salty effluent to be treated).

3.4 Cycle-ability and reversibility of the CDI process in the electrodes

Achieving a high adsorption–desorption reversibility of the ionic species retained at the

electrolyte/electrode interface with imposing an external electric field between two electrodes is an essential factor for the CDI process. Consequently, the performance of the electrodes was investigated through a number of charge/discharge cycles with the following voltage current profile: the voltage between the electrodes was set at 1 V during the charge step (ions electrosorption) for 80 min, followed by the release of the ionic species upon the voltage removal during 30 minutes (regeneration of the electrodes at OC conditions), and beginning of a new charge cycle at the same voltage.

Figure 4 compares the regeneration efficiency of the investigated materials over a few charge/discharge cycles -defined as the desalting capacity of each cycle vs the initial value-.

Figure 4. Regeneration efficiency of the carbon electrodes with the charge/discharge cycles at open circuit conditions. Applied voltage in the charge step= 1.0 V. Arrows indicate those cycles where regeneration was conducted upon reversal of polarization.

As the CDI process relies on electrostatic interactions, one would expect it to be fully reversible; however the experimental data showed that a fraction of the ionic species is not leached out upon the removal of the polarization.

Indeed the release of ions after removing the voltage was fast, but the conductivity of the solution did not recover its initial value. This trend was observed for the three materials tested, although with important differences between them. For instance, the recovery of the solution conductivity for XG electrode (ca. 90 % recovery) was almost complete during the first regeneration cycle, as opposed to ca. 23 % of the ions that were not released for the same cycle when CC was used as electrode (Figure 4). With the exception of the first cycle, the desalting capacity in XG was more or less constant, which indicates that the process (from the second cycle) is almost fully reversible.

In the case of CC and AC electrodes, besides the fall in the ionic removal during the first cycle, a gradual declining trend in the desalting capacity was also obtained for consecutive charge/discharge cycles. To further explore if this behavior is exclusively due to kinetic restrictions during the desorption of ions, the electrodes were characterized after several charge/discharge cycles by different techniques including gas adsorption (Table 2) and electrochemical tests (Figure 5). The cyclic voltammograms in the 3-electrode configuration (H_2SO_4 1M electrolyte) of the cycled electrodes (previous rinsing in distilled water) were run on both the positive and negative electrodes of each CDI system. Data showed that the CV of the negative electrodes (Figure 5 top) after a number of cycles practically superimpose to those of their corresponding electrodes in the initial

state. This demonstrates that the electrodes are rather stable under the cathodic potentials obtained for an applied voltage of 1.2 V. In contrast, a different trend was obtained for the positive electrodes (Figure 5 B). The intensity of the cathodic/anodic peaks assigned to quinone/hydroquinone groups increased with the number of cycles for AC and CC electrodes, confirming the gradual oxidation upon charging/discharging cycles.

Figure 5. Cyclic voltammograms (5mV/s) in 1M H₂SO₄ of the negative (left) and positive (right) electrodes at the initial state (circles) and after five (triangles) and ten (squares) CDI cycles.

Table 2. Evolution of the BET surface area [m^2g^{-1}] of the positive electrodes after several CDI cycles.

	initial	5 cycles	10 cycles	20 cycles
XG	753	733	719	707
AC	1048	865	821	814
CC	1018	789	765	759

This was further confirmed by thermal analysis of the cycled electrodes, with the appearance of high temperature desorption bands -identified as CO-evolving groups- in the thermogravimetric profiles (data not shown), suggesting that carbonyl-type groups are incorporated to the carbon electrodes as a result of the operation of the CDI system. Although the applied voltage was rather low (ca. 1.2 V), it seemed that the positive electrodes of CC and AC materials were gradually oxidized with the number of cycles. Similar findings have been reported for anodic treatment of carbon materials in NaCl [30], and interpreted in terms of the likely electro-generation of oxidant species (such as Cl_2 or chlorine radicals) that would react with the carbon matrix, as well as of the positive electrode potential.

On the other hand, no electrode degradation was observed for XG electrodes under the same operating conditions; neither the thermogravimetric profiles nor the electrochemical response of the cycled electrode (Figure 5) revealed any chemical or electrochemical modification, demonstrating the higher stability of this electrode material vs electrochemical corrosion.

A decrease in the surface area of the cycled electrodes (Table 2) also indicates their slight and gradual deterioration. Again this effect was more remarkable for the CC and the AC

electrodes, and it could be explained as a result of i) the incorporation of O-containing functionalities at the entrances of the pores -widely described in the literature for carbon materials [31], and/or ii) incomplete removal of the electro-sorbed ions during the OC regeneration.

If the fall in the ionic removal efficiency were only due to an incomplete desorption when zero-voltage regeneration of the electrodes is carried out, the complete rejuvenation of the carbon electrodes could be expected by reversing the polarity of the electrodes. The reverse voltage should be high enough to remove the accumulated ions but not too much, to avoid retro-diffusion of the ions (movement from one electrode to another during regeneration). Taking this into account, some regeneration cycles (corresponding to cycles marked with arrows in Figure 4) were conducted by intercalating reverse polarity pulses at controlled voltage (ca. 10 minutes) during the regeneration step. Under these conditions the solution conductivity increased, reaching values closer to the initial one. This confirmed the additional release of ionic species, particularly in the case of sample XG. The regeneration efficiency of CC and AC electrodes by polarization reversal was also enhanced, although the recovery of the solution conductivity was not as high as for XG electrode and still a gradual decreasing pattern was obtained with the number of cycles (Figure 4). This result suggests that either not all the ions are allowed to leach out after 10 minutes (kinetic restrictions) or that the oxidation of these electrodes is affecting their ionic removal capacity.

Although the application of an external voltage drove off a higher fraction of the accumulated ions (compared to zero-voltage conditions), the rejuvenation of the electrodes was not complete, which suggests that perhaps the retro-diffusion of ions

during the reversal of polarization should not (cannot) be considered negligible. Current studies are ongoing to detect the optimum reverse voltage at which rejuvenation could occur (based on the surface potential of the electrode material), with special emphasis on the porous and chemical features of the carbon electrodes.

4. Conclusions

This work describes the electrochemical behaviour of a porous carbon gel synthesized by the poly-condensation of resorcinol and formaldehyde as electrode for CDI of synthetic brackish water, compared to that of conventional microporous carbon materials. The results show that the carbon gel is a promising electrode material with a high CDI performance and good cycle-ability.

The desalting capacity of the electrode materials was found to depend on the applied voltage and the porous features of the carbons. In the absence of polarization (OC conditions), the fraction of ions physically adsorbed on the electrodes was strongly dependent on the porosity of the materials. When a voltage was applied, the desalting capacity largely increased due to the electrostatic interactions appearing at the electrode/electrolyte interface. The carbon gel showed a better electrochemical performance than the activated carbon and carbon cloth, both in terms of ionic removal efficiency, fast electrosorption kinetics and regenerability. The fast electro-assisted ion adsorption kinetics of the carbon gel electrode is due to the combination of an interconnected micro/mesoporous matrix.

The electrochemical performance of the carbon gel over a number of cycles exceeded that of AC and CC electrodes, with an almost fully reversible removal efficiency (ca.

90 % recovery) when regeneration was carried out at zero-voltage conditions. Characterization of the cycled electrodes revealed that the carbon gel is an electrochemically stable material, with an almost negligible deterioration (oxidation) upon several cycles of charge/discharge. In contrast, the AC and CC electrodes underwent severe oxidation during the CDI experiments.

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