CONDUCTIVE INKS WITH EPOXY RESIN BASED VEHICLES FOR PEROVSKITE SCREEN PRINTING METALLIZATION

C. Montes[1], A. Linares[2], E. Llarena[1], O. González[1], D. Molina[1], A. Pío[1], L. Ocaña[1], C. Quinto[1], M. Friend[1] & M. Cendagorta[1].

[1]Instituto Tecnológico y de Energías Renovables, S. A. (ITER)
[2]Agencia Insular de Energía de Tenerife (AIET)
Pol. Industrial de Granadilla, s/n
E 38600 Granadilla de Abona, España
Tlf. +34 922 747 700
Fax +34 922 747 701
E-mail iter@iter.es, agenergia@agenergia.org

ABSTRACT: The main objective of the present paper is to summarize the work done in the Laboratory of Solar Cells (SiCelLab) form the Instituto Tecnológico y de Energías Renovables (ITER) in order to enable the possibility of using screen printing techniques as an alternative to the actual methods, applied by the scientific community for producing the metal contacts in perovskite based devices. Thus, the deposition of contacts made by screen printing with inks such as the ones based on graphite powders, epoxy resins and anhydrous solvents, due to their inherent low cost and processing temperatures, could lead to reducing the manufacturing costs and, therefore, help with the future commercialization of this kind of solar cell technologies.

Bearing this in mind, optimal proportions of these three components have been combined, in order to obtain a basic ink recipe, suitable for printing purposes, which also provided the possibility to study the effect of using different solvents. The improvement of the derived ink recipes was achieved by producing samples, on the one hand, via screen printing so as to study their electric resistance and, on the other, via doctor blade so as to study their resistivity, in both cases by using a semiconductor characterization system, configured to operate as an ohmmeter. Also, a digital microscope was used to study in detail the homogeneity and adhesion characteristics of the deposited samples.

Finally, it was concluded that the N, N- dimethyl formamide (DMF) and N-methyl-2-pyrrolidinone (NMP) are the solvents that allow to add greater amounts of graphite to the final mixture and, thus, to improve its conductivity, without impairing its printing capabilities.

Keywords: Contact, Metallization, Screen Printing, Perovskite solar cells

1 INTRODUCTION

In the race for achieving higher Power Conversion Efficiencies (PCE) and regarding the need to provide the metal contacts required for completing the diverse fabrication architectures, most of the R&D efforts devoted to Perovskite solar cells have been focused on the use of thermal evaporation techniques [1]-[6]. However, if Perovskite solar cells are to reach the commercial stage, it is necessary to evaluate the introduction of alternative metallization techniques which could address larger active areas, while reducing the manufacturing costs. On the metallization side, one of these techniques is screen printing.

The Laboratory of Solar Cells (SiCelLab) [7][8] form the Instituto Tecnológico y de Energías Renovables (ITER) has been working on the screen printing approach for Perovskite solar cells by, originally, performing trials with different commercial frit based pastes and inks, such as aluminum and silver pastes, commonly used in crystalline silicon solar cell technologies, as well as silver inks, also commonly used in polyester and polymeric film depositions [9]. These trials were conducted applying low temperature and fast curing processes after the deposition stages, in order to preserve the Perovskite substrates qualities. However, it was found that, due to the chemical nature and physical morphology of such substrates, either the kind of vehicles or the size of the powders (or both) used in the composition of these pastes and inks failed to adhere to the substrates (after all, frit based inks require high curing temperatures in order to get tempered onto the substrates) or had water among its constituent elements, rendering them as too aggressive for being of any real use (as soon as they were deposited and cured over the perovskite substrates, they rapidly deteriorated the finished device) [9].

In order to overcome this problem, the Solar Cells Laboratory have been working on developing new conductive ink formulas that use, on the one hand, epoxy resin glues and anhydrous solvents as vehicles and, on the other, conductive powders and flakes of different purities and sizes. The reason for using resin glues lies in that it allows to produce inks with high adhesion capabilities which can be cured at low temperatures. The use of anhydrous solvents enables the possibility of tweaking the ink in order to incorporate higher amounts of conductive materials, while ensuring the absence of water based components in the final mix.

The present paper summarizes the methodology and first results achieved in this ongoing project.

2 METHODOLOGY

The inks were prepared by using a kitchen hand mixer [10], provided with stainless steel beaters, rotating at 200 RPMs, in order to combine the conductive powders with the epoxy resin together with the anhydrous solvent of choice. Finally, in order to perform characterization studies on the resulting contacts, samples were extracted from the blend, with the same mixing time, in order to make two kinds of contacts: via screen printing and via Doctor blade. Finally, the contacts were dried and cured in a drying oven [11] at low temperatures.

2.1 Screen printing study

It was performed over glass substrates with sizes 25mm x 25mm x 2mm by using screens [12] capable of handling inks with up to 67 microns particle sizes together with a screen printer [13], provided with a 70 durometer squeegee blade and a dial indicator for fine adjustment of the screen and the squeegee rod to the tool plate, which allows to control the thickness of the inks and pastes deposited with an accuracy of micrometers.

Figure 1 shows the appearance of the deposited contacts that, on average, were found to have a thickness of 10 microns.

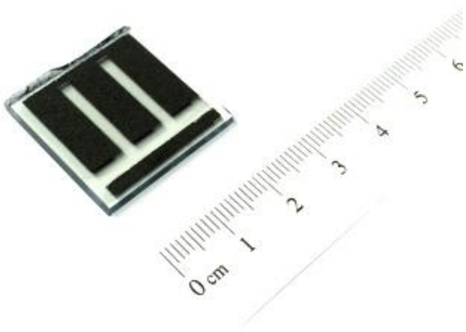

Figure 1: Example of a screen printed contact.

The characterization of the printed samples was performed by studying their visual appearance and electric resistance. The visual appearance assessment was performed by looking at the printed contacts with a microscope [14] in order to evaluate their homogeneity and degree of adhesion. The measurements were performed by using a semiconductor characterization system [15], configured to operate as an ohmmeter in order to obtain the resistance of the printed contacts.

2.2 Doctor blade study

In order to obtain resistivity values of the contacts derived from the different ink recipes, the standard F 1896 Test Method for Determining the Electrical Resistivity of a Printed Conductive Material [16] was considered. In this method it is required to print a determined kind of pattern, consistent of a straight trip, with known thickness. However, since no screen was available for that purpose, the alternative Doctor blade printing technique was performed. Thus, substrates with sizes 25mm x 75mm were prepared by covering them with cellulose tape [17], exposing only the pattern intended to be printed by using a glass rod in order to manually extend the ink over the substrate. The length (L) and width (W) of the printed pattern for the contacts was consistent with the minimum 50:1 size ratio, as it is specified by the above mentioned standard. As per the thickness of the resulting contact, it was estimated by considering the reported thickness of the tape (63.5 µm). As in the previous section, the measurements were performed by using semiconductor characterization system [15], configured to operate as an ohmmeter in order to obtain the resistance of the printed contacts and derive the corresponding resistivity values as per the standard method.

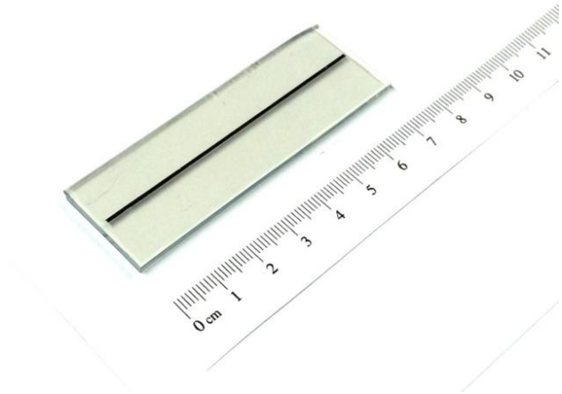

Figure 2: Example of a doctor blade printed contact.

3 EXPERIMENTAL

To get started, a basic ink recipe was obtained by trial and error, via mixing graphite powders [18] with epoxy resin [19] and toluene [20], almost to the point of saturation, before adding the hardener [19]. The reason for using toluene was due to its relatively low boiling point [21], in the assumption that it could speed up the curing process and help reducing the resistance of the resulting contacts.

After several trials, a procedure for elaborating the inks was established by dividing the actual mixing in four stages: At the first one, the resin and a part of the graphite was mixed by steadily stirring with a kitchen hand mixer for 10 minutes. In this phase is where most of the graphite is added. In the second stage, more graphite is added to the mix, followed by another 10 minutes of stirring. At this phase is when it was desired to reach the highest possible degree of saturation of graphite in the mixture. In the third stage, the remaining amount of graphite was added to the mix, together with the solvent of choice, continuing with the stirring but this time for 15 minutes. Finally the hardener was incorporated to the mix.

Notice that, in order to avoid spillage of graphite, every time that it is added to the mix, the first stirring stages were carried out by using a laboratory spatula.

Due to the nature of the chosen ink vehicle, which has a hardening time beyond which it renders quite unusable for printing purposes, a study of the print times for the mixtures was carried out by extracting samples at 5, 10, 20 and 30 minutes after adding the hardener and by trying to interrupt the mixing process as little as possible. For each sample, the two kind of printings explained in the previous section were performed.

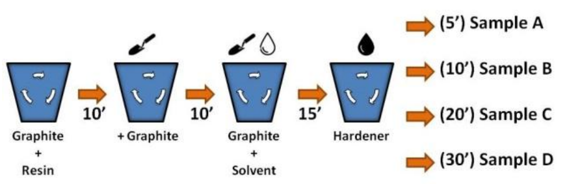

Figure 3: Mixing procedure.

The production of the contacts was concluded by a 10 minute curing process, performed in a drying oven at 100 ºC, following the recommendations of the manufacturer of the epoxy resin [19].

Once a basic ink recipe was developed, modifications were performed on it by keeping the weight concentration of its components, but changing the type of solvent. Thus, trials were performed with solvent with higher boiling points, such as chlorobenzene (ClBz) [22], N,N-dimethyl formamide (DMF) [23], and N-methyl-2-pyrrolidinone (NMP) [24]. To all mixes, the two printing processes were performed, together with their corresponding characterization and print time studies.

Finally, since the inks done with DMF and NMP had the appearance of being able to accommodate more graphite, the basic recipe was modified in order to do so and trials were carried out to conduct such study.

4 RESULTS AND DISCUSSION

4.1 Development of a basic ink recipe

The target was to obtain a basic recipe that could meet the two main requirements, that is, that it was suitable for screen printing and also that it was conductive. In order to do so, different mixtures were prepared, following the procedure described in the previous section, trying to determine an optimal ratio of graphite, resin and toluene.

Of all attempts, Table I summarizes the relevant information from those who gave as a result inks that were useable for screen printing purposes.

Table I: Basic ink recipe trials. “N/C” stands for non conductive and “N/A” for non available.

Mix code	Graphite (wt%)	Resin (wt%)	Solvent (wt%)	Resistance (kΩ)	Resistivity (Ω·cm)
M19	25.97%	74.03%	0.00%	N/C	N/C
M20	35.03%	64.97%	0.00%	N/A	821.82
M21	31.30%	58.13%	10.57%	127.65	50.47
M22	28.76%	53.37%	17.87%	217.92	19.31
M23	33.33%	49.95%	16.72%	300.04	6.40

As it can be seen in the data collected in Table I, different results were found, depending upon the kind of printing technique applied. So, for the screen printed contacts, the one obtained with the ink (M21) showed a better resistance than trials performed by either increasing the amount of vehicle, leading to a more fluid ink (M22) or by increasing the amount of graphite, producing a thicker ink (M23). However, for the doctor blade printed contacts, the key for reducing the resistivity in the printed contacts resided in decreasing the amount of resin in the corresponding ink vehicle (see M23 versus either M22 or M21).

Also, from the inks that were conductive, M21 presented a better behavior during the screen printing itself, showing superior material passage though the sieve of the screen, resulting on much more homogeneous contacts, as it can be seen in Figure 4

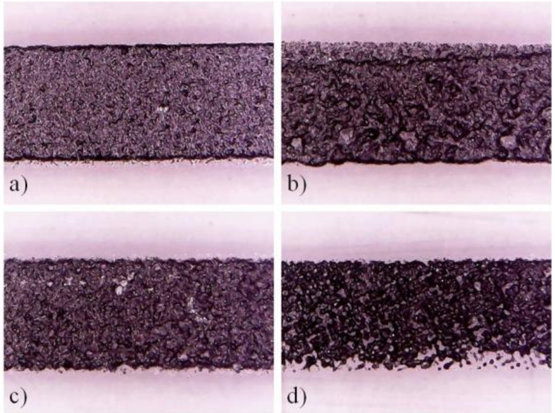

Figure 4: Microscope images showing contacts deposited by screen printing with inks M19 (a), M21 (b), M22 (c) and M23 (d).

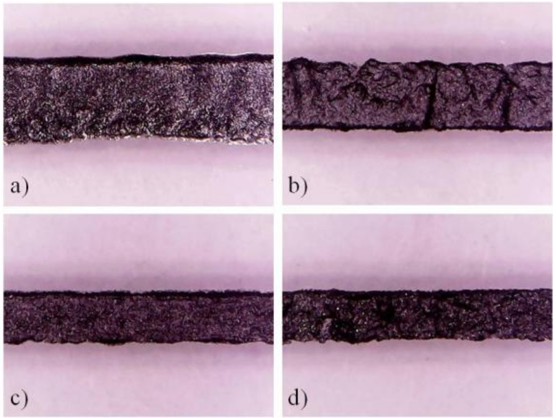

Figure 5: Microscope images showing contacts deposited by doctor blade with inks M19 (a), M21 (b), M22 (c) and M23 (d).

Since the purpose of the project was to develop inks for screen printing purposes, the mix M21, that is, the one with a weight concentration ratio of approximately 32%/58%/10% for graphite, epoxy and toluene, respectively, was considered as the best candidate to carry on with the next stage. Also, despite the differences observed between the contacts printed by screen printing and doctor blade, the possibility of studying the variations in the contact resistivity due to the use different ink recipes, was considered relevant enough to keep producing samples by doctor blade printing in the next stage of the project.

4.2 Ink trials with different solvents and printing times

Throughout the development of the basic ink recipe, it was clear that the mixtures had been affected by evaporating phenomena. Therefore, the addition of solvents with higher boiling point was studied in order to verify whether our original assumption for choosing toluene, so that it could speed up the curing process and help reducing the electric resistance of the resulting contacts, was correct.

Table II: Relevant properties [21][25] of the solvents used.

Properties	Toluene	ClBz	DMF	NMP
Boiling point (°C)	110.6	132	153	202-204
Density (g/mL)	0.867	1.106	0.944	1.028
Vapor pressure @ 20°C (hPa)	29	12	3.5	0.39
Surface tension @ 20 °C (mN/m)	28.4	33.6	37.1	40.79

Also, due to the use of an epoxy resin as part of the chosen vehicle for the inks, it was also required to examine for how long the mixed inks were still suitable for screen printing purposes, and how the differences on the bonding process could affect to the resistance, as well as the resistivity, for the resulting contacts.

Tables III and IV summarize the results obtained with the two printing processes:

Table III: Resistance measured in the contacts deposited via screen printing.

Time (min)	Toluene (kΩ)	ClBz (kΩ)	DMF (kΩ)	NMP (kΩ)
5	142.79	201.01	120.21	153.10
10	395.73	459.83	166.93	165.75
20	447.89	380.88	298.32	366.27
30	1632.20	947.15	273.85	364.18

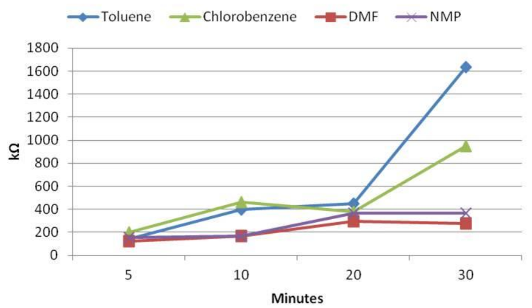

Figure 6: Resistance measured in the contacts deposited via screen printing.

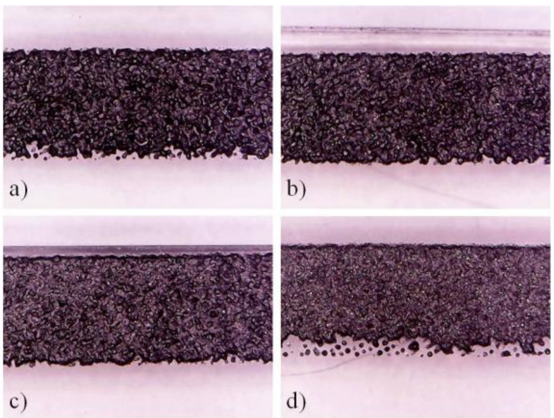

Figure 7: Microscope images showing contacts deposited by screen printing with Toluene (a), Chlorobencene (b), DMF (c) and NMP (d). All the contacts were deposited 20 minutes after adding the hardener.

By looking at the gathered data, it can be deduced that, for the screen printed contacts, which have considerably large surfaces but relatively short thicknesses, the differences in the solvent boiling temperature used are more relevant than the differences in their density, so that the inks which are more exposed to evaporation phenomena, both during the mixing and the contact curing processes, experience an acceleration in the resin bonding process which, due to the geometric nature of the printed contacts, became significant in the samples deposited at longer print times (from the addition of the hardener to the ink mixture). Therefore, contrary to what it was expected, an acceleration on the resin bonding process leads to an increase in the contact resistance, probably because more epoxide groups get in the way between the graphite stacks.

Table IV: Resistivity measured in the contacts deposited via Doctor blade.

Time (min)	Toluene (Ωcm)	ClBz (Ωcm)	DMF (Ωcm)	NMP (Ωcm)
5	27.43	33.79	18.02	15.22
10	40.38	64.58	23.47	23.09
20	59.62	88.08	45.52	46.26
30	57.62	164.51	119.49	59.16

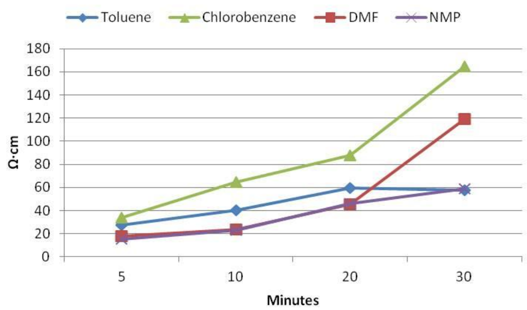

Figure 8: Resistivity measured in the contacts deposited via Doctor blade.

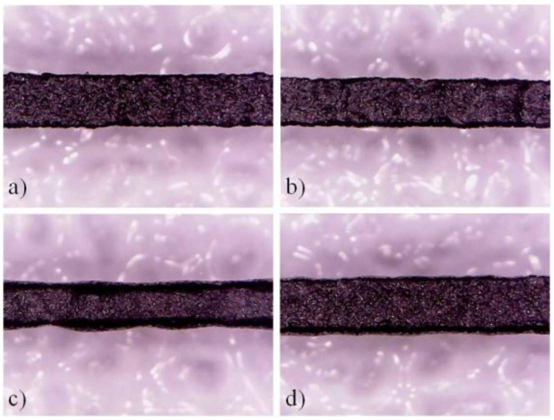

Figure 9: Microscope images showing contacts deposited by doctor blade with Toluene (a), Chlorobencene (b), DMF (c) and NMP (d). All the contacts were deposited 20 minutes after adding the hardener

By contrast, for the contacts printed with doctor blade, which have a much thicker nature than the screen printed ones (63.5 versus 10 µm, respectively), the gathered data suggest that, despite the differences in the boiling temperatures for the solvents, it was their density what helped to reduce the resin bonding speed during the curing process and, hence, also the resistivity of the contacts.

4.3 Ink trials with more graphite

The trials conducted at the previous section resulted in inks that, in the case of toluene and chlorobenzene, had an amount of graphite equal or near to the saturation level. However, this was not the case for the mixtures made with DMF and NMP (see Figure 7). Thus, since the purpose of the entire project was not only to obtain ink recipes suitable for screen printing purposes, but also that they were capable for producing contacts with the lowest resistance possible, a new set of trials were performed with these two last solvents in order to get closer to the desired level of ink saturation with graphite.

Table IV summarize the results obtained with contacts deposited via the two printing processes and by applying a recipe with a weight concentration ratio of approximately 35%/58%/7% for graphite, epoxy and solvent, respectively.

Table V: Resistance and resistivity measured in the contacts deposited via screen printing and doctor blade, respectively.

Time (min)	DMF Resistance (kΩ)	NMP Resistance (kΩ)	DMF Resistivity (Ωcm)	NMP Resistivity (Ωcm)
5	116.28	84.59	10.88	12.24
10	154.75	123.42	28.57	22.98
20	231.94	188.04	22.98	30.12
30	257.37	267.09	22.53	30.04

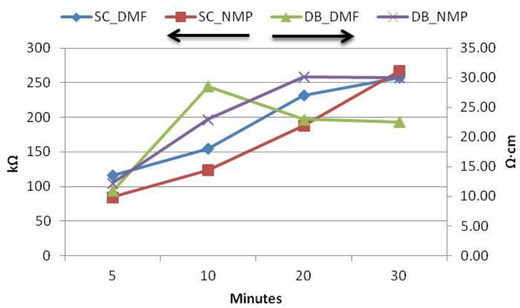

Figure 10: Resistance and resistivity measured in the contacts deposited via screen printing and doctor blade, respectively.

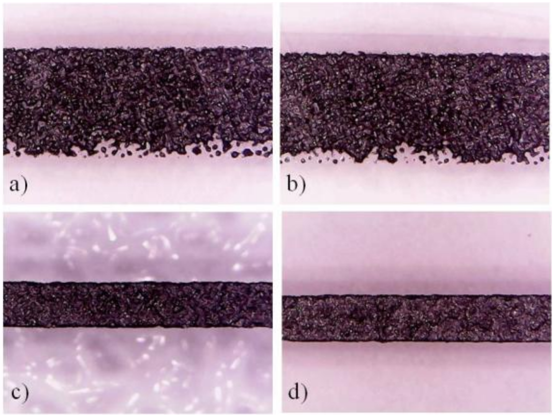

Figure 11: Microscope images showing contacts deposited by screen printing with DMF (a) and NMP (b) as well as doctor blade with DMF (c) and NMP (d). All the contacts were deposited 20 minutes after adding the hardener

As it can be seen in Table V, the obtained results do improve the ones referred in Table III and IV but not significantly. Therefore it can be assumed that the recipe proposed nearly matches the limits of the amount of graphite that these inks are capable of accommodating.

In order to further reduce the resistance of the printed contacts, the following options will be studied in this ongoing project:

- To use graphite powders with flakes made of shorter stacks, halfway between standard graphite and graphene, in order to improve the interconnections throughout the resulting contacts. To this end trials with this kind of graphite [26] have already been scheduled.
- To mix anhydrous solvents of different kinds in order to obtain better density to boiling point ratios so as to help accommodate more graphite during the mix while still facilitating the contact curing.
- To dissolve in the anhydrous solvent a quantity of conductivity improving species, such as ferrocene or graphene, prior to its addition to the ink mixtures. In this way it would be possible to reduce the electric resistance of the deposited contacts, without the need to add large amounts of graphite.
- To directly use powders and flakes of higher intrinsic conductivity, such as aluminium or silver.

On the other hand, and as it was explained in the Experimental section, the ink mixing throughout the project was done by means of a kitchen hand mixer. Although this technique provides fairly homogeneous blends, the mechanical action of the stirring beaters amalgamates the mix with small air bubbles. This phenomenon ultimately may be leading to a deterioration of the resulting inks, once cured, due to the existence of small air pockets within the contact. This was particularly noticeable for Doctor blade printed contacts. A way to overcome this phenomenon could be the use of a three roll mill in the final stages of the mixing process.

Finally, since the results obtained by screen printing seem to differ so much from the ones obtained by doctor blade, particularly at higher application times (that is, more than 20 minutes after adding the hardener to the mix), it would be very useful to obtain the resistivity values by screen printing. To that end, trials for using screens equipped with the necessary type of patterns have been scheduled.

5 CONCLUSIONS

A method for producing inks based upon the use of vehicles made with epoxy resins with anhydrous solvents, suitable for being used with perovskite substrates has been developed.

The entire study was carried out with graphite powders, as the conducting material of choice, which was due to their high purity and screen-compatible particle sizes.

In order to improve the derived recipes, samples were produced, on the one hand, via screen printing so as to study their electric resistance and, on the other, via doctor blade so as to study their resistivity.

With the methodology and the materials chosen, ink recipes were developed which were capable of producing contacts via screen printing with the lowest electric resistance possible. This was achieved by using DMF and NMP as the solvents of choice.

Finally, improvements on the methodology, as well as changes in the materials chosen, were proposed as ways for improving the accomplished results.

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