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FINAL DEGREE PROJECT

**[C<sub>2</sub>mpyr][FSI]/PEDOT-Cl composites as dual ionic and electronic  
conductors**

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# ABSTRACT

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Nowadays, it is quite common to see a wide range of investigations related to the development of technological devices that make use of clean energy, with the sole objective of decreasing unhealthy pollution emissions. Some of the most promising ones are related to rechargeable batteries, especially lithium ion batteries (LIBs), due to their high energy storage and cyclability. The electrodes of these kind of batteries still are design based on inorganic materials, such as carbon and polyvinylidene fluoride (PVDF), which in a future can finite and are not very environmental friendly. That is why there is an increased demand for a new kind of materials for electrodes, for example, polymeric materials that can conduct electrons and ions at the same time are a perfect option. These kind of materials improve the capacity of LIBs, making out the best of them. However, this is an area that still has a lot of research to be made, in order to be able to understand well the functionality of these kind of materials when using in organic electrodes.

The aim of this work is to investigate if the mixture of an organic ionic plastic crystal (OIPC) and a conducting polymer results in a composite that can be used as an organic battery electrode. The objective is to do the characterization of the created composites, which helps to understand their properties. For that, first of all, synthesizes of [C<sub>2</sub>mpyr][FSI] and PEDOT-Cl were done. Afterwards, composites of different weight ratios were prepared mixing both the mentioned materials. Finally, the characterization of the composites was carried out, using techniques like Fourier-transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and 4 point probe. The results of all these analyses demonstrate how the properties of the composites change varying the composition, as well as showing if the obtained results are good enough to be used as electrode materials. The results indicate that the mixture of [C<sub>2</sub>mpyr][FSI] and PEDOT-Cl is a good approach to obtain dual ionic and electronic conducting materials. However, there is a lot of research to be made yet, in order to be able to study and observe the applications of these new materials in battery electrodes.

# LABURPENA

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Gaur egun energia garbian oinarritzen diren gailu teknologikoen garapenean dihardute ikerketa talde asko, osasunerako kaltegarriak diren kutsadura emisioak jaisteko helburuarekin, hain zuzen ere. Berriz kargatzeko pilek interes handia piztu dute, zehazki litiozko bateriek (LIBs), beraien energia biltegitratzeko eta zikloak osatzeko kapazitate handiarengatik, beste gauza batzuen artean. Oraindik ere, bateria mota hauen elektrodoak material inorganikoetan oinarritzen dira, esaterako, karbonoan eta polibinilideno fluoruroan (PVDF), baina material hauek etorkizun batean amaitzeko aukerak asko dira, eta hori gutxi balitz, ingurumenarekiko kutsatzaileak dira. Hau guztia dela eta, elektrodoetarako material berriak sortzeko behar handia dago. Esaterako, material berdinean elektroiak eta ioiak garraiatzeko gaitasuna duten polimeroak aukera paregabeak dira aipatutako arazoari aurre egiteko. Material hauek litiozko baterien gaitasuna hobetzen dute, beraien alderdi hoberenak eskura ateraz. Hala eta guztiz ere, oraindik gai honen inguruko ikerketa asko egiteko daude, material mota hauek elektrodo organikoetan nola funtzionatzen duten ulertzeko, besteak beste.

Lan honen helburu nagusia, kristal plastiko organiko ioniko (OIPC) baten eta polimero eroale baten arteko nahasketen inguruan ikertzea da, konposatu mota hauek baterietan elektrodo organiko bezala erabili ote daitezkeen ikusteko asmoz. Helburua sortutako konposatuen karakterizazioa egitea izango da, elektrolito hauen propietateak nolakoak diren ulertzen laguntzeko. Horretarako, lehendabizi, [C<sub>2</sub>mpyr][FSI] eta PEDOT-Cl-ren sintesiak egin dira. Horren ostean, aipatutako bi materialak nahastuz pisu proportzio desberdineko konposatuak prestatu dira. Azkenik, konposatuen karakterizazioa burutu da, horretarako teknika desberdinak erabiliz: espektroskopia infragorriaren Fourier transformazioa (FTIR), analisi termo grabimetrikoa (TGA), ekortze kalorimetria diferentziala (DSC), ekortze mikroskopia elektronikoa (SEM), inpedantziaren espektroskopia elektrokimikoa (EIS), voltametria ziklikoa eta 4 puntazko proba. Analisi guzti hauen emaitzek konposizioak aldatuz konposatuen propietateak nola aldatzen diren frogatu dute; bai eta, ea lortutako emaitzak elektrodoetan material bezala erabiltzeko onak diren ikusten lagundu ere. Emaitzek erakutsi dutenez, [C<sub>2</sub>mpyr][FSI]-ren eta PEDOT-Cl-ren arteko nahasketa egitea material eroale ioniko eta elektronikoa lortzeko hurbilketa ona da. Hala eta guztiz ere, ikerketa gehiagoren beharra dago oraindik,

material berri hauek baterien elektrodoetan duten aplikazioak ikertzeko eta emaitzak ziurtatzeko.

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# 1. INTRODUCTION

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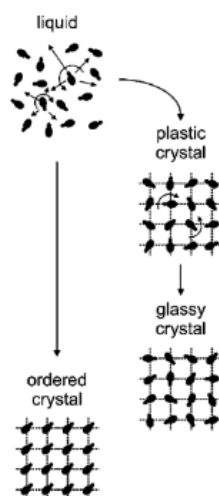
## 1.1. ORGANIC IONIC PLASTIC CRYSTALS (OIPC)

Currently, the climate change is a widely known problem that have to be affronted. There is a need of clean and renewable energy, at low cost and with high energy efficiency, to avoid the air pollution, water pollution and energy insecurity.<sup>1</sup> This is the reason why the development of electrochemical energy storage technologies is inevitable; fuels cells, supercapacitors and rechargeable batteries, to name a few. All of this demands electroactive materials and electrolytes with high energy-storage capacity and security.<sup>2</sup> There is also a need to take out the current flammable liquid battery electrolytes, switching to less volatile and solidified materials to increase safety.<sup>3</sup> Therefore, the electrolyte plays a very important role when increasing the efficiency of these technologies. In fact, there is a great interest in those electrolytes that can function in solid-state, as well as, in liquid-state.<sup>4</sup>

In recent years, ionic liquids (ILs) have become very interesting materials, using them to produce sustainable energy. ILs are perfect to synthesize electroactive materials and to use them as electrolytes in high energy-storage and low-cost batteries (Li-ion, Li-S, etc.). One of the main characteristics of most ILs is that at low temperatures they form a crystalline solid. When this is referred to organic salts, they are called organic ionic plastic crystals (OIPCs), which in other words, are the solid state analogues of the ILs. OIPCs are formed with multiple crystal solids, which contain plastic mechanical properties and significant ionic conductivity.<sup>2</sup>

Due to the fact that ILs and OIPCs have high decomposition temperatures and non-volatility, they are a good option to use as electrolytes in batteries (Li, Na batteries, for example), fuel cells and renewable energy devices. Both materials are composed of ions; the first ones are liquid at room temperature, while the others are solid.<sup>3</sup> It is interesting to highlight that OIPCs have not only long-range order and short-range disorder, but also the ability to produce ion conduction in the material.<sup>4</sup> The ionic conductivity of OIPCs is so thanks to their mechanical and transport properties, which

give the ions the ability to take advantage of the motional properties that are characteristic of liquids, without losing their 3D ordered structure<sup>2</sup> (**Fig. 1**)<sup>5</sup>.

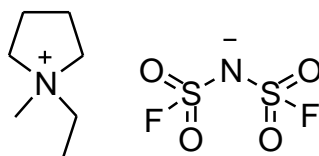


1. Fig. Schematic representation of possible transitions of a liquid in a crystalline system and a plastic crystal

Moreover, the term “plastic crystal” indicates that these materials have rotational, translational and conformational motions, allowing the ions to have good mobility.<sup>6</sup> As mentioned before, OIPCs contain only cations and anions that are solid at room temperature. Amongst the most used cations, are the pyrrolidinium, tetraalkyl ammonium and phosphoniums, combined with anions such as dicyanamide ([DCA]<sup>-</sup>), hexafluorophosphate ([PF<sub>6</sub>]<sup>-</sup>), bis(fluorosulfonyl)imide ([FSI]<sup>-</sup>) and tetrafluoroborate ([BF<sub>4</sub>]<sup>-</sup>).<sup>3</sup>

This report will be focused on the N-ethyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide, [C<sub>2</sub>mpyr][FSI], which is a plastic crystal (**Fig. 2**)<sup>7</sup> with two solid-solid phase transitions at -72 °C and -22 °C, and a melting point at 205 °C.<sup>8</sup> Moreover, this OIPC has a high ionic conductivity of 1,23 x 10<sup>-6</sup> S cm<sup>-1</sup> at room temperature.<sup>6</sup> It has been studied as a solid-state electrolyte for Li-ion batteries, mainly due to its practical use, its good stability and cycling performance.<sup>3</sup>





2. Fig. Chemical structure of the [C2mpyr][FSI] OIPC

## 1.2. CONDUCTING POLYMERS – PEDOT

Li-ion batteries are used worldwide, and this is due to their high energy, high power density and their versatility. These devices are normally based on inorganic materials, such as lithium phosphates, oxides and graphite materials. However, these materials, besides being very localized and low abundant in earth, are toxic; in fact, there is a need to look for alternative materials which are more sustainable in terms of raw materials, production and recyclability.<sup>9</sup>

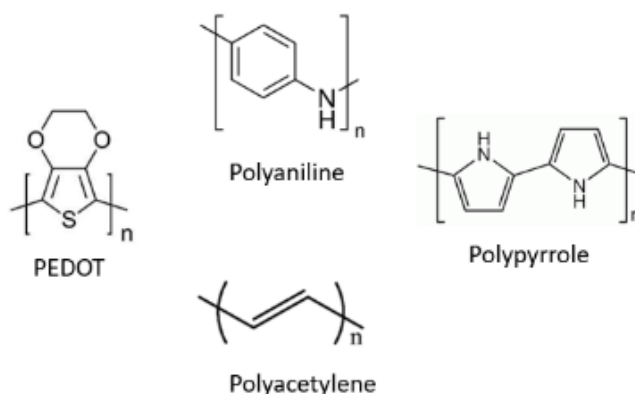
Conducting polymers (CPs) are organic macromolecules that can have high electronic conductivity, facile production, mechanical stability and light weight, at a fairly low cost.<sup>9</sup> They are a class of polymers with a conjugated backbone of adjoining  $sp^2$  hybridized orbitals, therefore, delocalized  $\pi$  electrons are formed along their backbone and are electronically conductive. Some examples of CPs are polyaniline, polypyrrole and polyacetylene (**Fig. 3**).<sup>10</sup>

CPs are one of the best options for that transformation, taking into account that they can be used in a wide range of technological applications. They are useful, for example, for electrochemical energy storage devices, supercapacitors, batteries and fuel cells.<sup>9</sup>

Nanostructured CPs are the best ones to use in previously mentioned applications. One of the reasons is that they have a high surface area in contact with the electrolyte, allowing high charge and discharge rates. Another reason is that as CPs show high tolerance towards the effort of the reaction that happens in the system, they provide high cycle life to the device. Last but not least, nanostructured CPs allow fast ionic diffusion, due to their short paths for the transport.<sup>9</sup>

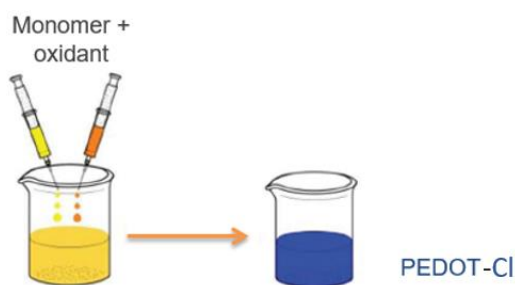
However, they also have some limitations.<sup>11</sup> One of them is the rapid degradation of properties like conductivity and the previously mentioned electrochemical cyclability.<sup>11-12</sup> During the cycles, when a CP is doped it expands, and when it is de-doped it shrinks; so with this repetitive behavior, the structure of the polymer goes slowly fading out.<sup>9</sup>

Poly(3,4-ethylenedioxythiophene), PEDOT (**Fig. 3**), is one of the most interesting CPs of the last years. It is electronically conductive, electroactive and it has high environmental stability. The PEDOT can be used in a lot of areas: batteries, chemical sensors, supercapacitors and conducting textiles, to name a few.<sup>2</sup> Focusing in batteries, PEDOT for example is used as electroactive material in electrodes; or as conductive binder with Li-ion materials, such as in lithium iron phosphate (LiFePO<sub>4</sub>) battery.



3. Fig. Chemical structures of PEDOT, polyaniline, polypyrrole and polyacetylene

The polymerization of the PEDOT can be done in three different ways; by oxidation, by electrochemical polymerization and by vapor phase polymerization. In this project it was done by the oxidation of the monomer 3,4-ethylenedioxythiophene (**Fig. 4**).



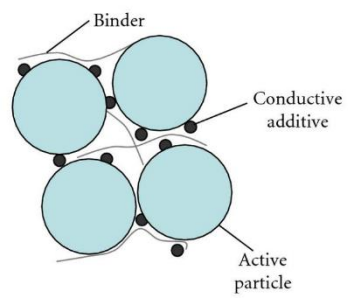
4. Fig. Schematic synthesis of PEDOT-Cl

### 1.3. MIXED IONIC AND ELECTRONIC CONDUCTORS

Mixed ion/electron conducting polymers (MIECPs) have recently been of great interest for many research groups. This is because they are unique materials that provide the ability to conduct ions and electrons in the same material, which gives the opportunity to use them in a wide range of electrochemical devices; however, the most studied ones are the batteries.<sup>13</sup>

The MIECPs are usually used as electrode binders (**Fig. 5**)<sup>14</sup> in batteries. As they provide ability of ion movement in the electrode and the removal of electrons, all in the same material, MIECPs are essential composites. Moreover, they increase de stability, longevity and the capacity of batteries' electrodes.<sup>13</sup> In resume, the combination of OIPCs and polymers provides safe and easy solid-state membranes with improved mechanical properties and ionic/electronic conductivities in batteries.<sup>6</sup> Curiously, the anions that are effective in forming ILs ([FSI], for example), are also those that are good intercalating ions (also known as dopants) for CPs.<sup>2</sup>

Although it is not the most common behavior, in some cases, the ionic conductivity decreases with MIECPs, while the ordering of the OIPC matrix improves. As there is little known about this yet, a lot of studies are being carried out to understand the results of the interactions between OIPCs and CPs. This will be one of the main goals of this report.



5. Fig. Illustration of a small part of an electrode, including the binder

## 2.OBJECTIVES

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The main objective of this report is to develop MIECs and perform their characterization, with the purpose of analyzing how these mixed composites function, how their properties change with composition and valuating their application in batteries. First, the main components of the composites will be synthesized, on one hand an organic ionic plastic crystal ([C<sub>2</sub>mpyr][FSI]), and on the other hand, a conducting polymer (PEDOT-Cl). After that, both of them will be mixed in different weight ratios to create a family of composites.

As it is known, PEDOT is electronically conductive, it is electroactive and it has high environmental stability. Instead, the [C<sub>2</sub>mpyr][FSI] OIPC has ionic conductivity, high decomposition temperature, it is non-volatile, it has a negligible vapor pressure and provides good contact with electrodes. So, the aim is to prepare a new family of composites, with different weight ratios and do their characterization. This way, it will be possible to see how the material properties change by modifying the ratios.

In the characterization of the prepared composites, electronic and ionic conductivities, electrochemistry, thermal properties and mechanical properties will be analyzed. In order to get these results, analyses such as FTIR, 4 point probe method, TGA, DSC, CV, EIS and SEM will be carried out. All these techniques and their specifications will be described later in the experimental part.

When creating the MIEC composites, an interphase is created between the OIPC and the polymer. So, by making all these analyses, it would be possible to understand, not only how the properties of OIPCs and polymers affect that interphase's properties, but also if the created interphase promotes order or disorder to the composites.

Summarizing, the principal goal of this project is to develop knowledge about [C<sub>2</sub>mpyr][FSI]/PEDOT composites, by their synthesis and full characterization. Moreover, by using and understanding the above mentioned characterization techniques, the skills and knowledge gained during the Chemistry degree will be put in practice.

## 3. EXPERIMENTAL PART

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### 3.1. REACTANTS AND SOLVENTS

The reactants and solvents that were used are the monomer 3,4-ethylenedioxythiophene (EDOT, Sigma Aldrich), potassium bis(fluoromethanesulfonyl)imide (Solvionic), *N,N*-dimethylpyrrolidinium bromide (abcr), dichloromethane (Scharlau), methanol (Scharlau), iron(III) chloride hexahydrate (Sigma Aldrich) and acetonitrile (Fisher). All reagents were used without further purification.

### 3.2. CHARACTERIZATION METHODS

The created mixed ion/electron conducting materials were characterized with different common methods and techniques. Exactly structural, thermal, morphological, transport and electrochemical properties were studied in the analyses. On the first part, the theory of these techniques is explained, mentioning how the experiments were carried out. On the next section, the obtained results and conclusions will be shown.

#### 3.2.1. Structural characterization

##### *Fourier-transform infrared spectroscopy (FTIR)*

Fourier-transform infrared spectroscopy (FTIR) is a technique in which, as a result of the absorption or emission of the material and measuring the molecular vibrations, an infrared spectrum is obtained. In the spectrum functional groups of a composite can be determined, and with this data, it is possible to obtain information about the chemical structure of the material.

In this project FTIR was done for each composite, and then, frequencies were analyzed in order to do a qualitative determination. Exactly, it was determined how the different amounts of PEDOT-Cl and OIPC in each composite affected the shifting of the frequencies. To be able to do the comparison, first of all, the spectra of the pure PEDOT-

Cl and [C<sub>2</sub>mpyr][FSI] prior to mixing were analyzed. After that, the most important peaks of them were selected, determining to what part of their chemical structure belong those characteristic frequencies.

To make the measurements KBr pellets were prepared for each composite, OIPC and PEDOT-Cl. Then, the spectra were registered in a *Nicolet Magna 6700 spectrometer* at room temperature. The results were obtained by Fourier transform at absorption terms.

### **3.2.2. Thermal characterization**

#### *Thermo-gravimetric analysis (TGA)*

Thermo-gravimetric analysis (TGA) is a thermal characterization technique in which, in a controlled atmosphere, the weight change of a material is determined with temperature. This way, the thermal degradation of the material is studied.

About 1-3 mg of the samples were dried in the *Büchi Glass Oven B-585* and were maintained in a glove box with an Ar atmosphere before the analysis. The thermo-gravimetric analysis was carried out on a *TGA Q500* from *TA Instruments*, and the samples were heated from room temperature to 800 °C in a rate of 10 °C/min under nitrogen atmosphere.

#### *Differential scanning calorimetry (DSC)*

Another thermal characterization technique is the differential scanning calorimetry (DSC). This method provides information about phase transitions (solid-solid, liquid-solid and melting point). In addition, it gives information about the enthalpy changes in the composites.<sup>6</sup> To obtain this information the samples are heated and cooled, taking into account an inert reference.

In this case it was seen how the different weight ratios of PEDOT-Cl and [C<sub>2</sub>mpyr][FSI] changed the phase transitions. For that, the measurements were carried out on a *DSC Q2000* from *TA Instruments*. In this case too about 1-6 mg of samples were dried and maintained in the glove box with an Ar atmosphere before the measurement. The method that was applied to each of them was: cooling in a rate of 10 °C/min from room temperature to -80 °C; then, heating at same rate from -80 °C to 225 °C; and finally,

a cooling in the same rate from 225 °C to 25 °C. In the case of 20/80 has been a little bit different because the results were wrong at first, so 5 scans were made in total. Instead of starting with the cooling, it started heating from room temperature to 190 °C, then the cooling to -80 °C and finally heating to 190 °C, all of them in a rate of 10 °C/min. Then the reported graphics were normalized to the mass of each composite.

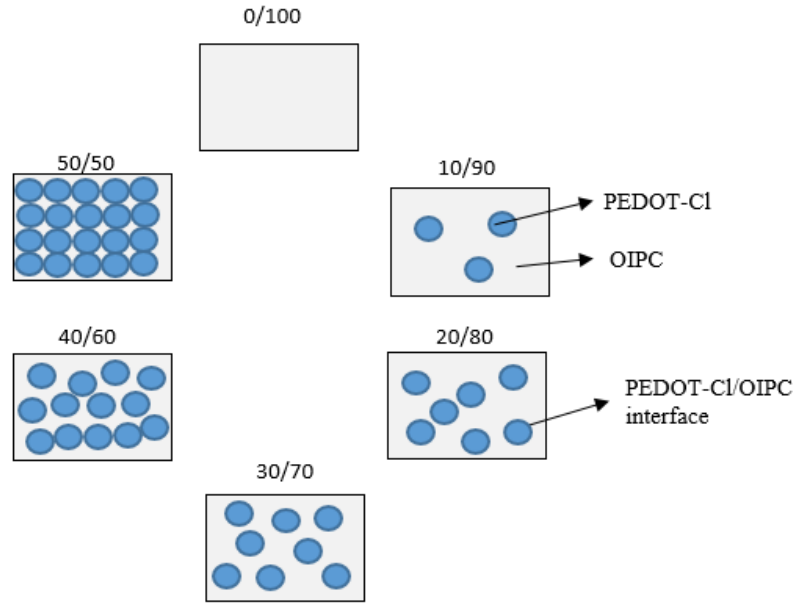
### **3.2.3. Morphological characterization**

#### *Scanning electron microscopy (SEM)*

One common morphological characterization technique is called scanning electron microscopy (SEM). It provides information about the superficial morphology and the topography of the material, allowing to image specimens at high magnifications (**Fig. 6**). This is useful when examining multi-component samples. Energy dispersive X-ray (EDX) also was carried out, which allows the collection of qualitative and quantitative information about the elemental composition of materials. Elemental analysis is based on the interaction of a high energy beam of electrons with the sample.

In this experiment it was possible to observe how the composites change their surface with different weight ratios. It was also understood better how the interface created between the polymer and the OIPC looked like. In addition, it was possible to obtain graphics in which qualitative and quantitative information of the composites was shown, providing mass percentages of elements in the samples.





6. Fig. Schematic showing of the packing of particles in the composites (PEDOT-Cl %/OIPC %)

Little amount of dried films were put in specimen holders using a conductive adhesive and carrying out the analyses in *HITACHI TM3030 Tabletop Microscope* at an accelerating voltage of 15 Kv for the SEM and at 8 Kv for the EDX.

### 3.2.4. Transport properties

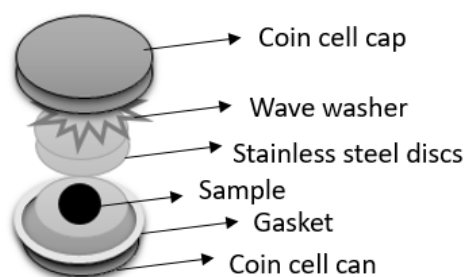
#### *Electrochemical impedance spectroscopy (EIS) analysis*

Electrochemical impedance spectroscopy (EIS) is a technique to analyze the transport properties, which in this case is referred to the ionic conductivity of a material. Impedance is usually measured by applying a frequency and a small amplitude voltage between electrodes, in different temperatures. In other words, it is a measurement of the ability of a circuit to resist the flow of electrical current.<sup>15</sup> This way, a semicircle graphic is obtained from which the resistance (R) value is taken. Once having this data the ionic conductivity is calculated using the **1. Equation**.

$$\frac{\text{Thickness (cm)}}{R (\Omega) * \text{area (cm}^2)} = \text{Ionic conductivity } \left(\frac{S}{\text{cm}}\right)$$

1. Equation. Equation to calculate the ionic conductivity from the resistance

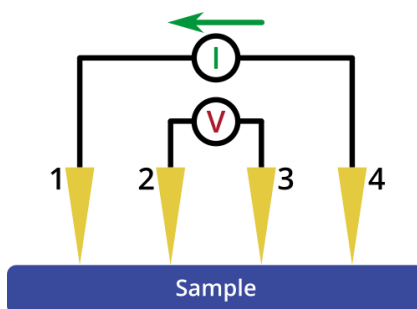
The composites, before being dried and saved in the glove box, were cut in circles. The 10/90, 20/80, 40/60 and 50/50 were cut with a diameter of 9 mm; 30/70 in a diameter of 8,5 mm; and finally, the OIPC in a diameter of 8 mm. Then, the measurements were done in *Biologic Science Instrument* for all the composites. To make the analyses samples were put between two stainless steel discs and sealed in a coin cell (**Fig. 7**). Then, the coin cell was put inside the *Büchi* as an oven and connected to the potentiostat. A frequency range of 1 MHz to 100 mHz was studied using a voltage amplitude of 10 mV. First of all, the heating was done from 25 °C to 40 °C and then from 40 °C to 90 °C with 10 °C steps; leaving 30 minutes to stabilize the temperature before the measurement. After that, the cooling was done using the same procedure but in the opposite direction (from 90 °C to 25 °C).



7. Fig. Schematic drawing of a coin cell with the sample in the middle

#### *Four point probe method (electronic conductivity)*

Another technique to analyze transport properties is the four point probe method, in which the electronic conductivity of a material is studied. The apparatus has four probes (**Fig. 8**) where a current is passed through the outer probes and the voltage difference is measured in the inner probes. Like this, the equipment provides the resistance (R) of the material from which the electronic conductivity is calculated.



8. Fig. Schematic drawing of four point probe machine

To make this analysis a piece of dried samples of each composite and of PEDOT-Cl were taken, measured the thickness with a micrometer and analyzed the resistance using a *FPP 5000 four point probe, Miller Design & Equipment, INC.*

The instrument gave the value of the resistance and for each sample three values of resistances were measured to calculate the electronic conductivity by making the promedium of the three measurements.

### 3.2.5. Electrochemical properties

#### *Cyclic voltammetry*

The electrochemical properties of the composites have been measured by cyclic voltammetry. This was made in a three electrode cell with Ag/AgCl as reference electrode, platinum wire as counter electrode and the sample was deposited in the working electrode made of platinum.<sup>16</sup> A solution of 0,1 M KFSI/H<sub>2</sub>O was used as electrolyte, in which N<sub>2</sub> was connected in each measurement to obtain an inert atmosphere.

To prepare the working electrodes with the samples, first of all, some solutions were prepared. 20 mg from each composite, except from 50/50, were taken and mixed with 200  $\mu$ l MeOH putting them into small vials. In the case of 50/50, 10 mg was mixed with 100  $\mu$ l MeOH (same proportion). After that, amounts between 3 and 5  $\mu$ l of the mixtures were deposited in the platinum working electrode. Then the current was normalized taking into account the mass of the composite added to have a better comparison between the composites. Finally, the electrodes were dried and the methanol

was evaporated leaving a thin layer of the sample in the electrode ready for the measurement.

The measurements were carried out in the *Biologic Science Instrument*, where cyclic voltammeteries were conducted from -1 V to 1 V vs. Ag/AgCl at different scan rates: 10 mV/s, 25 mV/s, 50 mV/s, 100 mV/s and 150 mV/s (4 cycles for each rate).

### 3.3. SYNTHESIS OF [C<sub>2</sub>mpyr][FSI]<sup>3</sup>

*N,N*-Dimethylpyrrolidinium bis(fluoromethanesulfonyl)imide, [C<sub>2</sub>mpyr][FSI], was synthesized by reacting *N,N*-Dimethylpyrrolidinium bromide, [C<sub>2</sub>mpyr]Br, with potassium bis(fluoromethanesulfonyl)imide, KFSI. [C<sub>2</sub>mpyr]Br (10,37 g, 53,4 mmol) was dissolved in 20 mL of distilled water taking a yellowish colour. KFSI (13 g, 58,8 mmol) was separately dissolved in another 20 mL of water being colourless. While the first solution was stirring, the second one was added to it slowly until a white precipitate was formed: [C<sub>2</sub>mpyr][FSI]. 5 mL more of water were added to the dissolution, in order to mix it properly. After that, taking into account that the product is soluble in the organic solvent dichloromethane, DCM, and not in water, 45 mL (same amount as the water) of DCM was added to the dissolution, in order to do the extraction. The solution was left stirring for an hour at room temperature. Then, the organic phase was washed with water (3 x 45 mL). All in all, there were two phases: on the one hand, a yellowish organic phase (DCM + [C<sub>2</sub>mpyr][FSI]); and on the other hand, a water phase (water + KBr). Finally, the DCM was evaporated in the rotary evaporator. A white and sticky precipitate was obtained. It was dried under vacuum for 24 h. (Yield: 66,2 %).

### 3.4. SYNTHESIS OF PEDOT-Cl<sup>17</sup>

The synthesis of PEDOT-Cl was done by the oxidation of the monomer 3,4-ethylenedioxythiophene, EDOT, with iron(III) chloride hexahydrate, FeCl<sub>3</sub> x 6H<sub>2</sub>O. FeCl<sub>3</sub> x 6H<sub>2</sub>O (15,2 g, 56,3 mmol) and 281,32 mL of acetonitrile, ACN, were put stirring in a flask at room temperature. EDOT (2 g, 14,1 mmol) was added to the flask and the solution was left stirring for 24 hours. The obtained product was filtrated in the Buchner funnel washing it with ACN and water, in order to obtain a pure PEDOT-Cl. A black/blue

precipitate was obtained, PEDOT-Cl, and it was put in the oven drying under vacuum for 12 hours. (Yield: 15,2 %).

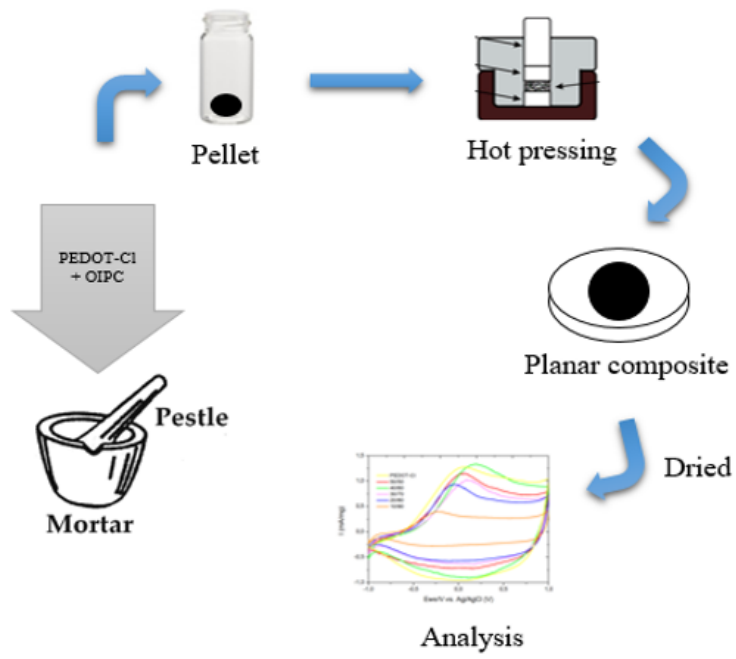
### 3.5. [C<sub>2</sub>mpyr][FSI]/ PEDOT-Cl COMPOSITES PREPARATION

When the syntheses of OIPC and PEDOT-Cl were done, some composites of them were prepared. The idea was to mix the two materials in different weight ratios (Wt %), beginning with 50 % of [C<sub>2</sub>mpyr][FSI] and with 50 % of the polymer. After that, the concentration of the PEDOT-Cl was going down and the weight of the plastic crystal up. In total 5 different composites were prepared: 50/50, 40/60, 30/70, 20/80 and 10/90 (the expressions come from PEDOT-Cl % / [C<sub>2</sub>mpyr][FSI] %).

To prepare them, the corresponding amount of each compound was taken and weighted in the balance, in order to obtain 100 mg in total. For example, in the case of 40/60, 40 mg of PEDOT-Cl and 60 mg of OIPC were taken. Then, they were dry mixed in an agate mortar converting them in a pellet. Finally, the pellet was saved in a glass vial and the next composite was prepared.

Once all the pellets were prepared, they were pressed by hot pressing in order to obtain planar composites. The hot pressing was done at 60 °C with the pressure of 4 tones during a minute.

Finally, the composites were dried in the oven being ready to do the characterization. However, for most of the techniques, after the oven the composites were dried in the *Büchi* and put them in the glove box with the Ar atmosphere. **Fig. 9** presents a schematic preparation of the composites.

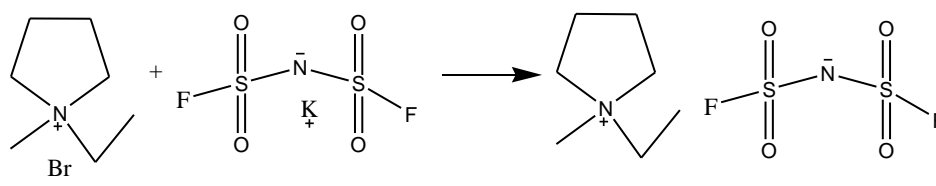


9. Fig. Schematic preparation of the composites

## 4. RESULTS AND DISCUSSION

### 4.1. SYNTHESIS OF [C<sub>2</sub>mpyr][FSI]<sup>3</sup>

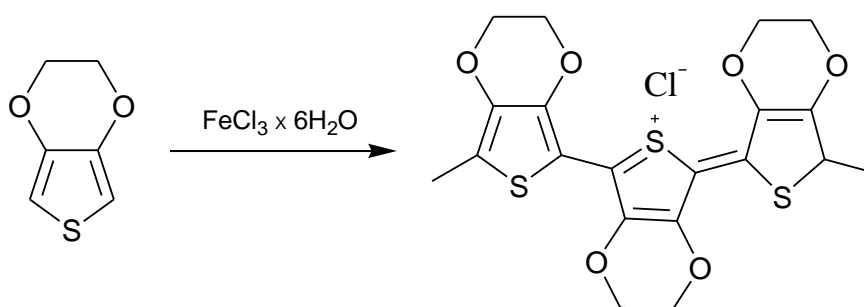
The OIPC was synthesized based in previously reported procedure<sup>3</sup> in good yield (66,2 %) by the direct reaction of *N,N*-Dimethylpyrrolidinium bromide with potassium bis(fluoromethanesulfonyl)imide as shown in **Scheme 1**. The obtained product, as it is previously said, it was white and very sticky.



1. Scheme. Reaction of the synthesis of [C<sub>2</sub>mpyr][FSI]

### 4.2. SYNTHESIS OF PEDOT-Cl<sup>17</sup>

PEDOT-Cl was also synthesized based in previous reports<sup>17</sup>, continuing the procedure shown in **Scheme 2**. The synthesis was done by the oxidation of EDOT with FeCl<sub>3</sub> x 6H<sub>2</sub>O. They were mixed and put stirring with ACN. The obtained product was filtrated in the Buchner funnel and washed with water and ACN. A black/blue precipitate was obtained, PEDOT-Cl, with a yield of 15,2 %.

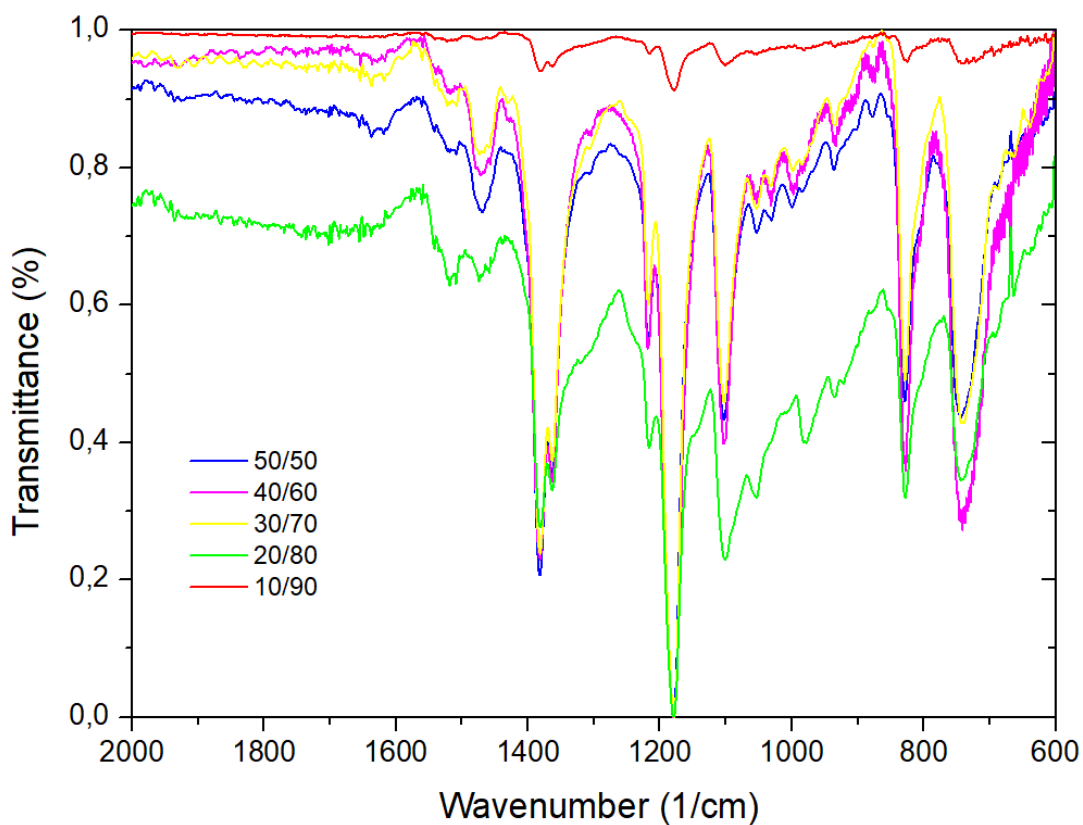


2. Scheme. Reaction of the synthesis of PEDOT-Cl

### 4.3. CHARACTERIZATION OF [C<sub>2</sub>mpyr][FSI]/ PEDOT-Cl COMPOSITES

#### 4.3.2. Structural characterization

The structural characterization of the composites was made by fourier-transform infrared spectroscopy (FTIR). For that, KBr pellets were prepared with each composite and pure PEDOT-Cl and [C<sub>2</sub>mpyr][FSI]. The measurements were carried out at room temperature. **Fig. 10** shows the spectra of all the composites, all of them measured between the wavenumber of 600 cm<sup>-1</sup> to 2000 cm<sup>-1</sup>. Each colour represents one of the different composites. However, to compare them properly, first of all the FTIR spectra of pure PEDOT-Cl and of OIPC (**Fig. 11**) were analyzed and the most important peaks were determined.



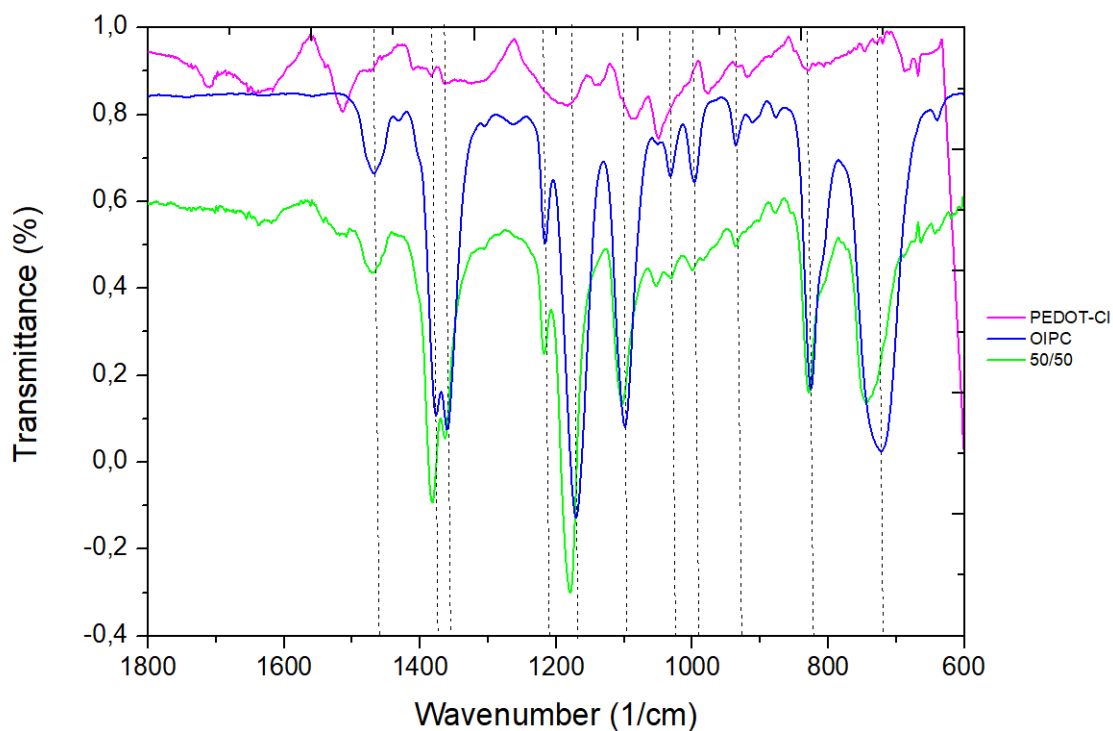
10. Fig. FTIR spectra of all composites



On the one hand, in **Fig. 11** the FTIR spectrum of PEDOT-Cl is shown. As it can be seen, the most important peaks are the C=C stretching at  $1640\text{ cm}^{-1}$ , the C-C bending at  $1500\text{ cm}^{-1}$ , at  $1179\text{ cm}^{-1}$  C-O stretching and to finish, C=S stretching at  $1045\text{ cm}^{-1}$ . However, it is important to say that in general the transmittance % is not very high in the peaks of PEDOT-Cl.

On the other hand, in **Fig. 11** appears also the illustration of FTIR spectrum of [C<sub>2</sub>mpyr][FSI]. In this case, the most important peaks are in the wavenumber of  $1465\text{ cm}^{-1}$ , which corresponds to C-C bending, R-SO<sub>2</sub>-N asymmetric stretching at  $1376\text{ cm}^{-1}$ , in  $1359\text{ cm}^{-1}$  the umbrella band of CH<sub>3</sub>, R-SO<sub>2</sub>-N symmetric stretching in  $1216$  and  $1165\text{ cm}^{-1}$ , the C-N stretching at  $1096\text{ cm}^{-1}$ , the pyrrolidinium ring bending at  $1031$  and  $997\text{ cm}^{-1}$ , C-C stretching band at  $936\text{ cm}^{-1}$ , S-F stretching at  $822\text{ cm}^{-1}$  and finally, the C-C rocking band at  $719\text{ cm}^{-1}$ .

After that, one FTIR spectrum from all the composites was chosen, in order to compare with the previous ones. The thing is that if all the composites are added to the graphic, as shown in the **Fig. 10**, the comparison and the conclusions can't be made properly. It was thought that 50/50 was the best option, taking into account that this composite had the same proportion of CP and of OIPC. In this way, it was possible to see how the wavenumbers changed mixing both materials in same proportion. This is also illustrated in **Fig. 11**, which shows the wavenumbers between  $600\text{ cm}^{-1}$  and  $1800\text{ cm}^{-1}$ , because in this interval are the most significant peaks.



11. Fig. Comparison of FTIR spectra of [C<sub>2</sub>mpyr][FSI] (blue), PEDOT-Cl (pink) and 50/50 composite (green)

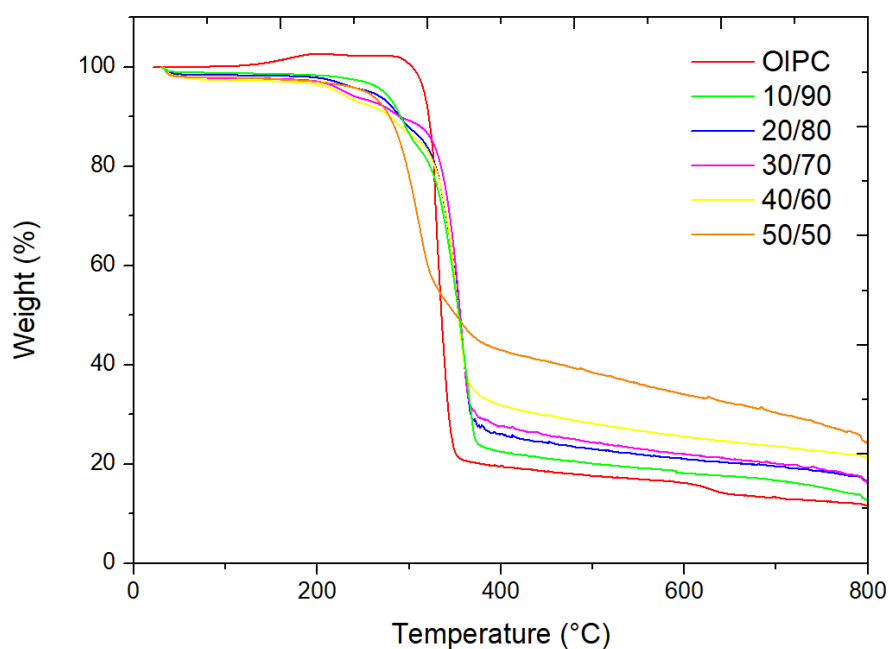
**Fig. 11** shows that the FTIR spectrum of 50/50 is very similar to the PEDOT-Cl and OIPC spectra. However, it has to be said that the wavenumbers are a little bit shifted to the left. This means that although the difference is small (**Table 1**), the wavenumbers in 50/50 are higher. In this interval, the main peaks correspond to the OIPC, that's why, its comparison with 50/50 is made in **Table 1**. The direction of the band shift is designated by (-) and (↑), representing no shift and a shift to higher wavenumber value. It can be observed that the biggest differences are in the peaks related to the FSI anion, such as the intensity of the peak at 1376 cm<sup>-1</sup> that is incremented in the composite and the peak at 1165 cm<sup>-1</sup> that is shifted to higher wavenumbers. These shifts suggest the presence of ion dipole interactions between the anion of OIPC and the charge of PEDOT.

1. Table. Comparison of wavenumbers in 1/cm of [C<sub>2</sub>mpyr][FSI] and 50/50

Type of peak <sup>18</sup>	OIPC wavenumber (1/cm)	50/50 wavenumber (1/cm)
C-C bending	1465	1466 (↑)
R-SO <sub>2</sub> -N stretching asymmetric	1376	1380 (↑)
CH <sub>3</sub> umbrella	1359	1363 (↑)
R-SO <sub>2</sub> -N stretching symmetric	1216	1217 (↑)
R-SO <sub>2</sub> -N stretching symmetric	1165	1177 (↑)
C-N stretching	1096	1102 (↑)
Pyrrolidinium bending ring	1031	1031 (-)
Pyrrolidinium bending ring	997	997 (-)
C-C stretching	936	936 (-)
S-F stretching	822	828 (↑)
C-C rocking	719	740 (↑)

#### 4.3.2. Thermal characterization

On the one hand, to do the thermal characterization the TGA was carried out for all the composites and for the OIPC. The analysis was done under nitrogen atmosphere in order to complete properly the degradation of the composites.



12. Fig. TGA analysis of the composites and the OIPC

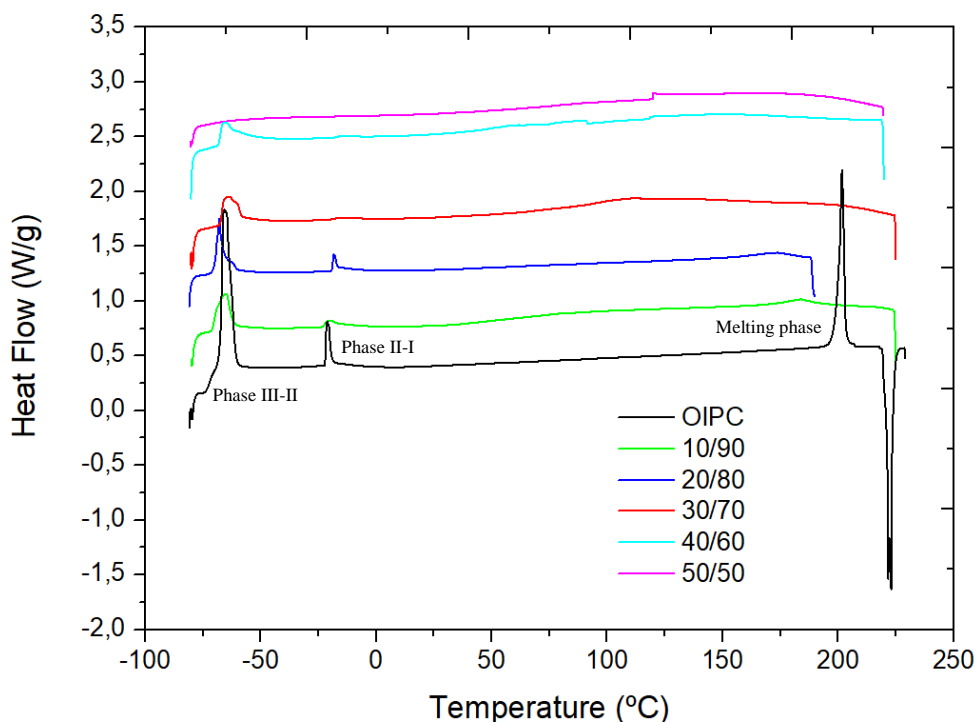
**Fig. 12** shows the results of the TGA analysis. The degradation of the materials, at which the 5 % of mass loss occurred, starts at high temperatures (between 250-320 °C) and they are not completely degraded until almost 400 °C. **Table 2** shows these exact degradation temperatures of the composites.

*2. Table. Degradation temperatures at which 5 % of mass loss occurred*

Composites	Degradation temperature (°C)
OIPC	316
10/90	271
20/80	257
30/70	227
40/60	223
50/50	250

The OIPC is the last starting to degrade and it is concluded that the more OIPC has de composite, the higher is the degradation temperature. However, there is an exception with 50/50, which has a similar degradation of 20/80 due to the interaction created between the PEDOT-Cl and the [C<sub>2</sub>mpyr][FSI]. In addition, it can be observed that with the increase of the amount of PEDOT-Cl the residue amount of the composites increases too, which can be seen in their weight values at 800 °C.

On the other hand, the differential scanning calorimetry, DSC, technique was used to complete the thermal characterization of the composites. The graphics obtained provide information about the enthalpy change ( $\Delta H$ ) and the peaks of phase transitions and the melting point ( $T_m$ ) for all the composites. The results were gathered in **Fig. 13**.



13. Fig. First scan of DSC results of the composites and of the OIPC carried out at 10 °C/min

In this graphic, the first scan of each composite's analysis is shown, because this is the best cycle to appreciate the melting point. It is concluded that increasing the percentage of PEDOT-Cl, the disorder created by the interphase is increased and the  $\Delta H$  and  $T_m$  are decreased. It is known that when both materials are mixed to create the composites, the OIPC's matrix starts to disorder. Having more PEDOT-Cl in the composite means that the polymer is doping more the OIPC, and so, changing more its surface. As a result, the intensity of the peaks decreased with the addition of the PEDOT-Cl.

In **Table 3**, the temperatures of the phase transitions and of the melting points are shown. This helps to see better the tendency of  $\Delta H$  and  $T_m$  among the composites. In the III-II and II-I phase transitions the values don't change very much between the composites. However, the melting temperature goes down when more PEDOT-Cl is added; this is also because of the disorder created. In the case of 50/50, it is not possible to distinguish well the peaks as they are very broad, so the values are not reported, but the same tendency is maintained.

3. Table. Temperature values of III-II, II-I phase transitions and melting phase of the composites and pure OIPC

Composite	III-II phase (°C)	II-I phase (°C)	T <sub>m</sub> (°C)
OIPC	-66	-21	202
10/90	-65	-20	184
20/80	-68	-18	174
30/70	-64	-14	111
40/60	-65	-14	61
50/50	-	-	-

As a conclusion, the first two significant peaks (III-II and II-I phases) demonstrate that there is OIPC in the composites and it maintains the crystal structure in most of the composites concentration but the 50/50, where all the OIPC is amorphous and solid-solid transitions are not observed in the DSC. It is also possible to see that changing the proportions of the composites, adding more PEDOT-Cl, the melting temperature starts to decrease and the peaks become more amorphous. Summarizing, with the rising of the amount of this material changes happened in the composites, decreasing the melting temperatures and the crystal phase ordering, which will provoke an increase in the ionic conductivity.

It is also concluded that the OIPC synthesis was correctly done, because the temperatures of its phase transitions are very similar to the ones that were previously mentioned in the introduction, which were values token from literature.

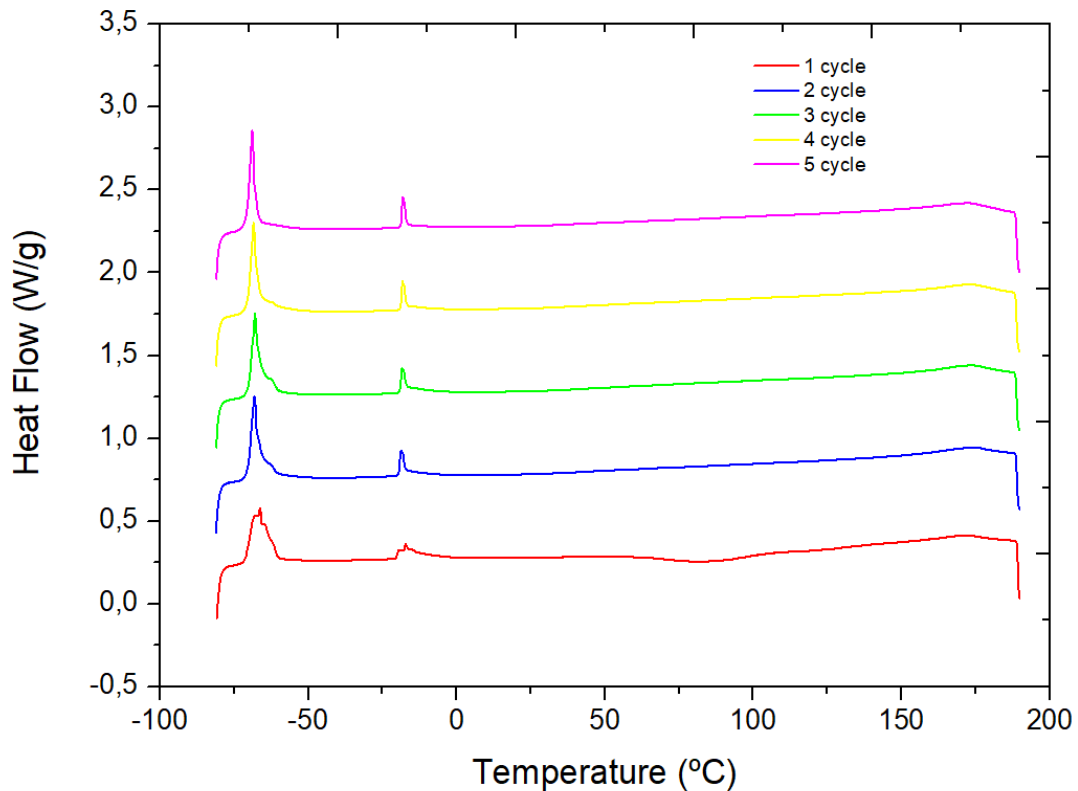
In **Table 4**, the enthalpy changes of each composite are shown. It is observed that when increasing the amount of PEDOT-Cl,  $\Delta H$  decreases and this is because there is more disorder in the composite.

4. Table. Enthalpy values of III-II, II-I phase transitions and melting phase of the composites and pure OIPC

Composite	III-II phase (J/g)	II-I phase (J/g)	T <sub>m</sub> (J/g)
OIPC	33	4	21
10/90	12	3	3
20/80	9	2	1,4

30/70	7	0,6	0,7
40/60	7	0,3	0,02
50/50	-	-	-

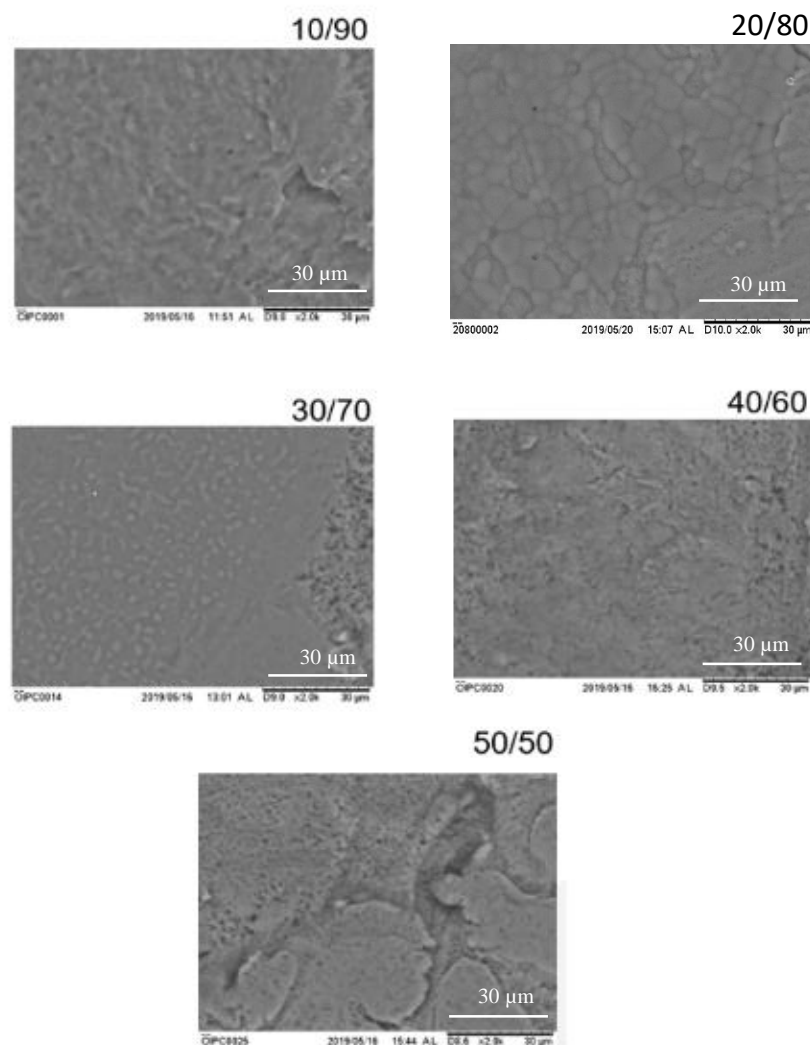
For the 20/80 composite, 5 cycles were made because the results were wrong at first. In **Fig. 14** is shown all the cycles of the 20/80. It can be observed that in the first cycle the melting phase is distinguishable and all the peaks are broader comparing to the other cycles. This is because, as in previous reports<sup>19</sup> is shown, the film released water during the heating process. As a result, the peaks are sharper in the last cycles and the melting peak is more difficult to distinguish.



14. Fig. DSC results of the composite 20/80 carried out at 10 °C/min (5 cycles)

## Morphological characterization

The morphological characterization was done by scanning electron microscopy (SEM). First of all, images (**Fig. 15**) with the magnification of x2000 were taken for each composite.



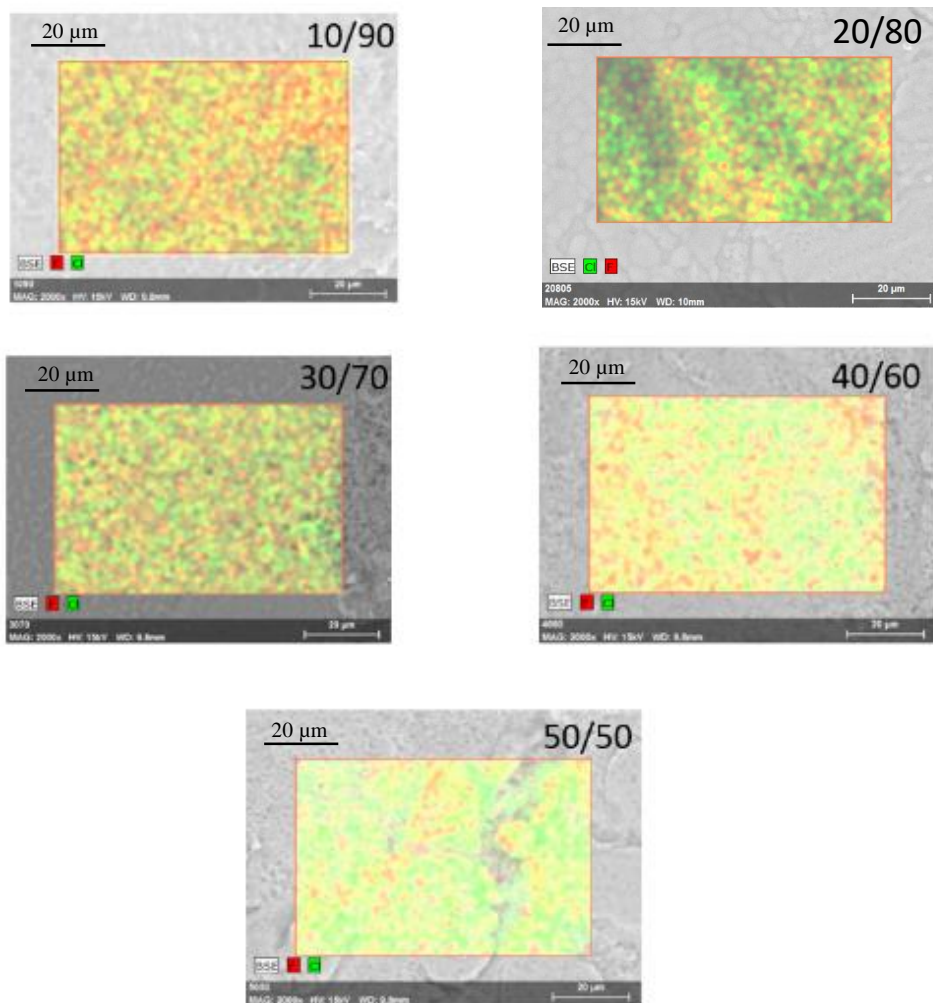
15. Fig. SEM micrographs of the composites

It is concluded that PEDOT-Cl particles are packed in the OIPC matrix, creating an interface between PEDOT-Cl and OIPC. In the cases of having low percentage of polymer, 20/80 for example, the particles are well dispersed with distance among them and they change the surface of the OIPC. With more percentage of PEDOT-Cl, the particles are packaged more closely, so the interfaces can touch between them. As a result, it can be observed a smooth surface morphology typical for interpenetrating network, where the OIPC and the polymer are well connected. However, the micrographs are not



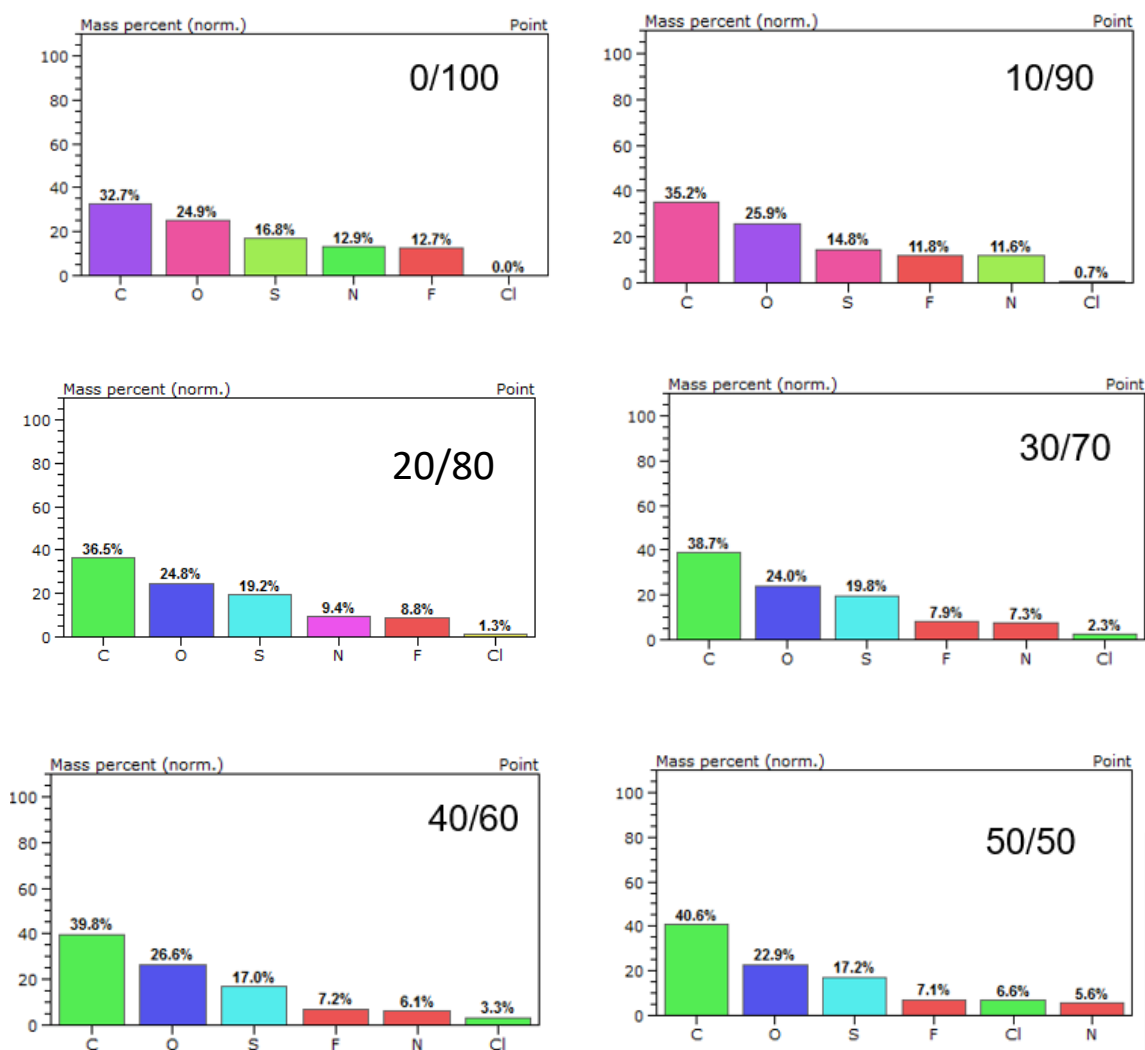
very clear and it is difficult to distinguish to which part of the images corresponds [C<sub>2</sub>mpyr][FSI] and to which part corresponds the PEDOT-Cl. The reason why the graphs are not clear is that the measurements were done at 15 Kv, which is a very high voltage to make properly the analysis. Due to the fact that the applied voltage was high, the organic phase (OIPC) was melted during the measurement and the images were not good enough, that's why, they will be repeated in a future with a lower voltage. In addition, the bigger the voltage, the deeper you penetrate in the sample providing unclear and more random micrographs. However, it is possible to conclude that the interconnection was good, as for example is possible to see in the 40/60 micrograph, because the materials are good mixed.

After that, energy dispersive X-ray spectroscopy (EDX) was carried out in each micrograph. The results can be seen in **Fig. 16**. Green colour represents the chloride (Cl) amount in the composite coming from the polymer and the red colour the fluoride (F) amount, which belongs to the anion of the OIPC. It can be seen that when the amount of the OIPC goes down, the red colour (F) is less remarkable and the green (Cl) more flashy, which correlates with the compositions of the composites. As in the SEM happened, here also the voltage used was high and the results were not as clear as expected.



16. Fig. EDX analyses of the composites

Finally, the graphs of the elements in the EDX were taken to see how the mass percentages of the elements change varying the amount of OIPC and PEDOT-Cl. This is illustrated in **Fig. 17**. (0/100 is the one that contains only OIPC).



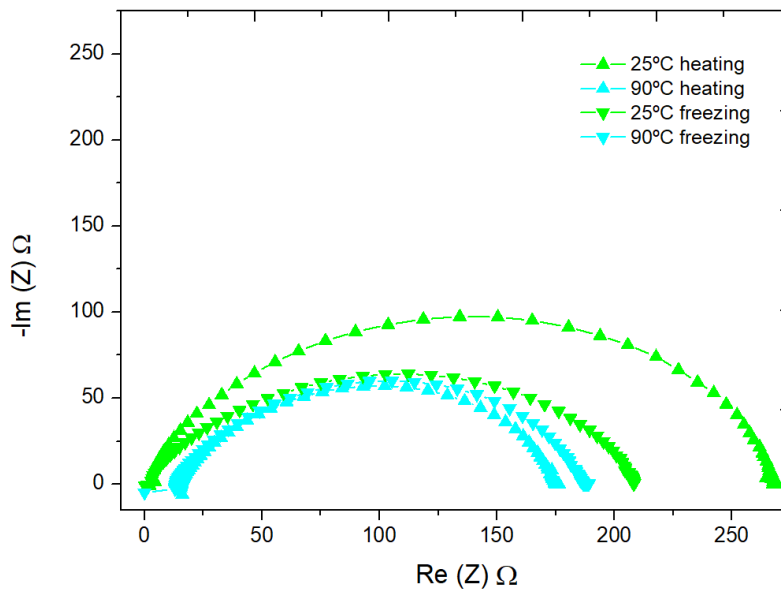
17. Fig. Graphics of the mass percentages of the elements in each composite

In these graphics it is important to highlight that when the proportion of the OIPC goes down, the F mass percentage decreases too. This is very similar to N proportions, due to the fact that in the anion of the OIPC, [FSI], both of the atoms are present, as it was possible to see in **Fig. 2**. Another remarkable data is the mass percentage of the Cl, which increases when the proportion of PEDOT-Cl goes up. This concludes that the composites were well prepared, as the results are in accordance to the proportions used for the preparation. In addition, carbon's (C) mass percentage also goes up and this is also because there is more PEDOT-Cl, which is the one that contains most of the C atoms. However, conclusions about sulfur (S) and oxygen (O) mass percentages cannot be obtained because both of them appear in the OIPC and in PEDOT-Cl, so the differences are not significant.

### 4.3.3. Transport properties

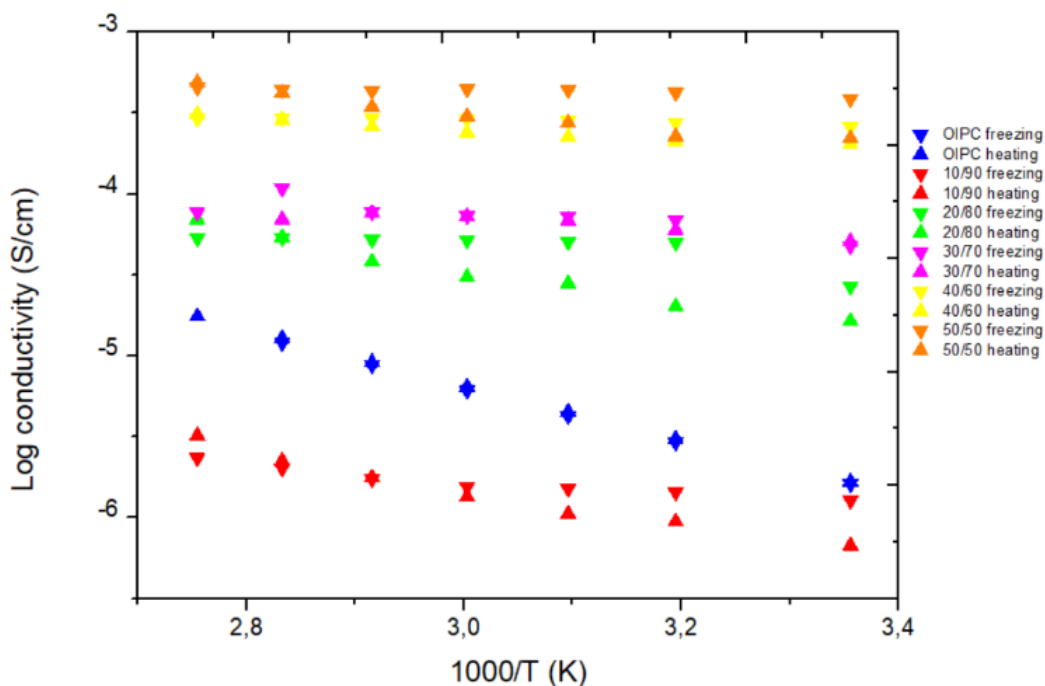
Electrochemical impedance spectroscopy (EIS) was one of the techniques used to analyze the transport properties. Firstly, the heating was measured from room temperature to 90 °C; and secondly, the freezing from 90 °C to room temperature. The same analysis was carried out for all composites and for OIPC.

The results were obtained from the Nyquist plots that provided the instrument (**Fig. 18**, 40/60 used as an example). The value of the resistance was taken from this graphics and then, the ionic conductivity and its logarithm were calculated.



18. Fig. Example of graphics obtained in the analysis of ionic conductivity (composite 40/60)

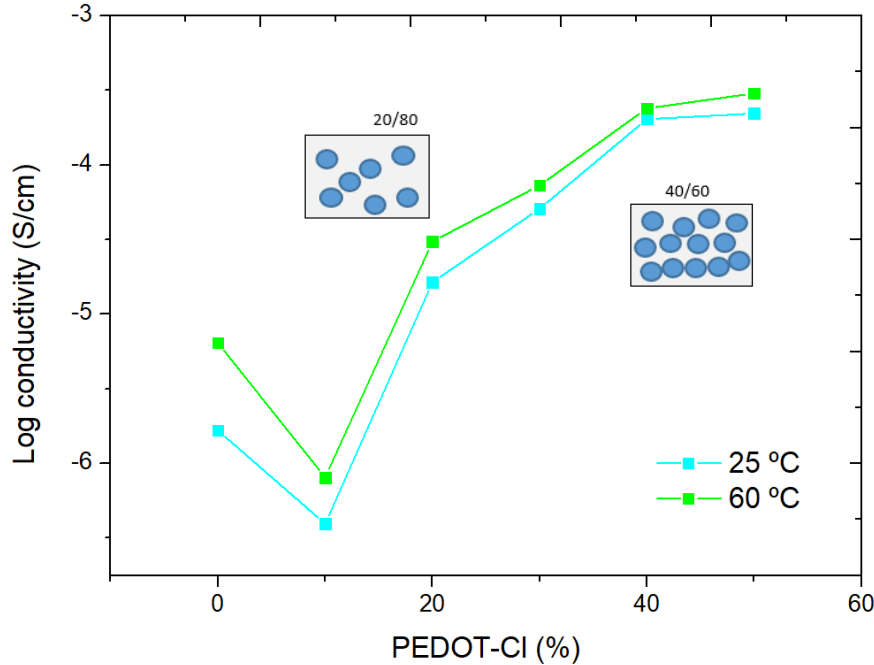
**Fig. 19** shows the logarithm of the ionic conductivity of the products in the function of the temperature in kelvins ( $1000/T$ ).



19. Fig. Log. ionic conductivities of the composites

As a conclusion, in the **Fig. 19** is seen that the OIPC has the lowest ionic conductivity and with the addition of PEDOT-Cl in the composites, the conductivity increases, having the best results with 40/60 and 50/50 composites. This is in good agreement with DSC results, where we observed that increasing the PEDOT-Cl percentage, crystallinity of OIPC decreased and thus, ionic conductivity increases. It can also be seen that the 40/60 results are very similar to the 50/50 ones, concluding that 40/60 is one of the best composites created. However, weirdly, the 10/90 composite's values are lower than the OIPC's ones. Due to the fact that it doesn't follow other composite's behavior, it will be repeated in the future. By increasing the amount of PEDOT-Cl in the composites, the conductivity is less dependent on temperature (the lines appear to be more horizontal), so the activation energy decreases and this is typical for liquid materials. So, it can be concluded that with more PEDOT-Cl, the composites have more liquid behavior being still a solid material, being that one of the objectives of the project and showing their potential application in solid-state batteries. In addition, the value of the OIPC at room temperature ( $1,61 \times 10^{-6} \text{ S}$ ) is very similar to the previously reported one ( $1,23 \times 10^{-6} \text{ S}$ )<sup>6</sup>, so it is concluded that the analysis and the synthesis of the  $[\text{C}_2\text{mpyr}][\text{FSI}]$  were made properly.

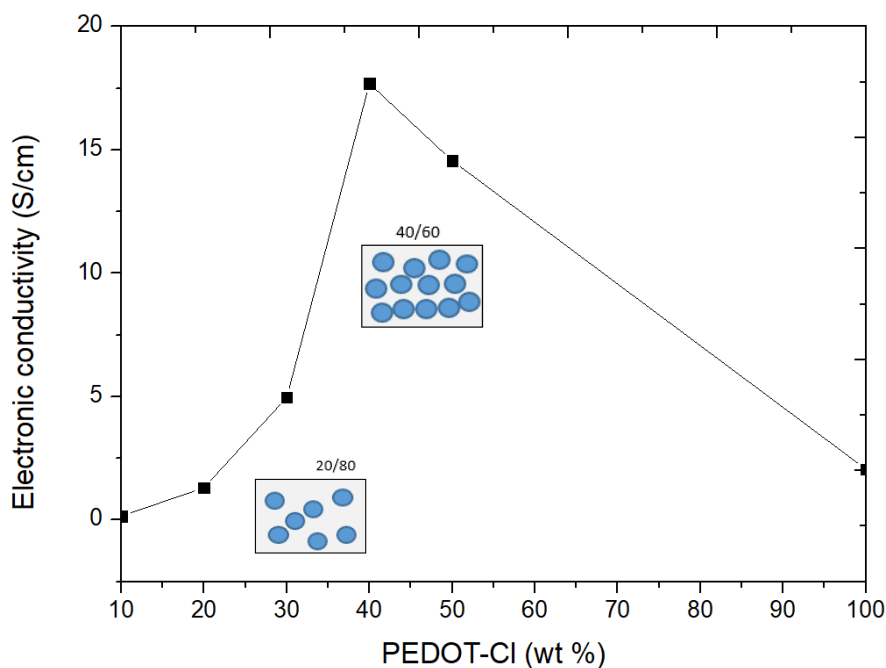
As summary, two different temperatures were selected to illustrate the logarithm of the ionic conductivities in the function of PEDOT-Cl concentration in weight percentage. This is predicted in **Fig. 20**.



20. Fig. Log. ionic conductivity in the function of PEDOT-Cl percentage, at 25 and 60 °C

In the graphic, schematic illustrations of the packing of PEDOT-Cl particles of 20/80 and 40/60 are shown, where blue circles represent PEDOT-Cl particles in OIPC matrix. These illustrations help to understand how with higher concentrations of PEDOT-Cl the interfaces can touch between them, creating more disorder and providing higher ionic conductivities. It can also clearly be seen that as it was shown in **Fig. 19**, the changes between 40/60 and 50/50 are minimum, comparing to other composites. This is because at 40/60 the composites behavior starts to stabilize, having similar behavior of 50/50 composites. So, here also can be concluded that 40/60 is one of the best composites, providing the highest ionic conductivity values. It can also be observed that with the increase of the temperature, the values of the ionic conductivities increase too. So as a conclusion, it is seen that **Fig. 20** looks like a semicircle, showing that at first there is some disorder in the composites, but not so much, having a normal conductivity. Then, the maximum of the semicircle is the place where there is a lot of disorder, having the highest conductivities. And finally, values should decrease again, having lower conductivities with pure PEDOT-Cl, which will be done in a future.

Another technique to analyze transport properties is the four point probe method, in which the electronic resistance to a current is measured and from this, electronic conductivities of the composites and of PEDOT-Cl can be obtained. Three measurements were done for each product, obtaining the values of the resistances (R). Then, making the median of them and having the thickness of the composites, the electronic conductivities were calculated, which are shown in **Fig. 21** in the function of PEDOT-Cl %.



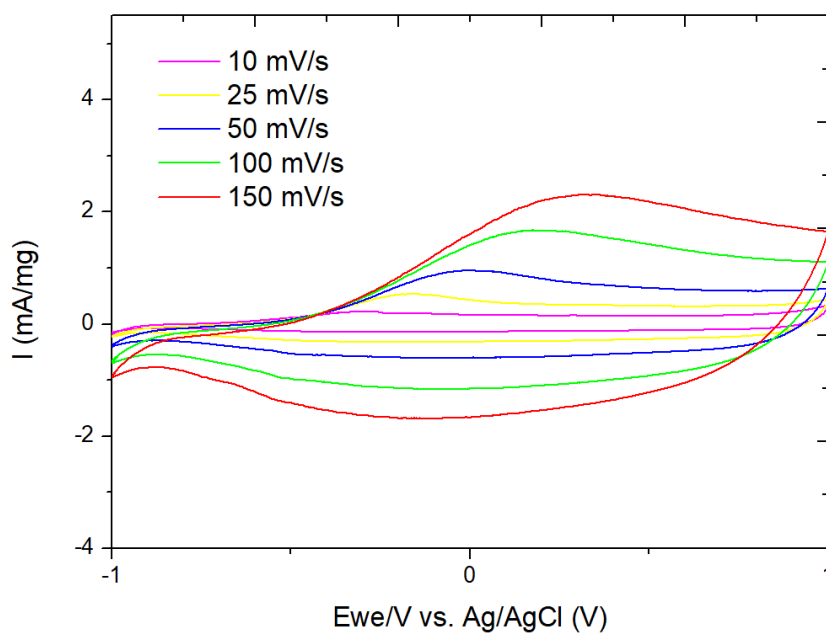
21. Fig. Electronic conductivities in the function of PEDOT-Cl % measured by 4 point probe method

It is clearly seen that the higher the amount of PEDOT-Cl in the composite, the higher the electronic conductivity. As in EIS, at low concentrations of the polymer the PEDOT-Cl particles are separated from each other and thus the electrons cannot flow through the different particles, resulting in low electronic conductivity. With higher concentrations of PEDOT-Cl, the interfaces of the particles can touch between them, creating longer electronic pathways and providing higher electronic conductivity, such as in 40/60 with a value of 17 S/cm. However, in the case of 50/50 the conductivity is a little bit lower than in 40/60 and this is probably because, as said before for the ionic conductivity, the composite's properties start to stabilize at that proportions. In addition, the material that only contained PEDOT-Cl without any OIPC has a value that is between 20/80 and 30/70. This demonstrates that with the addition of OIPC to the polymer, higher electronic conductivities are obtained due to the doping effect of the OIPC in the PEDOT

polymer, which helps to have higher charge carriers. Like this, it is demonstrated that it is achieved the main goal of this project; which was to develop dual ionic and electronic conducting materials, with improved transport properties compared to the individual components by each own.

#### 4.3.4. Electrochemical properties

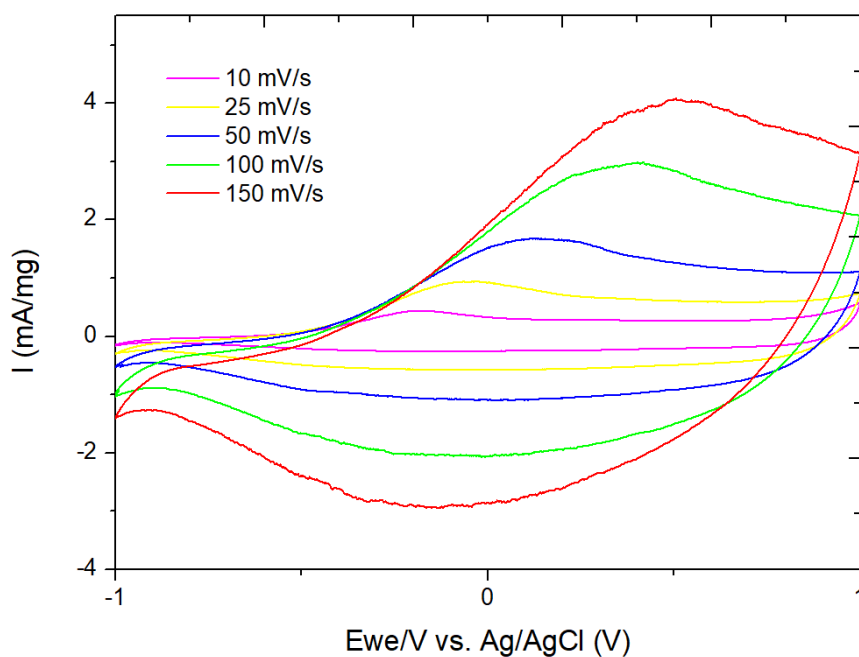
The electrochemical properties of the composites were analyzed by cyclic voltammetry (CV). The measurement was made in a three electrode cell with 0,1 M KFSI/H<sub>2</sub>O as electrolyte, Ag/AgCl as reference electrode and platinum working and counter electrodes. The composite was casted onto the working electrode and CV was applied in different scan rates which was conducted from -1 V to 1 V vs Ag/AgCl. The different scan rates were: 10 mV/s, 25 mV/s, 50 mV/s, 100 mV/s and 150 mV/s (4 cycles for each rate). In **Fig. 22** appears the second cycle of the scan rates of 10/90 composite.



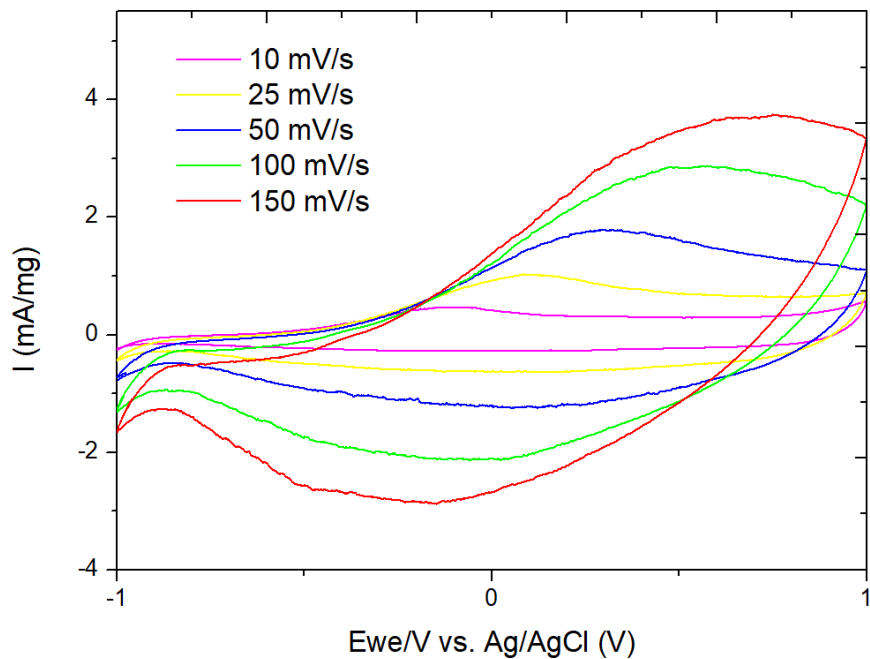
22. Fig. Cyclic voltammetry of 10/90, second cycle of the scan rates in different colours



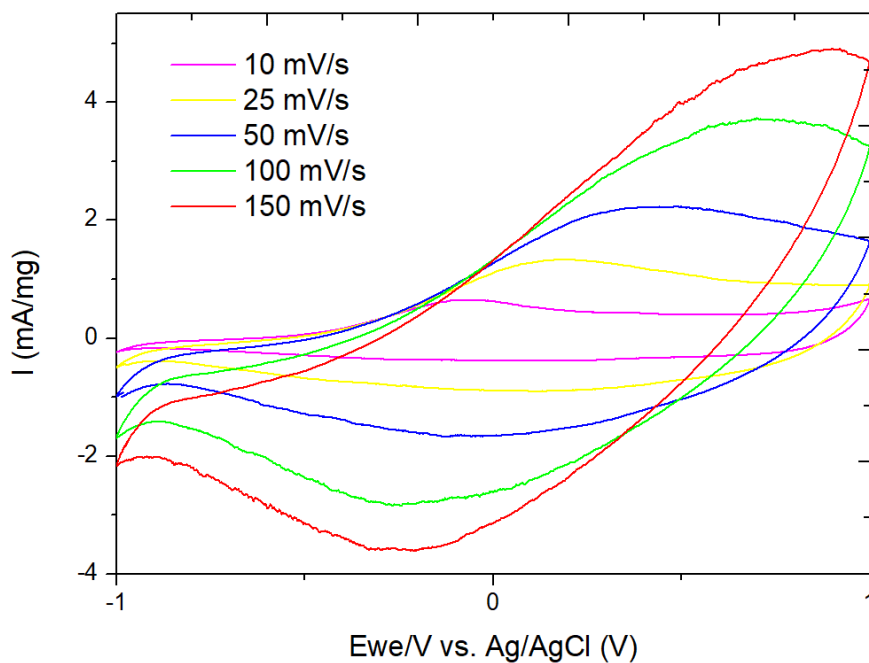
In this figure it is possible to distinguish the oxidation and reduction peaks of PEDOT in the composite. It can be observed that at 10 mV/s scan rate PEDOT oxidation peak appears at -0,3 V while the reduction peak is broader and it is around -0,4 V. It can also be observed that the current increases with the increment of the speed of the applied potential and oxidation peak shifts to higher potential, which means the redox reaction is limited by diffusion of ions. The same behavior is observed in the other composites as shown in **Fig. 23, 24, 25, 26 and 27** for the composites of 20/80, 30/70, 40/60, 50/50 and pure PEDOT-Cl, respectively.



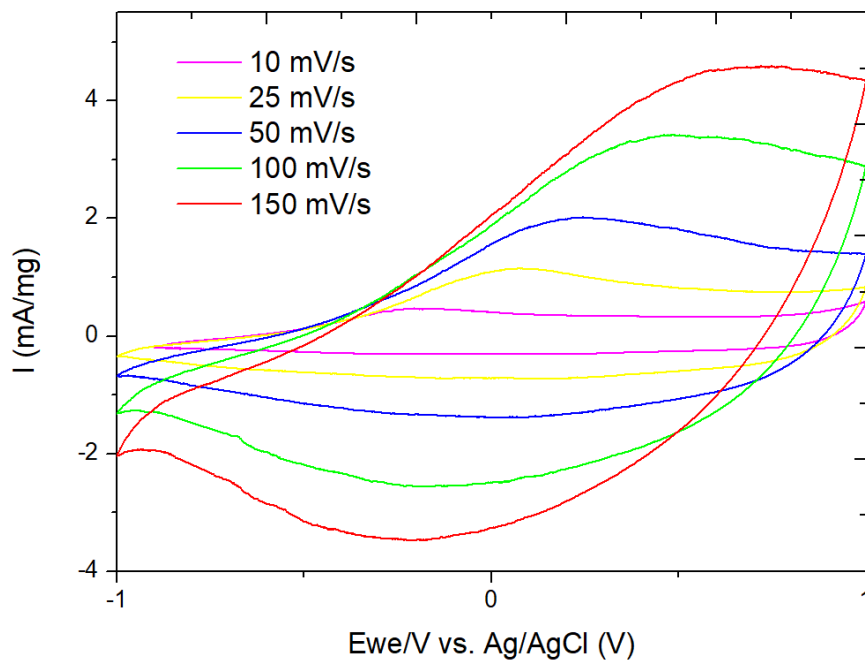
23. Fig. Cyclic voltammetry of 20/80, second cycle of the scan rates in different colours



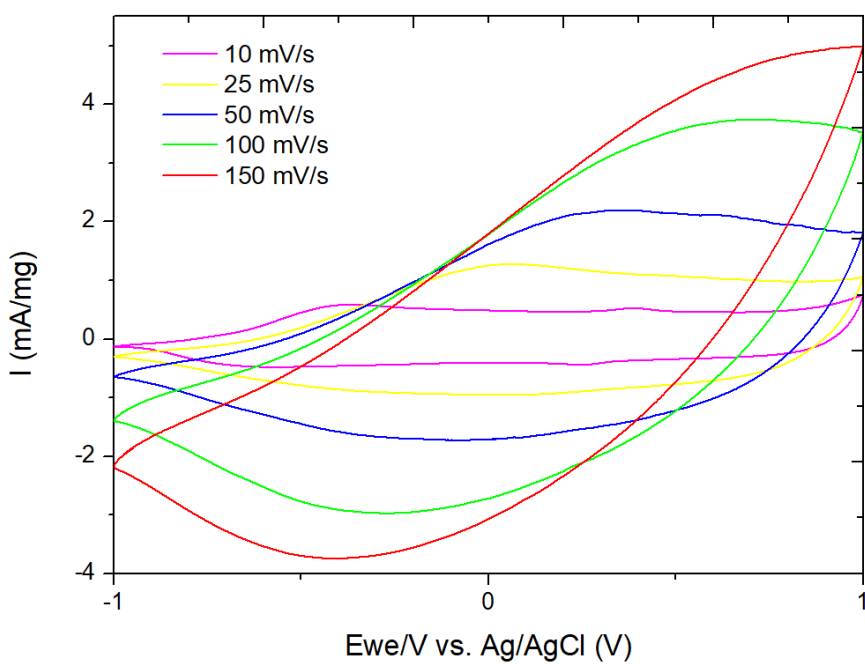
24. Fig. Cyclic voltammetry of 30/70, second cycle of the scan rates in different colours



25. Fig. Cyclic voltammetry of 40/60, second cycle of the scan rates in different colours

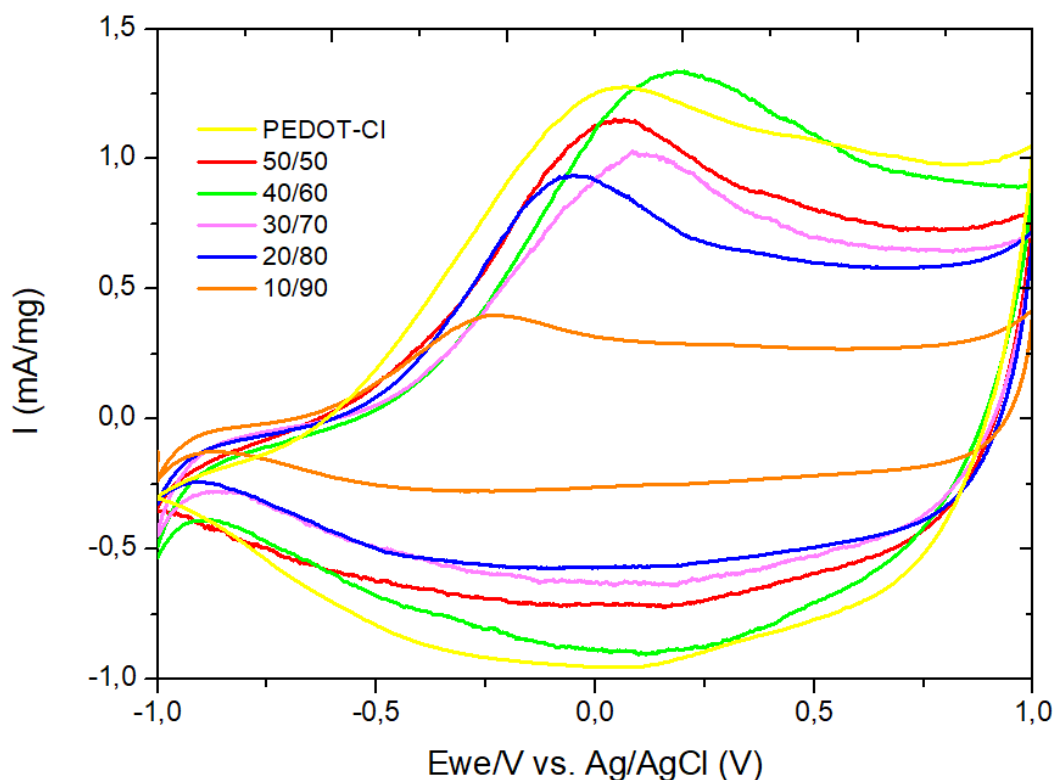


26. Fig. Cyclic voltammetry of 50/50, second cycle of the scan rates in different colours



27. Fig. Cyclic voltammetry of PEDOT-Cl, second cycle of the scan rates in different colours

PEDOT-Cl is the electroactive component, the one undergoing the redox reactions in the composite. In order to compare the results of the composites and pure PEDOT-Cl properly, one speed was selected, the 25 mV/s, and the second cycle of each composite at that speed was plotted in the same graphic, as is shown in **Fig. 28**. Like this, it can be observed that the current density increases with the PEDOT-Cl concentration in the composites due to higher electroactivity. Furthermore, it can be seen that the most similar CV of pure PEDOT-Cl is the one of 40/60, which means that at this composition the best electroactivity of the composites is obtained. These results are in good agreement with the electronic conductivity, as the higher electronic conductivity the higher the current density response of the composite.



28. Fig. Cyclic voltammetry at 25 mV/s of all the composites

In conclusion, it has been demonstrated that the 40/60 was the most electroactive composite, having the highest electronic conductivity and also ionic conductivity. The combination of all these properties make these materials very interesting to be used in electrochemical devices such as batteries and supercapacitors.

## 5. CONCLUSIONS AND FUTURE WORK

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In this project [C<sub>2</sub>mpyr][FSI] OIPC and PEDOT-Cl CP were synthesized firstly and then, a series of composites were prepared combining both of them in different weight ratios. Then, the characterization of these composites was carried out using some common techniques: FTIR, TGA, DSC, SEM, EIS, cyclic voltammetry and 4 point probe. In this way, the properties of the composites were analyzed and compared to see how these properties change with different materials' proportions.

It was concluded that the best results were obtained with the 40/60 composite, having the highest electronic and ionic conductivities and the best electrochemical performance, among other things. Furthermore, it was demonstrated that mixing OIPCs with CPs was an effective approach to develop high ionic and electronic materials which can be potentially applied in energy storage devices. It was also concluded that increasing the amount of PEDOT-Cl, the interphase created in the OIPC was more disordered, increasing the ionic conductivity and decreasing the enthalpy changes and the melting temperatures of the composites. It was also observed that when the amount of PEDOT-Cl was incremented, the electronic conductivity increased due to the interaction of PEDOT particles between them, generating more electronic pathways. All these characterization techniques lead to understand the properties of the composites and obtain the best performing one with 40/60 PEDOT-Cl/OIPC concentration. However, it has to be said that in a future SEM and EDX analyses will be repeated in lower voltage, with the aim of obtaining better results. Regarding the ionic conductivity, EIS analysis will also be repeated for 10/90 composite helping to understand why its values are so low.

As future work, it would be interesting to apply these materials in battery devices, for example, as cathode material in Li/Organic batteries or as conductive binder in Li-ion batteries. Another future work will be to add a redox active material to the composites, with the objective to improve charge-storage properties, and to be able to use them also as cathode materials in batteries. It would also be highly interesting to change the Cl anion in the PEDOT with others, in order to see the effects of this atom in the properties of the composites.

# KONKLUSIOAK ETA ETORKIZUNEKO LANA

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Proiektu honetan [C<sub>2</sub>mpyr][FSI] kristal plastiko organiko ionikoa (OIPC) eta PEDOT-Cl polimero eroalea sintetizatu dira lehendabizi, eta ondoren, bien arteko konbinazioak eginez, pisu kontzentrazio desberdineko konposatuen serie bat prestatu da. Horren ostean, konposatu horien karakterizazioa egin da ohikoak diren teknika batzuk erabiliz: FTIR, TGA, DSC, SEM, EIS, voltamperometria ziklikoa eta 4 puntazko proba. Modu honetan konposatuen propietateak analizatu dira eta kontzentrazio desberdineko materialen artean propietate hauek ea nola aldatzen diren ikusi ere.

Emaitza hoberenak 40/60 konposatuak ematen dituela ondorioztatu da, honek baititu konduktibitate elektronikoa eta ionikoa balio altuenak, bai eta, elektrokimikako emaitza hoberenak ere, beste gauza batzuen artean. Horretaz gain, OIPC eta polimero eroaleak nahastea energia biltegitzeko gailuetan aplikagarriak diren material ionikoa eta elektronikoa garatzeko hurrenkera ona dela frogatu da. PEDOT-Cl-ren kantitatea handitu ahala, OIPC-n sortutako interfasean desordena handiagoa dela ere ondorioztatu da, konposatuen konduktibitate ionikoa handituz eta entalpia aldaketak eta urte tenperaturaren balioak txikituz. Gainera, PEDOT-Cl-ren kantitatea handituz, konduktibitate elektronikoa ere handitu egiten dela ikusi da, PEDOT partikulen arteko interakzioarengatik bide elektronikoa gehiago sortzearen ondorioz. Teknika hauek guztiek konposatuen propietateak ulertzea ahalbidetu dute, 40/60 PEDOT-Cl/OIPC kontzentrazioarekin emaitza hoberenak lortuz. Hala eta guztiz ere, etorkizun batean voltaje txikiagoan SEM eta EDX analisiak errepikatuko dira, emaitza hobekien lortzeko helburuarekin. Konduktibitate ionikoari dagokionez, 10/90 konposatuaren EIS analisia ere errepikatuko da, bere balioak horren baxuak zergatik diren ulertzen laguntzeko.

Etorkizuneko lan bezala, interesgarria izango litzateke material hauek bateriak gailuetan aplikatzea, esaterako, Li/Organiko baterietan katodo bezala edo Li-ioniko baterietan lokailu eroale bezala. Etorkizuneko beste lan bat konposatuari erreox aktibo den material bat gehitzea izango litzateke, karga-biltegitze propietateak hobetzeko helburuarekin baita baterietan katodoetako material bezala erabili ahal izateko ere.

PEDOT-an Cl anioia beste batzuekin aldatzea ere oso interesgarria litzateke, horrela, konposatuen propietateetan atomo honek dituen efektuak ikusiko bailirateke.

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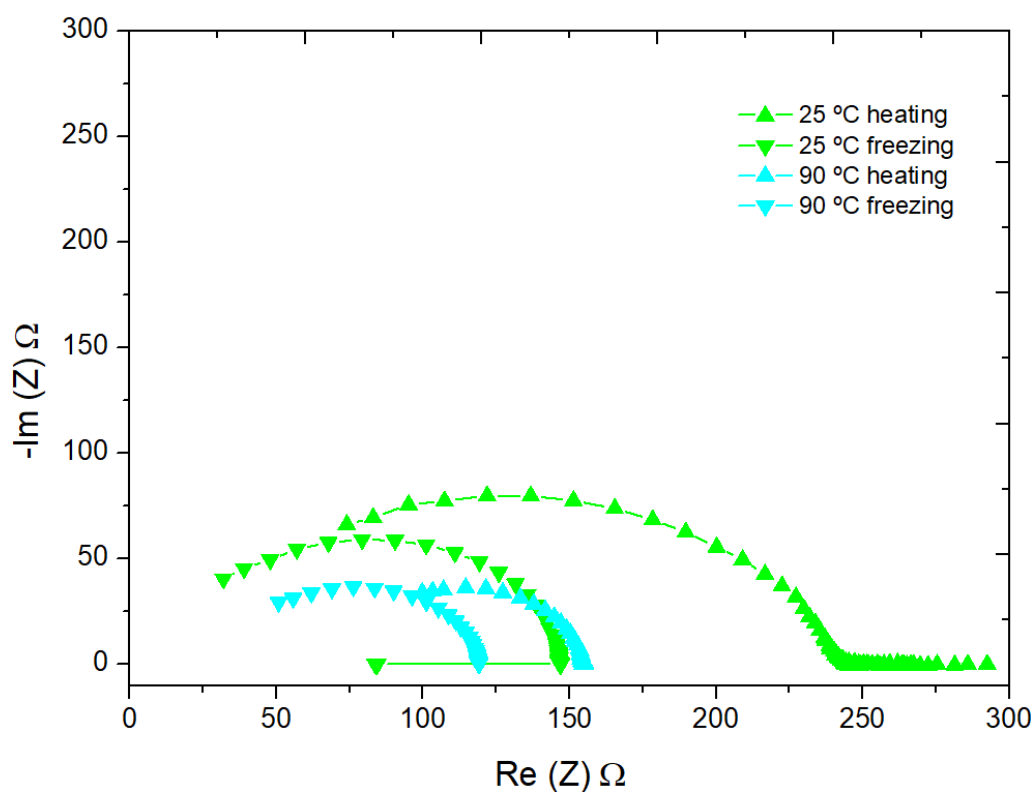
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## 7. ANEX

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Electrochemical impedance spectroscopy (EIS) was carried out for pure PEDOT-Cl too, however the results were not as expected. **Fig. 29** shows the Nyquist plot of the polymer at two different temperatures (20 °C and 90 °C). It can be observed that the graphic was not the same comparing to the ones obtained with the composites, as shown in **Fig. 18**. In PEDOT-Cl case, the semicircle does not start from 0  $\Omega$ , instead, it starts at higher values, so it is not obtained a complete semicircle. In **Fig. 29** is clearly seen that the Nyquist plot is too flat to be a proper result. In addition, the resistance values were too low to correspond only to ionic conductivity,



29. Fig. Nyquist plot obtained in the analysis of EIS (PEDOT-Cl)

The experiment was made twice and the same results were obtained. The conclusion was that the instrument was not only measuring the ionic conductivity, but maybe also the electronic conductivity. However, it is too early to confirm results, so much more research are needed to understand the values of **Fig. 29** and to make conclusions, that's why, it was included to future work.