**Universidad del País Vasco/Euskal Herriko Unibertsitatea**

**Facultad de Química/Kimika Fakultatea**

*Degree in Chemistry*

FINAL DEGREE PROJECT
Redox-active Ionic-Electronic Conducting Polymers For Batteries

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# ABSTRACT

High demand for consumer electronics combined with the need to substitute fossil fuels and migrate to a cleaner energy matrix make imperative the research for sustainable and efficient energy storage systems. Nowadays the most promising solutions are related to rechargeable lithium batteries, even though the usage of inorganic materials as electrodes is also not so good for the environment. The development of all organic batteries seems to be a better option when sustainability is considered. The stability and capacity of these materials as electrodes is still low compared to the lithium ion batteries, what makes the need for extensive research to be conduct in order to be possible to replace in the future the current inorganic batteries used nowadays.

The aim of this work was to investigate the performance of a new redox ionic electronic conducting polymer that is composed by well-known electronic conducting polymer (PEDOT), and a redox-active polyelectrolyte (PDADMA AQ). PEDOT has been extensively studied due to its high conductivity and applied in energy storage systems as binder and electrode material. Recently, a series of organic mixed electronic-ionic conductors (OMEIC) composed by PEDOT:PDADMA have been reported with inactive anions. In this work, we include redox active functionality in the polymer blends by incorporating an anthraquinone-sulfonate moiety as the counter anion. PEDOT:PDADMA AQ polymers were synthetized in different molar proportions and characterized using techniques like Fourier-transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), electrochemical impedance spectroscopy (EIS), and 4 point probe. The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV) in different electrolytes and finally, they were applied as cathode electrodes in lithium half cells, where galvanostatic charge/discharge tests and CVs were performed. The results of all these analyses confirm the ionic and electronic conducting properties, as well as the redox activity of the AQ moiety in the polymer blend. However, it was observed that the redox active molecule tend to elute to the electrolyte, indicating the need for further studies to avoid this elution and improve the capacity of the polymers.

# RESUMEN

La alta demanda de productos electrónicos de consumo combinada con la necesidad de sustituir los combustibles fósiles y migrar a una matriz energética más limpia hacen imperativa la investigación de sistemas de almacenamiento de energía sostenibles y eficientes. Hoy en día, las soluciones más prometedoras están relacionadas con las baterías de litio recargables, aunque el uso de materiales inorgánicos como electrodos tampoco es tan bueno para el medio ambiente. El desarrollo de todas las baterías orgánicas parece ser una mejor opción cuando se considera la sostenibilidad. La estabilidad y capacidad de estos materiales como electrodos sigue siendo baja en comparación con las baterías de iones de litio, lo que hace que sea necesario realizar una investigación exhaustiva para poder reemplazar en el futuro las baterías inorgánicas actuales que se utilizan en la actualidad.

El objetivo de este trabajo fue investigar el rendimiento de un nuevo polímero conductor electrónico iónico redox que está compuesto por un polímero conductor electrónico conocido (PEDOT) y un polielectrolito activo redox (PDADMA AQ). PEDOT ha sido ampliamente estudiado debido a su alta conductividad y se ha aplicado en sistemas de almacenamiento de energía como material aglutinante y electrodo. Recientemente, se ha informado de una serie de conductores iónicos electrónicos mixtos orgánicos (OMEIC) compuestos por PEDOT: PDADMA con aniones inactivos. En este trabajo, incluimos la funcionalidad activa redox en las mezclas de polímeros mediante la incorporación de un resto antraquinona-sulfonato como contra anión. PEDOT: Los polímeros PDADMA AQ se sintetizaron en diferentes proporciones molares y se caracterizaron mediante técnicas como la espectroscopia infrarroja por transformada de Fourier (FTIR), el análisis termogravimétrico (TGA), la espectroscopia de impedancia electroquímica (EIS) y la sonda de 4 puntos. Las propiedades electroquímicas de los polímeros se investigaron mediante voltamperometría cíclica (CV) en diferentes electrolitos y finalmente, se aplicaron como electrodos catódicos en semiceldas de litio, donde se realizaron pruebas de carga / descarga galvanostática y CV. Los resultados de todos estos análisis confirman las propiedades conductoras iónicas y electrónicas, así como la actividad redox del resto AQ en la mezcla de polímeros. Sin embargo, se observó que la molécula activa redox tiende a eluir al electrolito, lo que indica la necesidad de realizar más estudios para evitar esta elución y mejorar la capacidad de los polímeros.

# INDEX

# 1. INTRODUCTION

## 1.1. Electric Batteries

An electric battery can be defined as a power source consisting of one or more electrochemical cells with external connections for powering electrical devices [1]. Batteries have a positive and a negative terminal, where the positive terminal is called cathode and the negative terminal is called anode. The terminal marked negative is the source of electrons that will flow through an external electric circuit to the positive terminal. When a battery is connected to an external electric load, a redox reaction converts high-energy reactants to lower-energy products, and the free-energy difference is delivered to the external circuit as electrical energy [2].



(a)                  (b)                  (c)
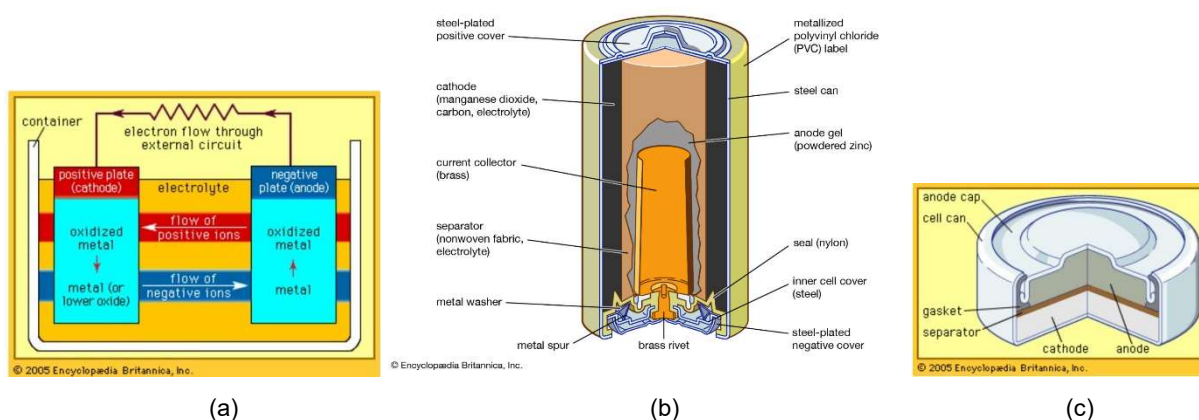
**Figure 1 -** *Three types of batteries. (a)Electrochemical cell; (b) Alkaline battery; (c) coin cell* [3].

Batteries may be classified as Primary (single-use or "disposable") or secondary (rechargeable). Disposable batteries are used once and discarded, as the electrode materials are irreversibly changed during discharge; a common example is the alkaline battery. On the contrary, rechargeable batteries can be discharged and recharged multiple times using an applied electric current; like this, the original composition of the electrodes can be restored by reverse current. A common example of a rechargeable battery is the lithium-ion battery [4].

Based on the application, the battery market is segregated as automotive, industrial, and portable. The automotive application segment led the market and accounted for 34.3% share of the total revenue in 2019. High demand for consumer electronics, including LCD displays, smartphones, tablets, and wearable devices such as fitness bands, is likely to drive the portable application

segment. This segment is expected to observe substantial growth in terms of consignments, though, with low revenues and small size, it does not subsidize a major share in the market. For these applications generally are used lithium-ion batteries as a product type. The market is expected to observe substantial growth on account of technological advancements in terms of enhanced efficiency, cost-effectiveness, and product innovation. The adoption of Li-ion batteries in electric vehicles, energy storage systems, and portable devices is expected to rise at a fast pace owing to their low maintenance properties and higher energy densities. Decreasing fossil fuel reserves, along with promising government initiatives and high $CO_2$ emissions, it is expected to propel the rechargeable batteries market growth in the next few years [4].

## 1.2. Organic batteries

The development of batteries and energy storage materials that are sustainable, nonhazardous, can be obtained from renewable sources, have easy processability and recycling potential that are economic viable is a global trend. It is necessary that these materials have high storage capacity and stability for their implementation in battery market.

Organic batteries, made from organic redox polymers, have been developed during the last decades for their potential application in energy storage devices. Organic redox polymers exhibit several advantages compared to the current lithium-ion battery technology (i.e., based on inorganic redox materials), such as easy processability, abundant and environmentally friendly precursors and excellent rate performance. The latter is inherent to the nature of the redox reactions occurring in the organic redox polymer, which is related to a change in the state of charge of the electroactive moiety, enabling fast electron-transfer kinetics. On the contrary, redox reactions in inorganic redox materials generally occur with a change of valence of the transition metal (i.e., cathode material), resulting in slow rate performance. Additionally, the intercalation of Li ions in inorganic intercalation electrodes (i.e., the anode in lithium-ion batteries) is usually accompanied with structural rearrangement of the lattice and layered structures, again resulting in slow kinetics and heat dissipation. Finally, inorganic redox materials are usually limited to lithium chemistries as the ion carrier, in contrast to organic redox polymers where the ion carrier can be either cationic (i.e., alkali metal, organic cation or even proton) or anionic, opening the range of battery configurations accessible, with low-cost and more environmentally friendly electrolyte systems [5].

### 1.3. Redox polymers

Polymers with redox properties are those with the ability of changing their electrochemical with the oxidation state due to the loss of electrons (oxidation) or the gain of electrons (reduction) [6]. For this reason, redox polymers can be applied as active electrode materials in electrochemical energy storage technologies [7].

In general, organic redox polymers can be classified into three classes, depending on the type of electrochemical reactions that they undergo during the discharge process of an electrochemical cell. N-type organic redox polymers are oxidized during discharge, while p-type organic redox polymers are reduced, and b-type organic redox polymers can be both oxidized and reduced, exhibiting both n-type and p-type redox features. Depending on the type of battery targeted (i.e., alkali metal–organic batteries, alkali ion– organic batteries and all-organic batteries, etc.), organic redox polymers can be either used as the anode or cathode, as long as sufficient potential difference is generated between the two electrodes [5].

The nonconjugated organic redox polymers generally consists of a nonconducting polymer backbone, bearing redox-active pendant moieties. Such a design concept allows the incorporation of a wide variety of electroactive functionalities, such as carbonyl, catechol, carbazole, phenazine, phenothiazine, triphenylamine and stable organic radicals, expanding the range of redox potentials accessible. In addition, these nonconjugated organic redox polymers exhibit well-defined redox potentials due to their inherent molecular design, since each redox site is not electrically connected through a conjugated system. This feature is highly favorable for battery applications, as this results in a constant cell voltage profile/plateau during the discharge process. Over the past two decades, nonconjugated organic redox polymers have been intensively investigated for their potential application in alkali metal–organic batteries, alkali ion–organic batteries and all-organic batteries [5].

Anthraquinone is a polycyclic aromatic hydrocarbon derived from anthracene or phthalic anhydride. Anthraquinone-based compounds have been regarded as the most important electrode materials in organic carbonyl electrode materials for batteries, which have demonstrated superior performance in terms of capacity and discharge voltage. However, anthraquinone (AQ) molecule also exhibits poor cycle performance because of its facile

dissolution in the organic electrolyte. The incorporation of the molecule to a polymer is a key strategy to solve this issue. Therefore, it is imperative to enhance other electrochemical properties, for example, specific capacity [8]. Anthraquinone contains two carbonyl groups able to form enolates upon two electron reduction which are stabilized by the neighboring aromatic rings [7].
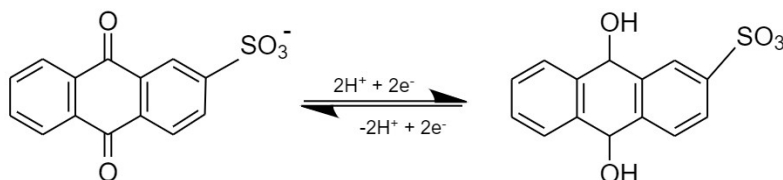


**Figure 2** - *Redox process of antrhaquinone-2-sulfonate.*

### 1.4. Conducting Polymers – PEDOT

Polymers were considered to be electrical insulators before the invention of conducting polymers (conjugated polymers), but these organic polymers have unique electrical and optical properties similar to those of inorganic semiconductors. A conjugated carbon chain consists of alternating single and double bonds, where the highly delocalized, polarized, and electron-dense p bonds are responsible for its electrical and optical behavior. Typical conducting polymers include polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH), poly(para-phenylene) (PPP), poly(-phenylenevinylene) (PPV), and polyfuran (PF) [9].

Among conducting polymers PEDOT (Poly(3,4-ethylenedioxythiophene) has drawn most of the attention in both academic studies and industrial applications due to its relatively high conductivity and remarkable stability in ambient conditions compared to other polymers, as well as its potential to be transparent in the visible spectrum. The main property of PEDOT that ensures its unique place among conducting polymers is its high and stable electrical conductivity. These conductivity values are remarkable since they are only one order of magnitude lower than the most conductive metals, namely silver and copper. Such large scale gives an overview of the remarkable advancement performed on the conductivity enhancement, but at the same time, the dispersion of data found in the literature suggests that there is still room for a better understanding of that material [10].

8

PEDOT is obtained from the oxidative polymerization of EDOT (3,4ethylenedioxythiophene). EDOT is not too stable against oxidation, and it may be completely decomposed by very strong oxidants. Peroxodisulfates (persulfates) are the best peroxidic oxidants for EDOT to form conductive PEDOT complexes [11].

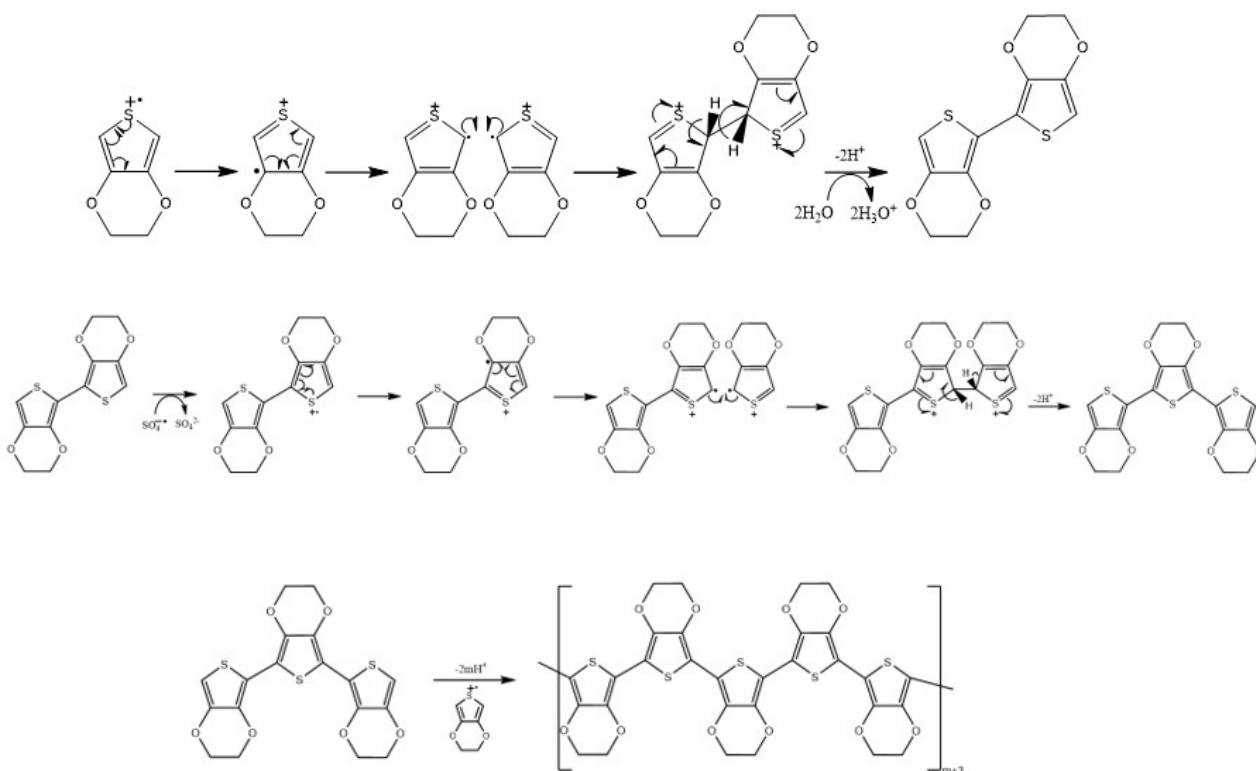(a) Dissociation of the initiator:

$(NH_4)_2SO_3 \rightarrow 2NH_4^+ + S_2O_8^{2-}$

$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$
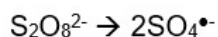
(b) Oxidation step of the Monomer:
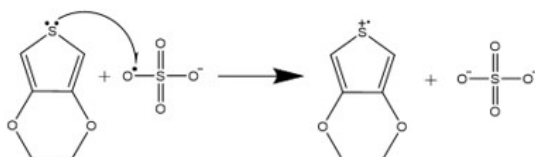
(c) Propagation step:



*Figure 3 - Proposed polymerization mechanism of PEDOT.*

Pure, freshly distilled EDOT is a nearly colorless liquid with an unpleasant odor. A small change in color to pale yellow is possible after extended storage, especially in the daylight, without significantly affecting the analytical purity. EDOT (3,4-ethylenedioxythiophene) chemistry started as early as the 1930s, when the corresponding 2,5-dicarboxylic acid esters were synthesized. The most remarkable EDOT reactions are its oxidation reactions, typically resulting in conductive oligomeric to polymeric materials in the presence of charge balancing, so-called doping counterions (anions). Although known for decades, the particular reactivity of 3,4-ethylenedioxythiophene (EDOT) with chemical oxidants was found not earlier than 1988 [11].

As PEDOT is a positively charged conjugated polymer, and being an insoluble polymer by itself, it is commercialized in form of a dispersion, stabilized with poly(styrene sulfonate (PSS), a negatively charged polymer that is a surfactant. This material has several applications in energy conversion and storage devices, such as solar cells, fuel cells and supercapacitors [12].

### 1.5. Poly(ionic liquids) - PDADMA

Poly(ionic liquids) (PILs), also called polymerized ionic liquids, refer to a subclass of polyelectrolytes that feature an ionic liquid (IL) species in each monomer repeating unit, connected through a polymeric backbone to form a macromolecular architecture. Some of the unique properties of ILs are incorporated into the polymer chains, giving rise to a new class of polymeric materials [13]. The incorporation of these properties improved mechanical stability, processability and spatial controllability over ionic liquids. PILs offer a wide range of applications in very different technological field such as energy, environmental science, analytical chemistry, polymer and colloidal science or biotechnology. In energy applications (energy conversion and energy storage) they can be used as polymer electrolytes or binders in batteries, supercapacitors, transistors, bioelectronic devices, light emitting electrochemical cells or solar cells [7].

Polydiallyldimethylammonium chloride (PDADMAC) is linear cationic polymer widely used for water purification. It can be synthesized using Hunter et al. method in terms of the free radical polymerization of diallyldimethylammonium chloride (DADMAC) [14].
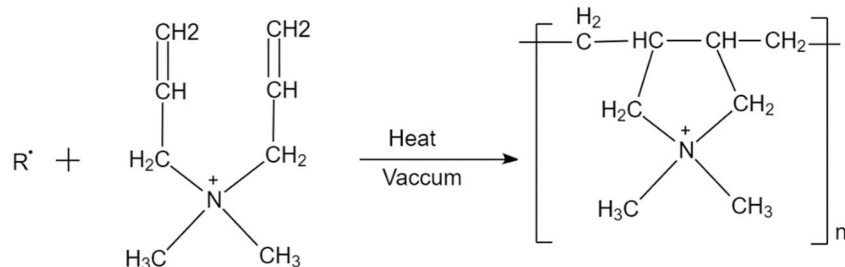
***Figure 4*** *- Radical polymerization of diallyldimethylammonium.*

PDADMA is also a popular type of poly(ionic liquid) which is commercially available and applied as a polymer electrolyte in lithium batteries [7]. Depending on the moiety attached to the polymer backbone it is possible to obtain different properties (chemical, electrical and mechanical) of the polymer.

### 1.6. OMIECs

Organic mixed ionic–electronic conductors (OMIECs) are electrical conductors, often polymers, that readily solvate and transport ionic species [15]. (OMIECs) has been highlighted because of their high electronic conductivity and flexibility in their synthesis and processability. Previous studies of inorganic MIECs illustrate the difficulties associated with OMIECs, with many factors affecting the ionic-electronic transport, such as the presence of solvent, mobile ions and temperature [1]. A steadily growing number of applications for π-conjugated polymers and small molecules where ion transport is crucial. The first of these applications investigated was π-conjugated polymer electrodes for batteries and super capacitors, where inducing charge within OMIECs was itself the goal. The field has rapidly grown to include actuators, light-emitting electrochemical cells, chemical sensors, sensing and stimulating bioelectronic probes, ion pumps ,and organic electrochemical transistors for sensing, circuits and neuromorphic computing applications, where induced charge has enabled further functionality [15].

OMIECs are predominated by π-conjugated polymers but also radical polymers and conjugated small molecule systems. Some of the π-conjugated polymers successfully employed are based on polyaniline, polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT) [16]. Several studies have been conducted to increase electronic conductivity and mechanical properties of OMIECs.

## 2. OBJECTIVES

The main objective of this report is to develop mixed organic ionic and electronic conducting polymers (OMIECs) with redox properties, perform their structural, thermal and electrochemical characterization, as well as evaluate their application in batteries.

First, polymer blends of a polyelectrolyte (PDADMAC) and a conducting polymer (PEDOT), will be synthesized with different molar ratios between both polymers, in order to study the influence of the different compositions in the final product properties. The chloride ion of the polyelectrolyte will be substituted with a redox active molecule, antraquinone-2-sulfonate (AQ). It will also be synthesized an OMIEC with a non-redox active moiety, such as TFSI, to be used as a reference.

A redox active poly(ionic liquid), PDADMA-AQ, was studied in previous work, presenting good capacity and stable life cycle as material for battery application. However, these electrodes need the addition of carbon and an extra binder to ensure the electronic conductivity and integrity of the cathode, respectively. The addition of PEDOT, to form a polymer blend has the objective to bring electronic conductivity to the material, and thus, have the three functionalities needed in a cathode in a single material polymeric blends containing PEDOT:PDADMA X were also previously studied, showing that for different substituent anions (X) the material present mixed conducting properties, but redox active molecules as the moiety attached to PDADMA were not evaluated. For that reason this report will also analyze the impact of adding a redox active molecule to the OMIEC PEDOT:PDADMA X.

In the characterization of the prepared polymers, electronic and ionic conductivities, electrochemical and thermal properties will be analyzed. In order to get these results, analyses such as Fourier-transform Infrared Spectroscopy (FTIR), 4 point probe method, Thermogravimetric Analysis (TGA), Cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic Charge Discharge will be carried out. All these techniques and their specifications will be described later in the experimental part.

As a Final Degree Project, this study has the aim to develop knowledge about innovative polymers for batteries, application of the topics learned during the first year of the Double Master in Polymer Science Course, such as characterization techniques, polymer properties, polymer synthesis and also research methodology.

## 3. EXPERIMENTAL

### 3.1. Reactants and Solvents

Poly(diallyldimethylammonium chloride) (PolyDADMAC) (Mw = 400,000–500,000 g mol$^{-1}$) 20 wt% in water, Sodium anthraquinone-2-sulfonate (> 98%) (AQ-Na), lithium perchlorate (LiClO$_4$), Tetrabutylammonium hexafluorophosphate (TBAPF$_6$), dimethyl sulfoxide (DMSO), 1,2-dimethoxymethane (DME), 1,3-dioxolane (DOL), ethyl methyl carbonate - anhydrous (EC), diethylcarbonate – anhydrous (DEC), acetonitrile – anhydrous (ACN) were purchased from Sigma-Aldrich as high purity chemicals. Ammonium persulfate (APS) and 3,4 - ethylenedioxythiophene (EDOT) (99%) were purchased from Acros Organics. Lithium hexafluorophosphate (1 M) in ethylene carbonate:diethylcarbonate 1:1 v/v  and potassium trifluoromethanesulfonimide (KTFSI) were obtained from Solvionic. Hydrochloric acid (HCl) (37%wt) was obtained from Fischer Chemical. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was purchased from IoLiTec.

### 3.2. Synthesis of PEDOT:PDADMA AQ

The polymeric mixture of PEDOT:PDADMA AQ was obtained through oxidative polymerization in acidic medium followed by a ionic exchange, following the procedure described by *Olmo et al* [16]. The oxidative polymerization was done in acidic medium once it was previously reported that the utilization of an acidic medium improves the doping of the PEDOTs chains [16].

Three different polymers were synthesized, with different molar ratios of PEDOT:PDADMAC, 1.13:1, 1.3:1 and 1.5:1 (mol/mol).

#### 3.2.1.  Oxidative Polymerization

In a first flask, 20 wt% PoliDADMAC in 50 mL of a solution of HCl 0.1 M in water were placed and EDOT was added to it. In a second flask, ammonium persulfate (APS) was dissolved in 20 mL of 0.1 M HCl. The quantities of added material for each synthesis can be found in **Table 1**.

**Table 1** – *Mass and volume of the reagents used for the oxidative polymerization of each polymer composite with different molar ratios.*

| PEDOT:PDADMA Ratio (molar) | 1,13:1 | | | 1,3:1 | | | 1,5:1 | | |
|---|---|---|---|---|---|---|---|---|---|
| Reagent | PDADMAC | EDOT | APS | PDADMAC | EDOT | APS | PDADMAC | EDOT | APS |
| Molar Concentration (mmol) | 2,480 | 2,800 | 4,210 | 2,480 | 3,220 | 4,840 | 2,480 | 3,720 | 5,590 |
| Mass (g) | 2,000 | 0,398 | 0,960 | 2,000 | 0,458 | 1,105 | 2,000 | 0,529 | 1,275 |
| Volume (mL) | 1,930 | 0,300 | | 1,930 | 0,340 | | 1,930 | 0,400 | |

Nitrogen gas was bubbled inside the flasks for 20 minutes to remove traces of oxygen once the polymerization of EDOT must occur in an inert atmosphere.



(a)                                                    (b)
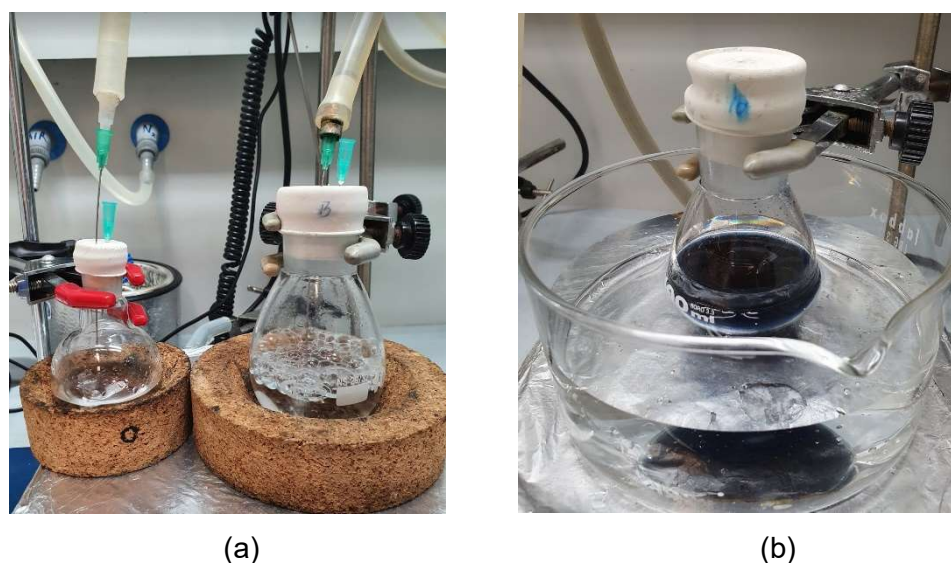
**Figure 5** – *(a) Flasks with APS+HCl 0.1M (left) and EDOT+PDADMAC+HCl 0.1M (right), during the nitrogen bubbling step. (b) Flask with the polymeric mixture, after 24 hours of the addition of the initiator.*

After the $N_2$ bubbling, the solution containing APS was added dropwise in the flask containing the PDADMAC and EDOT mixture with a syringe, to maintain the inert atmosphere. The flask was kept under mixing with a magnetic stirrer for 24 hours. During the addition of initiator and for the first hour the flask was in an ice bath. Initially the mixture was transparent, and as soon the initiator was added it turned white. After 24 hours of polymerization the mixture was dark blue characteristics of PEDOT.

### 3.2.2. Ionic Exchange

After 24 hours of polymerization, the ionic exchange reaction was done to change the chloride ion present in PDADMAC with anthraquinone-2-sulfonate (AQ). A quantity of 0.923 g of

anthraquinone-2-sulfonate sodium salt was initially dissolved in 20 mL of water Milli-Q (20 mol% in excess related to the PDADMAC content) and heated to 37°C to improve the dissolution. The content of the flask (polymeric blend) synthetized in step 3.2.1 was also heated to 37°C in a water bath. The dissolved anthraquinone salt was added dropwise to the content of the flask, that was kept under agitation. The system was maintained in 37°C and in agitation for 3 hours to ensure the ionic exchange.

### 3.2.3. Filtration and Drying

After 3 hours of agitation, the flask was kept in a refrigerator for 24 hours in order to precipitate the polymeric blend. The solubility of PEDOT:PDADMA X depends on the anion, which ranges from non-polar solvents (for example acetonitrile and acetone) or in polar solvents such as methanol and water [16]. As PEDOT:PDADMA AQ is insoluble in water, the polymer blend precipitates after the ionic exchange, and the polymer can be obtained through a vacuum filtration.



*Figure 6 – Arrangement used to perform a vacuum filtration.*

The polymer obtained in the filter was washed with Milli-Q water at 37°C to guarantee the removal of the salt generated (NaCl), the excess of anthraquinone-2-sulfonate sodium and APS, until the filtrated liquid was colorless, once the antraquinone-2-sulfonate sodium salt is yellowish. The filtered polymer blend was dried in a vacuum oven at 60°C for 24 hours.

### 3.3. Synthesis of PEDOT:PDADMA TFSI

To obtain PEDOT:PDADMA TFSI was followed the same procedure utilized to obtain PEDOT:PDADMA-AQ, described in the item 2.2 of this report (oxidative polymerization → ionic exchange → filtration → drying). The quantities added of PDADMA, EDOT and APS were the same used to obtain PEDOT:PDADMA AQ with the molar ratio of 1.13:1. In the ionic exchange, 0.950 g of KTFSI was added to the previously obtained PEDOT:PDADMAC.

### 3.4. Structural Characterization

#### 3.4.1. Infrared Spectroscopy Coupled to Attenuated Total Reflectance (ATR-FTIR)

The Infrared Spectroscopy Coupled to Attenuated Total Reflectance (ATR-FTIR) is a method used to determine organic and inorganic groups in liquid, gases and solids.

Most molecules absorb light in the infrared region of the electromagnetic spectrum, converting it to molecular vibration. This absorption is characteristic of the nature of the chemical bonds present in a sample. With the spectrometer, this absorption is measured as a function of wavelength. The result is an IR spectrum that serves as a characteristic "molecular fingerprint" which can be used to identify organic and inorganic samples. In the past, the samples were analyzed step by step, whereby the sample was irradiated with different single wavelengths (dispersive). FT-IR on the other hand, collects the spectral data of all wavelengths in one pass. A continuous source generates IR light over a wide range of infrared wavelengths. The infrared light then passes through an interferometer and is then directed at the sample. In contrast to dispersive measurements, we first obtain an interferogram, that needs to be converted to an IR spectra. This interferogram (a raw signal), represents the light intensity not as a function of wavelength, but as a function of the position of a mirror inside the interferometer. As a result, the signal must first be Fourier-transformed (FT) to produce the more familiar IR representation of intensity as a function of wavenumber [17].

ATR has become the standard technique for the measurement of FT-IR spectra. The infrared light passes through a crystal of a certain material (diamond, ZnSe or germanium) and interacts with the sample, which is pressed onto the crystal [17].

In the present study, the IR spectra for each polymer synthesized were obtained by ATR-FTIR analysis with a Bruker ALPHA Spectrometer, at room temperature, using a small sample of solid polymer, previously grinded in a mortar.

The objective of this analysis was to verify the success of the ionic exchange reactions, where the chloride ion in was supposed to exchange places with anthraquinone-2-sulfonate and TFSI as a moiety of PDADMA.

### 3.5. Thermal Characterization

#### 3.5.1.  Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an experimental technique in which the weight or strictly speaking the mass of a sample is measured as a function of sample temperature or as a function of the time in isothermal experiments. The instrument used to perform such measurements is called a thermogravimetric analyzer, TGA. The results of a TGA measurement are usually displayed as a TGA curve in which mass is plotted against temperature or time [18].

In the present report the TGA is used to determine the degradation temperature of the synthesized polymer blends in order to evaluate their thermal stability.

About 10 mg of each polymer blend was placed in vials. The vials were maintained in the vacuum oven at 60ºC for 24 hours prior to analysis. The thermogravimetric analysis was carried out on a TGA Q500 from TA Instruments, and the samples were heated from room temperature to 800ºC in a rate of 10ºC/min under nitrogen atmosphere.

### 3.6. Transport Properties

#### 3.6.1.  Electronic Conductivity – Four Point Probe Method

Electronic conductivity indicates how well electricity will travel through a material. Sheet resistance (or surface resistivity) is an important property of many materials, quantifying the ability for charge to travel along uniform thin films. Furthermore, resistivity (and hence conductivity) can

be determined from the measurement of the sheet resistance, enabling electrical characterization of a material [19].

The most common technique used for measuring sheet resistance is the four-probe method. This technique involves using four equally spaced, co-linear probes (known as a four-point probe) [19] where a current is forced through the two outer probes and the voltage generated across the two inner probes is measured.

The electronic conductivity measurements in this study were performed on a Ossila Four-Point Probe System using layer resistivity function. For each polymer studied 3 samples were prepared and each of the samples had the conductivity measured in 3 different zones of the film.

The samples used were prepared and the conductivity measured following the procedure:

1. In a vial, 0.5 g of the polymer was mixed with 1 mL of DMSO (Acetone for PEDOT:PDADMA TFSI).
2. For the complete dissolution, the mixture was kept under agitation with a magnetic stirrer for 24 hours.
3.  With a micropipette, 100 µL of the solution was added to a glass coverslip (17x17 mm).
4. The coverslips were placed above a heated plate at 60°C until all solvent had evaporated, forming a uniform film on the coverslips.
5. The coverslips were placed in the vacuum oven at 60°C for 24 hours.
6. The thickness of the polymer film was measured with a Digimatic micrometer from Mitutoyo Corporation.
7. The conductivity was measured sampling in different zones of the film 3 times.

***Figure 7*** *- The Ossila Four-Point Probe System.*

### 3.6.2. <u>Ionic Conductivity - Electrochemical Impedance Spectroscopy (EIS)</u>

Electrochemical Impedance Spectroscopy (EIS) is an electrochemical technique that measures impedance of a system as a function of a frequency at a constant potential [20]. This technic has several applications in studying batteries, as well as the determination of ionic conductivity in ionic conducting materials [21].

Electrical Impedance can be described as the resistance to an alternating current circuit [21]. Resistance is the "difficulty" of a current passing through a resistor due to a voltage, and can be described by Ohm's law:

$$E = IR$$

Once the impedance is the equivalent of resistance in an alternating current circuit, it can be defined as **Z**:

$$E = IZ$$

A potentiostat measures the impedance by applying a potential wave to the working electrode and records the resulting current wave. From these two waves the potentiostat calculates Z, Φ, Z' and Z''. The spectrum is made by measuring these parameters for potential waves with different frequencies.   The total impedance is the ratio of the potential's amplitude and the current's

amplitude. The resulting impedance is a complex number. This number can be expressed in the complex plane in polar coordinates by using Z as the length of the vector and Φ as the angle. With the common knowledge about calculations for complex numbers the impedance can also be expressed as the real part of the impedance Z', which is the resistance, and imaginary part Z'' [22].
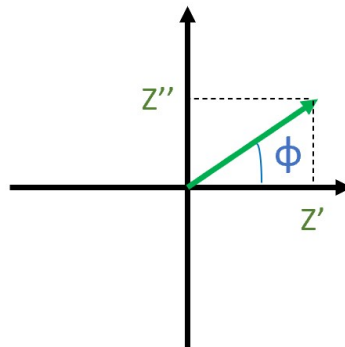


*Figure 8- Impedance represented in polar coordinates, where the real part is Z', the imaginary part Z'' and the phase shift φ.*

The Nyquist plots are a complex plane plot. They are plots of imaginary versus real impedance. In these plots -Z'' is plotted versus Z' as the imaginary impedances of the electrochemical systems are usually negative [20].
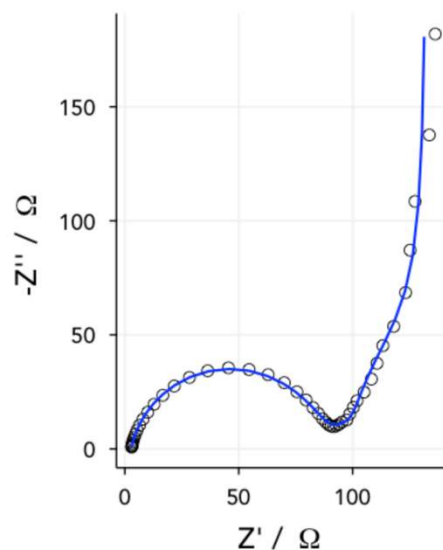


*Figure 9 - Example of a Nyquist Plot [21].*

In the present study, the ionic conductivity of the mixed conductors was investigated by EIS. EIS was performed on a AUTOLAB Potentiostat, between 25ºC and 90ºC, with frequency range from 100,000 Hz to 1 Hz. The films that were used in these experiments were drop casted directly on the electrode.

1. In a vial, 0.5 g of the polymer was mixed with 1 mL of DMSO (for PEDOT:PDADMA TFSI acetone was used as a solvent instead of DMSO).
2. For the complete dissolution, the mixture was kept under agitation with a magnetic stirrer for 24 hours.
3. With a micropipette, 10 µL of the solution was added the electrode.
4. The electrodes were placed above a heated plate at 60ºC until all solvent had evaporated, forming a uniform film.
5. The electrode was placed in the vacuum oven at 60ºC for 24 hours, to guarantee total evaporation of the solvent and avoid presence of humidity in the film.
6. The EIS was performed, following the procedure on **Figure 10**.
8. The thickness of both electrodes together was measured with a Digimatic micrometer from Mitutoyo Corporation.
7. The electrodes were cleaned, and the thickness was measured again.
8. The drop casted film thickness was calculated by the difference of thickness of the assembled electrodes before and after cleaning.
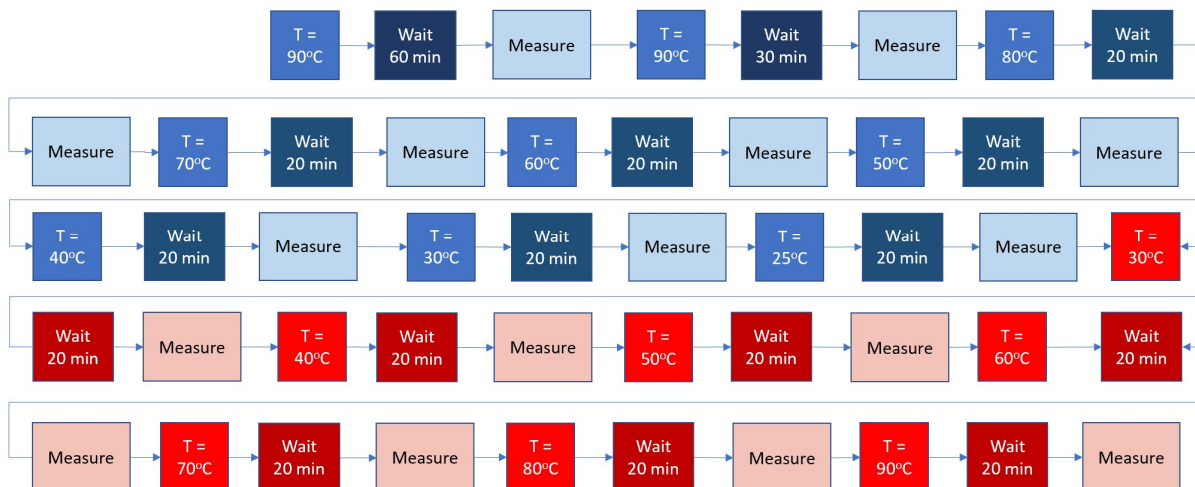


*Figure 10 - Procedure used in the potentiostat to measure impedance of the polymer film casted on the electrodes to obtain the Nyquist Plot.*

## 3.7. Electrochemical Properties

### 3.7.1. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species. To obtain the desired information, a potential is applied on a system, resulting in a current, that is measured. The result is represented as a graph, called voltammograms or cyclic voltammograms. The x-axis represents a parameter that is imposed on the system, here the applied potential (E), while the y-axis is the response, here the resulting current (i) passed. The oxidation and reduction peaks are separated due to the diffusion of the analyte to and from the electrode. If the reduction process is chemically and electrochemically reversible, the difference between the anodic and cathodic peak potentials, called peak-to-peak separation (ΔEp), is 57 mV at 25 °C (2.22 RT/F), and the width at half max on the forward scan of the peak is 59 mV. Chemical reversibility is used to denote whether the analyte is stable upon reduction and can subsequently be reoxidized. Electrochemical reversibility refers to the electron transfer kinetics between the electrode and the analyte. When there is a low barrier to electron transfer (electrochemical reversibility), the Nernstian equilibrium is established immediately upon any change in applied potential. By contrast, when there is a high barrier to electron transfer (electrochemical irreversibility), electron transfer reactions are sluggish and more negative (positive) potentials are required to observe reduction (oxidation) reactions, giving rise to larger ΔEp. Often electrochemically reversible processes where the electron transfers are fast and the processes follow the Nernst equation are referred to as "Nernstian" [23].
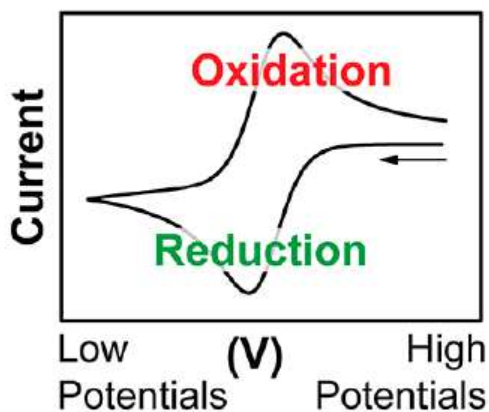


**Figure 11** - *Cyclic Voltammogram* [23].

Usually, an electrochemical cell is used for this type of experiment. The electrochemical cell consists in a vessel with an electrolyte solution, where 3 electrodes are immersed: a working electrode (WE), a counter electrode (CE) and a reference electrode (REF). The electrolyte solution is responsible to maintain electrical neutrality via migration of ions in solution. The working electrode (WE) carries out the electrochemical event of interest. A potentiostat is used to control the applied potential of the working electrode as a function of the reference electrode potential. A reference electrode (RE) has a well-defined and stable equilibrium potential. It is used as a reference point against which the potential of other electrodes can be measured in an electrochemical cell. The applied potential is thus typically reported as "vs" a specific reference. When a potential is applied to the working electrode such that reduction (or oxidation) of the analyte can occur, current begins to flow. The purpose of the counter electrode is to complete the electrical circuit. A platinum wire or disk is typically used as a counter electrode, though carbon-based counter electrodes are also available. [23]
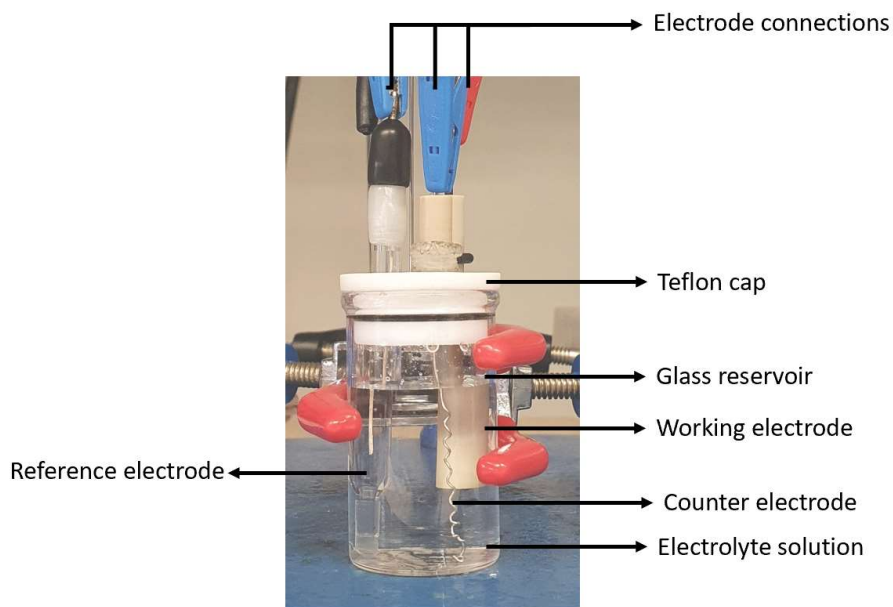


*Figure 12 - Schematic picture of an electrochemical cell.*

Cyclic voltammetry was performed to determine the redox potential of the reduction and oxidation reactions and the electrochemical window for all polymer blends. The CVs were performed on a BioLogic VMP3 instrument, between -1.5 V and 0.8 V vs. $Ag^+/Ag$ at a scan rate of 20 mV $s^{-1}$, for 30 cycles. The counter electrode used was platinum, the reference electrode $Ag/AgNO_3$ and the

electrolyte solution was 0.1M LiClO$_4$ in anhydrous acetonitrile. The electrochemical cell atmosphere was kept inert with nitrogen. The procedure for preparation of the electrochemical cell was:

1. In a vial, 0.5 g of the polymer was mixed with 1 mL of DMSO (Acetone for PEDOT:PDADMA TFSI).
2. For the complete dissolution, the mixture was kept under agitation with a magnetic stirrer for 24 hours.
3. With a micropipette, 1.5 µL of the solution was added to a Platinum Working Electrode.
4. The electrode was placed in the vacuum oven at 60°C for 1 hour.
5. The electrolyte was bubbled with nitrogen for 10 minutes prior to the addition of the working electrode to the cell.

### 3.8. Half Cell Lithium Batteries

#### 3.8.1. Coin Cell Preparation

To verify the performance of the synthetized polymers as cathodes for Lithium – Polymer batteries, coin cells were assembled and tested.
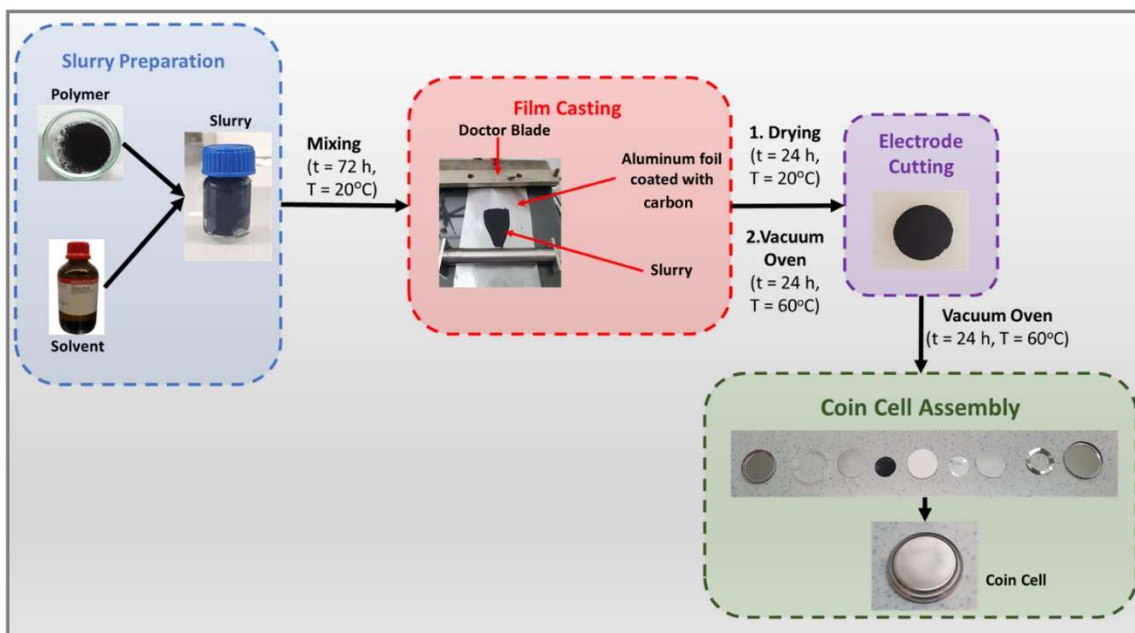


***Figure 13*** *- Illustrative flow chart of the coin cell preparation.*

1. First it was prepared a slurry mixing the synthetized polymer blends with a solvent (DMSO for PEDOT:PDADMA AQ and Acetone for PEDOT:PDADMA TFSI). As it is necessary to obtain a viscous mixture, it was mixed 0,5 g of polymer with 0,250 mL of solvent. The content of the vial was kept under agitation with a magnetic stirrer for 3 days.

2. Before use, the slurry was passed in a mortar to avoid solid that may compromise film integrity.

3. The film was casted in Doctor Blade, on an aluminum foil covered with carbon. The equipment was adjusted to obtain a wet thickness of 125 $\mu$m. The velocity of casting was 40 mm/s.

4. The foil was kept for 24 h in the chapel to evaporate the solvent and was after placed in the vacuum oven for 24 h at 60ºC to remove all traces of solvent and humidity from the film.

5. Circular electrodes were obtained with a hole puncher of 11 mm. Each electrode was weighted and kept in individual vials to dry for more 24 hours at the vacuum oven.

6. The electrodes were transferred to a glove box so the coin cells could be assembled in an inert atmosphere.

7. CR2032 coin cells were assembled following the scheme on **Figure 14**.

8. As electrolyte were used: LiPF6 1M in EC/DEC (1:1) v/v, LiTFSI 1M in DOL/DME (1:1) v/v and LiClO4 1M in EC/DEC (1:1) v/v. For each electrolyte, 2 coin cells were assembled.
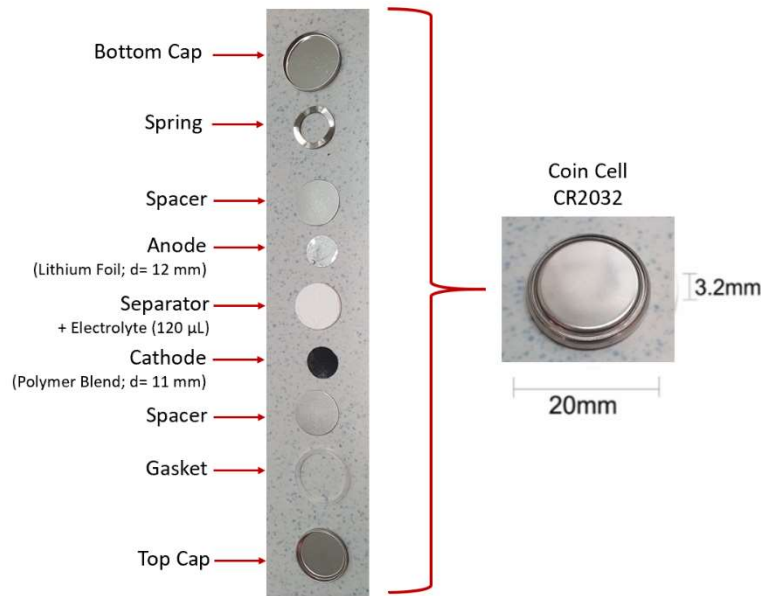
*Figure 14 - Coin Cell components.*

### 3.8.2. Batteries Testing - Galvanostatic Charge/Discharge

Cyclic Charge-Discharge (CCD) is the standard technique used to test the performance and cycle-life of batteries. A repetitive loop of charging and discharging is called a cycle. Most often, charge and discharge are conducted at constant current until a set voltage is reached. The charge (capacity) of each cycle is measured and the capacitance C, in farads (F), is calculated:

$$C = \frac{Q}{V}$$

where Q is the charge in coulombs, and V is the voltage window. Both are plotted as a function of cycle number. This curve is called the capacity curve [24].

During galvanostatic cycling of batteries, the charge and discharge current are often expressed as a C-rate, calculated from the battery capacity. The C-rate is a measure of the rate at which a battery is charged or discharged relatively to its maximum capacity. For example, a C-rate of 1 C means that the necessary current is applied or drained from the battery to completely charge or discharge it in one hour. C-rates multiples of 1 C are also exploited [25].

To verify the electrochemical activity of anthraquinone and PEDOT in the batteries assembled, a test protocol was followed for each battery. First, a cyclic voltammetry was performed on a BioLogic VMP3 instrument, between 1.5 and 3.6 V vs. Li+/Li at a scan rate of 5mV s-1, for 5 cycles. Then, galvanostatic charge/discharge measurements were carried on a Neware Battery Testing System at 0.3C, 0,5C, 1C, 2C, 4C and 0.3C rates (considering only AQ weight) between 1.5 and 3.6 V vs. Li+/Li, 5 cycles per C-rate. Then, a new CV was performed, with the same instrument and conditions of the first CV. Finally, galvanostatic charge/discharge measurements were carried on a Neware battery tester at 0.5C rate between 1.5 and 3.6 V vs. Li+/Li, for 100 cycles.

# 4. RESULTS AND DISCUSSION

## 4.1. Synthesis

The polymerization of EDOT in the presence of PDADMAC followed by the ionic exchange between PDADMAC and anthraquinone-2-sulfonate sodium salt was carried out to obtain new mixed ionic-electronic conductors. The blends obtained are formed by a conducting polymer (PEDOT) and a polyelectrolyte (PDADMA-AQ). PEDOT:PDADMA-TFSI was also synthesized through the same route in order to be used as a reference for comparison, as TFSI is not redox-active.
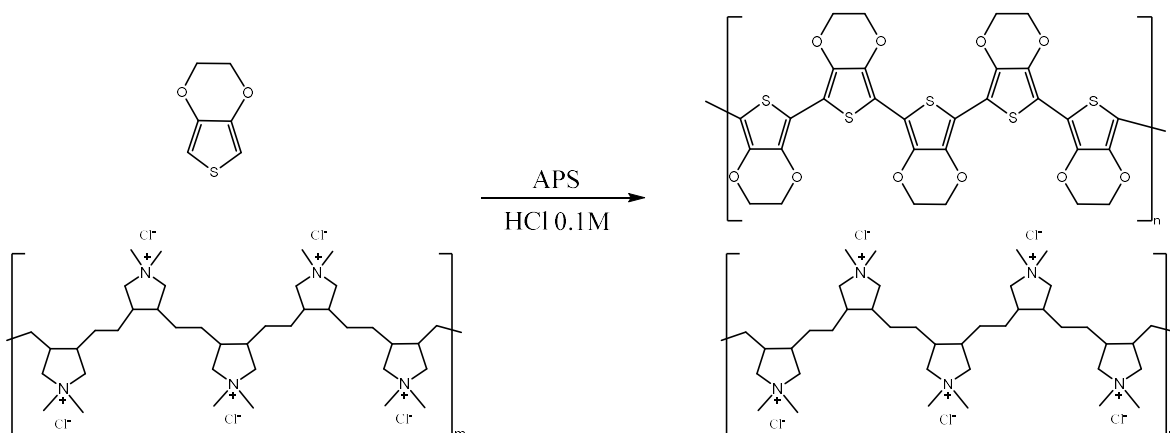


*Figure 15 – Oxidative polymerization of EDOT in the presence of PDADMAC to obtain a polymeric blend.*
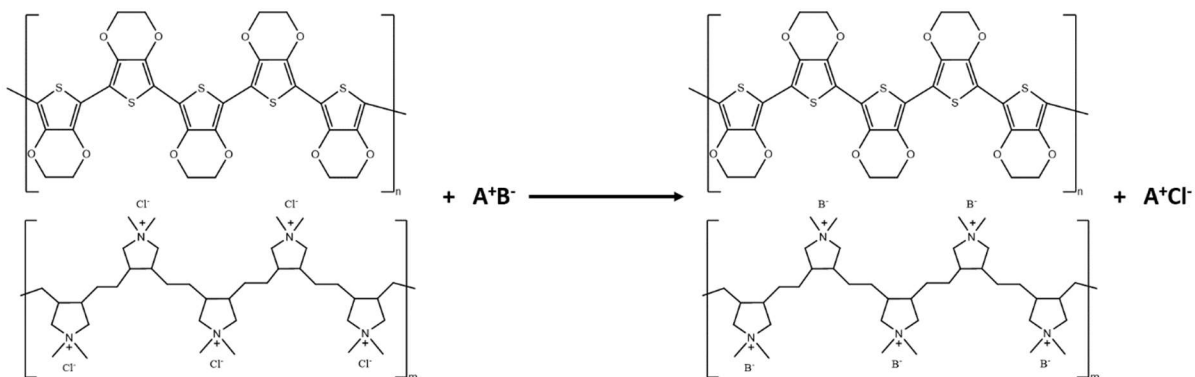


*Figure 16 – Ionic exchange reaction between the polymeric blend (PEDOT:PDADMAC) and a salt. In the present report A = Na⁺, K⁺ and B = AQSO₃⁻, TFSI⁻.*

Four different polymer blends of PEDOT:PDADMA-AQ with different molar ratios (1.13:1; 1.3:1; 1.5:1) were prepared to compare the effect of the composition on polymer properties. PEDOT:PDADMA-TFSI (1.3:1) was also synthesized to be used as a reference, once this polymer was previously studied by *Olmo et al* [16].

The yield for each polymer was calculated considering the polymerization of all EDOT added and total ionic exchange between the $Cl^-$ present in the PDADMAC with the anion of each salt used (TFSI and AQ). The mass of polymer blend was obtained after drying the product in the vacuum oven at 60°C for 24 h. The high values of yield obtained for all polymers indicate that the polymerization of EDOT and the ionic exchange were successful. Once the anion $Cl^-$ has a molar mass that is 12% of the molar mass of the anthraquinone-2-sulfonate, a low ionic exchange would impact directly on the yield. The difference between total conversion and obtained yield is due to losses during the process to obtain the final polymer blend and were considered reasonable for all polymers.

*Table 2* - *Yield for the synthesized polymer blends.*

| | PEDOT:PDADMA X | | | |
|---|---|---|---|---|
| **Moiety** | AQ | AQ | AQ | TFSI |
| **Molar Ratio** | 1.13:1 | 1.3:1 | 1.5:1 | 1.3:1 |
| **Yield (%)** | 92 | 93 | 87 | 91 |

The color of all polymer blends prepared were at observation black (**Figure 17**), the characteristic color of PEDOT. When diluted the polymer blend presented dark blue color. Regarding solubility all polymers were insoluble in water and non-polar solvents. The polymers that contained anthraquinone were soluble only in highly aprotic polar solvents, like DMSO, while the polymer blend containing TFSI also presented solubility in acetone (polar aprotic).
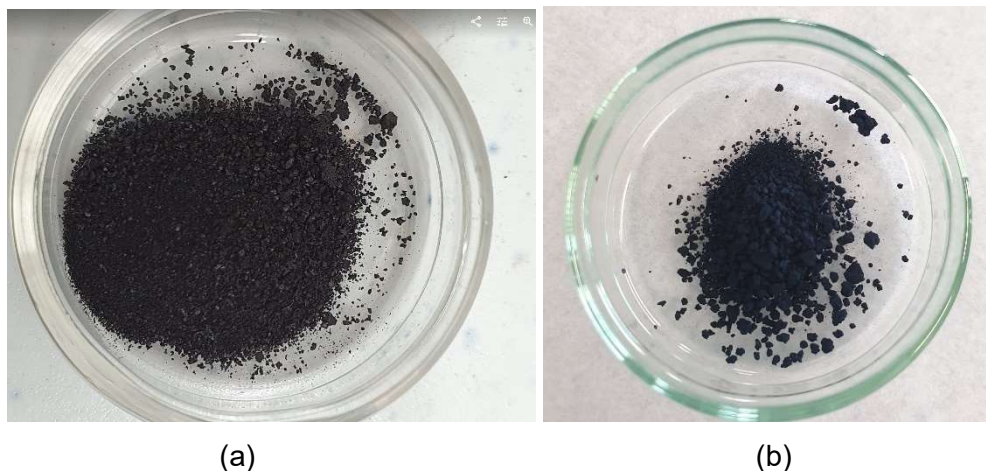
**Figure 17** - *Sample of (a) PEDOT:PDADMA-AQ (1.3:1) and (b) PEDOT:PDADMA-TFSI (1.3:1)*



**Figure 18** - *Solubility test for PEDOT:PDADMA-AQ. From left to right, Acetonitrile, DMSO, THF, Ethanol, Methanol.*

## 4.2. Structural Characterization - FTIR

The chemical nature of the synthesized polymers was confirmed by Infrared Spectroscopy Coupled to Attenuated Total Reflectance (ATR-FTIR). The IR spectra of the polymer blends are depicted in **Figure 19** and **Figure 20**.

For the three polymer blends synthesized that contain anthraquinone-2-sulfonate it is possible to observe the characteristic bands of this moiety (C=O stretching at 1664 cm$^{-1}$, C=C stretching at 1586 cm$^{-1}$ and SO$_3$ stretching at 1283 cm$^{-1}$). For the blend that contains TFSI anions the bands that appear are SO$_2$ symmetric stretching at 1130 cm$^{-1}$, SO$_2$ bending at 1318 cm$^{-1}$ and CF$_3$ asymmetric stretching at 1173 cm$^{-1}$. All of them show the same characteristic band of the pyrrolidinium backbone at 1472 cm$^{-1}$ (CH$_3$ bending vibration of the pendant methyl units). It is also

possible to observe the typical bands associated with thiophene ring vibrations (1506 cm$^{-1}$: C=C asymmetric stretching and 1320 cm$^{-1}$: C-C inter-ring stretching).
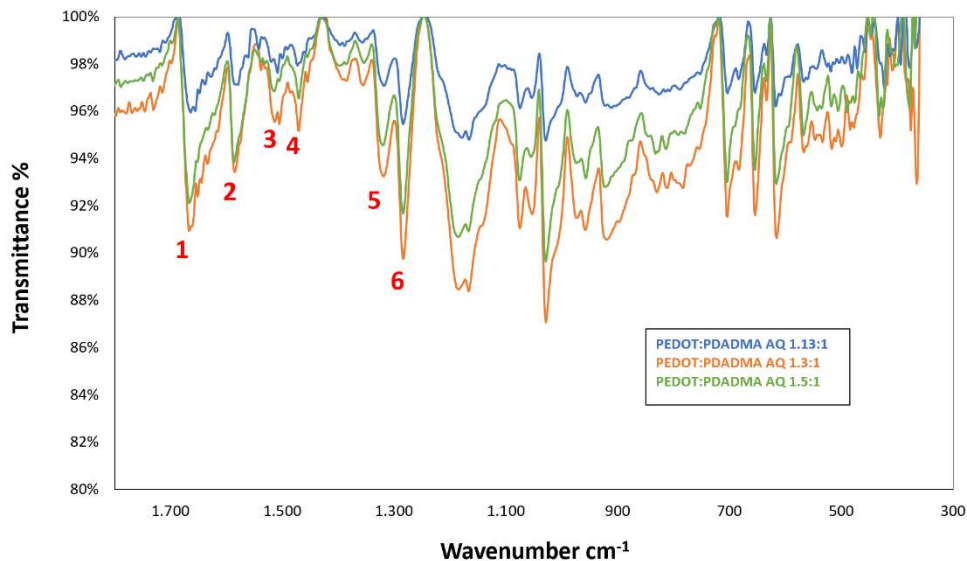


***Figure 19*** *- IR Spectra of PEDOT:PDADMA AQ. The characteristic bands observed are: 1: 1664 cm$^{-1}$, 2: 1586 cm$^{-1}$, 3: 1506 cm$^{-1}$, 4 : 1472 cm$^{-1}$, 5 : 1320 cm$^{1}$, 6 : 1283 cm$^{-1}$.*
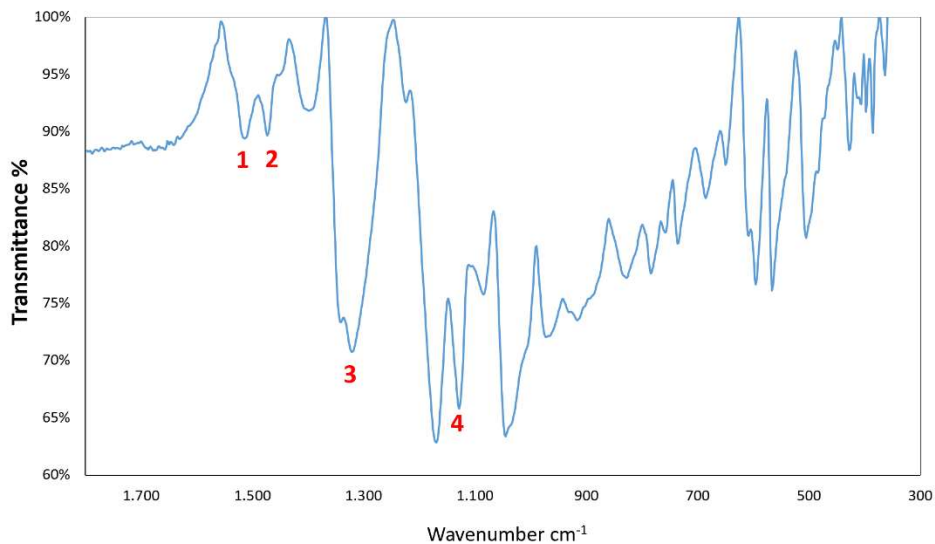


***Figure 20*** *- IR Spectra of PEDOT:PDADMA TFSI. The characteristic bands observed are: 1: 1506 cm$^{-1}$, 2: 1472 cm$^{-1}$, 3: 1318 cm$^{-1}$, 4: 1130 cm$^{-1}$.*

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## 4.3. Thermal Characterization - TGA

Thermogravimetric analysis (TGA) of the polymer blends samples were conducted to investigate their thermal stability in order to do an initial assessment of the relative impact of the different PEDOT:PDADMA ratios and the different anions (AQ and TFSI) on the thermal properties, determining the degradation temperature. Values obtained were also compared with the values obtained by previous studies for PEDOT:PDADMA-TFSI [16] and PDADMA-AQ [7].
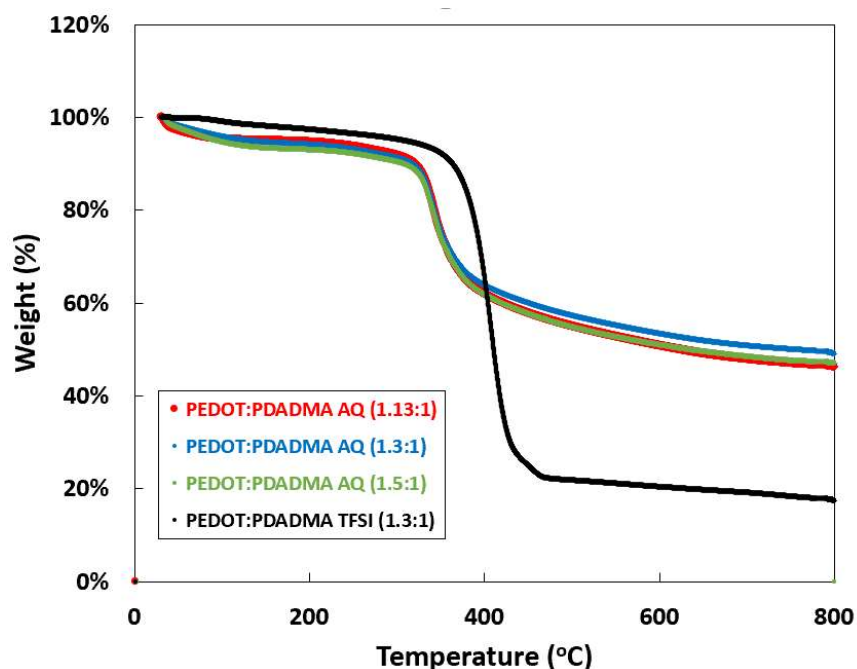


***Figure 21*** *- TGA of the synthesized polymer blends.*

All polymers analyzed presented 5% weight loss related to absorbed water. The redox-active polymer blends presented high thermal stability, with no difference regarding PEDOT:PDADMA molar ratio, as all had the same degradation temperature ($T_d$ = 330°C). PEDOT:PDADMA-TFSI presented the highest degradation temperature ($T_d$ = 370°C). It is also possible to observe that polymers that have AQ as moiety had a higher residual content than the polymer blend that contained TFSI, what is expected as AQ has in its structure aromatic rings. The values obtained are comparable with the data reported in the literature and can be found in **Table 3**.

**Table 3** – *Decomposition temperature (T$_{1,d}$ and T$_{2,d}$) and residual content after TGA for synthesized polymers (PEDOT:PDADMA AQ and PEDOT:PDADMA TFSI) and literature data (PEDOT Cl, PDADMA Cl, PDADMA AQ, PEDOT:PDADMA Cl and PEDOT:PDADMA TFSI).*

| Compound | Molar Ratio | T$_{1,d}$ (°C) | T$_{2,d}$ (°C) | Residual Content (%) |
|---|---|---|---|---|
| PEDOT Cl | 1:1 | 300 (16) | - | - |
| PDADMA Cl | 1:1 | 300 (16) | 450 (16) | - |
| PDADMA AQ | 1:1 | 320 (7) | - | - |
| PEDOT:PDADMA Cl | 1.13:1 | 378 (16) | - | - |
| PEDOT:PDADMA AQ | 1.13:1 | 330 | - | 46 |
| | 1.3:1 | 330 | - | 49 |
| | 1.5:1 | 330 | - | 49 |
| PEDOT:PDADMA TFSI | 1.13:1 | 423 (16) | - | - |
| | 1.3:1 | 370 | - | 17 |

As previously reported PEDOT:PDADMA-TFSI does not have a multi-step decomposition behavior, which is a characteristic of miscible blends, allowing this blend to form a coating via solvent casting[16]. The different polymer blends of PEDOT:PDADMA-AQ synthesized in this study presented a single step decomposition, being also miscible blends.

### 4.4. Transport Properties
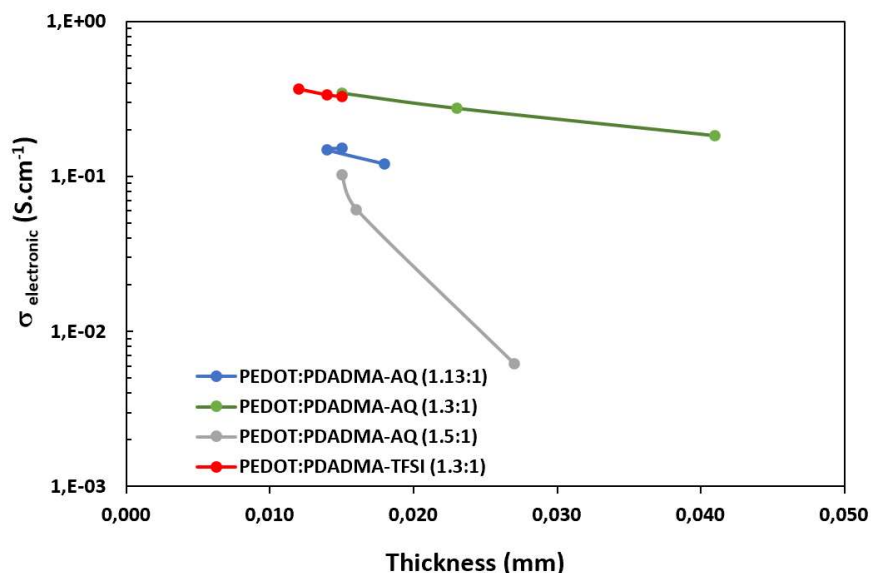
#### 4.4.1. Electronic Conductivity

In order to measure the electronic conductivity of the polymer blends synthesized, films were drop-casted on glass coverslips following the procedure described in section 3.6.1.

**Figure 22** – *Glass coverslips with thin film of PEDOT:PDADMA-AQ.*

The electronic conductivity of PEDOT comes from the existence of polarons and bipolarons formed in the chains, where charges can flow move through the backbone [16]. The electronic conductivity obtained for the different polymers showed that there is a decrease of conductivity

with the increase of film thickness. This effect is well known in the field of electronic conductors [16]. The decrease of thickness increases carrier mobility once larger film thickness allows random coil formation which will result in a much higher intercrystallite energy barrier [26].



**Figure 23** – *Electronic conductivity of PEDOT:PDADMA X.*

Comparing the thin films of similar thickness (15 μm) for different molar ratios of PEDOT:PDADMA it is possible to observe that all polymer blends present different electronic conductivity values, but with the same order of magnitude (between 0.1-1 S/cm). However, with the increase of thickness, each PEDOT:PDADMA ratio have a different behavior. With the increasing concentration of PEDOT there is an increase of the electronic conductivity, but after an optimum value there is an over-doping effect, decreasing the electronic conductivity ($\sigma_{electronic}$ 1.3:1> $\sigma_{electronic}$ 1.13:1 > $\sigma_{electronic}$ 1.5:1).

**Table 4** - *Electronic Conductivity of PEDOT:PDADMA X with varying molar ratios. Literature values for PEDOT:PDADMA TFSI were obtained from Olmo et al [16].*

| Compound | Molar Ratio | Thickness/ μm | Literature Values[16] $\sigma_{electronic}$/ S cm$^{-1}$ | Experimental Values $\sigma_{electronic}$/ S cm$^{-1}$ |
|---|---|---|---|---|
| PEDOT:PDADMA AQ | 1.13:1 | 15 | - | 0.15 |
| | 1.3:1 | 15 | - | 0.34 |
| | 1.5:1 | 15 | - | 0.10 |
| PEDOT:PDADMA TFSI | 1.13:1 | 75 | 0.25 | - |
| | 1.3:1 | 15 | - | 0.33 |

It was not observed a significant difference in the electronic conductivity for PEDOT:PDADMA-AQ 1.3:1 and PEDOT:PDADMA-TFSI, indicating that the content of PEDOT is more important to this property than the moiety present in the polymer blend. Also, when compared the electronic conductivity of PEDOT:PDADMA-TFSI 1.3:1 with literature data it is possible to see that the value obtained experimentally is lower than the reported, but has the same order of magnitude.

### 4.4.2. Ionic Conductivity - Electrochemical Impedance Spectroscopy (EIS)

EIS was performed for all mixed conductors, to determine the ionic conductivity at different temperatures. All Nyquist plots obtained were a closed semi-circle (**Figure 24**), typical of mixed ionic electronic conductors [16].
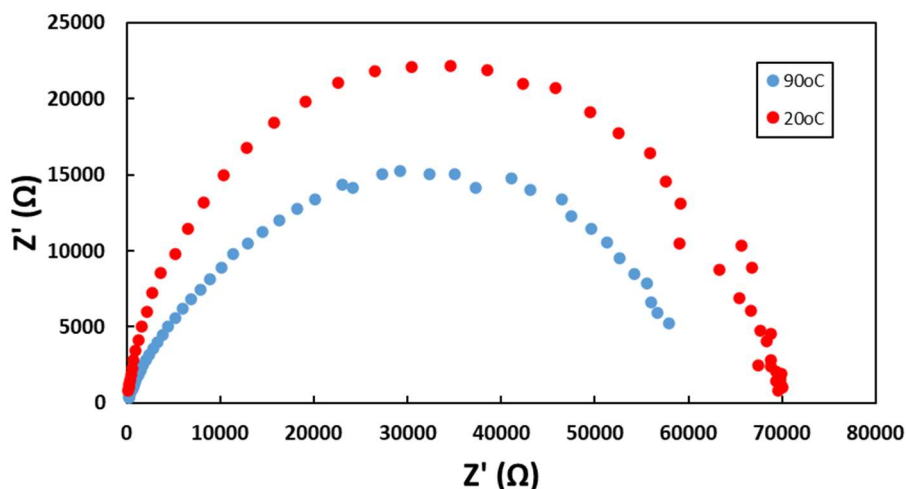


*Figure 24 - Nyquist plot of PEDOT:PDADMA AQ (1.3:1) for different temperatures.*

For all polymer blends the ionic conductivity increased with temperature once this parameter directly affects anion mobility. PEDOT:PDADMA TFSI presented higher values of ionic conductivity for all temperature range studied. The polymer blends containing AQ had close ionic conductivity values, with the same order of magnitude (**Figure 25**). At 70°C, PEDOT:PDADMA TFSI had the highest ionic conductivity value ($4.0 \times 10^{-6}$ S cm$^{-1}$) followed by PEDOT:PDADMA AQ 1.13:1 ($1.1 \times 10^{-7}$ S cm$^{-1}$), then PEDOT:PDADMA AQ 1.3:1 ($8.1 \times 10^{-8}$ S cm$^{-1}$) and finally PEDOT:PDADMA AQ 1.13:1 ($6.5 \times 10^{-8}$ S cm$^{-1}$).
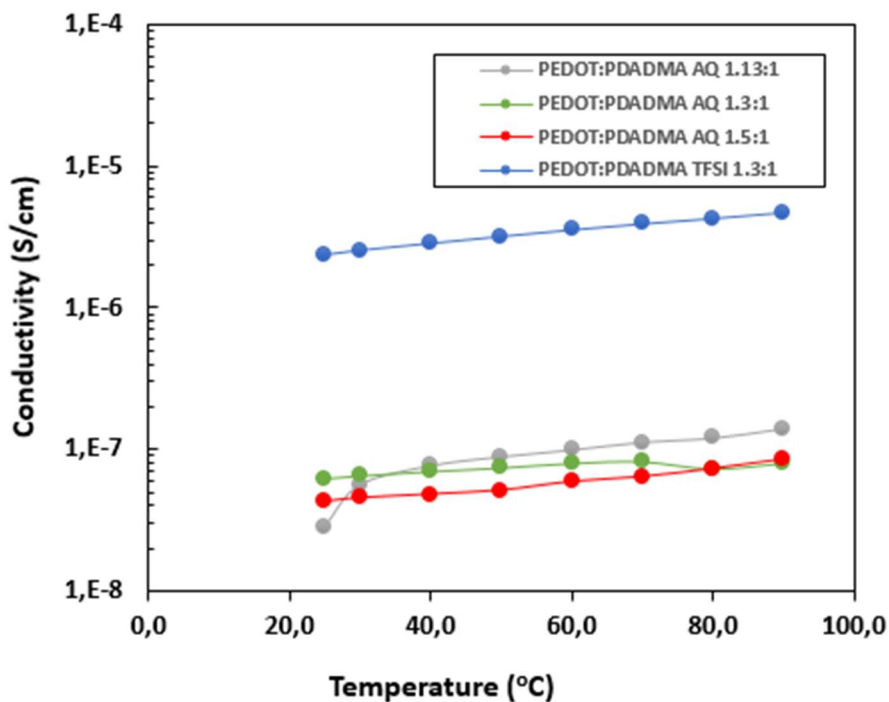
***Figure 25*** *- Ionic Conductivity of the mixed conductors studied.*

Comparing to literature data, the ionic conductivity of PEDOT:PDADMA TFSI at 70°C presented lower value that the previously reported (3 x 10$^{-5}$ S cm$^{-1}$) [16]. This could be related to the higher content of PEDOT in our blend, (PEDOT:PDADMTA TFSI 1.3:1 compared to 1.13:1) and thus, lower TFSI anion content, which is the main contributor to the ionic mobility.

The anthraquinone-2-sulfonate anion (266.4 Å$^3$) [27] is larger than TFSI (143 Å$^3$) [16], as well as more rigid, due to its aromatic rings. As the values for ionic conductivity obtained were lower for mixed conductors containing AQ, the reason can be related to lower mobility due to anion size and rigidity, as AQ is larger and more rigid than TFSI. The values of ionic conductivity for PEDOT:PDADMA AQ with molar ratios studied cannot be considered different.

### 4.5. Electrochemical Properties - CV

To study the electrochemical properties of the synthesized polymer blends, first it was performed a CV to determine the reduction and oxidation potentials for anthraquinone in the proposed arrangement of the electrical cell, that would be the same used for the CVs of the synthetized polymer blends. CVs were performed using a platinum counter electrode, a platinum working

electrode, a Ag/AgNO$_3$ reference electrode and an electrolyte of 0.1M of LiClO$_4$ in acetonitrile, with 1 mM of anthraquinone-2-sulfonate dissolved. **Figure 27** shows that the anthraquinone salt analyzed presented only one reduction and one oxidation peak, at -1.06 V and -1 V respectively. In nonaqueous media, the reductions of quinones (Q) take place by two successive one-electron reduction steps generating two separate cathodic waves. The first step corresponds to the formation of a semiquinone radical Q•− while the second step corresponds to the formation of quinone dianion, Q2−. Semiquinone radicals are short lived and readily undergo disproportionation generating a quinone and its corresponding dianion. Polarity of solvents, ion-pair formation, nature of supporting electrolyte, deprotonation equilibrium, intra- and intermolecular hydrogen bonding and addition of different acidic species or addition of water play important roles in determining the two formal reduction potentials [28]. As in the experiment was observed only one peak for reduction and one for oxidation it is assumed that for this arrangement the redox processes occur too fast to observe the two steps reduction and oxidation.
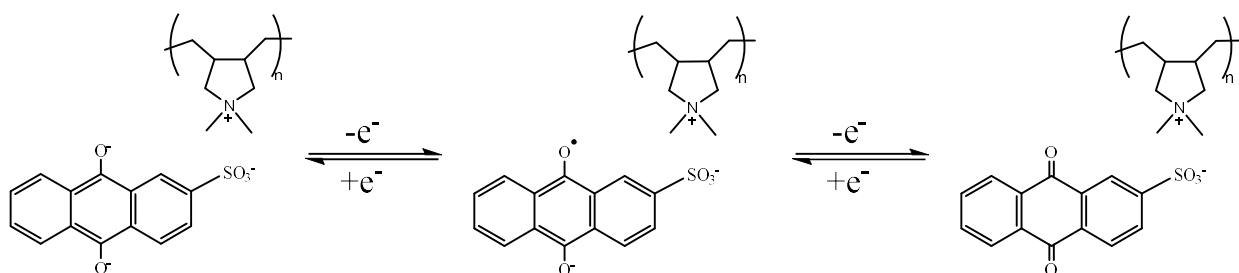


***Figure 26*** *- Redox process of anthraquinone-2-sulfonate as a moiety of PDADMA.*
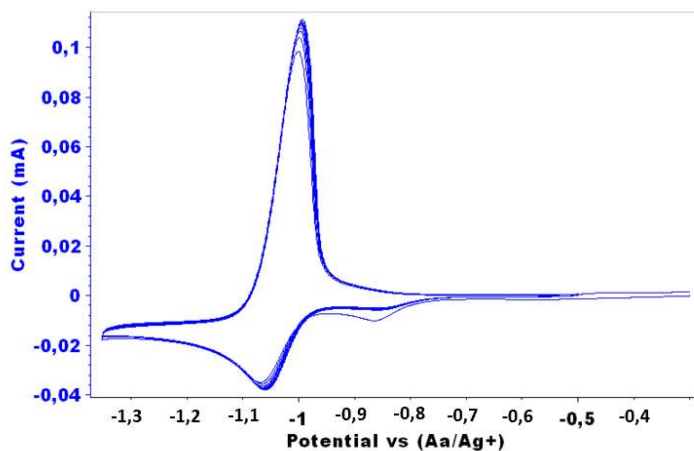


***Figure 27 -*** *Cyclic Voltammetry of anthraquinone-2-sulfonate sodium salt.*

The cyclic Voltammetry of the polymer blends synthesized was carried out in a three-electrode cell, following the procedure described in section3.7.1. Comparing the first cycle of each PEDOT:PDADMA AQ blend (**Figure 28**) it is possible to observe that all polymers present the characteristic redox peaks of anthraquinone and PEDOT. While for PEDOT:PDADMA AQ 1,3:1 and PEDOT:PDADMA AQ 1,5:1 there is only one oxidation peak and one reduction (-0.7 V and -1.0 V, respectively), for PEDOT:PDADMA AQ 1,13:1 it is possible to observe 2 peaks of oxidation and reduction for the AQ at around (-0.7 V, -0.4 V) and (-0.8 V and -0.45 V). The oxidation and reduction peaks of PEDOT polymer are observed in -0.2 V and -0.6 V, respectively in the three polymers. The lower concentration of PEDOT may facilitate the observation of double step of AQ redox process. It is possible to observe as the cycles occur that there was a reduction of AQ peaks intensity, and a shifting of the peaks to higher potentials (to the right of the x axis). This is explained by the dilution of AQ in the electrolyte during the CV, once the ion of the electrolyte, that is $ClO_4$, exchange places in the polymer with AQ, as it is a smaller ion. This behavior of AQ is well known and is one of the challenges to be solved in the development of redox active mixed electronic ionic conductors to be used in energy storage applications.

The CV of PEDOT:PDADMA TFSI was performed showing good stability of the polymer through the cycles. The peaks observed are related to PEDOT oxidation and reduction, while no peak at around -1 V can be observed due to the absence of AQ molecule in this polymer.
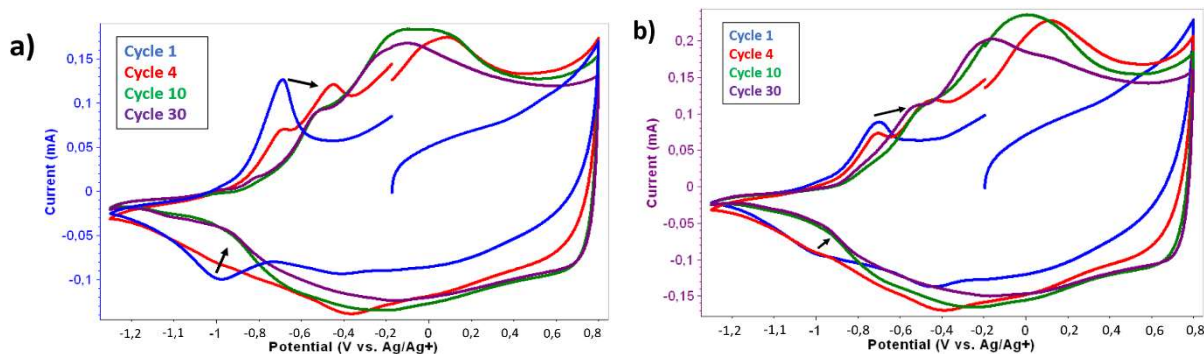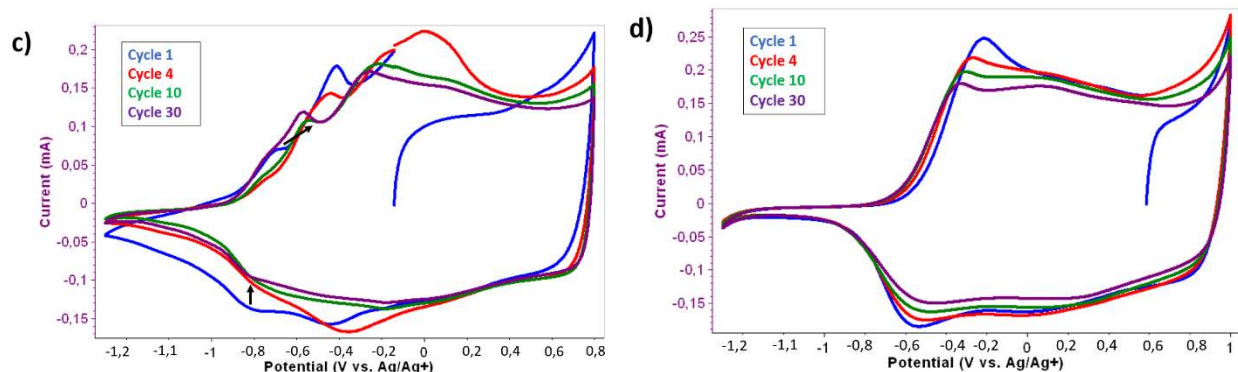
***Figure 28*** - *Cyclic Voltammetry at scan rate of 20 mVs⁻¹ and electrolyte solution of 0.1 M LiClO₄ in acetonitrile of a)
PEDOT:PDADMA AQ 1,3:1; b) PEDOT:PDADMA AQ 1,5:1; c) PEDOT:PDADMA AQ 1,13:1:1; d)PEDOT:PDADMA
TFSI*

### 4.6. Half Cell Lithium Batteries

As final application, the polymers were used as cathode materials for lithium batteries. For that, half Cell Lithium Batteries were assembled using the polymer blends as cathodes. For each polymer blend synthetized, two batteries were assembled for each of the electrolytes used (0.1M LiClO₄ in EC/DEC (1:1), 0.1M LiTFSI in DOL/DME (1:1) and 0.1M LiPF₆ in EC/DEC (1:1)), making a total of 6 batteries per polymer studied.

To verify the performance of this new materials as battery cathode the following tests were made. First, a CV of the battery was done between 0.5 V and 0.8 V vs. Li⁺/Li at a scan rate of 5 mV s⁻¹, for 5 cycles. Observing the CVs (**Figure 31**) it is possible to verify the AQ and PEDOT redox peaks.

After the CVs, a galvanostatic charge/ discharge test with different C-rates (0.3C, 0.5C, 1C, 2C, 4C) were performed. The C-rate was calculated considering AQ. For that it is necessary to also determine the theoretical capacity of the cell (C):

$$i\,(A) = C\text{-}rate \cdot \frac{C_{max}\,(Ah)}{1(h)} \qquad C\,(Ah) = \frac{i\,(A) \cdot t\,(s)}{3600\,(s/h)}$$

The value obtained for the theoretical capacity, considering only the AQ content was 187 mA h g⁻¹ (1C).

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**Figures 29** show that LiPF$_6$ had the higher values of specific capacity for every mixed conductor studied. For all coin cells the specific capacity found was lower than the theoretical. This can may be related to film quality. As expected, as higher the C-rate, lower the specific capacity.



**(a)**



**(b)**



**(c)**
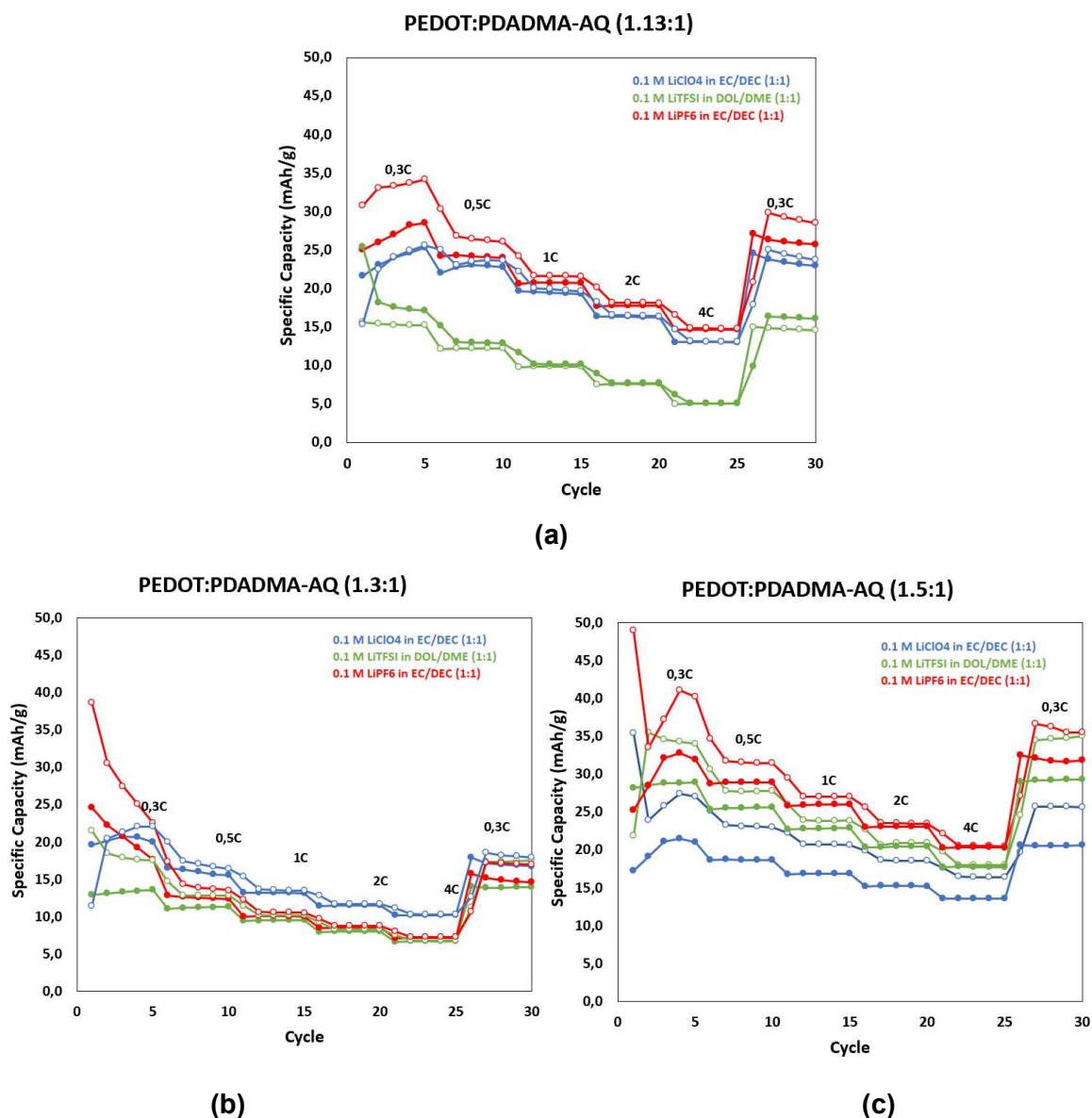
*Figure 29 - Specific capacity of the different polymer blends used as cathode in coin cells using lithium as anode and different electrolytes. Charge values are hollow markers and discharge values full markers. (a) PEDOT:PDADMA AQ (1.13:1); (b) PEDOT:PDADMA AQ (1.3:1); (c) PEDOT:PDADMA AQ (1.5:1)*

A comparison between the 3 polymer blends that contain AQ and the reference polymer blend that contain as moiety TFSI for the cells using the same electrolyte can be done. PEDOT:PDADMA AQ 1.5:1 had higher specific capacity of all polymer blend. PEDOT:PDADMA AQ 1.3:1 should have a higher capacity than PEDOT:PDADMA TFSI 1.3:1, as TFSI does not contribute to the capacity, showing that the influence of the quality of the film casted, as other influences during the preparation of the film, can affect specific capacity. It can also be concluded that the quantity of PEDOT had more influence in the capacity than content of AQ.

## 0.1M LiPF6 in EC/DEC (1:1)
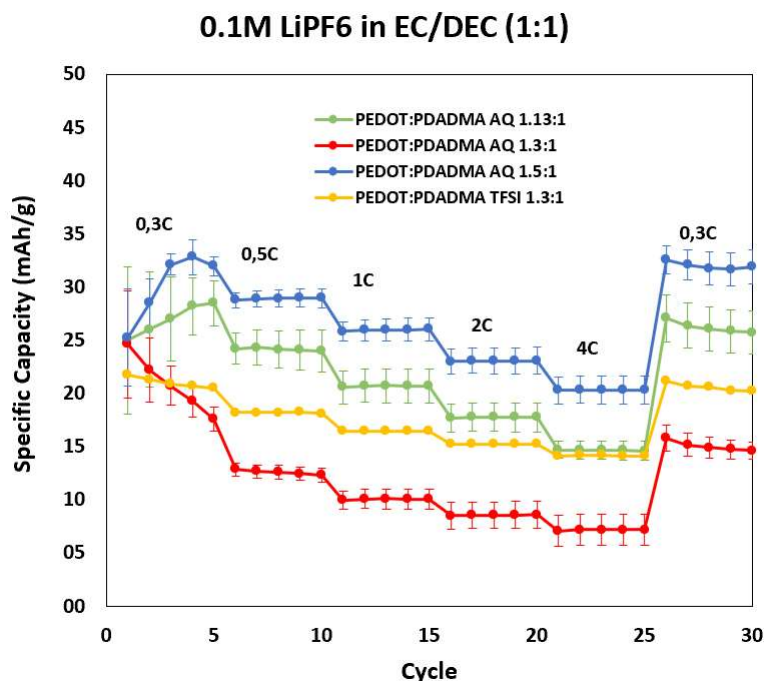


**Figure 30** – *Galvanostatic test results for the four polymer blends synthesized, in a coin cell using 0.1M LiPF$_6$ in EC/DEC (1:1) as electrolyte.*

A new CV was performed after the Galvanostatic charge/discharge test, and it was possible to observe that the AQ peaks when the electrolytes are LiClO$_4$ and LiPF$_6$ were used disappeared, once again showing that there was an ionic exchange between the polymer and the electrolyte. The electrolyte with LiTFSI the CV after charge/discharge presented even more pronounced the AQ redox peaks than the first CV performed, showing that there was not an exchange, but a swallow making possible to see anthraquinone's 2 step redox process. As it was not verified that the batteries containing this electrolyte had higher specific capacities, one conclusion is that the AQ content is not making difference in this property.

**(a)**



**(b)**



**(c)**
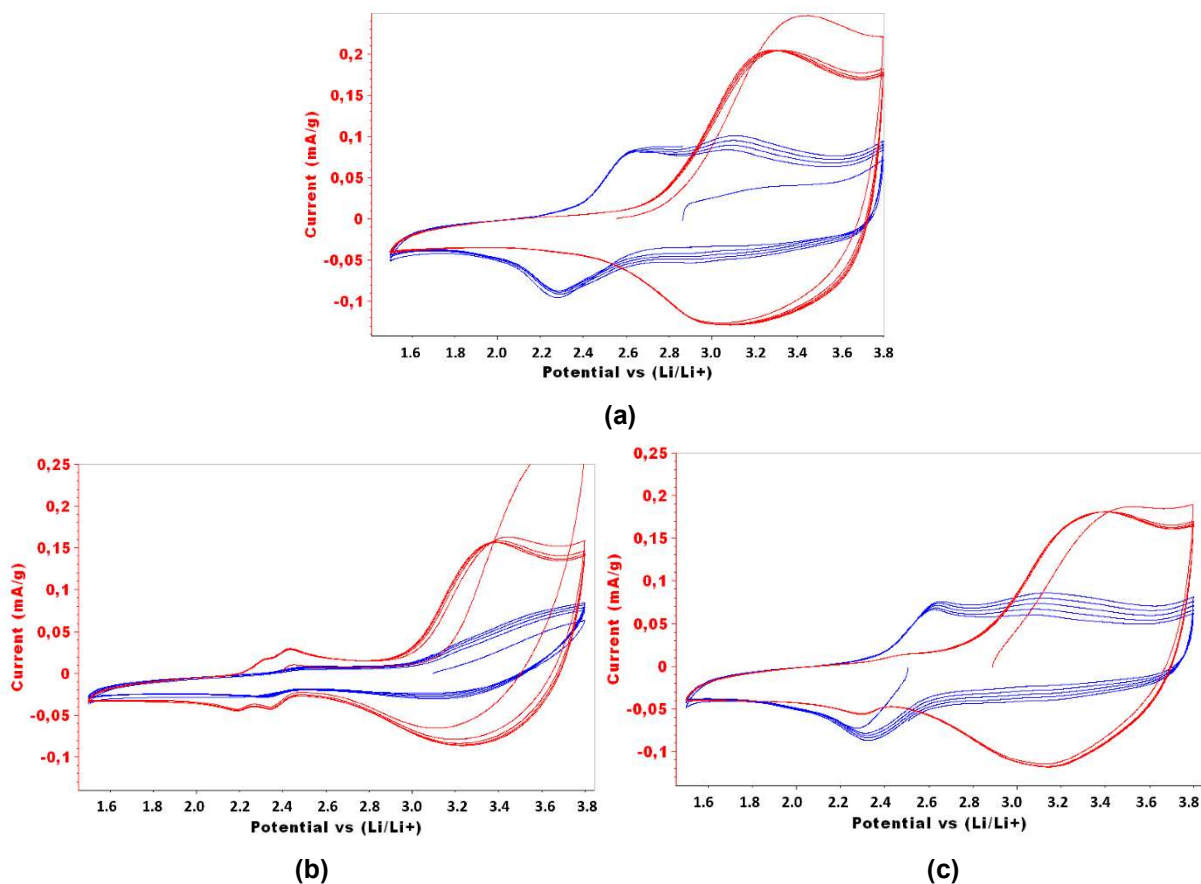
*Figure 31 – Cyclic Voltammetry of coin cells of PEDOT:PDADMA AQ 1.13:1 as a cathode and different electrolytes. Blue represent the CV done before galvanostatic charge/discharge and red the CV after charge/discharge. For the different electrolytes (a) 0.1M LiPF$_6$ in EC/DC (1:1); (b) 0.1M LiTFSI in DOL/DME (1:1); (c) 0.1M LiClO$_4$ in EC/DC (1:1)*

Last, the batteries then were cycled in another galvanostatic charge/discharge at fixed C-rate (0.5C) for 100 cycles (**figure 32**). The batteries presented good stability, with low values of capacity loss (**table 5**).

*Table 5 – Specific capacity loss after 100 cycles of charge/discharge for coin cells of different polymer blends as cathode, lithium as anode and 0.1M LiPF$_6$ in EC/DC (1:1) as electrolyte.*

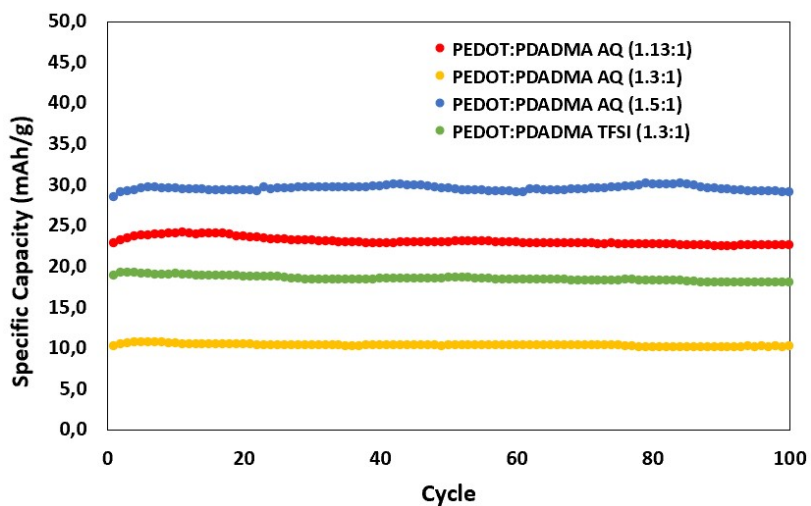| Long Cycling | |
|---|---|
| **Polymer** | **Capacity loss** |
| PEDOT:PDADMA AQ 1.13:1 | 4,7% |
| PEDOT:PDADMA AQ 1.3:1 | 4,1% |
| PEDOT:PDADMA AQ 1.5:1 | 0,3% |
| PEDOT:PDADMA TFSI 1.3:1 | 5,5% |

***Figure 32*** *– Specific capacity during 100 cycles of charge/discharge for coin cells of different polymer blends as cathode, lithium as anode and 0.1M LiPF$_6$ in EC/DC (1:1) as electrolyte.*

## 5. CONCLUSION

In this project PEDOT:PDADMA AQ was synthesized with different molar ratios. Then, the characterization of these polymer blends was carried out using some common techniques: FTIR, TGA, EIS, CV and 4 point probe. Batteries using these polymers as cathodes were also assembled and tested using CV and Galvanostatic Charge/Discharge technique. PEDOT:PDADMA TFSI was also synthetized and characterized to be used as a reference material. The main goal was to synthesize polymers with the 3 functionalities needed in a battery electrode, i.e. electronic and ionic conductivity, as well as redox properties. The incorporation of AQ moiety to PEDOT:PDADMA polymer, increased the redox properties of the polymer.

The incorporation of antrhaquinone-2-sulfonate to the three polymers was demonstrated by IR and by the presence of AQ redox peaks in CV of the polymer. It was observed that higher a PEDOT content derive to slightly higher electronic conductivity, while no differences were observed related to ionic conductivity. As a cathode, the values of specific capacity obtained for the polymer blends were below the theoretical capacity, being the polymer with the higher content of PEDOT the one that presented higher specific capacity. The reference polymer blend (PEDOT:PDADMA TFSI 1.3:1) presented higher capacity than the PEDOT:PDADMA AQ 1.3:1, which may be related to the preparation of the cathode. The small influence of the redox active moiety AQ may be to its elution on the electrolyte. The elution of AQ can be confirmed by CV of the polymer in electrochemical cells and the CVs preformed with the batteries before and after galvanostatic charge discharge tests.

For future works, it is necessary to increase the content of AQ in the polymer blends through the increase of excess anthraquinone-2-sulfonate salt in ionic exchange reaction. Solutions to minimize the elution of this moiety should also be studied to make viable the usage of this material as a cathode for energy storage applications.

## 6. REFERENCES

(1) Crompton, T. R. "Battery Reference Book — Second Edition." Fuel and Energy Abstracts, vol. 37, no. 3, 1996, doi:10.1016/0140-6701(96)88678-4.

(2) Schmidt-Rohr, Klaus. "How Batteries Store and Release Energy: Explaining Basic Electrochemistry." Journal of Chemical Education, vol. 95, no. 10, 2018, doi:10.1021/acs.jchemed.8b00479.

(3) Schumm, Brooke. "Battery". Encyclopedia Britannica, 5 Mar. 2021, Accessed 28 June 2021.<https://www.britannica.com/technology/battery-electronics>.

(4) Grandviewresearch. "Lithium-Ion Battery Market Size & Share Report, 2020-2027." Grandviewresearch.Com, 2020.

(5) Goujon, Nicolas, et al. "Chapter 8: Redox Polymers for All-Organic Batteries." RSC Polymer Chemistry Series, vol. 2021-January, no. 24, 2021, doi:10.1039/9781788019743-00288.

(6) Casado, Nerea, et al. "PEDOT Radical Polymer with Synergetic Redox and Electrical Properties." ACS Macro Letters, vol. 5, no. 1, 2016, doi:10.1021/acsmacrolett.5b00811.

(7) Hernández, G., et al. "Redox-Active Poly(Ionic Liquid)s as Active Materials for Energy Storage Applications." Journal of Materials Chemistry A, vol. 5, no. 31, 2017, doi:10.1039/c6ta10056b.

(8) Zhu, Limin, et al. "Anthraquinones with Ionizable Sodium Sulfonate Groups as Renewable Cathode Materials for Sodium-Ion Batteries." ChemElectroChem, vol. 6, no. 3, 2019, doi:10.1002/celc.201801252.

(9) Nezakati, Toktam, et al. "Conductive Polymers: Opportunities and Challenges in Biomedical Applications." Chemical Reviews, vol. 118, no. 14, 2018, doi:10.1021/acs.chemrev.6b00275.

(10) Gueye, Magatte N., et al. "Progress in Understanding Structure and Transport Properties

of PEDOT-Based Materials: A Critical Review." Progress in Materials Science, vol. 108, 2020, doi:10.1016/j.pmatsci.2019.100616.

(11) Elschner, Andreas, et al. "PEDOT: Principles and Applications of an Intrinsically Conductive Polyme." PEDOT: Principles and Applications of an Intrinsically Conductive Polymer, 2010, doi:10.1201/b10318.

(12) Sun, Kuan, et al. "Review on Application of PEDOTs and PEDOT:PSS in Energy Conversion and Storage Devices." Journal of Materials Science: Materials in Electronics, vol. 26, no. 7, 2015, doi:10.1007/s10854-015-2895-5.

(13) Yuan, Jiayin, et al. "Progress in Polymer Science Poly (Ionic Liquid) S : An Update." Progress in Polymer Science, vol. 38, no. 7, 2013.

(14) Assem, Yasser, et al. "Poly(Diallyldimethylammonium Chloride)/Clay Nanocomposites: Effect of Molecular Weight and Concentration of Polymer on the Structural, Thermal, and Dielectric Properties." Polymer Bulletin, vol. 74, no. 8, 2017, doi:10.1007/s00289-016-1873-2.

(15) Paulsen, Bryan D., et al. "Organic Mixed Ionic–Electronic Conductors." Nature Materials, vol. 19, no. 1, 2020, doi:10.1038/s41563-019-0435-z.

(16) Olmo, Rafael Del, et al. "Mixed Ionic-Electronic Conductors Based on PEDOT:PolyDADMA and Organic Ionic Plastic Crystals." Polymers, vol. 12, no. 9, 2020, doi:10.3390/polym12091981.

(17) Guide to Infrared Spectroscopy, Bruker, accessed 20 June 2021, < https://www.bruker.com>

(18) Wagner, M. (2017). "Thermogravimetric Analysis. Thermal Analysis in Practice", 162–186, 2018, doi:10.3139/9781569906446.010.

(19) Sheet Resistance Measurements of Thin Films, Ossila, acessed 20 June 2021, <https://www.ossila.com/pages/sheet-resistance-measurements-thin-films>

(20) Lasia, Andrzej. "Electrochemical Impedance Spectroscopy and Its Applications."

Electrochemical Impedance Spectroscopy and Its Applications, vol. 9781461489337, 2014, doi:10.1007/978-1-4614-8933-7.

(21) Lacey, Matt. The principles of electrochemical impedance spectroscopy, accessed 20 June 2021, < http://lacey.se/science/eis/eis-principles/>

(22) Electrochemical Impedance Spectroscopy (EIS), PalmSens, accessed 15 June 2021, <https://www.palmsens.com/knowledgebase-article/electrochemical-impedance-spectroscopy-eis/>

(23) Elgrishi, Noémie, et al. "A Practical Beginner's Guide to Cyclic Voltammetry." Journal of Chemical Education, vol. 95, no. 2, 2018, doi:10.1021/acs.jchemed.7b00361.

(24) Gamry Instruments. "Testing Electrochemical Capacitors Part 2 – Cyclic Charge Discharge and Stacks." Gamry Application Notes, no. V, 2012.

(25) Metrohm Autolab. "Galvanostatic Charge-Discharge of a Li-Ion Battery with Autolab." Autolab Application Note, 2014.

(26) Wang, Xiaoxue, et al. "High Electrical Conductivity and Carrier Mobility in OCVD PEDOT Thin Films by Engineered Crystallization and Acid Treatment." Science Advances, vol. 4, no. 9, 2018, doi:10.1126/sciadv.aat5780.

(27) Anusevičius, Žilvinas, et al. "Two-Electron Reduction of Quinones by Rat Liver NAD(P)H:Quinone Oxidoreductase: Quantitative Structure-Activity Relationships." Archives of Biochemistry and Biophysics, vol. 404, no. 2, 2002, doi:10.1016/S0003-9861(02)00273-4.

(28) Guin, Partha Sarathi, et al. "Electrochemical Reduction of Quinones in Different Media: A Review." International Journal of Electrochemistry, vol. 2011, 2011, doi:10.4061/2011/816202.