

# Conducting polymers as positive electrodes in rechargeable lithium-ion batteries

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## Abstract

The influence of the conditions of synthesis, such as both monomer and electrolyte concentrations, the electric potential of synthesis and temperature of work or the chosen solvent, on the properties of the polymeric material to be used as cathode of lithium-ion batteries, was studied. A similar study was performed to obtain three conducting polymers, as polypyrrole, polythiophene or poly-3-methylthiophene. Specific charges of the obtained materials, as a function of the conditions of synthesis were analysed. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Conducting polymers; Batteries; Li-ion; Rocking chair; Polypyrrole

## 1. Introduction

The batteries called ‘rocking-chair’ systems, are one of the most promising storage devices for the next years [1]. Schematically the operation of these batteries occurs together with an interchange of ions between the solution and the electrodes [2]. The direction of the ions depends on the electrode (anode or cathode) and the running way (charge or discharge) [3]. Different materials can be employed as electrode. In general they must be either conductive or porous in order to allow the interchange of the anions, and, if possible to have a high charge density with low weight [4]. Graphite and other carbonaceous materials are the most usual anodes [5]. As cathodes, two families of materials are mainly used: metal oxides [6] and conducting polymers [7–9]. Polyacetylene, polyaniline, polythiophene or polypyrrole [10] are some of the polymers able to conduct electrons and ions. The higher conductivities are related to an oxidation state of the material [11]. Then, positive charges are present along the polymer chains and anions from the electrolyte were inserted into the polymer in order to maintain the electrical neutrality [12–15]. These anions are eliminated from the film during reduction [16,17].

Conducting polymers obtained by both chemical or electrochemical synthesis are mixed materials: a result of the parallel crosslinking, degradation and chemical polymerizations triggered by the electrochemical synthesis. This means that properties of the final material can be altered by changing the conditions of synthesis [18–20]. The aim of this work is to evaluate the influence of the synthesis conditions on the specific charge of the polypyrrole, polythiophene and poly-3-methylthiophene.

## 2. Experimental

Polypyrrole, polythiophene and poly-3-methylthiophene films were electrogenerated and checked in a one-compartment electrochemical cell, connected to a PAR M273 potentiostat–galvanostat connected to a PC Pentium computer. The working electrode was a 1 cm<sup>2</sup> platinum sheet and as counterelectrode, a 2 cm<sup>2</sup> platinum sheet was used. A reference electrode of Ag/AgCl from Crison Instruments was used. It was directly put into the cell. Methanol (Lab Scan, HPLC grade), water (obtained from Milli Q Reagent Water System equipment, fed by Milli RO 4 water purification system), acetonitrile (Lab Scan, HPLC grade), *N,N'*-dimethylformamide (Panreac, for analysis) and anhydrous lithium perchlorate (Janssen, min 99% content) were used as received. All the solutions were deaerated by bubbling of N<sub>2</sub> gas for 20 min before the

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current flow. Once the polymer film is generated, the working electrode was dried in acetone, weighed and transferred into the background solution (0.1 M LiClO<sub>4</sub> in the studied solvent), in absence of monomer, where it was submitted to voltammetric analysis.

The specific charge (s.c.) is the electrical charge stored in a polymer film, per unit of mass. In this work, s.c. values (A h kg<sup>-1</sup>) were determined from the ratio between the stored charge, (anodic or cathodic) (A h) and the polymer weight (kg) adhered to the electrode along the electrogeneration process.

### 3. Results and discussion

The flow of an electric current through a solution containing a monomer, like pyrrole, thiophene or 3-methylthiophene, initiate a complex process, giving a polymeric film on the anode. During the process parallel reactions like electrogeneration of polyconjugated chains, cross-linking between chains, degradation processes and parallel chemical polymerisation occur [21]. The composition of the final material is a function of the relative rates of those simultaneous processes and those rates change when the conditions of synthesis change. Polymeric properties being a function of the material composition, the specific charge stored in the obtained polymers have to be related to the conditions of synthesis.

#### 3.1. Solvent influence

All the electropolymerisation processes occur from a solution. We studied the electrogeneration of polypyrrole films from acetonitrile, benzonitrile, dichloromethane,

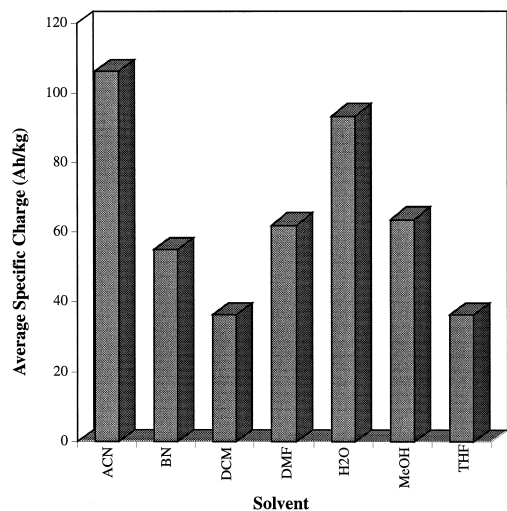


Fig. 1. Average specific charges obtained in polypyrrole films using different conditions in acetonitrile (ACN), benzonitrile (BN), dichloromethane (DCM), *N,N'*-dimethylformamide (DMF), water (H<sub>2</sub>O), methanol (MeOH) and tetrahydrofuran (THF).

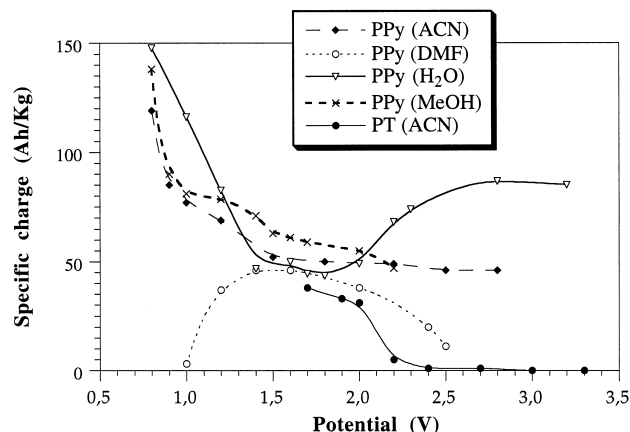


Fig. 2. Evolution of the specific charge with the potential of generation in polypyrrole films (using four different solvents during generation) and polythiophene films.

*N,N'*-dimethylformamide, methanol, tetrahydrofuran and water using lithium perchlorate as electrolyte. Films were electrogenerated from different concentrations of electrolyte, from different concentrations of monomer or using different temperatures, at different polymerisation times for each value of any variable. The average values of the specific charge stored in the different films obtained from every solvent are shown by Fig. 1. Acetonitrile and water resulted as the best solvents in producing films of conducting polymers for batteries.

#### 3.2. Potential of polymerisation

Previous results only represent average values. Some of the variables of synthesis have a strong influence on the relative rates of the parallel reactions, therefore likewise on the final composition and properties of the obtained films. One of those variables is the potential of polymerisation. Increasing current densities and increasing polymerisation rates are obtained at increasing potentials. Nevertheless, the higher oxidation power improves crosslinking and degradation reactions giving polymeric films with decreasing specific energies, as can be observed on Fig. 2. An exception to the general evolution is observed when DMF was used as solvent. This fact can be due to the nucleophilic character of this solvent. As conclusion, low potentials and low polymerisation rates result to the best conditions in order to obtain polymeric films having the higher specific charges. However, the oxidation potential of the monomer must be reached to obtain a polymer film. As is shown in Fig. 2 potentials under 0.8 V using pyrrole and 1.7 V using thiophene do not give any significant polymeric growth. The use of nucleophilic solvents does not favour the acquisition of good materials to store electrical energy. A fast degradation of the polymeric properties occurs when increasing potentials are used to generate the films.

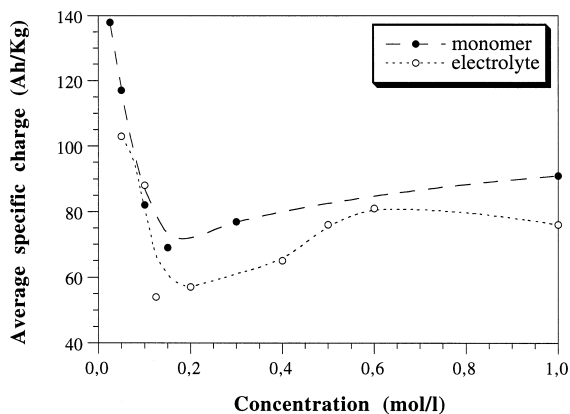


Fig. 3. Influence of the monomer and electrolyte concentrations in the specific charge of polypyrrole films. Every point represents an average value of the specific charge stored in the films generated at cited monomer or electrolyte concentrations.

### 3.3. Influence of the kinetic variables of synthesis

Similarly averaged were those values attained from films of polypyrrole obtained at different concentrations of electrolyte, or different concentrations of monomer (Fig. 3), keeping constant all the other variables. So, every point represents an average value of 15 films, obtained at different polarisation times. The fast initial decrease of the specific charge when any of those concentrations increases, seems related to the parallel fast increase of the polymerisation rate, with the subsequent fast pH variation in the polymer layer due to the deprotonation steps linked to the incorporation of every monomeric unit [16].

Fast variations of the polymerisation rate along the initial oxidation–polymerisation times, linked to the existence of a nucleation process, also seems the origin of the fast decrease on the average specific charge along the initial 10 s of polymerisation (Fig. 4). In the same figure, a

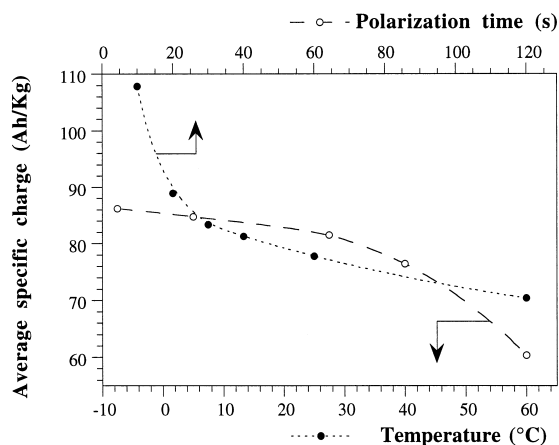


Fig. 4. Influence of the time and temperature in the specific charge of polypyrrole films. Every point represents an average value of the specific charge stored in the films generated at cited temperatures or polymerisation times.

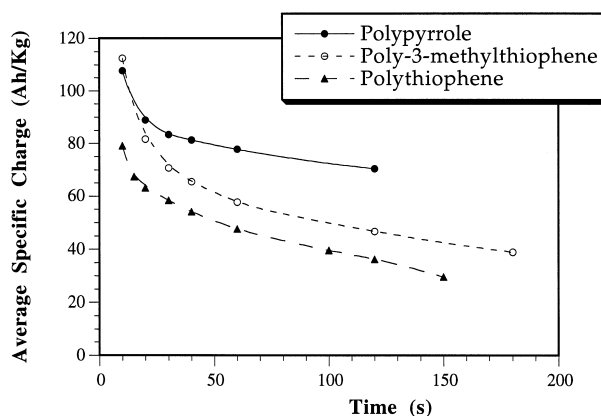


Fig. 5. Evolution of the average specific charge when polymerization time is increased using polypyrrole, poly-3-methylthiophene and thiophene films.

progressive decrease of the storage ability in films synthesised at increasing temperatures, from  $-10$  to  $25^{\circ}\text{C}$  can be observed. Higher temperatures promote a fast increase of the parallel degradation processes.

When thiophene or 3-methylthiophene are employed, similar evolution with the kinetic variables are obtained. In all cases, specific charges obtained in polythiophene show the lowest values keeping the poly 3-methylthiophene evolution in between the two other as can be seen in Fig. 5.

## 4. Conclusions

The specific charge stored in conducting polymers is under control of the conditions of polymeric synthesis. First of all, an adequate solvent has to be chosen, acetonitrile and water being the best in those studied here. Films having high specific charges were obtained at low potential of polymerization, short polymerization times and lower temperatures than  $30^{\circ}\text{C}$ . Very low monomer and electrolyte concentrations promotes the generation of films with very high specific charges but this polymer characteristic drops when both concentrations are increased. A higher increment of these concentrations attains the obtention of films with slightly higher specific charges.

The evolution of the influence of the synthesis variables in the polythiophene and poly-3-methylthiophene is similar to that obtained when pyrrole was employed. In general, polypyrrole films show the best specific charges and polythiophene the lowest.

## Acknowledgements

This work was developed with the economic support of the Industry Department of the Basque Country Govern-

ment (Project OD97UN17) and the collaboration of CE-GASA.

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