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**ELECTROCHEMICAL PERFORMANCE OF ORGANIC
ELECTROACTIVE MATERIALS FOR APPLICATION IN
RECHARGEABLE BATTERIES**

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ABSTRACT: Rechargeable batteries consisting of organic base electrodes are increasingly being studied as an alternative to conventional inorganic electrodes. The approach adopted in this work involves the development of new cathode organic materials based on polyimide derivatives with significant redox potential or capacity in order to increase stability and improve the energy density of current lithium ion cells. Preparation of organic polymeric polyimides was carried out, followed by their integration in an electrode structure that uses carbon nanofibers, as a support and as a means to increase conductivity. An electrochemical study based on cyclic voltammetry was conducted in order to evaluate the performance and redox capacity of the electrodes. The implemented strategy is based on the fact that the aromatic imide group may be electrochemically reduced and oxidized in a reversible manner, with each molecule of polyimide being able to transfer four electrons in two steps, accounting for a high specific capacity of the electrodes. Some of the composite electrodes studied in this work demonstrated good redox capacity, stability under potential cycling and higher current densities, 10-20X, than those reported in the literatures for similar compounds.

Keywords: organic electroactive materials, rechargeable batteries, polyimide.

1. INTRODUCTION

Lithium batteries have attracted considerable attention due to increasing demand for portable electronic devices and electric vehicles [1]. Secondary batteries have been regarded as an environmentally benign technology because of their rechargeability which contributes to reducing the amount of discarded primary batteries [2]. However, secondary batteries still remain immature from the viewpoints of green chemistry and safety concerns. Some electrode active materials in conventional batteries have been made from metals such as cobalt, manganese, and nickel [3]. Most of batteries have been landfilled (only part of them were recycled for the metals) [2]. Secondary batteries, such as Li-ion and Ni-Cd, face over-heating issues and the tightening of regulation issues of hazardous substances, respectively. Over-heating is a serious concern since it has resulted in a series of ignition accidents [4]. The regulations against hazardous substances have become stricter on a global scale [2].

While metal- or metal-based materials such as LiCoO_2 , LiMnO_2 , and V_2O_5 are widely exploited as electrode-active mate-

rials, they are limitations due to their toxicity and the limitation of natural metal resources [5].

Cathodes based on organic/polymeric materials are more advantageous than conventional cathode materials based on transition metal oxides, as they are lightweight, environmentally friendly and amenable to processing [6].

Redox-active organic polymers have been widely used as anti-oxidants and photostabilizers, as well as oxidizing agents for organic synthesis, due to their rapid and reversible oxidation and reduction processes [7]. Charge storage within the redox-active organic polymers could lead to new electrode-active materials for application in rechargeable batteries.

In this work, aromatic polyimide derivatives were synthesized with the objective of evaluating its electrochemical potential as an organic polymer cathode in rechargeable lithium batteries. These imide derivatives were chosen on the basis of their known good reaction reversibility of the imide group and the stability of the polymer framework [8]. Aromatic polyimides are known for their excellent thermal stability, chemical and solvent resistance. Furthermore, since the polyimide is hy-

drolysable, its use can also be considered environmentally friendly [2].

2. EXPERIMENTAL

To prepare the polyimide composite electrode, a layer of a polyamic acid (PAA) nanocomposite (2.8 mg) was applied on a glassy carbon plate (0.2 cm² geometric area).

The nanocomposite constituted by PAA, carbon nanofiber (VGCF) and polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) in the ratio of 1:2:1 (w/w/w). The mixture was treated in vacuum at 40°C for 12 hours to complete evaporation of the solvent. The composite was then subjected to dehydration at 400°C (furnace with forced Argon circulation) during 3.5 hours with further gradual cooling to room temperature, in inert atmosphere.

The electrochemical performance of the prepared electrodes was evaluated by cyclic voltammetry using a solution of tetrabutylammonium perchlorate in propylene carbonate, 0.1M, as electrolyte. An electrode of Ag / AgCl was used as a reference electrode and a platinum rod as an auxiliary electrode. Different tests were performed with scan rates varying from 1mVs⁻¹ and 10 mVs⁻¹ and potential ranges between -1.7 V and 1.7 V.

Analysis by scanning electron microscopy of the composite electrode before and after the cyclic voltammetry tests was carried out using a Phillips XL 30 Model FEG Scanning Electron Microscopy (SEM), coupled with Energy Dispersion Spectroscopy (EDS).

3. RESULTS

Aromatic polyimides were prepared by polycondensation of dianhydride **A** and diamine **B**, with *N,N*-dimethylacetamide as solvent, to form the corresponding polyamic acids (figure 1). These intermediates were converted to polyimides by thermal dehydration in inert atmosphere. The complete imidization was confirmed by FTIR analysis with the presence of characteristic imide absorption bands at 1680 and 1500 cm⁻¹.

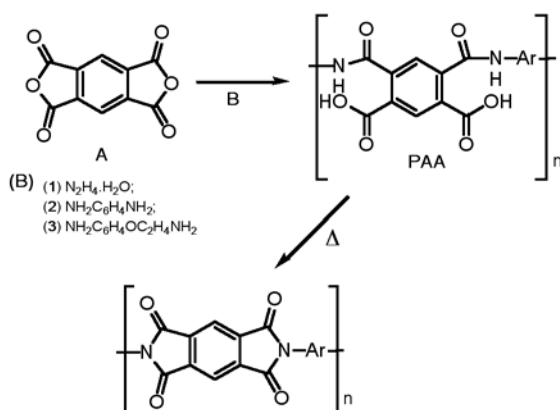


Fig. 1. Synthetic route chosen for the preparation of the polyimides of this work.

However, the obtained polyimides were shown to be completely insoluble materials and difficult to process. For the electrode manufacture it was used the soluble polyimide precursors, the polyamic acids (PAA). After casting, the PAA were heat treated to imidize the carboxylic groups. The radical-based electrodes were fabricated by blending the organic material (PAA), conductive carbon and poly(vinylidene fluoride) binder, mixed in NMP solvent. The viscous slurry was cast on a glassy carbon plate. Electroactivity of the materials was evaluated by cyclic voltammetry.

The electrode made from poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline) (compound **3**, figure 1) has shown the best performance and the results are presented herein. Cyclic voltammograms of this electrode at different scan rates is shown in figure 2.

The voltammograms show two oxidation peaks (A1 and A2) and two reductions peaks (C1 and C2) corresponding to electron transfer processes in two steps, involving the four carbonyl groups present in the molecule of the polyimide. The reduction and oxidation peaks are thought to correspond with the insertion and de-insertion of the tetrabutylammonium (TBA) ions. The reaction processes for are presented in figures 2b) and 2c).

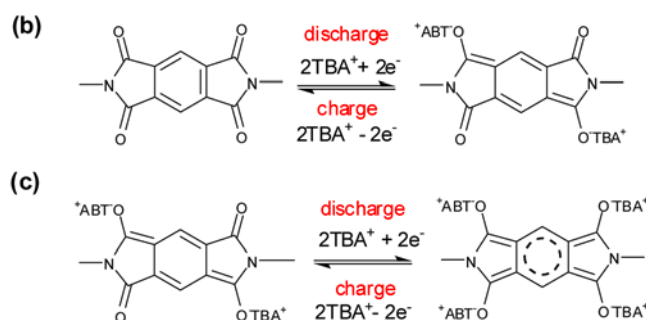
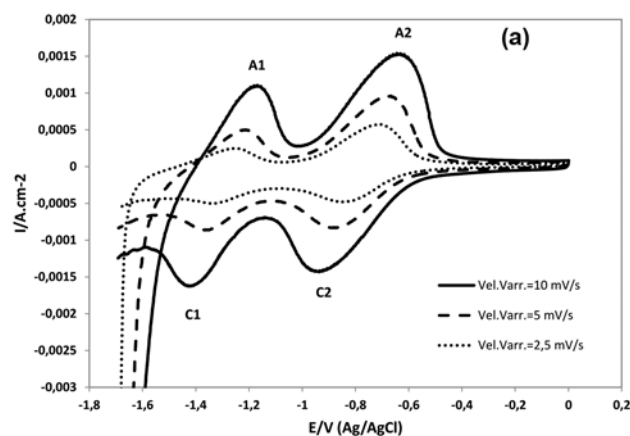


Fig. 2. (a) Cyclic voltammograms of compound **3**/carbon composite electrode, in 0.1M TBAClO₄ electrolyte solution, at various scan rates: 2.5, 5.0 and 10 mVs⁻¹; (b) and (c) schematic diagram for proposed reversible tetrabutylammonium (TBA) ion insertion/de-insertion mechanism.

During the stability study performed at 2.5 mVs⁻¹, 5 mVs⁻¹ and 10 mVs⁻¹, the peak potentials values were stable within the studied range. The change in the peak current density with the scan rate is indicative of the electronic transference processes without diffusion influence.

An electrochemical stability test was also carried out by cycling of the electrode at 10 mVs^{-1} , within the potential interval -1.7 to 0 V . As it is evident in figure 3, voltammograms appear virtually unchanged after 21 cycles.

In order to detect any morphological changes after cycling, the electrode composite was analyzed under the scanning electron microscopy (Fig. 4). Analyses were conducted on composite electrodes before (Fig. 4-a) and after the electrochemical tests had been performed (Fig. 4-b) which revealed agglomeration of the cathode material particles and apparent modification of the carbon nanofibers used as material's support.

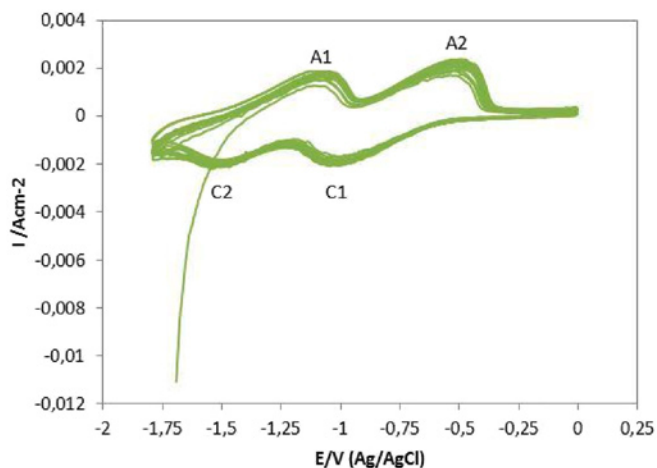


Fig. 3. Successive cyclic voltammograms for determination of electrochemical stability of the electrode at 10 mV s^{-1} (21 cycles).

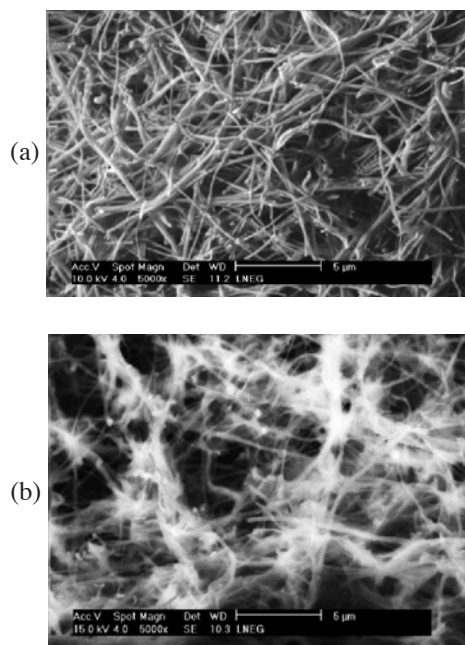


Fig. 4. Analysis by scanning electron microscopy of the composite electrode polyimide / carbon nanofiber (VGCF) before (a) and after (b) the electrochemical tests.

A more through study is in progress in order to evaluate the modifications suffered by the cathode under potential cycling, before proceeding to half-cell testing and battery constitution in a Swagelok type cell.

4. CONCLUDING REMARKS

Polyimide/carbon composites were prepared and electrochemically characterized in order to evaluate the performance and redox capacity of the corresponding electrodes. These imides have shown to possess stable doubly reduced dianions with properties suitable for high-density charge storage (two radicals for each repeat unit). The cyclic voltammograms showed two well separated reversible redox couples corresponding to electron transfer processes in two steps involving the four carbonyl groups present in the molecule of the polyimides. Current densities are reported to be higher, 10-20X, than those encountered in the literature for similar compounds, were found.

Stability under potential cycling was demonstrated.

Studies are in progress in order to clarify possible morphological modifications and evaluation of their potential use as a novel organic energy-storage system in Li-ion batteries.

The polyimide/carbon composites are expected to be highly promising as electro-active materials in organic rechargeable devices, owing to their excellent redox properties and environmental friendliness.

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