



Short communication

## Bilayered nanofilm of polypyrrole and poly(DMCT) for high-performance battery cathodes

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### ABSTRACT

Bilayered nanofilm electrodes made of polypyrrole (Ppy) and poly-2,5-dimercapto-1,3,4-thiadiazole (poly-DMCT) are produced by electrochemical means onto a carbon-fiber substrate, with the goal of preventing the loss of the electroactive mass of the disulfide and improving the electrode stability during the charge/discharge cycling process. Lightweight and high surface area composites are obtained by potentiostatically depositing a nanometric layer of Ppy onto a carbon fiber piece already supporting a layer of a potentiodynamically obtained poly(DMCT) film. The growth charge/mass ratio for the bilayered polymeric electrode is optimized, leading to a high electrochemical performance cathode with a stable specific capacity of  $\sim 320 \text{ mA h g}^{-1}$  after 100 cycles.

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## 1. Introduction

The production and development of new cathode materials for lithium-ion batteries is nowadays one of the most challenging research areas, partially due to specifications of modern portable electronic devices, but especially due to the increased demand for clean energy storage and the development of hybrid electric vehicles [1,2].

Since the 1990s disulfide compounds have been more intensively investigated as cathode materials due to their high theoretical specific capacity. Among the disulfides, 2,5-dimercapto-1,3,4-thiadiazole (DMCT) is known as the most promising cathodic material due to its theoretical capacity of  $362 \text{ mA h g}^{-1}$ , which exceeds those of conventional materials such as intercalation compounds and conducting polymers [3–6]. However, serious problems were found in attempts to construct a battery with disulfide electrodes due to the slow rate for their redox process at room temperature; this can lead to a very low energy density and poor capability for the electrochemical energy conversion system [7,8]. In order to enhance the rate of the poly(DMCT) redox reactions, conducting polymers such as polypyrrole (Ppy) [9–11] and polyaniline [12–14] combined with this disulfide have been successfully used as electrocatalysts.

The conducting polymer/disulfide materials still present poor performances that prevent their use in electrochemical energy conversion systems since the reduction products of poly(DMCT) are soluble in a great number of electrolytes, leading to a gradual loss of the electrode electroactive mass [15,16]. Therefore, an alternative way to avoid the loss of poly(DMCT) mass to the solution is the preparation of bilayered film electrodes, when a conducting polymeric film is deposited on top of the disulfide layer in order to improve the electrode properties such as charge retention for energy storage, conductivity, and ionic transport [17]. Another route to avoid the solubility of poly(DMCT) or analogous polymers is the preparation of hybrid guest–host nanocomposites [18,19].

An easy, fast, and clean preparation of the polymeric films is usually carried out by electrochemical means. However, the electrosynthesis conditions strongly affect the final properties of the polymer and therefore must be well controlled [20]. In the past we investigated and optimized some of these conditions for the electrochemical deposition of Ppy, poly(DMCT), and polyaniline onto carbon fiber (CF) and reticulated vitreous carbon substrates [13,14,21,22].

In this work, we propose the production of bilayered nanofilm electrodes made of Ppy and poly(DMCT) electrogenerated onto a CF substrate (CF/poly(DMCT)/Ppy) with the goal of preventing the loss of the electroactive mass of the disulfide and improving the electrode stability during the charge/discharge cycling process. Thus, aiming at obtaining a lightweight and high surface area material, a nanometric layer of Ppy was potentiostatically deposited onto CF already supporting a layer of a potentiodynami-

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cally obtained poly(DMCT) film. The best growth charge/mass ratio and charge–discharge features were investigated in order to attain the highest electrochemical performance possible from the light bilayered polymeric nanofilm.

## 2. Experimental

A 0.3-mm thick CF sheet (PWB-3, Stackpole, USA) was cut into 10 mm × 10 mm pieces, exposing a 2-cm<sup>2</sup> geometrical area to the electrolyte when used as substrates in the electrodeposition of the Ppy and poly(DMCT) films. Prior to their use, the CF pieces were chemically and thermally treated according to a procedure previously reported [14]. Prior to use, the pyrrole monomer (Acros Organics) was vacuum distilled at 65 °C and then stored at 0 °C.

The electrochemical syntheses were carried out in a conventional three-electrode Pyrex-glass cell containing, in addition to the respective electrolyte, CF as working electrode, a Pt sheet as counter electrode, and a saturated calomel electrode (SCE) as reference. The electrodes were connected to an Ecochemie/Autolab PGSTAT 30 potentiostat/galvanostat controlled by the GPES software. The solutions were kept at room temperature (ca. 25 °C) and thoroughly purged with nitrogen before each electrochemical run.

### 2.1. Potentiostatic deposition of Ppy

Ppy films were electrodeposited at 0.8 V (vs. SCE) onto CF in a 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> (Acros Organics) acetonitrilic solution (J.T. Baker, HPLC grade) containing 2% of deionized water, since it has been shown that the Ppy electroformation kinetics is thus favored [23]. Ppy films of different masses were obtained by fixing the total anodic charge at 1 C, 2 C, 5 C, or 10 C. These CF/Ppy electrodes were dried and kept under vacuum, prior to their characterizations.

### 2.2. Preparation of the CF/poly(DMCT)/Ppy electrode

The poly(DMCT) film was formed on the CF substrate by cycling the potential (30 voltammetric cycles) between -1.0 V and 0.69 V at 100 mV s<sup>-1</sup> in a 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> acetonitrilic solution saturated with DMCT powder (Acros Organics). The details of this preparation and the poly(DMCT) film characterization can be found in previous works [13,14].

Finally, a Ppy film was grown on the CF/poly(DMCT) electrode according to the procedure described above.

### 2.3. CF/Ppy and CF/poly(DMCT)/Ppy characterizations

The electrochemical characterizations of the composites were carried out by cyclic voltammetry in a 1 mol L<sup>-1</sup> LiClO<sub>4</sub> propylene carbonate solution at a scan rate of 10 mV s<sup>-1</sup> between -1.0 V and 0.8 V (vs. ECS). The total electrical charge stored in each film was determined by computer-assisted integration of its respective anodic and cathodic voltammetric waves.

The morphological characteristics of the composites were analyzed from SEM micrographs obtained using a 960-DSM Zeiss scanning electron microscope.

The charge and discharge cycles of the CF/Ppy and CF/poly(DMCT)/Ppy electrodes were carried out in a dry box under an argon atmosphere using a PARC 263A potentiostat/galvanostat. A standard three-electrode two-compartment electrochemical cell was used containing lithium as both reference and counter electrodes immersed in a 1 mol L<sup>-1</sup> LiClO<sub>4</sub> propylene carbonate solution. The bilayered polymeric cathodes were charged and discharged at a constant current density of 1 mA cm<sup>-2</sup> in the potential range 4.0–2.0 V. Prior to the charge–discharge cycling (up to 100 cycles), the composites were dried under vacuum at 60 °C for 48 h.

**Table 1**

Values of mass obtained for Ppy films potentiostatically (0.8 V vs. SCE) electropolymerized up to different charges (in coulombs) onto a 2-cm<sup>2</sup> carbon-fiber substrate.

1 C	2 C	5 C	10 C
0.30 mg	0.74 mg	2.19 mg	4.20 mg

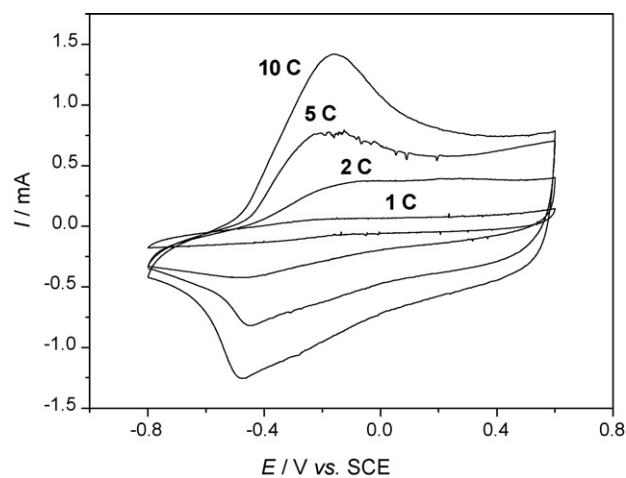
## 3. Results and discussion

### 3.1. CF/Ppy electrodes

Before preparing the bilayered electrodes, Ppy films were potentiostatically grown on the CF substrate using different total charges in order to optimize their performances. As shown in Table 1, the Ppy mass increases with the growth charge, indicating a well-ordered growth of the polymeric films without undesirable parallel reactions. This was confirmed by a gradual increase of the current found in the current–time transients for all the charge values employed in the Ppy electrodeposition process.

Fig. 1 shows cyclic voltammograms obtained at 1 mV s<sup>-1</sup> in a 1 mol L<sup>-1</sup> LiClO<sub>4</sub> propylene carbonate solution for CF/Ppy electrodes prepared using different total charges. These *I*–*E* profiles, which agree quite well with those previously reported in the literature [24–26], present broad current peaks related to the oxidation and reduction of Ppy and consequently to the ClO<sub>4</sub><sup>-</sup> doping and dedoping processes in the polymer, respectively. As it can also be seen in Fig. 1, the current increases as the film formation charge increases. This can be understood as due to the thickening and increasing surface area of Ppy as the total growth charge becomes larger. Indeed, this is corroborated by the SEM micrographs presented in Fig. 2, where the surface morphology of Ppy films on the CF substrate for the lowest and highest charge values are illustrated. Although both films present a uniform coverage, the characteristic nodular structure is more evident for the film prepared at the highest charge value (Fig. 2b), indicating a greater roughness and surface area. Similar results were found for Ppy grown at different charges in a NaPSS solution by Wallace and co-workers [27], who demonstrated from AFM results that both the roughness and the thickness of the polymer film increased as the polymerization charge was increased.

The high capacitive currents for potential values higher than 0.2 V (vs. SCE) are another interesting aspect of the voltammetric profiles in Fig. 1. Tanguy et al. [28] attributed this behavior to the charging of a pseudo-capacitance arising from the accumula-



**Fig. 1.** Cyclic voltammograms obtained at 1 mV s<sup>-1</sup> in a 1 mol L<sup>-1</sup> LiClO<sub>4</sub> propylene carbonate solution for CF/Ppy electrodes (*A*<sub>CF</sub> = 2 cm<sup>2</sup>) prepared using different total charges.

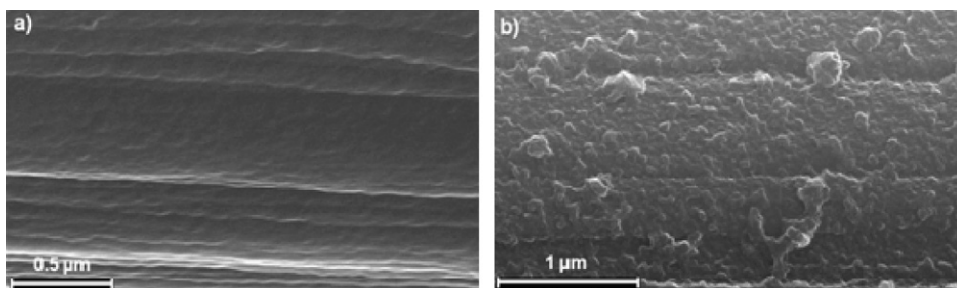


Fig. 2. SEM micrographs of Ppy films electropolymerized onto carbon fiber at 0.8 V vs. SCE using different total charges: (a) 1 C and (b) 10 C.

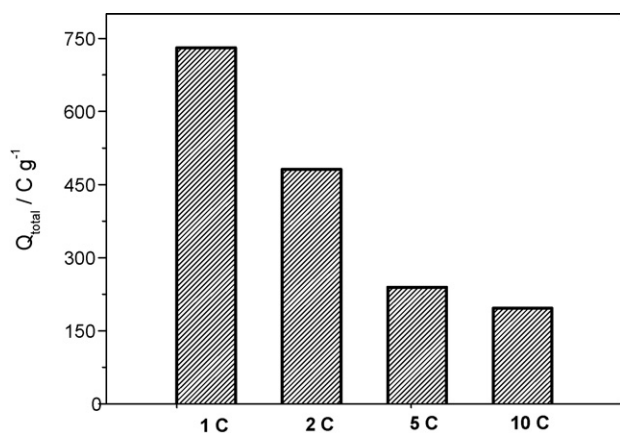


Fig. 3. Total specific charge (anodic and cathodic) obtained from the cyclic voltammograms shown in Fig. 1.

tion of trapped ions in the doped Ppy. These capacitive currents would also be responsible for the hysteresis and the broadening of the reduction peak in Fig. 1. Furthermore, an increase of the potential difference between the oxidation and reduction peaks is observed as the formation charge of Ppy films increases, indicating that counter-ion diffusion to/from the polymer becomes more difficult, as already observed for thicker films [29,30].

Fig. 3 shows the values of total specific charge (anodic and cathodic) obtained from the cyclic voltammograms shown in Fig. 1. Clearly, the charge/mass ratio is higher for the Ppy film formed at the lowest charge value possibly due to its thinner thickness, which will favor the polymer doping/dedoping process during the voltammetric cycle. Fig. 4(a) and (b) illustrates the cross-section of Ppy films potentiostatically grown on the CF substrate at the lowest and highest charge values, respectively. In both cases, the Ppy films are relatively well distributed around each individual fiber whose diameter is  $\sim 7 \mu\text{m}$ . From these images it is also possible to estimate the thickness of the Ppy films prepared at 1 C and 10 C as  $\sim 100 \text{ nm}$  and  $\sim 600 \text{ nm}$ , respectively. Wallace and co-workers [27] proposed, from electrochemical atomic force microscopy (EC-

AFM) results on Ppy films, that the path length for ion diffusion and the porous monolayer structure of nanometric films could positively affect the diffusion rate and the ionic and solvent access to the majority of the electroactive material. These ideas are consonant with the results shown in Fig. 3 for the thinner films, where the polymer/electrolyte interface is clearly more accessible to the redox reactions, a feature very important to the charge/discharge processes in a battery electrode.

Therefore, considering that the counter-ion diffusion into/out of the thinner films is facilitated for shorter polarization times and that a higher value of the charge/mass ratio was observed for the thinnest Ppy film, the charge value of 1 C was used in the subsequent electrodepositions of Ppy to produce the bilayered film on CF (CF/poly(DMCT)/Ppy).

### 3.2. CF/poly(DMCT)/Ppy electrodes

Fig. 5 illustrates a typical surface morphology of a bilayered electrode. Similarly to the CF/Ppy case (Fig. 2a), the bilayered film also presents a uniform coverage, although some disperse globular nanoparticles possibly related to poly(DMCT) can be observed. In this case, a thin layer of Ppy would cover such globular particles. Li et al. [9] also found globular particles of poly(DMCT) with an average diameter of  $\sim 500 \text{ nm}$  when a composite of Ppy-coated poly(DMCT) was examined by TEM. It is worthwhile to point out that the  $I-E$  profile of this electrode, in a  $1 \text{ mol L}^{-1} \text{ LiClO}_4$  propylene carbonate solution, was practically equal to that of the CF/Ppy electrode prepared with a charge of 1 C; hence, the outer layer of Ppy may be defining the voltammetric behavior of the bilayered electrode.

An exceptional performance was obtained when the CF/poly(DMCT)/Ppy electrode underwent charge–discharge tests, as demonstrated in Fig. 6. After the fortieth cycle, stable values of specific capacity of  $\sim 320 \text{ mA h g}^{-1}$  and  $\sim 140 \text{ mA h g}^{-1}$  with coulombic efficiencies of  $\sim 100\%$  were observed for the CF/poly(DMCT)/Ppy and CF/Ppy (1 C) electrodes, respectively. Such performance can be considered very good, especially when compared with those reported for other composite electrodes [6,9,31,32]. The increase of the specific capacity values until the

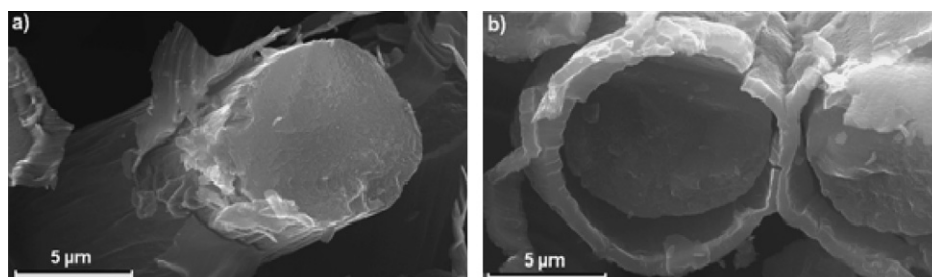
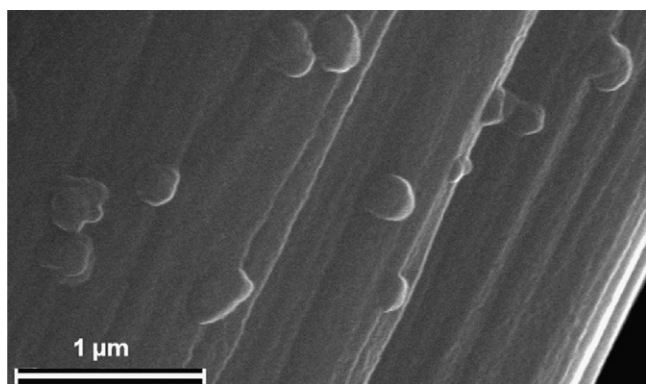
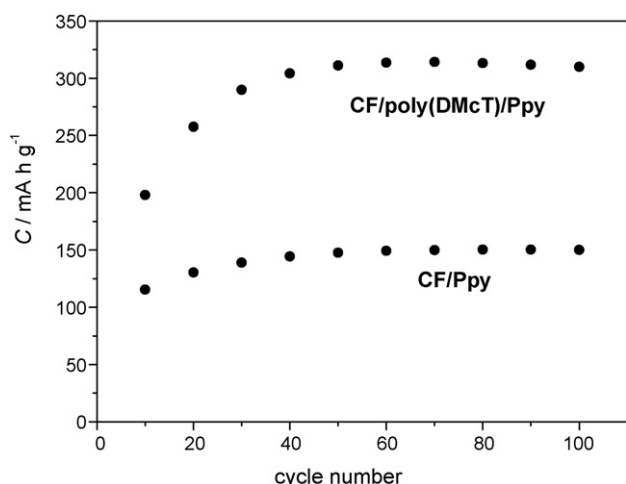


Fig. 4. Cross-sectional SEM micrographs of Ppy films electropolymerized onto carbon fiber at 0.8 V (vs. SCE) up to different total charges: (a) 1 C and (b) 10 C.



**Fig. 5.** Typical SEM micrograph of a CF/poly(DMcT)/Ppy electrode prepared by depositing Ppy onto carbon fiber already supporting a poly(DMcT) film.



**Fig. 6.** Specific capacity as a function of cycle number obtained for CF/poly(DMcT)/Ppy and CF/Ppy electrodes in a 1 mol L<sup>-1</sup> LiClO<sub>4</sub> propylene carbonate solution;  $i_c = i_d = 1 \text{ mA cm}^{-2}$ ; potential range: 4–2 V vs. Li/Li<sup>+</sup>.

fortieth cycle might be related to the increasing of the number of electroactive sites caused by the progressive electrosolvomechanical effect (polymer swelling) of Ppy during its multiple oxidation/reduction processes [33,34]. The high and stable specific capacity value found after the polymer swelling indicates that the interface generated between poly(DMcT) and Ppy favors possible synergic interactions and significantly improves the performance of the composite. Moreover, the electrode stability suggests that no significant loss of the disulfide electroactive mass occurs during the cycling process of the as-prepared bilayered polymeric cathode. Therefore, it can be concluded that a nanometric thickness of electrodeposited Ppy was enough to prevent the degradation of the inner poly(DMcT) layer, resulting in a high-performance disulfide/conducting polymer electrode.

#### 4. Conclusions

Bilayered nanofilm electrodes of Ppy and poly(DMcT) on a CF substrate (CF/poly(DMcT)/Ppy) were successfully produced by potentiostatic (0.8 V vs. SCE) polymerization of Ppy (total charge of 1 C) onto CF already supporting poly(DMcT) potentiodynamically formed at 100 mV s<sup>-1</sup> between -1.0 V and 0.69 V (vs. SCE). Under

SEM examination, these bilayered nanofilm electrodes (~100 nm) showed uniform coverage of Ppy with some disperse globular nanoparticles of poly(DMcT) on the high surface area CF substrate. In the charge and discharge tests, the CF/poly(DMcT)/Ppy electrode presented an exceptionally high specific capacity of ~320 mA h g<sup>-1</sup> with a coulombic efficiency of ~100% even after 100 cycles. Therefore, the proposed methodology can be considered for the production of high-performance electrodes made of a bilayer polymeric nanofilm of Ppy and poly(DMcT).

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