

Short communication

Performance of a polyaniline(DMcT)/carbon fiber composite as cathode for rechargeable lithium batteries

Sheila C. Canobre, Rogério A. Davoglio, Sonia R. Biaggio*,
Romeu C. Rocha-Filho, Nerilso Bocchi

Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13560-970 São Carlos – SP, Brazil

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Abstract

The redox reaction of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) is slow at room temperature, but it can be accelerated when the electron transfer reaction is coupled with that of polyaniline (Pani). Films of polyaniline were electrosynthesized onto carbon fiber substrates by cyclic voltammetry from a $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.1 \text{ mol L}^{-1}$ aniline aqueous solution; DMcT was incorporated into the films by two different procedures: A – previous adsorption on the carbon fiber substrate, and B – electropolymerization onto a Pani film from a 20 mmol L^{-1} DMcT solution in acetonitrile. The Pani(DMcT)/carbon fiber composites were tested as cathodes at 0.1 mA cm^{-2} in a cell containing lithium as anode in a $0.5 \text{ mol L}^{-1} \text{ LiClO}_4$ solution in propylene carbonate, in a dry box under an argon atmosphere at $25 \pm 2^\circ\text{C}$. Discharge capacity values of 159 mA h g^{-1} (after 90 cycles) and 39 mA h g^{-1} (after 50 cycles) were obtained for the composites prepared by procedures A and B, respectively. The high capacity value and the high electrochemical stability during the cycling indicate that there is a synergetic effect of Pani and DMcT in the composites prepared by procedure A.

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1. Introduction

The development of cathode materials with high energy density has been the subject of many rechargeable lithium batteries investigations [1]. As anodes of these batteries, lithium and lithium–intercalated carbon have been used due to their theoretical capacities of 3862 and 339 A h kg^{-1} , respectively [2]. On the other hand, organic polymers have been proposed as cathode materials, since some of their properties (as low mass, ease in blending, ability for molecular design, low pollution and low cost) are highly desirable.

Mercaptans with two or more $-\text{SH}$ groups have also attracted considerable attention as active materials for cathodes in lithium secondary batteries since they present a high theoretical capacity for energy storage, as, for

example, 362 mA h g^{-1} for the poly(2,5-dimercapto-1,3,4-thiadiazole) [3]. A series of compounds with $-\text{SH}$ groups is thought to have a significant potential as energy storage materials, whereby energy exchange occurs according to a reversible polymerization–depolymerization process ($2\text{SH} \leftrightarrow \text{S}-\text{S}$) [4–6]. Considering that the DMcT redox reaction rate is too slow for practical use at ambient temperature, Liu et al. [7] analyzed the use of DMcT as cathode material in a cell containing a solid polymer electrolyte operating at high temperatures; at 100°C , power densities of over 1800 W kg^{-1} (2200 W L^{-1}) at energy densities of 140 W h kg^{-1} (170 W h L^{-1}) were achieved with use of up to 96% of the cathode capacity. In order to enhance the redox kinetics of this polydisulfide, conducting polymers have been used as electrocatalysts [8–14]. Among them, the DMcT/Pani composite has an energy density as high as 600 W h kg^{-1} , which is much higher than the 400 W h kg^{-1} presented by a commercial LiCoO_2 cathode [15]. This might be due to a

* Corresponding author. Tel.: +55 16 3351 8086; fax: +55 16 3351 8350.
E-mail address: biaggio@power.ufscar.br (S.R. Biaggio).

synergetic effect of Pani and DMcT, i.e. the redox reaction of DMcT is accelerated by the polymer and the electrochemical activity of Pani is maintained by DMcT at high voltages in non-acidic media. This effect has been explained by postulating the formation of adducts between DMcT and the polymer chains [16–20].

For practical applications, the ratio electrode mass/electrochemical activity should be taken into account, since a high activity must be achieved with a minimum electrode mass. In order to reduce the electrode mass, the active polymeric film has to be detached from the metallic substrate, but sometimes this is limited by the mechanical properties of the polymeric film. Thus, if the substrate has to be maintained in the electrode structure, the choice of a light, porous and high surface area material is extremely important. These properties are easily found in carbon electrodes, which have been intensively studied as materials for energy storage applications such as batteries and capacitors. The possibility of using activated carbon without binding substances, as for example fibrous fabrics or felts, is an additional advantage from the device construction point of view [21].

Among the carbon substrates, carbon fiber has been used for the deposition of conducting polymers [22–24]. Films of polyaniline [22] and polypyrrole [23] electrodeposited onto carbon fiber substrates presented stable and high discharge capacities when tested as cathodes in lithium rechargeable batteries.

Intending to make a light, flexible and workable at room temperature organosulfur cathode, a new composite material consisting of DMcT and polyaniline prepared electrochemically onto a carbon fiber substrate is proposed in this work. Additionally, two different procedures for the DMcT incorporation into the composite are described and their influence on the cell charge–discharge performance is analyzed.

2. Experimental

The substrates for all the electrosyntheses were carbon fiber pieces (PWB-3, Stackpole, USA) with a geometrical area of 2 cm² exposed to the electrolyte. The carbon fiber was heat treated in an oven at 450 °C for 1 h, then immersed in a hot concentrated (50/50, v/v) H₂SO₄ aqueous solution for 1 h and kept overnight in purified water in order to increase its wettable surface. The preparation of polyaniline was made electrochemically by cyclic voltammetry. A disulfide, DMcT – 2,5-dimercapto 1,3,4-thiadiazole (Alfa Aesar), was incorporated into the polymeric matrix according to two procedures.

2.1. Procedure A: DMcT adsorbed onto the carbon fiber prior to the polyaniline electropolymerization

DMcT was adsorbed onto the carbon fiber pieces by keeping them immersed for 2 h in acetonitrile (Mallinckrodt, AR HPLC) containing 100 mmol L⁻¹ DMcT, according to

a procedure described before [22]. For DMcT concentrations higher than 100 mmol L⁻¹, an undesirable brown precipitate was formed, which is thought to be the dimeric form of the mercaptan [25]. The polyaniline films were grown onto the carbon fiber/DMcT electrodes by 300 voltammetric cycles, in 0.5 mol L⁻¹ H₂SO₄/0.1 mol L⁻¹ aniline aqueous solutions. For the first cycle, a scan rate of only 2 mV s⁻¹ was used between –0.4 and 0.8 V (versus SCE); for the other cycles the growth was continued at 100 mV s⁻¹ between –0.4 and 0.69 V (versus SCE), as reported before [22,26]. The anodic limiting potential was chosen in order to avoid the insulating oxidation state of polyaniline, pernigraniline [27].

2.2. Procedure B: DMcT added to the electrolyte after the polyaniline electropolymerization

A Pani film previously formed onto carbon fiber according to the cyclic voltammetric program described above was dried, placed in another cell containing a 0.1 mol L⁻¹ LiClO₄/20 mmol L⁻¹ DMcT solution in acetonitrile and cycled for 200 cycles at 100 mV s⁻¹ between –0.6 and 0.69 V (versus SCE) in order to obtain the poly(DMcT).

Electrochemical runs were conducted in a conventional three-electrode-Pyrex-glass cell containing Pani(DMcT)/carbon fiber composites as working electrode, a Pt sheet as counter-electrode, and a saturated calomel electrode (SCE) as reference, which were controlled by an EG&G PARC 273A potentiostat/galvanostat. The solutions were kept at room temperature (~25 °C) and thoroughly purged with nitrogen before each electrochemical run.

The morphological characteristics of the composites were analyzed using a 960-DSM Zeiss scanning electron microscope. The charge and discharge tests were carried out in a dry box under an argon atmosphere. A standard three-electrode, two-compartment electrochemical cell was used with a lithium reference electrode and lithium counter-electrodes as anodes in a 1 mol L⁻¹ LiClO₄ solution in propylene carbonate (PC). Two Pani(DMcT)/carbon fiber composites with active masses of 0.7 mg (proc. A) and 2.4 mg (proc. B) were tested as cathodes. The composites were dried under vacuum at 60 °C for 48 h prior to any charge/discharge run. Charging and discharging were performed at a constant current density of 0.1 mA cm⁻² in the potential range of 3.8–2.5 V versus Li/Li⁺ unless otherwise stated.

3. Results and discussion

The voltammetric responses of the carbon fiber (the blank) and the carbon fiber/adsorbed DMcT electrodes are shown in Fig. 1. The carbon fiber voltammetric profile presents its expected capacitive aspect, while two faradaic processes appear in the profile for the electrode containing-DMcT, whose anodic current peaks I and II can be assigned to DMcT dimerization and polymerization, respectively. It is widely

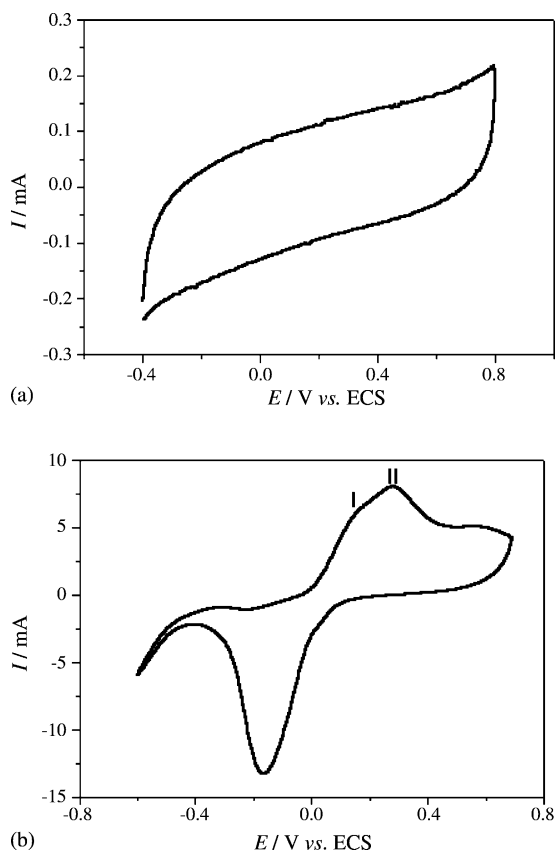
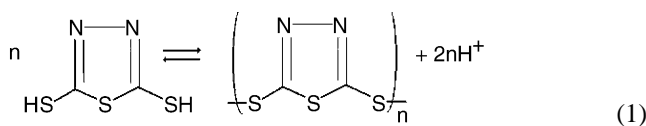


Fig. 1. Cyclic voltammograms of the working electrodes in a $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution: (a) carbon fiber; (b) carbon fiber/polyDMcT.

accepted that DMcT is polymerized upon oxidation and that the resulting polymer is depolymerized upon reduction [6], according to the reactions:



3.1. Composite A features

The composite A was prepared by electrosynthesizing polyaniline films onto a carbon fiber/adsorbed DMcT substrate, as described in procedure A in Section 2. Fig. 2 presents the evolution of the $I-E$ profile as the polymeric film thickness is increased within a maximum of 300 voltammetric cycles. The final profile shows peaks and features similar to those for a Pani film grown on a Pt substrate, well described in the literature: the anodic current peak corresponds to the Pani oxidation to its emeraldine conducting form while the corresponding cathodic peak to its reduction to the insulating leucoemeraldine form.

Fig. 3 shows SEM micrographs for the composite A prepared after different times of DMcT adsorption onto the carbon fiber substrate; a higher adsorption time allows the subsequent formation of a thicker Pani film that completely

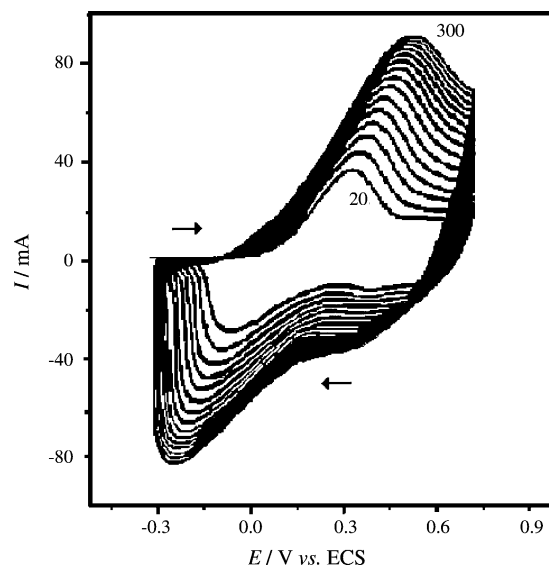


Fig. 2. Voltammetric profiles ($v = 100 \text{ mV s}^{-1}$) recorded during the formation of composite A: Pani growth onto a carbon fiber/adsorbed DMcT substrate, in a $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.1 \text{ mol L}^{-1}$ aniline aqueous solution.

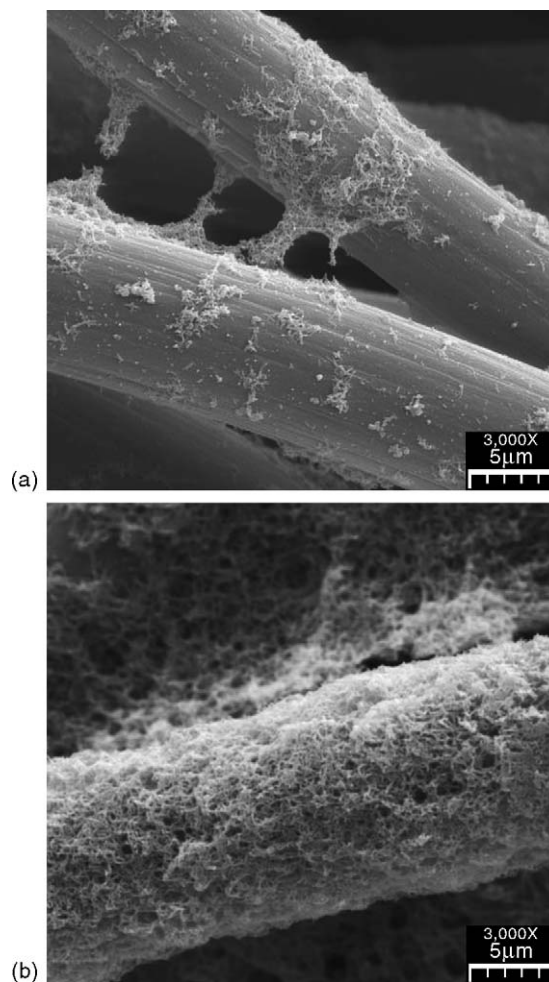


Fig. 3. SEM micrographs of the composite A surface, for DMcT adsorption times of 15 min (a) and 120 min (b). Magnification of $3000\times$.

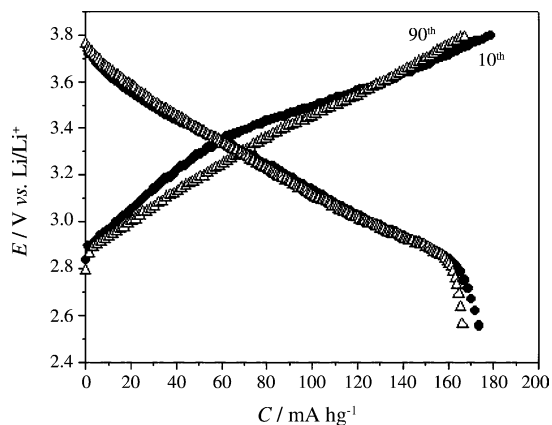


Fig. 7. Potential as a function of the specific capacity for the composite A, Pani(DMcT)/carbon fiber (0.7 mg of active mass), at 0.1 mA cm^{-2} , after 90 cycles.

analysis of the performance of composite A compared to other cathode materials can be done by assessing the data presented in Table 1 (see below).

Fig. 7 shows that after 90 cycles the specific capacity for composite A is yet 168 mA h g^{-1} , indicating that both materials, Pani and DMcT, remain active during the charge–discharge cycling. This result has been explained as due to a synergetic effect in which the redox reaction of DMcT is accelerated by polyaniline and the electrochemical activity of Pani is maintained by DMcT at potentials up to 3.8 V versus Li/Li⁺ in non-acidic media [3,6,15].

On the other hand, the charge–discharge results for the cell Li/1.0 mol L⁻¹ LiClO₄, PC/composite B (2.4 mg of active mass) are shown in Fig. 8. The performance of composite B was not as good as that for composite A, since the specific capacity decreased from 73 mA h g^{-1} (248 W h kg^{-1}) after 10 cycles to 36 mA h g^{-1} (122 W h kg^{-1}) after 50 cycles. The morphological differences of composite B with respect to composite A may possibly explain the distinct values of their initial specific capacity. While composite A presents a thick and porous surface film, as already shown in Fig. 3b, compos-

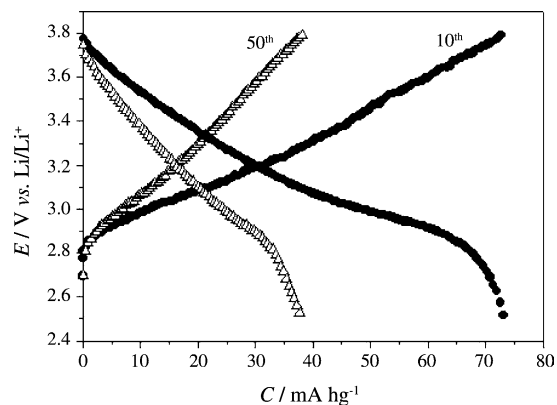


Fig. 8. Potential as a function of the specific capacity for the composite B, Pani(DMcT)/carbon fiber (2.4 mg of active mass), at 0.1 mA cm^{-2} , after 50 cycles.

ite B presents a less homogeneous surface film (see Fig. 5) leading to a much smaller active area in contact with the electrolyte. The capacity loss of composite B during the cycling may be due to the dissolution of DMcT, since the electrolyte became yellowish after some charge and discharge cycles.

Table 1 shows a summary of the theoretical discharge capacities of the materials more frequently employed as cathodes in secondary batteries, including the data of the two composites proposed in this work. The theoretical capacity value for poly(DMcT) suggests that it could be a promising material as cathode, though its slow redox reactions could be an inconvenience. However, due to the synergetic effect between Pani and poly(DMcT), this material became of large interest for application in rechargeable batteries. The incorporation of DMcT to the composite by the procedure A (previous adsorption of DMcT onto the carbon fiber) resulted in a DMcT/Pani film of high experimental discharge capacity which is $\sim 30\%$ higher than those observed for the cathode materials used in commercial secondary batteries.

4. Conclusions

The Pani(DMcT)/fiber carbon composites, electrochemically prepared by the procedures A and B, presented good charge–discharge characteristics as cathodes in lithium batteries: coulombic efficiency of 100%, reversibility and high initial discharge capacity. However, composite A presented a better performance compared to that of composite B due to their morphological differences and the dissolution of DMcT during the cycling of composite B. Furthermore, the high specific capacity of composite A (175 mA h g^{-1}) indicates that there is a synergetic effect between the materials Pani and DMcT, which remained active and presented a good electrochemical stability during the charge–discharge cycling. The good charge–discharge characteristics and high specific capacity suggest that composite A may be a promising material as cathode in rechargeable batteries.

Table 1

Theoretical and experimental discharge capacities of some cathodes tested in secondary batteries

Active material	Theoretical capacity (mA h g ⁻¹)	Experimental capacity (mA h g ⁻¹)	References
LiCoO ₂	274	120–130	[28]
LiMn ₂ O ₄	148	100–110	[28]
Polypyrrole (BF ₄ ⁻)	89	65	[2]
Polyaniline (BF ₄ ⁻)	100	77	[2]
Polyaniline	65	60	[29]
Poly(DMcT)	362	30	[2,12]
Pani(DMcT)	224	185	[15]
Pani(DMcT), procedure A	224	175 after 10 cycles	This paper
Pani(DMcT), procedure B	224	73 after 10 cycles	This paper

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