A new electrode for a poly(pyrrole)-based rechargeable battery

Rosa C. D. Peres and Marco-A. De Paoli*
Instituto de Química, UNICAMP, C. P. 6154, 13081 Campinas (Brazil)

S. Panero and B. Scrosati
Dipartimento di Chimica, Università di Roma 'La Sapienza', Rome (Italy)

Abstract

The use of dodecylbenzenesulfonate-doped poly(pyrrole) films, PPYDBS, as a secondary battery electrode was studied. The redox and morphologic properties of these films are suitable for battery application. Films were synthesized by electrolysis of pyrrole and sodium dodecylbenzenesulfonate aqueous solutions with a current density of 1.0 mA cm^{-2} and were switched in LiClO$_4$ 1.0 M propylene carbonate solutions (PC) by cyclic voltammetry. In these experiments an apparent diffusion coefficient of 3.7×10^{-9} cm^2 s^{-1} has been found. Charge/discharge tests at ±50, ±100, ±150 and ±200 μA cm^{-2} were done for a PPYDBS/LiClO$_4$, PC/Li battery. The open-circuit voltage was 3.2 V after 30 h, the specific capacity 53 A h kg^{-1} and the energy density 154 W h kg^{-1}. These values indicate that this polymer can be used as an electrode in a rechargeable battery.

Introduction

The great effort in the research of conducting polymers is in part due to their potential technological applications. The development of secondary batteries with these materials has advantages over those made with commonly-used materials, such as low specific weight and lower environmental impact when disposed. Poly(pyrrole), PPY, has been considered as an electrode in batteries because of its good chemical stability.

Many others have previously studied this polymer and have obtained good specific capacity and energy density but a poor cyclability due to a small holding charge [1–4]. The causes for these characteristics have been studied by Osaka *et al.* [5–8] who observed that parameters such as the doping anion, synthesis potential and the thickness of the film play an important role in the performance of the polymer. The influence of dopant ion was also studied by Nishio *et al.* [9] who found that perchlorate-doped PPY has a high coulombic efficiency up to 100 charge/discharge cycles. The solvent also influences the performance of the polymer film as electrode [10].

The use of high molecular weight anion-doped PPY, with a redox process involving cation insertion, is interesting because it allows obtaining high specific capacity values. Experiments with this type of PPY were done by Shimidzu *et al.* [11] who studied the cyclability of a poly(vinyl sulfate)-doped PPY/chlorine-doped PPY battery and found a potential of 1.7 V between the electrodes in 0.3 M aqueous KCl.

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*Author to whom correspondence should be addressed.

The aim of this work is the electrochemical characterization of a high molecular weight anion doped-PPY film in organic medium. We also studied its behaviour as a positive electrode in a lithium battery. Dodecylbenzene sulfonate anion (DBS) was used as doping agent.

Experimental

The dodecylbenzenesulfonate-doped poly(pyrrole) films (PPYDBS) were galvanostatically deposited onto both sides of platinum substracts at 1.0 mA cm^{-2} (total charge density of 360 mC cm^{-2}). A one compartment electrochemical cell was used. The synthesis electrolyte was a solution of pyrrole (Fluka, freshly distilled, 0.05 M) and NaDBS (Fluka, 0.025 M) in bidistilled water. After deposition, the films adhered to the electrode were washed with water and acetonitrile and left in propylene carbonate in a dry box for 3 days.

The electrochemical measurements were performed in a LiClO$_4$ 1,0 M propylene carbonate solution. Lithium has been used as counter and reference electrodes. The films were activated by cyclic voltammetry between 2.2 and 3.8 V (50 mV s^{-1}), with subsequent charge/discharge tests at ±50, ±100, ±150, ±200 μA cm^{-2}. The open-circuit voltages were measured with a zero shunt amperometer with a negligibly small internal resistance. All the potentials were referred to the Li/Li$^+$ electrode.

An Amel model 551 potentiostat coupled with an Amel model 567 function generator, and x–y recorder and an Amel 731 integrator were used. The charge/discharge tests were carried out using an Amel model 545 galvanostat.

Results and discussion

In Fig. 1 we show the first and 20th voltammetric curves for PPYDBS in LiClO$_4$-containing propylene carbonate. From the current density increase it can be seen that there is an activation process, which could be assigned to a modification of the polymer microstructure occurring in the early cycles. The apparent redox potential found in the 20th scanning is 2.7 V (versus Li/Li$^+$). An important aspect of Fig. 1 is that the ratio between the peak currents (and charge) is approximately 1, indicating that the number of electroactive sites in the PPYDBS film formed during the anodic and cathodic sweeps are the same.

In order to study the kinetics of the redox reaction, sweeping at different scan rates were done. In these cases, we observed a linear relationship between peak separation and the scan rate as a result of ohmic resistance limitations.

Figure 2 shows the variation of the anodic and cathodic peak currents as function of scan rate (ν) and scan rate square root ($\nu^{1/2}$). One can seen that for all scan rates studied the curves are approximately linear, although the intercept is near zero for I_p versus ν. Assuming that the polymer film electrode kinetics satisfy eqn. (1), the value of x can be a measure of the type of electrode process. The variables I_p, ν, x and k correspond to the peak current, the scan rate, the exponent of the scan rate and the proportionality constant, which includes the diffusion coefficient and number of electrons, respectively. The values of x can be calculated by using eqn. (2), obtained by rearranging eqn. (1), as the slope of the plot of $\log I_p$ as a function of $\log \nu$.

$$I_p = k\nu^x \tag{1}$$

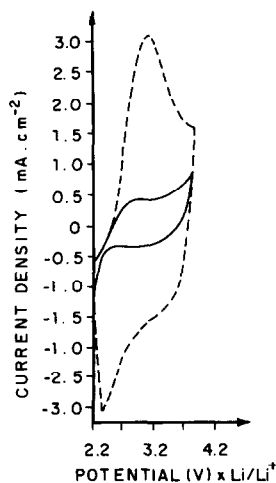Fig. 1. Cyclic voltammograms of PPYDBS in $LiClO_4$-containing propylene carbonate; $\nu =$ 50 mV s^{-1}, (——) 1st and (– – –) 20th cycle.
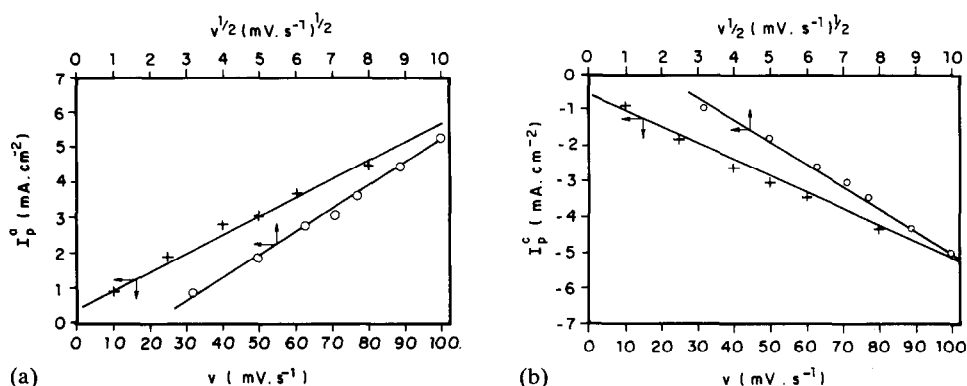

Fig. 2. Plots of the anodic and cathodic peak currents (a) I_p^a and (b) I_p^c, as a function of scanning rate (ν) and scanning rate square root ($\nu^{1/2}$).

$$\log I_p = \log k + x \log \nu \tag{2}$$

The exponent x may assume two values: 0.5 when I_p scales linearly with ν, and 1 when I_p scales linearly with ν. The value obtained in our study was 0.7 indicating that the kinetics of the redox process is complex. The best linear relationship observed for I_p versus ν suggests that the diffusion occurs only in a superficial layer of the film.

By using the slope of the straight part of the I_p versus ν curve and the relationship given by eqn. (3) [12] (the terms have the usual meaning, where C^* is the electroactive-site concentration calculated from the doping level, n is the number of electrons and A is the geometric area of the electrode in cm) we calculated the apparent diffusion coefficient (D_{ap}) at 25 °C given in Table 1.

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{ap}^{1/2} \nu^{1/2} C^* \tag{3}$$

An important feature from Table 1 is that D_{ap} for both processes are very similar, suggesting that the redox process is reversible.
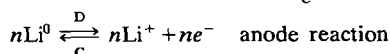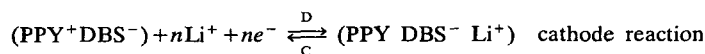
TABLE 1

Data obtained from cyclic voltammogram (lithium electrode as reference)[a]

E (V)	ΔE_p (V)	Y (%)	$D_{ap}^{ox} \times 10^9$ (cm^2 s^{-1})	$D_{ap}^{rd} \times 10^9$ (cm^2 s^{-1})
2.7	0.6	40	3.7	3.5

[a]E = potential, ΔE_p = difference between the oxidation and the reduction peak potentials, Y = doping level, D_{ap}^{ox} = apparent oxidation diffusion coefficient and D_{ap}^{rd} = apparent reduction diffusion coefficient.

According to our previous electrogravimetric results with dodecylsulfate-doped PPY [13, 14], we assume that during the redox process of PPYDBS the cation insertion/deinsertion is responsible for the charge electroneutrality, although the anion diffusion is also possible at high anodic potentials. This is reinforced by the low solubility of DBS in propylene carbonate. The reactions involved in these experiments are shown in Scheme 1. During discharge, D, the polymer is reduced with insertion of Li$^+$ ions in order to maintain electroneutrality. In the anode the discharge causes lithium oxidation with dissolution of Li$^+$ ions in the electrolyte. During charge, C, the opposite occurs.

$$(PPY^+DBS^-) + nLi^+ + ne^- \underset{C}{\overset{D}{\rightleftharpoons}} (PPY\ DBS^-\ Li^+) \quad \text{cathode reaction}$$

$$nLi^0 \underset{C}{\overset{D}{\rightleftharpoons}} nLi^+ + ne^- \quad \text{anode reaction}$$

Scheme 1.

The results of the charge/discharge tests at different current densities are shown in Fig. 3. A slow potential increase is observed at ± 50 μA cm^{-2}, indicating that the ion concentration gradient in the polymer/electrolyte interface is not high, i.e., ion diffusion is effective. Increasing the current density the slope of the curve is higher, probably due to the non-equilibrium between diffusion/redox reaction.

Figure 4 represents the charge used during the polymer discharge process at different current densities. Charge decrease, as a function of current-density increase, is indicative of a rate limitation for the discharge process.

The problem of using conducting polymers as electrodes in rechargeable batteries is their small retention of charge. Figure 5 shows the reduction charge as a function of number of cycles. Taking a current density of ± 100 μA cm^{-2} we observe a charge loss of 30% after 70 cycles of charge/discharge. This may be assigned to irreversible chemical changes of the polymeric electrode, probably cross-linking, causing degradation and loss of its electrochemical properties.

The coulombic efficiency (η) is a parameter used to characterize a battery and is obtained from the cathodic and anodic charge ratio. In these experiments we always obtained a value of 100%. However, polymer degradation will affect both processes (oxidation and reduction) causing the persistence of the value of η. In this case this parameter is not adequate to characterize a polymer battery.

The self-discharge process is another important effect to be checked when a material is used as a battery electrode. For the PPYDBS film studied the open-circuit voltage (OCV) is shown in Fig. 6, where one observed that the potential decreases faster in the first 6 h, and slower until 30 h, holding at 3.2 V. This self-discharge process has been assigned to impurities into the solvent. However, the curve behaviour
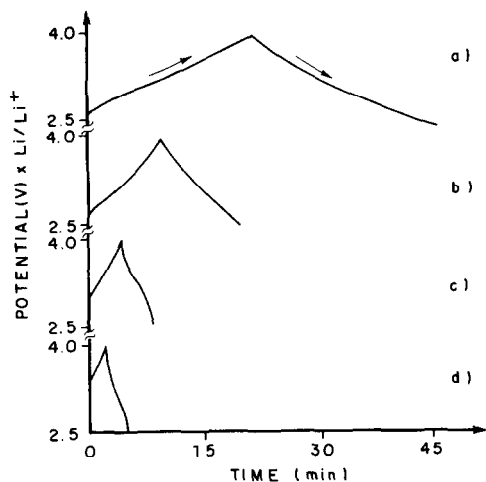
Fig. 3. Charge/discharge cycles of the battery PPYDBS/LiClO$_4$, propylene carbonate/Li; (a) ±50, (b) ±100, (c) ±150 and (d) ±200 μA cm^{-2}.
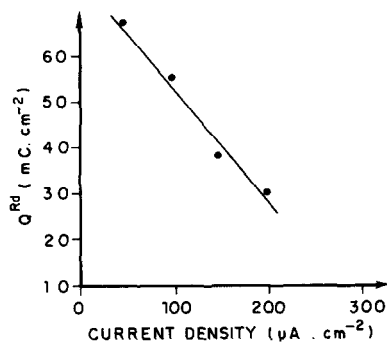
Fig. 4. Electrochemical charge during the discharge of the polymer at different current densities (2.5 to 4.0 V×Li/Li$^+$).
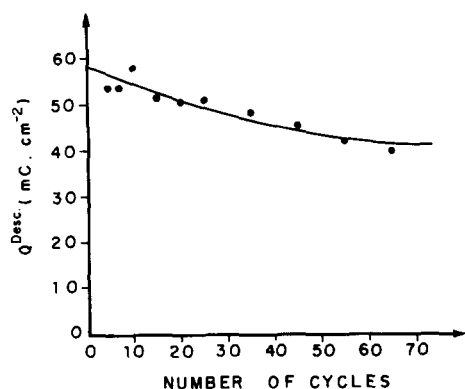

Fig. 5. Electrochemical reduction charge as a function of number of cycles.

suggests an equilibrium caused by the uniform distribution of ions in the polymer matrix. Besides, it might be accompanied by the relaxation of the pyrrolic rings.

Other parameters are also used to study the performance of the charge storage capacity of the polymer. The specific capacity C_s of the battery studied in this work is calculated using eqn. (4), where Y is the doping level, M_{pi} is the molecular weight of pyrrole and M_{dbs} is the molecular weight of the dodecylbenzene sulfonate anion. Taking a 40% doping level, C_s has the value of 53 A h kg^{-1}. An energy density, E_s, of 170 W h kg^{-1} was calculated by multiplying C_s by the OCV (3.2 V).

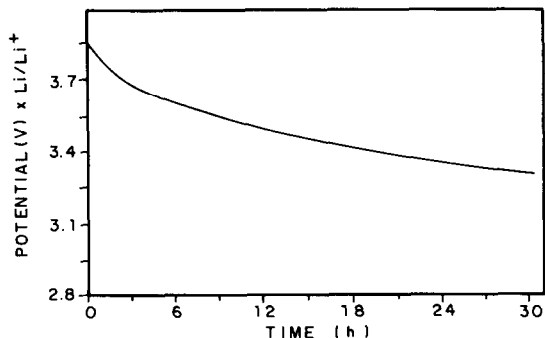$$C_s = \frac{YF}{(M_{pi}+YM_{dbs})3600} 10^3 \tag{4}$$

Fig. 6. Open-circuit voltage as a function of time.

The results presented in this work demonstrate that PPYDBS has a small capacity retention, probably due to irreversible chemical changes of the material. However, this effect is less pronounced in voltammetric experiments. In these experiments we observed that the redox reaction occurs only on the superficial layer. Thus, when the polymer undergoes an intense charge/discharge rate, there is a degradation caused by a shallow diffusion depth of ions into the polymer matrix. Possibly the use of thinner films could lead to better results.

Conclusions

The poly(pyrrole) synthesis was done in aqueous solution by applying a current of 1.0 mA cm^{-2}. By this technique a film has been obtained that could be switched by cyclic voltammetry in propylene carbonate and lithium perchlorate with a kinetics depending on ion diffusion into the polymeric matrix. In these conditions the film showed a good cyclability and a coulombic efficiency of 100%.

Charge/discharge tests at different current densities showed that the polymer undergoes an irreversible chemical change and therefore it has a small holding charge. This behaviour might be due to slow ion diffusion in the matrix. The OCV found was 3.2 V. There is a good agreement between our results and those previously reported for PPYClO$_4$ furnishing an energy density of 85.6 W h kg^{-1} at the first and 78 W h kg^{-1} at the 1500th chronopotentiometric cycle [5].

The values for theoretical specific energy and theoretical specific charge for a Pb/sulfuric acid battery are 161 W h kg^{-1} and 83.5 A h kg^{-1} [15]. Our results are very similar to these indicating the feasibility of a PPYDBS-based battery. However, the cyclability attained in this work is low in comparison to other works with the same polymer, where 20 000 voltammetric charge/discharge cycles were reported [10].

Acknowledgements

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