

## POLYMERIC MICROBATTERY BASED ON POLYANILINE COMPOSITE

Silmara Neves and Carla Polo Fonseca

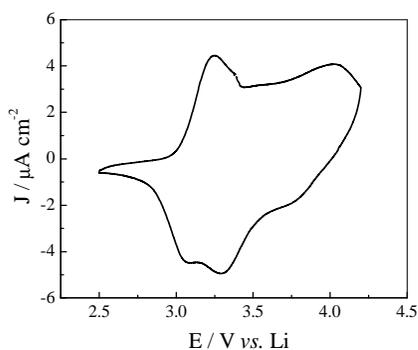
LCAM – Lab. Caracterização e Aplicação de Materiais  
Universidade São Francisco – 13251-900, São Paulo  
BRAZIL

e-mail: sneves@usf.com.br

In this work, we report the use of template synthesis to prepare conducting polymer composites by the electrochemical polymerization of aniline in the heterogeneous void spaces of inorganic (sol-gel Silica) porous films. Composites with conjugated polymers are interesting because of the perceived potential for combining properties that are difficult to attain separately from the individual components. We analyzed the electrochemical behavior of the PANi/Silica and its potential application in lithium polymeric microbattery. As electrolyte we used poly (dimetilsiloxano- co-ethylene oxide) - P(DMS-co-EO)/LiClO<sub>4</sub>. This complex was prepared by the mixture of the polymer and salt in THF. The solution was dried in vacuum for 48 h. The salt concentration was 5.0 % wt. LiClO<sub>4</sub>.

The polymerization of PANi inside the porous of Silica films/ITO [1] was carried out in the potentiodynamic mode by cycling the potential from 0.10 to 0.80 V vs. Ag|AgCl. The electrolyte consisted of 1.0 mol.L<sup>-1</sup> HCl and 1.0 mol.L<sup>-1</sup> NaCl containing 0.1 mol.L<sup>-1</sup> of distilled aniline. The polyaniline mass was calculated from the deposition charge [2]. After drying the films, the PANi-Silica / P(DMS-co-EO) / Li system was characterized into a dry box with argon atmosphere.

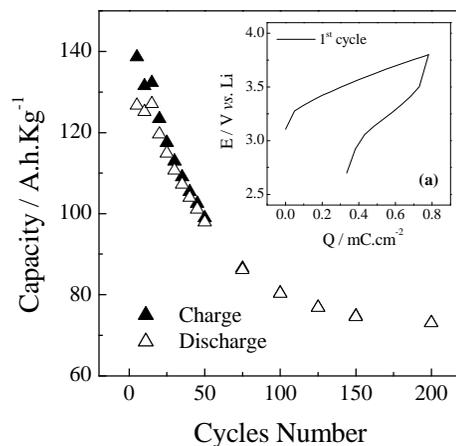
Figure 1 shows the cyclic voltammogram of PANi-Silica / P(DMS-co-EO) / Li system. The voltammetric peaks correspond to the changes in the oxidation state of the polyaniline that be related to the ratio between amine and imine content in the film [3].



**Fig. 1** – Steady state cyclic voltammogram of PANi-Silica / P(DMS-co-EO) / Li system, at 1 mV.s<sup>-1</sup>.

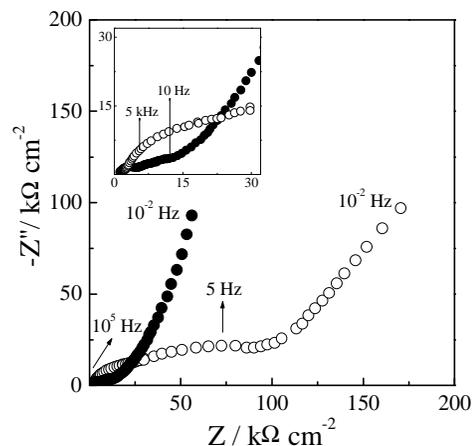
In Figure 2 the first charge/discharge cycle and the aging effect in the specific charge are shown. The initial open circuit potential was 3.35 V and the charging process was limited to 3.80 V cut-off potential, in order to avoid the over oxidation of polyaniline. The composite film presents an S-shaped charge/discharge curve, characteristic of a one-phase process. The initial capacity was 140 A.h.kg<sup>-1</sup> and it decreased with cycling remaining at 75 A.h.kg<sup>-1</sup> before 100 cycles. This behavior can be explained by two factors: polymer degradation and/or passivation of lithium electrode.

The charge efficiency for the first charge/discharge cycle was 90.7 % and it reached 100 % before 50 cycles.



**Fig. 2** – Dependence of the charge/discharge capacity with the number of cycle;  $i = \pm 1 \mu\text{A}$ . Insert (a) shows the first charge/discharge cycle.

The impedance spectra of PANi-Silica / P(DMS-co-EO) / Li system as maiden and before 100 cycles are shown in Figure 3. In high frequency range, the first intersection of the graph with the real axis corresponds to the resistance of the polymer electrolyte (1.5 k $\Omega$ .cm<sup>-2</sup>). The semicircle at medium frequency corresponds to the charge transfer resistance ( $R_{ct}$ ). The increase of  $R_{ct}$  was one order of magnitude with charge/discharge cycling. This behavior justifies the charge/discharge capacity decrease.



**Fig. 3** – Nyquist diagram at OCP potential (3.35 V) of system, after (●) and before (○) 100 charge/discharge cycles. Insert shows the high frequency range.

Based on these results, we concluded that as PANi-Silica composite as P(DMS-co-EO) – LiClO<sub>4</sub> are interesting potential materials to be used in polymeric microbatteries.

### Acknowledgements

The authors thank FAPESP (proc. 98/14756-8; 99/03330-2 and 99/05257-0).

- [1] S. Neves, C. Polo Fonseca, R.A. Zoppi, S.C. Torresi, *J. Solid State Electrochem.*, in press.
- [2] J. Koryta, J. Dvorák, L. Kavan Principles of Electrochemistry Second Edition, John Wiley & Sons, Chichester, chapter 5 (1993).
- [3] Snauwaert P, Lazzaroni R, Riga J, Verbist J, Gonbeau D (1989) Electronic Properties of Conjugated Polymers III, vol 91. Springer, Berlin, pp. 301-304.