Using Electrochemical Data to Obtain Energy Diagrams for Layer-By-Layer Films from Metallic Phthalocyanines

Frank N. Crespilho[1], Valtencir Zucolotto[2], José R. Siqueira Jr[2]., Antônio J. F. Carvalho[2], Francisco C. Nart[1] and Osvaldo N. Oliveira Jr[2]*.

[1]Universidade de São Paulo, IQSC, São Carlos, SP BR-13560970, Brazil
[2]Universidade São Paulo, IFSC, CP 369, São Carlos, SP BR-13560970, Brazil
*E-mail: chu@if.sc.usp.br

Energy diagrams have been obtained for iron tetrasulfonated phthalocyanine (FeTsPc) and nickel tetrasulfonated phthalocyanine (NiTsPc) from electrochemical and electronic absorption measurements in layer-by-Layer (LbL) films with chitosan in the cationic layers. This was made possible because the chitosan/FeTsPc and chitosan/NiTsPc modified electrodes exhibited a reversible, highly stable electrochemical response, with the voltammetric signal being preserved after several cycles in the range between 0 and 1.0V vs Ag/AgCl. The ionization potential (*IP*), electroaffinity (*EA*) and energy gap (E_g) were similar for both systems, suggesting that the coordinating metal atom does not play an important role in the elelctronic properties of the immobilized phthalocyanines. Chitosan was found suitable for the cationic layers as it did not affect the electrochemical current appreciably. The anodic peak current varied linearly with the scan rate for chitosan/NiTsPc and chitosan/FeTsPc films, denoting charge transport via electron hopping within the film, typical of a polymer-modified electrode.

1. INTRODUCTION

Porphyrins and phthalocyanines have found technological applications as photoresponsive materials in microelectronics, gas sensing, and modified electrodes for catalysis [1-3], especially due to their properties such as semiconductivity, well-defined redox activity and high thermal stability [3]. Metallic phthalocyanines and derivatives, in particular, are interesting for electrochemistry in addition to nonlinear optics, optical memories, sensors for toxic gases, organic solar cells and secondary batteries [1-5]. Phthalocyanine derivatives with suitable ionic groups can be fabricated using the layer-by-layer (LbL) technique, based on the adsorption of oppositely charged materials in alternating layers

[1-9]. This method is advantageous for the preparation of nanostructured films for electrochemical and spectroscopic studies, where parameters correlated with the electronic structure of the molecules can be determined. Nevertheless, only a few studies have appeared dealing with electrochemistry of LbL films from phthalocyanines [6-8].

Parameters such as ionization potential (*IP*), electroaffinity (*EA*) and energy gap (E_g) are important to understand and control the electrical, optical and chemical properties of phthalocyanine films [3]. They can be used to obtain energy level diagrams [10-13], which is important in the optimization of device performance. Both *IP* and *EA* are crucial for devices because they are major factors to determine electrode/electroactive molecule interfacial energy barriers [14], though other contributions may also be considered [15]. One of the most important requirements to build an energy diagram is the redox reversibility of the electrochemical species immobilized on the electrode. In addition, electrode stability is also required to determine the parameters for obtaining the energy diagram.

In this study, highly stable modified electrodes containing metallic phthalocyanines, viz. iron tetrasulfonated phthalocyanine (FeTsPc) and nickel tetrasulfonated phthalocyanine (NiTsPc), were assembled using chitosan as cationic polyelectrolyte. Optical and electrochemical techniques were employed to estimate E_g and *IP* of chitosan/FeTsPc and chitosan/NiTsPc, from which energy level diagrams were calculated.

2. EXPERIMENTAL PART

2.1 LbL chitosan-phthalocyanines films

FeTsPc and NiTsPc were purchased from Aldrich Co. and used without further purification. Nanostructured films comprising up to 20 bilayers of chitosan/FeTsPc and chitosan/NiTsPc were assembled onto hydrophilic glass and ITO-covered glass (indium-tin-oxide) substrates. The chitosan solution had concentration of 1 g L^{-1} and pH 4. FeTsPc and NiTsPc solutions were used at a concentration of 0.5 g/L and pH = 4. The sequential deposition of multilayers was carried out in a HMS series programmable slide stainer (Carl Zeiss Inc) by immersing the substrates alternately into the polycationic chitosan solution for 5 min. and in the anionic sulfonated phthalocyanine solution for 5 min. (Scheme 1). After each layer deposition, the substrate/film system was rinsed in the washing solution and dried under a N_2 flow.
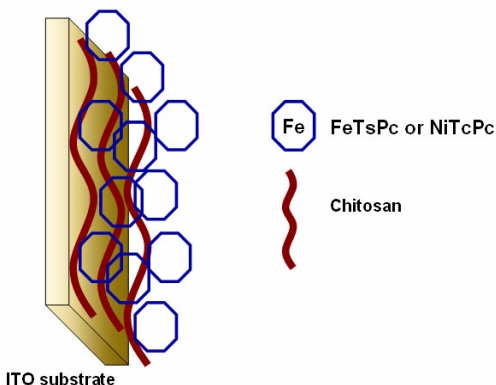
Scheme 1 - LbL films assembled with sulfonated phthalocyanines containing metal ions using chitosan as cationic polyelectrolyte.

2.2 Electrochemical measurements

The growth of the multilayers was monitored with cyclic voltammetry in an EG&G PAR M280 electrochemical analyzer for films containing 5, 10, 15 and 20 chitosan/FeTsPc or chitosan/NiTsPc bilayers deposited onto ITO-covered substrates. Use was made of a 3-electrode electrochemical cell, with Ag/AgCl reference electrode, Pt wire as counter electrode and ITO or ITO covered with LbL film as working electrode. All electrodes were inserted into the electrochemical cell containing a HCl (pH = 3.0) solution and the voltammogram was recorded immediately after insertion. The solid state absorption spectra were obtained with a Hitachi U2001 spectrophotometer, at room temperature, for 20-bilayer chitosan/FeTsPc or chitosan/NiTsPc LbL films deposited onto glass.

3. RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms for LbL films with different numbers of bilayers, where both chitosan/FeTsPc and chitosan/NiTsPc systems displayed well-defined electroactivity displaying one redox pair of peaks. For chitosan/FeTsPc films, the peak current increased non linearly with the number of bilayers, as indicated in the inset of Figure 1-a. In contrast, films containing NiTsPc (figure 1-b) exhibited a linear dependence. A possible explanation for the latter was the differences in the deposition kinetics for the two systems. While deposition of chitosan/FeTsPc was poor for the first bilayers, in NiTsPc films deposition was efficient from the start, as revealed by UV-VIS experiments. As expected, the resistivity of the films – indicated by the slope of the curve - increases with the number of deposited bilayers since chitosan is insulating.
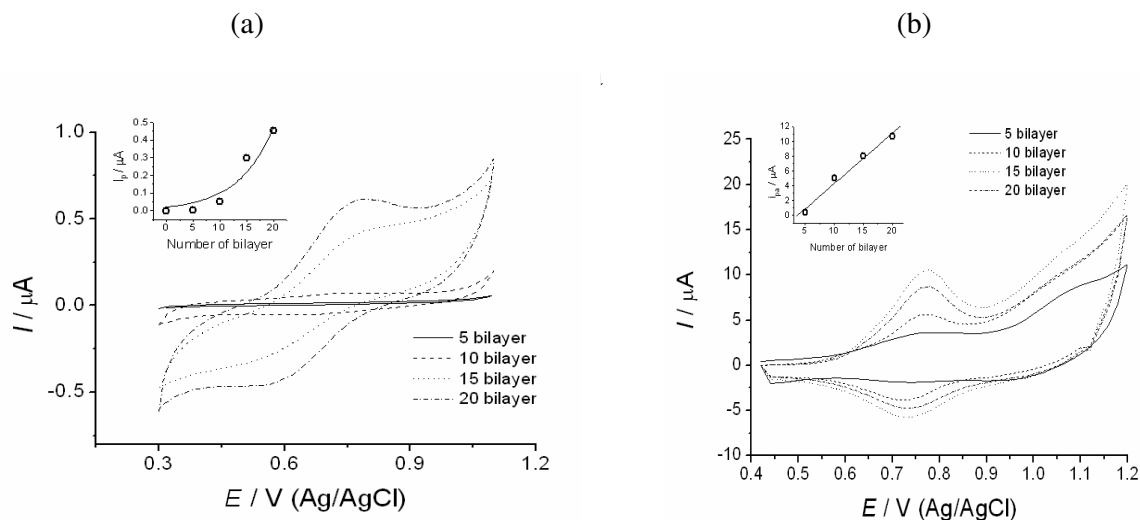

(a)   (b)

Figure 1 – Cyclic voltammograms for chitosan/FeTsPc (a) and chitosan/NiTsPc (b) LbL films with various numbers of bilayers. Inset: Oxidation peak current vs. number of bilayers. Electrolyte: HCl (pH=3.0). Scan rate: 50 mV s^{-1}.

The potential of the anodic current peak increased linearly with the scan rate, as shown in figure 2 for a 15-bilayer chitosan/FeTsPc and chitosan/NiTsPc films. The latter is an evidence of charge-transport mechanism, since if he process was diffusion-controlled a non-linear dependence with the scan rate should be observed.
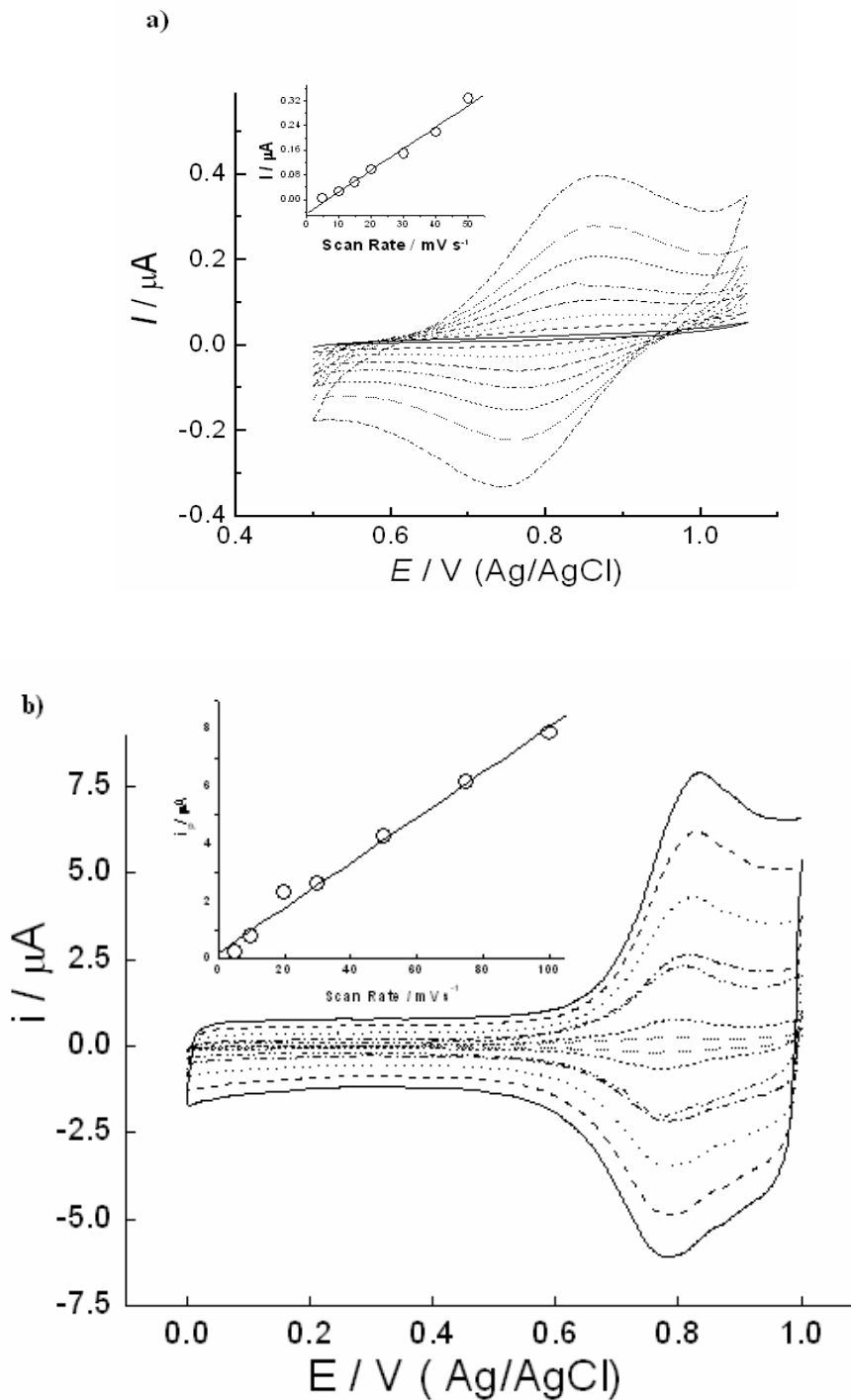

Figure 2 – Cyclic voltammograms for a 15-bilayer (a) chitosan/FeTsPc and (b) chitosan/NiTsPc film onto ITO with various scan rates. The inset shows that the oxidation peak current increases linearly with the scan rate. Electrolyte: HCl (pH=3.0).

Here we consider the system ITO-chitosan/NiTsPc and ITO-chitosan/FeTsPc as polymer-modified electrodes, more specifically as a redox polymer system [3,16,21]. In a polymer film electrode the electron transfer may occur at the two interfaces (phase boundaries) and as a mediated reaction inside the film. The mechanisms for charge transport within a redox polymer are electron hopping and ion migration [21]. In these systems, electron hopping is more likely to occur, since FeTsPc and chitosan/NiTsPc molecules are immobilized within the LbL films due to the ionic interactions between the amine groups of chitosan and the sulfonic groups of the phthalocyanine. These ionic interactions were confirmed by infrared spectroscopy (not shown). This conclusion is consistent with the work by Laurent and Schlenoff [16] who have shown that electrochemically active polyelectrolytes can be incorporated in multilayer structures in such a way that the redox active material throughout the multilayer is electrochemically addressable via electron hopping between neighboring sites. This kind of mechanism could account for the higher reversibility of the NiTsPc/chitosan film, since the higher concentration of this species facilitates the electron hoping in the insulating chitosan matrix.

The oxidation and reduction processes involving the chitosan/FeTsPc and chito-san/NiTsPc electrodes are reversible even at scan rates as high as 100mV/s, which indicates that charge transfer among phthalocyanine sites is fast and facilitated by the configuration of the LbL film. Chitosan also plays an important role: it does not interfere in the current, consistent with the findings by Huguenin et al. [22]. In order to check the reversibility of the electrochemical process in the course of the potential scan, we employ the concept of electrochemical reversibility [21], according to which $I_p \sim v$; E_p is independent of v; $\left| I_{pa} / I_{pc} \right| = 1$ and $E_{pa}\text{-}E_{pc} = 57 / n$ (mV). We observed that for chitosan/FeTsPc and chitosan/NiTsPc electrodes these requirements were met for the scan rates used, thus pointing to reversible reactions in the range of scan rates used. The experiments discussed above were possible because the chitosan/FeTsPc films were highly stable, as demonstrated in Figure 3a with almost identical voltammograms for 20 cycles. In addition, these films had the electrochemical properties preserved even after one month stored under room conditions. The same applies to the chitosan/NiTsPc LbL wich electrochemical stability as shown in figure 3b.

Even though the electrochemical properties are similar for chitosan/FeTsPc and chi-tosan/NiTsPc, important differences still exist which are related mainly to the type of metal in the phthalocyanine macrocycle. For instance, $E_{ox} \neq E_{red}$ for chitosan/FeTsPc points to different energies for oxidation and reduction. In contrast, $E_{ox} = E_{red}$ for chitosan/NiTsPc, which is typical of reversible systems with electroactive species adsorbed on the electrode. Owing to the reversibility and stability of chitosan/FeTsPc and chitosan/NiTsPc electrodes, a detailed study can be made of the energies involved in charge transfer. We have performed this by taking data from the electronic spectra and oxidation and reduction potentials. The onset potentials (E'_{ox}) of the LbL films were estimated by analyzing the intersection of the two slopes drawn at the rising oxidation current and background current in the cyclic voltammograms (not shown). Since the electrochemical charges for the anodic and cathodic peaks are the same, the redox process may be assumed to occur without film degradation. The latter suggests the presence of a fully outer sphere process, and therefore the oxidative potential is directly related to IP of the electrochemically active phthalocyanine.
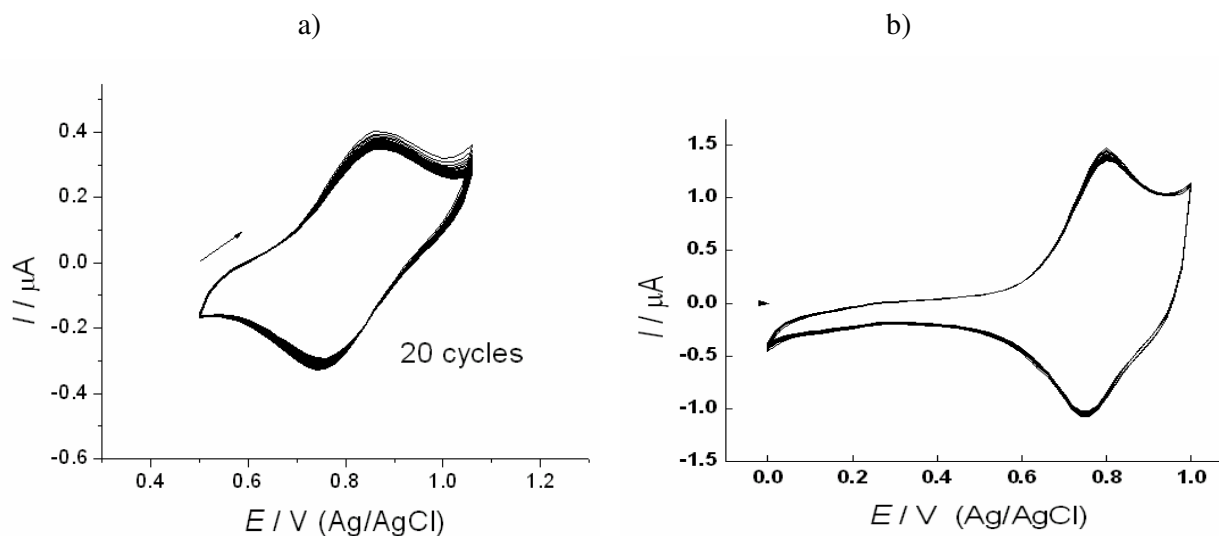
a)   b)

Figure 3 – Voltammograms with 20 cycles for 15-bilayer a) chitosan/FeTsPc and b) chitosan/NiTsPc films onto ITO. Electrolyte: HCl (pH=3.0). Scan rate: 50 mV s^{-1}.

To estimate the ionization potential (IP) and the electron affinity (EA) from the measured redox potentials, it is necessary to correlate the electrochemical potentials to the vacuum level. It is convenient to use the standard hydrogen electrode (SHE) as the reference for the potential values (*E*), and then correct these potentials using the vacuum level reference. The conversion from SHE to the vacuum reference has been discussed originally by Trasatti [23], who has determined the energy corresponding to the standard hydrogen electrode (SHE) as 4.6 ± 0.1 eV on the zero vacuum-level scale [17]. This is consistent with data in the literature, which point to an average of 4.6 eV [18], even though there may be dispersion in the quoted values from author to author [19]. Thus, it is possible to calculate the oxidation potential onset, relative to the vacuum level, since the oxidation potential onset *E'*$_{ox}$ in relation to the Ag/AgCl electrode (4.4 ± 0.1 eV on the zero vacuum-level) is known from eq. (1):

$$E_{OX} = E'_{OX} + E_{Ag/AgCl} \approx E'_{OX} + E_{vac} + 4.4$$ (1)

Assuming *E*$_{vac}$ = 0, then *IP* = *eE*$_{ox}$ - where *e* is the electron charge. This allows one to determine the HOMO level in an energy diagram. Thus, the energy of electronic transitions of the chitosan/FeTsPc and chitosan/NiTsPc was estimated from the intersection of the two slopes drawn at the maximum absorption and background absorption in the electronic spectra, as depicted in figure 4.
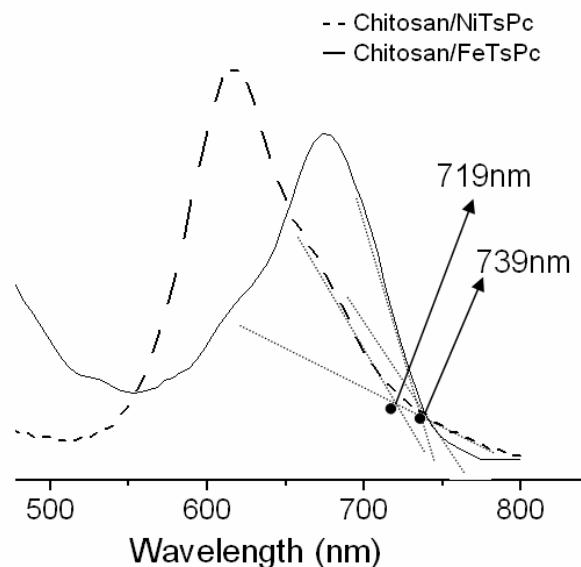
Figure 4 – Electronic spectra for 10-bilayer chitosan/FeTsPc and chitosan/NiTsPc LbL films.

In principle, the *EA* energy can be estimated by subtraction of the energy gap [20] from the electronic spectra, according to eq. 2:

$$EA = IP - E_g \qquad (2)$$

Table 1 summarizes the results obtained for the potentials measured at the onset of oxidation measured at 5 mV.s^{-1} (note that the same value can be obtained for 10 mV.s^{-1}, but for higher speed rate the value changes) for chitosan/NiTsPc and chitosan/FeTsPc LbL films and the absorption onset (λ') that yield the E_g values investigated in this work. E_g should be taken as corresponding to the onset of the absorption curves, rather than to the peak maxima.

Table 1 - The onset potentials for the electrochemical oxidation (E'_{ox}), the ionization potentials (*IP*), absorption onsets (λ') and energy gap (E_g) values for chitosan/FeTsPc and chitosan/NiTsPc.

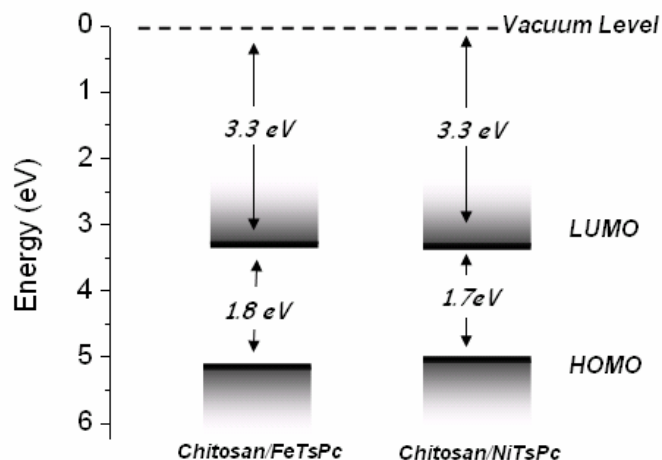| Parameters	chitosan/FeTsPc	chitosan/NiTsPc
E'_{ox} (V vs. Ag/AgCl)	0.7	0.5
IP (eV)	5.1	5.0
λ' (nm)	739	719
E_g (eV)	1.8	1.7
EA (eV)	3.3	3.3

Figure 5 – Diagram of energy levels for chitosan/FeTsPc and chitosan/NiTsPc films.

The energy level diagrams were then calculated on the basis of the experimental data for chitosan/NiTsPc and chitosan/FeTsPc. Figure 5 shows that the energy levels are similar for chitosan/NiTsPc and chitosan/FeTsPc, which should point to similar characteristics for the two systems. A higher energy for the HOMO level reveals the need of higher potentials to oxidize NiTsPc and FeTsPc molecules.

4. CONCLUSIONS

We have shown that LbL films can be prepared using FeTsPc or NiTsPc and chitosan as polyelectrolyte. Chitosan/FeTsPc and chitosan/NiTsPc modified electrodes exhibited high electrochemical stability, preserving the voltammetric signal after several cycles. For chitosan/FeTsPc films, a non-linear dependence of the current peak on the number of bilayers was observed and films comprising NiTsPc presented a linear dependence. The anodic peak current varied linearly with the scan rate, which indicates that the peak current was due to charge transport involving the chitosan/FeTsPc film. This is typical of polymer-modified electrodes, particularly for redox polymer systems, where charge transport occurs via electron hopping. Based on the electrochemical and electronic absorption experiments, parameters such as *IP*, E_g and *EA* could be estimated, which were similar for the two systems studied. Chitosan has proven suitable to produce LbL films for at electrochemical studies, particularly because it did not affect the Faradaic current appreciably.

References

1.   W. T Gao, S. F. Zhang, J. Z. Yang, L. Huang, *Dyes Pigm.* 44 (2000) 155.

2. V. R Albertini, A. Generosi, B.Paci, P. Perfetti, G. Rossi, A. Capobianchi, A. M. Paoletti, R. Caminiti, *Appl. Phy.s Lett*. 82 (2003) 3868.
3. C. C.Leznoff, A. B. P.Lever (Eds), Phthalocyanines: Properties and Applications, vols.1-4,Wiley-VCH, Cambridge, 1989-1996.
4. Y. Chen, S. M. O'Flaherty; M. Hanack, W. J. Blau, *J. Mater. Chem.* 13 (2003) 2405.
5. T. Tsujioka, Y.Hamada, K. Shibata, A. Taniguchi, T. Fuyuki, *Appl. Phys. Lett.* 78 (2001) 2282.
6. K. Shinbo, K. Kato, F. Kaneko, K. Onishi, R. C. Advincula, X. W. Fan, *Mol. Cryst. Liq. Cryst.* 407 (2003) 493.
7. V. Zucolotto, M. Ferreira, M. R. Cordeiro, C. J. L. Constantino, D. T. Balogh, A. R. Zanatta, W. C. Moreira, O. N. Oliveira Jr., *J. Phys. Chem.* B (107) 2003 3733.
8. V. Zucolotto, M. Ferreira, M. R. Cordeiro, C. J. L. Constantino, W. C. Moreira, O. N. Oliveira Jr. *Synth. Met.* 137 (2003), 945.
9. G. F. Decher, *Science* 277 (1997), 1232.
10. L. Micaroni; F. C. Nart, I. A. Hummelgen, *J. Solid State Electrochem.* 7 (2002) 55.
11. J. R.Garcia, L. O. Peres, M. R. Fernandes, J. Gruber, F. C. Nart, *J. Solid State Electrochem*. 8 (2004) 122.
12. H. Eckhardt, L. W. Shacklette, K. Y. Jen, R. L. Elsenbaumer, *J. Chem. Phys.* 91 (1989) 1303.
13. S. Janietz, , D. D. D. Bradley, M. Grell, C. Giebeler, M. Inbasekaran, E. P. Woo, *Appl. Phy.s Lett.* 73 (1998) 2453.
14. L. S. Roman, I. A Hümmelgen., F. C. Nart, L. O. Peres; E. L. Sá, *J. Chem. Phys.* 105 (1996) 10614.
15. H. Spaepen, I. H.Campbell, D. L.Smith, Physics of organic devices. In Ehrenreich F (ed) Solid state physics – advances in research and applications, vol. 55, Academic Press, London, 2001.
16. D. Laurent, J. B. Schlenoff, *Langmuir* 13 (1997) 1552.
17. Q. Xie, S. Kuwabata, H.Yoneyama, *J. Electroanal. Chem.* 420 (1997) 219.
18. J. L Bredas, Electronic structure of highly conducting polymers. In: Skotheim TA (ed) Handbook of conducting polymers, vol. 2, Dekker, New York, 1986,.
19. D. J. Fermin, H. Teuel, B. R. Scharaifker, *J. Electroanal. Chem.* 401 (1996) 207.
20. D.Stockert, R. Kessel, J. W.Schultze, *Synth. Met.* 41(1991) 1295.
21. C. M. A Brett, A. M. O. Brett, Electrochemistry: Principles, Methods and Applications, vol.1, Almedina, Coimbra, 1996.
22. F. Huguenin, E. R.Gonzalez, O. N. Oliveira Jr, *J. Phys. Chem.* B 109 (2005) 12837.
23. S. Trasatti, *J. Electroanal. Chem*. 150 (1983) 1.