J Solid State Electrochem (2002) 6: 391–395
DOI 10.1007/s100080100248

ORIGINAL PAPER

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A simple one-step electrosynthesis of poly(pyrrole-sulfated β-cyclodextrin) films

Received: 22 July 2001 / Accepted: 8 August 2001 / Published online: 17 November 2001

Abstract A functionalized stable film of poly(pyrrole-sulfated β-cyclodextrin) has been obtained electrochemically in $LiClO_4$ aqueous solution using a simple 1:1 mixture of pyrrole (Py) monomer and sulfated β-cyclodextrin (SβCD). Different cyclic voltammetric behavior is obtained for polypyrrole (PPy) and poly (Py-βSCD) during electrosynthesis. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) measurements on the two films have confirmed the presence of CD in the films and show that CD preferentially dopes the polymer even in the presence of a large excess of perchlorate supporting electrolyte. The morphology of the new polymers shows a more organized system under SEM examination. Contrary to conventional PPy films, this new polymer offers a wide potential range for electroanalytical exploration from selective electrodes to preconcentration/sampling devices.

Keywords Sulfated β-cyclodextrin · Polypyrrole conducting polymer · Electropolymerization · Doping anion · Cation uptake

Introduction

Electroanalytical chemists have always been attracted by novel electrode surfaces. The design of exotic molecular films at electrode/solution interfaces offers unlimited possibilities for specific molecular recognition, especially for electrochemical sensor applications. Among the wide range of electrode modifiers, perhaps one of the most attractive belongs to the cyclodextrin (CD) family, which has been extensively reviewed recently by Labuda [1]. The chemical reactivity of these cyclic 1,4-linked D(+)-glucopyranose oligomers has been also reviewed by Szejtli and Osa [2]. The α-, β- and γ-cyclodextrins contain respectively six, seven and eight glucose units and exhibit conical structures with a hydrophobic internal cavity and a hydrophilic exterior due to the presence of hydroxyl groups. The well-known ability of CDs to form supramolecular complexes with suitable organic and inorganic, neutral and ionic substances has resulted in the design of selective electrodes based on CDs [3, 4]. One approach to forming films used self-assembled monolayers (SAMs) of suitably substituted CD alkanethiols formed on metal substrate electrodes. Polymer films of β-CD have been prepared by a polycondensation method [5] on a platinum surface as a membrane for an amperometric glucose biosensor. The authors showed that the response of the sensor was improved using carboxymethylated β-CD, attributed to the introduction of a negative charge into the system. Rojas et al. [6] have studied the behavior of pure monolayers of CD bound on gold electrodes. All seven primary -OH groups of β-CD were converted into -SH groups for bonding. The results show that the organization of CDs yields density defects due to lack of favorable lateral interactions between the CD units. In other work, Wang and Kaifer [7] tried to immobilize positively charged β-amino-CD electrostatically as an adlayer on SAMs of thioctic acid on gold. Unfortunately, CD did not form a compact monolayer owing to repulsive coulombic interactions between the CD neighboring receptors. Polymeric films of CDs could constitute a unique system for redox mediation or enzyme immobilization. Thus the issue of CD monolayer stability needs to be addressed. Some researchers have also tried to use conventional polymers for the fabrication of CD films at electrode surfaces [8, 9, 10].

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A simpler synthesis method is desirable. There is little literature on the electrosynthesis of CD polymer systems using conducting polymers as starting materials for electrosynthesis at electrode surfaces. To the best of our knowledge, the only report is from Leprettre et al. [11], in which polymer films of CDs were prepared electrochemically on glassy carbon and platinum starting with a pyrrole-derivatized CD [12, 13]. The modified electrode exhibited molecular recognition for phenothiazine and naphthalenedisulfonate. However, CD derivatization is quite costly and complex for the preparation of routine devices.

In this paper, we present preliminary results on a very simple one-step electrochemical synthesis of highly stable polymer films based on the combination of pyrrole monomer and sulfated β-cyclodextrin (SβCD). This combination features both fast electrochemical synthesis with the conducting properties of polypyrrole (PPy) and incorporation of the supramolecular complexation/electrostatic interaction of the CD units enhanced by the presence of the negatively charged sulfate groups. The synthetic method, polymer morphology and speciation were investigated using cyclic voltammetry (CV), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The polymer counter ion doping property of the sulfate moiety of SβCD is also discussed.

Experimental

The sulfated β-CD (degree of substitution ~13–16 reported by vendor) was obtained from Aldrich (Milwaukee, Wis.) and pyrrole (99%) was from Acros (Morris Plains, NJ). The supporting electrolyte ($LiClO_4$) was from Alfa (Beverly, Mass.). All chemicals used were of analytical reagent grade and used without further purification. Deionized water (Sybron Barnstead) was used for the preparation of all solutions.

CV experiments were performed with a BAS CV-50W voltammetric analyzer (West Lafayette, Ind.). A conventional three-electrode 20-mL cell was used. A gold electrode (BAS MF2014, 1.6 mm diameter) was used as the working electrode and its surface was polished with 0.3 μm alumina powder (Buehler Gamma micropolish alumina no. 3). A Pt wire and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. Nitrogen (99.98%) was bubbled in solutions where O_2 was not desired.

Poly(Py-SβCD) electrosynthesis

A (1:1) (mole:mole) pyrrole/SβCD solution was prepared by mixing 2 g of SβCD and 71.4 μL of pyrrole (99%) in 50 mL of a 0.1 M $LiClO_4$ solution. After vigorous mixing and nitrogen sparging (15 min), cyclic voltammetric synthesis was initiated by scanning toward positive potentials from 0.0 to 1.8 V at a scan rate of 50 mV/s. The electrosynthesis was stopped after 80 cycles. The pure PPy film preparation method was similar to the one with SβCD. The electropolymerization medium was 71.4 μL of the monomer in 50 mL of 0.1 m $LiClO_4$.

SEM and EDAX measurements

The SEM instrument was a Philips XL30 ESEM (FEI, Peabody, Mass.). A 30 kV electron beam was used for the polymer surface analyses.

The EDAX detector was an EDAX Phoenix (Mahwah, NJ). The PPy and poly(Py-SβCD) films were first peeled from the electrode surface under a nitrogen stream and then introduced into the instrument with high vacuum before application of the electron beam.

Results and discussion

CV scans from 0 to 1.8 V for PPy and poly(Py-SβCD) electrosyntheses are compared in Fig. 1a and b, where quite different behavior of pyrrole electrooxidation under the two situations is seen. Figure 1a shows the electrooxidation of pure pyrrole in 0.1 M $LiClO_4$ aqueous solutions, with a first oxidation occurring between 0.8 and 1 V. The oxidation peak shifts to 1.35 V during further oxidative polymerization. A steady state occurs after about 80 cycles. A black/brownish film

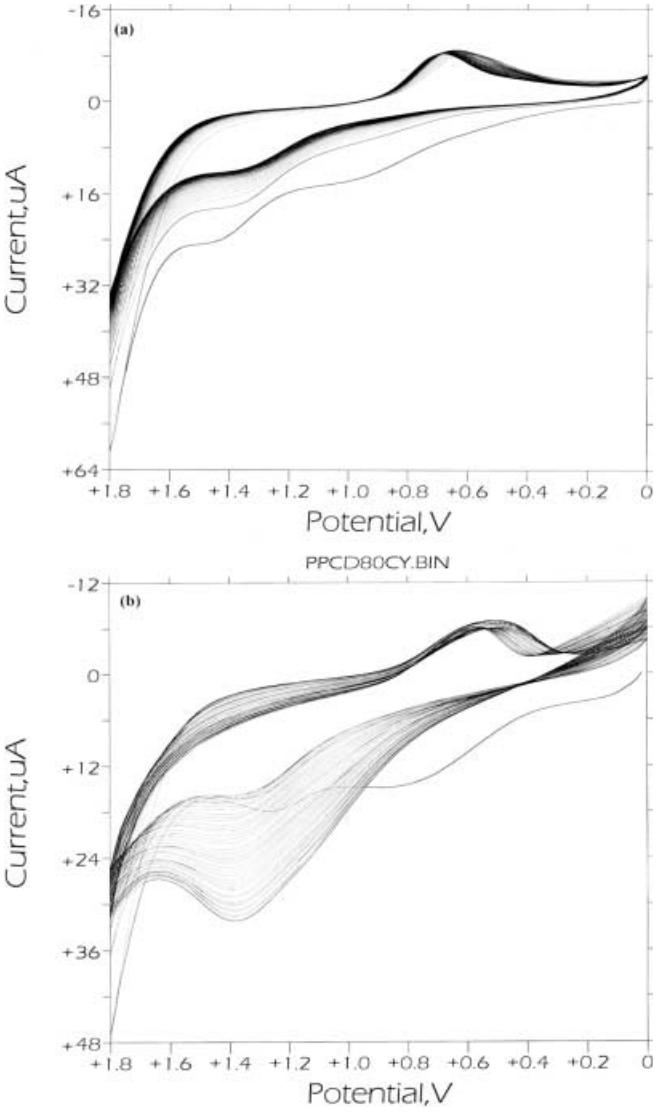

Fig. 1 Cyclic voltammograms for the electropolymerization of (**a**) pyrrole and (**b**) 1:1 pyrrole-SβCD in 0.1 M $LiClO_4$ aqueous solution; 80 sweep segments from 0 to 1.8 V. Solutions were bubbled with N_2 for 15 min before electrosynthesis

grows on the electrode surface during the process. In contrast, for the poly(Py-SβCD) (Fig. 1b), the CV shows a steady increase in current at 1.4 V, corresponding to growth of the polymer. The slight positive shift of the oxidation peak compared to PPy may be a result of the hydrophobic pyrrole partly or entirely included in the CD hydrophobic interior cavity. However, this interaction does not seem to inhibit the pyrrole units from polymerization. A compact stable black film is obtained after 80 cycles. CV performed on the polymer after several days of storage in deionized water on continued cycling shows no change in the poly(Py-SβCD) voltammograms.

To verify and confirm the SβCD presence in our polymer films, EDAX measurements were performed on both the SβCD-free and SβCD-containing films. Figure 2a shows the EDAX spectrum of the PPy film made in 0.1 M $LiClO_4$. As can be seen in the figure, no sulfur is present and, as expected, the film contains a significant amount of chlorine and oxygen from the ClO_4^- doping anion. Figure 2b clearly shows a very high sulfur content owing to incorporation of the SβCD in the polymer when the pyrrole/SβCD mixture is polymerized. However, an unexpected result is the total disappearance of the chlorine peak in the poly(Py-SβCD) films. Evidently, the negatively charged CD sulfate is selectively incorporated as the doping anions for the positively charged PPy. Bidan et al. [14] had previously reported that sulfonated β-CD could be used as a dopand in PPy films but did not report that it was selectively incorporated.

SEM measurements were also performed on both PPy and poly(Py-SβCD) films, as shown in Fig. 3a and b. The pictures clearly show different organization modes. The poly(Py-β-CDS) system seems to be a more organized system, while the PPy shows typical "cauliflower" morphology. Indeed, while the PPy films are very fragile and have powdery aspects at the solution interface, the poly(Py-SβCD) films are very compact, easy to handle and robust. The CDs appear to be permanently incorporated as no change in sulfur content on repeated charge/discharge cycling of the polymer was observed. Furthermore, the CD retains at least some of its supramolecular complexing ability on incorporation in the polymer. The CV behavior of racemic metanephrine (ME) at poly(Py-SβCD) (Fig. 4) is reversible

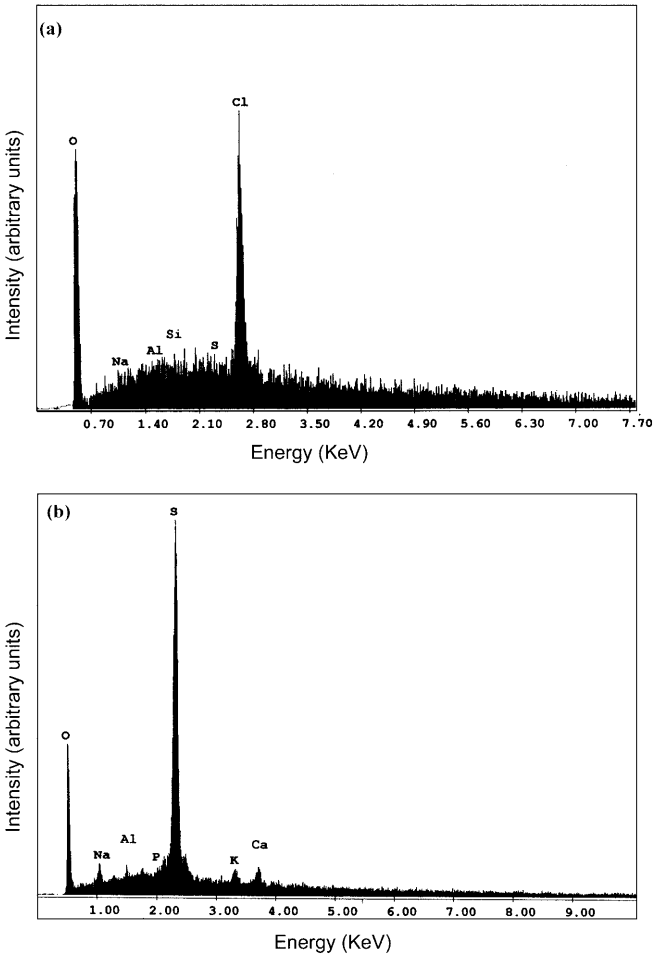

Fig. 2 EDAX spectra of (**a**) PPy and (**b**) poly(Py-SβCD) films made under conditions described in Fig. 1

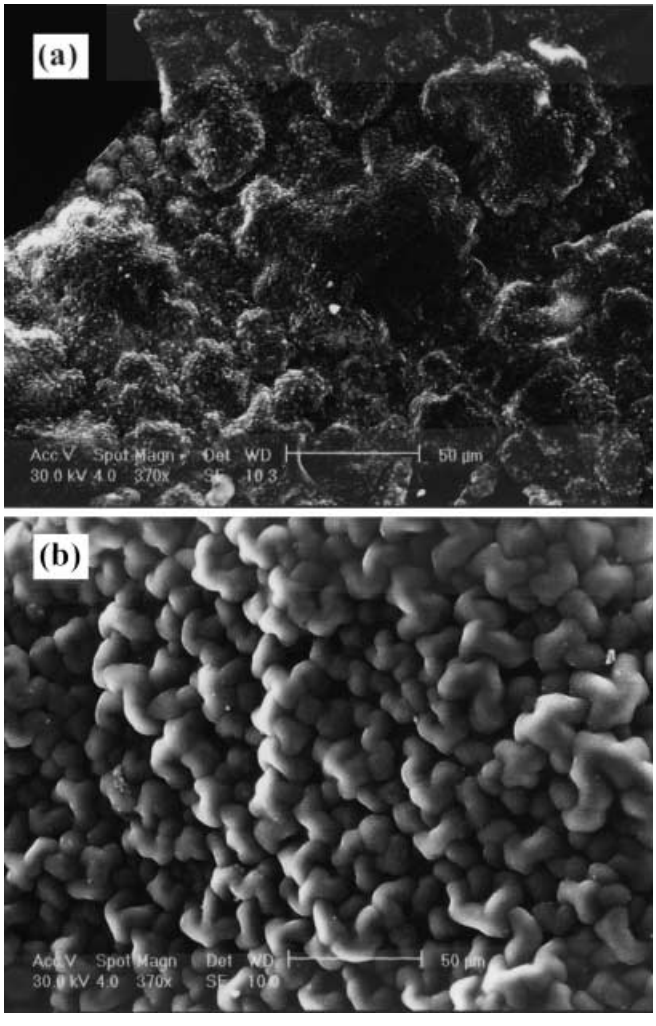

Fig. 3 Scanning electron micrographs of PPy (**a**) and poly(Py-SβCD) (**b**) films obtained at 30.0 kV with a 370× zoom

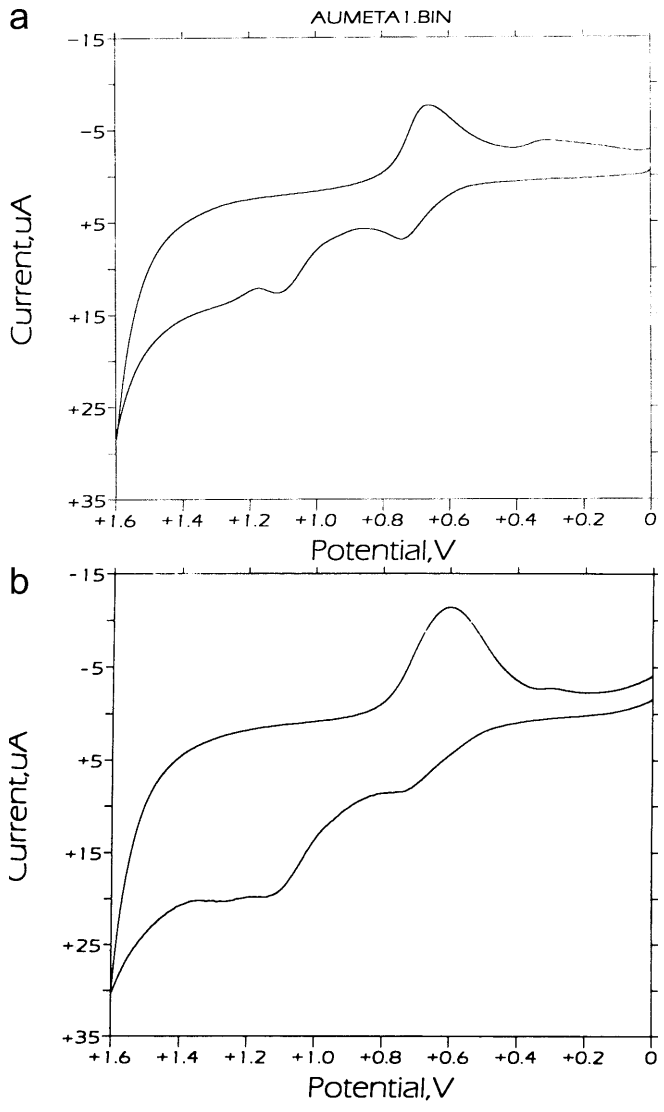

Fig. 4 Cyclic voltammograms of 0.2 mg/mL DOPA in 0.1 M $LiClO_4$ (**a**) at a bare gold electrode and (**b**) at a poly(Py-SβCD) electrode after 30 min incubation time

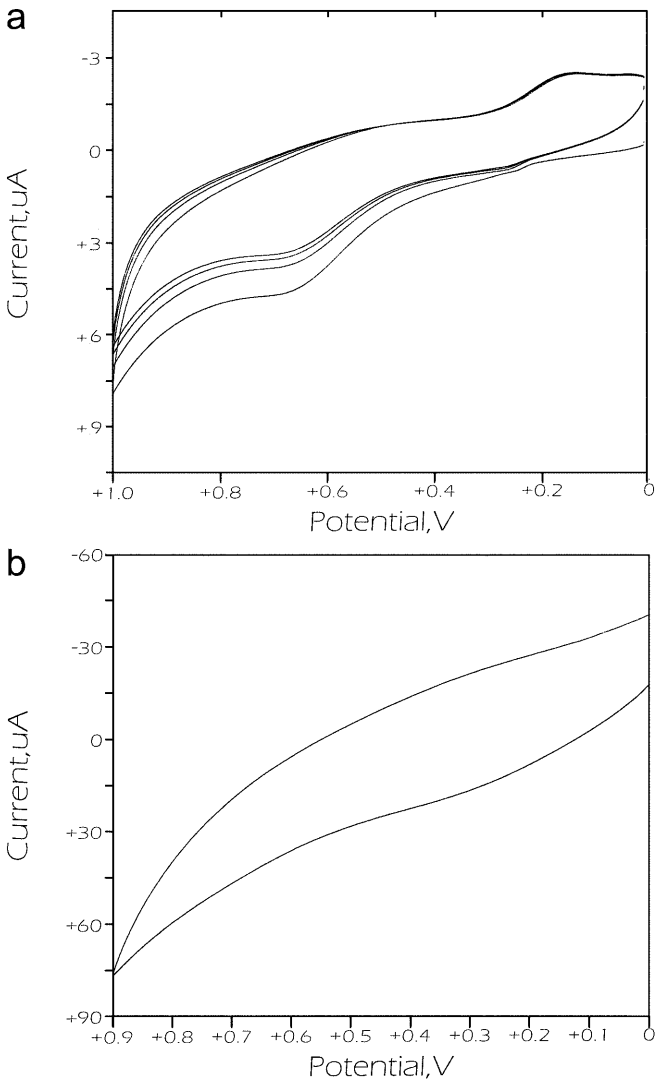

Fig. 5 Cyclic voltammograms of 0.2 mg/mL metanephrine in 0.1 M $LiClO_4$ (**a**) at a bare gold electrode and (**b**) at a poly (Py-SβCD) electrode after 30 min incubation time

for oxidation occurring at 0.7 V, while no electrochemical signal could be measured on the CV for racemic DOPA (Fig. 5). These results are in agreement with Gahm and Stalcup's [15] work focusing on the chiral separation of catecholamines using sulfated cyclodextrins. They observed that the charges on the sympathomimetic drugs seemed to be predominant in the binding process with the CD. The molecules without a carboxyl group (e.g. ME) seemed to bind more strongly to the CD than the ones with a carboxyl group (e.g. DOPA). These results suggest that the sulfate functionality remains active in the polymer film.

To verify the cation uptake and release properties of the negatively charged SβCD, calcium uptake was measured by EDAX on a poly(Py-SβCD) film initially in contact with a 1 ppm $CaCl_2/LiClO_4$ solution (Fig. 6a) under a negative potential of –0.6 V during 15 min. The results are compared to the expected release situation when the potential was switched to +1.2 V (Fig. 6b). As predicted, the EDAX spectra show that calcium is present in a high content on the poly(Py-SβCD) film during the uptake process, while a smaller peak was observed in the films corresponding to the release step.

The charge/discharge properties of the new films have been explored by chronoamperometry (data not shown) and they shows that the conversion from the positively charged polymer, under positive potential, to a neutral form, under negative potential (–0.6 V), and vise versa, is a very fast process that is complete on the order of seconds, which is important for solid phase micro extraction (SPME) applications [16].

Conclusion

A simple method for the electrochemical synthesis of poly(Py-β-CDS) is reported here. Using a 1:1

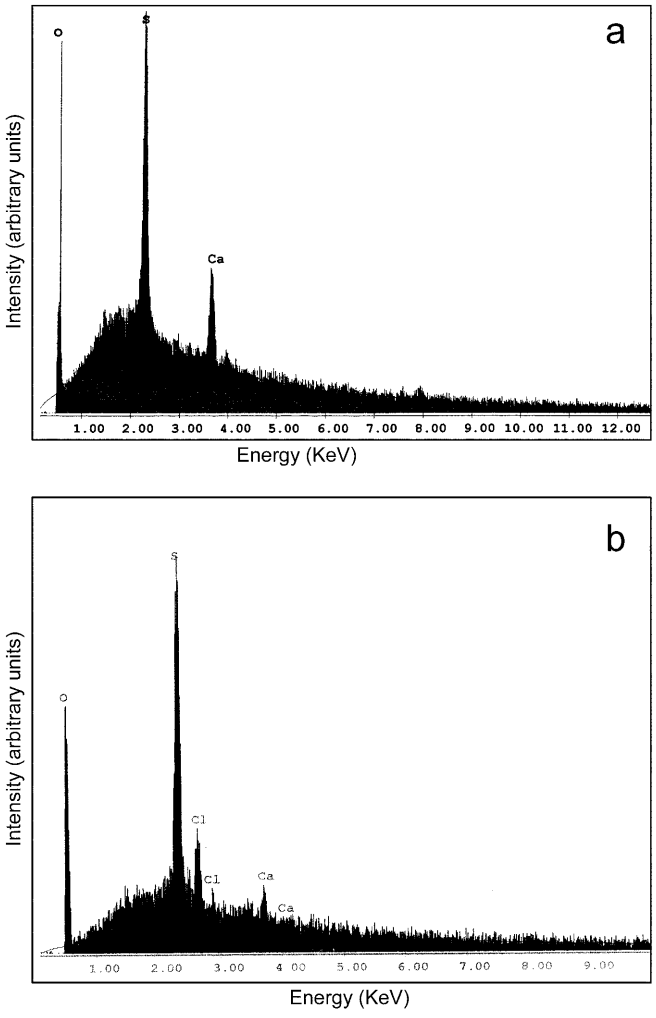

Fig. 6a, b EDAX spectrum of poly(Py-SβCD) films after uptake of calcium. Conditions are 1 ppm $CaCl_2$ in 0.1 M $LiClO_4$; potential applied was –0.6 V during 15 min

(mole:mole) ratio for Py/SβCD in 0.1 M $LiClO_4$ yields compact polymer films by electrooxidation. The perchlorate anion is selectively excluded as a dopant anion. We believe that the poly(Py-SβCD) system may offer a broad potential range for electroanalytical applications. Electrode selectivity and preconcentration/sampling properties are some of the experiments currently under way.

Acknowledgements This research was supported in part by a Research Corporation Research Opportunity Award, RA0275, and the Department of Chemistry, University of Cincinnati.

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