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## Electrochemically aided solid phase microextraction: conducting polymer film material applicable for cationic analytes

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**Abstract** The cation uptake and release properties of a poly(pyrrole-sulfated  $\beta$ -cyclodextrin) (PPy-S $\beta$ CD) film electrode have been investigated under both open circuit and controlled potential conditions for prospective applications in electrochemically aided solid-phase microextraction (EA SPME). The EDAX and ion chromatography results show that the K<sup>+</sup> and Na<sup>+</sup> cation uptake is enhanced if a small negative potential is applied to the electrode in the range where PPy is in its neutral form. These cations are released rapidly from the film if the applied potential is switched to the value at which PPy is converted to its positively charged form, i.e., oxidized state. The cation ingress and egress mechanism is affected both by the cation exchange at the negative sulfate moiety on the cyclodextrin sites and electrostatic interactions generated by the applied potential. The electrochemical “switching” capability increases the speed of the cation uptake and release, presumably due to electro migration, as compared to the open circuit ion exchange which is controlled solely by diffusion. Our preliminary fundamental results show that the PPy-S $\beta$ CD film is suitable for the future design of EA SPME devices.

**Keywords** Solid-phase microextraction · Sulfated  $\beta$ -cyclodextrin · Poly(pyrrole) · Conducting polymer · Electropolymerization

### Introduction

In a recent communication, we demonstrated that the electrochemical doping and undoping feature of the conducting polymer poly(3-methylthiophene) (P3MT) could have advantages as a solid-phase microextraction (SPME) film for anion analysis [1]. The favorable electrostatic properties of this film resulted in rapid (e.g., seconds) uptake and release of the anions. Such a SPME system is an electrochemically controlled analog of the mechanical syringe that is used for direct sample injection into a flow analytical system, such as HPLC or FIA. A polymer film, like P3MT, is applicable as an analytical tool for anion analysis as the p-type doped polymer, i.e., polymer in its cation radical form, being stable in aqueous solutions [2, 3]. However, this type of conducting polymer film would not be useful for cation uptake because the n-type doped polymer, i.e., polymer in its anion radical form, is not stable, generally, in aqueous solutions [2, 3].

Recently, Wu et al. [4] suggested that p-type poly(pyrrole) (PPy) with large-size anions used as the electropolymerization dopants could be switched to its neutral form, i.e., uncharged polymer, and retain the entrapped dopant anion. Thus, this polymer system would act as a cation-exchange film that might be useful for SPME. We have electropolymerized a PPy film with sulfated  $\beta$ -cyclodextrin (S $\beta$ CD) as the dopant anion [5]. The resulting poly(pyrrole-sulfated  $\beta$ -cyclodextrin) (PPy-S $\beta$ CD) film contains a very large excess of the sulfate anion sites, far above that necessary as the counter ions compensating the positive charge of the cation radicals of oxidized PPy. The S $\beta$ CD molecules are permanently trapped in the PPy matrix and make it a high-capacity cation exchanger film.

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We report here the effect of potential, applied to the PPy- $\beta$ CD film electrode, on the controlled uptake and release of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  cations in aqueous solutions. The rate enhancement of the cation ingress and egress due to the potential “switching” makes this polymer film a material which has potential for EA SPME applications.

## Experimental

The sulfated  $\beta$ -CD (substitution ca. 7–11 moles per mole of  $\beta$ -CD, as reported by vendor) was obtained from Aldrich (Milwaukee, Wis.), and the pyrrole (99%) was from Acros Organics (Morris Plains, NJ). The supporting electrolyte salt,  $\text{LiClO}_4$ , was from Alfa Inorganics Venton (Beverly, Mass.). The potassium chloride, sodium chloride, calcium chloride, and nitric acid were purchased from Fisher Scientific (Fair Lawn, NJ). Copper(II) sulfate pentahydrate, used for the HPLC mobile phase, was from J.T. Baker (Phillipsburg, NJ). All chemicals were of the analytical reagent grade and used without further purification. Deionized water (Sybron Barnstead) with a measured resistance of less than 18 M $\Omega$  cm was used for preparation of all solutions.

Cyclic voltammetry (CV) experiments were performed with a BAS CV-50 W voltammetric analyzer (West Lafayette, Ind.). A conventional three-electrode, 20 mL, cell was used. A gold disk electrode (BAS MF2014, 1.6 mm diameter) was used as the working electrode. Its surface was polished with a 0.05  $\mu\text{m}$  alumina slurry (Buehler Gamma micropolish alumina no. 3) and cleaned by ultrasonication prior to the polymer electrosynthesis. A Pt wire and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Purified nitrogen (99.98%) from Wright Brothers (Cincinnati, Ohio), was purged through the solutions for 15 min prior to all electrochemical experiments.

### Poly(pyrrole- $\beta$ CD) electrosynthesis

A 1:1 (mole:mole) pyrrole: $\beta$ CD solution was prepared by mixing 2 g of  $\beta$ CD and 71.4  $\mu\text{L}$  of pyrrole (99%) in 50 mL of a 0.1 M  $\text{LiClO}_4$  solution. After vigorous mixing and nitrogen purging for 15 min, the gold electrode was immersed in the solution together with the auxiliary and reference electrodes. The CV synthesis of the PPy- $\beta$ CD film was commenced by initial positive potential scanning, from 0 to 1.8 V, at a scan rate of 50  $\text{mV s}^{-1}$ . Then, electrosynthesis was stopped after 80 cycles [5].

### HPLC measurements

The separation of the potassium and sodium cations was performed with a Hamilton PRP-X800 cation-exchange column (Reno, Nev.), 250 $\times$ 4.6 mm. A 2 mM  $\text{CuSO}_4$  solution was used as the mobile phase at a flow rate of 1.0  $\text{mL min}^{-1}$ , at ambient temperature. Indirect UV detection at 220 nm was carried out with a Dynamax UV-C detector (Rainin Instrument, Woburn, Mass.), interfaced to a Dynamax PC HPLC Data System used to monitor the chromatograms. A Dynamax SD-200 Solvent Delivery System was used and the volume of the injected sample was 20  $\mu\text{L}$ .

### SEM-EDAX measurements

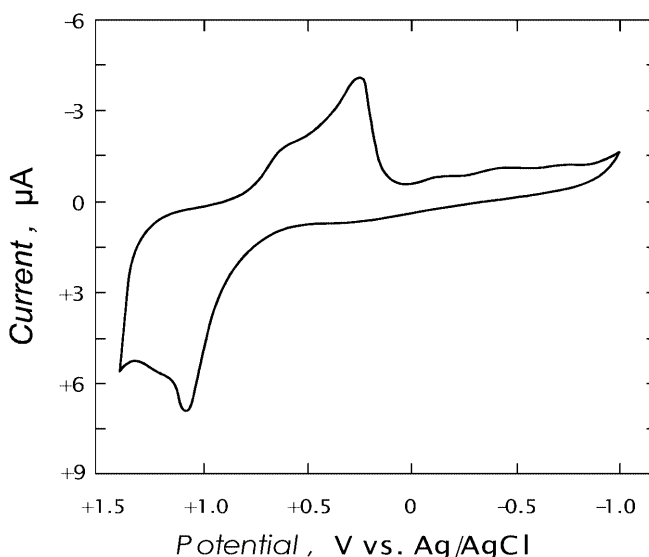
The SEM instrument was a Philips XL30 ESEM (FEI, Peabody, Mass.). A 30 kV electron beam was used for the polymer surface analyses. The EDAX detector was an EDAX instrument (Phoenix, Mahwah, NJ). The PPy and PPy- $\beta$ CD films were first washed, then dried, and peeled off from the electrode surface under a nitrogen stream. The films were then introduced into the SEM instrument under high vacuum before application of the electron beam.

## Results and discussion

The CV experiments with the PPy- $\beta$ CD film-coated electrode in 0.1 M  $\text{LiClO}_4$  were performed using a potential range of  $-1.0$  to  $+1.4$  V at 50  $\text{mV s}^{-1}$  scan rate. Figure 1 shows that PPy- $\beta$ CD is in its fully oxidized form at potentials exceeding  $+1.0$  V and in its totally neutralized form at potentials more negative than 0 V.

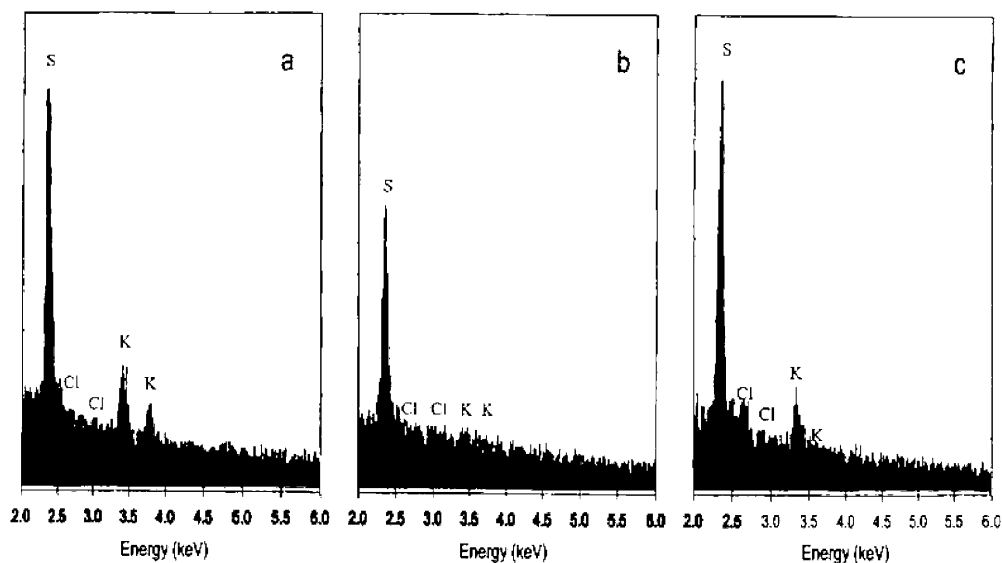
The electrochemical uptake and release of  $\text{K}^+$  by the PPy- $\beta$ CD film-coated electrode was examined both under the open circuit and controlled potential conditions. For the open circuit uptake of  $\text{K}^+$ , the PPy- $\beta$ CD film-coated electrode was immersed in a 5.36 mM KCl for 20 min. Figure 2c shows that the  $\text{K}^+$  uptake at open circuit is relatively slow and this slow  $\text{K}^+$  uptake at open circuit, even for times longer than 15 min, is a result of diffusion-controlled ion exchange alone. Importantly,  $\text{K}^+$  is not released, to any measurable extent, into deionized water at open circuit during a period of 20 min.

For the  $\text{K}^+$  uptake under potential control, the electrode was immersed in 2.68 mM KCl and a potential of  $-0.6$  V was applied for 15 min. Then, for the  $\text{K}^+$  release under potential control, the electrode was removed from this  $\text{K}^+$  uptake solution, rinsed with water, then transferred to deionized,  $\text{K}^+$ -free, water and a potential of  $+1.4$  V was applied for 15 min. As can be seen from Fig. 2a and Fig. 2b, under potential control, uptake of  $\text{K}^+$  by the PPy- $\beta$ CD film is appreciable and virtually no  $\text{K}^+$  remains in the film after electrochemical release. Most likely, migration contributes to the efficient cation ingress and egress. Thus, the potential applied to the PPy- $\beta$ CD film-coated electrode significantly increases both the rate of  $\text{K}^+$  uptake and release.



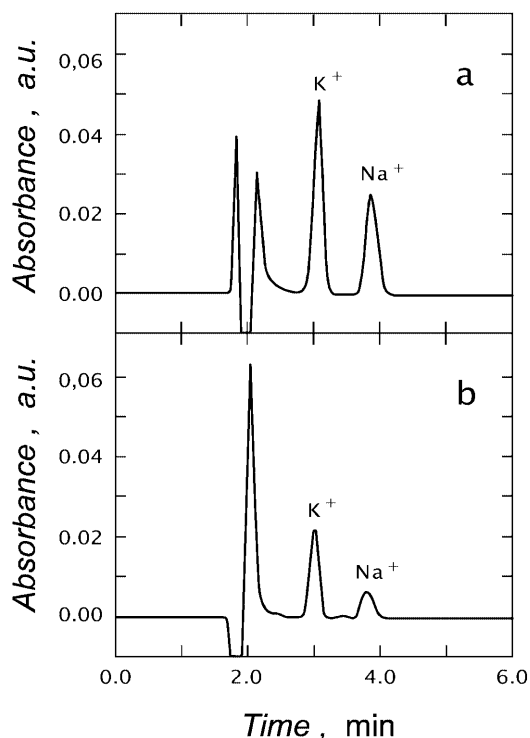
**Fig. 1** Cyclic voltammogram of a poly(pyrrole-sulfated  $\beta$ -cyclodextrin) film-coated Au electrode in 0.1 M  $\text{LiClO}_4$ . Potential sweep rate was 50  $\text{mV s}^{-1}$

**Fig. 2** The EDAX spectra of the PPy-S $\beta$ CD film after: **a** uptake of K<sup>+</sup> a 2.68 mM solution at -0.5 V for 15 min; EDAX plot: 597 counts full scale, 50 s measurement; **b** release of K<sup>+</sup> into deionized water at +1.4 V for 15 min; EDAX plot: 616 counts full scale, 38 s measurement; **c** uptake of K<sup>+</sup> from a 5.36 mM solution at open circuit for 20 min; EDAX plot: 514 counts full scale, 34 s measurement



The uptake and release of Na<sup>+</sup> and K<sup>+</sup> from the NaCl and KCl mixed solutions by the PPy-S $\beta$ CD film-coated electrodes was also examined. In these experiments, it was necessary to remove, first, all residual cations associated with the S $\beta$ CD sites remaining after the electrosynthesis of the film. For that purpose, the electrode was initially polarized at +1.4 V in 0.1 M HClO<sub>4</sub> for 30 min under a nitrogen atmosphere. That way, the remaining cations were exchanged with protons. Then, the electrode was rinsed with water and immersed in a 1.71 mM NaCl and a 1.34 mM KCl solution. After the controlled potential uptake and release (process as described above), both the uptake (standard) and the release solution were analyzed by HPLC using a cation-exchange column. The chromatogram in Fig. 3a, recorded for the uptake solution, shows two well-resolved peaks for Na<sup>+</sup> and K<sup>+</sup>. Figure 3b shows a similar chromatogram for the release solution. In the two chromatograms, the ratio of the peak heights for K<sup>+</sup>/Na<sup>+</sup> is higher for the release than for the uptake solution. This difference is, presumably, due to the difference in the uptake efficiency for Na<sup>+</sup> and K<sup>+</sup>.

Similar uptake and release experiments were performed for Ca<sup>2+</sup>. That is, a PPy-S $\beta$ CD film-coated electrode was loaded, first, with Ca<sup>2+</sup> in a 0.9 mM CaCl<sub>2</sub> solution under both open circuit and potential control conditions. Also, in this case, the Ca<sup>2+</sup> uptake is increased under controlled potential, compared to that at open circuit. However, once Ca<sup>2+</sup> was loaded into the PPy-S $\beta$ CD film, the potential switching to +1.4 V, even for a prolonged time, did not result in the release of Ca<sup>2+</sup>. Presumably, this effect is due to relatively high affinity of Ca<sup>2+</sup> for SO<sub>4</sub><sup>2-</sup>, as suggested by the low solubility of CaSO<sub>4</sub>. Hence, Ca<sup>2+</sup> may be irreversibly incorporated in the polymer matrix. At present, other multi-charge anions are being investigated for application for alkali earth and other multivalent cations.



**Fig. 3** HPLC chromatograms, for 20  $\mu$ L injections, on a Hamilton PRP-X800 cation exchange column, 250 $\times$ 4.6 mm, of **a** the K<sup>+</sup> and Na<sup>+</sup> uptake from a 1.34 mM KCl and a 1.71 mM NaCl mixed solution, and **b** the solid phase microextraction release solution. The flow rate of the 2 mM CuSO<sub>4</sub> mobile phase was 1 mL min<sup>-1</sup>

## Conclusions

Electrochemical control of the potential applied to a conducting organic polymer, like PPy, containing trapped multi-charged anions, such as S $\beta$ CD, does accelerate the rate of uptake and release of cations, like Na<sup>+</sup> and K<sup>+</sup>, as well as uptake of Ca<sup>2+</sup>, by the PPy-S $\beta$ CD

film. Thus, potential switching should be adaptable to the SPME conducting polymer devices for the analysis of cations, for instance, in flow analytical systems. Moreover, in this electrochemically aided SPME, accumulation in PPy- $\beta$ CD of organic cations of a size matching that of the  $\beta$ CD molecular cavity should be largely enhanced due to concurrent effects of ion exchange at the sulfate moieties and supramolecular complex formation with the  $\beta$ CD sites, similar to other anionic  $\beta$ CD polymeric systems [6, 7, 8].

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