Quantification of dopant ions in polypyrrole films with electrochemical ICP-atomic emission spectrometry and comparison to electrochemical quartz crystal microbalance studies

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Abstract

Quantification of electroinactive dopants in conductive polypyrrole (PPY) films was performed with electrochemistry combined on-line with inductively coupled plasma-atomic emission spectrometry (EC/ICP-AES). Anion (HSO$_4^-$) ejection out of a PPY film was first chosen as a model system and the results obtained with EC/ICP-AES were found to be comparable with values deduced by electrochemical quartz crystal microbalance (EQCM). The EC/ICP-AES approach was then extended to cases where EQCM findings become difficult to interpret (i.e. simultaneous insertion of Na$^+$ into and ejection of HSO$_4^-$ out of PPY film). It is demonstrated that EC/ICP-AES can simultaneously quantify both cationic and anionic species involved in the PPY redox switching. This is in contrast with EQCM studies that can only detect the net mass change from the two competing processes. This study shows that EC/ICP-AES is a viable technique for providing accurate information concerning the doping/dedoping processes without the necessity of removing the polymer-modified electrode from the electrochemical flow cell. More importantly, the species investigated do not need to be electroactive. It is clear that the comparative study between the two techniques can be powerful in unraveling relatively complicated redox reactions and ion-transport processes in conductive polymer films. © 2001 Published by Elsevier Science B.V.

Keywords: EQCM; Electrochemical ICP-AES; Ion-transport; Conducting polymer

1. Introduction

Several important physical properties of conductive polymer films (e.g. morphology, stability, and electrical conductivity) are highly dependent on the nature and quantities of ionic dopants inside the film matrices [1–9]. It is also known that ion-transport processes occurring during both the film formation and the redox switching of the polymer film affect the performance of conductive polymer films such as polypyrrole (PPY) or polythiophene in their applications as sensors, batteries, and electrochromic displays [10–15]. A number of techniques have been developed to examine various types of conductive polymer films. Generally, these techniques can be classified into two categories: ex situ and in situ. Examples of some ex situ techniques are X-ray photoelectron spectroscopy [7,16,17], Rutherford backscattering [18], energy dispersive X-ray spectroscopy [16], and radiotracer measurements [19]. The in situ methods include, but are not limited to, impedance spectroscopy [5,8,17,20,21], scanning electrochemical microscopy [22], rotating
ring-disk voltammetry [23,24], probe beam deflection [6], ellipsometry [25,26], and electrochemical quartz crystal microbalance (EQCM) [6,10,27–37]. While in situ methods undoubtedly provide more accurate information because ambiguities associated with transfer of films from the cell to the measuring devices are eliminated, they either are limited to the studies of electroactive dopants (e.g. rotating ring-disk voltammetry and scanning electrochemical microscopy) or do not provide quantitative information about the species of interest (e.g. ellipsometry, probe beam deflection, impedance spectroscopy, and EQCM). Traditionally, elemental analysis techniques have been impossible to use in situ (e.g. XPS) or less commonly used on-line (atomic spectroscopic techniques or mass spectrometry) with electrochemistry. Thus far, the most popular in situ method is still EQCM despite some of its intrinsic limitations [38–40]. The popularity of EQCM stems from its simplicity, sensitivity, and capability of studying both charge transfer and ion transfer processes. With the aid of information from other techniques and under favorable conditions, semi-quantitative measurements can be carried out [6,26,27,41,42].

Electrochemistry combined on-line with molecular mass spectrometry has been shown to be a useful technique to study electrode reactions [43–49]. Electrochemistry coupled with atomic mass spectrometry (e.g. inductively coupled plasma-mass spectrometry (ICP-MS)) [50–54], on the other hand, has primarily focused on the utilization of preconcentration for enhanced detection [52,53] and/or elimination of interfering species using the matrix-exchange procedure inherent in electrochemical stripping analysis [50,52,54]. To our knowledge, the only attempt that dealt with conductive polymers using electrochemistry combined on-line with molecular mass spectrometry (EC/MS) was the detection of permeable gaseous species through PPY films [55]. In that particular study, the experiments were qualitative, gearing towards proof of concept. A recent paper by Deng and Van Berkel demonstrated that electrochemical electrospray mass spectrometry can be used to study the initial oligomerization/polymerization of aniline monomer [43]. Thus far, electrochemistry used in conjunction with atomic mass spectrometry (e.g. ICP-MS) or ICP-atomic emission spectrometry (EC/ICP-AES) has not been shown for quantification of ionic dopants.

In this work, we applied EC/ICP-AES to the quantification of ionic dopants incorporated into PPY films. Particular emphasis is placed on the quantification of electroinactive species (which is not amenable to conventional voltammetric techniques) and on the study of cases that cannot be quantitatively examined by EQCM. We also show that EC/ICP-AES, when used in tandem with EQCM, can reveal new perspectives about the redox and ion-transport processes of the conductive PPY films.

2. Experimental

2.1. Reagents and chemicals

H₂SO₄ (95.8%) and pyrrole (Aldrich Chemicals, Milwaukee, WI) and Na₂SO₄ (Fisher Chemicals, Fair Lawn, NJ) were used as received. Hydrochloric acid used for preparing the carrier and sample solutions were double distilled from Vycor (GFS Chemicals, Powell, OH). All the solutions were prepared with deionized water (Millipore Corp.).

2.2. Instruments

A sequential, axially-viewed ICP-atomic emission spectrometer (Spectro Analytical Instruments, Fitchburg, MA) was used for sensitive detection of analytes of interest. A Microneb 2000 solvent delivery/flow-injection device, consisting of a gas displacement pump and a controller for the six-port rotary valve (Fig. 1a), and a model M2 microconcentric nebulizer were all from CETAC Inc. (Omaha, NE) and used as the sample introduction system. Throughout this work, 0.10 ml/min was chosen as the flow rate. The instrument used to monitor PPY growth in the chronopotentiometric QCM mode and to study the subsequent ion-transport processes using the potentiodynamic QCM mode was a CHI 440 galvanostat/potentiostat (CH Instruments).

2.3. Electrodes and cells

The QCM crystals used were AT-cut 7.995 MHz crystals that were coated with polished gold films.
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Fig. 1. (a) Valve configuration and flow system for introducing electrolyte solutions and for directing the plug of the ejected ions to the ICP-AES. The dotted lines show the valve configuration for introducing electrolyte solutions while the solid curves show that for delivering ejected dopants to the ICP-AES. (b) Schematic representation of the electrochemical flow cell for the EC/ICP-AES experiments. The darkened areas are the three electrodes and the shaded areas represent the Teflon gaskets. The gasket on the left had two small holes matching that on the Pt foil (auxiliary electrode) and the solution inlet and outlet, while the gasket on the right is a commercial gasket which has a diamond-shaped cavity.

(5 mm in diameter, ICM Technologies, Oklahoma City, OK). The crystal was mounted with O-rings on both sides into a cylindrical Teflon cell (CH Instruments, Austin, Texas) which also houses a Pt auxiliary electrode and a Ag/AgCl reference electrode. The area of the gold film disk was 0.212 cm$^2$ (QCM active area) and the portion of the stem of the keyhole that was exposed to solution constituted another 0.048 cm$^2$ (total conductive area = 0.26 cm$^2$).

The flow cell used for the EC/ICP-AES experiment was schematically shown in Fig. 1b. This design is similar to that used in [53] except that the PEEK cell body was part of a CHI130 thin-layer flow cell (CH Instruments). For this work, there are two additional changes. First, the Pt foil (25 μm thick, Aldrich), instead of being glued onto the cell body [53], was sandwiched between two Teflon gaskets. The Pt foil and the Teflon gasket behind it both have holes that match the inlet and outlet on the PEEK cell body. The other Teflon gasket separating the cell body and the working electrode was acquired from Bioanalytical Systems Inc. (BAS, West Lafayette, IN). The second change was that the reference electrode, a homemade PEEK screw-fitting embedding a 0.5 mm diameter Ag wire (Alfa-Aesar, Ward Hill, MA), was positioned upstream of the cell facing the inlet hole perpendicularly. With these two changes, replacing and cleaning of the counter electrode become easier (since the Pt foil was not permanently affixed onto the cell) and it is a tighter fit for applications in which higher backpressure exists downstream of the cell.

In order to have a consistent comparison with the EQCM experiments, the working electrode employed was a 6 mm diameter gold disk electrode (BAS Inc.). The total area, 0.28 cm$^2$, is very close to that of the gold film on the QCM crystals. Nevertheless, in order to make one-to-one comparison between EQCM and EC/ICP-AES, a correction factor of 0.26/0.28 was used when EC/ICP-AES results were interpreted.
2.4. Procedure

2.4.1. Electrode pretreatments

The gold films on the QCM crystals were cleaned with a piranha solution (30% H₂O₂ and 70% concentrated H₂SO₄). The gold disk electrode for the electrochemical flow cell was polished with diamond and alumina pastes down to 0.3 μm, followed by rinsing with and sonicating for 15 s in deionized water. Prior to screwing the reference electrode into the PEEK cell body, the Ag disk electrode was coated with a layer of AgCl using the coating solution (BAS Inc.).

2.4.2. Polypyrrole film formation

The PPY film doped with HSO₄⁻ was prepared in a 58 mM PY/0.5 M H₂SO₄ solution. Films at the both the gold disk electrode for EC/ICP-AES and the gold-coated QCM crystal were produced using the chronopotentiometric QCM mode using the same number of charges. At the QCM crystals, the charge for forming the PPY films was 0.0147 C and the amount of PPY–HSO₄⁻ deposited was about 5.1 μg. The average frequency decrease (ca. 3800 Hz) corresponds to the formation of films whose thickness is approximately 0.3 μm [32]. PPY films with such a thickness are generally considered to behave as rigid films [6]. Since the areas of the QCM crystal and the Au electrode for the EC/ICP-AES experiment are of similar size, the quantities of PPY per unit area should be close with the same current density and deposition time.

2.4.3. EQCM measurements

PPY films doped with different ions were transferred to a 0.1 M HCl solution. Multiple potential cycles were then conducted between PPY oxidized and reduced states. The number of potential cycles was chosen based on the nature of the film and the ions involved [20,56]. We cycled the electrode potential until there was little frequency hysteresis between the first and the last potential cycles. When such a “steady state” had been reached, the original cations or anions were ejected out of the film into the HCl solution and the charge compensation was achieved with the more abundant and favorable Cl⁻ and/or H⁺ [18,31,57] in the solution.

2.4.4. EC/ICP-AES measurements

The complete ejection of dopants such as HSO₄⁻ can be achieved by extensive potential cycling in a HCl solution because (1) both H⁺ and Cl⁻ are mobile and can replace dopants quite rapidly [18,31,57] and (2) redox switching expedites the expulsion of ions. Specifically, the PPY film-covered electrode containing dopants was mounted onto the flow cell that is connected to the six-port rotary valve (Fig. 1a). About 50 μl of HCl solution was then introduced into the cell with a syringe pump to ensure that the entire flow system was filled with solution. The pump was then stopped and the potential was cycled to eject the dopants into the quiescent solution confined within the cavity of the gasket (Fig. 1b). The combined volume downstream of the working electrode (including the volume of the gasket, the tubing connecting the cell to the valve, and the tubing connecting the valve to the ICP nebulizer) is about 16 μl. Upon switching the rotary valve to the inject position, ejected dopants were detected by the ICP-AES downstream of the flow cell (see Fig. 2). In experiments where PPY films were subject to partial exchange with ions in an electrolyte solution prior to switching to the HCl solution, introduction of the electrolyte solution and the subsequent washing of the cell system were carried out with syringes containing different electrolyte solutions without dismantling the flow cell.

Amounts of dopants were quantified using calibration curves constructed from separate flow-injection analyses of a series of standard solutions. Five standard solutions ranging from 1 to 150 ppm in 0.1 M HCl were injected through a 20 μl loop and the peaks were integrated to produce the calibration curves.

3. Results and discussion

3.1. Principle of and instrumental set-up for EC/ICP-AES

The principle of EC/ICP-AES for the quantification of dopant ions ejected from PPY films is illustrated in Fig. 2, using ejection of HSO₄⁻ into a HCl solution as an example. In step 1, HSO₄⁻, the primary species dissociated from the 0.5 M H₂SO₄/PY mixture, was incorporated into the oxidized PPY film during the
Fig. 2. Principle behind quantification of ions in PPY films by EC/ICP-AES, using $\text{HSO}_4^-$ ejection into the HCl carrier solution as an example. In step 1, the PPY formation brings the counteranion $\text{HSO}_4^-$ into the film, and in step 2, the counteranion will be ejected upon film reduction (neutralization). The $\text{Cl}^-$ anions in the HCl solution can be exchanged with the $\text{HSO}_4^-$ during the potential cycling experiments and eventually become the main dopant (indicated by the double arrow). At the completion of step 2, the cell content is diverted to the ICP-AES for subsequent analysis.

film formation as shown in the following reaction:

$$n\text{PY} + m(\text{HSO}_4^-) - (y + z)e^-$$

$$\rightarrow \text{PPY}^{x+}(\text{HSO}_4^-)_m + z\text{H}^+ \quad \text{(step 1)}$$

The number of charges consumed includes the charge needed for adding PY units to the polymer ($z$) and that needed to partially charge the PPY film ($y$). The loss of protons and the incorporation of $\text{HSO}_4^-$ help maintain the overall film neutrality. In step 2, the PPY film was cycled potentiodynamically in a HCl solution. The reduction causes the $\text{HSO}_4^-$ to be ejected, as shown in the following reaction, while the film reoxidation (not shown in Fig. 2) would lead to the incorporation of the more abundant $\text{Cl}^-$ from the solution.

$$\text{PPY}^{y+x+}(\text{HSO}_4^-) + xe^-$$

$$\rightarrow \text{PPY}^{(y-x)+} + x\text{HSO}_4^- \quad \text{(step 2)}$$

The partial loss of $\text{HSO}_4^-$ will occur in each reduction and through multiple potential cycles the $\text{HSO}_4^-$ will all be replaced by $\text{Cl}^-$. In this work, we terminated the potential cycles at the PPY reduced state so that any possible reincorporation of ions from solutions would not take place. After the dopant(s) of interest had been completely ejected, the valve (Fig. 1a) was switched to the inject position. The carrier solution from the gas displacement pump then delivers the cell content to the ICP-AES for quantification (Fig. 2).

3.2. Comparison between EC/ICP-AES and EQCM

Before discussing the experimental results, it is helpful to make a general comparison between EC/ICP-AES and EQCM for studies of ion-transport processes in conducting polymer films. The utilization of EQCM for studying redox switching and the accompanying dopant fluxes has been reviewed [39]. The quantitative aspect of EQCM is based on the Sauerbrey equation whose validity is highly dependent on various experimental factors [38–40]. These factors include the viscoelastic effect associated with the film swelling/deswelling [28,38,39], conductivity variation [58], and thickness and porosity of the films [6,28,38,55,59]. Another major disadvantage of EQCM is that it is not species-specific since only mass change at the electrode surface is measured. Finally, quantitative measurements and data interpretation might be difficult because of hydration of ions and competing processes that cause both mass gain and loss. Nevertheless, EQCM has been shown to...
provide valuable information about the electropolymerization processes (e.g. current efficiency and quantities of polymer and dopants deposited onto the electrode surface [26]) and to offer mechanistic insight into ion-transport processes within the polymer framework [35,39].

EC/ICP-AES can overcome some of the problems. ICP-AES is quantitative and selective. Owing to the high temperature of the plasma, all species are desolvated. Moreover, the detection is not electrochemically based. Therefore, certain processes occurring at the electrode surface that are detrimental to voltammetric measurements (e.g. film morphological and phase changes and charging current) will not interfere. In addition, simultaneous determination of multiple dopant ions, electroactive and/or electroinactive, is possible. However, EC/ICP-AES has certain limitations as well. Despite the fact that EC/ICP-AES allows quantification of species on-line, the results do not reflect certain important aspects of ion-transport (e.g. solvation of ions). In addition, the ICP-AES sample introduction system cannot tolerate high concentrations of some electrolytes (e.g. 0.17 M Na2SO4) for an extended measuring time. As a result, a solution more suitable for ICP-AES operation (e.g. HCl or HNO3) is preferred.

3.3. Calculation of amount of dopants incorporated into the pristine PPY films

In the electrodoposition of the PPY film with HSO4− as the dopant, we observed similar chronopotentiometric response and the mass–time behavior (not shown) to that reported by other researchers [10,26,31,33]. The experimental ratio between the mass change detected and the total charge consumed (Δm/ΔQ) in the PPY deposition was found to be 0.35 μg/C.

Baker and Reynolds [32] and Torresi and co-workers [33] derived and used Δm/ΔQ in attempt to relate the mass of the PPY–dopant mixture to the summation of charges for adding one PY unit (two electrons required) to the PY backbone and that for partially charging the PPY film. The number of charges used to partially oxidize the PPY film, n, has been reported to range from 0.2 to 0.5 electrons per PY [1,2,32,33,59–61]. The value of 0.33 is the most commonly used and the theoretical Δm/ΔQ for n = 0.33 would be 0.43 μg/C based on the following equation [33]:

\[
\Delta m = \frac{3(MW_{PY} + (1/3)MW(HSO_4^-) - 2AW_{H^+})}{7F}
\]

where MW_{PY} is the molecular weight of PY (67), MW(HSO4−) the molecular weight of HSO4− (97), AW_{H^+} the atomic weight of proton (1), and F is the Faraday’s constant (96,490 C/mol). Our experimentally measured Δm/ΔQ (0.35 μg/C) is smaller than the theoretical predication, suggesting that the electrolytic efficiency is less than 100%. This observation is similar to that reported to by other researchers [32,33].

The quantity of HSO4− can thus be calculated based on the total mass of the PPY–HSO4− deposit and the fraction of the HSO4− in the total deposit. According to the above equation, the fraction should be

\[
\frac{(1/3)MW(HSO_4^-)}{MW_{PY} + (1/3)MW(HSO_4^-) - 2AW_{H^+}} \times 100% = 33%
\]

Therefore, there will be about 1.68 μg of HSO4− in a 5.10 μg of PPY–HSO4− film. The actual amount of HSO4− should be less than the calculated value since the composite film is hydrated.

3.4. Detection and quantification of different ions ejected from PPY films

3.4.1. HSO4−-doped PPY films

To validate the methodology for quantification of ionic dopants in PPY films using EC/ICP-AES, we first chose HSO4− ejection from a reduced PPY film into a Cl−-containing solution as the model system. The choice of this system is based on the following two considerations: (1) HSO4− is a less favorable anion than Cl− [18,31,57,64]. Therefore, Cl− can replace HSO4− rapidly, especially during the redox switching processes, and (2) HCl is a suitable solvent system for introducing samples into ICP-AES and does not produce any background signal for sulfur.

Fig. 3a and b depict selected cyclic voltammograms (CVs) of a HSO4−-doped PPY film during multiple potential cycles in a 0.1 M HCl solution and the concurrent mass changes, respectively. In the first cycle (solid line curve), the PPY begins to undergo...
Fig. 3. (a) Cyclic voltammograms showing the redox switching of a PPY–HSO$_4^-$ film in a 0.1 M HCl solution and (b) the corresponding mass changes associated with the ion movements. The scan rate used was 0.1 V/s. For clarity, only the first (solid line curves), the 20th (curves with filled circles) and the 40th (dotted line curves) potential cycles are shown. Arrows indicate the scan directions. (c) Cyclic voltammograms (solid line curve for the first cycle and dotted line curve for the 40th cycle) obtained from the electrochemical flow cell and (d) the corresponding time-resolved ICP-AES response showing the elution of the HSO$_4^-$ (curve numbered with 1). The curve numbered with 2 shows the ICP-AES responses after each of the two separate sets of 20.5 cycles (corresponding voltammograms not shown).

The mass loss (solid line curve in Fig. 3b) is indicative of the HSO$_4^-$ dedoping for maintaining the PPY film neutrality. During the reoxidation (reversal scan), the PPY becomes positively charged and the charge-balance is achieved through the incorporation of the more abundant Cl$^-$ from the solution. Note that there was a net mass gain at the end of each cycle. The mass increase can be ascribed to the more extensive solvation of Cl$^-$ [62]. The observation that the second and later cycles (e.g. the 20th cycle shown as the curve with filled circles in Fig. 3b) caused smaller mass changes suggests that a large fraction of HSO$_4^-$ had been ejected in the first cycle. But the ejection of HSO$_4^-$ in one potential cycle is not complete as it generally takes more than 30–40 cycles to reach the “steady state” to attain a somewhat constant mass change. At the steady state, the Cl$^-$ doping/dedoping becomes the predominant process. The possible inclusion of H$^+$ during the film reduction might not be very important as mass loss during the film reduction was observed throughout the entire potential cycling experiment. This suggests that HSO$_4^-$ ejection is a slow process and multiple potential cycling between the oxidized and reduced states of PPY is deemed necessary if quantification of the total HSO$_4^-$ is desired. Since not all the HSO$_4^-$ has been ejected during the forward scan of the first cycle and incorporation of Cl$^-$ in the subsequent scan reversal brings more water molecules into the film, it is apparent that mass changes in Fig. 3b are not useful for deducing the total amount of HSO$_4^-$. 
Our EC/ICP-AES experiment provides a more reliable means to measure the amount of HSO$_4^-$ in the PPY film. Shown in Fig. 3c and d are some representative CVs of PPY obtained from a 0.1 M HCl solution in the flow cell and the time-resolved ICP-AES response for HSO$_4^-$ (monitored as sulfur), respectively. CVs in Fig. 3c are similar to that in Fig. 3a. The peak of curve 1 in Fig. 3d corresponds to the elution of the ejected HSO$_4^-$ after 40.5 potential cycles. The amount of HSO$_4^-$ upon cycling potentials for an additional 40.5 segments was not observable. We also carried out an experiment in which two separate sets of 20.5 cycles were applied consecutively while setting the ICP-AES to monitor the elutions of the cell contents. The data was presented as curve 2. We observed a smaller peak after the second set of 20.5 cycles (peak II in curve 2). Peak II is about 8–10% of peak I in curve 2. Therefore, we conclude that ejection of HSO$_4^-$ from the film is indeed a sluggish process and extensive potential cycling (40.5 cycles or more) is necessary for quantitative ejection of the total HSO$_4^-$.

Such a conclusion is in line with the EQCM observations. The average value of HSO$_4^-$ determined from five replicates and its uncertainty are listed in Table 1 for case (a).

As can be seen in Table 1, the value measured (0.969 μg), is in reasonable agreement with that predicted from the calculation based on the PPY–HSO$_4^-$ mass (1.68 μg), given the fact that the total mass of the PPY–HSO$_4^-$ composite should be less because of the water incorporation in the polymer film. Thus, the closeness between the value deduced from the EC/ICP-AES experiment and that calculated based on numbers acquired from the chronopotentiometric QCM experiment demonstrates that EC/ICP-AES is a reliable technique for quantifying the replaceable dopant ions in conductive polymer films. This also indicates that most of the HSO$_4^-$ in the pristine PPY–HSO$_4^-$ film has been replaced by Cl$^-$ through extensive cycling.

### 3.4.2. PPY films containing Na$^+$ and SO$_4^{2-}$

Once the EC/ICP-AES methodology has been established, we extended it to the study of competitive or simultaneous cation insertion (mass increase) and anion ejection (mass decrease), a case that is difficult for EQCM. In dealing with such systems, EQCM is a semi-quantitative technique at best and care must be exercised in interpreting the observed mass changes [38–40]. The specific case we chose is concerned with Na$^+$ insertion into and HSO$_4^-$ ejection out of reduced PPY films. Fig. 4a and b shows a CV and the corresponding mass–potential curve acquired at a PPY film in a monomer-free Na$_2$SO$_4$ solution, respectively. This is a non-steady state behavior since CVs and mass changes in later potential cycles (data not shown, but are consistent with that in [33]) are quite different. As can be seen during the forward scan,
there was a mass increase of 3.9 μg at ca. −0.38 V, followed by an abrupt mass decrease of 1.9 μg after −0.45 V. In this case, charge-balance in the reduced PPY−HSO₄⁻ film is fulfilled by concerted incorporation of Na⁺ and ejection of HSO₄⁻, a process that was proposed by Torresi and co-workers [33]. In the papers published by these researchers, however, quantitative information was not obtainable due to the complexity associated with the competitive cation insertion and anion ejection. Owing to such an uncertainty, most papers on the PPY doping/dedoping processes deal with the steady state (equilibrium) situation which is simpler to the interpretation of EQCM results. Fig. 4b suggests that the HSO₄⁻ ejection, though slow, could become pronounced at a more negative potential. In addition, extensive hydration of Na⁺ [62] and possible viscoelastic effects [38–40] resulted from the film redox switching could have introduced ambiguities since mass increase in Fig. 4b is greater than the value expected for charge-balance.
This assessment is made based on the following reasoning.

To deduce the maximum amount of Na\(^+\) that needs to be inserted for charge-balance, one can assume that all the PPY moieties in the film were reduced and little HSO\(_4^-\) was ejected. As mentioned in connection with the discussion of case (a), the amount of HSO\(_4^-\) in the pristine PPY–HSO\(_4^-\) was 1.16 \(\mu\)g. Therefore, the stoichiometric amount of Na\(^+\) should be 0.275 \(\mu\)g of Na\(^+\). Actually, the abrupt mass decrease in Fig. 4b indicates that a fraction of the HSO\(_4^-\) had been ejected. This implies that quantity of Na\(^+\) necessary for charge-balance should be even smaller than 0.275 \(\mu\)g.

Before we utilized EC/ICP-AES for the quantification of both Na\(^+\) and SO\(_4^{2-}\), we first conducted a potential cycling experiment in a 0.1 M HCl solution. Specifically, the PPY–HSO\(_4^-\) film was first reduced in the Na\(_2\)SO\(_4\) solution by terminating the potential scan at the negative potential limit (−0.75 V). This step was followed by thoroughly rinsing the resultant Na\(^+\)- and HSO\(_4^-\)-doped PPY film with water and transferring it to a 0.1 M HCl solution. The selected CV and QCM responses in the HCl medium are shown in Fig. 4c and d, respectively. In Fig. 4d, oxidation of the PPY film caused a mass decrease at ca. 0.20 V. This decrease continued throughout most of the reversal scan (from 0.5 to ca. −0.25 V). Therefore, it seems that reoxidation of the Na\(^+\)- and HSO\(_4^-\)-doped PPY film resulted in a major loss of Na\(^+\) and a follow-up loss of HSO\(_4^-\) during the scan reversal.

Our EC/ICP-AES experiment provides an attractive route for quantifying unequivocally the individual dopant ions. Shown in Fig. 4e and f are the simultaneously acquired time-resolved ICP-AES responses of the Na\(^+\) and HSO\(_4^-\) (as sulfur) ejected after multiple cycles in a 0.1 M HCl solution. The average values of Na\(^+\) and HSO\(_4^-\) from five replicates for the original 5.1 \(\mu\)g PPY–HSO\(_4^-\) film were therefore determined to be 0.103 and 0.397 \(\mu\)g, respectively. The R.S.D. (%) values (13% for Na\(^+\) and 15% for HSO\(_4^-\)) again suggest that the EC/ICP-AES measurements are precise. We believe that part of these variations stems from the variability in the reductions of different PPY films in the Na\(_2\)SO\(_4\) solution. The R.S.D. (%) associated with the areas of reduction peaks such as that in Fig. 4a is 11%. The more the charges consumed in the PPY reduction (i.e. larger reduction peak area in Fig. 4a), the higher the quantities of Na\(^+\) and HSO\(_4^-\) measured. This is expected since when more PPY units are reduced in Na\(_2\)SO\(_4\), more Na\(^+\) will be incorporated and more HSO\(_4^-\) will be ejected. Finally, it is worth mentioning two interesting points. First, in Table 1, compared to the amount of HSO\(_4^-\) measured in case (a), the amount of HSO\(_4^-\) quantified from the Na\(^+\)- and HSO\(_4^-\)-doped PPY film is smaller. Such a comparison indicates that an appreciable amount of the original HSO\(_4^-\) has departed the PPY film upon one potential scan to reduce PPY. The mass of HSO\(_4^-\) ejected should be the difference between the two values listed under the two cases (i.e. 0.969 − 0.397 = 0.572 \(\mu\)g). Therefore, about 59% of the original HSO\(_4^-\) has been ejected in one potential scan in the Na\(_2\)SO\(_4\) solution. Second, the ratio between the average mole of Na\(^+\) (0.103 \(\mu\)g/AM(Na\(^+\)) = 4.47 and that of HSO\(_4^-\) (0.397 \(\mu\)g/MW(HSO\(_4^-\)) = 4.09 nmol) is 1.09. This suggests that the amount of Na\(^+\) inserted is stochiometrically equivalent to the remaining HSO\(_4^-\). This can happen only when the PPY film is completely reduced. Therefore, it is obvious that the PPY reduction is rapid and the HSO\(_4^-\) departure is the rate-determining step. Since these additional points and those aforementioned observations are in line with general descriptions about PPY film redox switching in Na\(^+\)-containing electrolyte solutions [8,28,33,56,60], the viability of EC/ICP-AES for quantification of dopants in conductive polymer films is therefore consolidated. This also demonstrates that results extrapolated from EC/ICP-AES and EQCM can be highly complementary and can shed insight to the elucidation of the redox reaction of and ion-transport processes within conductive polymer films.

4. Conclusions

This work showed that EC/ICP-AES and EQCM are complementary to one another for the identification and quantification of ions inserted into or ejected from conducting PPY films during the film redox switching. While EQCM is simple and fast and can provide in situ information about the dominating mass transfer process during a redox reaction, it is not species-specific and only total mass change...
can be deduced. EC/ICP-AES, on the other hand, can provide unequivocal identification and accurate quantification of dopant ions involved during PPY deposition and redox-state alteration. We showed that EC/ICP-AES is a powerful hyphenated technique suitable for quantification of single or multiple species. A major advantage of this combination is that removal of the PPY-modified electrode from the electrochemical cell for elemental analysis of the film is avoided. Therefore, uncertainties inherent in certain ex situ methods (e.g., XPS) can be circumvented. Finally, the elemental analysis capability of ICP-AES allows species that are not electroactive to be determined, expanding the range of dopant types amenable to electrochemically-based methods. However, without the aid of EQCM, EC/ICP-AES cannot provide a comprehensive description of certain processes (e.g., amounts of PPY and the extent of hydration would not be known). Therefore, the tandem use of EQCM and EC/ICP-AES not only provides quantitative descriptions of each doping/dedoping process, but also allows certain complicated cases (e.g., the non-steady doping/dedoping of PPY in the present work) to be studied. Similar comparative studies should be applicable to the studies of other types of conductive polymers or redox polymers.

**Uncited reference**

[63].

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**References**


