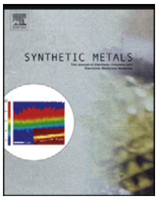
Synthetic Metals 159 (2009) 2590–2598

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Ion exchange behaviour and charge compensation mechanism of polypyrrole in electrolytes containing mono-, di- and trivalent metal ions

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ARTICLE INFO

Article history:
Received 9 June 2009
Received in revised form 30 August 2009
Accepted 10 September 2009
Available online 13 October 2009

Keywords:
Polypyrrole
Polystyrene sulfonate
Trivalent metal ion
Charge compensation
Quartz crystal microbalance

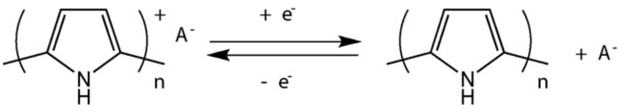
ABSTRACT

The electrochemical quartz crystal microbalance technique was used to examine the ion exchange behaviour and charge compensation mechanism of polypyrrole (PPy) doped with polystyrene sulfonate (PSS) immersed in electrolytes containing singly, doubly and triply charged metal ions. New insights were obtained concerning the mechanism of charge compensation and ion exchange behaviour of PPy/PSS films in electrolytes with triply and doubly charged transition metal ions. Understanding the ion exchange behaviour of conducting polymers immersed in these types of aqueous media could play a pivotal part in the development of methods for removing toxic metals from water supplies. Charge compensation occurred predominantly by means of cation movement for PPy/PSS films when the electrolyte was KNO_3, $Ca(NO_3)_2$, $Mn(NO_3)_2$ or $Co(NO_3)_2$. After prolonged redox cycling the electroactivity of the polymer decreases slightly, and the charge compensation mechanism becomes complex owing to movement of ions and neutral species in opposite directions. The charge compensation mechanism for PPy/PSS films immersed in aqueous $Cr(NO_3)_3$ and $Al(NO_3)_3$ solutions was also complex, with the ion exchange behaviour shifting towards anion movement to and from the polymer.

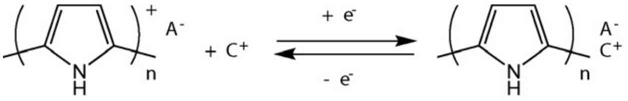
1. Introduction

Inherently conducting polymers (ICPs) such as polypyrrole (PPy), polyaniline (PAn), polythiophene (PTh) and their derivatives are attracting considerable attention for a myriad of applications in areas such as microelectronics, corrosion control, photochromic and photovoltaic devices, sensors, electromechanical actuators, batteries and capacitors [1,2]. This is a consequence of the unique blend of properties possessed by these materials, including strength, processability and electrical conductivity. Another feature of ICPs is their electroactivity, which is the ability to undergo reversible changes between two or more oxidation states. This is a very important characteristic of ICPs, as it provides a mechanism by which their chemical and physical properties, such as colour, volume, porosity, and electrical conductivity, can be altered by electrochemical means.

The reactions that accompany electrochemical switching of ICPs are often summarised using Eqs. (1) and (2), which use polypyrrole as an example. Immediately after their preparation by oxidative electrochemical polymerization, ICPs are present in a conducting, oxidised state. During electrochemical synthesis, anions (A^-) are incorporated (doped) into their structure to balance the positive charges present along the conducting polymer backbone. When the ICP is reduced, for example by applying a negative potential, the conducting polymer backbone becomes neutral. In order for the ICP to remain neutral either the anion, A^-, that was incorporated during synthesis must be expelled (Eq. (1)), or if the anion is immobile cations (C^+) present in the surrounding electrolyte will be incorporated (Eq. (2)). When the ICP is subsequently re-oxidised, and positive charges returned to the conducting polymer backbone, cations that were previously incorporated might be expelled, or alternatively anions present in the surrounding solution (either the original dopant A^- or another anion present in the electrolyte) are incorporated.



(1)



(2)

The above reactions allow ICPs to function as electrochemically controllable ion exchange membranes. Such materials are of interest for analytical applications, and also for recovery of toxic or

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doi:10.1016/j.synthmet.2009.09.019

precious metal ions from aqueous solutions. We have previously explored the use of ICP membranes as electrochemically controllable, selective barriers to ion movement [3–7]. The membranes used were thick enough to prevent metal ion transport under ordinary conditions, but allowed significant transport when either constant or pulsed potentials were applied. In early studies the flux of metal ions such as K^+ and Ca^{2+} across the membrane was found to be dependent upon a variety of factors, including the thickness of the membrane, and the type and duration of the electrochemical stimulus used [3,4]. More recently we have shown that transport of transition metal ions across polypyrrole membranes is significantly affected when anionic chelating agents, or other metal complexation agents such as cyclodextrins, are used as dopants [6,7].

In order to fully utilise ICP materials for membrane separation purposes, or other applications that takes advantage of the electroactivity of ICPs, it is essential to have a complete understanding of the processes that accompany oxidation and reduction of the polymer. A number of studies have showed that the size, and therefore the mobility, of the dopant anion incorporated during ICP synthesis plays a major role in determining which of the reactions depicted in Eqs. (1) and (2) is primarily responsible for maintaining charge neutrality upon redox cycling [2,8–15]. However, it has also been demonstrated that the ion exchange behaviour of ICP films is dependant on many other factors. These include the method used to prepare the polymer [14,16,17], the type, size and valency of the ions present in the surrounding electrolyte solution [18], the identity of the solvent [19], solution temperature [20], nature of the applied electrochemical stimulus [21], and the age and thickness of the film [22,23]. Not surprisingly under many circumstances movement of both cations and anions occurs simultaneously in order to bring about charge compensation [18,24,25], and ion movement is also accompanied by solvent transfer to and from the polymer [26–29].

A variety of models and schemes have now been proposed to account for the different charge compensation mechanisms observed for different ICPs including PPy and poly(3,4-ethylenedioxythiophene) (PEDOT), in the presence of different dopant/electrolyte combinations [18,25,30–32]. The development of these models represents a significant advancement in our understanding of the redox behaviour of ICPs. However, there still remain a number of areas that have not been explored in depth. This includes determining how charge compensation occurs when ICP polymer films are immersed in electrolytes containing transition metal cations. In addition, the relative extent of cation and anion movement can potentially be manipulated by the number of times an ICP film is subjected to redox cycling.

Therefore, in order to address these questions we have performed electrochemical quartz crystal microbalance (EQCM) experiments using polypyrrole films and a number of electrolytes including KNO_3, $Ca(NO_3)_2$, $Co(NO_3)_2$, $Mn(NO_3)_2$, $Al(NO_3)_3$ and $Cr(NO_3)_3$. These cations were chosen for study not only because of their environmental and toxic effects [33–35], but also because of their diversity in valency. In this study we provide new insights into the mechanism of charge compensation and ion exchange behaviour of polypyrrole films immersed in electrolytes containing triply and doubly charged transition metal ions. Developing a greater understanding in these areas could play a pivotal part in the development of methods for removing metal ions from water supplies using the ion exchange properties of ICPs [36–38].

2. Experimental

All reagents and chemicals used were of analytical reagent grade. Pyrrole was obtained from Merck and distilled before use. All other reagents including sodium polystyrene sulfonate (NaPSS) were purchased from Aldrich. All solutions were prepared using deionised water (18 MΩ cm). 5 MHz AT-cut, polished, quartz crystal with chromium/gold electrodes for use in EQCM experiments were supplied by Coherent Scientific, South Australia. The crystals had an overall diameter of 2.54 cm, while the electrochemically active area of the working gold electrode was 1.37 cm^2.

Prior to the polymerization, the crystals were cleaned by ultrasonication in ethanol for 5 min. The crystals were dried in a stream of N_2 and then placed in a UVO (ultra violet/ozone) cleaner for 5 min. The crystals were mounted into the crystal holder with the gold electrode facing upwards. The crystal holder was connected to the crystal oscillator, which was connected to the QCM controller (Stanford Research Systems). During electropolymerization, the crystals with the gold surface served as a working electrode, while Pt gauze was used as the auxiliary electrode and Ag/AgCl (3 M NaCl) was the reference electrode. The polymerization solution consisted of 0.1 M pyrrole and 0.1 M NaPSS. Electropolymerization was performed galvanostatically at room temperature, by using a EG&G PAR363 potentiostat/galvanostat to apply a constant current density of 0.5 mA cm^{-2} for 5 min to the working electrode in the polymerization solution. All polymerization solutions were deoxygenated with high purity N_2 gas before use. The EG&G PAR363 was equipped with a computer controlled eDAQ to monitor frequency variations of the crystal during polymerization.

After synthesis the polymer-coated crystals were washed thoroughly with deionised water in order to remove any remaining monomer, electrolyte or other impurities such as oligomers. In a similar set up to that used for electropolymerization, the PAR363 was used to apply a triangular potential waveform to the working electrode, with the potential limits initially being −1.0 V and +0.7 V, and the scan rate 100 mV s^{-1}, for 100 cycles. The electrolytes used were 0.1 M aqueous solutions of KNO_3, $Ca(NO_3)_2$, $Co(NO_3)_2$, $Mn(NO_3)_2$, $Cr(NO_3)_3$, and $Al(NO_3)_3$, representing mono-, di- and trivalent metal ions. By using the above electrolytes, variations in ion exchange behaviour and mechanism of charge compensation caused by changing the valency of the metal ion present could be investigated. The changes in frequency of the EQCM crystal were measured by a computer with the aid of an analogue to digital converter (eDAQ).

3. Results and discussion

3.1. Electropolymerization

Chronopotentiograms recorded during polymer growth showed that polymerization was initiated at +0.76 V, and that the film continued to grow uniformly over the surface at a constant potential of +0.6 V. The potential remained constant at +0.6 V throughout the rest of the polymerization process. At these potential values observed we can conclude that there was no over oxidation of the polymer.

The relationship between the observed change in oscillation frequency of the crystal and the change in mass per unit area is given by the Sauerbrey equation (Eq. (3)).

$$\Delta f = -C_f \Delta m \quad (3)$$

In this equation Δf is the observed frequency change, Δm is the change in mass per unit area, and C_f is the sensitivity factor for the crystal. The Sauerbrey equation is applicable only to thin, uniform and rigid films. Before proceeding with subsequent experiments, the Sauerbrey relationship was first verified by monitoring the amount of charge passed (the thickness of the film) and the relationship between the change in frequency (mass change) and the charge. A linear relationship was observed between the mass change due to polymer deposition on the crystal and the charge