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Metal transport studies on inherently conducting polymer membranes containing cyclodextrin dopants

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Abstract

Conducting polymer membranes consisting of polypyrrole (PPy) doped with sulfated α-cyclodextrin (α-CDS) or sulfated β-cyclodextrin (β-CDS) were prepared electrochemically using aqueous solutions, containing pyrrole and the respective cyclodextrins. The N:S ratio for both polymers were very similar and indicated that there was approximately 4.5 pyrrole for every deprotonated sulfate group. The electrical conductivities of PPy·α-CDS and PPy·β-CDS were found to be 0.7 S cm^{-1} and 0.4 S cm^{-1}, respectively. Cyclic voltammetry studies showed that the two polymers were electroactive and generally gave similar electrochemical responses when immersed in the same elecrolyte solution. Electrochemically controlled transport of alkali metal ions, alkaline earth metal ions and transition metal ions was demonstrated across composite membranes prepared by depositing PPy·α-CDS or PPy·β-CDS onto platinum sputter-coated polyvinylidene filters. PPy·β-CDS coated membranes proved to be significantly more permeable towards most metal ions examined than either PPy·α-CDS coated membranes or any other membranes previously examined. The one exception to this was copper ions, which were transported to a much greater extent across composite PPy·α-CDS membranes. Significant increases in the permeability of both membranes towards copper and in the case of composite PPy·β-CDS membranes iron, were obtained by altering the pulsed potential used to initiate metal ion transport.

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1. Introduction

Inherently conducting polymers (ICPs) are a unique class of materials that combine the electrical conductivity of metals with the strength and processability of traditional synthetic polymers. As a result, they have attracted considerable attention for potential applications in a variety of areas, including microelectronics, corrosion control, photochromic and photovoltaic devices, sensors, electromechanical actuators and novel batteries [1–7]. One of the most important properties of ICPs is electroactivity, which provides a mechanism by which their chemical and physical properties can be modified. For example, polyaniline can be switched between several different coloured oxidation states by using either chemical oxidants or reductants, or by applying suitable electrochemical potentials [2]. Immediately after preparation, ICPs are present in a conducting, oxidised state. During synthesis, anions (A^-) are incorporated (doped) into the structure of the ICP to balance the positive charges present along the conducting polymer backbone. When an ICP, such as polypyrrole (PPy) is reduced, the conducting polymer backbone becomes neutral. If the anion that was incorporated during synthesis of the ICP is relatively immobile, cations (C^+) present in the surrounding solution may be incorporated into the polymer to maintain overall charge neutrality (Eq. (1)). Subsequent re-oxidation of the ICP by application of a positive applied potential restores the conducting polymer to the initial, positively charged state, and results in cation expulsion from the polymer. Switching the redox state of the polymer by application of suitable potentials, therefore, enables ICPs to function as cation exchange materials. Reduction and subsequent re-oxidation of ICPs can also be accompanied by expulsion

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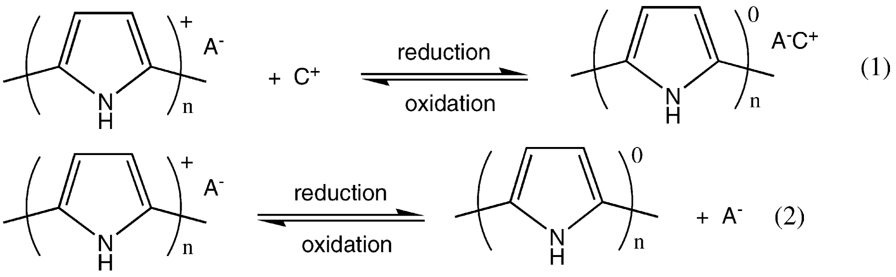
and incorporation of dopant anions (A^-) to maintain charge neutrality (Eq. (2)). The relative amounts of cation and anion movement that accompany redox cycling of the polymer have been shown to depend on the size of the anion initially incorporated [8–13]. When large, immobile dopants, such as polyelectrolyes are present charge neutralisation is believed to occur predominantly via movement of cations [2,8,11–13].



Cyclodextrins are a family of cyclic oligosaccharides containing different numbers of D-glucopyranose units linked by 1,4-glycosidic bonds [14]. Two of the most commonly used cyclodextrins are those containing six (α-cyclodextrin) and seven (β-cyclodextrin) glucose units. Unsubstituted cyclodextrins, such as α- and β-cyclodextrin have a structure resembling a truncated cone or torus, with hydrophilic hydroxyl groups lining both rims and a hydrophobic cavity. This makes these molecules ideal hosts for encapsulation of a wide variety of guest molecules, including aromatic molecules, dyes, indicators, amino acids, food additives, cations, anions, noble gases, drugs and fullerenes [14–17]. In some instances, a significant degree of discrimination between potential guest molecules is displayed by cyclodextrins, as a result of differences in intermolecular interactions between the host and guest molecules. The extent of discrimination is also influenced by the degree of steric complementarity between the cavity of the cyclodextrin and the shape and size of guest molecules. The cavities of cyclodextrins vary significantly as a result of differences in their diameters. For example, the volume of the cavities of α-cyclodextrin and β-cyclodextrin are 174 and 262 Å^3, respectively [15].

We have previously demonstrated that it is possible to use conducting polymer membranes as electrochemically controllable, semi-permeable barriers to the movement of metal ions from one solution to another [18–26]. The membranes used are thick enough to prevent movement of metal ions across the membrane in the absence of an applied electrical stimulus. In early studies, it was shown that the flux of alkali metal ions and alkaline earth metal ions across ICP membranes depended on a number of factors, including the nature of the applied electrochemical stimulus [19,20]. More recently, it was shown that a variety of transition metal ions, including for the first time Co^{2+}, Ni^{2+} and Zn^{2+}, could be transported across PPy membranes containing the chelating ligand bathocuproinedisulfonic acid (BCS) [25]. The flux of copper across PPy·BCS membranes was approximately 50 times larger than across any membrane previously studied, suggesting that the presence of suitable metal complexing dopants in ICPs can have a significant influence on their permeability In other work, involving mixtures of iron and either copper or gold, ICP membranes demonstrated a significant degree of selectivity in their metal ion permeability [23,24].

There is considerable interest in the development of niche methods for separation and recycling of precious metals from secondary sources, including jeweller's scrap, catalytic converters and waste produced by the semiconductor, photographic and electroplating industries. Such methods should be energy efficient, and use inexpensive materials that are also environmentally benign. Our previous research has demonstrated that membranes composed of ICPs are attractive materials for novel separation procedures based on their selective permeability towards metal ions. In this work, the synthesis and characterisation of PPys doped with either sulfated α-cyclodextrin (α-CDS) or sulfated β-cyclodextrin (β-CDS) is reported. Also included are the results of transport studies examining the permeability of PPy·α-CDS and PPy·β-CDS membranes towards a variety of metal ions. It was anticipated that the difference in size between the cavities of the two sulfated cyclodextrins would be similar to those of the corresponding unsubstituted cyclodextrins, and result in significant differences in the rate of transport of metal ions across the two membranes.

2. Experimental

2.1. Reagents

Pyrrole was obtained from Merck and distilled before use. Sulfated α-cyclodexrin (α-CDS), sulfated β-cyclodextrin (β-CDS) and all other reagents were obtained from the Aldrich Chemical Co. Solutions were prepared using deionised Milli-Q water (18 MΩ cm).

2.2. Preparation of polymers

Electropolymerisation was performed in aqueous solutions, containing 0.20 M pyrrole and 0.20% (w/v) sulfated cyclodextrin, using an EG and G Princeton Applied Research (PAR) Model 363 Potentiostat/Galvanostat. All solutions were deoxygenated with nitrogen prior to use. A three-electrode electrochemical cell consisting of a platinum work-

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