Electrochemical production of polypyrrole colloids

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An electrochemical method has been developed that enables production of conductive electroactive polymer colloids. This method involves the use of a flow-through electrochemical cell with a porous electrode. Polymerization is carried out in the presence of steric stabilizers. Colloids containing a range of different counterions can be produced.

(Keywords: electropolymerization; conducting polymer colloids; polypyrrole)

Introduction

It is recognized that severe limitations are imposed on the processing of conducting polymers by the lack of solubility and fusibility of these materials. The use of colloids to circumvent this problem has been advocated. The production of conducting polymer colloids is usually achieved via chemical oxidation of the appropriate monomer in the presence of a steric stabilizer[1-4]. This results in production of monodisperse colloidal sols in the size range 10–100 nm. Recently we have shown that conducting polymer colloidal sols are electroactive, and indeed electrodeposition of the colloids can be initiated at negative potentials to form a conductive film[5,6].

The use of chemical oxidation to produce these colloids has some limitations. Specifically, it is more difficult to control the oxidation potential throughout the polymerization and it is known that excursions to higher potentials will result in over-oxidation with a subsequent deterioration in electronic conductivity and mechanical properties[7,8]. In addition, only a limited number of counterions can be incorporated when chemical oxidation is employed, since the counterion of the oxidant will inevitably be incorporated.

The use of electropolymerization to produce conducting polymers is a more attractive option. Previously[9,10] we have shown that the presence of steric stabilizers or other additives in the electropolymerization solution prevents deposition of conducting polymers. We have now attempted to utilize these processes to produce conducting polymer colloids electrochemically.

Experimental

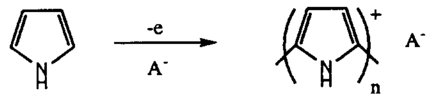
Reagent and standard solutions. All reagents were used as received without further purification, unless stated otherwise. Aqueous solutions were prepared using distilled deionized water. Pyrrole (Sigma) was freshly distilled and refrigerated. The materials used for preparation of colloids were: poly(vinyl alcohol) (PVA, $MW = 3 \times 10^4$–7×10^4); sodium nitrate ($NaNO_3$) (BDH); poly(ethylene oxide) (PEO, $MW = 3 \times 10^5$) (Aldrich); poly(vinyl pyrrolidone) (PVP, $MW = 1.2 \times 10^6$) (TCI); KI, $NaClO_4$ and NaCl (BDH); $C_6H_5SO_3Na$ (Aldrich); and $p-$toluenesulfonate (PTS) (Na^+) (Merck). Reticulated vitreous carbon (RVC) was obtained from Energy Research and Generation Inc.

Preparation of polypyrrole colloids. Sodium nitrate, potassium iodide, sodium perchlorate, sodium chloride, PTS and $C_6H_5SO_3Na$ were used as supporting electrolytes, and in addition PVP, PVA and PEO were considered for use as stabilizers. In a typical experiment, 4 ml of pyrrole was added to 200 ml of a stirred aqueous solution containing 1 M $NaNO_3$ and a minimum amount of the stabilizers PVP ($1.80\,g\,l^{-1}$), PVA ($3.0\,g\,l^{-1}$) and PEO ($3.20\,g\,l^{-1}$). This solution was recirculated through the electropolymerization cell. The flow rate was $25\,ml\,min^{-1}$. The polymerization reaction was carried out at room temperature for 3.5 h. A constant current density of $\sim 0.58\,mA\,cm^{-2}$ was used for these reactions. After electropolymerization the colloidal dispersions were ultracentrifuged ($55\,000\,rev\,min^{-1}$) for 1 h to produce a sediment. The supernatant was decanted and the sediment rinsed with distilled water.

Instrumentation. Electrochemical experiments were carried out in a three-electrode cell employing a working electrode (RVC), reference electrode Ag/AgCl (3 M NaCl) and an auxiliary electrode (RVC). Electrochemical control was achieved using either a Bioanalytical Systems BAS model 100A or BAS model CV 27. A Sorvall OTD ultracentrifuge was used. A JEOL 2000 FX transmission electron microscope or a Hitachi S 450 scanning electron microscope were employed. Transmission electron micrographs and scanning electron micrographs were obtained using dilute redispersed latex dried on carbon-coated copper grids and gold foil. An EG & G Princeton Applied Research potentiostat/galvanostat (model 363) and a Master Flex pump were used throughout this work.

Results and discussion

It is well known that polypyrrole can be produced electrochemically according to:



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where A^- is a counterion incorporated into the polymer during synthesis and *n* is normally between 2 and 4. The polymer product is an insoluble conductive, electroactive material deposited on the anode. However, this simplistic description belies the complexity of this electrochemical process. A more detailed examination reveals that initial polymerization actually occurs in solution[11] and the polymer is subsequently deposited. Solution additives that enhance the solubility of the oligomer or polymer, such as surfactants[8], or the nature of the product formed, for example steric stabilizers[9], have a marked effect on the polymer deposition step.

A flow-through electrochemical cell containing a porous electrode was constructed (see *Figure 1*). The electrolyte (containing the monomer and stabilizer) was directed through the porous working electrode. Preliminary experiments were performed using an RVC working electrode and a peristaltic pump. The cell volume was 265 ml. The surface area of the working electrode was approximately 858 cm^2 and the auxiliary electrode was approximately 1716 cm^2. The polymerization solution contained the pyrrole monomer (0.3 M), the steric stabilizer (PEO, PVP or PVA) and a supporting electrolyte. With all stabilizers, both constant potential and constant current polymerization were considered. It was found that although colloid could be produced by application of a potential between +0.70 and +1.00 V this did not produce colloid that was electroactive (as described later).

The use of constant current (applied current density between +0.40 and +0.60 mA cm^{-2}) also resulted in colloid production. In all cases, when colloid was produced it was more electroactive than that produced under constant potential conditions. Application of higher current densities resulted in a greater rate of production of colloid. However, at current densities above 0.60 mA cm^{-2} copious amounts of gas were evolved from the auxiliary electrodes, and this interfered with the production of colloids. Consequently a current density of 0.50 mA cm^{-2} was determined to be optimal for this cell design. Under these conditions the pH of the solution rose during the polymerization (up to 10.5) owing to the products produced at the auxiliary electrode; polymerization at such high pH values may degrade the properties of the conducting polymers. It was found that conducting polymer colloids could still be produced under these conditions. A constant current density of approximately 0.58 mA cm^{-2} was used.

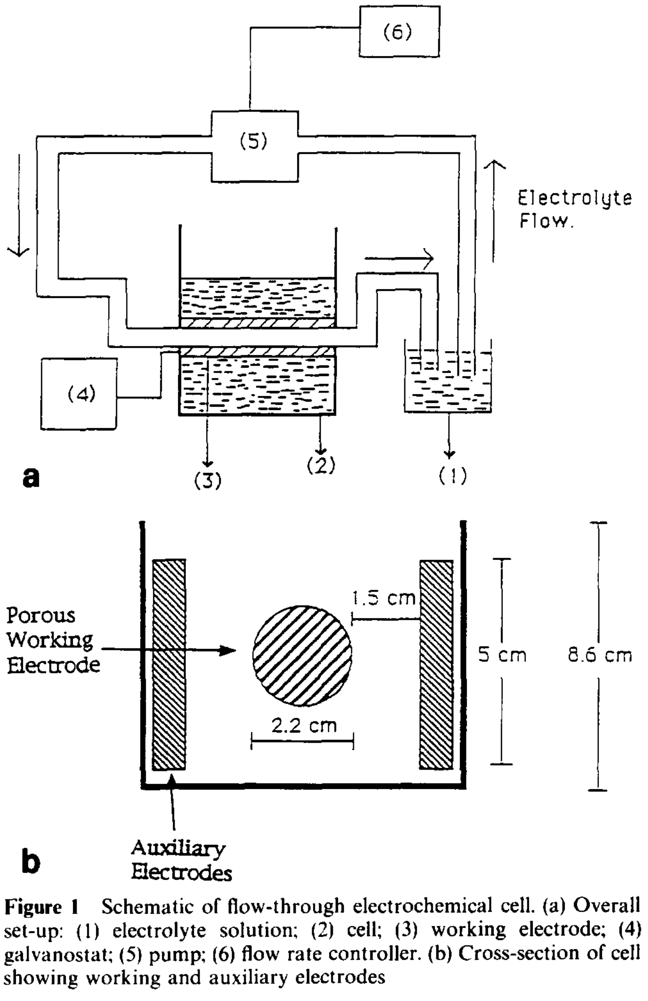


Figure 1 Schematic of flow-through electrochemical cell. (a) Overall set-up: (1) electrolyte solution; (2) cell; (3) working electrode; (4) galvanostat; (5) pump; (6) flow rate controller. (b) Cross-section of cell showing working and auxiliary electrodes

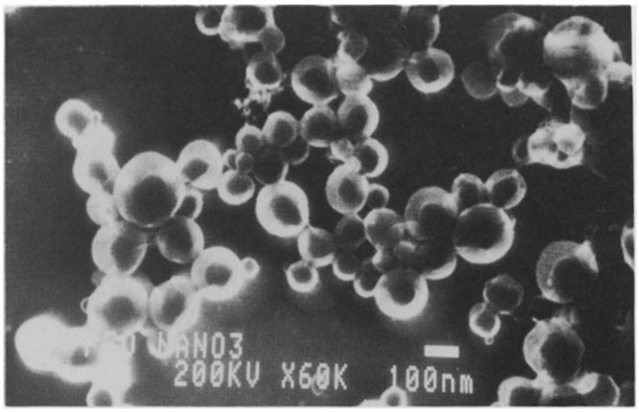
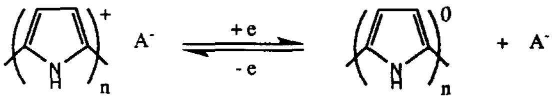


Figure 2 Transmission electron micrograph of colloid produced in the flow cell using PEO stabilizer (6 g l^{-1}). Supporting electrolyte was 1.0 M $NaNO_3$, monomer concentration was 0.3 M. Conditions for polymerization were as described in the Experimental section

The use of several counterions (NO_3^-, I^-, Cl^-, PTS^-, benzene sulfonate (BS^-) and ClO_4^-) was considered with each of the steric stabilizers. Constant monomer (0.3 M pyrrole) and supporting electrolyte (0.5–1.0 M) concentrations were employed throughout. The flow rate of the polymerization solution was 25 ml min^{-1} throughout this work. When polymerization was initiated in the flow-through cell with no stabilizer present then no colloid formation was observed.

The use of PEO (3.20–8.00 g l^{-1}) in the electrolyte solution was investigated. It was found that electroactive colloids could only be produced when $NaNO_3$ was employed as the electrolyte. In all other cases (except $NaNO_3$) the solution was not discoloured after 3 h of polymerization, indicating little colloid formation. With $NaNO_3$, 0.25 g of colloid was produced from 1 ml (~1 g) of monomer after 3.5 h. The transmission electron micrograph of colloids produced in this way is shown in *Figure 2*. Spherical colloids in the 10–200 nm size range were produced. As described previously[4], these colloids could be redispersed; using cyclic voltammetry they were shown to be electroactive since the expected polymer oxidation/reduction responses due to:



(2)

were observed.

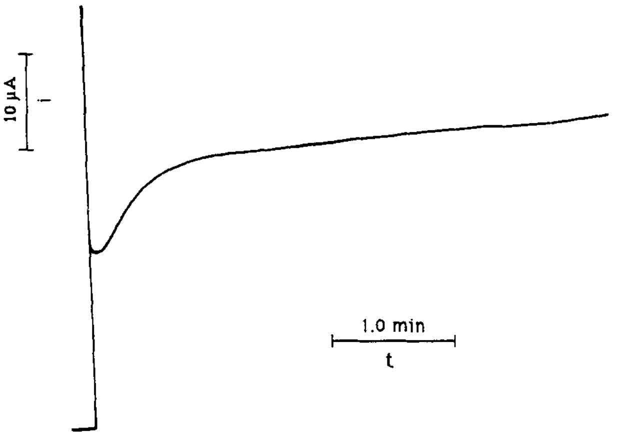


Figure 3 Chronoamperogram obtained for deposition of colloids prepared using PVA stabilizer ($8\,g\,l^{-1}$). Colloid sol was redispersed in distilled deionized water ($5\,g\,l^{-1}$). All other conditions as described in the Experimental section. Applied potential was −1.65 V for 4 min

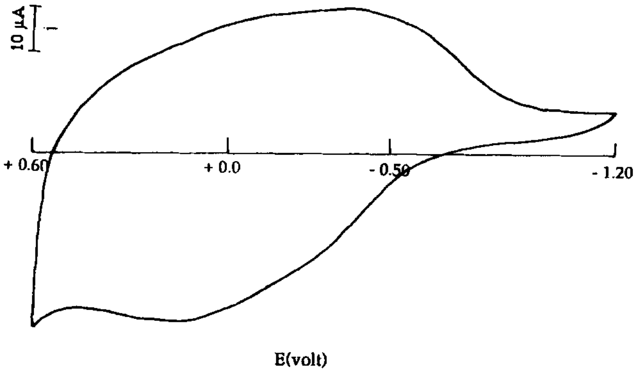


Figure 4 Cyclic voltammogram obtained for material deposited as in *Figure 3*. Supporting electrolyte 1.0 M $NaNO_3$. Scan rate $100\,mV\,s^{-1}$

Using PVA (3.00–$8.00\,g\,l^{-1}$) colloidal material was only produced when either nitrate or iodide were used as the anion in the supporting electrolyte.

The yield of colloid was observed to increase and the amount of polymer deposited on the working electrode (as observed visually) decreased with greater stabilizer concentrations. Use of PVP (1.80–$8.00\,g\,l^{-1}$) as stabilizer enables production of colloids with all of the counterions studied. All of these colloids formed stable electroactive dispersions. Again, the yield of colloid increased and the amount of polymer deposited on the working electrode decreased with greater stabilizer concentrations.

As reported previously[5], it is possible to deposit conductive electroactive colloids on to stainless steel by imposition of a negative potential. It was found that all of the colloids produced in this work could be deposited in this way. For example, *Figure 3* shows the chronoamperogram obtained for deposition of colloids prepared using PVA stabilizer. The cyclic voltammogram (*Figure 4*) indicated that a conductive electroactive film was deposited at these negative potentials, since redox responses attributed to the processes described in equation (2) were clearly observed.

Conclusion and future work

The ability to generate conducting polymer colloids electrochemically has been demonstrated for the first time.

The colloids produced are sterically stabilized, are electroactive, and can be electrodeposited onto electrode surfaces. The use of electropolymerization methods to prepare the colloids means that a range of counterions can be incorporated and (particularly when PVP is used as the steric stabilizer) the process lends itself to continuous on-line production of colloids. Preliminary work has shown that a range of other conducting polymer colloids (e.g. polyaniline) can be produced using this approach.

We are at present concerned with the design and construction of a more efficient flow-through electrochemical synthesis cell. In particular, it is envisaged that the use of a porous working electrode with a more well-defined flow path will be advantageous.

The use of a separated or divided cell may result in higher quality colloids since the pH near the working electrode can be kept low.

Acknowledgements

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