2934 *Chem. Mater.* **1997,** *9,* 2934−2939

Size Control of Polypyrrole Particles

Zhigang Qi and Peter G. Pickup*

Department of Chemistry Memorial University of Newfoundland St. John's,
Newfoundland, Canada A1B 3X7

Received May 1, 1997. Revised Manuscript Received July 14, 1997⊗

Size control of polypyrrole particles prepared by chemical polymerization was achieved by varying the concentration of the oxidant in the presence of poly(styrenesulfonate). At higher concentrations, smaller polypyrrole particles are formed. Poly(styrenesulfonate) functions as a molecular template, causing local preconcentration of both pyrrole and Fe^{3+}. These increased local concentrations result in faster nucleation and polymerization, which favors the formation of small particles. Average particle sizes ranging from ca. 40 nm to 1 μm have been obtained.

Introduction

Polypyrrole is one of the most widely investigated conducting polymers.[1−3] It can be generated both chemically and electrochemically.[2,4−6] Electrochemical polymerization leads to formation of a polymer film on the working electrode. Although this technique has many advantages, including control of the film's thickness, morphology, and conductivity and the incorporation of selected ions, it is not suitable for mass production. In contrast, chemical polymerization is simple, cheap, and fast and can easily be scaled up. Unfortunately, conventional chemical polymerization produces a nonprocessable conducting polymer precipitate without controllable shape and size, which seriously restricts its applications.

Certain efforts have succeeded in producing conducting polymers with some degree of controlled dimensions and shapes.[7−11] Conducting polymer fibrils and tubules with nanometer-scale diameters have been synthesized using microporous membranes as templates.[7,8] Encapsulation of conducting polymers in the channels of zeolites[9,10] and a porous glass composite[11] has also been reported. All these fabrications used a similar templating concept where the guest conducting polymers are synthesized within the channels or pores of a host material. The size and shape of the resulting polymers are determined and limited by the channels or pores. Such a host−guest inclusion templating idea is probably the most popular strategy used today by chemists and materials scientists to synthesize nanostructures.[12]

Colloidal polypyrrole particles with diameters between 50 and 400 nm have been synthesized in the presence of various steric stabilizers such as poly(vinyl alcohol), poly(vinylpyrrolidone), and poly(vinyl acetate).[13−19] The polypyrrole colloids are believed to be two-component systems, consisting of an inner core of polypyrrole and an outer layer of adsorbed stabilizer.[20,21] The stability of the dispersions arise from steric repulsion between the stabilizer molecules. Colloids have the advantage of being processable, but their dispersion in aqueous media will not be acceptable for applications that require the polymer particles to stay in the solid state.

We report here a simple procedure for preparing polypyrrole (PPy) particles with controllable dimensions down to tens of nanometers. The presence of poly(styrenesulfonate) (PSS) in the reaction medium allows the size of chemically synthesized PPy/PSS particles to be controlled by varying the concentration of the Fe(III) oxidant. The higher the concentration, the smaller the resulting polymer particles.

The particles are insoluble in both water and organic solvents and do not form colloidal dispersions. This is an advantage over colloidal polypyrrole particles for certain applications (e.g., as a catalyst support in polymer electrolyte fuel cells[22]). Because of their insolubility, they can be easily and quickly separated from the reaction medium and washed using either filtration or centrifuging. In contrast, colloids are normally washed by dialysis, which normally takes several days. Even with a ultrahigh-speed centrifuge, washing would

---

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) Street, G. B. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, pp 265−292.

(2) Heinze, J. *Synth. Met.* **1991**, *41−43*, 2805−2823.

(3) Curran, D.; Grimshaw, J.; Perera, S. D. *Chem. Soc. Rev.* **1991**, *20*, 391−404.

(4) Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1984**, *23*, L899−L900.

(5) Myers, R. E. *J. Electron. Mater.* **1985**, *15*, 61−69.

(6) Stanke, D.; Hallensleben, M. L.; Toppare, L. *Synth. Met.* **1995**, *72*, 159−165.

(7) Martin, C. R. *Science* **1994**, *266*, 1961−1966.

(8) Martin, C. R. *Acc. Chem. Res* **1995**, *28*, 61−68.

(9) Wu, C.-G.; Bein, T. *Science* **1994**, *264*, 1757−1759.

(10) Bein, T.; Enzel, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1692−1694.

(11) Maia, D. J.; Zarbin, A. J. G.; Alves, O. L.; De Paoli, M.-A. *Adv. Mater.* **1995**, *7*, 792−794.

(12) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612−649.

(13) Vincent, B. *Polym. Adv. Technol.* **1994**, *6*, 356−361.

(14) Bjorklund, R. B.; Liedberg, B. *Chem. Commun.* **1986**, 1293−1295.

(15) Armes, S. P.; Vincent, B. *Chem. Commun.* **1987**, 288−290.

(16) Armes, S. P.; Miller, J. F.; Vincent, B. *J. Colloid Interface Sci.* **1987**, *118*, 410−416.

(17) Cawdery, N.; Obey, T. M.; Vincent, B. *Chem. Commun.* **1988**, 1189−1190.

(18) Armes, S. P.; Aldissi, M. *Polymer* **1990**, *31*, 569−574.

(19) Digar, M. L.; Bhattacharyya, S. N.; Mandal, B. M. *Chem. Commun.* **1992**, 18−20.

(20) Armes, S. P.; Aldissi, M.; Idzorek, G. C.; Keaton, P. W.; Rowton, L. J.; Stradling, G. L.; Collopy, M. T.; McColl, D. B. *J. Colloid Interface Sci.* **1991**, *141*, 119−126.

(21) Armes, S. P.; Aldissi, M.; Agnew, S. F. *Synth. Met.* **1989**, *28*, C837−C848.

(22) Qi, Z.; Lefebrve, M.C.; Pickup, P. G. *J. Electroanal. Chem.*, submitted.

S0897-4756(97)00280-9 CCC: $14.00

Table 1. Effect of Reagent Concentration on the Average Polypyrrole Particle Size and Electronic Conductivity at 120 kg cm^{-2}

sample	[PSS]	[pyrrole]	[Fe^{3+}]	Fe^{3+}/Py/PSS	size (nm)	conductvity (S cm^{-1})
1	0.042	0.14	0.70	5.0/1.0/0.30	40	3
2	0.015	0.14	0.15	1.1/1.0/0.11	180	0.71
3	0.015	0.035	0.15	4.3/1.0/0.43	150	*a*
4	0.015	0.035	0.15	4.3/1.0/0.43	180	0.12
5	0.015	0.014	0.15	11/1.0/1.1	180	0.035
6	0.018	0.053	0.13	2.5/1.0/0.34	*a*	0.46
7	0.015	0.035	0.05	1.4/1.0/0.43	550	*a*
8	0.0015	0.0035	0.01	2.9/1.0/0.43	850	*a*

[a] Not measured.

take several hours. Our procedure is also easy to perform and control. It is much cheaper than templated-fabrication methods, where the cost of the template may limit the commercial viability.

Experimental Section

Chemicals. Sodium poly(styrenesulfonate) (Aldrich, $M_W \approx$ 70 000), Nafion 117 membrane (Ballard Power Systems), PTFE (poly(tetrafluoroethylene), 15% solution, Ballard Power Systems), carbon fiber paper (Toray TGPH090 + 10% PTFE; Ballard), and other chemicals were used as received. Pyrrole (Aldrich) was purified by passing through a SiO_2 (230−400 mesh) column and was used immediately.

Preparation of Polypyrrole Particles. Pyrrole was dissolved in an aqueous sodium poly(styrenesulfonate) solution. After a few minutes to allow equilibration, $Fe(NO_3)_3$(aq) in 0.1 M HNO_3 (or $FeCl_3$ in HCl for samples 3, 7, and 8) was added as an oxidant. Polymerization of the pyrrole was observed immediately, as a darkening of the reaction mixture, and was complete within ca. 30 min. The polymer particles were separated from the reaction medium by centrifuging, washed three times with water, and dried overnight at room temperature under vacuum. The concentrations of the reagents are specified in Table 1.

Electron Microscopy. A Hitachi S-570 scanning electron microscope and a Zeiss EM 109 transmission electron microscope were used to examine the shape and size of the polypyrrole particles.

X-ray Emission Analysis. Energy-dispersive X-ray analysis was performed with a Tracor Northern 5500 energy-dispersive X-ray analyzer associated with the scanning electron microscope. Relative elemental concentrations were estimated using Tracor Northern's software package "SQ" Standardless Quantitative Analysis.[23] This program provides a rapid, easy, and standardless analysis of X-ray spectra acquired from a bulk specimen. It removes background, extracts peak areas, calculates normalized intensity ratios, and corrects for matrix effects.

Cyclic Voltammetry. The electrochemistry of the polypyrrole particles was investigated in a gas-diffusion electrode (Figure 1). The polymer powder was mixed with a PTFE solution to form a sticky slurry, which was spread on a 4 cm^2 area of a Toray TGPH090 carbon fiber paper containing ca. 10% PTFE. A Nafion 117 membrane was then hot-bonded on the polymer side of the carbon paper at a pressure of ca. 3000 psi and a temperature between 120 and 130 °C for 90 s. Circular sections (1 cm^2) of the carbon paper/polymer/Nafion membrane assembly were tested in the cell illustrated in Figure 1. A Pt wire was used as the counter electrode, and a saturated sodium chloride calomel electrode (SSCE) was used as the reference electrode. All potentials are quoted with respect to the SSCE reference electrode. Voltammetric measurements were made using a Solartron electrochemical interface (Model 1286).

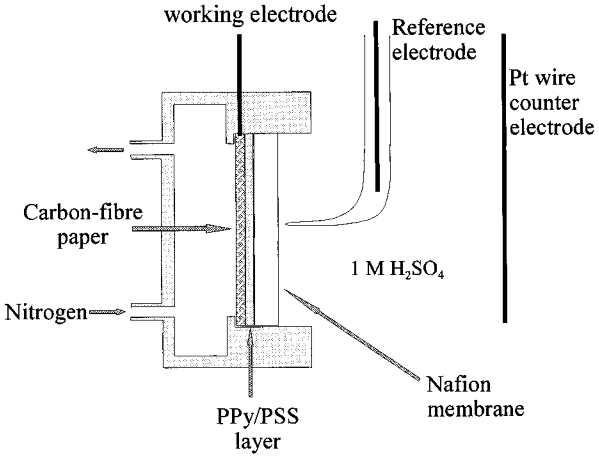

Figure 1. Schematic diagram of the gas diffusion electrode cell.

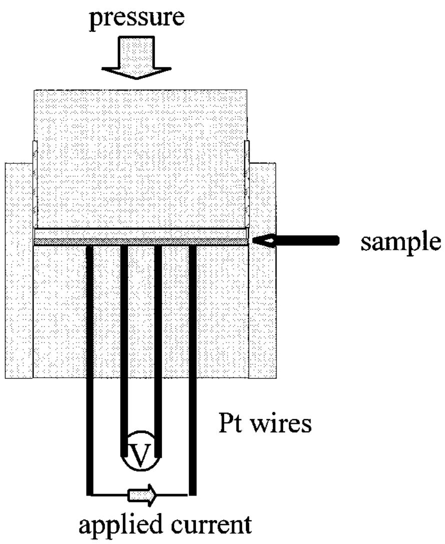

Figure 2. Schematic diagram of the four-point probe.

Infrared Spectroscopy. KBr pellets were used for FTIR spectra. About 0.4 mg of the polymer was ground with 300 mg of KBr and pressed under vacuum with several increments in pressure to 3.5×10^5 psi. The sample was kept at each intermediate pressure for 5 min. Spectra were collected using a Mattson Polaris FTIR spectrometer at a nominal resolution of 4.0 cm^{-1}.

Conductivity Measurements. A modified four-point probe assembly (Figure 2) was designed to measure electronic conductivities. The problem with a conventional four-point probe[24,25] when applied to conducting polymers is that the needles penetrate the sample and cause it to crack. In the modified device (Figure 2), the electrodes are flush with the base surface and the powder is pressed into a pellet in situ, avoiding a separate pressing step. The pressure was controlled by a torque wrench, which enabled the study of the effect of pressure on conductivity. Such information will be important for applications in gas diffusion electrodes (e.g., in PEM fuel cells[22]), where the pressure applied to the electroactive polymer layer may be quite low.

For the device used in this work, the distance between each electrode was 1.3 mm, and the diameter of the sample chamber (and pellet) was 16 mm. The thickness (d) of the sample was

---

(23) Qi, Z.; Pickup, P. G. *Anal. Chem.* **1993**, *65*, 696−703.

(24) Smits, F. M. *Bell Syst. Techn. J.* **1958**, *37*, 183−190.

(25) Blythe, A. R. In *Measurement Techniques for Polymeric Solids*; Brown, R. P.; Read, B. E., Eds.; Elsevier Applied Science Publishers: London, 1984; pp 195−209.

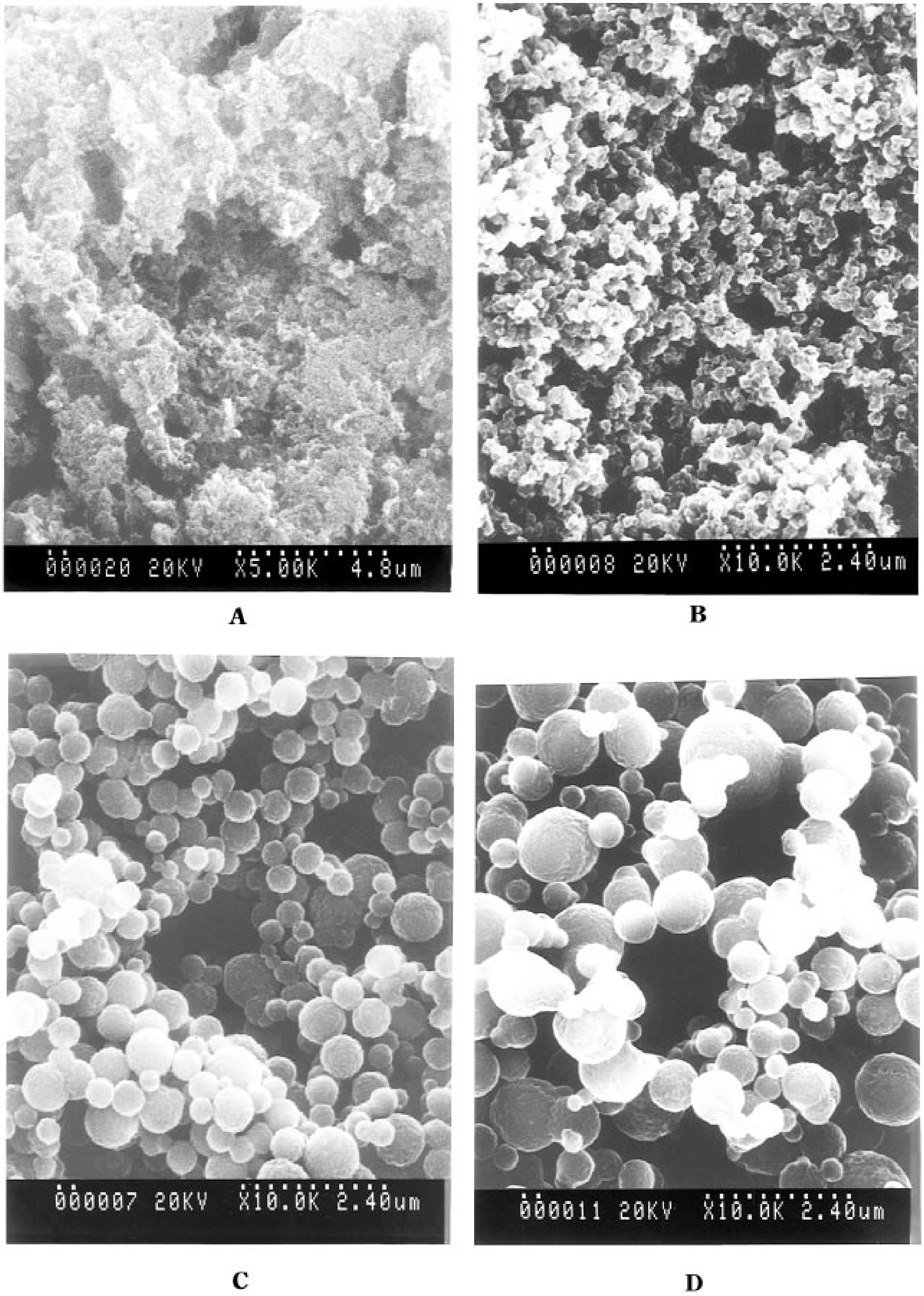

Figure 3. Scanning electron micrographs of PPy/PSS samples 1 (A), 3 (B), 7 (C), and 8 (D) prepared using the various reagent concentrations given in Table 1.

measured using a Linear Vernier Microscope (Griffin) while still in the device. For pellet thickness/electrode distance ratios below 0.7, the conductivity is given by the following equation:[24]

$$\sigma = I/4.27Vd \tag{1}$$

where I is the current applied between the outer two electrodes and V is the voltage drop between the inner two electrodes.

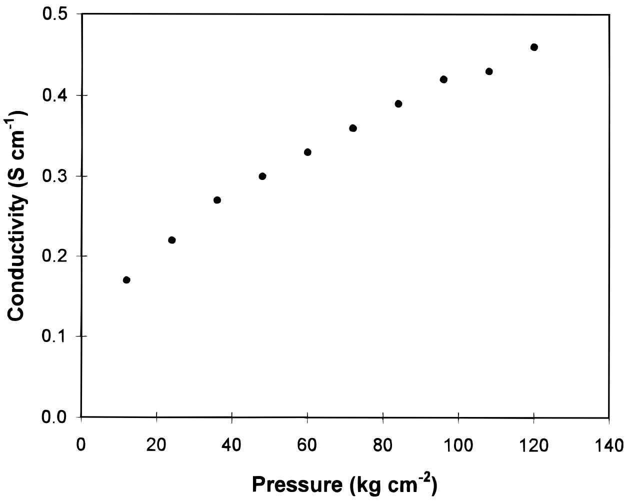

Figure 4. Conductivity vs pressure for PPy/PSS sample 6.

Results

Electron Microscopy. Figure 3 shows micrographs of four polypyrrole samples prepared using different reagent concentrations. The reagent concentrations along with the average particle size are summarized in Table 1. The particle size of sample 1 was estimated from a transmission electron micrograph.[22] When the PPy/PSS particles are small (e.g., samples 1−5), they are of irregular shape and tend to agglomerate. The larger particles (samples 7 and 8) are spherical. It is clear from the data in Table 1 that higher concentrations of oxidant result in smaller PPy/PSS particles. The pyrrole concentration and Py:PSS ratio have no noticeable effect. A comparison of samples 3 and 4, prepared at the same concentrations but with different Fe^{3+} salts, shows that the counteranion added with the Fe^{3+} has little effect.

Elemental Analysis and X-ray Emission Analysis. Elemental analysis (Canadian Microanalytical Service Ltd.) of sample 1 gave a S:N atomic ratio of 0.18. If the sulfonate groups of the PSS are the only counterions in the oxidized PPy, then its oxidation level was ca. 0.18, i.e., ca. five pyrrole units share each positive charge. This is a typical oxidation level for chemically prepared polypyrrole.[26]

X-ray emission spectroscopy indicated that there was residual Fe, from the oxidant, in the polymer powders. Semiquantitative analysis indicated a S to Fe atom ratio of ca. 8. The Fe species is probably Fe^{3+} associated with sulfonate groups of the PSS. This would lower the calculated doping level to 0.11, but the uncertainty in the X-ray emission results makes such a calculation unreliable.

Conductivity. Figure 4 shows the conductivity vs pressure relationship for sample 6. The conductivity calculation was based on the thickness of the sample pellet at the final pressure (e.g., 120 kg/cm^2), so it overestimates the conductivity slightly at lower pressures. The conductivity increases with pressure but begins to level off at the highest pressures used. The density of the pellet at the final pressure was ca. 0.5 g cm^{-3}, suggesting that it was quite porous. Polypyrroles typically have densities of ca. 1.5 g cm^{-3}.[27]

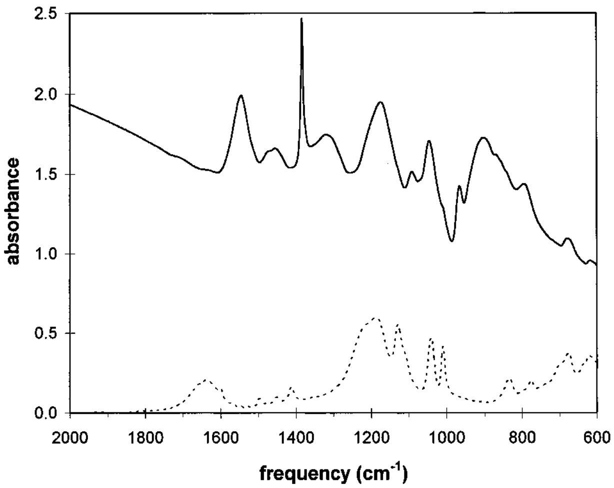

Figure 5. FTIR spectra of PPy/PSS sample 1 (—) and PSS (– –).

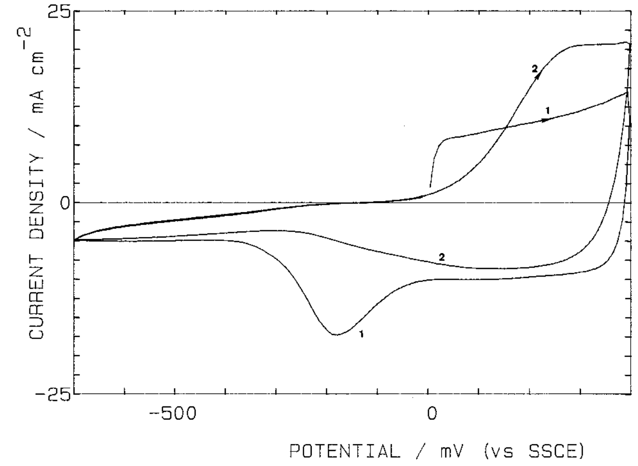

Figure 6. Cyclic voltammograms of PPy/PSS sample 1.

The conductivities of the PPy/PSS powders at a specific pressure were found to increases with increasing oxidant (compare samples 1 and 2) and pyrrole (samples 2, 4, and 5) concentration (Table 1).

Infrared Spectroscopy. Figure 5 shows the FTIR absorption spectra of sample 1 and NaPSS. Except for the sharp peak at 1384 cm^{-1}, the PPy/PSS sample shows an IR spectrum of characteristic of PPy alone,[28−35] with the IR absorption of the PSS being completely suppressed, as reported previously.[36] The origin of the peak at 1384 cm^{-1} is unclear.

Cyclic Voltammetry. Figure 6 shows cyclic voltammograms of sample 1 in a gas-diffusion electrode (Figure 1). These voltammograms are quite characteristic of polypyrrole.[2] The cathodic peak at ca. −0.20 V

---

[26] Roncali, J.; Yasser, A.; Garnier, F. *Chem. Commun.* **1988**, 581−582.

[27] Salmon, M.; Diaz, A. F.; Logan, A. J.; Krounbi, M.; Bargon, J. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 265−276.

[28] Street, G. B.; Lindsey, S. E.; Nazzal, A. I.; Wynne, K. J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 137−148.

[29] Qian, R.; Qiu, J. *Polym. J.* **1987**, *19*, 157−172.

[30] Jin, J.-Y.; Ando, T.; Teramae, N.; Haraguchi, H. *Anal. Sci.* **1991**, *7*, 1593−1594.

[31] Tian, B.; Zerbi, G. *J. Chem. Phys.* **1990**, *92*, 3892−3898.

[32] Pei, Q. B.; Qian, R. Y. *J. Electroanal. Chem.* **1992**, *322*, 153−166.

[33] Lei, J. T.; Liang, W. B.; Martin, C. R. *Synth. Met.* **1992**, *48*, 301−312.

[34] Lei, J. T.; Martin, C. R. *Synth. Met.* **1992**, *48*, 331−336.

[35] Lei, J. T.; Cai, Z. H.; Martin, C. R. *Synth. Met.* **1992**, *46*, 53−69.

[36] Arribas, C.; Rueda, D. *Synth. Met.* **1996**, *79*, 23−26.

during the first scan can be assigned to the uptake of protons by the polymer.[37,38] Since the PPy/PSS layer contains immobile polyanions and was separated from an acid electrolyte solution by a Nafion film, which is impermeable to anions, protons are the only charge-compensating ion that are likely to be involved.

Discussion

Table 1 clearly shows that the size of the PPy/PSS particles is controlled by the concentration the oxidant: the higher the concentration, the smaller the particles. Qi[39] has proposed that there is a nucleation process in the chemical polymerization of conducting polymers. It becomes more easily observable if the polymerization rate is slowed by reducing the concentrations of both pyrrole and the oxidant. We assume here that the number of nuclei will determine the average size of the PPy/PSS particles. Increasing the oxidant concentration will generate a large number of nuclei, and thus the average particle size will decrease.

PSS plays a critical role in the polymerization and size-controlling processes. Without PSS, it is very difficult to control the shape and size of PPy. It was found that pyrrole polymerized much faster in the presence of PSS, and almost no polymerization occurred on the surface of the reaction vessel. Similar results were observed when PPy colloids were prepared using anionic surfactants or polyelectrolytes as stabilizers.[39] It is believed that PSS functions as a molecular template.[39] Pyrrole is accumulated around the PSS chains via a hydrophobic interaction, resulting in a higher local concentration. Such an interaction is supported by the fact that pyrrole dissolves much more rapidly in NaPSS(aq) solutions than in pure water. When a ferric salt is added, the mixture immediately becomes cloudy due to the coagulation of PSS by the Fe^{3+}, and the coagulate blackens quickly due to polymerization of the associated pyrrole. The coagulation implies that the electrostatic interaction between PSS and Fe^{3+} concentrates the Fe^{3+} around the PSS. Therefore, PSS causes a local preconcentration of both pyrrole and Fe^{3+} and enhances the polymerization rate. The absence of polymerization on the surface of the reaction vessel in the presence of PSS is an indication that the PSS provides nucleation sites for the polymerization. In the absence of PSS, the first sign of polymerization usually appears on the surface of the reaction vessel.

Since polymerization is accompanied by parasitic side reactions such as overoxidation,[40] the properties of the final polymer will be affected by their extent. Martin et al.[35] have studied the effect of reagent concentration on the properties of PPy and found that lower initial concentrations of Fe^{3+} and pyrrole result in a lower yield of PPy, shorter conjugation lengths, lower doping levels, and lower conductivity. The conductivity results presented in Table 1 are consistent with this.

Planche et al.[41] showed that overoxidation occurred mainly at the beginning of the polymerization and was enhanced by low oxidant ($FeCl_3$) concentrations. Quantitative measurements indicated that the polymerization followed second-order kinetics with respect to $FeCl_3$, while overoxidation appeared to be first order.[41] This explains why a higher oxidant concentration results in higher conductivities. Since PSS has the ability to preconcentrate both Fe^{3+} and pyrrole, their local concentrations are much higher than normal, and so the resulting PPy would be expected to exhibit high conductivity.

The maximum conductivity reported here (3 S cm^{-1}) is not particularly high. This in part arises from our measurement technique in which the sample is pressed at a relatively low pressure. Our conductivity measurements therefore underestimated the inherent conductivity of the materials.

Under the condition employed in this work PSS is the main counterion incorporated into the oxidized PPy particles during their formation. Its presence modifies the properties of PPy and can be very important in certain applications. Most importantly, the PPy/PSS composite is a cation-exchanger under most conditions because reduction or partial reduction of the PPy leaves an excess of immobile sulfonate groups.[42] Also, since cations normally move faster than anions, the charge transport rate in the PPy/PSS composite will be faster.[43]

There are numerous reports on the electrochemical generation of PPy in the presence of PSS, and the exploration of the properties and applications of PPy/PSS composites,[44-59] but there is only one report describing the chemical synthesis of PPy in the presence of PSS.[36]

Our current interest in PPy/PSS is as a catalyst support in proton-exchange membrane fuel cells.[22] Its ability to conduct both electrons and protons should provide significant advantages over carbon supports.

Because the use of PSS to control the size of PPy particles is much simpler and cheaper than using microporous membranes[7,8] or zeolites[9,10] as templates,

---

(37) Duffitt, G. L.; Pickup, P. G. *J. Chem. Soc., Faraday. Trans.* **1992**, *88*, 1417–1423.

(38) Beck, F.; Dahlhaus, M. *J. Electroanal. Chem.* **1993**, *357*, 289–300.

(39) Qi, Z. Ph.D. Dissertation, McGill University, Montreal, 1996.

(40) Pud, A. A. *Synth. Met.* **1994**, *66*, 1–18.

(41) Thieblemont, J. C.; Gabelle, J. L.; Planche, M. F. *Synth. Met.* **1994**, *66*, 243–247.

(42) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Electroanal. Chem.* **1987**, *224*, 123–135.

(43) Ren, X.; Pickup, P. G. *J. Phys. Chem.* **1993**, *97*, 5356–5362.

(44) Iyoda, T.; Ohtani, A.; Shimidzu, T.; Honda, K. *Chem. Lett.* **1986**, 687–690.

(45) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *Chem. Commun.* **1987**, 327–328.

(46) Glatzhofer, D. T.; Ulanski, J.; Wegner, G. *Polymer* **1987**, *28*, 449–453.

(47) Ulanski, J.; Glatzhofer, D. T.; Przybylski, M.; Kremer, F.; Gleitz, A.; Wegner, G. *Polymer* **1987**, *28*, 859–862.

(48) Shimidzu, T.; Ohtani, A.; Honda, K. *J. Electroanal. Chem.* **1988**, *251*, 323–337.

(49) Zhong, C.; Doblhofer, K.; Weinberg, G. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 307–316.

(50) Kuramoto, N.; Michaelson, J. C.; McEvoy, A. J.; Gratzel, M. *Chem. Commun.* **1990**, 1478–1480.

(51) Li, F.; Albery, W. J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2949–2954.

(52) Iyoda, T.; Alba, M.; Saika, T.; Honda, K.; Shimidzu, T. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1765–1769.

(53) Yang, R.; Naoi, K.; Evans, D. F.; Smyrl, W. H.; Hendrickson, W. A. *Langmuir* **1991**, *7*, 556–558.

(54) Hepel, M.; Seymour, E.; Yogev, D.; Fendler, J. H. *Chem. Mater.* **1992**, *4*, 209–216.

(55) Momma, T.; Nishimura, K.; Osaka, T.; Kondo, N.; Nakamura, S. *J. Electrochem. Soc.* **1994**, *141*, 2326–2331.

(56) Stephan, O.; Carrier, M.; Page, J.; Frontier, J. P.; Trouslard, P. *Synth. Met.* **1995**, *75*, 181–185.

(57) Otero, T. F.; Olazabal, V. *Electrochim. Acta* **1996**, *41*, 213–220.

(58) Ren, X.; Pickup, P. G. *Electrochim. Acta* **1996**, *41*, 1877–1882.

(59) Otero, T. F.; Bengoechea, M. *Electrochim. Acta* **1996**, *41*, 1871–1876.

this procedure is more suitable for commercial production. As an extension of this approach, molecular assemblies such as micelles or vesicles formed from surfactants, lipids, or polymers can be used as templates.[60−62] These assemblies are easy to obtain since they form spontaneously, and their shape and size are controllable by changing the concentration.[63,64] Qi has produced conducting polymer nanofibers and nanorings using $DC_{8,9}PC$ lipid tubules as templates.[39] The nanofibers were of a length of hundreds of microns, and the diameter could be controlled to as thin as 10 nm. It is believed that using molecular assemblies as templates in the fabrication of conducting polymer nanostructures will be very fruitful.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada and Memorial University. We thank Ballard Power Systems Inc. for providing materials for construction of gas diffusion electrodes.

CM970280Q

---

(60) Schnur, J. M. *Science* **1993**, *262*, 1669−1676.

(61) Singh, A.; Markowitz, M.; Chow, G. M. *Nanostruct. Mater.* **1995**, *5*, 141−153.

(62) Kim, A.; Bruinsma, P.; Chen, Y.; Wang, L.-Q.; Liu, J. *Chem. Commun.* **1997**, 161−162.

(63) Lindman, B.; Wennerstrom, H. *Top. Curr. Chem.* **1980**, *87*, 1−83.

(64) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728−1731.