Chapter 4: Polypyrrole Synthesis

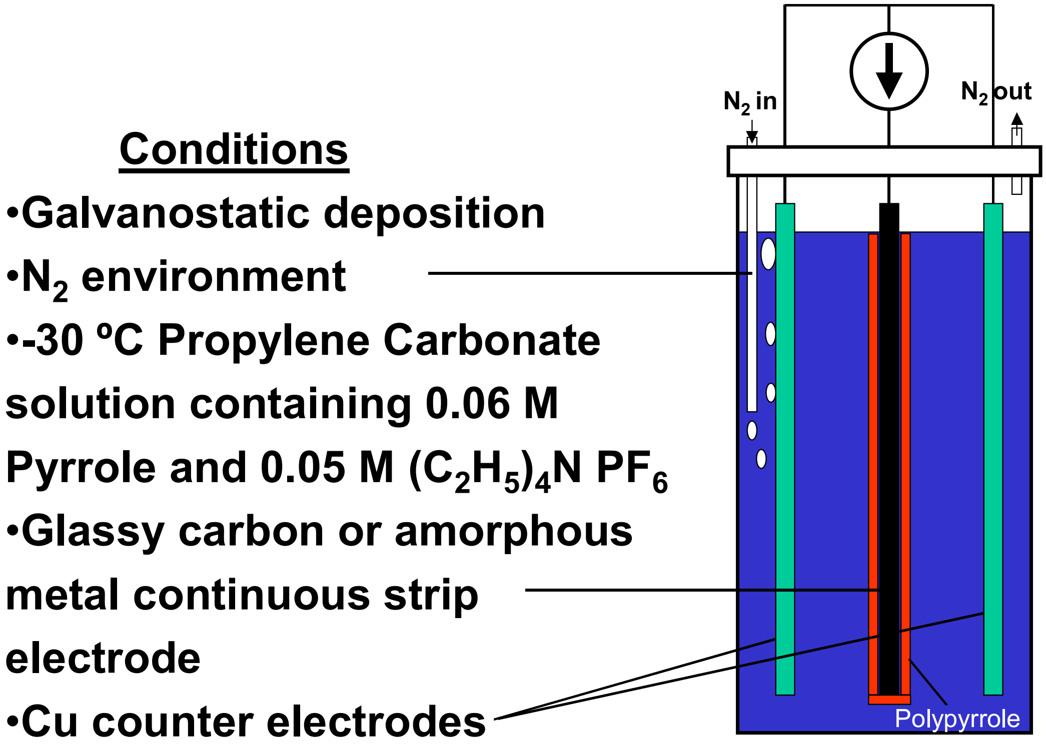
This chapter describes the synthesis procedures used to produce the polypyrrole films employed in the experiments presented throughout the thesis. Some characterization is also included. The synthesis follows the methods of Yamaura and colleagues (Yamaura, Hagiwara and Iwata 1988).

The development of the specifics of the synthesis procedure and the construction of the apparatus was done by a number of people, including the author. Others who have contributed include Dr. Tanya Kanigan, who identified the Yamaura method of synthesis as a promising approach and performed the early synthesis. Peter Madden developed, built and tested the apparatus for growing long films on the surface of a crucible. Patrick Anquetil, Ryan Cush, Kevin Joyce, Yun-Ju Lee and Gerda Nolan are among those who synthesized films for this study.

Polypyrrole is chosen for testing for a number of reasons. Early experiments showed that rapid contractions, and large deflections could be obtained using polypyrrole (Madden, Lafontaine and Hunter 1995). Further experimentation showed that strains of 2 % are obtainable at stresses of 5 MPa or more. Polypyrrole also exhibits the highest conductivity of any intrinsically conducting polymer apart from polyacetylene. High conductivity is advantageous, as it enables films and fibers to be electrochemically activated without concern for potential drops, which reduce efficiency and cause activation to be non-uniform. Finally, the electrochemistry and electrical properties of polypyrrole have been extensively studied (Arbizzani, Mastragostino and Scrosati 1997; Doblhofer and Rajeshwar 1998; Kohlman and Epstein 1998; Menon, Yoon, Moses and

Heeger 1998; Winokur 1998). The primary disadvantage of polypyrrole is that it is insoluble, making basic characteristics such as molecular weight difficult to determine, and eliminating some candidate methods of mass production, including casting, spin coating and solution drawing as methods.

The electrodeposition method employed produces high conductivity films (2-4.5×10^4 S·m^{-1}), with good mechanical properties (e.g. 30-50 Mpa tensile strength, 0.8 GPa elastic modulus wet).



Conditions

- **Galvanostatic deposition**
- **N_2 environment**
- **-30 °C Propylene Carbonate solution containing 0.06 M Pyrrole and 0.05 M $(C_2H_5)_4N\ PF_6$**
- **Glassy carbon or amorphous metal continuous strip electrode**
- **Cu counter electrodes**

Figure 1: Polypyrrole synthesis conditions. The diagram summarizes the conditions used in the synthesis of the hexafluorophosphate doped polypyrrole films employed in this study.

4.1 Electrodeposition

Films are grown from a solution of 0.06 M freshly distilled pyrrole monomer (Aldrich, Milwaukee, WI, USA, www.aldrich.com) and 0.05 M tetraethylammonium hexafluorophosphate (Aldrich) in propylene carbonate, following the procedure of Yamaura and colleagues (Yamaura and others 1988). Polypyrrole is deposited galvanostatically on to polished glassy carbon substrates (Alfa Aesar, Ward Hill, MA, USA, www.alfaaesar.com) at current densities of between 1 and 2 $A{\cdot}m^{-2}$, resulting in film thickness of between 8 and 100 μm. A copper counter electrode is used. Deposition takes place at temperatures between -30 °C and –45 °C in a nitrogen saturated solution. The resulting films have conductivities of between 20 and 45 $kS{\cdot}m^{-1}$, densities of 1500 to 1800 $kg{\cdot}m^{-3}$ dry and tensile strengths of 30 to 50 MPa.

The polished glassy carbon substrates take the form of either 100 mm × 100 mm × 1mm thick plates, or a crucible. The crucible is employed to obtain films that are up to 1.5 m in length, with a width of 4 mm. Figure 1 shows the crucible after deposition, including the kapton© tape that is spirally wound to masks the surface so that a continuous film is electrodeposited. Also shown is a 1.3 m long film that has been removed from the crucible.

4.2 Film Characterization

X-ray diffraction analysis of the material reveals that the material is ~50% crystalline, containing ordered regions that are ~2 nm across (Lee 1999; Nogami, Pouget and Ishiguro 1994; Pouget, Oblakowski, Nogami, Albouy, Laridjani, Oh, Min, MacDiarmid, Tsukamoto, Ishiguro and Epstein 1994). The proposed lattice structure is discussed in

Chapter 2. Based on the x-ray data, and conductivity data, it has been suggested that the structure is inhomogeneous, containing ordered conductive, crystalline and disordered regions with incoherent chain orientation (Kohlman and Epstein 1998). Electronic conductivity is achieved by percolation through the ordered regions.

The temperature dependence of electronic resistance down to liquid helium temperatures is shown in Figure 3. The measurement is courtesy of Peter Madden and Cynthia Chiang. The resistance data agrees with measurements performed by other on polypyrrole synthesized in the same manner (Kohlman and Epstein 1998; Menon and others 1998). Note that the conductivity shows metal-like behavior below 15 K, and the

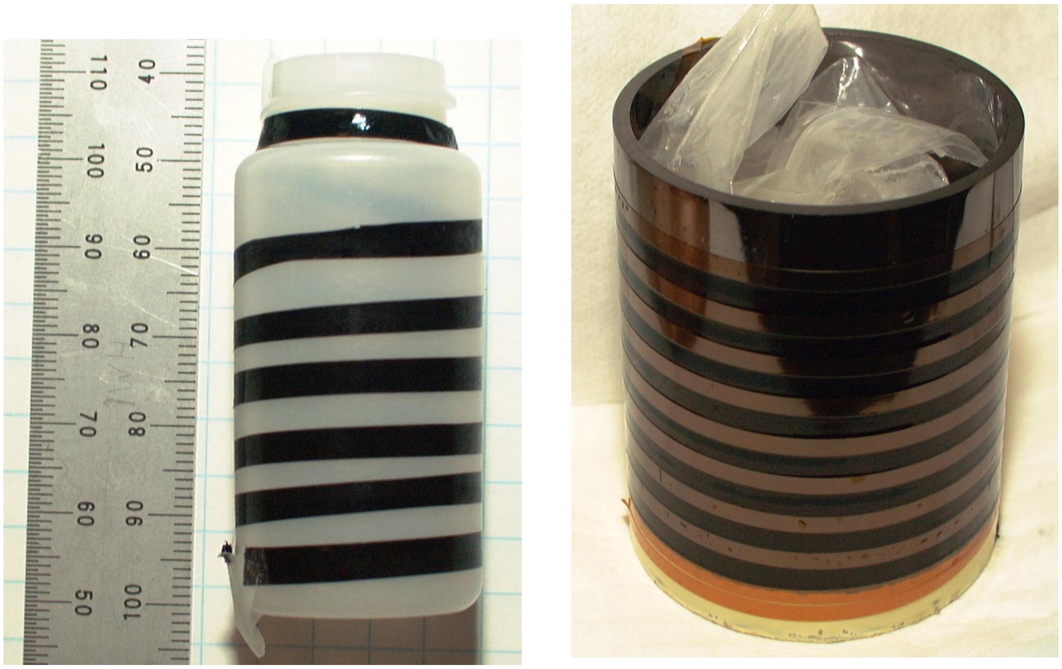


Figure 2: Synthesis of long films on a crucible. At right is the glassy carbon crucible employed to electrodeposit polypyrrole films of up to a meter in length. The crucible is masked using Kapton © tape, resulting in a film a shown at left. Photos courtesy of Patrick Anquetil.

ratio of 6 K resistance to room temperature resistance is 2.0. The fact that the polymer conductivity does not drop to zero at low temperature, and in fact increases as absolute zero is approached, suggests metallic behavior.

Elemental analyses show that dry films have an oxidation state of between 0.3 and 0.4 charges per monomer as grown. Films are dried by baking under vacuum or in a nitrogen environment at between 90 ºC and 100 ºC. The elemental analyses are performed by Galbraith Laboratories, Knoxville Tennessee, and agrees with the range of oxidation levels reported by Yamaura (Sato, Yamaura and Hagiwara 1991; Yamaura and others 1988; Yamaura, Sato and Hagiwara 1990; Yamaura, Sato and Iwata 1992).

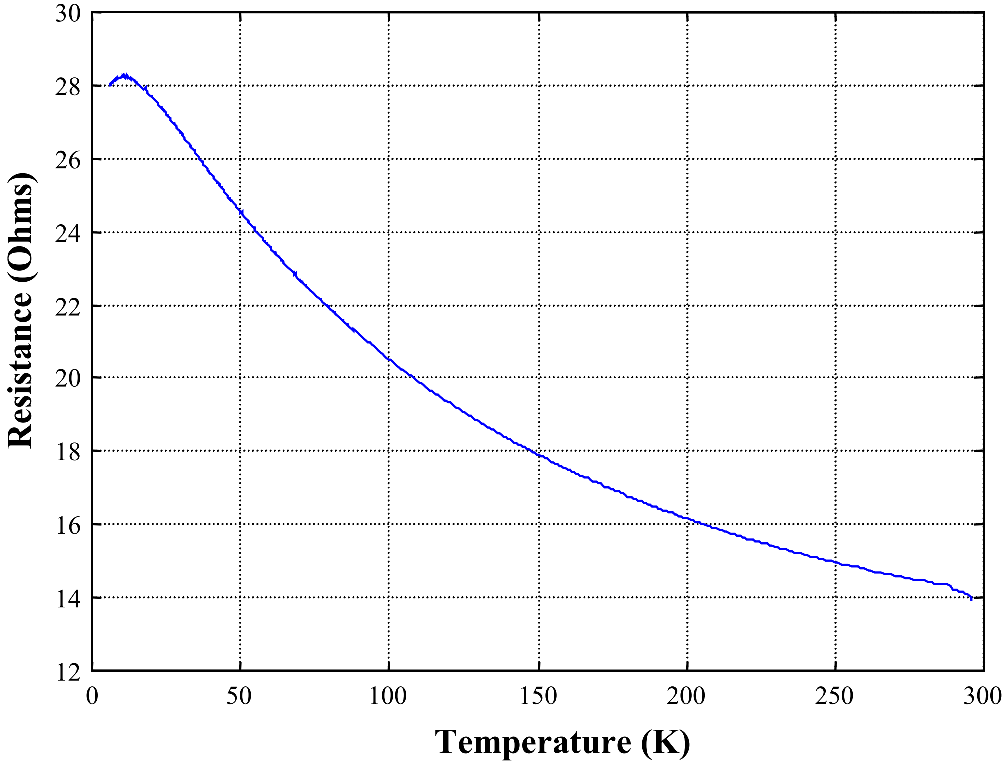


Figure 3: Temperature dependence of polypyrrole resistance. Courtesy of Peter Madden and Cynthia Chiang.

Thermal gravimetric analysis combined with mass spectroscopy and, separately, infra-red absorption spectroscopy, indicate that polypyrrole backbone does not thermally degrade appreciably under nitrogen until 375 ºC. Some fluorine and hydrogen fluoride is detected at temperatures of 110ºC and higher, suggesting that the hexafluorophosphate dopant ion may decompose, or have decomposed during electrodeposition.

Characterization of film mechanical properties and solvent content are presented in Chapters 5 and 10.

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