Solution−Surface Electropolymerization: A Route to Morphologically Novel Poly(pyrrole) Using an Ionic Liquid

Jennifer M. Pringle,*,† Maria Forsyth,†
Gordon G. Wallace,§ and Douglas R. MacFarlane‡

Australian Centre of Excellence in Electromaterials Science, Department of Materials Engineering and School of Chemistry, Monash University, Wellington Road, Clayton, VIC 3800, Australia, and Australian Centre of Excellence in Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

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The continually increasing interest in the use of conducting polymers, which now encompasses a wide range of applications,[1,2] is fuelling a continued need for materials with improved physical and chemical properties. In particular, there is a recent drive toward nanostructured and reduced dimensionality materials, such as thin films, nanotubes, wires, particles, etc., which can exhibit markedly different properties from those of the bulk materials.[3−5] The use of a template can be effective in such synthesis, but with the disadvantage of having to subsequently remove the template to obtain the nanostructured polymer. We have been investigating the use of ionic liquids for the electrochemical synthesis of conducting polymers,[6] and here we report an unusual growth process of poly(pyrrole) in this medium, which can result in the formation of a free-standing polymer film with an extended fine structure, without the aid of a template. In addition, SEM analysis of the materials provides insight into the growth mechanism of such electrochemically synthesized poly(pyrrole) films.

Ionic liquids are a relatively new class of solvent, composed entirely of ions, whose advantageous physical properties can in some cases include negligible vapor pressure, nonflammability, and good electrochemical stability.[7−9] The use of ionic liquids as the supporting electrolyte for conducting polymers has been shown to be extremely beneficial to performance and device lifetimes,[10,11] and studies have more recently focused on the potential benefits of using ionic liquids as the growth media for conducting polymers.[12−15] We have previously observed significant morphological differences between poly(pyrrole) films grown onto a stainless steel working electrode from ionic liquids compared to those grown in conventional molecular solvent/electrolyte systems.[6] However, if the electrochemical polymerization of pyrrole in the ionic liquid is performed using a platinum wire as the working electrode, the polymer forms an initial layer on the section of working electrode that is submerged into the monomer/ionic liquid solution, but then grows along the surface of the ionic liquid. This solution−surface electropolymerization is explored in more detail in this paper.

The ionic liquid used here was 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, prepared using the literature procedure,[16] dried (water typically <40 ppm by Karl Fisher), and degassed with dry and oxygen-free nitrogen before use; other ionic liquids are also being investigated. The working electrode was a 0.5 or 0.25 cm Pt wire. The first counter electrode used was platinum mesh (parallel to the working electrode) and then a PVDF membrane sputter-coated with platinum. The working electrode was placed vertically into the cell, completely through the ionic liquid containing 0.1 M pyrrole, touching the bottom of the cell. The film was grown either using constant potential or potential pulses (0.8 V), either 100 ms or 10 ms long with the same time resting at 0 V between pulses, versus a Ag wire pseudo-reference electrode. The films were grown for a number of hours depending on the growth technique (longer for voltage pulses), until the film extended sufficiently far across the surface of the ionic liquid to allow subsequent analysis. The film, still attached to the working electrode, was removed from the growth solution, washed repeatedly with ethanol to remove the ionic liquid, and dried under vacuum at room temperature. A JEOL 840A scanning electron microscope was then used for morphological analysis.

We have found that this solution−surface polymerization phenomenon only occurs in ionic liquids when the growth solutions are deaerated, but the polymerizations are performed in air rather than under nitrogen. Under a dry nitrogen atmosphere the polymer only forms on the submerged body of the electrode; this also occurs when a water-saturated ionic liquid is used. We believe that the presence of some water is necessary for the surface polymerization, to react with the H^+ produced in the reaction (water being a stronger base than the bis(trifluoromethanesulfonyl)amide anion), and when a dry ionic liquid is used this is provided by absorption from the atmosphere. We have observed this solution−surface polymerization phenomenon in a number of hydrophobic ionic liquids, such as *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)amide, 1-butyl-3-methylimidazolium hexafluorophosphate, and tri(hexyl)tetradecylphosphonium bis(trifluoromethanesulfonyl)amide, although growth in the latter is hindered by very high IL viscosity. This report details the results obtained using 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, which we have previously found to be an excellent choice for the electropolymerization of pyrrole and various thiophene derivatives.[6,17,18]

There are a small number of reports of similar phenomena observed in aqueous solutions of pyrrole, referred to as solution−surface polymerization.[19−21] Lee et al.[20] suggest that a large solution−surface tension is required to observe this effect. However, ionic liquids generally have quite modest surface tensions compared to molecular solvents; 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide is ∼40 mN m^{-1} compared to 72.7 mN m^{-1} for water at 20 °C.[22] The authors report that, of the solvents they tested, solution−surface polymerization was observed only in water and not in any of the molecular solvents (and only for pyrrole, not thiophene or methylthiophene). The authors use deaerated aqueous solutions and perform the polymerization under a nitrogen atmosphere. Thus, this present work is the first report of solution−surface polymerization in a nonaqueous solvent, which may be particularly beneficial in preventing the overoxidation of the polymer that can occur during polymerization in water.

The morphology of the poly(pyrrole) films formed on the surface of the ionic liquid, using constant potential growth and

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[†] Department of Materials Engineering, Monash University.
[‡] School of Chemistry, Monash University.
[§] University of Wollongong.
* Corresponding author: e-mail Jenny.Pringle@eng.monash.edu.au; Fax (+613) 9905 4597; Tel (+613) 9905 4599.

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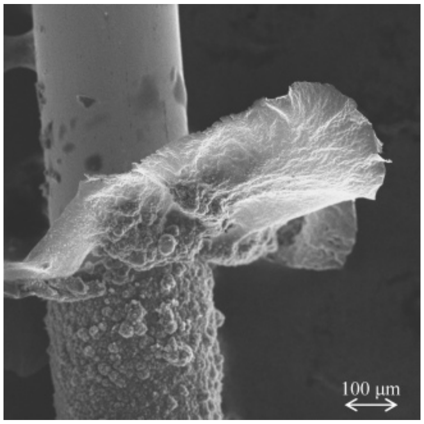

Figure 1. Poly(pyrrole) grown onto a Pt wire working electrode from the surface of an ionic liquid.

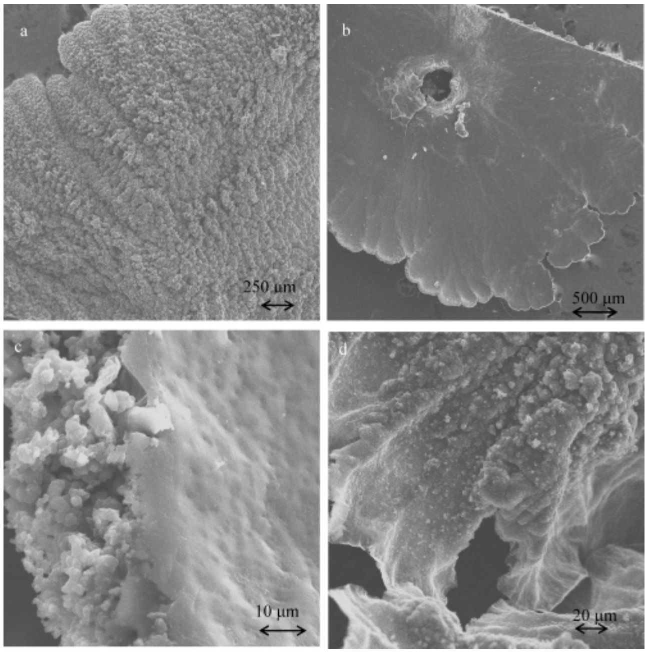

Figure 2. Poly(pyrrole) films grown at constant potential on the surface of the ionic liquid, cut in two to show (a) the ionic liquid side of the film and (b) the air side of the same film (the hole in the center of the film is where the Pt wire working electrode was). Second poly(pyrrole) film: (c) side view and (d) outer edge, indicating progression of growth morphology from working electrode (top right-hand side) to edge.

a platinum mesh counter electrode, were examined using scanning electron microscopy, SEM (Figure 2). This shows marked differences between the morphology of the upper and lower surface of the polymer film. The side grown into the ionic liquid shows the traditional cauliflower morphology of poly(pyrrole) grown in molecular solvents or water (Figure 2a), which is rougher than that previously observed for poly(pyrrole) films grown directly onto a working electrode from this ionic liquid,[17] further suggesting a role of water in this film growth process. In contrast, the air side is exceptionally smooth (Figure 2b) as the traditional 3D nucleation and growth mechanism with which the polymer grows into the ionic liquid/monomer solution is not possible in the opposite direction due to the lack of monomer. SEM analysis of the edge of the film (Figure 2c) shows the striking difference in morphology of the two surfaces, with a smooth, compact upper layer and the traditional globular morphology below. Examination of the outer edge of the film (Figure 2d) indicates that the flat, compact layer of the film grows first, followed by a transition from 2D to 3D growth, which results in the sequential formation of polymer with globular morphology visible in the regions of film closer to the working electrode (top right-hand side).

To encourage this surface growth and manipulate the morphology, a Pt-coated PVDF membrane was then used as a counter electrode, positioned around the inner wall of the electrochemical cell to completely circle the working electrode. SEM analysis of the poly(pyrrole) films grown using this setup (constant potential) show significant directional growth (Figure 3). This is of interest with respect to improving the conductivity of the films—it is well known that increasing the alignment of conducting polymers, e.g. by stretching, can enhance electrical transport because conducting polymers can be considered to be quasi-1D conductors.[23]

The microstructure of the poly(pyrrole) films can be further enhanced by polymerization using voltage pulses rather than a constant potential. SEM analysis of polymer films grown using voltage pulses (Figure 4) indicate that the polymer forms first as a series of fibrils, which can extend over a significant portion of the film before filling to form a complete film. This fine structure imparts a larger surface area to the polymer than would be present in a solid, homogeneous film. The electrochemical activity of a film grown using voltage pulses has been analyzed (see Supporting Information), and a cycling efficiency of more than 60%, with respect to the theoretical maximum, was observed. This is difficult to achieve for conventional poly(pyrrole) films, prepared by conventional electropolymerization, which show a significant decrease in electrochemical efficiencies once they exceed ca. 0.5 μm in thickness.[24]

In summary, we have observed an unusual mechanism of growth during the polymerization of pyrrole in an ionic liquid, with the polymer growing along the surface of the solution.

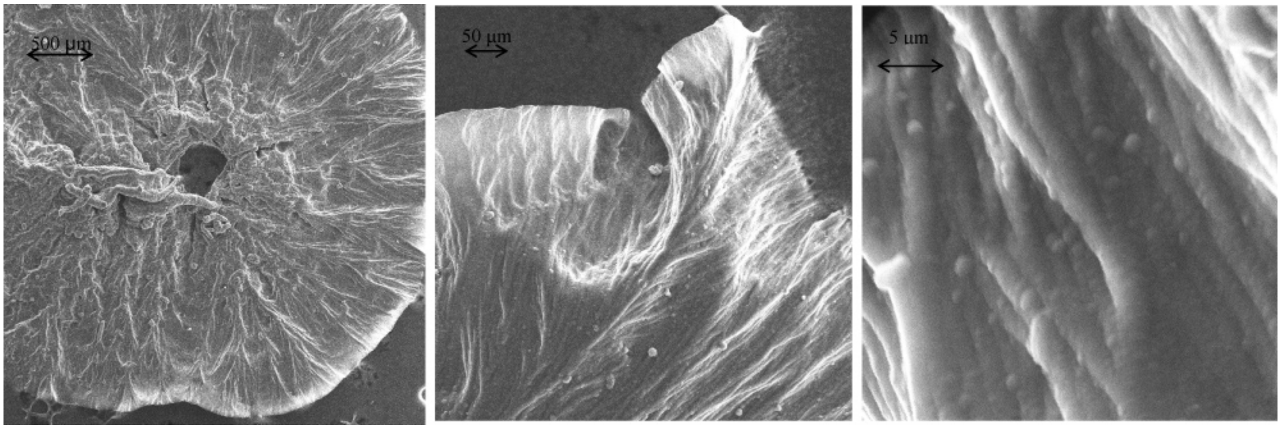

Figure 3. Directional growth on the poly(pyrrole) films grown using a circular counter electrode.

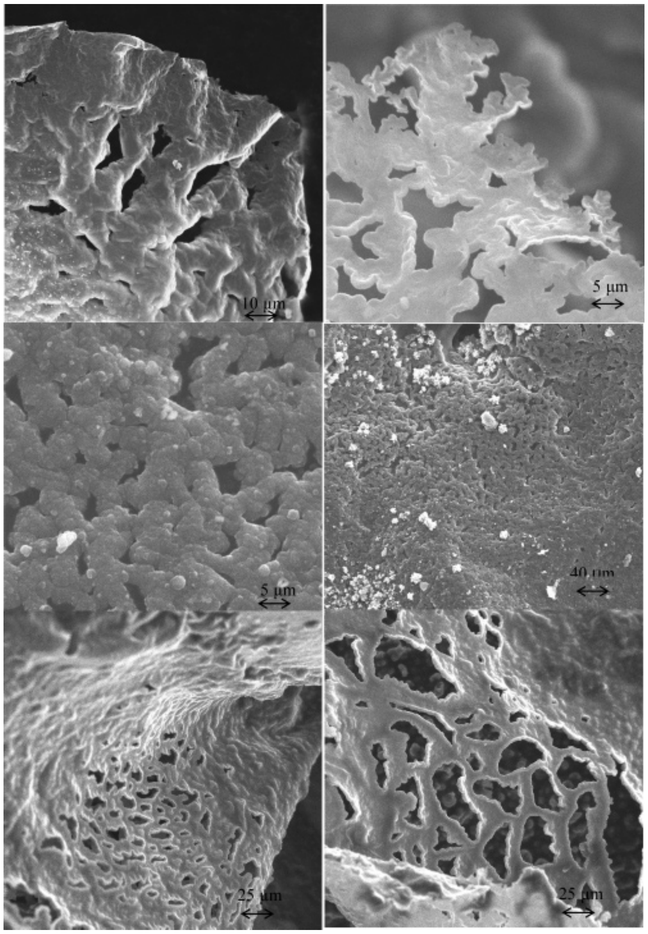

Figure 4. Different fine-structured poly(pyrrole) films formed on the ionic liquid surface using voltage pulses (100 ms pulses, top; 10 ms, lower four).

This phenomenon can be encouraged using different electrode setups and electrochemical techniques to produce free-standing films with desirable morphological features such as directional growth or fine-structured, larger surface area films. This surface polymerization methodology also has the potential to allow growth of poly(pyrrole) into porous structures for electrode applications or to incorporate other surface-active materials into the film. Such experiments are underway.

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Supporting Information Available: Cyclic voltammogram of a polypyrrole film, grown by solution−surface electropolymerization using 0.1 s voltage pulses, cycled in 0.1 M acetonitrile/tetrabutylammonium hexafluorophosphate (Figure S5); calculation of the cycling efficiency of this film. This material is available free of charge via the Internet at http://pubs.acs.org.

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