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Electrochemical synthesis of polypyrrole in ionic liquids

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Abstract

Electrochemical synthesis of inherently conducting polymers such as polypyrrole is traditionally performed in a molecular solvent/electrolyte system such acetonitrile/lithium perchlorate. We report the use of ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide and *N*,*N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide, both as the growth medium and as an electrolyte for the electrochemical cycling of polypyrrole films. Use of the ionic liquid as the growth medium results in significantly altered film morphologies and improved electrochemical activities.

Keywords: Polypyrrole; Ionic liquids; Conducting polymers

1. Introduction

Inherently conducting polymers (ICPs) are organic materials that not only display electrical, electronic, magnetic and optical properties similar to metals, but also have the mechanical properties and low density of a polymer. These materials, such as polyaniline, polypyrrole or polythiophene, have a conjugated structure; hence delocalisation of electrons occurs along the polymer backbone.

Polypyrrole is an especially promising ICP, as it is highly conducting, environmentally stable and relatively easy to synthesise. It has recently found use in a wide range of applications, including chemical and biological sensors, [1,2] light emitting diodes, [3] electromagnetic interference shielding [4] and advanced battery systems, [5,6] and the widespread interest in this and other ICPs is reflected in the extensive publications in this area [7–9]. One of the most exciting recent developments in the field of electroactive polymers, and polypyrrole in particular, is the fabrication of electromechanical actuators, where the polymer can be made to bend and straighten on application of a small potential [10]. This has particular significance in the medical field, where electroactive polymers are being investigated as artificial muscles for a range of prosthetic and therapeutic uses.

Electrochemical polymerisation of pyrrole is traditionally performed in an electrolyte/molecular solvent system. The processing parameters, particularly the size and nature of the dopant counter-ions from the solvent/electrolyte system, and the nature of the solvent itself, can have a marked influence on the properties of the resultant polymer film [11]. When the electroactive polymer films are oxidised in an appropriate electrolytic medium, positive charges are generated along the backbone and, typically, solvated anions enter the polymer from the solution, to effect charge balance. It has been shown that the size and nature of the dopant counter-ion incorporated during synthesis can have a dramatic effect on the ion movement occurring during redox processes [12–14]. Recent work has suggested that in some cases, when the film is oxidised and reduced in an ionic liquid, the intercalation/de-intercalation of a cation rather than the anion occurs [15]. Ionic liquids have a number of

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advantages over conventional solvents such as the negligible vapour pressure, which overcomes the problem of solvent evaporation that exists with the long-term use of volatile solvents in electrochemical applications. Additionally, they have a wide liquid range, good thermal stability and, of particular importance, good electrical stability, with electrochemical windows typically over 4 V wide [16–18]. They are also recyclable and more environmentally benign than most conventional organic solvents. Films prepared in conventional solvents but cycled in an ionic liquid show improved actuator performance and significantly increased lifetimes, to up to a million cycles [15].

The ionic liquids used in this investigation are 1-butyl-3-methylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide and *N*,*N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide. The PF_6^- anion has previously been studied in some detail as a dopant for polypyrrole films, traditionally from solutions of a tetraalkylammonium PF_6 salt in a molecular solvent such as acetonitrile or propylene carbonate (PC) [22]. More recently, utilisation of the bis (trifluoromethanesulfonyl) amide (TFSA) anion, from LiTFSA solutions, has also been reported to produce doped polypyrrole films with high electrical conductivity [23].

The use of ionic liquids for the growth of electroactive polymers was initially investigated in 1985 by Pickup et al. [23,24] but was hindered by the moisture sensitivity of the chloroaluminate ionic liquids being used. The use of ionic liquids in electrochemical devices that utilise electroactive polymers is also starting to be recognised, [25,26] driven by the wide electrochemical window and low volatility of the solvents.

Sekiguchi et al. [27] recently reported the electropolymerisation of pyrrole in 1-ethyl-3-methylimidazolium triflate, both neat and as a 0.1 M solution in either acetonitrile or water, and observed an improvement in the morphology and electrochemical capacity of the films. In this communication, we report the use of ionic liquids as both a growth medium for the electrochemical polymerisation of pyrrole, and as an electrolyte for the electrochemical cycling of the films, and compare this to the use of conventional solvent/electrolyte systems. Use of the ionic liquid as the growth medium results in significantly altered film morphologies and improved electrochemical activity.

2. Experimental

Films of polypyrrole were prepared from 0.1 M solutions of freshly distilled pyrrole either in an ionic liquid, a solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in propylene carbonate, or a solution of 0.1 M lithium perchlorate in acetonitrile. The films were grown over 30 potentiodynamic cycles at room temperature unless stated otherwise. The ionic liquids were prepared using published procedures and were thoroughly dried and degassed before use [19–21]. All cyclic voltammograms (CVs) were recorded using a platinum working electrode, platinum coil counter electrode and silver pseudo-reference electrode. The scan rate used was $100\ mV\ s^{-1}$ with a starting potential of 0 V, scanning first to positive potentials and then to negative potentials on the return scan as indicated by the arrow on the *x*-axis. Larger films for analysis by SEM and XPS were grown potentiostatically for 2 h, at 1 V from the ionic liquids or at 0.85 V from the molecular solvents. The slightly higher potentials used in the ionic liquid reflect the increased IR drop in these solvents due to the higher viscosity. The risk of overoxidation of the films was minimised by growing the films at the lowest possible potentials and by thoroughly drying and degassing the ionic liquids before use to remove any traces of water. Prior to XPS analysis, the films were washed well with acetonitrile and dried under vacuum at 30 °C for 48 h.

3. Results and discussion

Comparison of the growth cycles recorded during the electropolymerisation of pyrrole in ionic liquids compared to those recorded during film growth in a conventional solvent/electrolyte system is shown in Fig. 1.

The current onset at about 0.75 V indicates the oxidation of the pyrrole monomer, i.e. the onset of film growth. CVs recorded during film growth are sensitive to the nature of the electrolyte, concentration, solvent viscosity etc. hence comparison of different systems is normally more effective by comparison of post-polymerisation CVs. However, it is interesting to note that while film growth in a conventional solvent results in a steady and significant increase in current and capacitance with increasing cycles (Fig. 1(c)), this is not so apparent during film growth in the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid and even less so in the *N*,*N*-butylmethylpyrrolidinium TFSA. This may initially suggest that the films produced are either thinner or less electrochemically active, but this is contradicted by the post-polymerisation analysis, discussed below. Growth in the less viscous, more conductive 1-ethyl-3-methylimidazolium TFSA is more comparable to that of molecular solvents, suggesting faster growth of rougher, less dense films and this is reflected in the morphology of the films produced, as discussed below. The slight increase in the oxidation potentials observed in an ionic liquid compared to molecular solvents is probably a result of the higher viscosity and, therefore, increased IR drop across the ionic liquids, although it may also reflect a change in the stability of the pyrrole radical cation, which is the reactive species during electropolymerisation.

The wider electrochemical window of the ionic liquid allows access to higher potentials, and it is interesting to note that polypyrrole films can be grown at higher potentials than those used conventionally without any

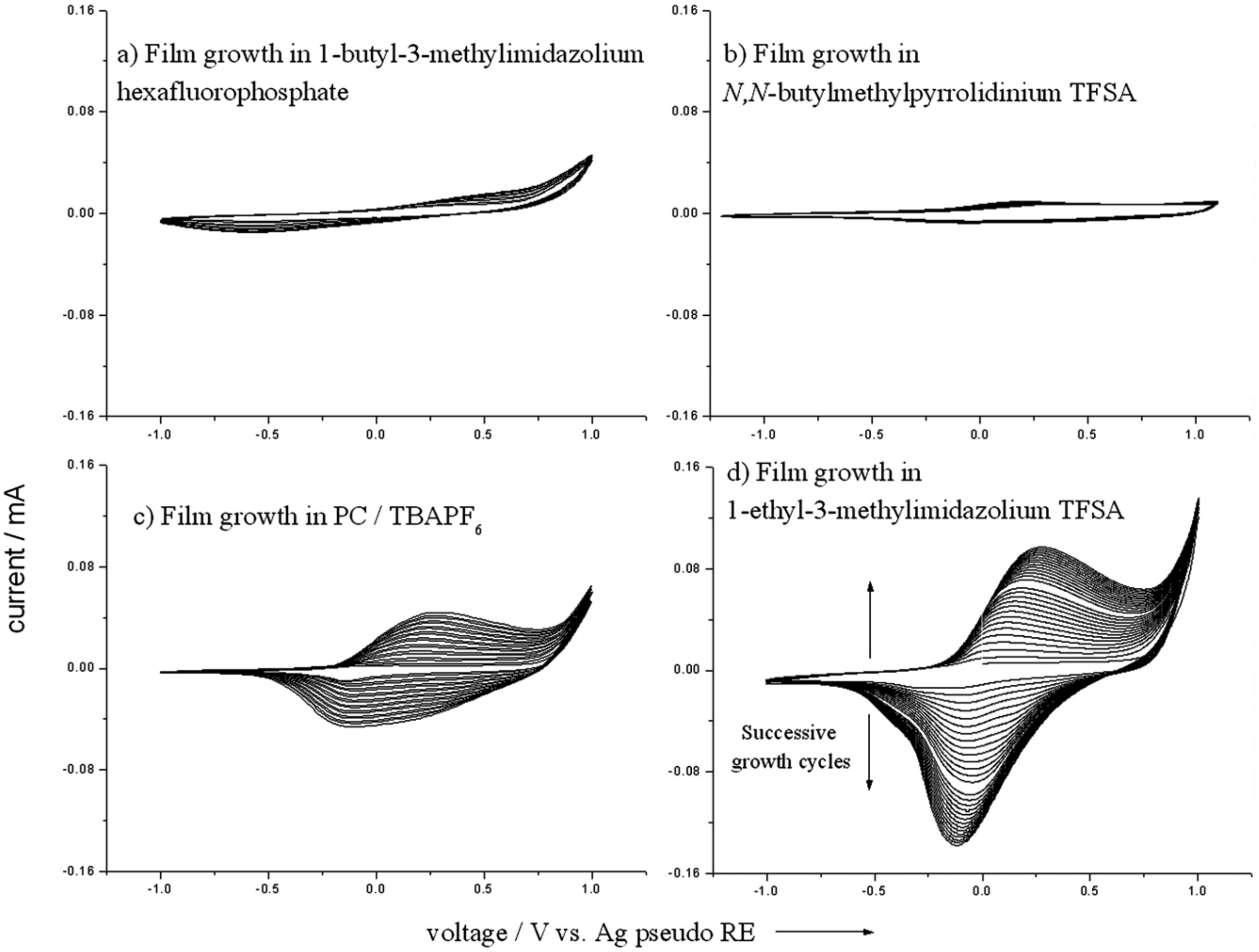

Fig. 1. Potentiodynamic growth of polypyrrole films in 0.1 M solutions of pyrrole in (a) 1-butyl-3-methylimidazolium hexafluorophosphate (b) *N*,*N*-butylmethylpyrrolidinium TFSA (c) PC/$TBAPF_6$ and (d) 1-ethyl-3-methylimidazolium TFSA. Scan rate 100 mV s^{-1}.

impairment of the film properties. After electropolymerisation, the working electrode with the films attached was removed from the growth solution, rinsed with a little propylene carbonate or acetonitrile, and the electrochemical properties of the films assessed. Surprisingly, the different polypyrrole films showed little electrochemical response when cycled in either 1-butyl-3-methylimidazolium hexafluorophosphate or *N*,*N*-butylmethylpyrrolidinium TFSA. However, the electrochemical response of the films when cycled in a conventional solvent system is dramatically different (Fig. 2).

It is clear from the post-polymerisation cyclic voltammograms in $TBAPF_6$/PC that the use of ionic liquids as the growth solvent for the electropolymerisation of pyrrole results in films that are significantly more electrochemically active than those prepared in the conventional PC/$TBAPF_6$ solvent system under comparable conditions. The peak currents of the anodic wave of the polypyrrole film grown in *N*,*N*-butylmethylpyrrolidinium TFSA are more than three times that of the film from PC/$TBAPF_6$. The considerable increase in capacitance of the polypyrrole films is of particular interest as polypyrrole, and other ICP materials, have recently found application in solid-state redox supercapacitors [28].

The improved electrochemical performance of polymer films grown in ionic liquids was further confirmed by comparison with polypyrrole films grown from a lithium perchlorate/acetonitrile solvent system. Post-polymerisation CVs of the films recorded in a lithium perchlorate/acetonitrile solution are shown in Fig. 3. In this solvent system, the advantages of using the ionic liquid as the growth solvent are even more striking.

The exceptional electrochemical response of the polypyrrole films produced from the ionic liquid solutions prompted us to return to the issue of the electrochemical cycling of these films in an ionic liquid. It is proposed that when the *N*,*N*-butylmethylpyrrolidinium TFSA or 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquids are used as the growth solvent, the films produced are so dense that, when they are cycled in ionic liquids, only the redox behaviour of the outer polypyrrole layers are measured. However, when these films are placed in a molecular solvent, such as PC or acetonitrile, swelling of the polypyrrole film occurs, allowing movement of dopant

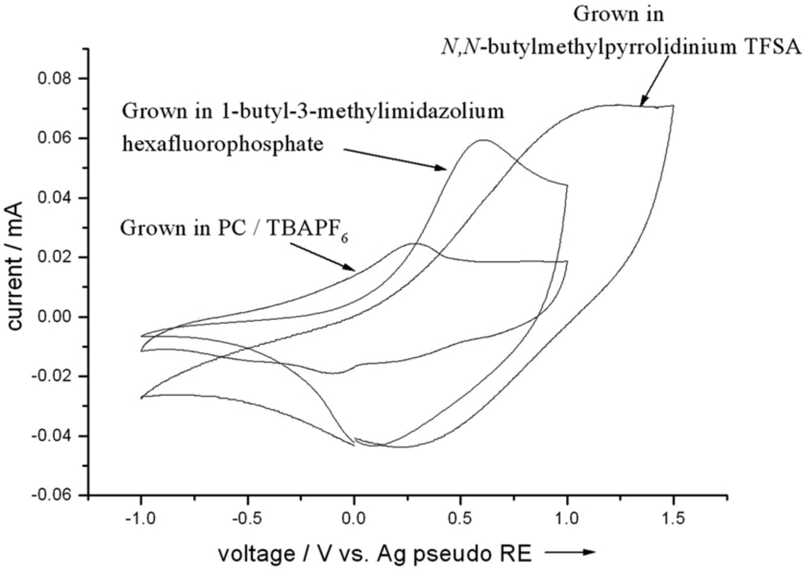

Fig. 2. Comparison of the electochemical activity of the polypyrrole films in PC/TBAPF$_6$ solution. Scan rate 100 mV s^{-1}.

ions and the oxidation and reduction of all of the polymer layers. This seems to be consistent with the growth CVs of the polymer films in the ionic liquid, where the first few cycles show a steady increase in the anodic current, after which it remains constant, suggesting that only the electrochemical response of the outer layers is being recorded.

To test this hypothesis, a thinner polypyrrole film was grown from *N*,*N*-butylmethylpyrrolidinium TFSA, over only five potentiodynamic cycles, and this thin film did indeed show a significantly improved electrochemical response when cycled in *N*,*N*-butylmethylpyrrolidinium TFSA (Fig. 4(a)). In contrast, the films grown in 1-ethyl-3-methylimidazolium TFSA, which show a more significant increase in the oxidation/reduction current during film growth (Fig. 1(d)), shows a notable electrochemical response when cycled in the ionic liquid, even when thicker films are grown (Fig. 4(b)). This seems to indicate that a limit is reached during film growth beyond which further addition of polymer does not add to the electrochemical response of the film in the ionic liquid, and that this limit is strongly dependant on the nature of the ionic liquid.

The electronic properties of polypyrrole films are intricately linked to the morphology; a smoother, more dense film will generally be more conductive as it is likely to be less porous and more ordered, which can facilitate charge transport through the film [11]. In trying to understand the role that the ionic liquid plays in producing such electrochemically active polymer films, electron microscopy was used to investigate the surface morphology. Conducting

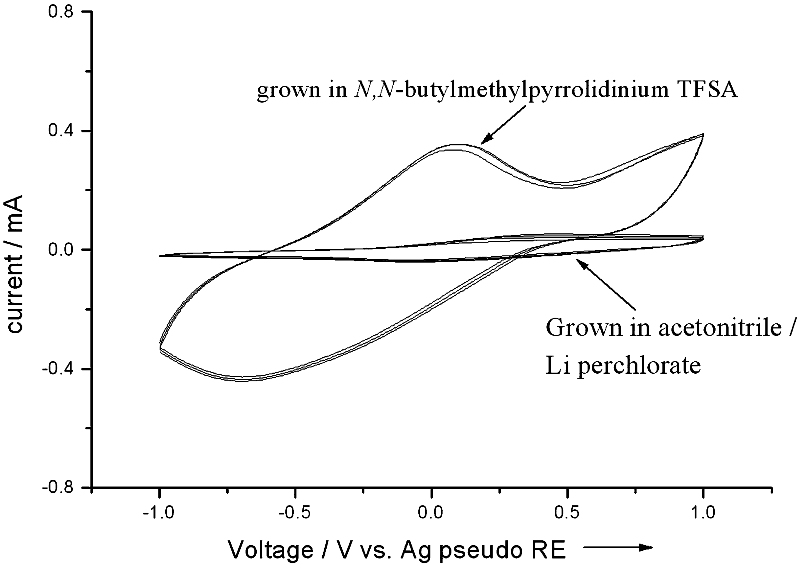

Fig. 3. Comparison of the cycling of films in an acetonitrile/Li perchlorate solution. Scan rate 100 mV s^{-1}.

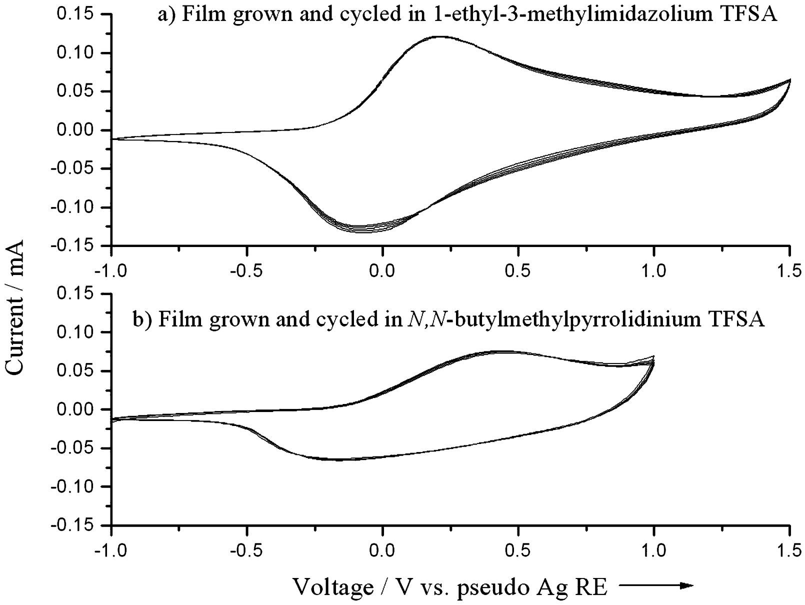

Fig. 4. (a) Post-polymerisation CV of polypyrrole film in *N*,*N*-butylmethylpyrrolidinium TFSA, grown over only five cycles in *N*,*N*-butylmethylpyrrolidinium TFSA. (b) Post-polymerisation CV of polypyrrole in 1-ethyl-3-methylimidazolium TFSA, grown over 30 cycles in 1-ethyl-3-methylimidazolium TFSA.

polymers typically show a nodular surface morphology, the origin of which is not well understood [11]. However, the films grown in the *N*,*N*-butylmethylpyrrolidinium TFSA ionic liquid are strikingly different to those grown in conventional solvent systems. Scanning electron microscopy shows that the films grown in *N*,*N*-butylmethylpyrrolidinium TFSA are considerably smoother than those grown in the PC/TBAPF$_6$ solution (Fig. 5).

At 100 μm resolution it can be seen that the films grown in the *N*,*N*-butylmethylpyrrolidinium TFSA ionic liquid are relatively uniform in morphology, whereas the polypyrrole film from the PC/TBAPF$_6$ shows the typical nodular, 'cauliflower' appearance, with large variations in surface structure across the film and nodules up to ca. 100 μm in diameter. Even at 2 μm resolution the polypyrrole film from the ionic liquid appears reasonably homogeneous, with only small nodules, whereas the film from the PC/TBAPF$_6$ appears very rough and pitted. The difference in morphology of the two films is consistent with the significant differences in the electrochemical properties of these two films. Further, the film grown in 1-ethyl-3-methylimidazolium TFSA is more similar in appearance to that grown in the molecular solvent system. The rougher surface of this film may explain the improved response, when cycled in an ionic liquid, compared to the smoother film produced from the *N*,*N*-butylmethylpyrrolidinium TFSA ionic liquid. Indeed, the striking differences in the morphology and electrochemical behaviour of the films indicate that the chemical structure of the materials made in ionic liquids may also be significantly altered. A change in the distribution of αα, αβ and ββ type linkages within the polypyrrole, [11] which would arise if the stability of the respective radical cations in the ionic liquid were different from the stability in molecular solvents, could be expected to change the film morphology, although the link between the extent of branching and macroscopic structure is not well understood.

During film growth in an ionic liquid, the polypyrrole is exposed to a considerably greater concentration of potential dopant ions, in this case both the cation and the anion of the ionic liquid, compared to film growth in the 0.1 M solution of TBAPF$_6$ in PC. This may be expected to allow a greater degree of doping of the polymer film, which would result in a significant increase in the electrochemical response of the material. The concentration and nature of dopants within the polypyrrole films is presently being investigated in detail using NMR and XPS spectroscopy. Solid-state ^{13}C NMR spectroscopy allows the detection of both intercalated TFSA anions and pyrrolidinium or imidazolium cations within the polymer films. Preliminary XPS analysis of films grown at constant potential from both *N*,*N*-butylmethylpyrrolidinium TFSA and 1-ethyl-3-methylimidazolium TFSA revealed one TFSA anion for every N$^+$ species, consistent with doping by the TFSA anion. When the films are grown in a quaternary ammonium ionic liquid, it is possible that some of the N$^+$ species detected by XPS is not oxidised pyrrole but rather dopant cations from the ionic liquid. However, this is unlikely for the films grown at a constant potential that were never cycled in the ionic liquid. XPS and NMR analysis is being continued to further investigate the nature and concentration of dopants in polypyrrole films grown under a range of conditions.

It is also interesting to note that although polypyrrole films grown in ionic liquids are predicted to contain more dopant ions than those grown in molecular solvents, movement of these ions within the polymer appears to

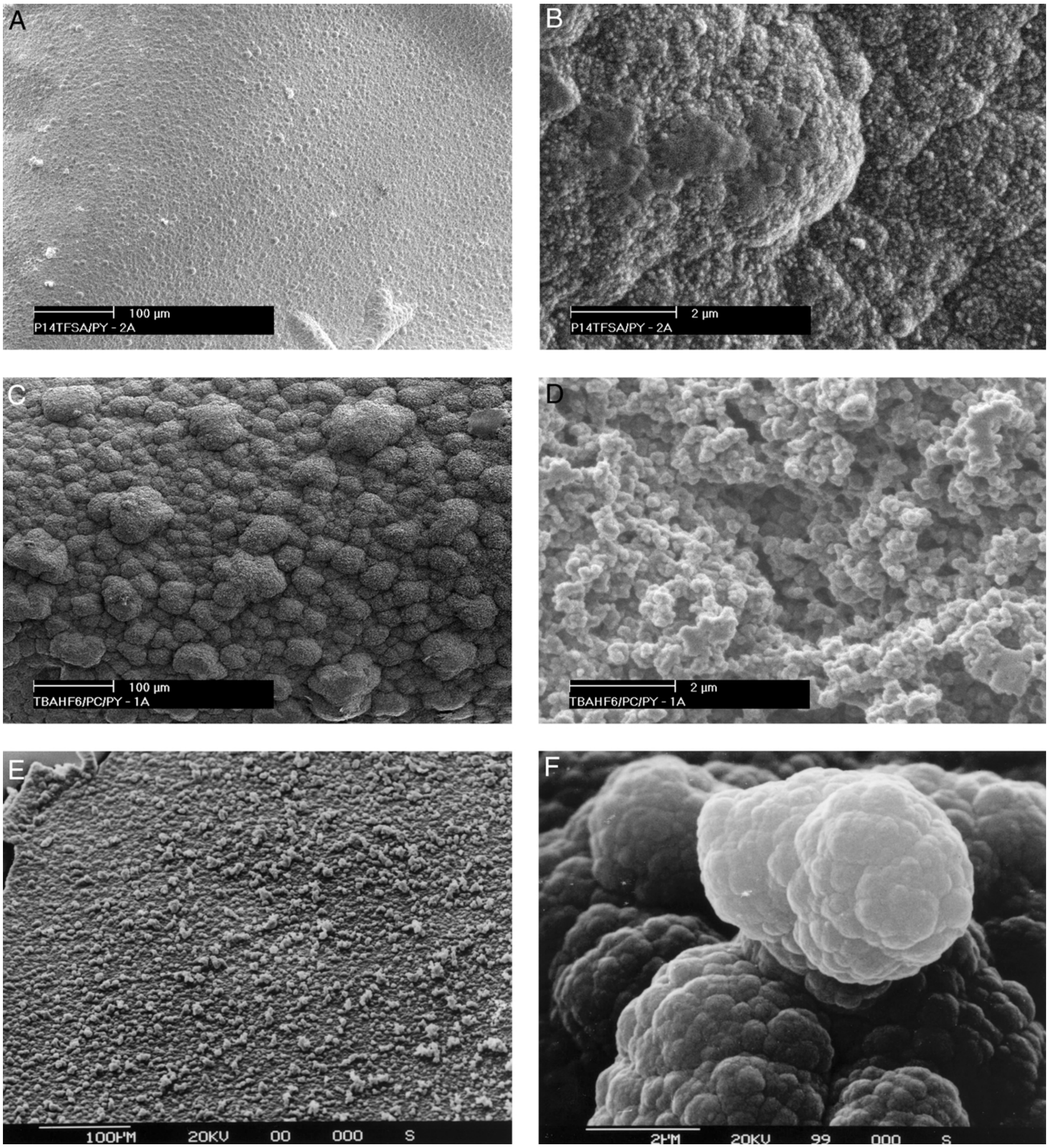

Fig. 5. Scanning Electron Micrographs of the polypyrrole films grown in *N*,*N*-butylmethylpyrrolidinium TFSA (100 μm (A) and 2 μm (B)) compared to those grown in $TBAPF_6$ (100 μm (C) and 2 μm (D)) and 1-ethyl-3-methylimidazolium TFSA (100 μm (E) and 2 μm (F)) (all solution side).

require some solvent swelling—the improved electrochemical response of the films grown from the *N*,*N*-butylmethylpyrrolidinium TFSA or 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquids is only observed during cycling in molecular solvents and not to such a large extent during cycling in the ionic liquids themselves. This need for significant solvent swelling is probably exacerbated by the fact that films grown in these ionic liquids are particularly smooth and dense. Consistent with this, the films grown in the more conductive, less viscous 1-ethyl-3-methylimidazolium TFSA have a much rougher surface structure, and these show a more significant response when cycled in the ionic liquid.

4. Conclusions

Three different ionic liquids have been used as the growth medium for the electrosynthesis of polypyrrole and a dependence on the nature of the ionic liquid was observed. All ionic liquids produced films with considerably smoother surface morphology and significantly enhanced electrochemical activity than films grown in conventional molecular solvent/electrolyte systems, with the more viscous, less conductive ionic liquid producing the smoothest films. The chemical nature of the new polypyrrole films and the nature and concentration of dopants is being investigated in more detail, and the significantly improved morphology of these materials suggest that they will also display significantly higher conductivity and better mechanical behaviour than those prepared in conventional solvents.

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References

[1] Ramanaviciene A, Ramanavicius A. Crit Rev Anal Chem 2002;32: 245–52.
[2] Bhat NV, Gadre AP, Bambole VA. J Appl Polym Sci 2003;88:22–9.
[3] Shen Y, Wan M. Synth Met 1998;98:147–52.
[4] Kim SH, Jang SH, Byun SW, Lee JY, Joo JS, Jeong SH, Park M-J. J Appl Polym Sci 2003;87:1969–74.
[5] Levi MD, Gofer Y, Aurbach D. Polym Adv Technol 2002;13: 697–713.
[6] Kuwabata S, Masui S, Tomiyori H, Yoneyama H. Electrochim Acta 2000;46:91–7.
[7] Sabouraud G, Sadki S, Brodie N. Chem Soc Rev 2000;29:283–93.
[8] Heeger AJ. J Phys Chem B 2001;105:8475–91.
[9] Jagur-Grodzinski J. Polym Adv Technol 2002;13:615–25.
[10] Baughman RH. Synth Met 1996;78:339–53.
[11] Wallace GG, Spinks GM, Kane-Maguire LAP, Teasdale PR. Conductive electroactive polymers, 2nd ed. Boca Roton: CRC Press; 2003.
[12] Tanguy J, Slama M, Hoclet M, Baudouin JL. Synth Met 1989;28: C145–50.
[13] Naoi K, Lien M, Smyrl WH. J Electrochem Soc 1991;138:440–5.
[14] Zhao H, Price WE, Wallace GG. J Membr Sci 1994;87:47–56.
[15] Lu W, Fadeev AG, Qi B, Smela E, Mattes BR, Ding J, Spinks GM, Mazurkiewicz J, Zhou D, Wallace GG, MacFarlane DR, Forsyth SA, et al. Science (Washington, DC) 2002;297:983–7.
[16] Wasserscheid P, Welton T, editors. Ionic liquids in synthesis. 2003.
[17] Welton T. Chem Rev (Washington, D.C.) 1999;99:2071–83.
[18] Endres F. Chem Phys Chem 2002;3:144–54.
[19] MacFarlane DR, Meakin P, Sun J, Amini N, Forsyth M. J. Phys. Chem. B 1999;103:4164–70.
[20] Suarez PAZ, Dullius JEL, Einloft S, De Souza RF, Dupont J. Polyhedron 1996;15:1217–9.
[21] Bonhote P, Dias A-P, Papageorgiou N, Kalyanasundaram K, Graetzel M. Inorg Chem 1996;35:1168–78.
[22] Joo J, Lee JK, Lee SY, Jang KS, Oh EJ, Epstein AJ. Macromolecules 2000;33:5131–6.
[23] Garcia B, Belanger D. Synth Met 1998;98:135–41.
[24] Pickup PG, Osteryoung RA. J Electroanal Chem Interfacial Electrochem 1985;195:271–88.
[25] Lu W, Fadeev AG, Qi B, Mattes BR. Synth Met 2003;135–136: 139–40.
[26] Lu W, Mattes BR, Fadeev AG, Qi B. PCT Int Appl 2002;50.
[27] Sekiguchi K, Atobe M, Fuchigami T. Electrochem Commun 2002;4: 881–5.
[28] Hashmi SA, Latham RJ, Linford RG, Schlindwein WS. Polym Int 1998;47:28–33.