Use of Ionic Liquids as Electrolytes in Electromechanical Actuator Systems Based on Inherently Conducting Polymers

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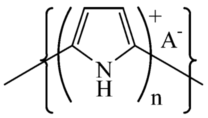
The use of ionic liquids (ILs) as electrolytes for electromechanical actuators based on polypyrroles (PPy's) is described. The composition of the electrolytes has a significant effect on the electrochemical properties of the PPy actuator and subsequently on actuator performance, improving cycle life and strain generated. The actuator performance in ionic liquid electrolytes is significantly better than that in traditional organic and aqueous electrolytes.

Introduction

Inherently conducting polymers (ICPs) such as polypyrroles, polythiophenes, and polyanilines (I−III shown below) have attracted considerable attention over the past 2 decades.[1−3]



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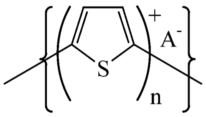

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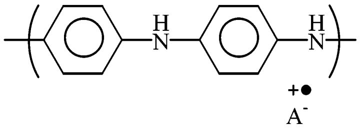
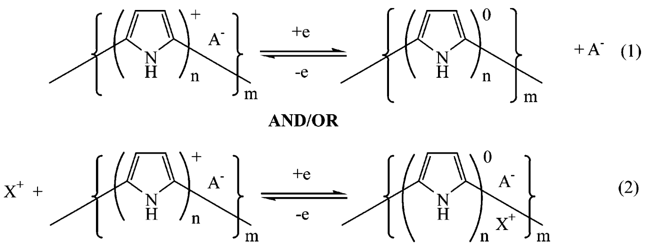


(III)

The remarkable electronic and ion exchange redox properties of these materials have led to their use in application areas as diverse as chemical sensors,[4,5] polymer batteries,[6,7] polymer-containing supercapacitors,[8−11] membrane separations,[12,13] and artificial muscles.[14,15]

All of these applications utilize the chemical or physical changes that accompany the facile redox processes occurring in these polymers. The oxidation/reduction process may involve either anion (eq 1) or cation (eq 2) exchange or a mixture of both.



[n = 2-3, m – determines molecular weight,
A^- = dopant anion, X^+ = cation from electrolyte]

Obviously, the electrolyte used to facilitate these redox processes plays a critical role. If the original

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dopant anion (A^-) is released during the reduction process, subsequent ICP oxidation will involve uptake of electrolyte anions. If on the other hand the reduction process leads to cation (X^+) incorporation (i.e., the anion is not expelled during reduction), then X^+ will be taken up from the electrolyte source.

The electrolyte also plays a critical role in determining the performance of ICPs at extreme potentials. For example, at extreme anodic potentials polypyrroles undergo irreversible degradation, which is attributed to nucleophilic attack on the polymer from solvent or electrolyte ions.[16,17] Breakdown of the solvent or electrolyte can also prevent some of the electronic properties of ICPs from being accessed. For example, at extreme negative potentials some polythiophenes can be n-doped,[18−20] provided the solvent or electrolyte does not break down before this occurs.

Interestingly, the electrolyte can also have a direct impact on the mechanical properties of ICPs, even after simple immersion, before any electrical stimuli are applied.[21] Given the well-known effect of the chemical environment on conducting polymer composition (via ion exchange and/or adsorption) as well as the influence on conformation, the observed changes in properties are not unexpected. Variation in mechanical properties as the oxidation state of the polymer is changed has also been found to be electrolyte-dependent.[21]

In some electrochemical systems containing ICPs the use of conventional liquid electrolytes is not practical, with leakage or loss due to evaporation resulting in limited working life. Thus, there has been some attention paid to alternatives and a number of solid polymer electrolytes (SPEs) have been investigated. For example, both poly(vinyl alcohol) (containing H_3PO_4) and poly(ethylene oxide) (containing $LiCF_3SO_3$) plasticized with poly(ethylene) glycol have been evaluated for use in polypyrrole-based redox supercapacitors[22] with specific capacitances in the range 40−84 F g^{-1} being obtained. These electrolytes have ionic conductivities in the range 10^{-4}−10^{-3} S cm^{-1}. Alternatively, poly(ethylene oxide)-based solid polymer electrolytes have been used in polypyrrole-based batteries.[23] The importance of chemical and electronic (band gap) compatibility of the polymer electrodes and polymer electrolyte has also been acknowledged.[24]

The stringent requirements for an electrolyte to be used in electromechanical actuators include adequate conductivity, mechanical properties, adhesion during flexing, and mechanical/electrical stability and it must be easily processible and able to function in air. Poly(ethylene glycol) containing $LiClO_4$ has been used as a solid polymer electrolyte for polypyrrole-based microactuators.[25] We have investigated[26] the use of polyacrylonitrile- or Kynar-based nonaqueous SPEs and water-based polyacrylamide hydrogel ion source/sinks containing various perchlorate salts for their applicability in polypyrrole-based actuators. The results indicated that the optimum electrolyte for use with polypyrrole-based actuators was a polyacrylonitrile plasticized with propylene carbonate and ethylene carbonate containing 1.0 M $NaClO_4$.

Unfortunately, the use of a SPE decreased the degree and rate of actuation in comparison to that possible in liquid solution-based electrolytes. The SPE both slows ion movement (cations in one direction and anions in the other) and adds stiffness to the device. However, on the positive side, SPEs allow the use of these actuators as free-standing devices in air. An all-polymer solid-state actuator has been constructed and tested.[27]

Previous workers have shown that ionic liquids (ILs) function well as electrolytes in electrochemical systems[28−30] with unprecedented environmental and electrochemical stability. It has been shown that dramatically improved electromechanical efficiency and lifetime can be achieved when ILs are used as the electrolyte in artificial muscle systems based on ICPs and that electrochromic windows based on ICPs using ILs as electrolytes can be cycled in excess of 1 000 000 times.[31] In that work limitations on the use of a PF_6^--containing ionic liquid were noted due to breakdown of the anion leading to the formation of HF. Consequently, in this work the electrochemical and electromechanical performance of polypyrrole actuators in the more environmentally stable 1-ethyl-3-methyl imidazolium bis(triflouromethanesulfonyl) amide was investigated. Performance is compared with that observed in a more conventional electrolyte (propylene carbonate containing *tert*-butylammonium hexafluorophosphate).

Experimental Section

Reagents, Standard Solutions, and Conducting Polymer Preparation. Pyrrole, tetrabutylammonium hexafluorophosphate ($TBA{\cdot}PF_6$), and propylene carbonate were obtained from Sigma. Pyrrole was distilled before use. 1-Butyl-3-methylimidazolium hexaflourophosphate ($BMI{\cdot}PF_6$)[32,33] and 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl) amide (EMI·TFSA)[34] were synthesized as described previously. It is known that PF_6^- salts can form HF under hydrolyzing conditions and so consideration should be given to the long-term storage of ionic liquids based on this anion.

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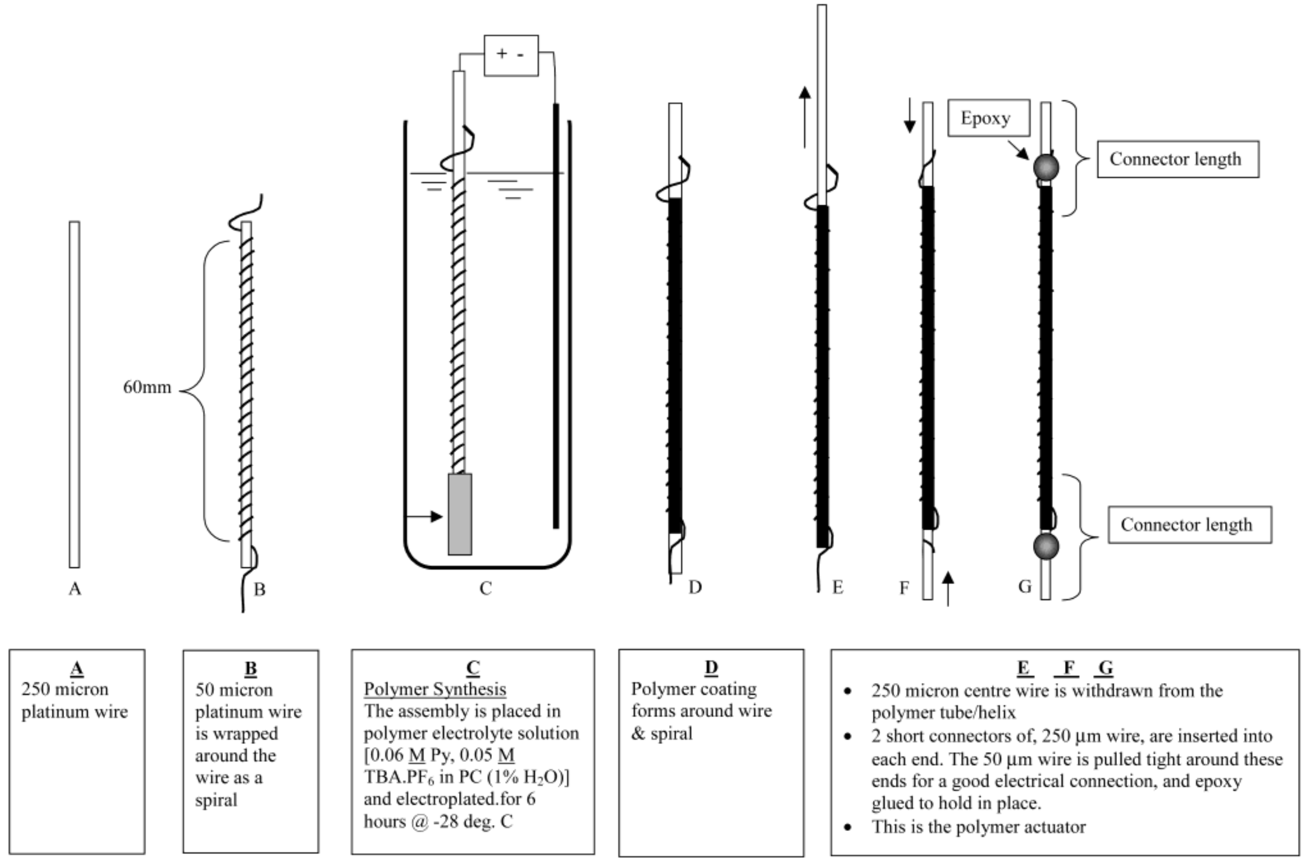

Figure 1. Schematic diagram showing method of construction for these actuators: (A) 250-μm platinum wire. (B) 50-μm platinum wire is wrapped around the 250-μm wire as a spiral. (C) Polymer synthesis: the assembly is placed in polymer electrolyte solution and electroplated for 6 h at −28 °C. (D) Polymer coating forms around wire and spiral. (E) 250-μm center wire is withdrawn from the polymer tube/helix; (F) Two short connectors of 250-μm wire are inserted into each end. (G) 50-μm wire is pulled tight around these ends for a good electrical connection and glued to hold in place.

For UV−visible absorption studies of PPy/PF_6 films were obtained after deposition onto transparent indium tin oxide (ITO) coated glass electrodes galvanostatically (1 mA cm^{-2} for 3 min).

Polypyrrole Actuator Preparation. The actuator was prepared as described in Figure 1.[35] Platinum wire (50 μm) was wound tightly around the 250-μm platinum wire core. This electrode set-up was then cleaned with acetone and left to dry in air before use as the working electrode in electropolymerization. A current density of 0.15 mA/cm^2 was applied. The polymerization solution consisted of propylene carbonate containing 0.06 M pyrrole monomer and 0.05 M TBA·PF_6. 1% (v/v) H_2O was added to ensure that the water content was constant. The cell temperature was controlled at −28 °C. The polymerization process was maintained for 6 h. The polymer tube formed around the inner core. Following electrodeposition, the platinum core was removed. The hollow tube with the thin helical platinum wire interconnect embedded in the inner wall was then washed with propylene carbonate and stored wet. All characterization was performed at room temperature.

An electrical connection to the hollow tube was obtained using two shorter platinum wires (1−1.5 cm) inserted into each end of the tube and subsequently fixed with polystyrene hot melt on each side. The electrical contact was checked by measuring the electrical resistance between the two ends. Values of 4−8 Ω were typically obtained.

Instrumentation. *Cyclic Voltammetry of Polymers.* Cyclic voltammetry studies were conducted in a three-electrode electrochemical cell using a platinum working electrode onto which the PPy/PF_6 composite had been deposited. A Ag/Ag^+ reference electrode and platinum mesh auxiliary electrode were used and measurements conducted in propylene carbonate (TBA·PF_6) or ionic liquid electrolyte.

Electropolymerization of PPy/PF_6 was performed using an EG & G Princeton Applied Research Model 363 potentiostat/galvanostat together with a conventional one-compartment electrochemical cell and three-electrode system. All solutions were thoroughly deoxygenated with nitrogen prior to use, and experimental data were collected using a MacLab A/D and D/A data collection system. Galvanostatic methods (1 mA cm^{-2} for 3 min) were used for depositing thin polymer films onto platinum electrodes from propylene carbonate solution containing 0.06 M Py, 0.05 M TBA·PF_6 and 1% H_2O onto a platinum working electrode. A Ag/Ag^+ reference electrode and platinum mesh auxiliary electrode were used.

UV−Visible Absorption Spectra. Absorption spectra (250−1100 nm) were obtained using a Shimadzu Model UV-1601 spectrophotometer and polymer films grown galvanostatically (1 mA/cm^2 for 3 min) on indium tin oxide (ITO) coated glass.

Actuation Test. Actuation/displacement tests were carried out using two different systems. The first involved the use of a two-electrode cantilever system (see Figure 2). The amount of displacement was measured from a video recording of the cantilever movement and the strain calculated according to the original length of the actuator component. The weight applied to the PPy tube during actuation was 5.0 g.

Actuator strain data in PC and IL was also obtained using a beam balance as described previously.[36] The extension/contraction of the polymer was recorded using a linear variable distance transducer when a ±2.5 V triangle waveform with a potential scan rate of 50 mV/s was applied. For EMI·TFSA this experiment was repeated under different loads.

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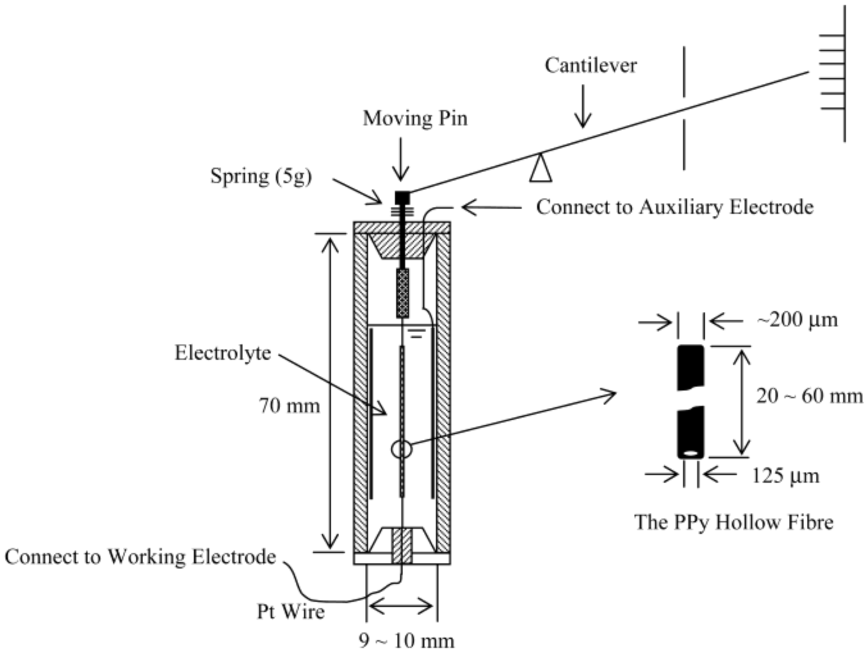
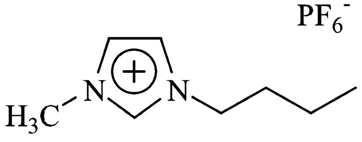


Figure 2. Two-electrode cantilever set-up.

Results and Discussion

Initially, the electrochemical properties of PPy−PF_6 were examined using cyclic voltammetry in the propylene carbonate-based electrolyte and each of the ionic liquids **IL1** and **IL2** shown below.



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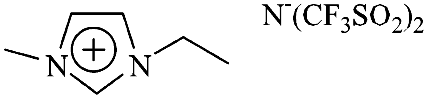
1-butyl-3-methylimidazolium hexaflourophosphate (BMI·PF_6) [IL1]



2

1-Ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl) amide (EMI·TFSA) [IL2]

When propylene carbonate containing TBA·PF_6 was used as an electrolyte, degradation in the polymer electroactivity was observed if the anodic potential range was extended beyond +1.30 V. This degradation is attributed to the irreversible "overoxidation" previously observed for polypyrroles at anodic potentials where the polymer backbone becomes susceptible to attack from nucleophiles in the electrolyte. When the limit was extended to +1.55 V (Figure 3a), the breakdown was rapid and all electroactivity was lost after six potential cycles.

When the polypyrrole was deposited on ITO glass and cycled over the same potential range, the changes in the UV−visible spectra observed at long wavelengths (Figure 4) are related to a decreased absorption due to the bipolarons. The spectral changes are consistent with the nucleophilic attack reducing π-conjugation length and bipolaron activity. The loss of conjugation leads to reduced conductivity and electroactivity.

When **IL1** (BMI·PF_6) was used as the electrolyte, no such degradation was observed over this same potential range (Figure 3b). The increased stability was confirmed when the experiment was repeated on PPy-coated ITO glass with no changes in the UV−visible spectra observed. In fact, when BMI·PF_6 was used, the potential could be scanned to +1.75 V without any change in the cyclic voltammetry being observed. Similarly, in EMI·TFSA (Figure 3c) no degradation of electroactivity was observed with a +1.55 V potential limit. With this electrolyte the upper limit could be extended to +2.0 V without degradation being observed. Again, UV−visible spectra obtained for film deposited on ITO glass confirmed that no degradation occurred after cycling the potential to those extended anodic regions for six cycles. These results indicate a greater degree of polymer stability to potential cycling over extreme limits when these very electrochemically stable IL electrolytes are used.

Actuator Experiments

The two-electrode actuator (Figure 2) set-up was used to evaluate the performance of hollow fiber PPy actuators in each of the electrolytes. A repetitive pulse (500-ms duration) was applied over a number of potential ranges and the maximum strain as well as the average strain rate over the 500-ms period determined. The electrolytic efficiency [EE% = (actual charge (Q) passed during oxidation or reduction cycle/Q needed to oxidize or reduce all of polymer) × 100] was determined during these experiments. As expected, in all electrolytes the electrolytic efficiency, strain, and strain rate increased with increased magnitude of the applied potential (Table 1). At most potentials (all except ±5 V) there is a higher

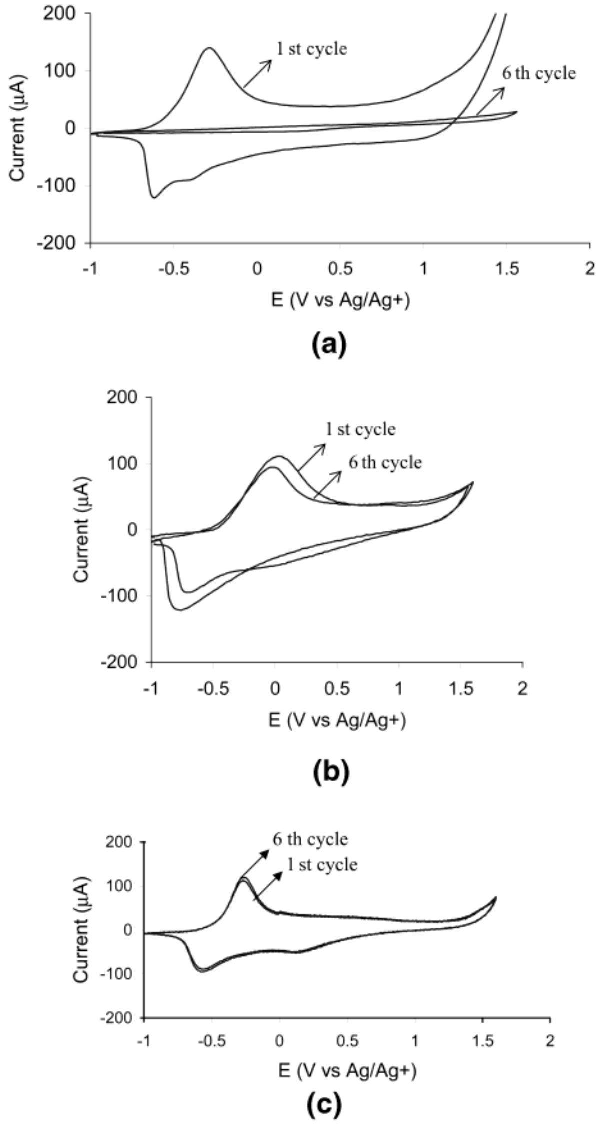


Figure 3. (a) Cyclic voltammogram obtained using a PPy/PF$_6$-coated platinum electrode in PC (0.25 M TBA PF$_6$). Scan rate = 100 mV/s. PPy/PF$_6$ was prepared galvanostatically (1 mA cm^{-2} for 5 min) using a solution containing 0.06 M Py, 0.05 M TBAPF$_6$, and 1% H_2O. Potential range: −1 to +1.55 V. (b) Cyclic voltammogram obtained using a PPy/PF$_6$-coated platinum electrode in **IL1** (1-butyl-3-methylimidazolium hexaflourophosphate). Scan rate = 100 mV/s. PPy/PF$_6$ was prepared galvanostatically (1 mA cm^{-2} for 5 min) using a solution containing 0.06 M PPy, 0.05 M TBAPF$_6$, and 1% H_2O. Potential range: −1 to +1.55 V. (c) Cyclic voltammogram obtained using a PPy/PF$_6$-coated platinum electrode in **IL2** (1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl) amide). Scan rate = 100 mV/s. PPy/PF$_6$ was prepared galvanostatically (1 mA cm^{-2} for 5 min) using a solution containing 0.06 M PPy, 0.05 M TBAPF$_6$, and 1% H_2O. Potential range: −1 to +1.55 V.

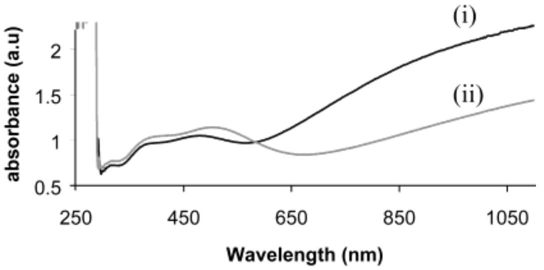


Figure 4. UV−visible spectra of a PPy/PF$_6$ deposited galvanostatically (1 mA/cm^2 for 3 min) onto ITO-coated glass: (i) Polymer in the oxidized state; (ii) oxidized polymer after CV in PC (0.25 M TBA.PF$_6$) solution for six cycles over the potential range −1 to +1.55 V and scan rate = 100 mV/s. PPy/PF$_6$ was prepared galvanostatically (1 mA cm^{-2} for 5 min) using a solution containing 0.06 M Py, 0.05 M TBAPF$_6$, and 1% H_2O.

Table 1. Effect of Electrolyte Used on Electrolytic Efficiency and Strain Obtained[a,b]

	electrolyte					
	PC (TBA·PF$_6$)		**IL1** (BMI·PF$_6$)		**IL2** (EMI·TFSA)	
applied potential[c] (V)	electrolytic efficiency (%)	max. strain (%)	electrolytic efficiency (%)	max. strain (%)	electrolytic efficiency (%)	max. strain (%)
±1	9.4	0.4	5.3	0.2	0.50	0.01
±2	18.3	0.4	12.1	0.3	7.3	0.2
±3	37.8	0.6	20.2	0.5	15.8	0.3
±4	51.4	0.9	42.7	0.9	34.6	0.7
±5	56.3	1.0	56.6	1.4	51.0	1.5

[a] All data obtained using the two-electrode moving pin system. Potential pulse is applied for 0.5 s positive and then 0.5 s negative. Electrolytic efficiency calculated from current flow over that period. Strain and strain rate are average values over the 0.5 s period. [b] Growth conditions for actuator: Polymerization solution contained 0.06 M pyrrole, 0.05 M TBA·PF$_6$ in PC (1% H_2O). Current density: 0.15 mA/cm^2. Growth time: 6 h. Temperature: −25 to 28 °C. [c] 100 cycles were applied at each potential range starting with ±1 V and increasing to the largest range ±5 V, so data collected at ±5 V is in fact after 500 cycles.

electrolytic efficiency in PC than either IL, reflecting the higher ionic conductivity of the propylene carbonate electrolyte compared with that of the ionic liquids. Interestingly, at ±5 V the electrolytic efficiencies observed are approximately the same (50−56%) in all electrolytes, yet there is significant differences in the strain generated. In IL a higher strain is generated for a given charge passed when a large potential is applied. These different characteristics reflect fundamental differences in the actuation mechanism of PPy·PF$_6$ in ionic liquids compared with the propylene carbonate-based electrolyte. The results may also be affected by Faradaic reactions occurring in the PC electrolyte that do not contribute to actuation but still consume charge. This is confirmed by the increased oxidation current observed above 1.00 V in propylene carbonate-based electrolyte (Figure 3a) compared to the IL electrolytes (Figure 3b,c).

The actuator was then cycled over a few thousand cycles using propylene carbonate (TBA·PF$_6$) as the electrolyte. After 3600 cycles the strain recorded was just 0.3% (Figure 5), a greater than 4-fold decrease compared with those of the initial cycles. These experiments were then repeated in BMI·PF$_6$ (Figure 5). The strain attainable over several thousand cycles was significantly more consistent in the ionic liquids, reflecting the higher electrochemical stability of the PPy in these electrolytes.

Plots of strain versus potential were then obtained using the beam-balance set-up described in the Experimental Section (Figure 6). Here, the direction of actuation was clearly shown to be reversed in the ILs compared with that in the PC-based electrolyte. These results show that the movement of the IL cation in/out of the polymer at negative potentials is the dominant mechanism leading to actuation. Conversely, in PC it is the anion (PF$_6^-$) that is induced to move into (positive

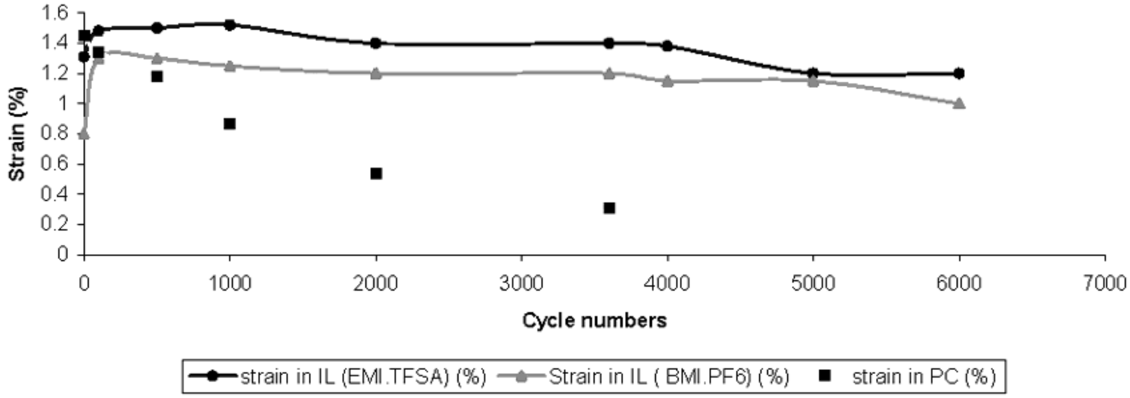


Figure 5. Strain versus cycle number observed for the polymer actuator in PC (0.25 M TBA·PF_6) and the two ionic liquids. One cycle involved application of ±5 V (1 Hz). Strain measured at the positive potential for propylene carbonate electrolyte and the negative potential for the ionic liquids.

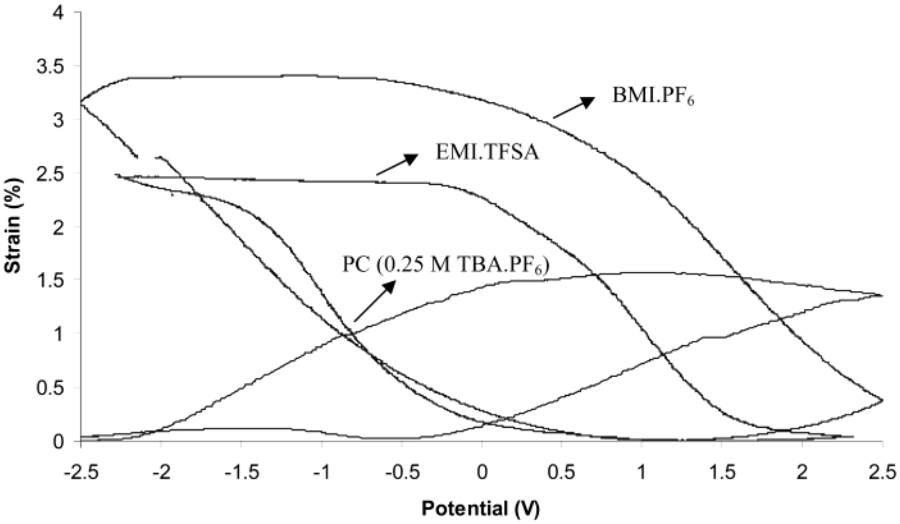


Figure 6. Strain–potential curves observed when a ±2.5 V cyclic waveform was applied with a scan rate of 50 mV/s.

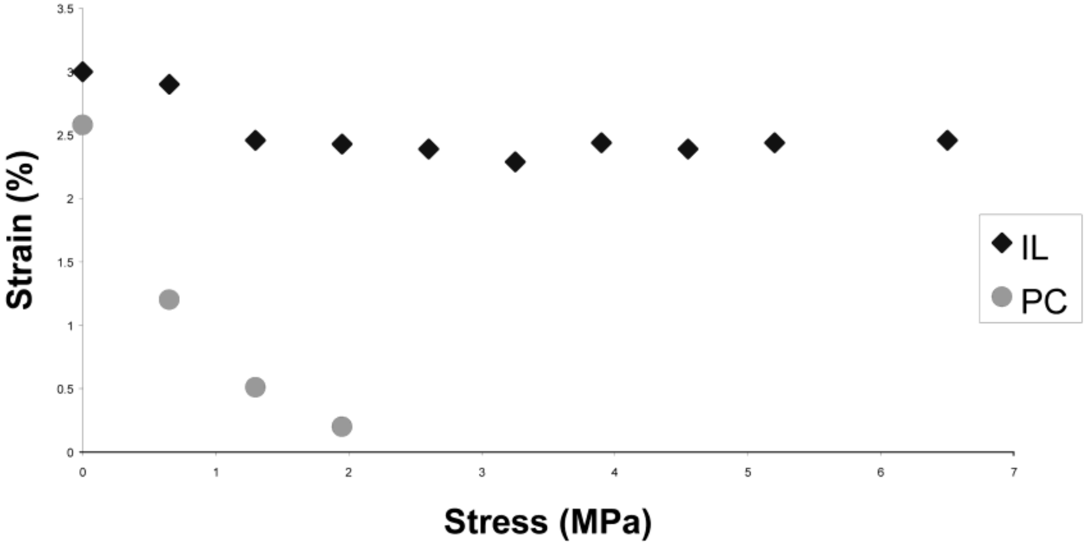


Figure 7. Strain observed under load for PPy–PF_6 in EMI·TFSA (**IL2**) compared to the propylene carbonate electrolyte (containing 0.25 M TBA·PF_6) using a triangular waveform (±2.5 V) applied at a scan rate of 50 mV/s.

potentials) and out of (negative potentials) the polymer. Even using the larger BMI molecule it is cation movement that predominates and the amount of strain (>3%) was increased compared with that observed (2.5%) using the EMI cation. For EMI·TFSA this experiment was repeated under load with the strain decreasing from 3.0% (no load) to 2.5% (6.5 MPa stress applied) (Figure 7). A much higher decrease in strain was observed when a propylene carbonate-based electrolyte was used from 2.5% (no load) to 0.5% at 2.5 MPa.

Further evidence that the cation motion dominates the actuation mechanism can be observed from the contrast in the maximum strain obtained form the two ILs under conditions of rapid testing (such as cycling shown in Figure 5) as compared with a slower potential scan (Figure 6). In the latter experiment, the BMI·PF_6 ionic liquid shows significantly larger strains at negative potentials as compared with EMI·TFSA and a greater positive potential is required to complete the charge/discharge cycle with the BMI-containing system. Given the relative size of BMI and EMI, the latter is considerably smaller and may be incorporated more rapidly into the polypyrrole, whereas the BMI ultimately shows a larger response (due to its larger size) but achieves this response more slowly. NMR diffusion experiments aimed at determining the diffusion coefficients of the cations and also anions in the ICP are currently underway to investigate this hypothesis. In Figure 5 we observe that the EMI·TFSA IL maintains a higher strain than the other electrolyte systems.

A final, unique feature of actuation in ionic liquids compared to other electrolytes is the absence of osmotic effects. Recently, there have been reports that osmotic processes contribute considerably to the actuation in PPy.[37] In ionic liquids there is no solvent present, so osmosis does not occur. Interestingly, the strain amplitude, under equivalent conditions, is slightly higher for ionic liquid electrolytes (where osmosis is absent) compared with that of TBA·PF_6 in PC (where osmosis is expected).

Conclusions

Ionic liquids provide an interesting alternative electrolyte for electromechanical actuators. The wide electrochemical potential window provides an added degree of stability, enabling many thousands of actuator cycles. In addition, an unexpected result has been obtained in terms of actuator mechanism where cation inclusion/expulsion predominates in determining the mode of actuation. The actuator performance in terms of strain under load and cycle lifetime was significantly improved in the IL electrolytes compared with that of a conventional organic electrolyte.

The use of the EMI·TFSA ionic liquid is preferred due to the enhanced environmental stability of this ionic liquid compared to that of the PF_6^--containing material. The use of EMI·TFSA also results in improved electromechanical performance.

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