Stability of polypyrrole soft actuators in ionic liquids

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Abstract. Characteristics of electrochemomechanical deformation (ECMD) of polypyrrole films using ionic liquids are reported. The PPy film prepared by electrodeposition in an ionic liquid (1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, BMPTFSI) was compact and high density. The other film prepared from LiTSFI/methyl benzoate and dimethyl phthalate mixed solvents was porous and low density. Both films demonstrated a stable ECMD in the ionic liquid. The strain of ECMD was 3-5% and superimposed on a creeping, showing a typical behaviour of cation movement. The Strains of ECMD in both films operated in a mixed electrolyte of BMPTFSI and propylene carbonate were enhanced up to 17-25%, showing anion movement. However, the large strain decreased upon several electrochemical cycles. The results were discussed in terms of swelling of the PPy film by solvents and loss of electrochemical activity.

1. Introduction
Electrochemomechanical deformation (ECMD) of conducting polymers[1] are interested in application to artificial muscles or soft actuators for robots, since the strain and the stress have been achieved more than 30% and 22MPa[2,3], respectively. These figures are comparable or even better than those of typical skeletal muscles. The ECMD is mainly generated by insertion of counter ions into polymer matrix as well as by the conformation change of polymer backbone due to the delocalization of π-electron upon oxidation. However, the short cycle life, which results mostly from the degradation of π-electron system[4], has been the issue to be solved for the practical use.

Recently, ionic liquids (ILs), which show non flammability, non volatility, high ionic conductivity and wide potential window, are interested and employed as electrolytes for electrochemical reactions [5-8]. Few studies on ECMD of conducting polymers prepared from ionic liquids are found in literatures. Characteristics of ECMD or actuation of conducting polymers[7-14], polypyrrole (PPy)[8] polyaniline[9] and poly(3-methythiophene)[10] in ionic liquids have been reported. These materials were prepared electrochemically using conventional electrolyte solutions[11-13,14] and chemical polymerization[9]. The ionic liquids employed commonly were 1-ethyl-3-methylimidazolium (EMI+) and 1-buthyl-3-methylimidazolium (BMI+) as cations. As anions trifluoromethansulfonic (CF3SO3−), bis(trifluoromethylsulfonyl)imide (TFSI−) and PF6− were used. The chemical structures of ionic liquids and materials used in this study are depicted in Fig.1.

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The ECMD of these polymers in ionic liquids demonstrated excellent cycle stability even more than million times[9,11-13], compared with those cycled in conventional electrolyte[2-4]. However, the overall performances of ECMD in ionic liquids were not satisfactorily regarding with the strain, which was less than ca. 3% along the film length[12]. Possibly, this is a reason why the ECMD using ionic liquid has not been studied intensively, so far. Recently, 11% strain of thickness direction (estimated by ellipsometry) in PPy films cycled in EMITSFI was reported[14]. The result indicated the anisotropic deformation of the PPy film during the electrochemical cycles.

PPy films prepared from LiTFSI/methyl benzoate (MB) was low density and high porosity in the surface morphology[3], demonstrating the world record of largest strain, viz. 39%. The study motivated us to see the enhanced strain and increased stability of ECMD by using porous PPy films and ILs. In this paper, characteristics of ECMD in PPy films electrodeposited from ILs of BMPTFSI and LiTFSI/MB operated in the IL is reported, comparing with the results operated in the mixture of IL and propylene carbonate (PC).

2. Experimental

Pyrrole, LiTFSI, MB, dimethyl phthalate (DP) and PC were purchased from Wako Pure Chemical Industries Ltd., and used without further purification. IL of BMPTFSI was obtained from Fuluka Co., Ltd. PPy films were prepared by two methods of electro polymerizations of pyrrole from #1: pure BMPTFSI and #2: mixed electrolyte solution of 0.2 M LiTFSI/MB&DP (=1/5). The concentrations of pyrrole in solutions were 0.1M for #1 and 0.25 M for #2, and these polymerizations were carried out at constant current of 0.2 mA/cm² for 6 h at 0°C.

The test piece of films was 15 x 2 mm and set in a electrochemical cell for the measurement of ECMD same to that in our previous papers[2-4]. The electrolytes for ECMD measurement were the pure BMPTFSI and the mixture of BMPTFSI and PC by the ratio of 1:1. A Ag/AgCl wire was used as a pseudo-reference electrode[2-4,8]. Measurements of cyclic voltammetry (CV) and strain of ECMD were carried out at the ambient condition. The strain was defined by $\Delta l/l_0$, where $\Delta l = l - l_0$, $l$ and $l_0$ were the film lengths at the time measured and the original, respectively.

3. Results and discussion

Table 1 shows characteristics of the obtained films containing TFSI as the dopant for their densities, conductivities ($\sigma$) and film morphologies by scanning electron micrograph (SEM). As seen in SEM the morphologies of films were apparently different between #1 and #2. Namely, the #1 film was dense and compact compared with #2 film being porous and rough surface, which were consistent
with their densities and conductivities. The thickness of films was ca. 20 and 40 µm for #1 and #2 films, respectively.

Figure 2(a) depicts the CV and strain of ECMD in compact #1 film in the IL of BMPTFSI at the potential between -1.5V and +1.3V and the scan rate of 2mV/s. The film showed the cyclic strain, $\Delta l/l_0$ of 3-5 %, responding to oxidation and reduction. The cyclic strain was superimposed on a creep up to 10 %. The expansion of the film by reduction indicates the cation movement and insertion into the film[15]. The similar results of cation movement have been also reported by other groups[9-12,14], indicating immobilized TFSI in the film. The current peak of oxidation shifted to higher potentials without dropping the magnitude, and the reduction peak was almost unchanged. On the other hand, in the mixed solution of BMPTFSI/PC as shown in Fig.2 (b), the cyclic strain increased by oxidation, indicating the anion movement and insertion. It is noted that the cyclic strain was more than 17% at the beginning, however, faded out into the creep of 7% in a few cycles. The oxidation peak in the CV shifted to higher potentials and decreased in the magnitude. The reduction current also decreased similarly. The results indicate that the film apparently degraded in the activity upon electrochemical cycling.

Table 1. Scanning electron micrographs of PPyTFSI films obtained from #1IL and #2 mixed solution of MB&DP

| PPyTFSI Film | Surface (Scale 10 µm) | Cross section (Scale: 20 mm) |
|--------------|-----------------------|-----------------------------|
| #1 IL        | Liquid side           | Electrode side              |
|              | Density (g/cm³)       |                             |
|              | 1.67                  |                             |
|              | $\sigma$ (G/ cm)      |                             |
|              | 99                    |                             |
| #2 MB&DP     | Liquid side           | Electrode side              |
|              | Density (g/cm³)       |                             |
|              | 0.89                  |                             |
|              | $\sigma$ (G/ cm)      |                             |
|              | 57                    |                             |

**Figure 2.** CVs and ECMD strains in #1 PPyTFSI/IL film operated in (a) Ionic liquid of BMPTFSI and (b) mixed BMPTFSI/PC (=1/1) electrolytes. Broken lines are the first cycle.
Figure 3 (a) shows the CV and ECMD of porous #2 film operated in the pure ionic liquid, indicating similar behaviour to #1 film except for the magnitude of cyclic strain and the small shift of oxidation current peak. The cyclic strain was about 5% and was kept almost constant upon many cycles. On the other hand as depicted in Fig.3 (b) in the mixed electrolyte of BMPTFSI/PC, it is noted that the magnitude of cyclic strain was enhanced to be more than 25%. However, by cycling the strain gradually faded out to the creep of 16% similarly to that of Fig.2 (b).

Figure 4 (a) and (b) summarize cyclic stabilities of ECMD, Δl of #1 and #2 films as the function of charge for the pure IL and the mixed electrolyte for comparison. The charge is estimated from the total consumed electric charges during cycling, and the negative direction corresponds to reduction. The shift to negative direction in the charge indicates over reduction due to the unbalanced electrochemical cycles. In other words, the smaller shift implies the better cycle stability. Upward shift until levelling off is due to a creep, in this case, swelling of films by sorption of ionic liquid and solvents as discussed in our previous paper [15]. The shift was larger in porous #2 film than that of compact #1 film.

**Figure 3.** CVs and ECMD strains in #2 PPyTFSI/MB&DP film operated in (a) ionic liquid of BMPTFSI and (b) mixed BMPTFSI/PC (=1/1) electrolytes. Broken lines are the first cycle.

**Figure 4.** Deformation, Δl of PPy/TFSI film operated in (a) ionic liquid of BMPTFSI and (b) BMPTFSI/PC mixed solution for #1 (lower curves) and #2 (upper curves) films.
Figure 5 shows the stability of cyclic strain as the function of electrochemical cycle. It is apparent that the cyclic strains in #1 and #2 films behaved similar manner in the same electrolyte solutions. Again the porous film exhibited larger strain compared with that obtained from the IL by 1.5-2 times at the beginning of cycling, then, the strains resulted in the similar magnitude. The cyclic strains of both films in the mixed solvent of IL/PC were larger than those in IL. It is conjectured that by use of the mixed solution the PC swollen the films and accommodated with TFSI, resulting in TFSI anion insertion and the large strain. The shrinking of cyclic strain was resulted from the degradation of films, being due to lose of the conductivity [4]. This was confirmed by the fact that the conductivity of #2 film after the ECMS measurement was 1.7 S/cm. The degradation of films in the mixed solution may be initiated by the over oxidation of π-conjugation with the existence of PC, as supposed from the variation of CV curves in Fig.2 and Fig.3. The detail mechanisms for the degradation in the mixed solution may be complicated and not be discussed at the present stage. We are expecting, however, that the performance of ECMD in pure ILs could be improved by controlling the film morphology and tuning the operation potentials appropriately, as well as choosing suitable ILs.

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