Enhanced electrochemical strain in polypyrrole films

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Abstract

Electrochemomechanical characteristics of polypyrrole (PPy) films, electrodeposited from tetra-*n*-butylammonium trifluoromethane-sulfonate dissolved in methyl benzoate (PPyFMS), have been investigated using a simultaneous measurement of electrochemomechanical deformation (ECMD) with cyclic voltammetry (CV) by comparing with PPy films deposited from *p*-phenol sulfonate in aqueous media (PPyPPS). The ECMD magnitude of PPyFMS film was reached around 9% at 1st cycle and was decreased to be about 3.2% at 20th cycle with electrochemical cycling in 1 M $NaPF_6$. While in 1 M NaCl solution, the ECMD magnitude was 1.9% at 20th cycle in CV measurement. In the case for the PPyPPS film, ECMD magnitude at 20th cycle was around 0.8% and 1.1% in 1 M $NaPF_6$ and 1 M NaCl solutions, respectively. The results indicate that the combination of electrolytes employed in both the electrodeposition and the device actuation plays the very important role for achieving the enhancement of ECMD magnitudes. In the case of ECMD behaviors, it was found that the electrolyte used in the film actuation determines the ECMD characteristics.
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1. Introduction

Functional polymers, exhibiting film deformation, are candidate material applicable to the soft actuator fabrication in the feature of intrinsic flexibility. From this viewpoint, variety kinds of soft actuators have been investigated by many researchers [1–4]. In the area of the soft actuator development, conducting polymer (CP) has the advantage in terms of the intrinsic volume change, resulting in the generation of extra-large force [5]. For the advantage of electrochemical activity in neutral electrolyte [6], polypyrrole has been mostly investigated as the candidate material for actuator fabri-

cation [7–10]. CP films deform during the electrochemical process; therefore, this phenomenon can be expressed as the electrochemomechanical deformation (ECMD). One of the important issues of ECMD behavior in CP is the small deformation [11]. For focusing this point, several investigations have been carried out by several researchers [12].

Recently, Hara and co-workers have reported that the film deposited from the electrolyte with methyl benzoate exhibits extra-large magnitude in ECMD [13]. This article reports the ECMD and CV characteristics in PPy film electrodeposited in tetra-*n*-butylammonium trifluoromethanesulfonate (PPyFMS) [13] in comparison with that in PPy film deposited in *p*-phenol sulfonate (PPyPPS) [14]. ECMD magnitudes are also discussed in terms of the dependence of supporting electrolyte and surface morphology.

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2. Experimental

Electrodepositions of freestanding PPy films were carried out galvanostatically with a current density of 0.2mA/cm^2 for 4 h at room temperature. Two types of electrolytes were used for deposition, namely, 0.2 M tetra-*n*-butylammonium trifluoromethanesulfonate with 0.25 M pyrrole dissolved in methyl benzoate (PPyFMS) and 0.25 M *p*-phenol sulfonic acid with 0.15 M pyrrole (PPyPPS) in distilled water. Detail of deposition and physical parameters are listed in Table 1.

In-situ measurement system of ECMD behavior with cyclic voltammetry (CV) was employed for measurement with a custom-made electrochemical cell as reported in the previous papers [15,16]. ECMD measurements with CV cycling were performed in electrolyte solutions having 1 M concentration of electrolyte. In this study, NaCl and NaPF$_6$ were employed for supporting electrolyte in CV measurement. Ag wire, on which AgCl was anodically electrodeposited in HCl [16], and Pt foil were used for reference and counter electrodes, respectively. Laser displacement meter (Keyence LB-040/LB-1000) was used for detecting the change in length of the film. Electrochemical potential was applied by a potentio/galvanostat (Hokuto Denko HA-501) with a function generator (Hokuto Denko HB-105). A 2mV/s of scan speed was employed for all CV measurements.

Surface morphology was examined with Scanning Electron Microscope (SEM: Shimadzu SS-550). Energy dispersive analysis of X-rays (EDX: EDAX Inc. Genesis2000) was also performed for elemental analysis during SEM observation.

3. Results and discussion

3.1. ECMD responces of PPy films

As already reported the detail of ECMD characteristics in PPyPPS film [6,14], the PPyPPS film tends to exhibit the co-expansive behavior at both the anodic and cathodic potentials. Thereofore, the ECMD response clearly exhibited double peaks during redox cycling as

shown in Fig. 1(a). The similar co-expansive behavior was also observed in PPyFMS film with NaCl solutions (Fig. 1(b)). The relative intensity of each expansive peak can be estimated as the ratio (r) of anodic expansion (D_{anodic}) to the sum of D_{anodic} and cathodic one ($D_{cathodic}$) by the following equation:

$$r = \frac{D_{anodic}}{D_{anodic} + D_{cathodic}} \times 100(\%).$$

Relative large r in PPyFMS as compared to that in PPyPPS listed in Table 2 indicates the PPyFMS film having the effective anodic expansion.

In the case of PPyFMS film, however, the base length of the film was drastically decreased in the 1st cycle, while it was almost stationary in the followed CV cycling. The ECMD response of PPy film tends to involve creeping behaviors [14]. The base length of the film, which is defined to 0% in deformation magnitude as shown in Fig. 1, was monotonically decreased with cycling in PPyPPS film. This can be explained as the elution of initial dopant anion (PPS$^-$) from the net polymer as discussed in the literature [14]. This implies that in the case of PPyFMS film, the initial dopant anion (CF$_3$SO$_3{}^-$) would be ejected swiftly at cathodic potential application in the first cycle, resulting in the rapid decrease of base length to be about 5%. The ejection of large amount of initial dopant well converts the PPy as anion exchanger. This speculation is also supported by relative large anodic expansion observed in PPyFMS.

In 1 M NaPF$_6$, both the films exhibited simple anodic expansion as shown in Fig. 2. It is interesting to note that the base length was clearly decreased with potential cycling in PPyPPS film, while in the case of PPyFMS film, no clear creeping in film length was observed. This implies that in the case of PPyPPS film, the initial dopant has the dipole moment, which prevents the dopant from eluting during the redox process. Meanwhile, in the case of PPyFMS film, the initial dopant has the uniform distribution of electron, resulting in the swift removal of the dopant in the oxidation process. The creeping behaviors, therefore, might not be appeared in the following potential cycling.

Table 1
Deposition condition and physical parameters of PPy films

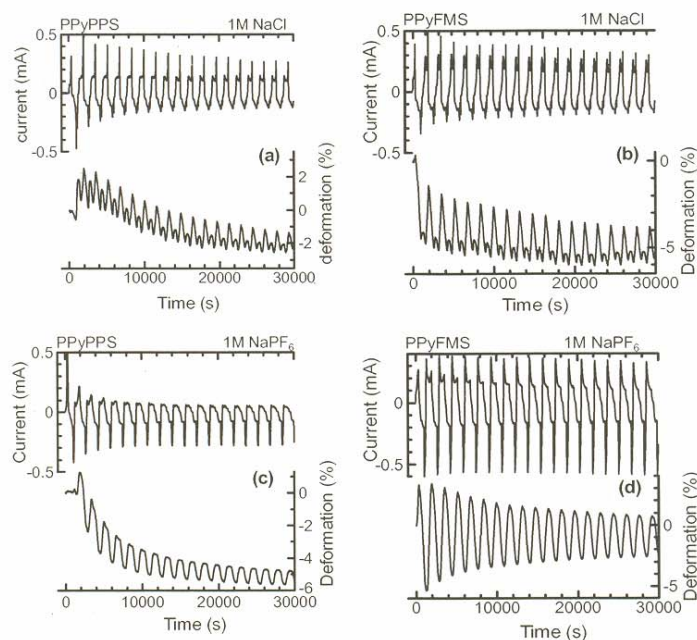| Abbreviation	PPyPPS	PPyFMS
Electrolyte	*p*-phenol sulfonic acid	Tetra-*n*-butylammonium trifluoromethanesulfonate
Concentration	0.25 M	0.2 M
Solvent	Distilled water	Methyl Benzoate
Current density (mA cm^{-2})	0.2	0.2
Deposition time (h)	4	4
Thickness (μm)	17	18
Film conductivity (S/cm)	70	56

Fig. 1. ECMD responces of (a) PPyPPS film in 1 M NaCl, (b) PPyFMS film in 1 M NaCl, (c) PPyPPS film in 1 M $NaPF_6$ and (d) PPyPPS film in 1 M $NaPF_6$, respectively.

Table 2
Summary of ECMD parameters in all the films tested

Film/electrolyte	Cyc	Q_{redox} (mC)	ECMD (%)	r (%)	η (%/mC)
PPyPPS/NaCl	3	95	1.8	60	0.052
	10	83	1.7	70	0.052
	20	70	1.1	70	0.046
PPyPPS/NaPF$_6$	3	76/94[a]	3.3	100	0.050
	10	38/79[a]	1.2	100	0.042
	20	29/74[a]	0.8	100	0.041
PPyFMS/NaCl	3	108	3.4	82	0.047
	10	108	2.7	80	0.042
	20	105	1.9	76	0.034
PPyFMS/NaPF$_6$	3	162	7.6	100	0.089
	10	138	4.5	100	0.061
	20	121	3.2	100	0.052

[a] Including over-oxidation charge.

3.2. ECMD and CV curves

The first potential cycle tends to exhibit specific ECMD and CV characteristics. The typical ECMD behaviors, therefore, can be found in the 2nd and the following redox cycles. As shown in Fig. 2(a), the cathodic expansions in PPyPPS film exhibited the similar ECMD magnitudes in 1 M NaCl. In the case of PPyFMS film, it was shown that the anodic expansion was dominant and the cathodic one was small in 1 M NaCl. Therefore, the main and sub peaks discussed in Fig. 1 can be assigned to the anodic and cathodic expansions, respecively. The small cathodic expansion retains in the 20th of potential cycle in both films. The persistent cathodic expansion, therefore, characterizes the co-expansive behaviors in NaCl solutions.

In the case of the solution using $NaPF_6$ as supporting electrolyte, the simple anodic expansions were only observed in both PPyPPS and PPyFMS films. In the 1st cycle, no ECMD behavior appeared except in PPyFMS during the oxidation process. When it tuned to the reduction process, the films started to exhibit the
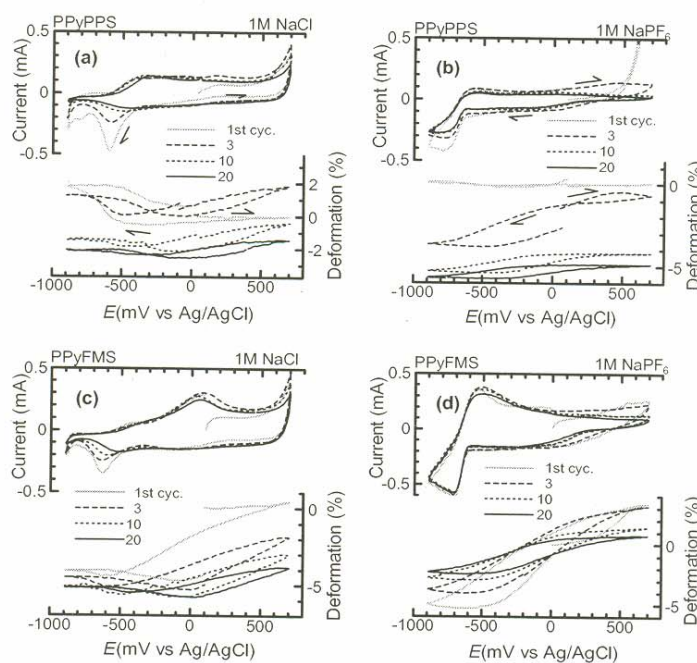
Fig. 2. ECMD and CV curves of (a) PPyPPS in 1 M NaCl, (b) PPyPPS in 1 M NaPF₆, (c) PPyPPS in 1 M NaCl and (d) PPyFMS in 1 M NaPF6.

contractive behavior. It should be noted that the rest-potentials in all the films are located at around −100 to +100 mV vs Ag/AgCl. This indicates that the as deposited PPy films are commonly in the highly doped state. However, PPyFMS film exhibited the remarkable anodic expansive behavior even in the initial oxidation process (Fig. 2(d)). This might cause the extra-large deformation in PPyFMS film.

3.3. Deformation-redox charge curves

For PPyPPS film in NaCl solution, the clear co-expansion at both anodic and cathodic potentials was observed as shown in Fig. 3(a). Cathodic expansion at 3rd CV cycle (1.2%) is quite large as compared to the other one and is comparable magnitude to that of anodic expansion (1.8%) as compared to that in the other films, while it was decreased strongly to be 0.46% at 20th cycle. Anodic expansion also decreases its magnitude with cycling. Redox charge (Q_{red}) also decreased at the same time. Therefore, the slope of deformation per Q_{red} in the linear correlation, which determines the efficiency of deformation (η) [16], tends to be in constant (Table 2).

In 1 M NaPF₆, ECMD characteristics of PPyPPS film exhibited a simple anodic expansion as shown in Fig. 3(b). ECMD magnitude was also enhanced about 3%. As reported in the previous paper, anodic expansion is characterized with the anion of electrolyte in both PPy and polyaniline films [6,11,17]. Therefore, this enhance-

ment also can be attributed to the anion size effect. The enhanced magnitude, however, decreased to 1.2% at 10th cycle and 0.8% at 20th cycle, which is smaller than that in 1 M NaCl. It should be noted that the redox charge in oxidation process was also smaller as compared to that in the reduction process. In this case, Q_{redox} tends to show the over-oxidation phenomena. As can be seen in Fig. 3(b), Q_{redox} in the strongly reduced region did not contribute for the ECMD behavior. Decrease of substantial amount of Q_{redox} for ECMD behavior will depress the ECMD magnitude. It is interesting to note that the film clearly contracted at highly oxidzed region at 3rd cycle in Fig. 3(b). At both the 10th and 20th cycles, the film also tends to show the saturation of expansion at higly oxidized region. This behavior seems to change drastically from 3rd to 10th or 20th cycle. Therefore, the highly oxidized state of PPyPPS in NaPF₆ will change in the deforming characteristics, inducing the irreversible deformation to the decrease of ECMD magnitude.

In the case of the PPyFMS film, co-expansive behavior was observed in 1 M NaCl similar to that in PPyPPS film. By comparison to the mono-expansive behavior of PPyPPS in NaPF₆, the fundamental ECMD characteristics should be determined by the supporting electrolyte. The ECMD magnitude of anodic expansion in PPyFMS films tends to be larger than that in PPyPPS film. Q_{redox} in PPyFMS is also larger as compared to that in PPy-PPS. It has been already reported that the deformation magnitude can be associated to the amount of
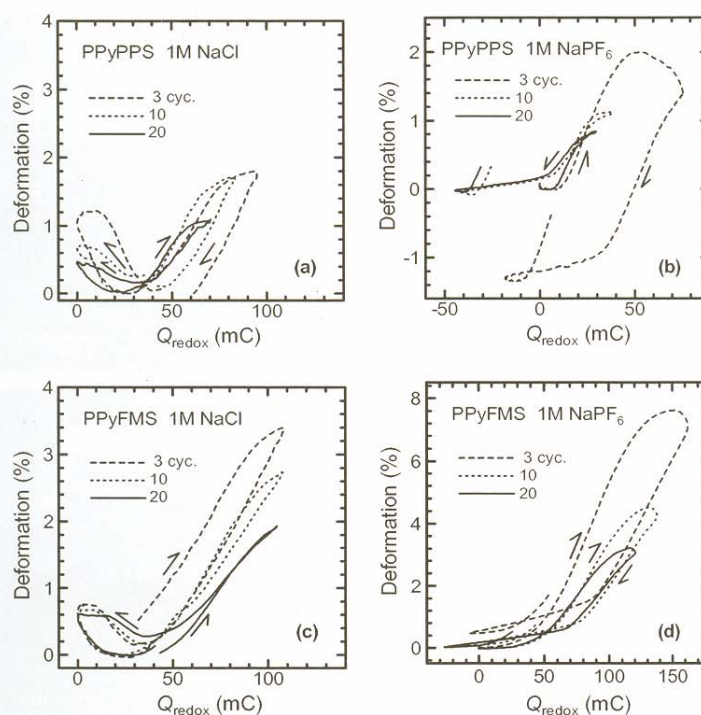
Fig. 3. Deformation-charge curves of (a) PPyPPS in 1 M NaCl, (b) PPyPPS in 1 M NaPF$_6$, (c) PPyPPS in 1 M NaCl and (d) PPyFMS in 1 M NaPF6.

injected/ejected charge [15]. This is also supported by the relative linear correlation between the film deformation and Q_{redox} as shown in Fig. 3. Therefore, the enhanced deformation in PPyFMS film can be explained by the increase of Q_{redox} namely, the large redox activity in PPy system will induce the effective enhancement of ECMD magnitude. In the case of expansive ratio at anodic potentials, it was larger in PPyFMS than that in PPyPPS at all CV cycle (Table 2). It should be noted that η at 3rd cycle in PPyFMS is in the similar value of that in PPyPPS. This indicates that both the PPyPPS and PPyFMS films have the similar expansion ratio in ECMD per Q_{redox}. Therefore, the enhanced fraction in Q_{redox} will directly contribute to the increase of anodic expansion. It is interesting to note that in PPyFMS film, Q_{redox} was remarkably in constant at all CV cycles, indicating the reversible redox reactions. Meanwile the ECMD magnitude was monotonically decreased. This implies that the ECMD magnitude will be depressed by irreversible factors different from redox activities, such as mechanical deterioration.

The ECMD behavior of PPyFMS in 1 M NaPF$_6$ exhibited a simple anodic expansion as shown in Fig. 3(d). This ECMD characteristic is well associated with that of PPyPPS film in 1 M NaPF$_6$ as described above, namely, the ECMD behaviors are well characterized by the supporting electrolyte similar to those in 1 M NaCl

as described above. The anodic expansion was reached to be around 7.6% at 3rd cycle, which is quite large as compared to those in the other system (Table 2). The fact that Q_{redox} in this system were quite larger than the other system indicates that the large amount of injected/ejected ions strongly contributed to the enhancement of ECMD magnitude. The enlargement of redox activity, therefore, is one of the important terms for achieving the large deformation.

The ECMD magnitude of PPyFMS film in 1 M NaPF$_6$ decreased with cycling. In this case, both Q_{redox} and η were also decreased at the same time. Concerning the results of the ECMD characteristics for both the PPyPPS and PPyFMS films in 1 M NaPF$_6$, the decreases in Q_{redox} ECMD and η as a function of CV cycle might be assigned to the decrease of redox activities by the over-oxidation of PPy in NaPF$_6$ solution and/or some essential decrease of film deformation with potentially increased cathodic expansion.

3.4. EDX analysis

EDX analysis is the easy method to detect the atoms inserted and/or ejected to the films during redox process [18]. Fig. 4 show the detected element on film surface by means of EDX analysis. As deposited PPyFMS film exhibited F and S atoms, which can be associated to
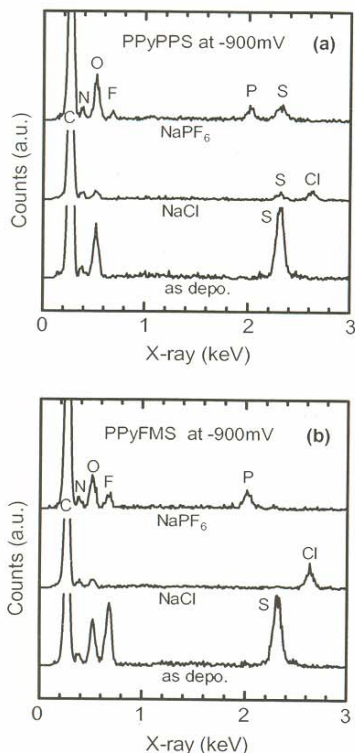
Fig. 4. EDX profiles of (a) PPyFMS film actuated in 1 M NaCl, (b) PPyFMS film in 1 M NaPF6 and (c) PPyPPS film in 1 M NaCl and NaPF6 after 20 CV cycles. Described voltages are the potentials at terminated CV measurement.

Fig. 5. SEM micrographs of the surface of as deposited (a) PPyPPS and (b) PPyFMS films.

the initial dopant ($CF_3SO_3^-$), while both peaks are clearly disappeared in both NaCl and $NaPF_6$ solutions, indicating the rapid removal of $CF_3SO_3^-$ from the film. This can be correlated with the swift creeping observed in Fig. 1(b) as discussed in the previous section. The large electrochemical activities as listed in Table 2 also indicate the prompt motion of mobile ion in PPyFMS film during CV cycling.

It should be noted that the EDX profiles of PPyFMS films terminated at strong reduced potential of −900 mV vs. Ag/AgCl still did not exhibit sodium atom, In contrast, anion-related atom peaks persistently appeared to be in relative small in both NaCl and $NaPF_6$ solutions. This implies that cations penetrated in PPy will remove in ease with counter anion as salt form during wash in distilled water. While, some dopant anions will be encapsulated or bound to net PPy polymer, which might cause the decrease of Q_{redox} with CV cycling.

3.5. Surface morphologies

SEM micrographs elucidate that the PPyFMS film has the different surface morphology from that of PPy-
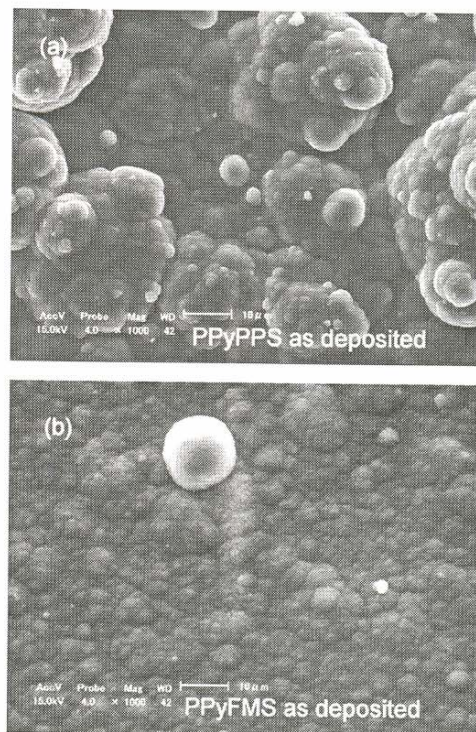
PPS. As shown in Fig. 5, PPyPPS possesses a coarse surface. Therefore, the SEM image predicts the enlargement of electrochemical activity in PPyPPS as compared to that in PPyFMS. This picture, however, conflicts with the result of Fig. 3. As discussed in Section 3.3, the enhancement of ECMD magnitude in PPyFMS can be supported as the increase of redox activity as well. Therefore, the roughness of PPyPPS film in SEM images of Fig. 5 will not depict directly the enhancement of redox activity. In contrast, the relative flat surface of PPyFMS is preferred to be anomalous. A subtle perusal corroborates that the elemental circular structure consisted of surface seems to be smaller on PPyFMS as compared to that on PPyPPS. Substantial porosity contributed for ion exchange, therefore, might be large in PPyFMS, resulting in the increase of Q_{redox}. In the case of the ECMD magnitude, the flat surface might be effective for the film deformation because of the small loss in dimensional change.

4. Conclusions

Electrochemomechanical deforming (ECMD) characteristics in polypyrrole films were investigated in terms of the effect of supporting electrolyte employed in both

the processes of electrodeposition and cyclic voltammetry (CV). It was found that PPy film deposited with tetra-*n*-buylammonium trifluoromethane sulfonate (PPyFMS) exhibited the large ECMD magnitudes as compared to those in PPy film deposited with *p*-phenol sulfonate (PPyPPS) in both NaCl and NaPF$_6$ solutions. Comparison of redox charge (Q_{redox}) collected from CV curve in each film revealed that PPyFMS film has the large amount of Q_{redox} than that in PPyPPS, indicating that the increase of Q_{redox} effectively enhances the ECMD magnitude. Comparison of deformation-redox charge curves in each film elucidates that the ECMD characterisitics are strongly depended upon the employed electrolyte, while the similar ECMD characteristics are obtained in the PPy films deposited from different electrolytes. The results indicate that the supporting electrolyte used in the deposition process is essentially determined in the ECMD characteristics in PPy film. The combination of electrolytes in the electrodeposition and the redox reaction processes plays the important role for optimizing the enhancement of ECMD behavior. EDX analysis elucidated the swift exchange of anion in PPyFMS during the redox process, which supports for anodic expansion in ECMD behaviors. The flatness in surface morphology implies the effective expansion during deforming process in NaPF$_6$ solution, which will give the large efficiency (η) in PPyFMS film.

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