Supporting Information

5/18

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Mass change of a film during its electropolymerization. We presented that the PPhPy film grown in a PF_6^--containing solution (PPhPy/PF_6) shows larger charge capacity than the film grown in a ClO_4^--containing solution (PPhPy/ClO_4) and that the PPhPy film grown in a PC solution (PPhPy/PC) shows similar behavior with or larger charge capacity than the film grown in an AN solution (PPhPy/AN). We suggested that the difference is due to the different morphology of a film depending on the electropolymerization condition. However, the different polymerization efficiency may be responsible for the different charge capacity. It is possible that the amount of an electropolymerized PPhPy/PF_6 or a PPhPy/PC film is larger than that of a PPhPy/ClO_4 or a PPhPy/AN film, respectively. To check this possibility, we performed the EQCM experiments during the electropolymerization of PPhPy films.

Figure S1 shows mass change diagrams during the electropolymerization of PPhPy films. The masses are not linearly proportional to the charge over the whole electropolymerization process, indicating that the mechanism of the polymerization is not simple. When assuming 100 % polymerization efficiency, the theoretical mass of PPhPy film (M_{PPhPy}) is obtained as below,

$M_{PPhPy} = \Delta Q\,(W_{PhPy} + d\,W_{-}) / (2 + d)F$

Where ΔQ is the charge consumed during the electropolymerization that is fixed to 96 mC (300 mC/cm^2, electrode area = 0.32 cm^2) in this study, d is the doping level, W_{PhPy} is the molar mass of PhPy, W_{-} is the molar mass of dopant anion, and F is Faraday constant. When d is regarded as 0.2, M_{PPhPy} is 77.9 μg for a PPhPy/PF_6 film and 73.8 μg for a PPhPy/ClO_4 film.

As seen in Figure 1, however, the total mass change (ΔM) is much larger than M_{PPhPy} in all cases. Moreover, ΔM depends highly on the type of dopant anion and solvent used in the electropolymerization. These mean that the incorporation of electrolyte or solvent within PPhPy films occurs during the electropolymerization. On the contrary, the mass of a dry film (ΔM_{dry}), which was measured after drying an electropolymerized film in air, is smaller than M_{PPhPy} (Table S1). It is interesting to note that ΔM_{dry} does not change with the dopant anion and solvent significantly. Therefore, it seems that ΔM_{dry} rather than ΔM represents the real amount of an electropolymerized film.

The ratios of ΔM_{dry} to M_{PPhPy} are calculated as shown in Table S1. The ratios are around 0.8 and do not vary significantly with the type of dopant anion and solvent used in the electropolymerization. It means that the amount of an electropolymerized film is almost similar irrespective of the electropolymerization conditions. To compare the charge capacity of films, the total charge change during the cathodic scan (ΔQ_t) obtained from the cyclic EQCM experiment is shown in Table S1. The ΔQ_t ratio of a PPhPy/PF_6 film and a PPhPy/ClO_4 film is 1.42 (= 6.4/4.5) in PC and 1.27 (= 7.5/5.9) in AN. These values are much larger than the ΔM_{dry} ratio of a PPhPy/PF_6 film and PPhPy/ClO_4 film, which is 1.12 (= 64.5/57.5) in PC and 1.08 (= 64.1/59.2) in AN. The mass of a PPhPy/PF_6 film is slightly larger than that of a PPhPy/ClO_4 film because the molar mass of PF_6^- is larger than that of ClO_4^-. Although the exact *d* value can not be determined easily, *d* is known to be near 0.2 for a PPhPy film.[1] If *d* is assumed to range from 0.1 to 0.3, the M_{PPhPy} ratio of a PPhPy/PF_6 film and a PPhPy/ClO_4 film ranges from 1.05 to 1.08. They are very similar to the ΔM_{dry} ratio of a PPhPy/PF_6 film and a PPhPy/ClO_4 film in both solvents. In conclusion, the dependence of charge capacity on the electropolymerization condition seems to be due to the different morphology depending on the electropolymerization condition as pointed out in this paper, not to the different amount of an electropolymerized film.

References and Notes

(1) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W. *J. Electroanal. Chem.* **1981**, *129*, 115.

TABLE S1.

film[a]	M_{PPhPy}[b] (μg)	ΔM_{dry}[c] (μg)	$\Delta M_{dry}/M_{PPhPy}$	ΔQ_t[d] (mC)
PPhPy/PF_6/PC	77.9	64.5±1.3	0.83	6.4±0.2
PPhPy/ClO_4/PC	73.8	57.5±1.8	0.78	4.5±0.4
PPhPy/PF_6/AN	77.9	64.1±2.2	0.82	7.5±0.1
PPhPy/ClO_4/AN	73.8	59.2±0.9	0.80	5.9±0.1

a. The charge consumed during the electropolymerization was fixed to 96 mC.
b. The mass of a PPhPy film calculated according to Eq. S1, when regarding *d* as 0.2.
c. The mass of a dry PPhPy film.
d. The total charge change during the cathodic scan obtained from the cyclic EQCM experiment.

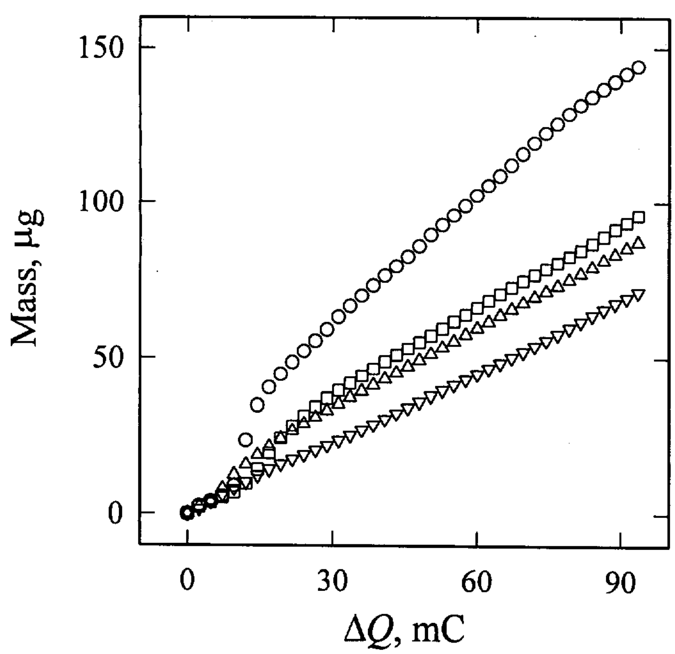

Figure S1. Mass change diagram during the electropolymerization of PPhPy/PF_6/PC (○), PPhPy/ClO_4/PC (□), PPhPy/PF_6/AN(△), and PPhPy/ClO_4/AN (▽) films.