

## Supporting Information

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**Capacitance Data Treatment.** It was shown that, when only one kind of ion takes part in ion transport, the  $(\Delta Q/\Delta E)$  data can be related to the  $(\Delta M/\Delta E)$  data without consideration of  $R_s$ .<sup>17a</sup> But, when two kinds of ion transport take place, the influence of  $R_s$  on the  $(\Delta Q/\Delta E)$  and  $(\Delta M/\Delta E)$  data must be corrected. Figure S1 shows flow diagram of capacitance data treatment procedure for obtaining the capacitance data of a cation and an anion. In the first step, the influence of  $R_s$  is corrected. The  $(\Delta Q^f/\Delta E^f)$  and  $(\Delta M^f/\Delta E^f)$  data are obtained from the  $(\Delta Q/\Delta E)$  and  $(\Delta M/\Delta E)$  data, respectively. And then, the  $(\Delta Q^f_{+}/\Delta E^f)$ ,  $(\Delta Q^f_{-}/\Delta E^f)$ ,  $(\Delta M^f_{+}/\Delta E^f)$ , and  $(\Delta M^f_{-}/\Delta E^f)$  data are calculated from the  $(\Delta Q^f/\Delta E^f)$  and  $(\Delta M^f/\Delta E^f)$  data.

**Ion Transport in PPy/PSS Films.** In Figure 6c, there is a small semicircle in the low frequency region. But, it is not certain whether cation transport is present in the slow charge transport process or not, because the  $(\Delta M^f/\Delta E^f)$  data in the low frequency region are noisy. Figure S2a shows  $(\Delta Q^f/\Delta E^f)$  plots and Figure S2b shows  $(\Delta M^f/\Delta E^f)$  plots at 0.1 V for PPy/PSS films in a 0.5 M Cs<sub>2</sub>SO<sub>4</sub> solution. At this potential, the  $(\Delta Q^f_{-}/\Delta E^f)$  plot consists of two semicircles. It indicates that anion transport occurs in the fast as well as slow charge transport process though it is small in the fast charge transport process. In the  $(\Delta Q^f_{+}/\Delta E^f)$  plot, the low frequency data is noisy. It is also uncertain whether cation transport is present in the slow charge transport process or not. Figure S3 shows  $(\Delta Q^f/\Delta E^f)$  and  $(\Delta M^f/\Delta E^f)$  plots for 0.2 μm thick PPy/PSS films. In case that the film thickness is small, the slow charge transport process is observed more easily in a frequency range between 2.7 Hz and 0.04 Hz. Thus, the presence of cation transport in the slow charge transport process can be elucidated more evidently. At -0.3 V in a 0.5 M Cs<sub>2</sub>SO<sub>4</sub> (Figure S3a,b), the  $(\Delta Q^f_{+}/\Delta E^f)$  and  $(\Delta Q^f_{-}/\Delta E^f)$  plots consist of one semicircle, respectively. It shows that cation transport is negligible in the slow charge transport process and that anion transport is negligible in the fast charge transport. When the  $(\Delta Q^f_{+}/\Delta E^f)$  and  $(\Delta Q^f_{-}/\Delta E^f)$  data at -0.3 V (Figure 6c,d) and the  $(\Delta Q^f_{+}/\Delta E^f)$  at 0.1 V (Figure S2c) in a Cs<sub>2</sub>SO<sub>4</sub> solution are fitted with only  $Z_{D+}$  or  $Z_{D-}$ , the data are not fitted well. Thus, the equivalent circuit of Figure 1c is used, so the some fitted values in Table 1 are meaningless. Consequently, it seems that the presence of  $Z_{D+2}$  and  $Z_{D-1}$  at -0.3 V and  $Z_{D+2}$  at 0.1 V in a Cs<sub>2</sub>SO<sub>4</sub> solution is due to the experimental error whereas the

presence of  $Z_{D-1}$  at 0.1 V is due to some anion transport in the fast charge transport process.

At  $-0.3$  V in a 1.0 M  $\text{CsNO}_3$  (Figure S3c,d), the  $(\Delta Q^+/\Delta E^f)$  plot consists of two semicircles, and the  $(\Delta Q^-/\Delta E^f)$  plot consist of one semicircle which is shifted along the real axis. If higher frequency data were obtained, there would be another semicircle in the  $(\Delta Q^-/\Delta E^f)$  plot. It is evident that, in a solution containing monovalent anion, both cation transport and anion transport occur in the fast and slow charge transport processes, resulting in complex ion transport behavior.

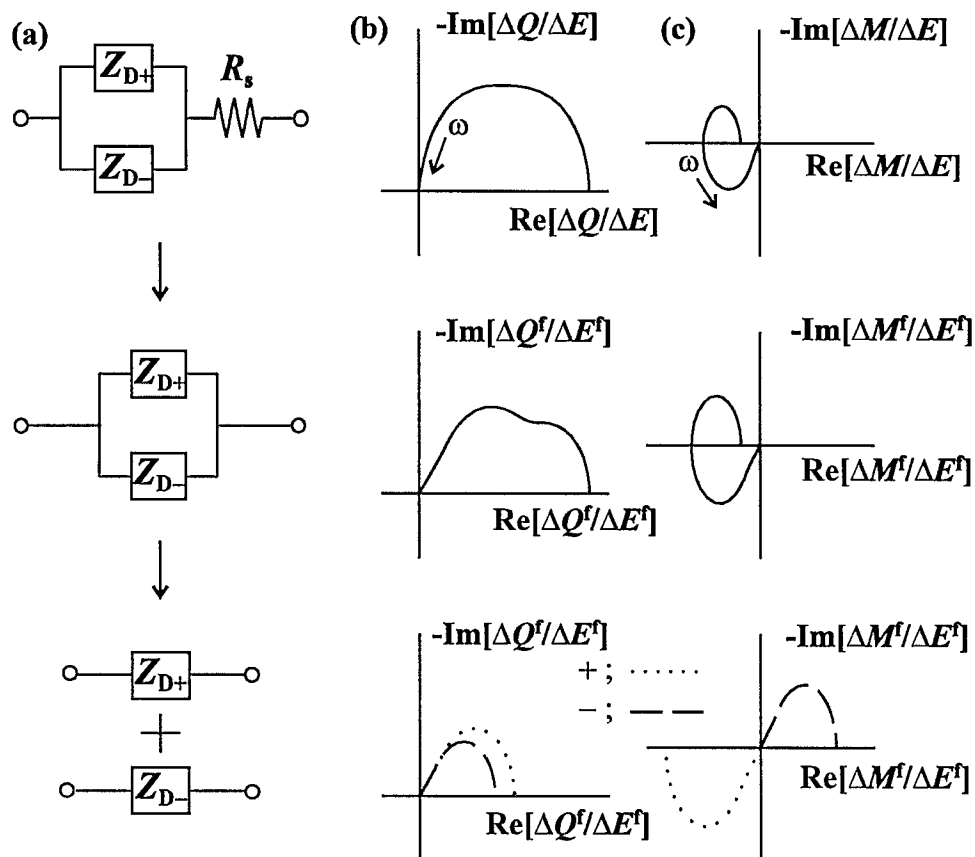
**Fast vs Slow Charge Transport Processes.** The charge transport of the PPy/PSS film consists of the fast and slow charge transport processes. It is shown that electron transport in the fast charge transport process is much faster than ion transport, whereas electron transport in the slow charge transport process is much slower than ion transport (Figure 8b). Thus, the apparent diffusion coefficient of an ion in the fast charge transport process is different from that in the slow one. And also, both anion and cation transport are possible in the fast and slow charge transport processes. Therefore, four kinds of ion transport are present in a  $\text{CsNO}_3$  solution. Even though one ion has only one diffusion coefficient, we can measure two apparent diffusion coefficient for the same ion (Table 1).

When the fast charge transport process is independent of the slow charge transport process, the charge transport impedance of PPy/PSS films can be represented by Figure S4a where the fast charge transport impedance ( $Z_1$ ) and the slow charge transport impedance ( $Z_2$ ) are connected parallel. When ion transport is much faster than electron transport or electron transport is much faster than ion transport, the charge transport impedance is represented by  $Z_D$  (Figure S4d).<sup>7d</sup> It is shown that the fast charge transport process is governed by ion transport and that the slow charge transport process is governed by electron transport. And also, ion transport in the fast charge transport process consists of two kinds of ion transport. Thus, the charge transport impedance of PPy/PSS films can be described by Figure S4b. In the slow charge transport process, there are two kinds of ion transport. It is possible to divide one  $Z_{D2}$  into  $Z_{D+2}$  and  $Z_{D-2}$  connected parallel, only if  $R_{D+2}C_{D+2}$  time and  $R_{D-2}C_{D-2}$  time are the same as  $R_{D2}C_{D2}$  time. Finally, the charge transport impedance of PPy/PSS films can be represented by Figure S4c, where  $C_{D2} = C_{D+2} + C_{D-2}$  and  $1/R_{D2} = 1/R_{D+2} + 1/R_{D-2}$ . Thus, the equivalent circuit of Figure 1c is used to fit the experimental data.

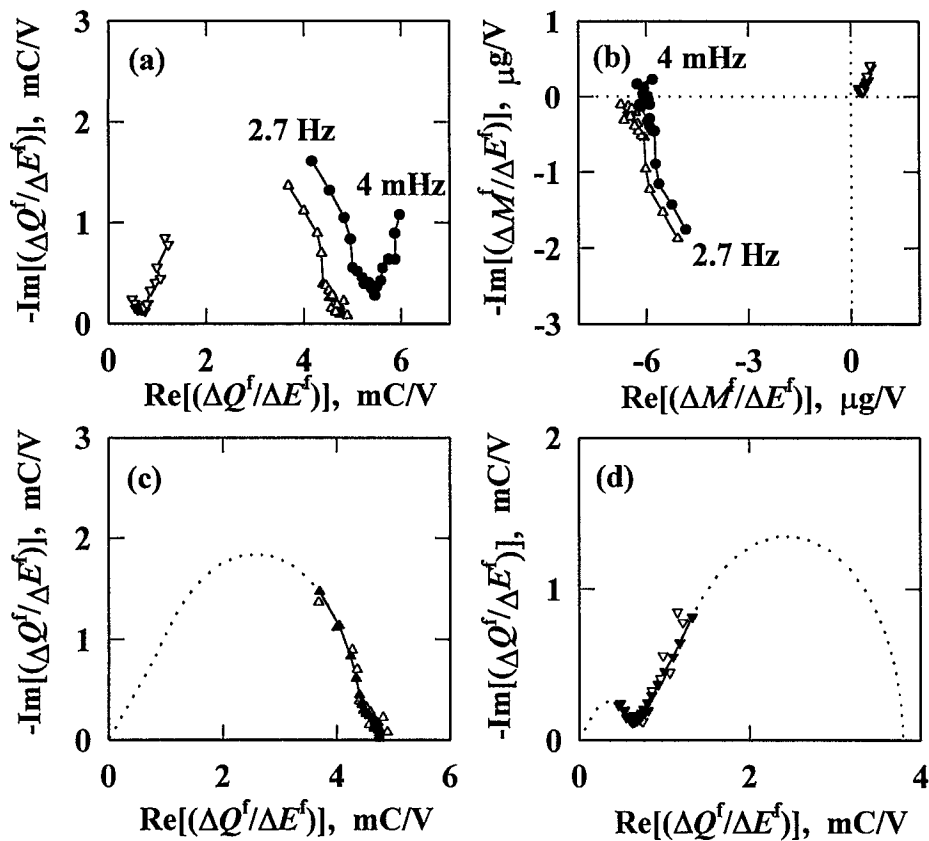
It is interesting to note that  $R_{D+2}C_{D+2}$  time (=510 s) in a  $\text{CsNO}_3$  solution is similar to  $R_{D-2}C_{D-2}$  time (=340 s) (Table 1). That is because the slow charge transport process is limited by electron transport and independent of ion transport.  $R_{D-2}C_{D-2}$  time (=410 s) in a  $\text{Cs}_2\text{SO}_4$  solution is similar to  $R_{D-2}C_{D-2}$  time (=340 s) in a  $\text{CsNO}_3$  solution irrespective of anion. It was shown that divalent anion or cation is much slower than monovalent one in the fast charge transport process that is limited by ion transport.<sup>14</sup> Thus, it is

evident that the slow charge transport process is limited by electron transport.

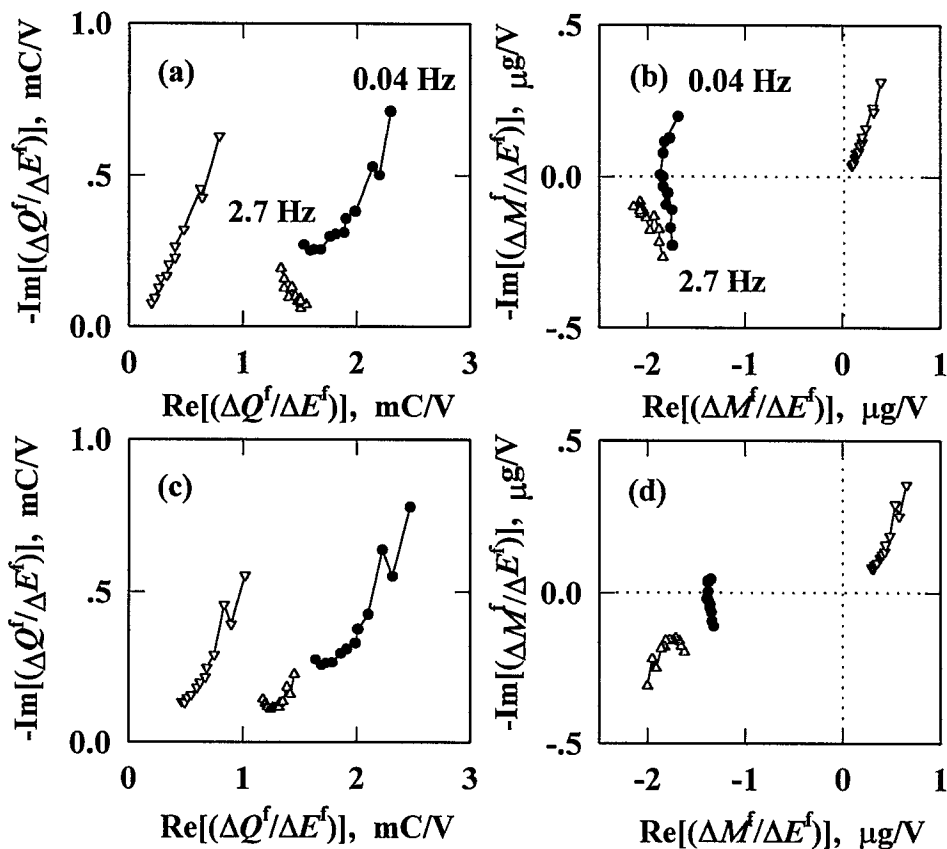
Actually,  $R_{D2}$  is related to the electronic resistance, not the ionic resistance in a film, while  $R_{D+1}$  and  $R_{D-1}$  are related to the ionic resistance of an ion. That is because the slow charge transport process is governed by electron transport. But, we do not differentiate  $R_{D+2}$  and  $R_{D-2}$  with  $R_{D+1}$  and  $R_{D-1}$ , because on a phenomenological point ion transport and electron transport occur simultaneously. The fast and slow charge transport processes are limited by ion and electron transport, respectively. Thus, we can obtain only the diffusion coefficient of an ion in the fast charge transport process and the diffusion coefficient of an electron in the slow charge transport process. But, all data have been processed in connection with ion transport. Thus, we used the term 'the apparent diffusion coefficient' in order not to be confused with the diffusion coefficient.



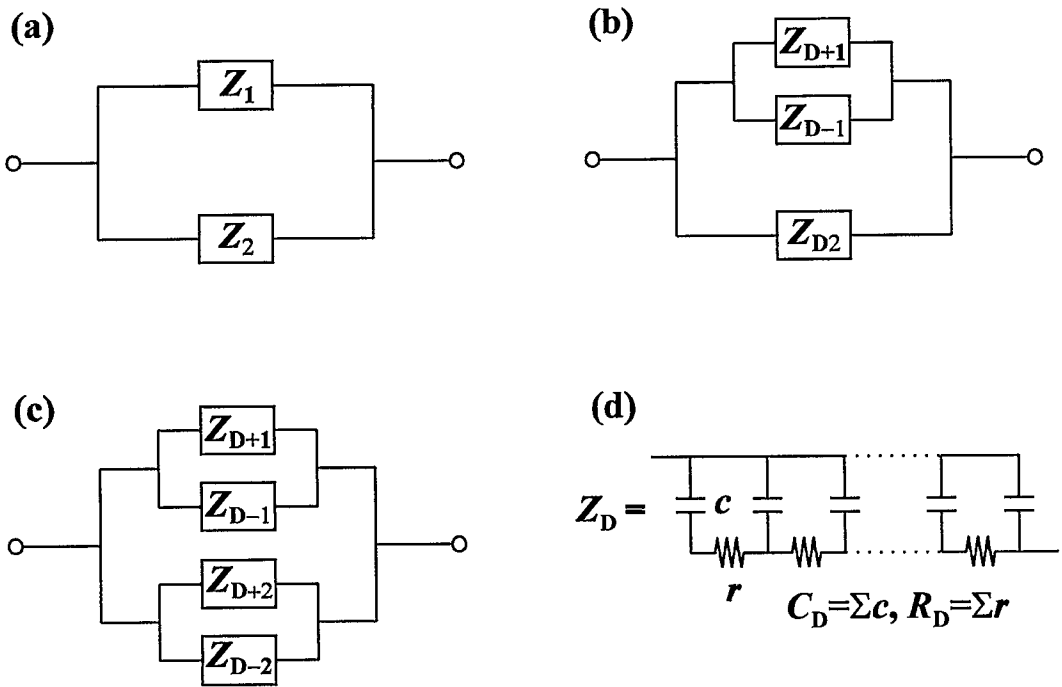
**Figure S1.** Flow diagram of capacitance data treatment for obtaining the capacitance data of a cation and an anion; (a) equivalent circuits, (b) electrochemical capacitance ( $\Delta Q/\Delta E$ ) plots, and (c) electrogravimetric capacitance ( $\Delta M/\Delta E$ ) plots.



**Figure S2.** (a, c, d) Faradaic electrochemical capacitance ( $\Delta Q^f/\Delta E^f$ ) plots and (b) faradaic electrogravimetric capacitance ( $\Delta M^f/\Delta E^f$ ) plots at  $E = 0.1$  V for PPy/PSS films (film thickness =  $1.0 \mu\text{m}$ ) in  $0.5 \text{ M Cs}_2\text{SO}_4$  ( $W_+^+ = W_{\text{Cs}^+} = 132.9$  and  $W_-^- = W_{\text{SO}_4^{2-}} = 96.0$ ); ( $\Delta Q^f/\Delta E^f$ ) and ( $\Delta M^f/\Delta E^f$ ) ( $\bullet$ ), ( $\Delta Q_+^f/\Delta E^f$ ) and ( $\Delta M_+^f/\Delta E^f$ ) ( $\triangle$ ), ( $\Delta Q_-^f/\Delta E^f$ ) and ( $\Delta M_-^f/\Delta E^f$ ) ( $\nabla$ ), simulated ( $\Delta Q_+^f/\Delta E^f$ ) ( $\blacktriangle$ ), and simulated ( $\Delta Q_-^f/\Delta E^f$ ) ( $\blacktriangledown$ ).



**Figure S3.** (a, c) Faradaic electrochemical capacitance ( $\Delta Q^f/\Delta E^f$ ) plots and (b, d) faradaic electrogravimetric capacitance ( $\Delta M^f/\Delta E^f$ ) plots for PPy/PSS films (film thickness = 0.2  $\mu\text{m}$ ) at  $E = -0.3$  V in (a, b) 0.5 M  $\text{Cs}_2\text{SO}_4$  ( $W_+ = W_{\text{Cs}^+} = 132.9$  and  $W_- = W_{\text{SO}_4^{2-}} = 96.0$ ) and (c, d) 1.0 M  $\text{CsNO}_3$  ( $W_+ = W_{\text{Cs}^+} = 132.9$  and  $W_- = W_{\text{NO}_3^-} = 62.0$ ); ( $\Delta Q^f/\Delta E^f$ ) and ( $\Delta M^f/\Delta E^f$ ) ( $\bullet$ ), ( $\Delta Q_+^f/\Delta E^f$ ) and ( $\Delta M_+^f/\Delta E^f$ ) ( $\triangle$ ), ( $\Delta Q_-^f/\Delta E^f$ ) and ( $\Delta M_-^f/\Delta E^f$ ) ( $\nabla$ ), simulated ( $\Delta Q_+^f/\Delta E^f$ ) ( $\blacktriangle$ ), and simulated ( $\Delta Q_-^f/\Delta E^f$ ) ( $\blacktriangledown$ ).



**Figure S4.** (a) Charge transport impedance when charge transport consists of the fast and slow charge transport processes. (b) Charge transport impedance when the fast and slow charge transport processes are limited by ion and electron transport, respectively, and the fast charge transport process consists of two kinds of ion transport. (c) Charge transport impedance when the fast and slow charge transport processes are limited by ion and electron transport, respectively, and both fast and slow charge transport processes consist of two kinds of ion transport. (d) Charge transport impedance when ion transport is much faster than electron transport or electron transport is much faster than ion transport.