Temperature-Controlled Charge Transfer Mechanism in a Polymer Film Incorporating a Redox Molecule As Studied by Potential-Step Chronocouloabsorptometry

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Charge transport (CT) in a Nafion film incorporating $[Ru(bpz)_3]^{2+}$ (bpz = 2,2′-bipyrazine) was investigated using a potential-step chronocouloabsorptometry technique. The reductive CT by $[Ru(bpz)_3]^{2+/+}$ was found to take place by a combination mechanism of physical displacement of the complex and charge hopping between the molecules of the complex. This is a different mechanism from that of the oxidative CT (occurring by a charge hopping mechanism) in an earlier reported Nafion/$[Ru(bpy)_3]^{2+/3+}$ (bpy = 2,2′-bipyridine) system. The combination mechanism in CT was also reported in an earlier Nafion/$[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$ (Ru-red) system. In the present $[Ru(bpz)_3]^{2+}$ system, the activation energy (E_a = 78 kJ·mol^{-1}) of physical displacement is higher than that (40 kJ·mol^{-1}) of charge hopping. In the Ru-red system, on the contrary, the E_a (13 kJ·mol^{-1}) of physical displacement is lower than that (55 kJ·mol^{-1}) of charge hopping. As a result, the fraction (Φ_c) of the contribution of charge hopping to the initial CT rate decreased with increasing temperature for the $[Ru(bpz)_3]^{2+}$ system, whereas it increased with increasing temperature for the Ru-red system. The physical displacement was enthalpy-controlled in the $[Ru(bpz)_3]^{2+}$ system at 25 °C. By contrast, it was entropy-controlled in the Ru-red system. The featured factors influencing physical displacement and charge hopping were discussed.

Introduction

In the recent quarter century, works concerning developments and characterizations of polymer-modified electrodes have been reported vigorously.[1,2] The wide range of their promising applications in the field of electroanalysis,[2] electrocatalysis,[3,4] photoelectrochemistry,[5] and solar energy conversion[6,7] has given impetus to develop these kinds of electrodes. The elucidation of the nature of charge transport (CT) in electroactive polymer films is the most interesting fundamental subject in the field, as well as a question of practical importance for the development of new electrode systems, because CT in the films is a key process for the films to work efficiently in most cases. Lots of trailblazing great works on the nature of CT in the polymer films have been reported.[8−17] However, ambiguous issues on the mechanism still remain.

We have reported CT analyses in polymer-modified electrodes using some potential-step electrospectrophotometric techniques for the specific purpose of evaluation of a CT mechanism in a non-electroconductive polymer film incorporating a functional redox molecule,[18−22] in which CT takes place by physical displacement of the molecules and charge hopping between them, as shown in Figure 1. The analyses of an initial CT rate and its dynamics worked for providing mechanistic insights into the CT in the film. Our analysis showed that in a Nafion/$[Ru(bpy)_3]^{2+}$ system the oxidative CT by $[Ru(bpy)_3]^{2+/3+}$ occurs by a charge hopping mechanism,[18,19] which is consistent with the previous results in Nafion/$[Ru(bpy)_3]^{2+}$ systems reported elsewhere.[9,15,23] In a Nafion/$[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$ (Ru-red) system, CT was found to take place by a combination mechanism of physical displacement of the complex and charge hopping between the molecules of the
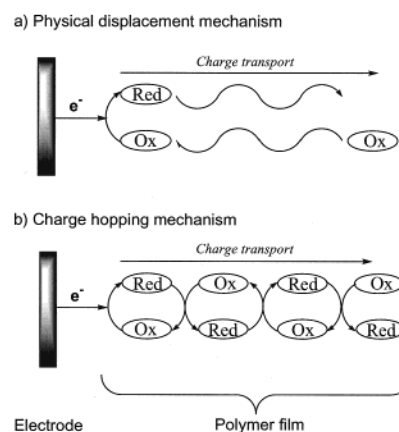
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a) Physical displacement mechanism

b) Charge hopping mechanism

Electrode   Polymer film

Figure 1. Illustration for charge transport in a polymer film by (a) physical displacement and (b) charge hopping mechanisms.

complex.[20] In these works, we obtained activation energies and other activation parameters of each mechanism for the CT to afford a clue to evaluate factors that control the CT. However, a clear conclusion has not been drawn because of the limited cases of the CT systems investigated.

Zhang et al. reported that the reductive CT by $[Ru(bpy)_3]^{3+/2+}$ in a Nafion film takes place by a physical displacement mechanism, as contrasted to a charge hopping mechanism in the oxidative CT by $[Ru(bpy)_3]^{2+/3+}$.[24] In our earlier works, CT in a Nafion film containing $[(bpy)_2(H_2O)Ru-O-Ru(H_2O)(bpy)_2]^{4+}$ (abbreviated to $Ru^{III}-O-Ru^{III}$) was investigated to find that the CT by reduction of $Ru^{III}-O-Ru^{III}$ to form $[Ru(bpy)_2(OH_2)_2]^{2+}$ monomers in the film takes place by physical displacement of the complex, which is in distinction from the CT mechanism of oxidation of $Ru^{III}-O-Ru^{III}$ in the same film, in which charge is transported by charge hopping between $Ru^{III}-O-Ru^{III}$ and

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Ru^{III}−O−Ru^{IV}.[21,22] These results are undoubtedly informative to understand the CT in the film. However, the factors influencing the CT have been difficult to evaluate without the activation parameters.

The comparison between the oxidative (based on [Ru-(bpy)$_3$]$^{2+/3+}$) and reductive (based on [Ru(bpy)$_3$]$^{2+/+}$) CT in the Nafion/[Ru(bpy)$_3$]$^{2+}$ film would provide mechanistic insights into the CT nature coming from the difference in the redox reaction. Unfortunately, it is difficult to investigate the reductive CT by [Ru(bpy)$_3$]$^{2+/+}$ in the film dipped in an aqueous solution because the redox potential (−1.33 V vs SCE [25]) of [Ru(bpy)$_3$]$^{2+/+}$ is out of the potential window of the aqueous solution even if it is highly basic. [Ru(bpz)$_3$]$^{2+}$ possesses similar photoelectronic properties to those of [Ru(bpy)$_3$]$^{2+}$ and is also an attractive molecule in photochemistry and electrochemistry,[26−28,29] but its redox potential (−0.86 V vs SCE [26]) of [Ru(bpz)$_3$]$^{2+/+}$ is much lower than that of [Ru(bpy)$_3$]$^{2+/+}$, which enables us to investigate the reductive CT of [Ru(bpz)$_3$]$^{2+/+}$ in a Nafion film dipped in an aqueous solution. We herein present that in a Nafion/[Ru(bpz)$_3$]$^{2+}$ film the reductive CT takes place by a combination of physical displacement of the complex and charge hopping between the molecules of the complex, compared with earlier results on the oxidative CTs in the Nafion/[Ru(bpy)$_3$]$^{2+}$ and Nafion/Ru-red systems. We will report a first finding that the predominant mechanism of CT in the polymer film is controlled by temperature, depending on the features of the redox molecule and its reaction in the film. The temperature-controlled CT mechanism is discussed here.

Experiments

Materials. [Ru(bpz)$_3$]Cl$_2$ was synthesized by the method reported elsewhere.[28,29] Nafion 117 solution (5 wt % alcoholic solution) was purchased from Aldrich Chemical Co. Inc. and diluted to 2.5 wt % with methanol before use.

Preparation of a Nafion Film Incorporating [Ru(bpz)$_3$]$^{2+}$. A Nafion film was prepared by casting a 2.5 wt % Nafion solution (10 μL) onto an indium tin oxide (ITO) electrode (area 1 cm^2) followed by air-drying. The film thickness was calculated as 1.0 μm using the volume (10 μL) and density (0.83 g·cm^{-3}) of the Nafion solution cast, the density (2.0 g·cm^{-3})[12] of the Nafion film, and the electrode area (1.0 cm^2).[30] A Nafion-coated ITO electrode incorporating [Ru(bpz)$_3$]$^{2+}$ (ITO/Nf-[Ru(bpz)$_3$]$^{2+}$) was prepared by adsorbing [Ru(bpz)$_3$]$^{2+}$ from its aqueous solution into the Nafion film. The amount of the complex incorporated into the film was varied by changing the dipping time or concentration of the complex solution. It was calculated from the visible absorption spectral change of 3.0 mL of the aqueous solution (λ_{max} = 443 nm, ϵ = 15 000 M^{-1}·cm^{-1}) before and after the adsorption, and the absorbance change by the adsorption is more than 25% in all experiments employed. The complex concentration in the film was obtained from its amount in the film and the film volume.

Measurements. Potential-step chronocouloabsorptometry (PSCCA) measurements were carried out by combining a photodiode array spectrophotometer (Shimadzu, Multispec-1500) with an electrochemical analyzer (Hokuto Denko, HZ-3000). A conventional single-compartment cell was equipped with a modified working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. A 0.1 M KOH supporting aqueous electrolyte solution (pH = 13) was used to suppress reduction of proton when applying a negative potential.[31] The electrolyte solution was deaerated by bubbling argon gas for ∼30 min before the measurements.
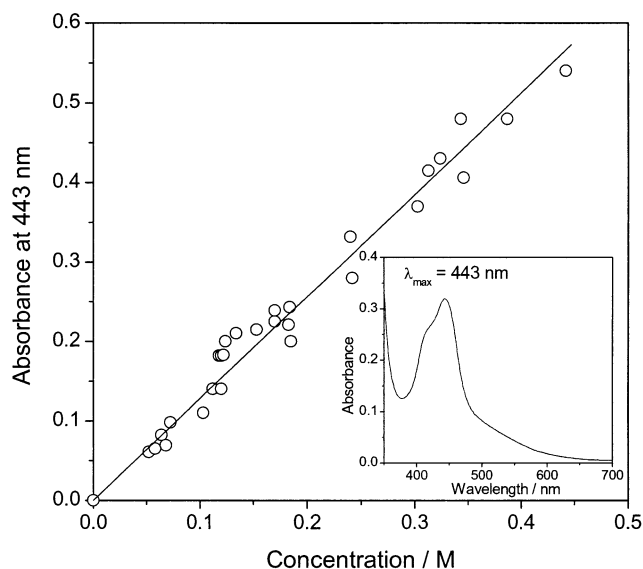

Figure 2. Plots of absorbance at 443 nm of ITO/Nf-[Ru(bpz)$_3$]$^{2+}$ vs complex concentration in the film. The inset illustrates a visible absorption spectrum of ITO/Nf-[Ru(bpz)$_3$]$^{2+}$.

Results

A Nf-[Ru(bpz)$_3$]$^{2+}$ film exhibited an absorption spectrum with λ_{max} = 443 nm shown in the inset of Figure 2, which is almost the same as that in an aqueous solution. Plots of the absorbance at 443 nm versus the complex concentration in the film gave a straight line in Figure 2, corroborating the homogeneities of the confined complex and the film thickness. The slope of the straight line gave a molar absorption coefficient (ϵ_{bpz} = 12800 ± 200 M^{-1}·cm^{-1}) of [Ru(bpz)$_3$]$^{2+}$ in the film that is very close to the value (λ_{max} = 443 nm, ϵ = 15 000 M^{-1}·cm^{-1}) in an aqueous solution.

The cyclic voltammogram (CV) of an ITO/Nf-[Ru(bpz)$_3$]$^{2+}$ film dipped in a 0.1 M KOH electrolyte solution exhibited a reversible redox wave at −0.88 V SCE (see Figure 1 in the Supporting Information). This was assigned to reduction/oxidation of a bpz/bpz$^{\bullet-}$ ligand on the complex on the basis of a previously reported CV of [Ru(bpz)$_3$]$^{2+}$ in an acetonitrile solution showing a reversible reduction of one of the three bpz ligands to bpz$^{\bullet-}$ at −0.86 V vs SCE.[26] The CV of the film was stable in repetitive scans of several times.

The in-situ absorption spectral change of the ITO/Nf-[Ru(bpz)$_3$]$^{2+}$ under a potential step from 0.0 to −1.0 V (vs SCE) in a PSCCA measurement is shown in Figure 3. The absorbance at 443 nm decreased, and the absorbances at 368 and 494 nm increased with isosbestic points at 401 and 457 nm. This spectral change is quite similar to that observed in photochemical reduction of [Ru(bpz)$_3$]$^{2+}$ to [Ru(bpz)$_3$]$^{+}$ in methanol (The isosbestic points are 400 and 459 nm).[26] This clearly shows that [Ru(bpz)$_3$]$^{2+}$ was electrochemically reduced to form [Ru(bpz)$_3$]$^{+}$ in the PSCCA measurement. The absorption spectrum (absorbance = 0.247 at 443 nm) after a back potential step from −1.0 to 0.0 V following the PSCCS measurement was confirmed to be almost identical to that (absorbance = 0.240 at 443 nm) before the PSCCA measurement, showing the stability of the film during the measurement (see Figure 2 in the Supporting Information).

An example of PSCCA measurements is shown in Figure 4. The absorbance at 443 nm decreased, and the amount (Q/C·cm^{-2}) of passed charge simultaneously increased with time after the potential-step, showing that the absorbance change accords with the electrochemical reaction. The coulometric data provided
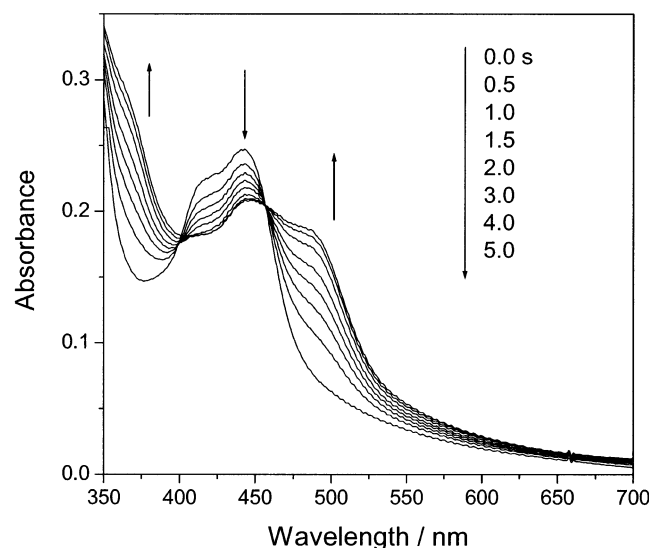
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Figure 3. In situ absorption spectral change of ITO/Nf-[Ru(bpz)$_3$]$^{2+}$ dipped in 0.1 M KOH aqueous solution (pH = 13) in a PSCCA measurement after a potential step from 0.0 to −1.0 V vs SCE. The complex concentration is 0.20 M.
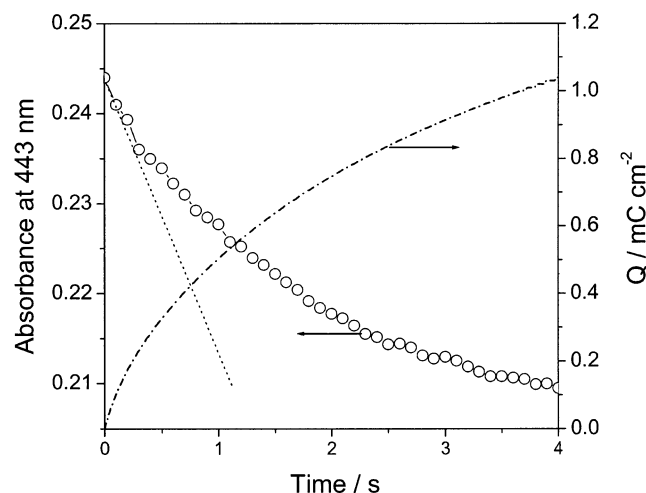

Figure 4. Changes of absorbance at 443 nm and the amount (Q/C·cm^{-2}) of charge passed with time after a potential step. The conditions are indicated in Figure 3. The tangent line estimating {d($A_0 − A_t$)/dt}$_{initial}$ was indicated by a dotted straight line.

a linear relationship between Q and $t^{1/2}$ according to the Cottrell equation, and the slope of the line yielded an apparent diffusion constant, $D_{app} = 7.3 \times 10^{-10}$ cm^2·s^{-1} for the CT in the Nafion/[Ru(bpz)$_3$]$^{2+}$ film.

On the other hand, absorptometric data can also yield the corresponding D_{app} (cm^2·s^{-1}) using the modified Cottrell equation (eq 1):

$$A_0 - A_t = 2c_0(\epsilon_{bpz} - \epsilon_{bpz^{\bullet-}})(D_{app}t/\pi)^{1/2} \qquad (1)$$

where A_0 and A_t are the absorbances at 443 nm of the film at times zero and t, respectively, c_0 (M) is the initial concentration of [Ru(bpz)$_3$]$^{2+}$ in the film, ϵ_{bpz} and $\epsilon_{bpz^{\bullet-}}$ (M^{-1}·cm^{-1}) are the molar absorption coefficients at 443 nm of [Ru(bpz)$_3$]$^{2+}$ and [Ru(bpz)$_3$]$^+$, respectively, and t (s) is reaction time. ϵ_{bpz} is 12 800 M^{-1}·cm^{-1} (vide supra), and $\epsilon_{bpz^{\bullet-}}$ was obtained to be 9500 M^{-1} cm^{-1} from the absorbance after completion of the electrochemical reaction. The plots of $A_0 − A_t$ versus $t^{1/2}$ in Figure 5 gave a linear relationship according to eq 1, and the slope of the line
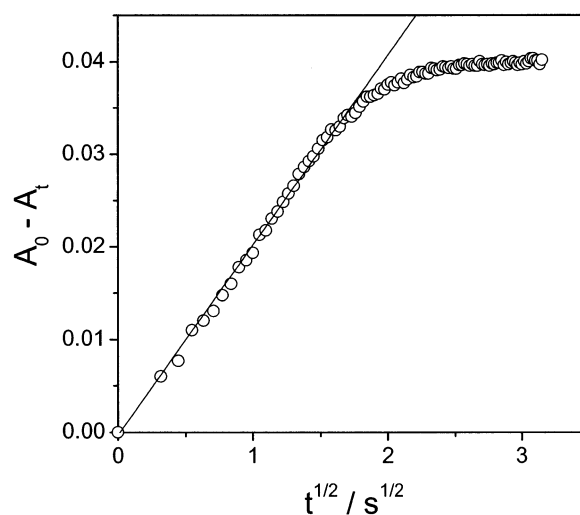

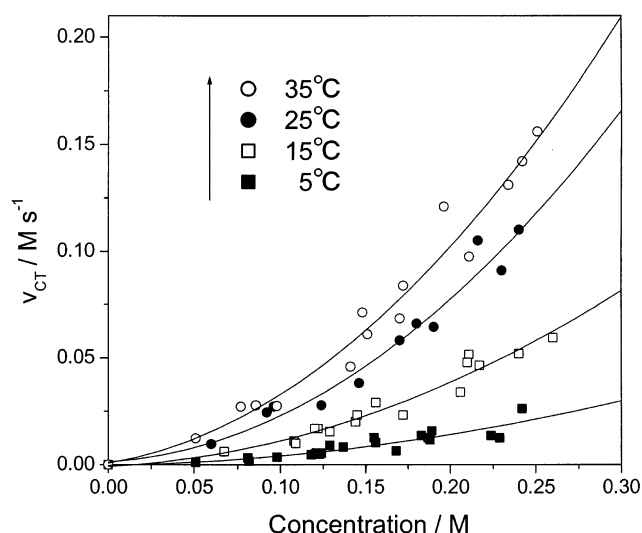**Figure 5.** Plots of $A_0 − A_t$ vs $t^{1/2}$ according to eq 1.

Figure 6. Plots of initial CT rate (v_{CT}/M·s^{-1}) vs complex concentration for various temperatures: 35 °C (○); 25 °C (●); 15 °C (□); 5 °C (■).

yielded $D_{app} = 7.6 \times 10^{-10}$ cm^2·s^{-1}, close to that (7.3 × 10^{-10} cm^2·s^{-1}) obtained from coulometric data. This reveals the quantitative correspondence between the coulometric and absorptometric data.

We have successfully evaluated the CT mechanism in polymer films on the basis of analysis of the initial CT rate [32] (v_{CT}/M·s^{-1}).[18−22] v_{CT} was defined as eq 2 and estimated from the tangent of the initial absorbance change at 443 nm, as shown by a dotted line in Figure 4:

$$v_{CT} = \frac{\{d(A_0 - A_t)/dt\}_{initial}}{(\epsilon_{bpz} - \epsilon_{bpz^{\bullet-}})L} \qquad (2)$$

where L is the film thickness (1.0 μm). The plots of v_{CT} versus c_0 in Figure 6 showed an upward curve for each temperature, suggesting a contribution of a multimolecular process to v_{CT}. Figure 6 also showed that v_{CT} depends on temperature, noting the presence of an activation process in the CT.

CT by physical displacement in the film is treated as a unimolecular process because it is based on physical diffusion of the complex, though it involves diffusions of both the oxidized and reduced species of the redox couple. CT by charge hopping that is based on self-exchange electron transfer between

TABLE 1: Rate Constants of Charge Transport by Physical Displacement and Charge Hopping in a Nafion Film

	reductive CT of [Ru(bpz)$_3$]$^{2+/+}$		oxidative CT of [Ru(bpy)$_3$]$^{2+/3+}$ [a]		oxidative CT of [Ru(NH$_3$)$_5$−O−Ru(NH$_3$)$_4$−O−Ru(NH$_3$)$_5$]$^{6+/7+}$ [b]	
T/°C	k_p/10^{-2} s^{-1}	k_c/M^{-1}·s^{-1}	k_p/10^{-2} s^{-1}	k_c/M^{-1}·s^{-1}	k_p/10^{-2} s^{-1}	k_c/M^{-1}·s^{-1}
5	0.67 ± 0.99	0.32 ± 0.064	0.055		0.37	0.014
15	2.5 ± 1.9	0.84 ± 0.11	0.10		0.35	0.039
25	9.0 ± 3.9	1.49 ± 0.23	0.25		0.57	0.12
35	16.6 ± 4.2	1.69 ± 0.25	0.56		0.59	0.13

[a] Reference 19. [b] Reference 20.
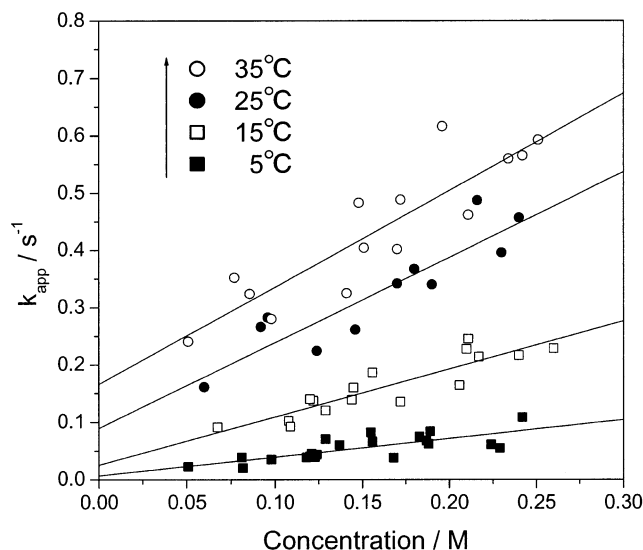
Figure 7. Plots of apparent CT rate constant (k_{app}/s^{-1}) vs complex concentration: 35 °C (○); 25 °C (●); 15 °C (□); 5 °C (■).

Figure 8. Arrhenius plots of the first-order rate constant (k_p/s^{-1}) of the physical displacement (●) and the second-order rate constant (k_c/M^{-1}·s^{-1}) of the charge hopping (○). T/K is absolute temperature.
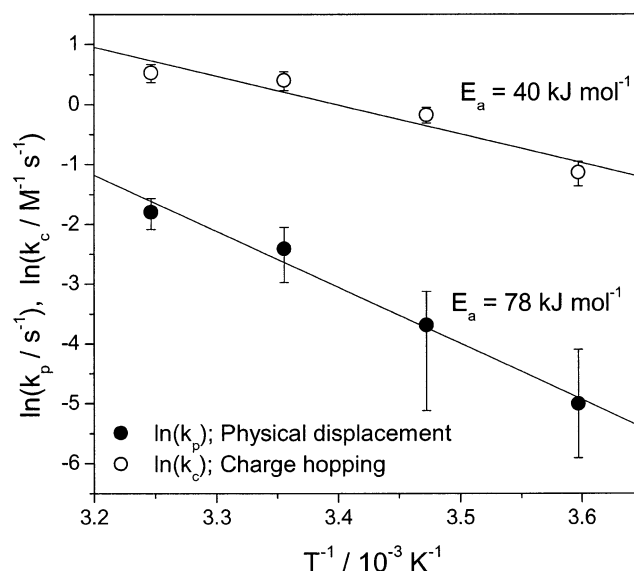
the redox couples should be a bimolecular process (see Figure 1). When CT takes place by both physical displacement and charge hopping, v_{CT} can be represented by eq 3, which is a combination of first-order physical displacement and second-order charge hopping:[18−22]

$$v_{CT} = k_p c_0 + k_c c_0^2 \qquad (3)$$

where k_p (s^{-1}) and k_c (M^{-1}·s^{-1}) are the first-order rate constant for CT by the physical displacement and the second-order rate constant by the charge hopping, respectively. To make the contributions of each mechanism to v_{CT} clearer, an apparent first-order CT rate constant, k_{app} (s^{-1}), is defined as

$$k_{app} = v_{CT}/c_0 = k_p + k_c c_0 \qquad (4)$$

The k_{app} versus c_0 plots gave a straight line with a distinguishable intercept and slope at each temperature according to eq 4, which shows that the CT takes place by both physical displacement and charge hopping.[33] The k_p and k_c values[34] were obtained from the intercept and slope of the lines, respectively, and summarized in Table 1 together with the results reported in earlier systems. For the [Ru(bpz)$_3$]$^{2+}$, the k_p value increased by 25 times with a temperature increase from 5 to 35 °C, with k_c values increasing by 5 times with the same temperature change. Arrhenius plots for k_p and k_c exhibited straight lines in Figure 8, showing that the physical displacement and charge hopping in the film are of the Arrhenius type. The activation energies (E_a) for physical displacement and for charge hopping obtained from the slopes of the lines were 78 ± 7 kJ·mol^{-1} and 40 ± 8 kJ·mol^{-1}, respectively. The activation energies and other activation parameters at 25 °C for each mechanism are summarized in Table 2 including those reported in earlier systems.

Discussion

We first discuss the comparison between the reductive CT of [Ru(bpz)$_3$]$^{2+/3+}$ and the oxidative CT of the [Ru(bpy)$_3$]$^{2+/3+}$ system. The CT mechanism for the former is a combination of physical displacement and charge hopping (presently shown), whereas it is a sole charge hopping mechanism for the latter. Relative kinetics between physical displacement and charge hopping under the complex concentration conditions employed should be important for the predominant CT mechanism. Physical diffusion of the redox couples could be a possible contributing factor for the predominant CT mechanism. To evaluate the interaction between [Ru(bpz)$_3$]$^{2+}$ or [Ru(bpy)$_3$]$^{2+}$ and Nafion, we examined adsorption equilibria of the complexes from their aqueous solutions to their films. The adsorption equilibrium constant ($K = 4.5 \times 10^4$) of [Ru(bpz)$_3$]$^{2+}$ is smaller by a factor of 6.0 than that ($K = 2.7 \times 10^5$) of [Ru(bpy)$_3$]$^{2+}$,[35] suggesting weak interaction of [Ru(bpz)$_3$]$^{2+}$ with Nafion relative to that of [Ru(bpy)$_3$]$^{2+}$. Both [Ru(bpz)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ are supposed to be attached by electrostatic interaction with anionic sulfonate groups of Nafion as well as by hydrophobic interaction between bpz or bpy ligands and its fluorocarbon chain.[36,37] The hydrophobic interaction of bpz ligands with its fluorocarbon is considered to be weak relative to that of bpy ligands though electrostatic interaction should be comparable for both the complexes, making [Ru(bpz)$_3$]$^{2+}$ easier to diffuse in the film than [Ru(bpy)$_3$]$^{2+}$.

The change in the total charge on the complexes in redox reactions could affect the diffusion of the complexes in addition to the nature of the ligands. In principle, the CT by physical displacement should involve diffusions of both oxidized and

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TABLE 2: Summary of Activation Energy (E_a) and Activation Parameters at T = 25 °C

complex	redox reaction	mechanism	E_a/ kJ·mol^{-1}	$\Delta G^{\ddagger}$ a/ kJ·mol^{-1}	$\Delta H^{\ddagger}$ b/ kJ·mol^{-1}	$\Delta S^{\ddagger}$ c/ J·K^{-1}·mol^{-1}	$-T\Delta S^{\neq}$/ kJ·mol^{-1}	ref
[Ru(bpz)$_3$]$^{2+}$	bpz/bpz$^{\bullet-}$	physical displacement	78 (±7)	79 (±1)	75 (±7)	−13 (±1)	3.8 (±8)	present work
		charge hopping	40 (±8)	72 (±0.4)	37 (±8)	−116 (±30)	35 (±9)	
[Ru(bpy)$_3$]$^{2+}$	Ru^{II}/Ru^{III}	physical displacement						19
		charge hopping	55	76	53	−79	24	
[Ru(NH$_3$)$_5$−O−	Ru^{III}Ru^{IV}Ru^{III}/	physical displacement	13	86	11	−252	75	20
Ru(NH$_3$)$_4$−O−Ru(NH$_3$)$_5$]$^{6+}$	Ru^{IV}Ru^{III}Ru^{IV}	charge hopping	55	78	53	−86	26	

^{a} $\Delta G^{\ddagger}$ was calculated by k = kT/h exp($-\Delta G^{\ddagger}/RT$), where k, k, h, and R are rate constant (k_p or k_c), Boltman constant, Planck constant, and gas constant, respectively. ^{b} $\Delta H^{\ddagger}$ was calculated by $\Delta H^{\ddagger} = E_a - RT$ (RT is zero-point energy). ^{c} $\Delta S^{\ddagger}$ was calculated on the basis of $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

reduced species of a redox couple. In the oxidative CT of [Ru(bpy)$_3$]$^{2+}$, the charge on [Ru(bpy)$_3$]$^{2+}$ changes to more positive to form [Ru(bpy)$_3$]$^{3+}$, which could be more difficult to diffuse in the anionic polymer film relative to [Ru(bpy)$_3$]$^{2+}$ due to its high positive charge. By contrast, the reductive CT of [Ru(bpz)$_3$]$^{2+}$ produces [Ru(bpz)$_3$]$^+$ that could be easier to diffuse there than the dication species. Thus, a physical displacement mechanism could be much more favorable in the reductive CT of [Ru(bpz)$_3$]$^{2+}$ than the oxidative CT of [Ru(bpy)$_3$]$^{2+}$.

The k_c values in the [Ru(bpz)$_3$]$^{2+}$ system are higher by 3.0−5.8 times than those in the [Ru(bpy)$_3$]$^{2+}$ system at the temperatures employed. The positive $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ for charge hopping could be explained by the intermediate formation involving solvation (aquation) in the self-exchange electron-transfer reaction between the redox couples. $\Delta S^{\ddagger}$ (−116 J·K^{-1}·mol^{-1}) for charge hopping in the reductive CT of [Ru(bpz)$_3$]$^{2+}$ is lower than that (−79 J·K^{-1}·mol^{-1}) in the oxidative CT of [Ru(bpy)$_3$]$^{2+}$ (Table 2). The lower $\Delta S^{\ddagger}$ would be responsible for the higher degree of reorganization of the solvent in the intermediate formation for the [Ru(bpz)$_3$]$^+$ system compared with the [Ru(bpy)$_3$]$^{2+}$ system. This is consistent with the charge hopping reaction involving the polarized [Ru(bpz)$_3$]$^+$ [38] that requires more reorganization of the solvent than that in charge hopping between nonpolarized [Ru(bpy)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{3+}$. $\Delta H^{\ddagger}$ (37 kJ·mol^{-1}) in the [Ru(bpz)$_3$]$^{2+}$ system is lower than that ($\Delta H^{\ddagger}$ = 53 kJ·mol^{-1}) for the [Ru(bpy)$_3$]$^{2+}$ system, making the charge hopping for [Ru(bpz)$_3$]$^{2+}$ enthalpically easier than that for [Ru(bpy)$_3$]$^{2+}$. The higher k_c values in the [Ru(bpz)$_3$]$^{2+}$ system could be explained by the lower enthalpic factor for the intermediate formation that overcomes the corresponding entropic one at the temperatures employed. In the [Ru(bpz)$_3$]$^{2+}$ system, physical displacement and charge hopping are kinetically comparable for the CT, whereas, in the [Ru(bpy)$_3$]$^{2+}$ system, CT by physical displacement is extremely slower than that by charge hopping (negligible contribution of physical displacement), which explains the difference in the CT mechanism between both the systems.

In the Nafion/Ru-red system, the CT mechanism is a combination of physical displacement and charge hopping, in contrast to a sole charge hopping mechanism for the Nafion/ [Ru(bpy)$_3$]$^{2+}$ system. Ru-red could be much easier to diffuse in the film than [Ru(bpy)$_3$]$^{2+}$ due to the hydrophilicity of its ammine ligands. The activation parameters for charge hopping in the Ru-red system are quite similar to those in the [Ru(bpy)$_3$]$^{2+}$ system, which might suggest a dynamically similar charge hopping process in the film for both the systems.

In the Nafion/[Ru(bpz)$_3$]$^{2+}$ system, as well as the Nafion/ Ru-red system, CT takes place by a combination mechanism of physical displacement and charge hopping. However, for the former system, E_a (78 kJ·mol^{-1}) of physical displacement is higher than that (40 kJ·mol^{-1}) of charge hopping, whereas, for the latter system, E_a (13 kJ·mol^{-1}) of physical displacement is
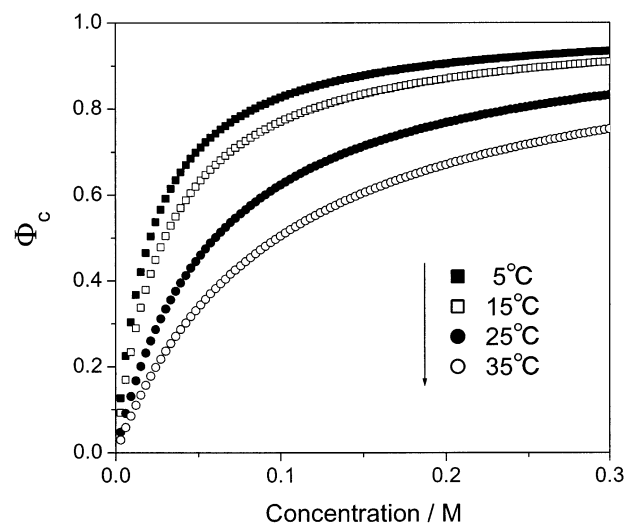

Figure 9. Concentration dependence of the fraction (Φ_c) of the contribution of charge hopping to v_{CT} for various temperatures in the Nafion/Ru[(bpz)$_3$]$^{2+}$ system.

lower than that (55 kJ·mol^{-1}) of charge hopping (Table 2). This provides a striking difference in the temperature dependence of the fraction (Φ_c) of the contribution of charge hopping to v_{CT}. The Φ_c was calculated by the following equation (eq 5).

$$k_c c_0{}^2/(k_p c_0 + k_c c_0{}^2) \tag{5}$$

Figure 9 depicts the relationship between Φ_c and c_0 at each temperature for the Nafion/[Ru(bpz)$_3$]$^{2+}$ system. The Φ_c increased with c_0, since charge hopping is a second-order process with respect to c_0 against a first-order physical displacement. It draws close to unity, at which the concentration is high enough for $k_c c_0{}^2 \gg k_p c_0$. The Φ_c decreased with the increase in temperature for the Nafion/[Ru(bpz)$_3$]$^{2+}$ system, as shown in Figure 9, in contrast with the Φ_c increase with the temperature increase for the Nafion/Ru-red system.[20] This is illustrated by the temperature dependences of Φ_c (at 0.1 M of complex concentration) shown in Figure 10.

As for the temperature-controlled predominant CT mechanism shown above, it is particularly notable that the physical displacement is enthalpy-controlled in the Nafion/[Ru(bpz)$_3$]$^{2+}$ system at room temperature ($\Delta H^{\ddagger}$ = 75 kJ·mol^{-1} is much larger than $-T\Delta S^{\ddagger}$ = 3.8 kJ·mol^{-1} at 25 °C), whereas it is entropy-controlled in the Nafion/Ru-red system ($-T\Delta S^{\ddagger}$ = 75 kJ·mol^{-1} is much larger than $\Delta H^{\ddagger}$ = 11 kJ·mol^{-1} at 25 °C). The cationic complex is electrostatically attached to the anionic sulfonate groups of Nafion, and physical displacement should require the dissociation of the complex from the sulfonate groups in an intermediate state involving reorganization of the solvent, which is responsible for the positive $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ for physical displacement. The higher $\Delta H^{\ddagger}$ (75 kJ·mol^{-1}) for the
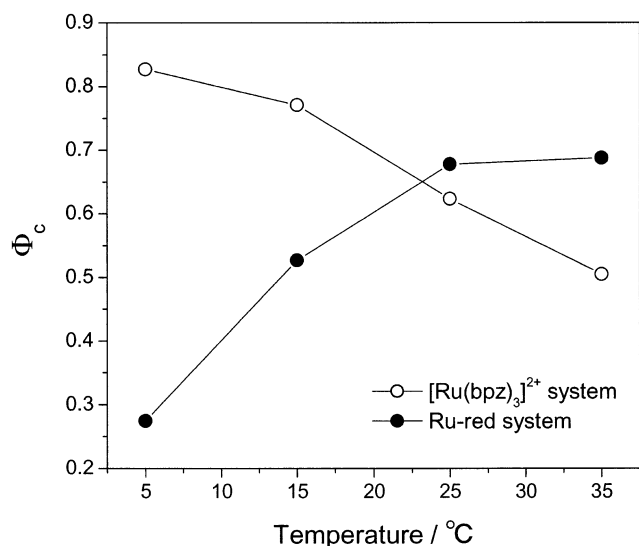
Figure 10. Plots of Φ_c vs temperature for Nafion/Ru[(bpz)$_3$]$^{2+}$ (○) and Nafion/Ru-red systems (●). The complex concentration is 0.1 M.

[Ru(bpz)$_3$]$^{2+}$ system than that (11 kJ·mol^{-1}) for the Ru-red system would suggest the stronger attachment of Ru(bpz)$_3$$^{2+}$ to the Nafion film than that of Ru-red by hydrophobic interaction of bpz ligands with its fluorocarbon as well as the electrostatic interaction. The much lower $\Delta S^{\ddagger}$ (-252 J·K^{-1}·mol^{-1}) for the Ru-red system than that (-13 J·K^{-1}·mol^{-1}) for the [Ru(bpz)$_3$]$^{2+}$ system could be explained by the higher degree of solvation required in dissociation of the redox couple of [Ru-red]$^{6+/7+}$ from the sulfonate groups of Nafion than that for [Ru(bpz)$_3$]$^{2+/+}$ due to the highly positive charge.

The k_p values in the reductive CT in the [Ru(bpz)$_3$]$^{2+}$ system are higher by 1.8−28 times than those in oxidative CT in the Ru-red system at 5−35 °C. The higher $\Delta H^{\ddagger}$ (75 kJ·mol^{-1}) for physical displacement of [Ru(bpz)$_3$]$^{2+}$ than that (11 kJ·mol^{-1}) of Ru-red suggests that physical displacement of [Ru(bpz)$_3$]$^{2+}$ is enthalpically unfavorable by the stronger attachment of [Ru(bpz)$_3$]$^{2+}$ to the Nafion film than that of Ru-red. However, the much higher $\Delta S^{\ddagger}$ (-13 J·K^{-1}·mol^{-1}) in the [Ru(bpz)$_3$]$^{2+}$ system than that (-252 J·K^{-1}·mol^{-1}) in the Ru-red system makes physical displacement of [Ru(bpz)$_3$]$^{2+}$ entropically easier compared with that of Ru-red. The entropic factor overcomes the corresponding enthalpic one to provide higher k_p for the [Ru(bpz)$_3$]$^{2+}$ system around room temperature.

Conclusion

Charge transport (CT) in a Nafion film incorporating a redox molecule was investigated using potential-step chronocoulo-absorptometry. Concentration dependences of the initial CT rate (v_{CT}/s^{-1}) provided a distinguishable CT mechanism, and temperature dependences of v_{CT} yielding E_a and other activation parameters allowed us to figure out the factors influencing the CT. It was first reported that the predominant mechanism of CT in the polymer film is controlled by temperature, depending on features of the redox molecule and its reaction. The result reported here should shed light on the ambiguous issues of a CT mechanism in a polymer film.

Supporting Information Available: CV and absorption spectra of ITO/Nf-[Ru(bpz)$_3$]$^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Molecular design of electrode surface*; Murray, R. W., Ed.; John Wiley and Sons: New York, 1992; Vol. 22.

(2) *Electroanalytical chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1996; Vol. 18.

(3) Zen, J.-M.; Kumar, A. S. *Acc. Chem. Res.* **2001**, *34*, 772.

(4) Yagi, M.; Kinoshita, K.; Kaneko, M. *J. Phys. Chem.* **1996**, *100*, 11098.

(5) Torres, G. R.; Dupart, E.; Mingotaud, C.; Ravaine, S. *J. Phys. Chem. B* **2000**, *104*, 9487.

(6) Kaneko, M.; Woehrle, D. *Adv. Polym. Sci.* **1988**, *84*, 141.

(7) Li, W.; Osora, H.; Otero, L.; Duncan, D. C.; Fox, M. A. *J. Phys. Chem. A* **1998**, *102*, 5333.

(8) Majda, M.; Faulkner, L. R. *J. Electroanal. Chem.* **1984**, *169*, 77.

(9) Buttry, D. A.; Anson, F. C. *J. Electroanal. Chem.* **1981**, *130*, 333.

(10) Blauch, D. N.; Saveant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 3323.

(11) Blauch, D. N.; Saveant, J. M. *J. Phys. Chem.* **1993**, *97*, 6444.

(12) White, H. S.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4811.

(13) Leddy, J.; Bard, A. J. *J. Electroanal. Chem.* **1985**, *189*, 203.

(14) Oyama, N.; Ohsaka, T.; Kaneko, M.; Sato, K.; Matsuda, H. *J. Am. Chem. Soc.* **1983**, *105*, 6003.

(15) Martin, C. R.; Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4817.

(16) Anson, F. C.; Saveant, J. M.; Shigehara, K. *J. Phys. Chem.* **1983**, *87*, 214.

(17) Anson, F. C.; Saveant, J. M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096.

(18) Yagi, M.; Mitsumoto, T.; Kaneko, M. *J. Electroanal. Chem.* **1997**, *437*, 219.

(19) Yagi, M.; Mitsumoto, T.; Kaneko, M. *J. Electroanal. Chem.* **1998**, *448*, 131.

(20) Yagi, M.; Yamase, K.; Kaneko, M. *J. Electroanal. Chem.* **1999**, *476*, 159.

(21) Yagi, M.; Yamase, K.; Kaneko, M. *Electrochim. Acta* **2002**, *47*, 2019.

(22) Kinoshita, K.; Yagi, M.; Kaneko, M. *Electrochim. Acta* **1999**, *44*, 1771.

(23) He, P.; Chen, X. *J. Electroanal. Chem.* **1988**, *256*, 353.

(24) Zhang, J.; Zhao, F.; Abe, T.; Kaneko, M. *Electrochim. Acta* **1999**, *45*, 399.

(25) Hemingwey, N. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.

(26) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128.

(27) Kalyanasundaram, K. *J. Phys. Chem.* **1986**, *90*, 2285.

(28) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.

(29) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.

(30) It was calculated by the equation: $(1.0 \times 10^{-2}$ cm^3) × (0.83 g cm^{-3}) × $0.025/\{(2.0$ g cm^{-3}) × $(1.0$ cm^2)$\} = 1.0 \times 10^{-4}$ cm.

(31) The potential for H$^+$ reduction to H$_2$ is -0.767 V vs NHE (converted to -1.01 V vs SCE) at pH = 13. H$^+$ reduction is sufficiently suppressed at the applied potential (-1.0 V vs SCE) employed in the PSCCA measurements when taking an overpotential into account.

(32) v_{CT} is convenient for comparison with any case of an electrochemical reaction that cannot be analyzed by a simple diffusion process. We have adapted v_{CT} in the CT analysis for the wide range of its application to electrochemical research.

(33) The k_p could be independent of the complex concentration under the present conditions. This is supported by the linear plots of k_{app} versus c_0 in Figure 7. Many previous studies relating to CT in a polymer film reported that the physical diffusivity of the redox molecule depends on its concentration, which was explained by the interaction between the complex and the polymer matrix, such as cross-linking in many cases. These studies employed a wide range (10^{-3} to 10^{-1} M) of concentration conditions, but the present study adapted the narrow concentration range 5.0×10^{-2} to 2.6×10^{-1} M. In a similar concentration range to that for the present work, we reported that the first-order rate constant for physical displacement of a redox molecule in a Nafion film is independent of its concentration.

(34) The k_p and k_c obtained are phenomenological values including equilibria, the reorganization of the solvent, and counterion migration involved in CT rather than real rate constants, so these values should be sensitive to solvent and a supporting electrolyte. However, in the present Nafion/[Ru(bpz)$_3$]$^{2+}$ system we did not observe any distinguishable changes in charge transport kinetics when NaOH was used instead of KOH. In the

Nafion/[Ru(bpy)$_3$]$^{2+}$ and Nafion/Ru-red systems the electrochemical reaction is corroborated not to change when the electrolyte solutions of KNO$_3$, NaNO$_3$, K$_2$SO$_4$, and NaClO$_4$ were used. These results show that counterion migration does not influence significantly phenomenological CT under the conditions applied in these systems though it should be involved in the CT. v_{CT} significantly increased with the complex concentration in these three systems. The different v_{CT} values as well as its different dependencies on the complex concentration were exhibited between the Nafion/[Ru(bpy)$_3$]$^{2+}$ and Nafion/Ru-red systems, indicating the different CT mechanism, though an aqueous 0.1 M KNO$_3$ solution is used as a supporting electrolyte solution in both the systems. These results reveal that the CT mechanism in the film is exclusively limited by reactions of the complex.

Thus, the k_p and k_c reflect the CT dynamics arising from the nature and reactions of the complexes.

(35) The adsorption equilibrium constant (K) is defined as $K = c_m/c_s$, where c_m and c_s are the complex concentrations in the film and aqueous solution at an equilibrium state.

(36) Yagi, M.; Nagai, K.; Onikubo, T.; Kaneko, M. *J. Electroanal. Chem.* **1995**, *383*, 61.

(37) Yagi, M.; Nagai, K.; Kira, A.; Kaneko, M. *J. Electroanal. Chem.* **1995**, *394*, 169.

(38) The oxidation state of the Ru center is II, and one of three bpz ligands was 1-electron reduced to bpz$^{•-}$, so [Ru(bpz)$_3$]$^+$ is exactly represented as [Ru^{II}(bpz)$_2$(bpz$^{•-}$)]$^+$.