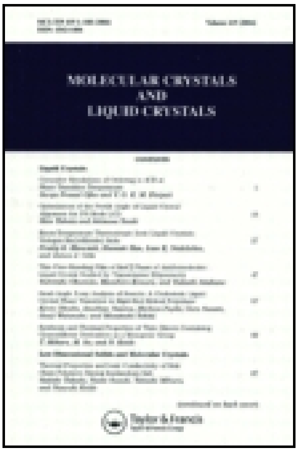

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# Speculation on Nanochannels in Polymer Electrolyte Membranes

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# Speculation on Nanochannels in Polymer Electrolyte Membranes

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*We investigated the interaction of excited ruthenium complexes with quenchers in nanochannels of Nafion-cation-conductive membranes by using luminescence quenching measurements. The quenching rate is reflected by mobility of ions in Nafion nanochannels, which depends on the relationship between the ion size and diameter or structure of the nanochannels. The quenching of excited pyrene sulfonic acid by the quencher* $NO_2^-$ *in anion-conductive membranes is also discussed.*

**Keywords** Luminescence quenching; nanostructures; polymer electrolyte; proton channel

## Introduction

Because of their potential high efficiency, small size, and environmental friendliness, proton exchange membrane fuel cells (PEMFCs) are of great interest [1]. However, the high price and limited supply of platinum (Pt) constitute a barrier to their use, so a reduction in the Pt loading of the electrocatalyst is desirable. Such a reduction would require an improvement in cell performance per unit mass Pt; cell performance is known to be related to polymer electrolytes such as Nafion. Modifications of the Nafion surface [2] or addition of hydroxide to Nafion [3] has been attempted to improve cell performance. We brought attention to the fact that cell performance is related to the texture of proton channels in the polymer electrolyte Nafion. Fullerene derivatives added to the Nafion ionomer to produce membrane electrode assemblies (MEAs) affect the texture of ion channels in the Nafion and enhance the proton transport efficiency, which explains the high performance of the MEAs [4].

To design polymer electrolytes for promising high-performance MEAs, it is important to elucidate the nature of the microenvironment of proton channels in an electrolyte membrane. Ionomer solution properties may also provide useful information about proton channels. For example, rod-like aggregation particles are found in Nafion ionomer solutions because of hydrophobic interactions of fluorocarbon backbones. Ionic side chains are located near the surface of the rod, and thus, the surface is considered to be a reverse model of the inner wall of the proton channels. In a previous publication [5], we demonstrated

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*Address correspondence to H. Shioyama, National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan. E-mail: shioyama.h@aist.go.jp luminescence quenching in a tris(2,2′-bipyridine)ruthenium(II) [$Ru(bpy)_3^{2+}$)]–methyl viologen ($MV^{2+}$) system in ethanol-containing Nafion aggregates and showed that $Ru(bpy)_3^{2+}$ and $MV^{2+}$ are adsorbed onto the aggregates [6]. Furthermore, we reported that the diffusion constant of $Ru(bpy)_3^{2+}$ and $MV^{2+}$ in the nanochannels of a Nafion membrane is one tenth or less than that of the bulk solvent.

In the present study, we analyze differences in luminescence quenching of ruthenium complex–quencher systems in Nafion membranes. We also analyze quenching of a pyrene sulfonic acid ($PyS^-$)–$NO_2^-$ system occluded into the nanochannels of anion-conductive membranes.

These analyses provide information about a new method to determine the mobility of ions in polymer electrolytes to subsequently determine the structure of nanochannels, which could not be analyzed by conventional impedance measurements [7]. The structure of nanochannels is useful in designing high-performance polymer electrolytes for advanced fuel cells. The design of nanochannel structures to increase the mobility of ions may bring about an improvement in fuel cell performance.

## Materials and Methods

Tris(2,2′-bipyridine)ruthenium(II) dichloride [$Ru(bpy)_3^{2+}$, Tokyo Kasei], tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride ($Ru(dp\text{-}phen)_3^{2+}$, Alfa), methyl viologen dichloride ($MV^{2+}$, Tokyo Kasei), ethyl viologen diperchloride ($EV^{2+}$, Sigma-Aldrich), pyrene sulfonic acid hydrate ($PyS^-$, Sigma-Aldrich), and sodium nitrite ($NO_2^-$, Sigma-Aldrich) were used as received. A Nafion membrane (Nafion 117, $1.78 \times 10^{-4}$ m thick) was obtained from Du Pont. Anion-conductive membranes (A-201 and A-202, $2.8 \times 10^{-5}$ m thick) were supplied from Tokuyama Corp.; alkyl ammonium groups provide anion conduction in this resin. A-201 is the prototype membrane, and A-202 is a membrane modified for low methanol crossover.

Luminescence spectra were measured with a fluorescence spectrometer (Perkin Elmer LS50B). All solutions for luminescence measurement were deoxygenated by flushing with Ar gas for $\geq$20 min. To occlude luminescence probes into the polymer electrolyte membrane, a membrane section ($2 \times 2$ cm$^2$) was immersed in an aqueous solution or in ethanol of a weighted quantity of luminescence probes for $\geq$2 days. Occlusion of quenchers was carried out in a similar manner. All luminescence measurements were performed at room temperature. The lifetime of excited ruthenium complexes was determined by exciting the sample with the second harmonic (wavelength = 401 nm) of a Ti:sapphire femtosecond laser pulse (fwhm = 130 fs) and observing the decay curve at a wavelength of 600 nm with a photomultiplier combined with a storage oscilloscope. Because the lifetime of excited $PyS^-$ cannot be obtained by this apparatus, $K_{SV}$ values are discussed instead of $k_q$.

## Results and Discussion

### *Luminescence Quenching of Ruthenium Complex–Quencher Systems in Nafion Membrane*

$MV^{2+}$ is a popular electron acceptor that can quench fluorescence from the excited state of $Ru(bpy)_3^{2+}$. This electron-transfer quenching is described by the Stern–Volmer equation:

$$I_0/I = 1 + K_{SV}[MV^{2+}], \tag{1}$$

$$K_{SV} = k_q \tau_0, \tag{2}$$

where $I_0$ is the luminescence intensity in the absence of a quencher, $I$ is the intensity in the presence of a quencher, $K_{SV}$ is the Stern–Volmer constant, $k_q$ is the rate constant of the quenching reaction, and $\tau_0$ is the luminescence lifetime in the absence of a quencher. The reaction rate is known to consist of the intrinsic part and the diffusion factor. If the luminescence probe and the quencher are fixed and the quenching reactions are performed in different media, $K_{SV}$ or $k_q$ depends merely on the diffusion factor because the intrinsic part is the same. In a previous publication, we reported these luminescence quenching reactions for a $Ru(bpy)_3{}^{2+}$–$MV^{2+}$ system [5]. The value of $K_{SV}$ was ca. 18 for the luminescence quenching in the Nafion membrane. Because the value of $K_{SV}$ for quenching in bulk ethanol solution is ca. 330, the quenching reaction in the Nafion membrane is considerably suppressed.

To investigate the nature of proton channels in Nafion, we examined the luminescence quenching of some ruthenium complex–quencher systems. Pieces of Nafion membrane ($2 \times 2 \times 0.0178$ cm$^3$, 130 mg) were used as specimens. The amount and the concentration of sulfonic acid in the specimens were $1.0 \times 10^{-4}$ mol and 1.4 M, respectively. After immersion in an aqueous solution containing $3 \times 10^{-7}$ mol of ruthenium complex for 2 days, all ruthenium complex ions were occluded into the membrane. The specimen turned a homogeneous yellow color, and the concentration of ruthenium complex was calculated to be $4.2 \times 10^{-3}$ M. The luminescence from the excited ruthenium complex in the Nafion membrane was similar to that in bulk aqueous solution. Subsequent immersion for 2 days in aqueous solutions containing a quencher caused the quencher ions to also be occluded into the membrane, which resulted in luminescence quenching. As an example of luminescence quenching in the Nafion membranes, the Stern–Volmer plot of the $Ru(dp\text{-}phen)_3{}^{2+}$–$MV^{2+}$ system is shown in Fig. 1.

The values of $K_{SV}$ and $k_q$ obtained by the Stern–Volmer Equations (1) and (2) for individual systems are listed in Table 1. In the $Ru(bpy)_3{}^{2+}$–$Cu^{2+}$ system, the value of $k_q$ in the Nafion membrane is the same as that in bulk aqueous solution. Numerous studies demonstrate that the Nafion membranes exhibit a bicontinuous structure involving a hydrophobic matrix and ionic domains of nanochannels. Because the ratio of ionic domains in the membrane cannot be estimated, we determined the quencher concentration in Nafion by assuming that the quencher exists throughout the membrane. Although the value of $k_q$ in the Nafion membranes appears to be the same as that in the bulk solution, the quencher concentration in the ionic nanochannel is higher and the ion mobility in the nanochannel is therefore expected to be lower.

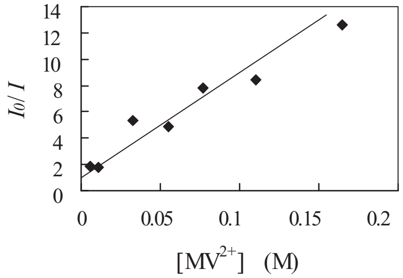

**Figure 1.** Dependence of $I_0/I$ on quencher concentration for luminescence quenching in a $Ru(dp\text{-}phen)_3{}^{2+}$–$MV^{2+}$ system in a Nafion membrane. The concentration of $Ru(dp\text{-}phen)_3{}^{2+}$ is $4.2 \times 10^{-3}$ M and that of the sulfonic acid chain is 1.4 M.

**Table 1.** Comparison of $K_{SV}$ for luminescence quenching of each system in polymer electrolyte with luminescence quenching of each system in solution

| Luminescence probe | Quencher | Medium | $K_{SV}$ | $\tau_0$ (ns) | $k_q$ ($\times 10^9$ $M^{-1}s^{-1}$) | Order of quenching depression ($k_q$ in Nafion/$k_q$ in solution or $K_{SV}$ in anion-conductive membrane/$K_{SV}$ in solution) |
|---|---|---|---|---|---|---|
| $Ru(bpy)_3{}^{2+}$ | $Cu^{2+}$ | $H_2O$ | 43 | 850 | 0.051 | 1 / 1.1 |
| | | Nafion membrane | 29 | 630 | 0.046 | |
| $Ru(bpy)_3{}^{2+}$ | $MV^{2+}$ | $H_2O$ | 330 | 850 | 0.39 | 1 / 13 |
| | | Nafion membrane | 18 | 630 | 0.029 | |
| $Ru(bpy)_3{}^{2+}$ | $EV^{2+}$ | $H_2O$ | 370 | 850 | 0.43 | 1 / 27 |
| | | Nafion membrane | 10 | 630 | 0.016 | |
| $Ru(dp\text{-}phen)_3{}^{2+}$ | $MV^{2+}$ | EtOH | 1750 | 3670 | 0.48 | 1 / 11 |
| | | Nafion membrane | 73 | 1700 | 0.043 | |
| $PyS^-$ | $NO_2{}^-$ | $H_2O$ | 300 | - | - | 1 / 3 |
| | | Anion-conductive membrane – A-201 | 100 | - | - | |
| | | Anion-conductive membrane – A-202 | 55 | - | - | 1 / 5 |

In the Ru(bpy)$_3{}^{2+}$–MV$^{2+}$ system, the quenching reaction is depressed in the Nafion membrane compared with the bulk solution because of its narrow ion channels. The degree of depression is pronounced when MV$^{2+}$ is replaced by the larger quencher EV$^{2+}$. However, the degree of $k_q$ depression is not affected when Ru(bpy)$_3{}^{2+}$ is replaced by the more bulky luminescence probe Ru(dp-phen)$_3{}^{2+}$. In the quenching process, the reaction rate is independent of the luminescence prove with concentration as low as $4.2 \times 10^{-3}$ M but does depend on the quencher with much more high concentration.

The value of $k_q$ is associated with the mobility of ions in the nanochannels, and the mobility depends on the relationship between the ion size and the diameter or structure of the nanochannels. The structure of nanochannels in Nafion membrane has been extensively debated over recent decades [8–10]. As the nanochannels in the polymer electrolyte membrane cannot be analyzed with transmission electron microscopy, small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS) data are used to determine the structure of nanochannels in Nafion. K. Schmidt-Rohr and Q. Chen have lately concluded that the nanochannels with a tubular structure have diameters of between 1.8 and 3.5 nm, with an average of 2.4 nm, which was derived from a precise analysis of SAXS [10]. Adopting this tubular structure, the dependence of the ion size on the quenching reaction shown in Table 1 could be favorably explicable. The tubular structure with the diameter of 2.4 nm seems to affect the mobility of Cu$^{2+}$, MV$^{2+}$, and EV$^{2+}$ in the nanochannels, on the basis of the ion size ordering. The mobility of a large quencher ion is lower than that of smaller ion, and hence the degree of quenching depression in the Nafion membrane compared with its quenching in solution is more pronounced.

### *Luminescence Quenching of PyS$^-$–NO$_2{}^-$ System in Anion-Conductive Membranes*

Quite recently, some researchers have proposed alternative approaches to reduce Pt loading that uses anion-conductive membranes [11]. An important advantage of these membranes is that electrocatalytic reactions take place in an alkaline media, which allows us to select a wide range of catalysts such as non-noble metals. Nevertheless, no information of the ion channels in these membranes has been reported.

To investigate the nature of ion nanochannels in an anion-conductive membrane, we examined the luminescence of PyS$^-$ [12]. Pieces of the anion-conductive membranes A-201 and A-202 ($1 \times 2 \times 0.0028$ cm$^3$, 6.1 mg) were used as specimens. The amount and concentration of alkyl ammonium group in the specimens were $1.1 \times 10^{-5}$ mol and 2.2 M, respectively. After immersion in an aqueous solution (PyS$^- = 4.4 \times 10^{-7}$, $2.2 \times 10^{-6}$, and $1.1 \times 10^{-5}$ mol) for over 2 days, almost all PyS$^-$ anions were occluded in the membrane and their concentration was 0.088, 0.44, and 2.2 M, respectively. Luminescence spectra from the excited PyS$^-$ at each concentration in the membrane are shown in Fig. 2. In solution, excimer fluorescence is observed if the PyS$^-$ concentration is as high as $1 \times 10^{-3}$ M [13]. The concentration of PyS$^-$ that gives excimer fluorescence is much higher, which suggests that the mobility of PyS$^-$ in the membrane is lower than that in the solution. Because of the low mobility, the diffusion length of excited PyS$^-$ is shorter in the membrane than that in the solution, so an excited PyS$^-$ could not encounter a ground state PyS$^-$ to form an excimer at low PyS$^-$ concentration in the membrane.

To discuss the effect of the nanochannel structure, the ratio of excimer emission intensity to monomer emission intensity is compared in Figs. 2(b) and (e). Being different from Nafion, the structure of nanochannels in these anion-conductive membranes is not elucidated. The manufacturer shows that the alternative current (ac) impedance of A-201 and A-202 at 1 kHz is 0.3 and 0.6 ohmcm$^2$, respectively. The A-202 membrane is shown

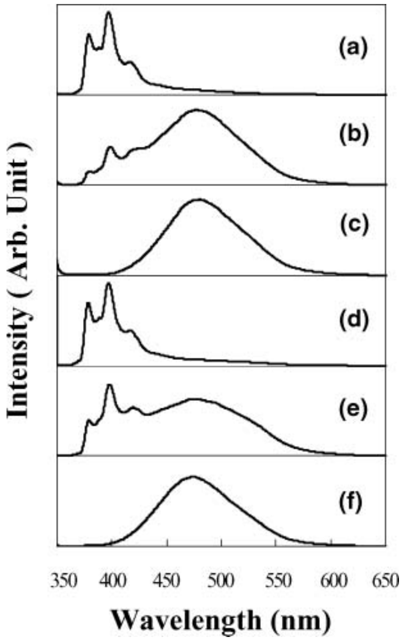

**Figure 2.** Steady-state luminescence spectra of $PyS^-$ in anion-conductive membrane A-201. The concentrations of $PyS^-$ in A-201 are (a) 0.088, (b) 0.44, and (c) 2.2 M. The concentrations of $PyS^-$ in A-202 are (d) 0.088, (e) 0.44, and (f) 2.2 M.

to be designed to reduce methanol crossover when it is used as the polymer electrolyte of a direct methanol fuel cell, which is a type of PEMFC. In practice, A-202 reduces the methanol crossover rate ca. 20% compared with A-201. Although further details of these membranes are not disclosed by the manufacturer, it is presumed that the ion channel diameter of A-202 is narrower than that of A-201. The excimer emission in the A-202 membrane is weaker than that in the A-201 membrane, which means that the mobility of $PyS^-$ in A-202 is lower than that in A-201. This result is explained by the narrow ion channels in the A-202 membrane.

The low mobility of anions in the anion-conductive membrane is likewise confirmed by luminescence quenching. The Stern–Volmer plots for quenching of $PyS^-$ luminescence by $NO_2^-$ in the A-201 and A-202 membranes are shown in Fig. 3. The electron donor $NO_2^-$ can quench fluorescence [14] from the excited state of pyrene chromophores. For luminescence quenching in the A-201 [15] and A-202 membranes, $K_{SV}$ is 100 and 55, respectively. These values are one third and one fifth of that obtained for quenching in the solutions that are listed in Table 1. It is interesting to note that $K_{SV}$ is smaller when the A-202 membrane is used. This difference in $K_{SV}$ can be understood on the basis of the ion channel diameter, i.e., the mobility of $NO_2^-$ in the A-202 membrane with narrower ion channels is lower than that in the A-201 membrane.

As mentioned above, luminescence quenching of the ruthenium complex–quencher system in the Nafion membrane is depressed compared with its quenching in the solution and the degree of depression is more pronounced for larger ionic quenchers. The degree of quenching depression for the $PyS^-$–$NO_2^-$ system in the anion-conductive membranes listed in Table 1 can be understood on the basis of the ion size ordering: $EV^{2+} > MV^{2+} > NO_2^- > Cu^{2+}$, which determines the ion mobility in the nanochannels. More accurately,

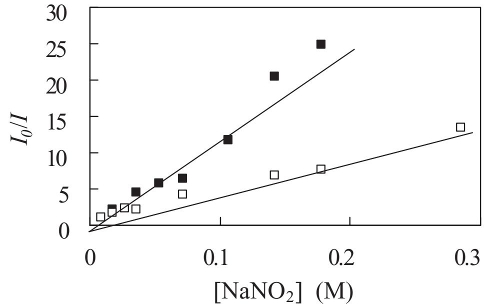

**Figure 3.** Dependence of $I_0/I$ on quencher concentration for luminescence quenching in a $PyS^-$–$NO_2^-$ system in anion-conductive membranes (■) A-201 and (□) A-202. The concentration of $PyS^-$ is $8.8 \times 10^{-3}$ M.

the quenching rate is also affected by the diameter or structure of the nanochannels in an ion-conductive membrane. Although nanochannels in Nafion membranes and anion-conductive membranes should not be studied with the same criterion, the mobility of $NO_2^-$ in anion-conductive membranes is intermediate between the mobility of $MV^{2+}$ and $Cu^{2+}$ in Nafion membranes, and the order is interpreted to first approximation due to the ion size. Conversely, this order of ion mobility predicts that the size of nanochannels in the anion-conductive membranes is approximately identical with that in Nafion membrane.

## Conclusion

In the present study, we discuss the luminescence quenching of ruthenium complex–quencher systems in Nafion membranes and a $PyS^-$–$NO_2^-$ system in anion-conductive membranes. We conclude that ion mobility is more hindered in the nanochannels of an ion-conductive membrane than in the solution; the degree of hindrance depends on the relationship between the ion size and the diameter or structure of the nanochannels. This finding should be helpful in the design of polymer electrolytes for the development of high-performance MEAs of fuel cells.

From another viewpoint, we succeeded in detecting the ion mobility in the nanochannels of polymer electrolyte membranes, by applying conventional luminescence measurements. This analytical technique should be useful for estimating the diameter or structure of the nanochannels. Monte Carlo simulation studies of ions in the nanochannels will be undertaken to determine the nanochannel structure more precisely.

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