Influence of Immersion of Polyethyleneimine Thin Film Modified with Gold Nanoparticles in $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ Aqueous Solution on Redox Reaction on AuNPs

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ABSTRACT

The influence of immersion in a hexaammineruthenium chloride ($[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$) aqueous solution on the redox reaction on a polyethyleneimine (PEI) thin film modified with gold nanoparticles (AuNPs) is investigated for the electrochemical analysis of the conjugated reaction area of electronic and electrochemical conduction. The PEI thin film is electrodeposited on a glassy carbon (GC) electrode in an ethylenediamine acetonitrile solution. AuNPs were prepared by Frens's method and loaded onto the PEI thin film on the GC (GC/PEI) electrode. The redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ on AuNPs loads onto a PEI film on a GC (GC/PEI/AuNPs) electrode is observed by cyclic voltammetry and electrochemical impedance spectroscopy. The apparent electron transfer rate constant at a single AuNP, calculated from the charge transfer resistance and AuNP number density, increases during immersion of GC/PEI/AuNPs in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. It is suggested that the redox reaction occurs not only at the AuNPs by the tunneling effect, but also at the GC electrode due to the ionic transport of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ during the immersion in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. Care should be taken that the electrochemical reaction is measured as soon as possible when using PEI films before the electrolyte can penetrate the film completely, because the ionic conduction of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution in the PEI thin film cannot be ignored during immersion in the electrolyte solution.

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1. Introduction

Metal nanoparticles are utilized to increase the reaction area and the electrochemical activity for electrochemical reactions and can function as catalysts for fuel cells,^{1,2} electrolyzers,³ electrochemical sensors,⁴ and other applications. Not only metal nanoparticles, but nanoparticles made of metal oxides⁵ or semiconducting materials^{6,7} have also been studied in nanoelectrochemistry as single electron transfer media.⁸ However, such nanoparticles are unstable due to their surface activities, and ripening and coagulation phenomena usually occur.⁹ Therefore, in order to maintain their electrochemical activity, such particles are supported on a current collector such as a metal or carbon material with polymer materials as a binder; for example, polyvinylidene difluoride (PVDF) is used for various batteries¹⁰ and polytetrafluoroethylene (PTFE) is used for low-temperature fuel cells.^{11,12} Briefly, these systems can be classified as current collectors serving as electron transfer media, coated polymer materials serving as insulators, and nanoparticles serving as reaction media. From this viewpoint, composite electrodes or metal supported electrodes containing an insulator layer are located on the substrate and contain nanoparticles as the electron transfer material, which might be isolated spatially from the current collector; it is thought that these nanoparticles do not participate in the electrochemical reactions.

On the other hand, it is well-known that tunneling behavior can occur between isolated electron transfer materials separated by a few nanometers.^{13–26} If there are the insulating materials between the metal nanoparticles and current collectors, the nanoparticles can still be involved in the electrochemical reactions, even when isolated from the collectors. Here, there may be more electrical conduction routes than just direct contact with conductive materials.

Numerous studies have been carried out to understand electronic tunneling phenomena. In such studies, various kinds of precisely size-controlled molecular structures, such as self-assembled monolayers (SAMs)^{13–18,21} or metal oxide thin films deposited by electrodeposition^{22–25} and atomic layer deposition (ALD) processes²⁶ have been utilized. However, from a practical viewpoint, it might be interesting to use conventional polymer materials, such as polyethyleneimine (PEI), deposited on planar electrodes by electrochemical polymerization.^{27,28} PEI thin films can be easily prepared by electrodeposition in organic solvents containing ethylenediamine.^{27,28} Also, PEI thin films modified with metal nanoparticles are commonly used in applications including electrochemical catalysts^{29,30} and sensors.³¹ They are also used as model electrodes to investigate the electrochemical properties of nanoparticles.³² However, the structures of the electrodeposited PEI thin film on carbon electrodes are very complex in terms of the orientation of molecules in the thin film compared with SAMs.^{33,34} Because of the concern that ions can penetrate the PEI thin film, the durability of the thin film in the electrolyte solution influences the ionic transport, which is coupled with electron transfer at the nanoparticles deposited on the PEI thin film. In a previous study, Downard et al. reported that ionic permeation occurred in PEI thin films electrodeposited on glassy carbon (GC) electrodes only when the films were immersed in the electrolyte solution.³⁵ The durability of a barrier layer, such as a polymer thin film electrodeposited on the electrode, has not been taken into account when investigating electron transfer across polymer thin films modified with nanoparticles to the best of our knowledge.³² In such studies of tunneling behavior between isolated electron transfer materials, electrolyte solutions containing ferricyanide ions, $[\text{Fe}(\text{CN})_6]^{3-}$,^{13,14,16,17,21} and hexaammineruthenium ions, $[\text{Ru}(\text{NH}_3)_6]^{3+}$,^{15,18,24,32} are often uti-

lized, because of the highly reversible nature of their reactions. In such cases, the electrochemical reaction might also occur by ionic charge transfer between the isolated particles and the active surface coupled with electron migration via tunneling from the nanoparticles. It might be important to understand the reaction kinetics in such systems.

In this study, PEI thin films modified with gold nanoparticles (AuNPs) were immersed in an aqueous hexaammineruthenium chloride ($[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$) solution to study the effects of immersion on their redox reaction by the electrochemical analysis of the conjugated reaction area which is involved in electronic and electrochemical conduction. The redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ on Au nanoparticles loaded on PEI prepared by electropolymerization on GC electrodes was observed by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The durability of the PEI layer and reaction conditions governed by tunneling in the nanoparticles and ionic charge transfer were discussed based on the variations in the charge transfer resistivity.

2. Experimental

2.1 Preparation of PEI thin films electrodeposited on the electrode

PEI thin films were electropolymerized on GC electrodes (BAS Inc.), as reported elsewhere previously.^{28,29,32,35} The surface of the GC electrodes (diameter: 3 mm) was polished by diamond paste (mean particle size: ca. 1 μm) and alumina paste (mean particle size: ca. 0.05 μm). The polished surface was washed with distilled water and dried in atmosphere. The PEI thin film was electropolymerized in 9.0 mmol L⁻¹ ethylenediamine (EDA, Nacalai Tesque Inc.) in acetonitrile (AN, Nacalai Tesque Inc.) containing 0.1 mol L⁻¹ tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4 , Tokyo Chemical Industry Co., Ltd.) as a supporting electrolyte. The electrolyte solution was degassed by N_2 gas bubbling for 20 min prior to electrodeposition. During electrodeposition of PEI, the glass cell with a water jacket containing the electrolyte solution was purged by N_2 gas flow. An electrochemical analyzer (VoltaLab PGZ-402, Radiometer Analysis) was used for electrodeposition. The scanning potential ranged from 0 to +2.3 V vs Ag quasi reference electrode (QRE) in an anodic scan with a 40 mV s⁻¹ scanning rate. The current number density, j , was obtained from the measured current during the scanning potential. After electrodeposition, the electrode was sequentially rinsed with AN and water, and then dried in atmosphere. The electrodeposited PEI thin films on GC electrodes are referred to as GC/PEI $_x$ in which the number “ x ” denotes the number of electrodeposition cycles.

The optical thickness of the PEI thin films was obtained from ellipsometry using a JASCO M-220K ellipsometer. PEI was deposited on Si wafers as well as on GC surfaces for electrochemical deposition. The PEI films were irradiated with a He-Ne laser ($\lambda = 632.8 \text{ nm}$) at a 45 degree incident angle. The obtained optical parameters were simulated by the complex diffraction index using the optical constants of refractive index (n) and extinction coefficient (k) as follows: $n = 3.865$, $k = 0.020$ for Si substrate, $n = 1.50$, $k = 0$ for SiO_2 oxidized surface layer, and $n = 1.45$, $k = 0$ for deposited PEI.

2.2 Modification of AuNPs on the PEI thin film electrodeposited on the electrode

AuNPs were synthesized from an HAuCl_4 solution by Frens's method.³⁶ Four milliliters of a 1 wt% sodium citrate (Nacalai Tesque Inc.) aqueous solution as a reductant reagent was added to 100 mL of a 1 mmol L⁻¹ HAuCl_4 (Nacalai Tesque Inc.) solution in a three-neck flask with an Allihn reflux condenser, which was held in a heating oil bath at 98°C while being stirred by a magnetic stirrer. A solution with dispersed AuNPs was obtained after 15 min of

reducing reaction. The size distribution of the obtained AuNPs was determined by field emission transmittance electron microscopy (FE-TEM; JEOL JEM2100F). The mean particle size of used AuNPs for surface modification of GC/PEI electrode was $38 \pm 6 \text{ nm}$.

The electrodeposited PEI thin films on GC electrodes were immersed in the dispersed AuNP solution for 5–120 min.

The temperature was kept at 25°C. After modification, the electrode was rinsed with water carefully and was dried in atmosphere. The surface of the PEI thin film modified with AuNPs on the GC electrode was observed by field emission scanning electron microscopy (FE-SEM) JEOL JSM-6335F with an accelerating voltage of 15 kV. The number of AuNPs was counted in the SEM images to estimate the number density, Γ , of AuNPs. The electrodeposited PEI thin film (GC/PEI10) modified with AuNPs on the GC electrode is designated as GC/PEI10/AuNPs.

In order to confirm the existence of the PEI thin film on the GC electrode, X-ray photoelectron spectroscopy measurements (XPS, JPS-9010MC, JEOL Ltd.) were carried out using an Al-K α X-ray source (1486.6 eV).

2.3 Electrochemical analysis of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox reaction

An electrolyte solution containing $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ (Mitsuiwa Chemicals Co., Ltd.), phosphate buffer solution (pH 7), and Na_2SO_4 (Nacalai Tesque) was used for electrochemical reactions on the GC/PEI electrodes. The concentrations of $[\text{Ru}(\text{NH}_3)_6]^{3+}$, PO_4^{3-} , and SO_4^{2-} were 1, 10, and 200 mmol L⁻¹, respectively. The phosphate buffer solution was prepared from equimolar mixed salts of NaH_2PO_4 (Nacalai Tesque) and Na_2HPO_4 (Nacalai Tesque). The electrolyte solution is denoted as the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution as necessary. An electrochemical analyzer (VoltaLab PGZ-402, Radiometer Analysis) was used for electrochemical measurements of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ redox reaction. The reference electrode consisted of an Ag/AgCl electrode in a 3 mol L⁻¹ NaCl aqueous solution using BAS RE-1B with a glass separator. A Pt wire was used as a counter electrode.

In order to confirm the durability of the PEI thin film in solutions, cyclic voltammetry in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution was carried out while repeatedly immersing the GC/PEI electrode in pure water or $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The potential scanning from +300 to -500 mV (vs Ag/AgCl) in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution was carried out ten times. The scanning rate was 100 mV s⁻¹. After cyclic voltammetry, the PEI thin film on the electrode was immersed in pure water (Scheme 1(i)) or a 1.0 mmol L⁻¹ $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution (Scheme 1(ii)) for 30 min. Also, pure water was prepared using distilled water production equipment (GSH-200 and RFD240RA, AVANTEC). Ten scans were carried out in every 30 min immersion period 5 times during the cyclic voltammetry experiments, as shown in Scheme 1(i) and 1(ii).

EIS with potential scans of cyclic voltammetry in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution was carried out to obtain the charge transfer resistance (R_{ct}) of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ on the PEI thin films modified with AuNPs during immersion in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The frequency range of EIS was from 100 kHz to 0.1 Hz. The amplitude of the impedance measurement was 10 mV. The potential for EIS was -210 mV corresponding to the original midpoint potential in the redox of $[\text{Ru}(\text{NH}_3)_6]^{3+}$. After EIS, the potential was returned to -500 mV (vs Ag/AgCl) and 10 cyclic voltammetry scans were carried out from -500 mV to +300 mV (vs Ag/AgCl). EIS was conducted for 10 cycles with 10 scans of cyclic voltammetry in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution as shown in Scheme 1(iii). The results shown in Fig. 5, as discussed later, obtained using the experimental procedures outlined in each scheme are also represented in Scheme 1.

A summary of the various electrochemical experimental conditions and sample conditions is shown in Table 1. In order to discuss the influence of immersion in ionic electrolyte species containing $[\text{Ru}(\text{NH}_3)_6]^{3+}$, the PEI thin film was immersed in pure

Scheme 1. Schemes of the electrochemical measurement; 10 times scan in cyclic voltammetry of GC/PEI10 for every 30 min of the immersion time for 5 times in (i) pure water and (ii) $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. (iii) 10 times EIS with 10 scans of cyclic voltammetry in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The result obtained in the experimental procedure with each scheme is also represented.

Table 1. Summary of the experimental conditions in the cyclic voltammograms in various conditions in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution using GC/PEI10 and GC/PEI10/AuNPs.

Condition	Solvent	PEI	AuNPs	EIS
(a)	Pure water	✓		
(b)	$[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution	✓		
(c)	$[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution	✓		✓
(d)	$[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution	✓	✓	
(e)	$[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution	✓	✓	✓

Solvent; the solution where the sample electrode is immersion. EIS; the electrochemical impedance spectroscopy is carried out during the immersion in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. (See in Scheme 1(iii)).

The alphabets in column of condition in Table 1 correspond to Figs. 5a–e.

water repeatedly and cyclic voltammetry measurements of the PEI thin film were carried out in a 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. This experimental condition is referred to as (a). In addition, a PEI thin film was immersed in an $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution repeatedly and cyclic voltammetry measurements of the PEI thin film were carried out in a 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, referred as (b). Next, cyclic voltammetry measurements of the PEI thin film were carried out in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, while EIS measurements were carried out during the immersion in a 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution in order to discuss the influence of the electrochemical perturbation on the ionic transport of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in the PEI thin film, referred to as (c). The AuNP-modified PEI thin film on a GC electrode was immersed in a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution and cyclic voltammetry was carried out in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, referred to as (d), in order to discuss the influence of AuNPs on ionic transport in the PEI thin film. Furthermore, cyclic voltammetry measurements of the PEI thin film modified with AuNPs were also carried out in a 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution and EIS measurements were obtained during the immersion in the 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution in order to discuss the influence of AuNPs and the electrochemical perturbation of ionic transport of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in the PEI thin film, referred to as (e).

GC/PEI10/AuNPs (AuNP number density, $\Gamma = 12 \mu\text{m}^{-2}$) was immersed into a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution repeatedly and cyclic voltammetry was carried out according to the procedure of Scheme 1(ii). The AuNP number density was estimated from SEM observations.

The current number density, j , was obtained from the measured current during the scanning potential experiments. It was noticed that the first measurements of cyclic voltammetry and EIS for each procedure in Scheme 1 should be started simultaneously while dipping the electrode into the electrolyte solution in order to avoid the influence of the penetration of the electrolyte solution.

3. Results and Discussion

3.1 Reversible redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in cyclic voltammetry and EIS repeatedly

Figures 1a and 1b show the cyclic voltammograms and Nyquist plots of the bare GC electrode in a 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution using the measurement procedure of Scheme 1(iii). It is well-known that $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions react reversibly. The sweep number is defined as the cyclic voltammetry scan number. As shown in Fig. 1a, all the cyclic voltammograms were those of an ideal reversible redox reaction, because the peak-to-peak potential difference was almost 60 mV. The redox reaction maintained its reversibility in repeated cyclic voltammetry and EIS measurements. The solution resistance (R_{sol}) was 60Ω in Fig. 1b. The semicircle due to the charge transfer resistance was almost not observed in repeated CV and EIS measurements, because the charge transfer process is very fast and the ideal reversible redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was maintained.

3.2 Electropolymerization and characterization of PEI on GC electrode

Figure 2 shows the cyclic voltammogram obtained during the electropolymerization of a PEI thin film recorded over 10 cycles of potential scanning. Ag QRE was calibrated by the CV of 10 mmol L^{-1} ferrocene in an AN-containing 0.1 M Bu_4NBF_4 solution, as shown in the inset. The electrochemical reaction of ferrocene is reversible with a formal potential = 380 mV; the potential is close to the previously reported value (400 mV).³⁷ In this experiment, the anodic peak appeared at ca. 1.5 V vs Ag QRE in the first cycle and the intensity of the peak rapidly decreased until the peak was eliminated. In the case of the preparation of a GC/PEI electrode, it is important to maintain the insulating condition of the PEI layer. For this purpose, we confirmed the conductivity of the GC/PEI electrode in a $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ solution, and the results are discussed later. In any case, most samples had insulating PEI surfaces after at least 10 scanning procedures.

Figure 3 shows the variations in the integrated intensity of the N1s peak as a function of the electrodeposition cycle. XPS spectra in the N1s region of the electrodeposited PEI thin film on GC electrode are inserted in Fig. 3. The peak at 399.6 eV which appeared after

Figure 1. Reversible redox reaction in $1.0 \text{ mmol L}^{-1} [\text{Ru}(\text{NH}_3)_6]^{3+}$ solution on GC electrode (a) the cyclic voltammograms are shown at 1st, 20th, 40th, and 90th sweep number. Scanning rate is 100 mV s^{-1} . (b) Nyquist plots are shown at 0th, 20th, 40th, and 90th sweep number. The electrochemical measurement is carried out in Scheme 1(iii). Open symbols show the impedances at each decade. The immersion time in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during the measurements is represented in bracket.

Figure 2. Cyclic voltammogram of electrodeposition of EDA in 10 cycles in 9.0 mmol L^{-1} EDA in AN containing $0.1 \text{ mol L}^{-1} \text{Bu}_4\text{NBF}_4$. Scanning rate is 40 mV s^{-1} and scanning potential range is $0 \rightarrow +2.3 \text{ V}$ (vs Ag QRE). The numbers are denoted as the electrodeposition cycles in figure. Inset represents the cyclic voltammogram of 10 mmol L^{-1} ferrocene in AN containing $0.1 \text{ mol L}^{-1} \text{Bu}_4\text{NBF}_4$ on bare GC electrode. The reference electrode is Ag QRE. Scan rate is 100 mV s^{-1} .

electrodeposition was assigned to PEI. The N1s peak was confirmed after only the first cycle of electrodeposition, and the peak intensity slightly increased even as more cycles of electrodeposition were performed. The integrated intensity increased during the first cycle of electrodeposition and was nearly constant after two cycles of electrodeposition. It is suggested that PEI thin film almost covered the GC electrode during the first cycle and only slightly more PEI was deposited after two cycles.

To confirm the insulating properties of the electrodeposited PEI thin films in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, cyclic voltammograms of the electrodeposited PEI thin films on GC electrodes (GC/PEI x) are shown in Fig. 4. The cyclic voltammograms are 1st sweep curve in Scheme 1(iii). The redox current of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was observed in GC/PEI1. It is suggested that there are some defects in the electrodeposited PEI thin film with 1 electrodeposition cycle, as $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is reached and reacted at the GC electrode. In the previous report, the redox current of $[\text{Ru}(\text{NH}_3)_6]^{3+}$, especially the cathodic current, was observed from the PEI thin film electro-

Figure 3. Variation of the integrated intensity in N1s region against the electrodeposition cycle. Inset; XPS spectra of bared GC and GC/PEI1, 2, 5, and 10 in N1s region.

Figure 4. Cyclic voltammograms of GC/PEI1, 5, and 10 in $1 \text{ mmol L}^{-1} [\text{Ru}(\text{NH}_3)_6]^{3+}$ solution at 1st sweep (Scheme 1(iii)). Scan rate is 100 mV s^{-1} . The black dash line is $0 \mu\text{A cm}^{-2}$ in each cyclic voltammogram.

deposited on a GC electrode in the first few electrodeposition cycles.³² Whereas there is a possibility that the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ occurs at the GC electrode with the PEI thin film electrodeposited after 1 cycle, the redox current was hardly confirmed in GC/PEI10. GC/PEI10 is suitable for examining the electrochemical activity of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ on PEI thin films modified with nanoparticles because there is enough insulation from the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The thickness of the PEI thin (GC/PEI10) film was estimated to be 2.9 nm by ellipsometry.

3.3 CV measurements for comparison of sample durability for GC/PEI10 and GC/PEI10/AuNPs

The cyclic voltammograms for the redox reaction of 1 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution under various circumstances using GC/PEI10 and GC/PEI10/AuNPs electrodes are shown in Fig. 5. The letters in the column marked “condition” in Table 1 correspond to each Figure in Fig. 5a–e.

As shown in Fig. 5a for which electrode was penetrated in water during interval time, small redox peaks of the reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ complex were observed in the initial state and the intensity of the reduction peak rarely increased as the measurements were repeated every 30 min. On the other hand, the intensity of the redox peak gradually increased as the measurements were repeated for Fig. 5b. For the measurement of CV with EIS as shown in Fig. 5c, the intensity of the redox peak also gradually increased as the measurements were repeated as similar as the results of Fig. 5b. It is suggested that the penetration of ionic species into the PEI thin film is not influenced very much by potential scanning with the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$, which only occurs when the PEI thin film is immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. In order to compare the results with the existence of AuNPs, the changes of cyclic voltammogram of GC/PEI10/AuNPs (AuNP number density, $\Gamma = 12 \mu\text{m}^{-2}$) are shown in Fig. 5d. The redox current of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ increased, compared to that in the absence of AuNPs (Fig. 5b). It is suggested that electrons can be transferred between AuNPs and the GC electrode owing to the tunneling effect, and that the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ occurs at the AuNPs. The redox current of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ also gradually appeared with an increase in immersion time in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. Thus, ionic penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ into the PEI thin film occurred in the PEI thin film modified with AuNPs. The same GC/PEI10/AuNPs electrode was also immersed in a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during all measurements with an impedance measurement for Fig. 5e according to the procedure of Scheme 1(iii). In this case, the intensity of the redox peak also gradually increased as the measurements were repeated, and the change in the redox peak is similar to that observed with no EIS measurements during the immersion in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution (Fig. 5d). Therefore, it is suggested that the penetration of ionic species into PEI thin films is not influenced very much by the electrochemical perturbation, while the penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ only occurs when the PEI thin film is immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution.

Considering the data in Fig. 5, we suggested that the penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ into the electrodeposited PEI thin film and the PEI thin film modified with AuNPs can occur under various conditions, as shown in Scheme 2. When the PEI thin film on the GC electrode is immersed in pure water and then immersed in a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution only during electrochemical measurements, corresponding to the procedure in Scheme 1(i), $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetrates slightly the PEI thin film because the PEI thin film is immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution for a short time, as shown in Scheme 2(I), corresponding to Fig. 5a. On the other hand, when the PEI thin film on the GC electrode was immersed in a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, corresponding to the procedure in Scheme 1(ii) and 1(iii), $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is able to gradually penetrate the PEI thin film, as shown in Scheme 2(II). The corresponding results are shown in

Fig. 5b and c. In addition, as further discussed in the following section, with the modification of the PEI thin film by AuNPs, the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ occurs on AuNPs in the PEI thin film modified with AuNPs. During the immersion of the PEI thin film modified with AuNPs in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, $[\text{Ru}(\text{NH}_3)_6]^{3+}$ gradually penetrates the PEI thin film as shown in Scheme 2(III), corresponding to the results of Fig. 5d and e.

If the intensity of the redox current is larger for thinner PEI thin films during immersion in solutions, it is expected that the change in the redox current when the PEI thin film is immersed in pure water is similar to that when it is immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. But the redox current when the PEI thin film is immersed in pure water (Fig. 5a) did not increase significantly compared to the current observed when it was immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution (Fig. 5b). It is suggested that whereas the electronically insulating condition was maintained in the PEI layer during the measurements, the ionic species reached the GC electrode substrate after immersion in the electrolyte solution for ca. 30 min. Actually, during the operation for Fig. 5a, since the GC/PEI10 electrode was totally immersed in the electrolyte solution for 800 s ($= 8 \text{ sec} \times 2 \times 10 \times 5$) only, the penetration of the electrolyte might be avoidable. It is suggested that the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions slightly penetrated the electrode during immersion in the electrolyte solution. The oxidized species, $[\text{Ru}(\text{NH}_3)_6]^{3+}$, can be reduced on the electrode slightly, but the reduced species formed, $[\text{Ru}(\text{NH}_3)_6]^{2+}$, was removed during the immersion in pure water. Therefore, the intensity of the cathodic peak might be increased slightly in Fig. 5a.

Additionally, in order to confirm the effects of perturbation by electrochemical measurements using CV and EIS, the electrode was immersed in a 1 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during all measurements with the impedance measurement shown in Fig. 5c following the procedure of Scheme 1(iii). The indicated times in each index are the immersion periods in the electrolyte solution. In this case, the intensity of the redox peak also gradually increased as the measurements were repeated. It is suggested that the penetration of ionic species into the PEI thin film is not influenced very much by potential scanning with the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$, which only occurs when the PEI thin film is immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The oxidation current peak was not well defined compared to the reduction current peak in Fig. 5c. It is suggested that the behavior of ionic transport in the PEI thin films is different between the oxidized species, $[\text{Ru}(\text{NH}_3)_6]^{3+}$, and the reduced species, $[\text{Ru}(\text{NH}_3)_6]^{2+}$.

According to previous studies performed by Downard et al. using a hydroxymethyl ferrocene (FcOH) solution and a PEI insulating layer, the GC/PEIs electrode was immersed in a buffer solution and in a FcOH-buffer solution during the measurement period for the redox reaction of FcOH only.³⁵ This condition was similar to our experiment shown in Fig. 5a. Comparing with the previous case, it is suggested $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is hardly able to penetrate the PEI thin film in a short period, in contrast to the FcOH species. It is considered that not only does $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetrate the PEI thin film, but anions (such as Cl^-) also penetrate the PEI thin film to provide charge compensation. Thus, there are some barriers to the penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$. On the other hand, FcOH is a neutral molecule and is thought to penetrate the thin film alone.

We also investigated the difference in the ionic penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ into PEI thin films in the presence of AuNPs on the PEI thin film. The redox currents in GC/PEI10/AuNPs (Fig. 5d) are larger than those in GC/PEI10 (Fig. 5b) for each immersion time. This suggests that the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ occurs at the AuNPs owing to nanoparticle-mediated electron transfer. The change in the cyclic voltammogram in the presence of AuNPs with respect to immersion time is similar to that observed without AuNPs. Therefore, it is suggested that the influence of AuNPs on ionic penetration into PEI thin films is negligible.

Figure 5. Cyclic voltammograms in various conditions in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution; (a) GC/PEI10 was immersed in pure water for 30, 60, 90, and 120 min (Scheme 1(i)) (b) GC/PEI10 immersed in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution for 30, 60, 90, and 120 min (Scheme 1(ii)) (c) GC/PEI10 in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during all measurements with an impedance measurement (Scheme 1(iii)). (d) GC/PEI10/AuNPs was immersed in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution for 30, 60, 90, and 120 min (Scheme 1(ii)). (e) GC/PEI10/AuNPs in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution (Scheme 1(iii)). In (c) and (e), sweep number denotes the scan number in cyclic voltammetry and the immersion time in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during the measurements is also represented in bracket. The black dash line is $0 \mu\text{A cm}^{-2}$ in each cyclic voltammogram.

Nyquist plots corresponding to Fig. 5c and the inverse values of calculated charge transfer resistance ($1/R_{ct}$) are shown in Fig. 6. The values of $1/R_{ct}$ were obtained from the semicircular shape in the results of Fig. 6a, which increased as the sweep number was gradually increased. These values correspond to the intensity of the redox peaks in Fig. 5c as shown in Fig. 6b. It is suggested that the current in the redox peaks is caused by the reaction of penetrated

electrolyte solution into PEI layer on the GC substrate, as shown in Scheme 2(II).

Here, ionic species can transfer into the PEI thin film in small amounts, and it was found that the measurement of the electrochemical reaction which relies on tunneling across the insulating PEI should be carried out within 30 min. The historical influence of the electrochemical reaction on the GC/PEIs electrode might not be

Scheme 2. Schematic of the penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in the PEI thin film electrodeposited on GC electrode (I) The PEI thin film on GC electrode is immersed in pure water and immersed in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution only during electrochemical measurement, corresponding to Fig. 5a. (II) The PEI thin film on GC electrode is immersed in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, corresponding to Figs. 5b and c. (III) The PEI thin film modified with AuNPs is immersed in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is not only at AuNPs by tunneling effect but also GC electrode by penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$, corresponding to Figs. 5d and e. The alphabets in the bottom of the each scheme denote the corresponding results in Fig. 5.

Figure 6. (a) Nyquist plots of GC/PEI10 in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution at 0th, 20th, 40th, and 90th sweep, corresponding to the Fig. 5c. Open symbols show the impedances at each decade. The immersion time in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during the measurements is represented in bracket. (b) The inverse of the charge transfer resistance ($1/R_{\text{ct}}$) calculated from the Nyquist plots in Fig. 6a are plotted as a function of sweep number.

taken care very much. The following discussion of GC/PEIs with loaded gold nanoparticles will consider the circumstances of limited immersion time in the electrolyte solution, which was indicated by the redox peaks.

3.4 Durability of the PEI thin film modified with AuNPs on GC electrode

TEM images of AuNPs, their size distribution, SEM images of

the PEI thin film modified with AuNPs (GC/PEI10/AuNPs) with adsorption times from 5–120 min, and the size distribution of the AuNPs adsorbed on the GC/PEI electrode surface are shown in Fig. 7. The mean particle size of the AuNPs in this study was $38 \pm 6 \text{ nm}$, as shown in Fig. 7b. Since the mean particle size of adsorbed AuNPs was similar to the original distribution, this value was used for the calculation of reaction area on the surface of Au particles.

Figure 7. (a) TEM image of the synthesized AuNPs. (b) The histogram of particle size of AuNPs in TEM images. (c)–(f) SEM images of GC/PEI10/AuNPs. The adsorption time of GC/PEI10/AuNPs in AuNPs dispersed solution is (c) 10, (d) 20, (e) 30, and (f) 120 min, respectively. The AuNPs number density (Γ) is calculated from SEM images. Γ is (c) 11, (d) 14, (e) 21, and (f) $32 \mu\text{m}^{-2}$.

Adsorbed AuNPs were dispersed uniformly on the PEI thin film, although partial aggregation was observed sometimes, as shown in Figs. 7c–f. The number density of AuNPs, Γ , gradually increased with the adsorption time, and the Γ value reached to ca. $40 \mu\text{m}^{-2}$, which is similar to the number that was reported in the previous study.³²

Cyclic voltammograms of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution with GC/PEI10/AuNPs are shown in Fig. 8 following the procedure of Scheme 1(iii). The cyclic voltammograms at the 1st and 90th sweeps are shown in Figs. 8a and 8b, respectively. The redox currents at the 1st sweep obviously increased after modification with AuNPs, which can be seen by comparing with the results of Fig. 5c. The thickness of the PEI thin film was estimated to be ca. 3 nm by ellipsometry. Thus, electrons can be transferred between the AuNPs and the GC electrode in this range of thickness, as attested by previous studies.^{19,26,32} It is suggested that the redox reaction on the surface of the AuNPs might be caused by electron transfer between nanoparticles and the GC electrode via tunneling, based on the result

in Fig. 8a. Here we should compare with the results of Fig. 5a. The possibility that the aqueous solvent of the AuNP dispersion solution may penetrate the PEI thin layer, which might cause the increase in the anodic current in Fig. 8a, is rejected. This is because there is no effect of the aqueous solvent, even when the GC/PEI electrode was immersed in water for 120 min, as shown in Fig. 5a. Although the redox current is small in the case of AuNPs number density $\Gamma = 11 \mu\text{m}^{-2}$, the reduction current is still larger than that of the electrodeposited PEI thin film during immersion in pure water.

The redox current is larger for the GC/PEI/AuNPs electrode with a large AuNP number density. In this case, since the reaction area on the surface of the AuNPs on the PEI thin film might be larger, it is necessary to normalize the surface area of the nanoparticles geometrically. This is discussed in the following section.

In Fig. 8b, the redox current in the cyclic voltammograms of GC/PEI10/AuNPs at the 90th sweep is higher than that at the 1st sweep. In the electrodes with fewer AuNPs, the reaction area on the

Figure 8. Cyclic voltammograms of GC/PEI10/AuNPs and GC/PEI10 electrode at (a) 1st and (b) 90th sweep in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The AuNPs number density (Γ) on the PEI thin film on GC electrode is represented in figure. Scan rate is 100 mV s^{-1} .

Figure 9. (a) Typical Nyquist plots of GC/PEI10/AuNPs in case of $\Gamma = 14 \mu\text{m}^{-2}$ in 1.0 mmol L^{-1} $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution at 0th, 20th, 40th, and 90th sweep. Open symbols show the impedances at each decade. The immersion time in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution during the measurements is represented in bracket. (b) The inverse of the charge transfer resistance ($1/R_{\text{ct}}$) as a function of sweep number.

AuNPs where the redox reaction can occur by nanoparticle-mediated electron transfer is small. When immersed in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution for a longer time, the redox reaction occurs not only at the surface of the AuNPs due to the tunneling effect, but also at GC electrode via the penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$, so that the redox current at the 90th sweep is higher than that at the 1st sweep. It is suggested that the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ also occurs at the interface between AuNPs and the PEI thin film due to the penetration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ into the PEI thin film. However, in the case of $\Gamma = 32 \mu\text{m}^{-2}$, the redox current at the 90th sweep is slightly larger compared to that at the 1st sweep. It is suggested that the tunneling effect is enough to achieve current saturation, and it reached the level of that of the bare GC electrode as shown in Fig. 1a.

Variations in Nyquist plots and the inverse value of the charge transfer resistance R_{ct} , of GC/PEI10/AuNPs with sweep number are shown in Fig. 9, which can be compared with the results in Fig. 6 for GC/PEI10 electrodes with a AuNP number density $14 \mu\text{m}^{-2}$. The changes in the Nyquist plots in Fig. 9a obviously indicate the process of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetration into the PEI thin film modified with AuNPs during immersion in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. The semicircles assigned to the charge transfer resistance and Warburg impedance caused by diffusion on the electrode were confirmed in

all plots for each sweep number. The $1/R_{\text{ct}}$ values increased with sweep number for each value of AuNP number density, as shown in Fig. 9b. Compared to the result of Fig. 5b in which a GC/PEI electrode was used, the values of $1/R_{\text{ct}}$ are larger in Fig. 9b, even immediately after dipping and at increasing sweep numbers. It is suggested that the adsorbed AuNPs contribute as areas for both the redox reaction and electrical conduction to the GC substrate. Also, even though the PEI thin film was modified with AuNPs, $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetration in the thin film occurred similarly to the case of an unmodified PEI thin film, as shown in Fig. 6b. The difference is caused by the redox reaction on the AuNPs by nanoparticle-mediated electron transfer, and at the surface of the GC electrode by $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetration in the PEI thin film while immersed in a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, as shown in Scheme 2(III).

3.5 Influence of interparticle distance between AuNPs on kinetic parameter

In order to discuss the relationship between electron transfer and reaction area of the AuNPs, we calculated the kinetic parameter normalized by the number density and projected area of the AuNPs, and applied it to the effective redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions.

Figure 10. (a) Variations of the apparent electron transfer rate constant ($k^{\text{app}}_{\text{et AuNP}}$) in GC/PEI10/AuNPs as a function of sweep number. (b) Variation of $k^{\text{app}}_{\text{et AuNP}}$ at 0th sweep number against an interparticle distance between AuNPs.

Generally, the R_{ct} value is calculated by the following equation based on the limiting conditions of the Butler-Volmer equation which depend on the exchange current density, i_0 , as follows:

$$R_{\text{ct}} = RT/nFi_0 \quad (1)$$

where R , T , n , F are the gas constant, the absolute temperature, the number of exchanged electrons, and Faraday constant, respectively. The value of i_0 is defined as

$$i_0 = nFAk^0c \quad (2)$$

where A , k^0 , and c are the electrode surface area, the electron transfer rate constant at the equilibrium potential, and concentration of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions, respectively. Substituting Eq. (2) into Eq. (1) yields

$$k^0 = RT/n^2F^2R_{\text{ct}}Ac \quad (3)$$

In the case of using AuNPs on an insulating layer, such as SAMs and polymer thin films, the apparent electronic conduction should be considered, because it is not possible to clearly define the geometric conduction route of single electron transfer. Here, the rate constant of electron transfer is calculated. The apparent rate constant of electron transfer; k^{app} , instead of the electron transfer rate constant at the equilibrium potential, k^0 , is defined from the mean size of the AuNPs and their number density, Γ , among other parameters. Therefore, as in previous studies,^{13,14,16–18,21,32} the $k^{\text{app}}_{\text{et AuNP}}$ was calculated from the following relations. Equation (3) can be modified with k^{app} as follows:

$$k^{\text{app}} = RT/n^2F^2R_{\text{ct}}Ac \quad (4)$$

As a normalized apparent reaction rate constant for one AuNP, $k^{\text{app}}_{\text{et AuNP}}$ is calculated as follows:

$$\begin{aligned} k^{\text{app}}_{\text{et AuNP}} &= k^{\text{app}}/\Gamma\pi r^2 \\ &= RT/n^2F^2\Gamma\pi r^2R_{\text{ct}}Ac \end{aligned} \quad (5)$$

The dependence of $k^{\text{app}}_{\text{et AuNP}}$ on sweep number at different number densities is shown in Fig. 10a. The values of $k^{\text{app}}_{\text{et AuNP}}$ for each number density, Γ , have similar values and gradually increase with an increase in a sweep number.

Generally, the diffusion behavior of ionic species on the metal nanoparticles dispersed on a substrate as a current collector depended on the number density of the nanoparticles, in other words, the inverse of the interparticle distance.¹⁵ Also, the diffusion region of ionic species which react on a nanoparticle depends on the CV sweep rate, ranging from hemispherical diffusion to planar steady-state diffusion, for which the diffusion layers overlap with each other when the interparticle distance, d , is relatively small in

the case that the AuNP number density is large.¹⁵ The interparticle distance is calculated from the following equation on the assumption that nanoparticles are modified with hexagonal close packing:

$$d = (2\sqrt{3}/3\Gamma)^{1/2} - 2r \quad (6)$$

where r is the radius of the AuNPs. The variation in initial values of $k^{\text{app}}_{\text{et AuNP}}$ with d values are shown in Fig. 10b. The values of $k^{\text{app}}_{\text{et AuNP}}$ tend to increase with a small interparticle distance. The interparticle distance was in the range from 100 to 300 nm in this study. It is suggested that electrons cannot be transferred between AuNPs by the tunneling effect because the interparticle distance is too large. On the other hand, electron transfer between AuNPs and the GC electrode occurs because the thickness of the PEI thin film is ca. 3 nm, and the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ occurs at the AuNPs. Watanabe et al. suggested that the inactive area between nanoparticles was caused by the overlap of the diffusion layers, so that the electrochemical activity of the nanoparticles declined for small interparticle distances.³⁸ In the present work, the result in Fig. 10(b) seems to be different from that of Watanabe's report. The diffusion layer of each particle will overlap with each other when the interparticle distance satisfies the following relationship:^{15,39}

$$d < 12r \quad (7)$$

Then, the diffusion layer of each AuNP will overlap within an interparticle distance of $d < 228$ ($= 12 \times 19$) nm. In this study, the largest AuNP number density (Γ) was $40 \mu\text{m}^{-2}$ (interparticle distance; $d = 131$ nm) and this value of d reaches the same degree of the interparticle distance where the diffusion layer of each nanoparticle overlaps. It is difficult to discuss the influence of the overlapping of the diffusion layers on the electrochemical activity of AuNPs because there are small numbers of plots at a smaller interparticle distance where the diffusion layer can be overlapped. The influence of the diffusion layer around AuNPs on the electrochemical reactivity on AuNPs is thought to appear in the case of a very small interparticle distance between AuNPs. We will discuss the electrochemical behavior of AuNPs on the PEI thin films at shorter interparticle distances in detail elsewhere. In the case of a AuNP number density of $\Gamma = 8 \mu\text{m}^{-2}$ ($d = 340$ nm), the value of $k^{\text{app}}_{\text{et AuNP}}$ is very small compared with those values with more AuNPs. The small value of $k^{\text{app}}_{\text{et AuNP}}$ in the case of $\Gamma = 8 \mu\text{m}^{-2}$ was obtained because the prepared PEI thin film had a large film resistance and/or the modification of AuNPs was not uniform due to the small number density.

We need to discuss that the value of $k^{\text{app}}_{\text{et AuNP}}$ in GC/PEI10/AuNPs electrodes increases with an increase in sweep number. As discussed above, the value of R_{ct} changes during only immersion in

the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution due to ionic penetration. The value of $k_{\text{et AuNP}}^{\text{app}}$ is dependent not only on the charge transfer process between the redox species and AuNPs, which is due to nanoparticle-mediated electron transfer between AuNPs and the GC electrode via tunneling, but also strongly dependent on charge transfer at the GC electrode due to $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetration. Therefore, the determined value of $k_{\text{et AuNP}}^{\text{app}}$ did not represent the real electron transfer rate constant of AuNPs on the PEI thin film.

The obtained $k_{\text{et AuNP}}^{\text{app}}$ rapidly increased until 20 sweeps (corresponding to an immersion time of 25 min in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution), and gradually increased thereafter. It is suggested that the $k_{\text{et AuNP}}^{\text{app}}$ within 25 min of immersion time in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution approximately represents the electron transfer rate constant of AuNPs on the PEI thin film. This result indicates that the electrochemical reaction should be measured as soon as possible before penetration of the electrolyte solution for discussions of the tunneling effect using insulating polymer films.

4. Conclusion

The PEI thin films electrodeposited on GC electrodes were able to almost entirely block the electrochemical activity of the GC electrode during immersion in pure water. Therefore, electrodeposited PEI thin films on GC electrodes are durable in pure water. On the other hand, $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was able to penetrate the PEI thin film and react on the GC substrate electrode during immersion in a $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetration in the PEI thin film occurs without any electrochemical perturbation. The electrodeposited PEI thin film on the GC electrode was not able to passivate the electrochemical activity of the GC electrode due to $[\text{Ru}(\text{NH}_3)_6]^{3+}$ penetration. With the addition of AuNPs to the PEI thin film, the redox reaction mainly occurs at the surface of the AuNPs on the PEI thin film due to nanoparticle-mediated electron transfer via the tunneling effect, which occurs even for short immersion times in the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution. Thus, for studying the conjugated reaction area of electronic and electrochemical conduction on PEI thin films modified with AuNPs, the electrochemical measurements, such as cyclic voltammetry and impedance measurement, should be carried out immediately upon immersion in the electrolyte solution. In reactions for practical electrochemical devices, such as those involving composite electrodes, ionic penetration into the conventional polymer might provide greater electrochemical activity on the active materials by increasing the reaction area. When using insulating PEI films, care should be taken to ensure that the electrochemical reaction is measured as soon as possible before the electrolyte solution can penetrate the film completely, because the ionic conduction of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution in the PEI thin film cannot be ignored during electrode immersion in the electrolyte solution.

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