Effect of an Underlying Monolayer of a Nafion Film upon Redox Reaction of Methyl Viologen on a Au Electrode

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ABSTRACT

To explore the effect of the presence of a self-assembled monolayer (SAM) of an alkyl thiol derivative as an underlayer of a Nafion film, redox reaction of methyl viologen (MV) at the Au/SAM/Nafion (1 μm -thick) interface was characterized using the results of the voltammetric and electroreflectance measurements. The perfluorinated SAM slowed the kinetics of the interfacial electron transfer process compared to a Au/Nafion electrode, whereas 1-dodecanethiol SAM accelerated it. However, both the SAMs decreased the voltammetric current by half. Importance of the approach to underlay a SAM was discussed.

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Keywords : Methyl Viologen, Self-assembled Monolayer, Nafion Film, Electroreflectance

Nafion[®] is the most widely used functional cation exchange polymer for various applications such as proton transporting membranes, sensors, and supporting materials for catalysts. Nafion coatings on catalysts have been an important approach to enhance the activity and selectivity.^{1,2} When one needs to regulate the electron or proton transfer at a catalyst/Nafion interface, insertion of a self-assembled monolayer (SAM) in between would be an important method of choice. It would be as a promising mean to optimize the electron and proton transfer processes as well as film micro-structures. Cha et al. used an alkanethiol SAM on a Au electrode to reinforce the adhesion of the Nafion film without degradation of the redox of cationic species across the film.³ After their work, however, the merits and problems in the use of the electrode/SAM/Nafion structure and its electrochemical characteristics have been left unexplored.

A solid/Nafion interfacial structure depends on the chemical nature of the substrate and atmosphere for the processing. The examples include humidity dependent formation of an interlaminated structure of water-rich layers and fluoroalkyl phase layers on a SiO₂ hydrophilic surface,⁴ substrate surface chemistry dependent abundance and connectivity of water-filled proton conducting channels in Nafion films,⁵ and the effect of an *n*-octyltrichlorosilane layer on the orientation of the ion-channels.⁶ Most likely, a thin SAM underlayer also affects the properties and electrochemistry of a thick Nafion overlayer.

In this work, we explore the effect of the pre-modification of the electrode surface by SAMs before casting a Nafion film (ca. 1 μm -thick) upon the electrochemistry of cationic species.

Before casting Nafion on a polished polycrystalline Au electrode surface (0.0201 cm²), formed was one of the three SAMs of alkyl thiol derivatives: 1-decanethiol (C10-SH), ω -hydroxy-hexanethiol (HO-C6-SH), and 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (Perfluoro-C10-SH). HO-C6-SH was one of our choices because of its non-ionic hydrophilicity and affinity to Nafion especially at the ionic channel sites. The last one is used to see the perfluoro-interaction between the SAM and the perfluoro-phase region in the Nafion film in reference to our previous reports.^{7,8} The Au electrode was modified by a SAM in 1 mM ethanoic solution ($M = \text{mol dm}^{-3}$) of one of the three thiol compounds for 12 h. The Au/SAM/Nafion interfaces were characterized in the solution of methyl viologen (MV) as a redox probe by combined use of voltammetric and electroreflectance (ER)⁹ measurements. A Nafion 5 wt% solution and the three alkyl thiol derivatives were purchased from Sigma Aldrich. MV dichloride salt was home synthesized.

When casting Nafion dispersion, the Au/SAM was inevitably brought into contact with 2-propanol, because it is the solvent of the Nafion dispersion. To see whether the immersion in 2-propanol deteriorates the SAM, cyclic voltammograms (CVs) of the Au/SAM electrodes in 0.050 mM MV aqueous solution were measured before and after immersing the electrodes in 2-propanol for 2 h. A three-electrode configuration with a Ag|AgCl|sat'd KCl reference electrode and a coiled Au wire counter electrode was used under an Ar gas (>99.998 %) atmosphere at $25 \pm 2^\circ\text{C}$. The base supporting electrolyte was 0.10 M KCl prepared from reagent grade KCl (Nacalai) and Milli-Q water.

Figure 1. Time course CVs at Au/Nafion (a) and Au/SAM/Nafion systems (b and c) at $v = 200 \text{ mV s}^{-1}$.

Table 1. Characteristic of CV response in 0.05 mM MV solution at $v = 200 \text{ mV s}^{-1}$.

Before Nafion coating*			With Nafion coating**		
Electrode	$-i_{pc}/\mu\text{A}$	$\Delta E_p/\text{mV}$	underlayer SAM	$-i_{pc}/\mu\text{A}$	$\Delta E_p/\text{mV}$
bare Au	0.30	66	none	29	72
Au/C10-SH	0.29	65	C10-SH	15.5	57
Au/Perfluoro-C10-SH	0.22	86	Perfluoro-C10-SH	16.3	85

*Without immersion in 2-propanol. CVs of Au/SAM/MV solution are shown in Fig. S2.

**Data after saturation obtained in the same experiments in Fig. 2 (vide supra).

Immersion of a Au/HO-C6-SH electrode in 2-propanol turned out an approximately doubled CV peak current of the MV redox, a decrease in the separation between anodic and cathodic CV peak potentials (ΔE_p) from 69 to 63 mV at $v = 200 \text{ mV s}^{-1}$, and a tripled double-layer capacitance of $17 \mu\text{F cm}^{-2}$ at 0.1 V. The other two Au/SAM showed no apparent change in the same immersion test. We excluded the use of HO-C6-SH thereafter because of the instability of its SAM.

On a bare Au electrode and SAM-covered electrodes without pre-immersion in 2-propanol, Nafion film coating was made by casting 0.5 wt% Nafion/2-propanol solution and drying in air for 2 h to attain $1.0 \pm 0.2 \mu\text{m}$ dry-state thickness as measured by AFM (Fig. S1). The film showed a continuous and homogeneous light-interference pattern. Before use, the Nafion film on the electrode was swelled by immersing it in MV-free KCl solution. The time zero ($t = 0 \text{ min}$) was set when a Nafion-coated electrode was immersed in a pre-deaerated MV solution. At certain times, a single potential-cycle CV was recorded at $v = 200 \text{ mV s}^{-1}$. The details of the combined CV and ER train measurements were fully described in our previous reports.⁸

The time course CVs are shown in Fig. 1. In the first scan CV at Au/Nafion at $t = 2 \text{ min}$, a redox peak pair appeared with the midpoint potential, E_m , of -0.670 V of viologen radical cation/dication (V^{+}/V^{2+}) redox couple. Because a bare Au electrode gives $E_m = -0.623 \text{ V}$, the CV revealed no appreciable existence of pores, being far greater in size than ionic channels, in the Nafion film to give direct contact of the MV solution to the bare part of the Au surface. This was also the case for the Nafion overlayers on the SAMs (Fig. 1). Note that in the early stage after immersion, MV dication-sulfonate electrostatic attraction under small MV/sulfonate ratio shifts E_m to negative.

Table 1 shows the characteristics of CV before Nafion coating and after saturation with Nafion coating. All the voltammetric peak currents (represented by cathodic peak current, i_{pc} , in Table 1) were proportional to $v^{1/2}$, indicating that the redox reactions are largely controlled by diffusion. Before Nafion coating, the Perfluoro-C10-SH SAM showed a weak blocking against redox of MV, while C10-SH did not. Approximately 100 times as much reversible current response at Au/Nafion as at bare Au indicates that the product of MV concentration and the square root of the apparent diffusion coefficient, D_{app} , of MV in the Nafion film is 100 times greater than in solution, provided that the whole electrode surface area is active. Because D_{app} is four order of magnitude smaller in the film than in the solution,¹⁰ over two order of magnitude of MV concentration occurred in the present condition. Note that the diffusion layers develop only within the Nafion film in the present systems.⁸

Time course changes of $-i_{pc}$, ΔE_p , E_m , and the content of MV dimer (f_{dimer}) are shown in Fig. 2. As shown in Figs. 1 and 2, the CVs of three systems reached saturation in 150–250 min after immersion. From ER spectra (Fig. S3), we can calculate f_{dimer} as the number of viologen units in dimer of V^{+} relative to all the electroactive viologen units using the signals at 603 and 537 nm.¹¹

The pieces of important information in regard to the comparison of the three systems we obtained from these results include:

- (1) Almost the same f_{dimer} reveals nearly the same concentration of MV in the ionic channels.
- (2) The micro-environments for MV are also nearly the same because of the coincidence of the E_m values.
- (3) On the basis of ΔE_p , because diffusion coefficient of MV in the bulk of Nafion cannot be lowered by the insertion of the SAM, the interfacial electron transfer rate constant is greater for C10-SH but smaller for Perfluoro-C10-SH than that at Au/Nafion.

Figure 2. Characteristics of voltammetric response (a–c) obtained from the CVs and the fraction of viologen unit in dimer form (d) obtained from ER spectra for the three systems notified in the figure in 0.050 mM MV + 0.1 M KCl.

(4) Therefore, additionally taken the same level of saturated i_{pc} for the two SAMs, being about half of i_c at the Au/Nafion system, C10-SH accelerates the interfacial electron transfer but presumably reduces the number of ionic channels in the Nafion film in the proximity to the SAM surface. On the other hand, Perfluoro-C10-SH slows the interfacial electron transfer process but would increase the number of the channels. This may originate from the perfluoro affinity between the Perfluoro-C10-SH SAM terminal group and the perfluoro phase of Nafion, whereas the details should be clarified in due course. The surface chemistry-dependent growing of the covering area by the water-rich ion-channel on the electrode was reported by Ohira and colleagues.⁴ Our above-mentioned result is in line with the claim of Ohira and colleagues. The use of Perfluoro-C10-SH SAM for the reinforcement of the double layer structure does not negatively affect electron transfer processes in/through Nafion.

In summary, we have evaluated the effect of insertion of the SAMs in between the Au electrode surface and Nafion film on the redox processes of MV in the film using voltammograms and ER spectra. The time course of the redox response was monitored until saturation. We gained insights into the insertion effect on the density of active ionic channels and the heterogeneous electron transfer kinetics. We further need to shed light on the molecular level structure of SAM/Nafion interfaces in due course, because we found clearly the terminal group dependence in this preliminary study.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00132>.

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