

Voltammetric and Spectroelectrochemical Studies of Viologen Monolayers on Electrode Surfaces

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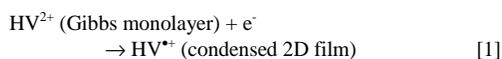
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We investigated the behavior of viologen monolayers at well-defined electrode surfaces. Our focuses include the anion effect on the electrochemistry of a self-assembled monolayer of a thiol-functionalized viologen (viologen-thiol) at an Au(111) electrode and the dynamics of faradaic phase transition of heptyl viologen at a highly oriented pyrolytic graphite (HOPG) electrode.

We previously demonstrated that a monolayer of a viologen-thiol, $C_5V^{2+}C_{11}SH$ (see Scheme 1), at a *poly-crystalline* Au electrode shows an anion dependent redox reaction¹ and that the monolayer memorizes the anion present during formation of the monolayer in an acetonitrile solution.² It is worthwhile to see the anion effect at a *single crystal* Au(111) electrode surface. At a better-defined Au(111) surface, we can describe the anion effect more clearly, because the heterogeneity of the film structure is largely eliminated. In fact, the properties of the viologen-thiol modified Au(111) electrodes were highly reproducible. The formal potentials obtained for the $V^{2+}/V^{•+}$ couple (E^{0*}) were summarized in Table 1. In KBr solution, the differential interfacial capacity at $E < E^{0*}$ is much smaller than that at $E > E^{0*}$, and that adsorption-desorption of Br⁻ takes place at positive potentials. This indicates that the monolayer is permeable to Br⁻ for it to adsorb on the exposed Au(111) substrate, confirming that even at a single crystalline surface, ingress/egress of anions into/from the monolayer occurs. The results of film transfer experiments (Table 1) revealed that the voltammetric behavior depends strongly on the history of the electrode, while the memory effect is weaker than that at a polycrystalline electrode.²

Viologens in aqueous solutions exhibit spike responses in cyclic voltammograms (CVs) at Hg and HOPG electrodes.³ We investigated the electrochemistry of a basal plane HOPG electrode horizontally touching a gas/heptyl viologen (HV) dibromide aqueous solution (G/S) interface.⁴ The spike response was observable only under restricted conditions. The experimental electroreflectance spectrum at the spike potential was agreed well with the simulated spectrum, indicating that the redox reaction of HV takes place at the spike potential and that HV^{•+} adsorbs onto the electrode surface in a non-upright orientation. The CV and potential step responses suggested that the kinetics of the spike response can be explained by a nucleation-growth-collision (NGC) mechanism. The transient of reflectance in response to the potential step synchronizes with the NGC current component. The plot of the charge as a function of the final potential in the potential step coulometry measurement exhibited a transition point at which the interconversion of the oxidation state amounts to more than half of the adsorbed viologen. The spike response was assigned as the first-order faradaic phase transition, presumably between a Gibbs monolayer and a Langmuir monolayer. The presence of the Gibbs monolayer of HV²⁺ at the G/S interface was supported by surface tension measurement.

The process giving the spike response is therefore represented by Eq. 1, though the possibility that the process represented by Eq. 2 can occur remains undened.



The decay time of the cathodic transients as the response of the potential step was shorter than the period required for the diffusion-controlled adsorption when the concentration of heptyl viologen was as low as 0.1 mM. Addition of a surfactant (tetradecyltrimethylammonium chloride) at a concentration much less than *cmc* strongly inhibited the sharp spike response in HV²⁺ 2Cl⁻ solution. These facts support the interpretation of the process of interest being represented by Eq. 1 rather than Eq. 2.

On a basis of Eq. 1, the CV wave may be understood in the context of a strong lateral interaction of viologen moieties in the monolayer. When the difference of cathodic and anodic transition potentials was adopted to the theory of voltammetry for an adsorption layer of the Frumkin-type, we obtain $a_R = a_{OR} + 5.2 = a_O + 7.7$ from the transition potentials and their temperature dependence, where a is the interaction parameter (if positive, the interaction is attractive).⁵ These values of a are indicative of two-phase equilibrium, in accordance with our interpretation as a phase transition.

Scheme 1: $C_5V^{2+}C_{11}SH 2PF_6^-$

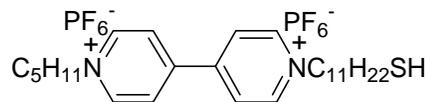


Table 1. Values of E^{0*} in various electrolyte solutions. The results of film-transfer experiments^a are also included.

E^{0*} / mV in 0.1 M electrolyte solutions					
Electrode-N ^b		Electrode-Br ^b			
1st	2nd	3rd	1st	2nd	3rd
KBr -329	KPF ₆ -515	KBr -369	KBr -345	KPF ₆ -511	KBr -370
KPF ₆ -514	KBr -364	KPF ₆ -518	KPF ₆ -517	KBr -402	KPF ₆ -521
KF -215	KBr -352	KF -224	KF -250	KBr -341	KF -283

^aThe initial cyclic voltammetry measurement was made in the 1st electrolyte solution, and sequentially transferred into the 2nd and 3rd electrolyte solutions. ^bElectrode-N was prepared in the absence of additive salt in an acetonitrile solution of viologen-thiol, while Electrode-Br was prepared in the presence of Et₄N⁺Br⁻.

References: 1) T. Sagara *et al.*, *Langmuir*, **15**, 3823 (1999). 2) T. Sagara *et al.*, *J. Electroanal. Chem.*, **500**, 255 (2001). 3) K. Arihara *et al.*, *J. Electroanal. Chem.*, **473**, 138 (1999). 4) T. Sagara *et al.*, *Langmuir*, **17**, 1620 (2001). 5) E. Laviron, *J. Electroanal. Chem.*, **63**, 245 (1975).