

## Voltammetric Study of Viologens Possessing Aromatic Groups on a HOPG Electrode Surface

Tomohiro Higashi, Takamasa Sagara\*

*Department of Applied Chemistry, Faculty of Engineering,  
Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan  
Tel: +81-95-819-2676, E-mail: sagara@nagasaki-u.ac.jp*

### Introduction

At a well-defined solid electrode surface in contact with an aqueous solution of viologens possessing long alkyl chains, a faradaic phase transition of the first order showing a nucleation-growth type current transient is observed [1]. This phase transition takes place between a gaseous expanded adsorption layer of oxidized form (dication:  $V^{2+}$ ) and a 2D insoluble condensed monolayer of one-electron reduced form (radical cation:  $V^{\bullet+}$ ). The transition is represented by sharp spike peaks in cyclic voltammograms (CVs). The behavior of this phase transition is governed by the strength of attractive interaction between radical cation molecules.

The aim of this work is at the elucidation of the phase change behavior of viologens possessing aromatic groups. We use dibenzyl viologen (1,1'-dibenzyl-4,4'-bipyridinium dichloride: dBV) and diphenyl viologen (1,1'-diphenyl-4,4'-bipyridinium dichloride: dPhV). We examined both viologens in regards to the effect of  $\pi$ - $\pi$  stacking in between molecules and also between HOPG and viologen molecules upon the phase change.

### Experimental

A basal plane HOPG electrode surface was brought into contact with dBV + KCl solution or dPhV + KCl solution to make electrochemical, electroreflectance (ER) and *in situ* electrochemical scanning tunneling microscopic (*in situ* EC-STM) measurements. These measurements were carried out by the use of an Ag/AgCl/sat'd KCl reference electrode in an Ar gas atmosphere at room temperature.

### Results and Discussions

The results of CV and potential step (PS) measurements enabled us to assign the monolayer redox process of dBV on a HOPG electrode to a faradaic phase transition of the first order. The current transients in response to PS exhibited nucleation-growth type curves. The peak separation of the CV response,  $\Delta E_p$  was 40 mV at a potential

sweep rate  $\nu = 70 \text{ mV s}^{-1}$ , being greater than that of heptyl viologens [1]. This fact suggests effective contribution of  $\pi$ - $\pi$  stacking interaction between one-electron reduced forms of dPhV to the increase in the width of bi-stable potential region of the phase transition.

In the case of dPhV, CVs depend strongly on  $t_w$  ( $< 30 \text{ min}$ ), where  $t_w$  is the time period spent after the contact of HOPG surface to  $0.3 \text{ mM dPhV} + 0.3 \text{ M KCl}$  solution until the start of potential sweep. This fact suggested the time change of the dPhV adsorbed films structure occurs on the HOPG surface. When repeating multiple potential sweeps, the cathodic peak I at  $-0.2 \text{ V}$  has increased while decreasing of the cathodic peak II at  $-0.3 \text{ V}$  (Fig. 1). When equilibration was reached at the potentials more negative than  $-0.2 \text{ V}$ , CV curve was superimposable to the finally converged one in Fig.

1. The value of  $\Delta E_p$  at  $\nu = 70 \text{ mV s}^{-1}$  for dPhV is almost comparable to that of HV [1], suggesting that the contribution of  $\pi$ - $\pi$  stacking interaction between molecules is minor. In the PS current transient curves, no signification of nucleation-growth-collision process was seen. In addition, the CV peak width of dPhV is wider than that of HV under the same condition. To attain the peak width near to that of HV, we need to set  $t_w < 3 \text{ min}$ , complete equilibration at the negative potentials, or the experience of multiple potential sweeps. These facts suggest that the redox mechanism of dPhV is different from that of viologens possessing long alkyl chains. We cannot, therefore, conclude as to whether dPhV exhibits the first order phase transition or not. We further need *in situ* observation of a molecular-level structure of the adsorption film. We are currently underway of *in situ* EC-STM measurements, especially in order for the adsorption structure of dPhV molecules to be figured out.

## References

- [1] K. Arihara, F. Kitamura, K. Nukanobu, T. Ohsaka, K. Tokuda, *J. Electroanal. Chem.*, **1999**, 473, 138.; T. Sagara, S. Tanaka, Y. Fukuoka, N. Nakashima, *Langmuir*, **2001**, 17, 1620.

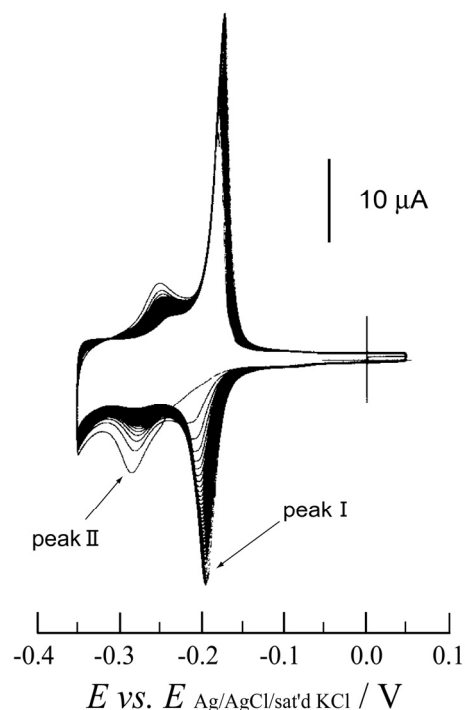


Fig. 1. Cyclic voltammogram of a HOPG electrode ( $A = 0.79 \text{ cm}^2$ ) on  $0.3 \text{ mM dPhV} + 0.3 \text{ M KCl}$  solution at  $\nu = 70 \text{ mV s}^{-1}$ .