Drastic Enhancement of Cycle Lifetime of Electrochromic Devices Using Polysilsesquioxane as an Anchoring Agent

Ichiro Imae,* Youichi Takenaka, Daisuke Tokita, Yousuke Ooyama,
Kenji Komaguchi, and Yutaka Harima
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University,
1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527

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Polysilsesquioxanes were obtained by hydrolysis of viologens having one or two triethoxysilyl groups, followed by their polycondensation, and anchored on the surface of an ITO electrode. The electrochromic properties of the polysilsesquioxanes were investigated and its component was optimized to enhance the cycle lifetime.

Electrochromism is the phenomenon of reversible color change in electrochemical redox reactions, and can be applied to smart windows and to automatic tint rear-view mirrors of automobiles.[1] Organic electrochromic materials are of interest due to the variety of possible chromophores and for their potential capability of multicolor display.[2] Among them, polymeric materials, e.g. polythiophenes and polyanilines as conducting polymers, are actively investigated, because they can easily form homogeneous and smooth films by coating their solution onto electrodes. However, there is a problem that polymeric materials peel off in solution when used for an extended period, because the organic polymers are incompatible with the inorganic electrode. This problem makes the polymer electrochemically inactive, and causes the low cycle lifetime of the devices. To overcome this problem, we focused on the reactivity of polysilsesquioxanes (PSQs). PSQs are well-known as an organic–inorganic hybrid polymer with a three-dimensional siloxane network, and can be easily synthesized by the hydrolysis of trialkoxysilanes having one organic substituent, followed by polycondensation of the formed silanols. Since PSQs also possess a silanol group at the terminal, it is expected that they can react with hydroxy groups on the surface of a metal–oxide electrode, such as ITO.[3] However, there is no report on the role of PSQs from the viewpoint of the cycle lifetime. Thus, in order to improve the cycle lifetime of electrochromic devices, we are studying the synthesis of PSQs having electrochromic chromophores and their electrochromic properties.

Here, we report the preliminary results of the electrochromic properties of PSQs containing viologen, which is the most widely studied as a typical electrochromic chromophores,[4] to justify our concept.

For the precursor of PSQs bearing viologen, 1-butyl-1′-[5-(triethoxysilyl)pentyl]-4,4′-bipyridinium dibromide (**1**) and 1,1′-bis[5-(triethoxysilyl)pentyl]-4,4′-bipyridinium dibromide (**2**) (Figure 1) were synthesized according to the Ref. 5 and characterized by ^{1}H NMR.[9] Hydrolysis and polycondensation of **1** and **2** were carried out in MeOH/MeCN (2/98 by volume) to form PSQ. By soaking ITO electrode in this solution, PSQ-coated ITO electrode was obtained.[6] For convenience, PSQ-coated ITO electrodes obtained from **1**, **2**, and their mixture were named as PSQ–**1**, PSQ–**2**, and PSQ–**12**, respectively.

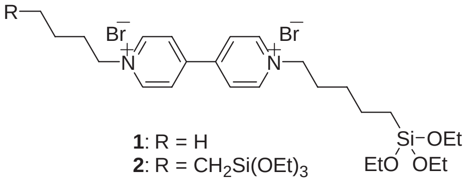

Figure 1. Chemical structure of viologens having triethoxysilyl group at the terminal of alkyl chain.

Cyclic voltammetry was carried out in an acetonitrile solution of tetraethylammonium perchlorate (0.1 M) acting as an electrolyte under Ar atmosphere, using a two-compartment cell equipped with PSQ-coated ITO, platinum plate, and Ag/Ag^{+}, as working, counter, and reference electrodes, respectively.

Figure 2 shows cyclic voltamograms of PSQ–**2**. In the first scan, one cathodic peak was observed at around -0.85 V vs. Ag/Ag^{+} due to the reduction of the dication to form radical cations of viologen, and the corresponding oxidation peak was observed at around -0.75 V vs. Ag/Ag^{+}. When the redox cycle was repeated, the redox peaks gradually became smaller. For the quantitative discussion, we estimate the ratio of cathodic peak current in the cycle number of n [$i_{pc}(n)$] to that in the first cycle [$i_{pc}(1)$] as the index of electrochemical activity, and found that $i_{pc}(10)/i_{pc}(1)$ and $i_{pc}(20)/i_{pc}(1)$ were 0.16 and 0.06, respectively. Even though the reaction time of polycondensation was elongated, the absolute value of $i_{pc}(1)$ was increased reflecting the formation of thicker films by longer reaction time, but the ratio of $i_{pc}(n)/i_{pc}(1)$ was not increased. An explanation for this may

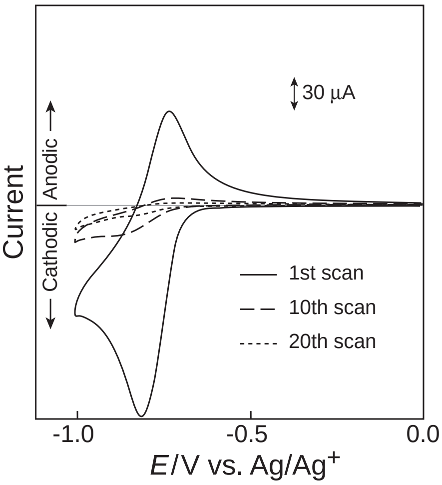

Figure 2. Cyclic voltamograms of PSQ–**2** (solid: 1st scan, dash: 10th scan, and dot: 20th scan).

be that the rigid PSQ network prevents the counter ions from injecting into the film. Once viologen is reduced to form radical cation, the counter anion is dedoped from the film and diffused away to the bulk of the electrolyte solution. However, the diffused anion will not be perfectly returned to the film because of the rigidity of polymer network. Thus, even though the redox potential was repeatedly applied, the actual redox reaction did not perfectly occur. Accordingly, the peak current became smaller reflecting the decrease of the concentration of the viologen dication.

To make the PSQ network more flexible, we tried to prepare the PSQ film from **1**, which has only one triethoxysilyl group. Cyclic voltamograms of PSQ–**1** showed almost reversible redox peaks.[9] However, the apparent surface of film was gummy, and a part of the film dissolved into the electrolyte solution during the measurement. Thus, even though the cycle lifetime was slightly improved compared with PSQ–**2**, the peak current ratio was not sufficiently improved [$i_{\mathrm{pc}}(10)/i_{\mathrm{pc}}(1)$ and $i_{\mathrm{pc}}(20)/i_{\mathrm{pc}}(1)$ are 0.54 and 0.21, respectively]. These results suggest that the reactivity of **1** is much lower than that of **2**, and that the cross-linked three-dimensional network is not fully expanded. To obtain an insoluble film, PSQ–**1** was annealed at 100 °C for 72 h, but the dissolution of the film was still observed.

To form a moderate PSQ film to be both flexible and insoluble, PSQ was prepared from a mixture of **1** and **2**. After optimization to form an insoluble film,[9] it was found that the feed ratio of **1**:**2** = 12:2 by mole gave the best results. Cyclic voltamograms of PSQ–**12** showed reversible redox peaks and their intensities were not changed during 10–20 cycles. This result was improved by lengthening the polymerization time from 3 to 12 h. Even after 100 and 200 cycles, the peak current ratio was found to be 0.93 and 0.88, respectively (Figure 3). In situ electronic absorption spectra of PSQ–**12**,[9] to which voltages at 0 and -0.9 V vs. Ag/Ag$^+$ were applied, showed typical color changes due to the redox reaction of viologens, which suggests that the introduction of PSQ does not affect the electrochemical and optical properties of the original viologen.

To confirm the effect of chemical bonding between PSQ and ITO electrode, we also synthesized poly([4,4′-bipyridinium]-1,1′-diyl-1,4-butanediyl dibromide) (PBV, $M_{\mathrm{n}} = 2800$ estimated by ^{1}H NMR) as a polymeric material which has no chemical bonding to the electrode,[7] and investigated its electrochromic properties.[9] During the redox cycles, it was observed that the polymer partially peeled off from the electrode. As a result, even though the redox cycles were reversible, the peak current ratio was gradually decreased [$i_{\mathrm{pc}}(10)/i_{\mathrm{pc}}(1)$ and $i_{\mathrm{pc}}(20)/i_{\mathrm{pc}}(1)$ are 0.70 and 0.59, respectively], which we ascribe to the electrochemical inactivity.

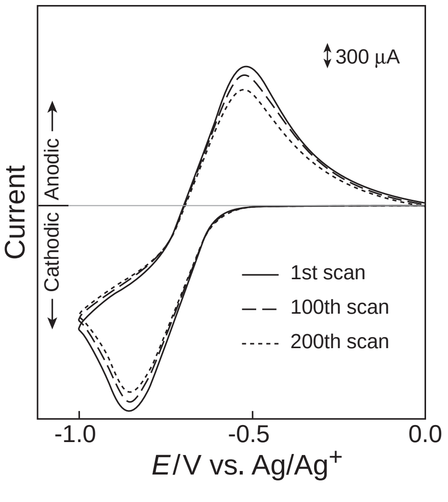

Figure 3. Cyclic voltamograms of PSQ–**12** (solid: 1st scan, dash: 100th scan, and dot: 200th scan).

The response time of color changes was determined by monitoring $\lambda_{\max}$ of absorption due to viologen radical cation (600 nm), and found to be 8 s (coloration) and 30 s (decoloration).[9] These values are much faster than those of low-molecular-weight viologens, such as 1,1′-dibutyl-4,4′-bipyridinium dibromide, and similar to those of PBV.

In conclusion, it is suggested that the introduction of chemical bonding between the electrochromic material and the electrode leads to an improvement of cycle lifetime due to the prevention of peeling off of the materials, and that the PSQ network needs to be flexible enough to enable the transport of the counter ions. These results give a useful basis to develop excellent electrochromic materials for a long cycle lifetime. However, cycle lifetime and response time are not sufficient for commercialization. This may be due to instability of the radical cation of viologen and the low electrical conductivity of film. For further improvement of electrochromic properties, we are trying to synthesize PSQ having other chromophores, such as oligothiophenes.[8] Also, we need to further investigate the effect of spacers, size of counter ions, and film thickness, and optimize them.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.