IMPROVING SPECTROELECTROCHEMICAL PROPERTIES OF POLYVIOLOGEN FILMS THROUGH ELECTROPOLYMERIZATION WITH FERROCYANIDE

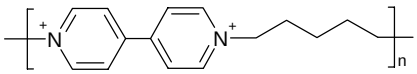
*Ying-Chan Hsu and Kuo-Chuan Ho**

Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan
**Corresponding author: E-mail: kcho@ms.cc.ntu.edu.tw; Fax: +886-2-2362-3040; Tel: +886-2-2366-0739.*

Introduction

Viologen is a well-known electrochromic species and electron transfer mediator due to its reversible redox behavior [1]. Recently, effort has been made to fabricate the modified electrode based on viologen films, like polyviologen-polyanion complexes [2-3], viologen-substituted conducting polymers [4], and electropolymerized films [5-6]. Although the polyviologen (PV) film electroreduced from monomers was successful [5], the spectroelectrochemical properties, including the charge capacity and absorbance, were less studied. In this study, it is suggested that the dimerization occurs during the electropolymerization of PV film and decreases the deposition efficiency. The dimerization of viologens to radical cation dimer often takes place in aqueous solution and results in the electrochemical irreversibility [1]. The electrodeposition efficiency and the electrochromic coloration efficiency could be increased if the dimerization is reduced.

Ferrocyanide acts as a charge transfer donor with the viologen [7] and forms a conducting bridge between two viologens [8]. It is believed that ferrocyanide can prevent the dimerization of viologen radical cation. In this study, the poly(butyl viologen) (PBV) film, **1**, was electropolymerized from bis(4-cyano-1-pyridino)butane dibromide on a conducting substrate. Encouraging by the improvement of ferrocyanide on the performance of a viologen-based device [8], this work is aimed at depositing a stable and high charge capacity PBV film with ferrocyanide (denoted by FeCN-PBV hereafter). In this paper, spectroelectrochemical properties of FeCN-PBV films, including the *in situ* dynamic and static optoelectrochemical characteristics and the coloration efficiency, are discussed.



Experimental

The indium tin oxide (ITO) conducting electrode was obtained from a local supplier (Ritek Co., Hsinchu, Taiwan), and the sheet resistance was around 30 /sq. PBV or FeCN-PBV films were deposited onto the ITO substrates (active area of 2.0×1.5 cm^2) by applying a constant potential of -0.75 V (*vs.* Ag/AgCl/Sat'd KCl) to a predetermined charge capacity and then stepping to 0 V for 5 min. The deposited charge capacities of both films were controlled either at 75 or 100 mC/cm^2 at -0.75 V. PBV film was electrodeposited from a solution containing 20 mM 1,4-bis(4-cyano-1-pyridino)butane dibromide, 50 mM KH_2PO_4 and 50 mM K_2HPO_4. 1,4-bis(4-cyano-1-pyridino)butane dibromide was synthesized from 4-cyanopyridine and 1,4-dibromobutane in acetonitrile [5]. For plating FeCN-PBV film, a concentration of 100 mM $K_4Fe(CN)_6$ was added to the above solution.

The three-electrode cyclic voltammetry (CV) was performed to characterize both PBV and FeCN-PBV films in 0.1 M KCl aqueous solution. The *in situ* spectroelectrochemical measurements for both films were recorded with a potentiostat/galvanostat (Autolab, model PGSTAT 30) and a spectrophotometer (Jasco, model V-570).

Results and Discussion

Figure 1(a) shows typical CVs for PBV and FeCN-PBV films obtained in a 0.1 M KCl electrolyte at a scan rate of 50 mV/s, respectively. The deposited charge capacities for both films were 75 mC/cm^2. It is

noticed from Fig. 1(a) that both anodic and cathodic current peaks of FeCN-PBV film were about twice as large as those of PBV film. The active charge capacity of FeCN-PBV film was determined from the CV and was found to be about twice as large as that of PBV film. The first cathodic peaks at –0.52 and –0.60 V, showing purple colors, correspond to the reduction of viologen di-cation unit to form radical cation unit. The second cathodic peaks at –0.95 and –1.17 V, showing brownish colors, correspond to the reduction of viologen radical cation unit to di-reduced species. The absorption spectra of PBV and FeCN-PBV films, at a potential of –0.6 V, were shown in Fig. 1(b). The spectra were confirmed as the radical cation of polyviologen [2-3, 5]. Obviously, the electropolymerization or electrodeposition efficiency of FeCN-PBV film was higher than that of PBV film.

Absorption spectra of FeCN-PBV film in a 0.1 M KCl solution, with reducing potentials varied from -0.2 to -1.1 V, were shown in Fig. 2(a). The absorbance at 535 nm increased when the potential was decreased to –0.8 V. When the potential is more negative than –0.8 V, the peak at 535 nm decreased but the absorption band at 405 nm increased. The color of FeCN-PBV film changed from dark purple to brownish, which was consistent with the CV results. Figure 2 (b) plots the absorbencies at 405 and 535 nm, obtained from Fig. 2(a), as a function of the applied potential. The results indicate that the radical cation unit of viologen was formed at –0.5 V and began to form di-reduced species at –0.9 V.

Figures 3(a) and 3(b) show the responses of the active charge capacity and the absorbance for a FeCN-PBV film cycled in a 0.1 M KCl solution under double potential-step switchings. The deposited charge capacity of the film was 100 mC/cm^2. The stepping conditions were –0.7 V for 10 sec and 0 V for 10 sec. The active charge capacity during bleaching at 0 V was about 1 mC/cm^2 less than that of darkening at –0.7 V. Presumably, the excess reduction charge is due to the reduction of dissolved oxygen in the solution by viologen radical cation [9]. The coloration efficiency of a FeCN-PBV film at 535 nm was about 140 cm^2/C, as calculated from Fig. 3.

To sum up, a stable, high charge capacity polyviologen thin film was electrodeposited successfully from viologen monomer-ferrocyanide complex. This is useful in practice for modified electrodes, including possible applications in electrochromic device and electron transfer mediator.

Acknowledgement

This research was supported by the National Research Council of the Republic of China under grant numbers NSC 91-2622-E002-006-CC3 and NSC 92-2623-7-002-005-NU.

References

[1] P. M. S. Monk, *The Viologens*, John Wiley & Sons, New York (1998).

[2] H. Akahoshi, S. Toshima, and K. Itaya, *J. Phys. Chem.*, **85**, 818-822 (1981).

[3] H. Kim and M. Pyo, *J. Appl. Electrochem.*, **30**, 49-53 (2000).

[4] C.-F. Shu and M. S. Wrighton, *J. Phys. Chem.*, **92**, 5221-5229 (1988).

[5] T. Saika, T. Iyoda, and T. Shimidzu, *Bull. Chem. Soc. Jan.*, **66**, 2054-2060 (1993).

[6] K. Kamata, T. Suzuki, T. Kawai, and T. Iyoda, *J. Electroanal. Chem.*, **473**, 145-155 (1999).

[7] A. Nakahara and J. H. Wang, *J. Phys. Chem.*, **67**, 496-498 (1963).

[8] P. M. S. Monk, *J. Electroanal. Chem.*, **432**, 175-179 (1997).

[9] P. Martigny and F. C. Anson, *J. Electroanal. Chem.*, **139**, 383-393 (1999).

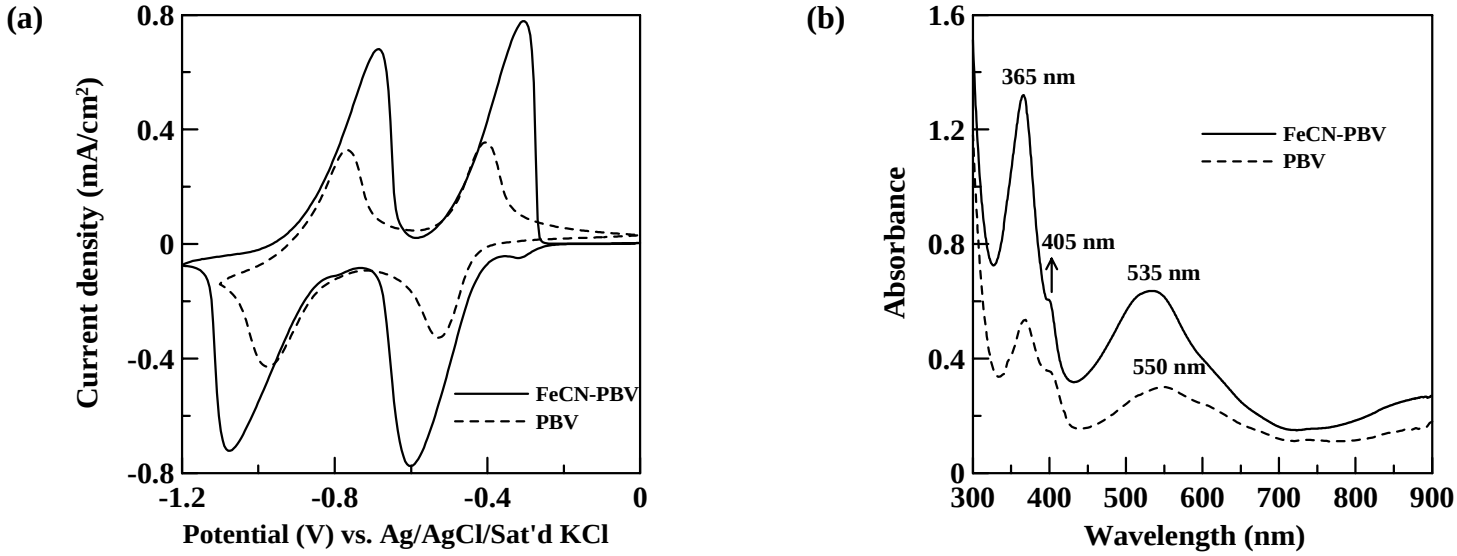


Fig. 1 *(a) Typical cyclic voltammograms of FeCN-PBV and PBV films in a 0.1 M KCl solution at a scan rate of 50 mV/s.*
(b) Absorption spectra of FeCN-PBV and PBV films measured at -0.6 V vs. Ag/AgCl/Sat'd KCl.

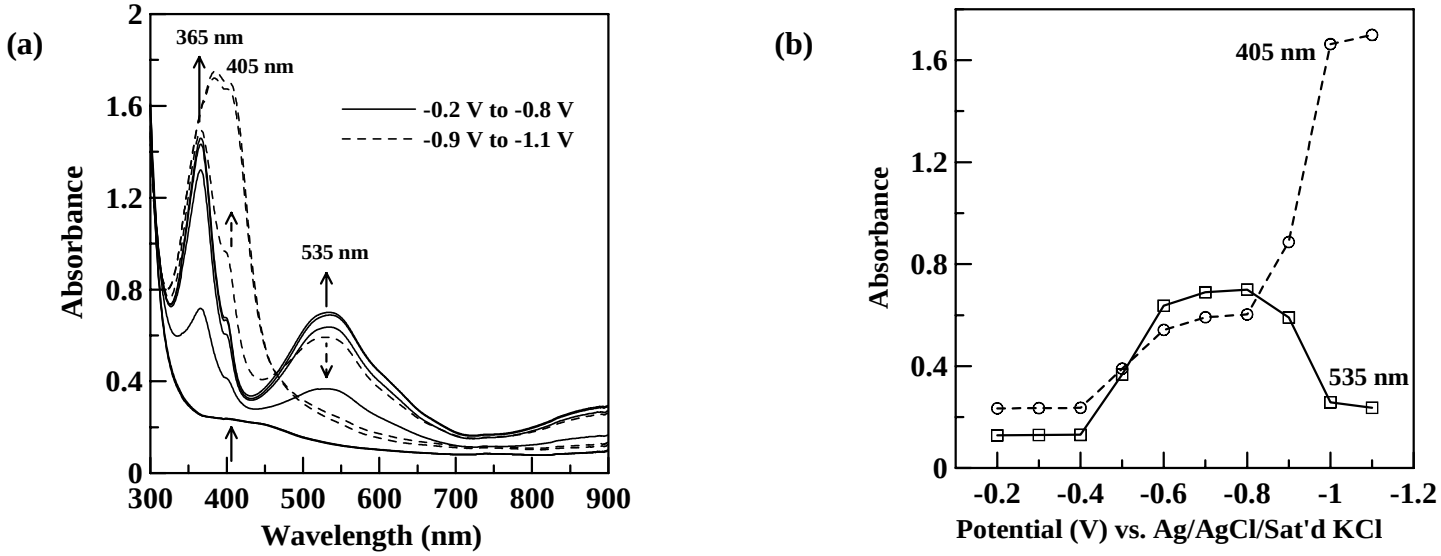


Fig. 2 *(a) Absorption spectra of FeCN-PBV film measured at different reducing potentials from -0.2 to -1.1 V vs. Ag/AgCl/Sat'd KCl in a 0.1 M KCl solution.*
(b) Absorbance at 405 (○) and 535 nm (□) as a function of the applied potentials.

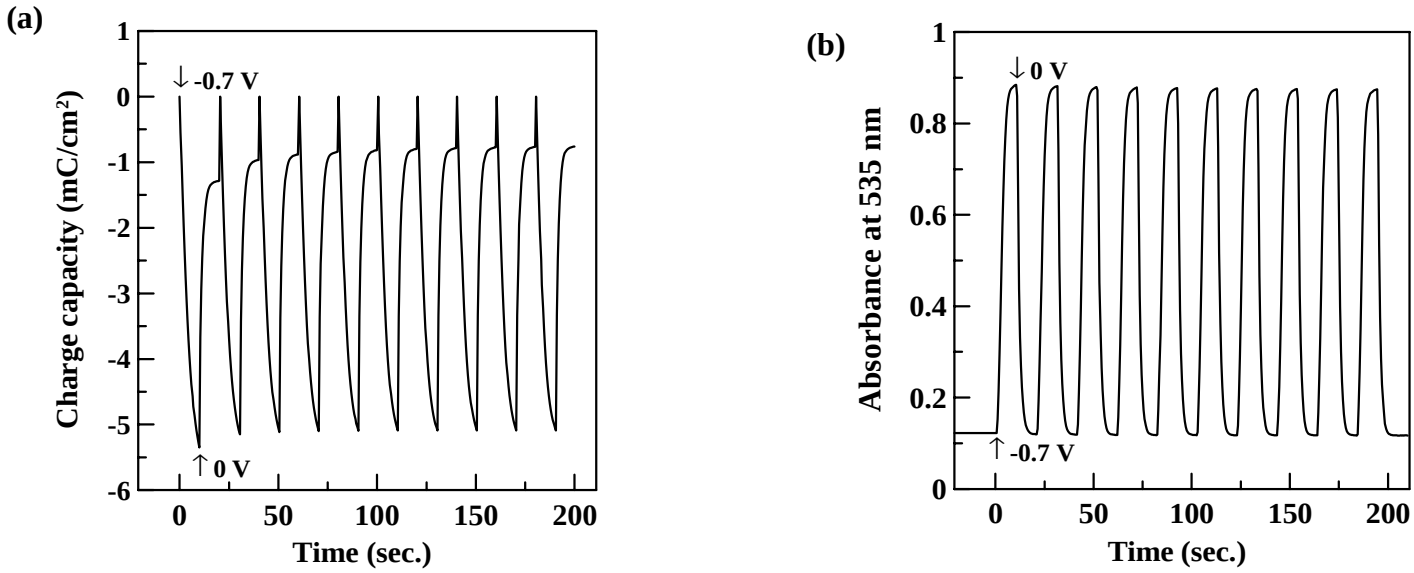


Fig. 3 *(a) Charge capacity – time response, and*
(b) absorbance of FeCN-PBV film for the first 10 cycles at the stepping potentials of -0.7 V for 10 sec and 0 V for 10 sec.