

Electrochemical Polymerization of Methylene Green

ZHU, Hong-Ping(朱红平) MU, Shao-Lin*(穆绍林)

Department of Chemistry, School of Science, Yangzhou University, Yangzhou, Jiangsu 225002, China

The electrochemical polymerization of methylene green has been carried out using cyclic voltammetry. The electrolytic solution consisted of 4×10^{-3} mol/L methylene green, 0.1 mol/L NaNO_3 and 1×10^{-2} mol/L sodium tetraborate with pH 11.0. The temperature for polymerization is controlled at 60°C . The scan potential is set between -0.2 and 1.2 V (vs. Ag/AgCl with saturated KCl solution). There are an anodic peak and a cathodic peak on the cyclic voltammogram of poly(methylene green) at $\text{pH} \leq 3.8$. Both peak potentials shift towards negative potentials with increasing pH value, and their peak currents decrease with increasing pH value. Poly(methylene green) has a good electrochemical activity and stability in aqueous solutions with $\text{pH} \leq 3.8$. The UV-Visible spectrum and FTIR spectrum of poly(methylene green) are different from those of methylene green.

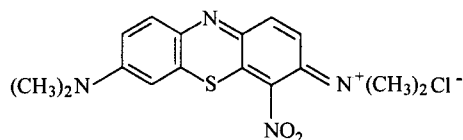
Keywords Electrochemical polymerization, poly(methylene green), electrochemical properties, UV-Visible spectrum, FTIR spectrum

Introduction

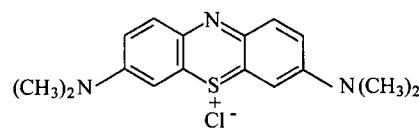
After doping, polyacetylene was converted from insulator into conductor.¹ This discovery has revealed a new research field of conducting polymers. Since then, some organic polymers, such as polypyrrole,^{2,3} polyaniline,^{4,5} and polythiophene,⁶ etc, have been proven to be interconvertible between insulator and conductor through doping and dedoping. The conducting polymers have been attracting significant interest in research areas such as chemistry, physics and bioelectrochemistry due to their high conductivity, high redox reversibility, fast change in film color with potential⁷ and strong tensile strength.⁸ Therefore, there are possible applications in the electrodes of battery, electrochromic devices, elec-

tronic devices and immobilization of enzymes.⁹⁻¹¹

The conducting polymer possessing different properties is very important for various purposes of application. For example, the conducting polymers used for fabricating biosensors require the good redox reversibility in an approximate neutral solution. Thus, the synthesis of a new type of conducting polymer is very significant. Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new system. We have used cyclic voltammetry to look for the electrochemical polymerization from over eighty monomers. Among them, we found that several new monomers including methylene green can be polymerized. The structure of methylene green is similar to that of methylene blue:



Methylene green



Methylene blue

The electrochemical polymerization of methylene blue has been reported.¹² Poly(methylene blue) can be used as a biomaterial due to its bioelectrochemical activity¹² and has a good reversibility in the pH region between 2.0 and 8.0.¹³ Recently, Karyakin *et al.* reported that

* E-mail: slmu@yzu.edu.cn

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azines including methylene blue, methylene green, toluidine blue, thionine, brilliant cresyl blue, meldola blue, oxazine 170 and neutral red could be polymerized electrochemically,¹⁴ but no experimental results about the electrochemical polymerization of methylene green were presented in their paper. We also found that neutral red could be polymerized electrochemically in the aqueous acidic and basic solutions, but its polymer had a little electrochemical activity. In this paper, we report the conditions of the electrochemical polymerization of methylene green, UV-Visible spectrum, FTIR spectrum and electrochemical properties of poly(methylene green).

Experimental

Chemicals and polymerization

The chemicals used were all of reagent grade. Doubly distilled water was used to prepare solutions. The pH values of the solutions were determined using a PXD-12 pH meter.

The electrolysis cell for the electrochemical polymerization of methylene green consisted of two platinum foils and a reference electrode. The area of the working electrode was $4 \times 4 \text{ mm}^2$. Potentials given here were referred to the Ag/AgCl electrode with saturated KCl solution. The electrolysis was performed using cyclic voltammetry in the potential region between -0.2 and 1.2 V . Cyclic voltammetry was carried out using an HPD-1 A potentiostat-galvanostat. A YEW 3086 X-Y recorder was used to record the cyclic voltammograms. The scan rate was 80 mV/s . The temperature for electrolysis was set at 60°C .

Measurement of spectra and equipment

The measurement of the UV-Visible spectrum of poly(methylene green) film polymerized on platinum deposited on quartz glass was carried out using an MPS 2000 spectrometer. FTIR spectra of methylene green and poly(methylene green) were measured on pressed pellets with KBr using an IFS66 V instrument.

Results and discussion

Film growth of poly(methylene green)

Fig. 1 shows the electrolytic process of methylene

green during repeated potential cycles. The electrolytic solution for the electrolysis consisted of $4 \times 10^{-3} \text{ mol/L}$ methylene green and 0.1 mol/L NaNO_3 with pH 11.0. Two anodic peaks near 0 and 0.12 V , and a cathodic peak at -0.09 V appear on the cyclic voltammograms in Fig. 1. As the scan potential passes the anodic peak potential, the oxidation current decreases quickly with increasing potential, and then increases again at 0.75 V for the first cycle (curve 1). Also the oxidation current at 1.2 V decreases with the number of potential cycles. The anodic peak current near 0 V increases first and then decreases with increasing the number of potential cycles (curves 3 and 4) in Fig. 1. The former is caused by the scan potential direction for the first cycle, which will be explained in the following experiment. The latter is due to the formation of the polymer on the platinum electrode. The conductivity of the polymer is rather lower than that of platinum. However, the anodic peak at 0.12 V in curve 1 disappears after the first cycle. This is caused by formation of poly(methylene green). After

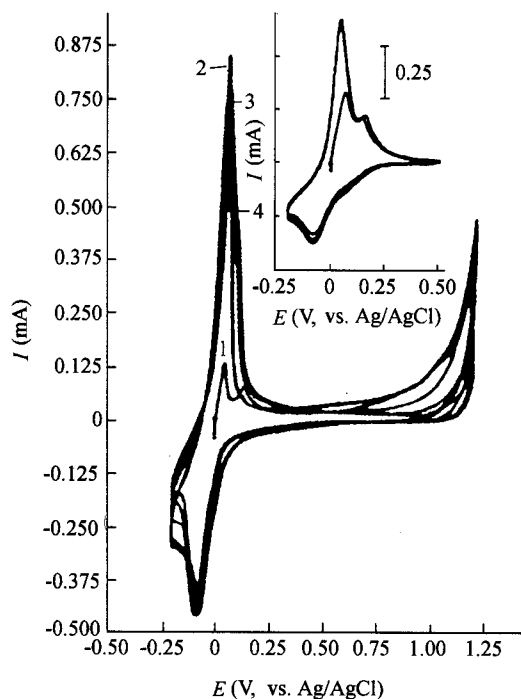


Fig. 1 Film growth of poly(methylene green) during electrolysis of the solution consisting of $4 \times 10^{-3} \text{ mol/L}$ methylene green and 0.1 mol/L NaNO_3 with pH 11.0, scan rate 80 mV/s , at 60°C . Curves: (1) the first scan, (2) the second scan, (3) the third scan, (4) the fiftieth scan.

fifty cycles, a blue film was found at the working electrode, which is poly(methylene green).

Fig. 2 shows the electrolytic process of methylene green. The electrolytic conditions were the same as those shown in Fig. 1, but the electrolytic solution contained 1×10^{-2} mol/L sodium tetraborate. The difference between Fig. 1 and Fig. 2 is that a pair of redox peaks around 0 V disappear in Fig. 2, and the current at 0.75 V is larger in Fig. 2 than in Fig. 1. Also a blue film was formed after fifty cycles, but this film is much thicker than that obtained in the absence of sodium tetraborate, which indicates that the polymerization rate of methylene green is faster in the presence of sodium tetraborate than in the absence of sodium tetraborate. This is caused by adsorption of methylene green on the platinum electrode, which inhibited the electrochemical polymerization of methylene green. Thus, to prove this suggestion, a separate experiment for electrolysis of methylene green was carried out in the absence of sodium tetraborate. The scan potential region was set between -0.2 V and 0.5 V, where there were still two anodic peaks around 0 and 0.12 V and a cathodic peak at -0.09 V in the cyclic voltammograms (the inset in Fig. 1). The i - E curve in the inset in Fig. 1 is very similar to that in Fig. 1. This indicates that two anodic peaks and a cathodic peak on curve 1 in Fig. 1 are caused by the redox of methylene green itself. After

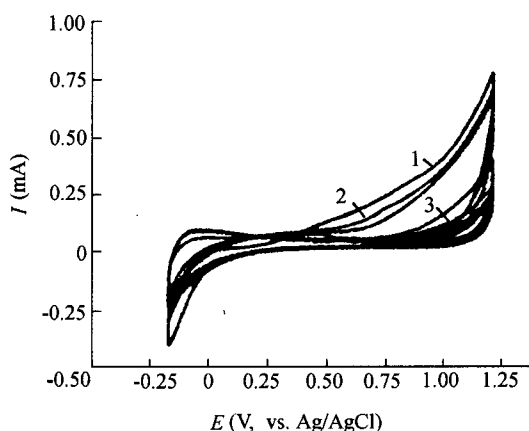


Fig. 2 Film growth of poly(methylene green) during electrolysis of the solution consisting of 4×10^{-3} mol/L methylene green, 0.1 mol/L NaNO_3 and 1×10^{-2} mol/L $\text{Na}_2\text{B}_4\text{O}_7$ with pH 11.0, scan rate 80 mV/s, at 60°C . Curves: (1) the first scan, (2) the second scan, (3) the fiftieth scan.

electrolysis, no polymer film was formed in this potential region, only an electrochemical redox of methylene green took place in the potential range between -0.2 and 0.5 V, which is very similar to the electrochemical redox of methylene blue at the same potential range.¹² It is clear that sodium tetraborate plays an important role in removing adsorption of methylene green on the platinum electrode. As a result, the presence of sodium tetraborate promotes the electrochemical polymerization of methylene green.

A remaining question is that why the anodic peak current near 0 V increases first and then decreases with increasing the number of potential cycles in Fig. 1. This experimental result is dependent on the scan potential direction at the first cycle. We have proved that the anodic oxidation current near 0 V for the first cycle is much larger at the potential scan from 0 V to negative potentials and then on scan reversal than at the potential scan from 0 V to positive potentials. This is because when the potential was first scanned from 0 V to negative potentials, methylene green was reduced first. Thus, the concentration of the reduced methylene green at the electrode surface was increased, which led to the increase in the anodic peak current near 0 V for the first cycle compared with the first cycle in Fig. 1, and then the anodic peak current decreased with increasing the number of potential cycles. The cyclic voltammogram for the electrolysis of methylene green in this case is omitted here.

Now, we can explain why the anodic peak current near 0 V increases first and then decreases with the number of potential cycles in Fig. 1. This is because the concentration of the reduced methylene green at the electrode surface was increased after the first reverse scan from 1.2 to -0.2 V. As a result, the anodic peak current of the second scan (curve 2) is much higher than that of the first scan (curve 1) in Fig. 1.

The effects of temperature, pH value and potential on the electrochemical polymerization of methylene green have been examined in our experiments. The electrochemical polymerization rate increased with increasing temperature from 20 to 60°C , and with increasing pH value from 6.0 to 11.0 . Over pH 11.0 , the solubility of methylene green decreased. Thus, this is not favorable for polymerization. Methylene green could not be polymerized below 0.6 V, and its polymerization rate increased with increasing potential from 0.6 to 1.2 V. Therefore, poly(methylene green) film used for the fol-

lowing experiments was obtained in the solution consisting of 4×10^{-3} mol/L methylene green, 0.1 mol/L NaNO_3 and 1×10^{-2} mol/L sodium tetraborate with pH 11.0; the temperature and potential region for electrolysis were controlled at 60°C and -0.2 to 1.2 V, respectively.

The structure of methylene green is similar to that of methylene blue. A suggestion for the electrochemical polymerization of methylene blue was carried out via coupling of phenyl rings followed by coupling of phenyl ring and $-\text{N}(\text{CH}_3)_2$,¹⁴ or via coupling between two $-\text{N}(\text{CH}_3)_2$ groups.¹³ Therefore, the polymerization of methylene green is also very complicated.

UV-Visible spectra

Curves 1 and 2 in Fig. 3 show the UV-Visible spectra of methylene green dissolved in the solution of NaNO_3 and $\text{Na}_2\text{B}_4\text{O}_7$, and dried poly(methylene green) film, respectively. There are three peaks at 247.8, 288.9 and 595.6 nm with a shoulder peak at 645.9 nm in curve 1 for the solution of methylene green and three peaks at 247.8, 280.0 and 590.0 nm in curve 2 for poly(methylene green). In fact, the peak at 247.8 nm is very small and almost disappears in curve 2. This result is similar to polymerization of methylene blue. There are two peaks at 245 and 292 nm for methylene blue, but the peak at 245 nm disappears after polymerization.¹³ The aqueous solution of methylene green is blue, which is caused by chromophores and auxochromes in

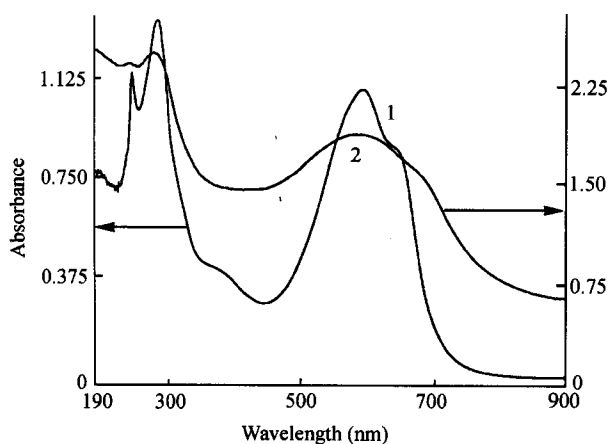


Fig. 3 UV-Visible spectra. Curves: (1) methylene green solution, (2) poly(methylene green) polymerized on platinum deposited on quartz glass.

methylene green. After polymerization, only a broad band at 590 nm appears in curve 2, which may be caused by the change of auxochromes in poly(methylene green). The difference between curves 1 and 2 indicates that methylene green is polymerized after the electrolysis.

FTIR spectra

Curves 1 and 2 in Fig. 4 show the FTIR spectra of methylene green and poly(methylene green). Both of FTIR spectra are very complicated. For simplicity, we only discuss the main difference between curve 1 and curve 2. After polymerization, a broad band at 3434 cm^{-1} is very strong with respect to other peaks in curve 2. The retention of a strong OH stretch region in the polymer suggests that water is still contained in the polymer, and the internal hydrogen bond in the polymer was enhanced. The peaks at 1354 (s), 1291 (s), 1241 (w) and 1215 (w) cm^{-1} disappear in curve 2 compared with curve 1. This phenomenon is usually observed in some polymers, since vibrational models could be reduced after polymerization; a very strong peak at 1600 cm^{-1} (curve 1) attributable to stretching vibration of $\text{C}=\text{C}$ in aromatic rings is split into two weak peaks at 1628 and 1603 cm^{-1} in curve 2; and new small peaks at 1161 and 930 cm^{-1} appear in curve 2.

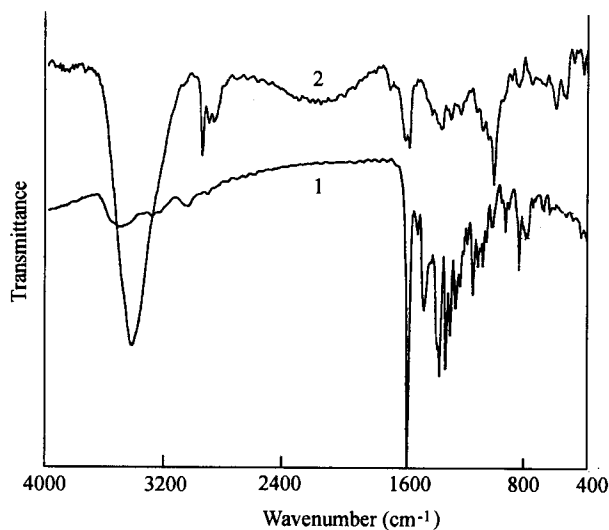


Fig. 4 FTIR spectra. Curves: (1) methylene green, (2) poly(methylene green).

The IR spectrum of methylene blue at wavenumber

greater than 3100 cm^{-1} shows a broad band between 3400 and 3500 cm^{-1} ,¹⁵ which is caused by water. The structure of methylene green is similar to that of methylene blue. Thus the broad band at 3508 cm^{-1} in curve 1 is also attributed to water. However, after polymerization, this band becomes very strong, and the peaks at 2972 , 2928 and 2894 cm^{-1} attributable to stretching vibration of C—H in $-\text{CH}_3$ groups become more prominent in curve 2 compared with curve 1. This difference may be caused by the formation of polymer chains, which leads to that these vibration models predominate over the vibration models of aromatic rings in poly(methylene green). In fact, the IR spectra of methylene green and poly(methylene green) are very complicated as mentioned above, but the difference between them, especially the peaks in curve 2 less than in curve 1 at the wavenumber less than 1600 cm^{-1} , indicates that methylene green is polymerized after electrolysis.

Electrochemical properties of poly(methylene green)

Curves 1 and 2 in Fig. 5 show the cyclic voltammograms of poly(methylene green) in the solution of $0.3\text{ mol/L H}_2\text{SO}_4$ and $0.5\text{ mol/L Na}_2\text{SO}_4$, and in the solution of $0.2\text{ mol/L H}_2\text{SO}_4$ and $0.5\text{ mol/L Na}_2\text{SO}_4$, respectively. Curves 3, 4, 5, 6 and 7 show the cyclic

voltammograms of poly(methylene green) in $0.5\text{ mol/L Na}_2\text{SO}_4$ with pH 1.0, 2.0, 3.0, 3.6 and 4.0, respectively. Both of the anodic and cathodic peak potentials change hardly from curve 1 to curve 3. However, the shift of the anodic peak from 0.33 to 0.23 V , and the shift of the cathodic peak from 0.18 to -0.063 V were observed as the pH value increased from 1.0 (curve 3) to 3.6 (curve 6), respectively. This indicates that the redox of poly(methylene green) is related to the concentration of protons. This behavior is similar to that of polyaniline.⁵ From Fig. 5, we can see that their peak currents decrease with increasing pH value. This means that the electrochemical activity of poly(methylene green) decreases with increasing pH value.

The cyclic voltammograms of poly(methylene green) at pH 3.6 (curve 6) and pH 4.0 (curve 7) are a little different from other curves. In the curves 6 and 7, the anodic current increases markedly at about 0.6 V , and the cathodic current also increases rapidly at about -0.2 V . The former may be caused by the overoxidation of poly(methylene green) at higher pH values; the latter may be ascribed to the decrease in the activity of poly(methylene green) at higher pH values, which leads to the reduction of protons at the polymer electrode. This means that a usable potential range for poly(methylene green) is between 0.55 and 0.18 V .

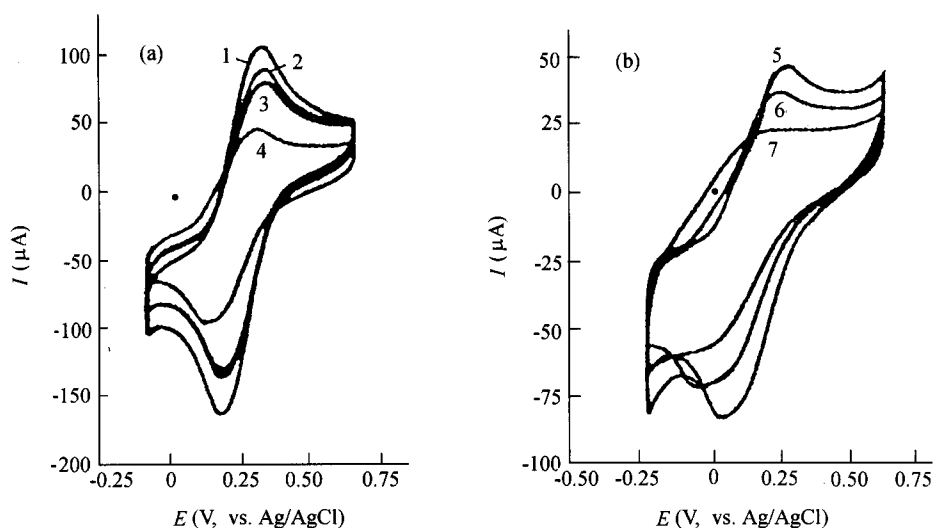


Fig. 5 Cyclic voltammograms of poly(methylene green) polymerized on platinum foil, in the solution of $0.5\text{ mol/L Na}_2\text{SO}_4$ at various pH values, scan rate 80 mV/s , at 25°C . Curves: (1) $0.3\text{ mol/L H}_2\text{SO}_4$ and $0.5\text{ mol/L Na}_2\text{SO}_4$, (2) $0.2\text{ mol/L H}_2\text{SO}_4$ and $0.5\text{ mol/L Na}_2\text{SO}_4$, (3) pH 1.0, (4) pH 2.0, (5) pH 3.0, (6) pH 3.6, (7) pH 4.0.

Fig. 6 shows the cyclic voltammograms of poly-

(methylene green) in the solution of $0.3\text{ mol/L H}_2\text{SO}_4$

and 0.5 mol/L Na_2SO_4 at various scan rates. Fig. 7 shows the cyclic voltammograms of poly(methylene green) in 0.5 mol/L Na_2SO_4 solution with pH 3.8. Their peak currents in both plots increase with the scan rate, and the both peak potentials change a little as the scan rate increases from 25 to 600 mV/s. This means that poly(methylene green) has a good electrochemical reversibility.

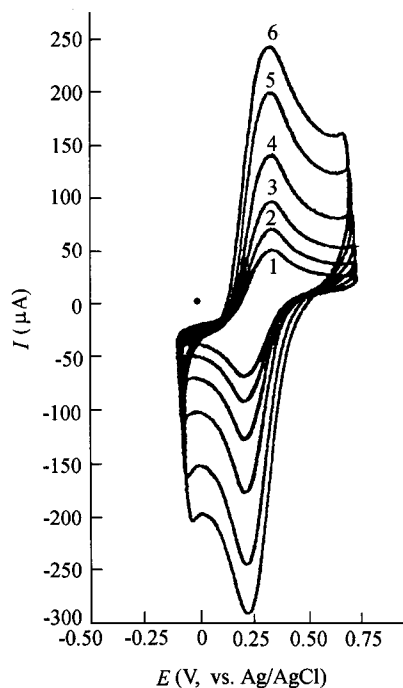


Fig. 6 Cyclic voltammograms of poly(methylene green) polymerized on platinum foil, in the solution of 0.3 mol/L H_2SO_4 and 0.5 mol/L Na_2SO_4 at various scan rates. Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400, (6) 600 mV/s, at 25°C.

In both plots, there are still a sharp anodic peak and a sharp cathodic peak at 600 mV/s. This proves that the electrochemical reaction is controlled by mass transfer at such a high scan rate. This result is supported by the plots of both peak currents i_p versus $\nu^{1/2}$ based on the results from Fig. 6 and Fig. 7, since the plots (omitted here) of i_p versus $\nu^{1/2}$ are all straight lines. This is a characteristic property of mass transfer controlled process, and indicates that poly(methylene green) has a good ability of the fast charge transfer. The result from Fig. 7 also proves that poly(methylene green) has a good electrochemical activity at pH 3.8.

Curves 1 and 3 in Fig. 8 show the cyclic voltam-

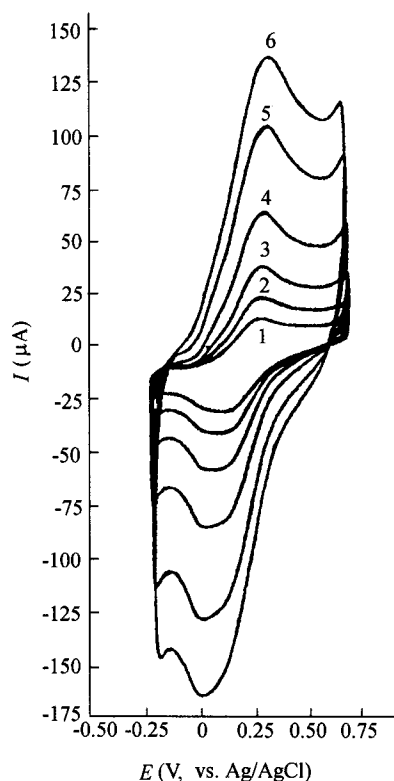


Fig. 7 Cyclic voltammograms of poly(methylene green) polymerized on platinum foil, in the solution of 0.5 mol/L Na_2SO_4 with pH 3.8 at various scan rates. Curves: (1) 25, (2) 50, (3) 100, (4) 200, (5) 400, (6) 600 mV/s, at 25°C.

mograms of poly(methylene green) in the solution of 0.3 mol/L H_2SO_4 and 0.5 mol/L Na_2SO_4 at the first cycle and fiftieth cycle, respectively. Curves 1 and 3 in Fig. 9 show the cyclic voltammograms of poly(methylene green) in 0.5 mol/L Na_2SO_4 solution with pH 3.6 at the first cycle and fiftieth cycle. From Fig. 8 and Fig. 9, we can see that both peak currents change a little after fifty cycles. Thus, poly(methylene green) has a good stability.

Conclusion

The electrochemical polymerization of methylene green is significantly affected by many factors, such as pH value and the composition of the electrolytic solution, temperature and potential. An optimum condition for the electrochemical polymerization of methylene green is that pH value, temperature and scan potential were

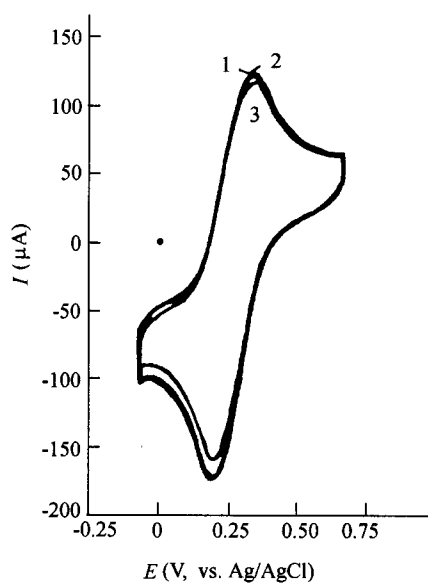


Fig. 8 Cyclic voltammograms of poly(methylene green) polymerized on platinum foil, in the solution of 0.3 mol/L H_2SO_4 and 0.5 mol/L Na_2SO_4 , scan rate 80 mV/s. Curves: (1) first scan, (2) second scan, (3) fiftieth scan.

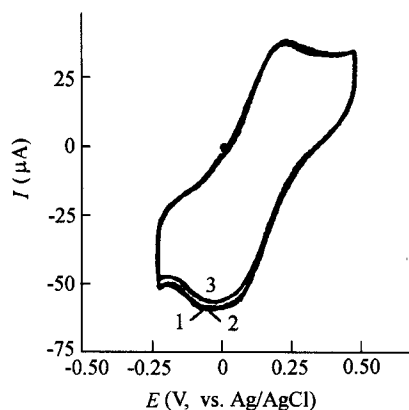


Fig. 9 Cyclic voltammograms of poly(methylene green) polymerized on platinum foil, in the solution of 0.5 mol/L Na_2SO_4 with pH 3.6, scan rate 80 mV/s. Curves: (1) first scan, (2) second scan, (3) fiftieth scan.

controlled at 11.0, 60°C and -0.2 to 1.2 V, respectively. Sodium tetraborate plays an important role in re-

moving adsorption of methylene green on the platinum electrode and promoting polymerization of methylene green. Poly(methylene green) has a high electrochemical activity and a good stability at $\text{pH} \leq 3.8$. However, the polymerization mechanism of methylene green and the structure of poly(methylene green) are rather complicated. Thus, the further study for the polymerization mechanism and the structure of poly(methylene green) is required.

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