

Study on Electrochemical Oxidation of *m*-Nitrophenol on Various Electrodes Using Cyclic Voltammetry

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ABSTRACT: The electrochemical oxidation behavior of *m*-nitrophenol (*m*-NP) was studied comparatively on glassy carbon electrode, Pt electrode, PbO₂ electrode, SnO₂ electrode, and graphite electrode using cyclic voltammetry. The cyclic voltammetry measurements were performed in acidic (1 M H₂SO₄, pH 0.4), neutral (1 M Na₂SO₄, pH 6.8), and alkaline (1 M NaOH, pH 12.0) media to investigate the effect of pH value on the oxidation of *m*-NP. The fouling of electrodes was also studied during cyclic voltammetry measurements. The results indicate that both of the electrode material and the pH value of supporting electrolyte had significantly influence on the oxidation of *m*-NP. In acidic medium, *m*-NP was irreversibly oxidized on glassy carbon electrode, Pt electrode, SnO₂ electrode, and graphite electrode at 1.23, 1.26, 1.26 and 1.27 V, respectively, while there was no any oxidation peak for PbO₂ electrode. In a neutral medium, *m*-NP yielded well-defined oxidation peaks on all electrodes, although the height and potential of the peaks depended on the material of electrodes. In the alkaline medium, the *m*-NP could be directly oxidized only on glassy carbon electrode and graphite electrode, but their peaks were not well defined because the oxidation of *m*-NP occurs closer to oxygen evolution potential region. In addition, the oxidation peaks appeared at the lower potential value in the alkaline medium than in neutral and acidic media. Under all conditions, except in the alkaline solution and on glassy carbon electrode, the passivation of electrodes occurred during continual scans.

KEYWORDS: Electrochemical oxidation; Cyclic voltammetry; *m*-nitrophenol; Electrode material; pH value.

INTRODUCTION

Nitrophenols (NPs) are widely used in the manufacture of pesticides, dyes, textile, and pharmaceuticals [1,2].

Considering their toxicity and supposed carcinogenic effects on living organisms, the US Environmental

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Protection Agency has listed 2-NP, 4-NP and 2,4-dinitrophenol in the priority pollutant category [3-5]. However, NPs are one kind of the most challenging pollutants because the presence of a nitro-group confers to the aromatic compounds strong chemical stability and resistance to biological methods [5]. Thus, in the recent years, lots of researches have been focused on the destruction of these organic pollutants using different methods, such as adsorption [6], Fenton [7], electro-Fenton [3], photocatalytic oxidation [8], ozonation [2], catalytic wet peroxide oxidation [9], and electrochemical oxidation [5], etc. Among these technologies, the electrochemical oxidation is one of the most promising technologies for the treatment of toxic organic wastewater due to its high energy efficiency, versatility, and environmental compatibility [10].

During the electrochemical oxidation process, the nature of anode material is crucial to determine the anodic reactions and the productions of pollutants. There is a wide variety of electrodes used in electrochemical oxidation. They are noble metal electrodes (Pt, Au), carbon and graphite electrodes, Mixed Metal Oxide electrodes (MMO, the commercial name is dimensionally stable anodes (DSA)), Boron-Doped Diamond (BDD) electrodes, etc. [11]. *Quiroz et al.* studied the electrocatalytic oxidation of *p*-NP using Pb/PbO₂ anode in acidic and alkaline media. Under the alkaline condition, almost complete chemical demand abatement was attained, with a high level of *p*-NP mineralization [5]. A ternary oxide electrode Ti/IrO₂-SnO₂-Sb₂O₅ showed high catalytic activity for the electrochemical oxidation of nitrophenolic compounds 4-NP and 2-NP [12]. In recently several years, the boron-doped diamond electrode was extensively tried as anode material [13]. In an investigation, nearly complete degradation of *o*-NP was achieved using boron-doped diamond anode [4]. Thus, NPs can be degraded on various electrode materials.

Cyclic voltammetry, as one of the main electrochemical technologies, has often been used to characterize the activity of electrodes or study the oxidation behavior of organics. The electrochemical oxidation of *p*-NP was studied comparatively on a graphene modified electrode and a carbon nanotube electrode by cyclic voltammetry [14]. In order to investigate nitro-substituent's effect on degradation of phenols at BDD anode, cyclic voltammeteries of three nitrophenol isomers: 2-NP, 3-NP,

and 4-NP were studied [15]. Rabi-Stnković studied the electrochemical-oxidation of *p*-NP on a BTMA⁺-bentonite-modified electrode in H₂SO₄ solution by cyclic voltammetry [16]. The electrochemical behavior of *o*-NP on hexagonal mesoporous silica modified carbon paste electrode was also reported [17]. Besides, the Ti/Pt anode was also used to study the electrochemical behavior of *p*-NP [18]. However, the comparative study of

the electrochemical oxidation behavior of *m*-NP on various electrodes has rarely been investigated by cyclic voltammetry in great detail before.

Thus, in this work, the *m*-NP was used as the target pollutant. We chose the typical noble metal electrode (Pt sheet), carbon electrodes (glassy carbon electrode and graphite electrode) and DSA (PbO₂ and SnO₂ electrodes) to investigate the oxidation behavior of *m*-NP using cyclic voltammetry. Noting that, we did not choose BDD electrode in this study due to its high cost. We investigated the influence of pH value of medium on the oxidation of *m*-NP on the various electrodes by adopting different electrolytes. Besides, the passivation reaction of electrodes during cyclic voltammetry measurements was also studied.

EXPERIMENTAL SECTION

In this study cyclic voltammetry was exclusively applied. Cyclic voltammetry measurements were carried out in a conventional three-electrode cell using the PGSTAT302 electrochemical workstation. Glassy carbon electrode, Pt electrode, PbO₂ electrode, SnO₂ electrode, and graphite electrode were used as working electrode, a platinum sheet as an auxiliary electrode and a Saturated Calomel Electrode (SCE) as a reference electrode. The glassy carbon had a geometric area of 0.0707 cm², and the effective areas of other electrodes were 1 cm².

Cyclic voltammetry measurements were performed in 1 M H₂SO₄ (pH 0.4), 1 M Na₂SO₄ (pH 6.8) and 1 M NaOH (pH 12.0) aqueous solutions containing 500 mg/L of *m*-NP at the scan rate of 50 mV/s at 25 °C.

RESULTS AND DISCUSSION

Cyclic voltammograms on the glassy carbon electrode

The electrochemical behavior of *m*-NP on glassy carbon electrode was first studied by cyclic voltammetry. Fig. 1a1, b1, and c1 shows the continuous cyclic voltammograms of 500 mg L⁻¹ *m*-NP in 1 M H₂SO₄, 1 M

Na₂SO₄ and 1 M NaOH aqueous solutions on glassy carbon electrode, respectively. Also, the voltammograms were recorded in the absence of *m*-NP for the three media as shown in Fig. 1a2, b2, and c2 for comparison.

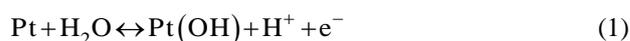
In acidic medium containing 500 mg/L *m*-NP (Fig. 1 a1), during the first cycle, the anodic branch exhibits two oxidation peaks A₁ and A₂ at 0.48 and 1.23 V, respectively, while a weak reduction peak (B₁) at 0.38 V on the cathodic branch. Compared with the cyclic voltammograms for a blank solution (Fig. 1 a2), it can be determined that the oxidation peak (A₂) at 1.23 V was attributed to the oxidation of *m*-NP. It also can be seen that the electro-oxidation of *m*-NP and oxygen evolution are in different potential regions, the potential of *m*-NP oxidation is lower than the oxygen evolution potential, implying that the oxidation process was caused by direct electron transfer. However, in the subsequent cycles, the current oxidation peak A₂ gradually decreased with increasing the number of scans. This means the phenoxy radicals were indeed formed and these polymerized radicals resulted with a strongly adherent film on the surface of the electrode, which prevented the further oxidation of *m*-NP on the surface of the electrode. It is also noted in Fig. 1a1 that the peak currents of oxidation peak (A₁) and the corresponding reduction peak (B₁) increased at the expense of decrease of the irreversible oxidation peak current (A₂), and this reversible redox couple also existed on the cyclic voltammograms obtained in blank H₂SO₄ solution (Fig. 1a2). Thus, it can be determined that this reversible redox couple did not result in the redox of *m*-NP or the production of *m*-NP, and it may be due to the production of H₂ gas and the hydrogen oxidation [19].

The results in Na₂SO₄ solution are shown in Fig. 1b1 and b2. No any redox signal was observed in blank Na₂SO₄ solution. After *m*-NP was added into the Na₂SO₄ solution, an obvious oxidation peak at 1.04 V was obtained. It is no doubt that the oxidation peak should be attributed to the oxidation of *m*-NP, and its potential is lower by 190 mV than that in H₂SO₄ solution. Similar to the H₂SO₄ medium, as the number of cycles increased, the anodic current peak decreased due to the passivation of the electrode. However, this phenomenon will not occur in actual electrochemical oxidation process because the electrode surface can produce hydroxyl radicals which can oxidize the polymeric film on the surface and the activity of electrode can be restored in the same electrolyte at high potentials.

Fig. 1c1 and c2 show the cyclic voltammograms of the glassy carbon electrode in 1 M NaOH solution with and without 500 mg/L *m*-NP. As shown, an oxidation peak of *m*-NP appeared at 0.96 V in curves c1 while no redox peaks were found in curves c2. The oxidation potential for *m*-NP on glassy carbon electrode is lower by 260 and 70 mV than those in H₂SO₄ and Na₂SO₄ media, which indicates that the oxidation of *m*-NP on glassy carbon electrode will be enhanced with increasing pH value of electrolyte. However, as the oxidation peak for *m*-NP occurs closer to the oxygen evolution potential region in alkaline medium, distinct anodic peaks cannot be observed. As the oxidation reaction of *m*-NP produces phenoxy radicals which can be further polymerized in acidic and neutral media, 10 successive cyclic voltammetric measurements were also performed in NaOH solution. It is interesting that the *m*-NP oxidation peak and oxygen evolution peak current of repeated curves did not decrease, which is quite different from the substantial decrease of the peak current in H₂SO₄ and Na₂SO₄ media, demonstrating that the *m*-NP can be continually degraded and the passivation of glassy carbon electrode did not occur in alkaline medium. This phenomenon is in agreement with our earlier report on the cyclic voltammetric study of 4-chlorophenol on glassy carbon electrode [20].

Cyclic voltammograms on Pt electrode

Cyclic voltammograms for Pt electrode in H₂SO₄ solution with and without *m*-NP are shown in Fig. 2 a1 and a2. In two cyclic voltammograms, a not well-defined oxidation peak both presented from 0.9 to 1.2 V in the anodic scan, and corresponding well-defined reduction peak both occurred from 0.6 to 0.2 V in the subsequent back scan. In addition, the oxidation and reduction peaks did not disappear with increasing scan times. These results indicate that this redox couple corresponds to the formation of mono layer oxide such as PtO on the Pt electrode in the anodic scan and the reduction of oxide in the reverse scan [21-23]. The electrochemical generation of the oxide layer at the Pt surface can be represented as follows [24]:



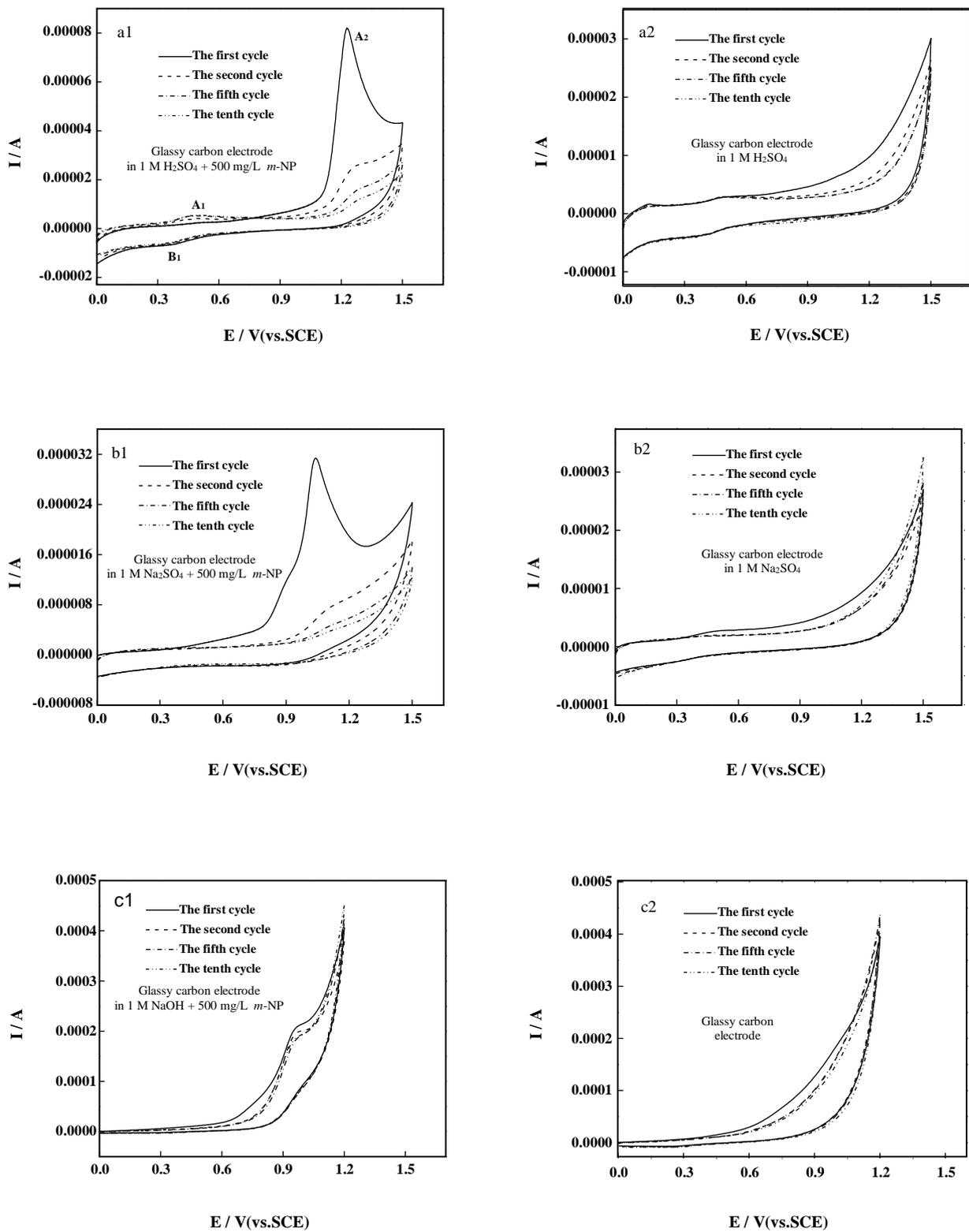


Fig. 1: Cyclic voltammograms of glassy carbon electrode in 1 mol/L H₂SO₄, Na₂SO₄, and NaOH solutions with (a1, b1, c1) and without (a2, b2, c2) 500 mg/L *m*-NP. Scan rate: 50 mV/s.

It can be seen that similar scenarios also take place in the blank Na₂SO₄ solution (Fig. 2b1 and b2). Only due to the different pH value of electrolyte, the potential of redox peaks presented at more negative potentials.

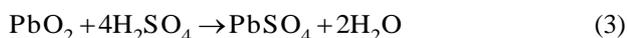
When the *m*-NP was added into H₂SO₄ and Na₂SO₄ solutions, in the first cycle, new well-defined oxidation peaks occurred at the potential of 1.27 V in H₂SO₄ (Fig. 2 a1) and 1.14 V in Na₂SO₄ (Fig. 2 b1) solutions, respectively, indicating the oxidation reaction of *m*-NP on Pt sheet. However, no corresponding reduction peak was observed in the following reverse scan from 1.5 to 0 V, indicating that the oxidation of *m*-NP is a totally irreversible electrode process under the above experimental conditions. However, in the second scan cycle, the oxidation peak almost disappeared completely, indicating the polymer was also formed on Pt electrode under acid and neutral conditions.

In the case of the alkaline medium, the results are fairly different. In the NaOH solutions with and without 500 mg/L *m*-NP, the scans towards positive potentials both feature in the absence of any oxidation peak, and only a steep rise in anodic current value due to the oxygen evolution reaction. This can be explained by considering that at increasing potential, the •OH-based mechanism competes with the plausible direct oxidation by electron transfer from the substrate, which was undetectable due to the corresponding low limiting current density.

Cyclic voltammograms on PbO₂ electrode

Cyclic voltammetry measurements of *m*-NP aqueous solutions with H₂SO₄, Na₂SO₄ and NaOH as supporting electrolytes were also performed on PbO₂ electrode. Interestingly, a very different behavior was observed in three media, as shown in Fig. 3, indicating that the pH value of solution has a significant effect on the oxidation process of *m*-NP on the PbO₂ electrode.

Similar cyclic voltammograms were obtained in H₂SO₄ solutions with and without *m*-NP (Fig. 3 a1 and a2). There was not any peak on the anodic branches of the curves, while a reduction peak can be observed at potentials between 0.9 to 1.1 V on the cathodic branches of the curves. It indicates that *m*-NP cannot be directly oxidized on the PbO₂ electrode in acidic condition. The occurrence of this cathodic peak is due to the reduction of PbO₂ to PbSO₄ according to the following scheme [1,25]:



In addition, it also can be observed that the reduction peak disappeared in the second scan, which indicates that the transformation of PbO₂ to PbSO₄ was irreversible in the potential range of this experiment.

The cyclic voltammograms in blank Na₂SO₄ solution were shown in Fig. 3b2. There were three oxidation peaks on the anodic branch and one reduction oxidation on the cathodic branch in all curves. According to the previous literature, the first oxidation peak was corresponding to the generation of hydrogen peroxide following the reaction [26]:



The second and third oxidation peaks might be a result of a reversible surface reaction between sulfate and lead oxides, that is, the second oxidation peak was responsible for the formation of PbO and the third oxidation peak represented the formation of PbO₂ [23,27]. The reduction peak was attributed to the electrochemical reduction of Pb (IV) and Pb (II) to Pb (0).

Fig. 3 b1 shows the cyclic voltammograms in Na₂SO₄ solution containing 500 mg/L *m*-NP. There were both three oxidation peaks on the anodic branches in the first scan. The potential of peaks was similar to those of blank Na₂SO₄ solution (Fig. 3 b2), but the current response of the third peak is much higher than that in blank Na₂SO₄ solution. In addition, there were significant differences in the subsequent scans between curves of two systems. With the present of *m*-NP, all these three peaks decreased significantly and shifted negatively during second cycling. After five cycles, three peaks almost disappeared. While with the absent of *m*-NP, these peaks were weak in the first cycle, and increased slowly and moved negatively as the number of scans increased, especially for the second and third oxidation peaks. These differences indicate that the third oxidation peak in Fig. 3a1 should be attributed to the oxidation reaction of *m*-NP on the surface of the electrode, which may overlap the oxidation peak of the formation of PbO₂ in Fig. 3b1. The disappearance of all peaks in Fig. 3b1 means that a passivation film was formed on the surface of PbO₂ electrode during the oxidation of *m*-NP in Na₂SO₄ solution, which prevented all the reactions further occurring on the surface of the electrode.

Comparing the cyclic voltammograms on PbO₂ electrode in NaOH solution with and without *m*-NP

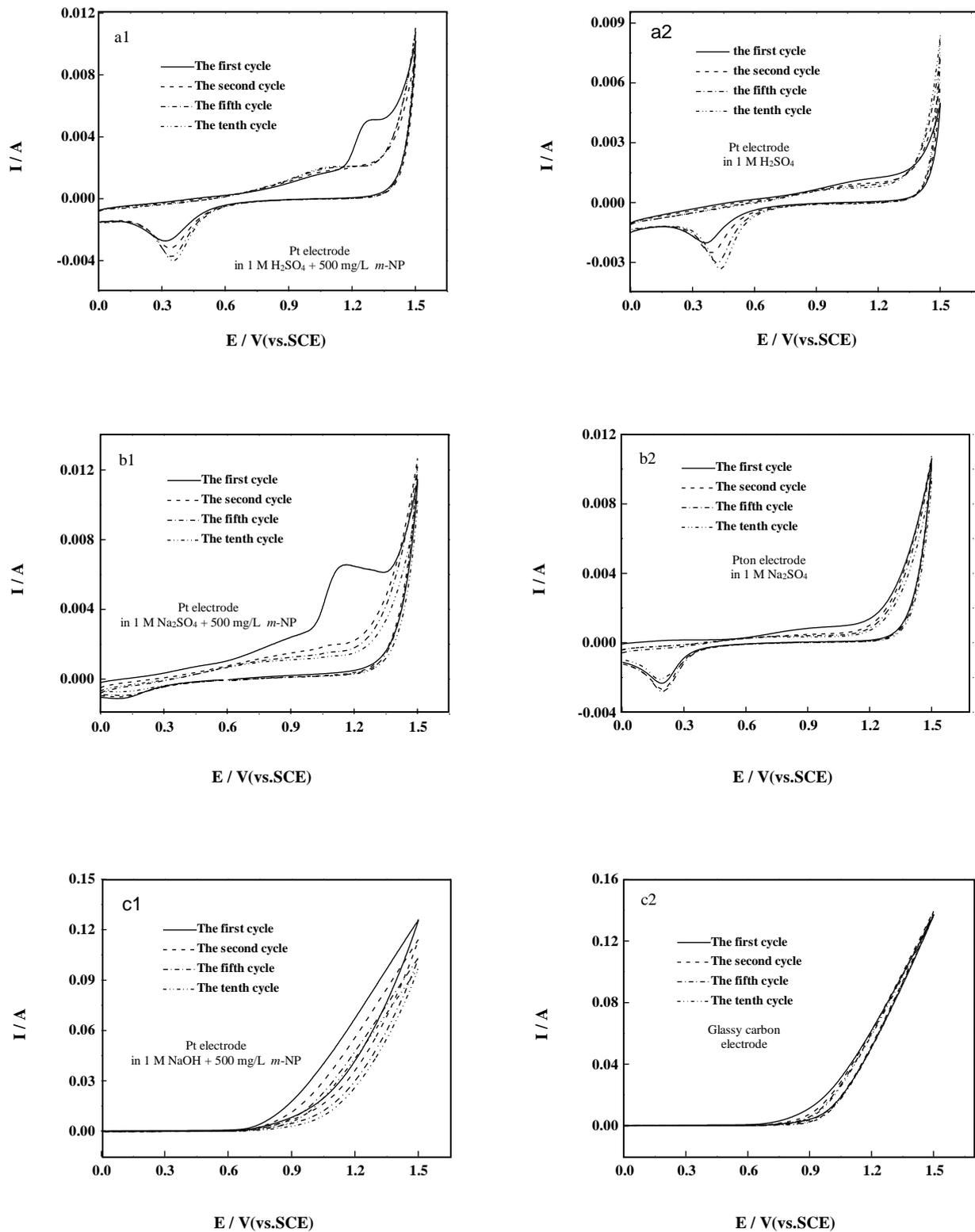


Fig. 2: Cyclic voltammograms of Pt electrode in 1 mol/L H_2SO_4 , Na_2SO_4 , and $NaOH$ solutions with (a1, b1, c1) and without (a2, b2, c2) 500 mg/L m-NP. Scan rate: 50 mV/s.

shown in Fig. 3c1 and c2, it was found that all the anodic branches of the curves featured an exponential current growth corresponding to the oxygen evolution at potentials higher than 0.7 V, and there was no any difference except the different current value of oxygen evolution between two groups of curves. This means that *m*-NP cannot be directly oxidized on PbO₂ electrode in an alkaline medium like Pt electrode. It also should be noted that there was an oxidation peak at about 0.34 V on anodic branches in both of two systems, as shown in the inserts of Fig. 3 c1 and c2. The appearance of oxidation peak in the blank NaOH solution shows that the oxidation did not result in the oxidation of *m*-NP, and it may due to the formation of PbO [28].

Cyclic voltammograms on SnO₂ electrode

Fig. 4a1, b1, c1 shows cyclic voltammetric behavior of SnO₂ electrode in H₂SO₄, Na₂SO₄ and NaOH solutions containing *m*-NP. The curves obtained under the same experimental conditions but without *m*-NP are also shown in Fig. 4a 2, b2, c2. The similar curves were obtained in Fig. 4 a1 and b1. The voltammograms both show an irreversible oxidation peak at 1.25 and 1.15 V, respectively, in the first cycle. Compared with the curves in blank H₂SO₄ (Fig. 4 a2) and Na₂SO₄ (Fig. 4 b2), it can be determined that these two oxidation peaks were ascribed to the oxidation of *m*-NP on the surface of SnO₂ electrode in acidic and neutral media. It also can be observed that, in the subsequent cycles, the oxidation peaks decreased remarkably and completely disappeared during the successive cyclic voltammetric scans, which shows that the passivation also occurred on SnO₂ electrode in acidic and neutral media.

However, there was no any redox peak in the cyclic voltammograms in blank NaOH solution (Fig. 4 c2) and NaOH solution with 500 mg/L *m*-NP (Fig. 4 c1), which demonstrates that the *m*-NP cannot be directly oxidized on SnO₂ electrode, or the *m*-NP oxidation current did not be detected due to the rapid increase of oxygen evolution current, just the same as the Pt electrode.

Cyclic voltammograms on graphite electrode

The same experiments were also carried out on graphite electrode in H₂SO₄, Na₂SO₄ and NaOH solutions. Fig. 5 a1 and a2 show the cyclic voltammograms in 1 M H₂SO₄ solution with and without

500 mg L⁻¹ *m*-NP. As can be seen in Fig. 5 a2, in the absence of *m*-NP, all curves show an oxidation peak at about 0.49 V on the anodic branch and reduction oxidation at about 0.35 V on the cathodic branch. This reversible redox couple could be ascribed to the formation of sulfuric acid-graphite intercalation compound (H₂SO₄-GIC) in the anodic polarization and partial reduction of the H₂SO₄-GIC during the cathodic scan [29,30], which can be expressed by the following equation:



Compared with Fig. 5a2, Fig. 5a1 not only shows the oxidation peak and reduction peak corresponded to the redox reaction of graphite oxide, but also there was an anodic peak at 1.27 V due to the oxidation of *m*-NP. Furthermore, as seen in Fig. 5 a1, the oxidation peak current of *m*-NP gradually dropped with the increase of scan number, and it presented a wavy peak until the tenth cycle, indicating that the oxidation of *m*-NP in H₂SO₄ medium did not cause the complete passivation of the graphite electrode in the experiment. This result may be related to the redox of graphite oxide.

For the cases of Na₂SO₄ and NaOH as supporting electrolytes, typical cyclic voltammograms of graphite electrode were observed. In blank Na₂SO₄ and NaOH solution, there was no any oxidation and reduction peak occurred. When 500 mg/L *m*-NP was added into the electrolyte, well-defined and single oxidation peaks were observed with E_{pa} at 1.06 and 1.01 V during the anodic sweeps from 0 to 1.5 V, respectively. The oxidation peak potential of *m*-NP shifted to a less positive potential with increasing pH value, but the oxidation peak was very weakly defined in the alkaline medium due to the oxygen evolution as the parallel process. These results were consistent with the oxidation of *p*-NP on graphene-Nafion electrode [14]. In their study, the pH value also has a significant influence in the oxidation of *p*-NP. The oxidation peak potential of *p*-NP is shifted to a less positive potential with increasing pH from 5 to 9, then at pH 11 the oxidation peak is very weakly defined. It also can be observed that, on the following reverse scan from 1.5 to 0 V, no corresponding reduction peak was observed, indicating that the oxidation of *m*-NP on the graphite electrode is totally irreversible under these experimental conditions. Similar to other electrodes, the fouling phenomenon also occurred on the graphite electrode in Na₂SO₄ solution. In the second cycle, the oxidation peak current

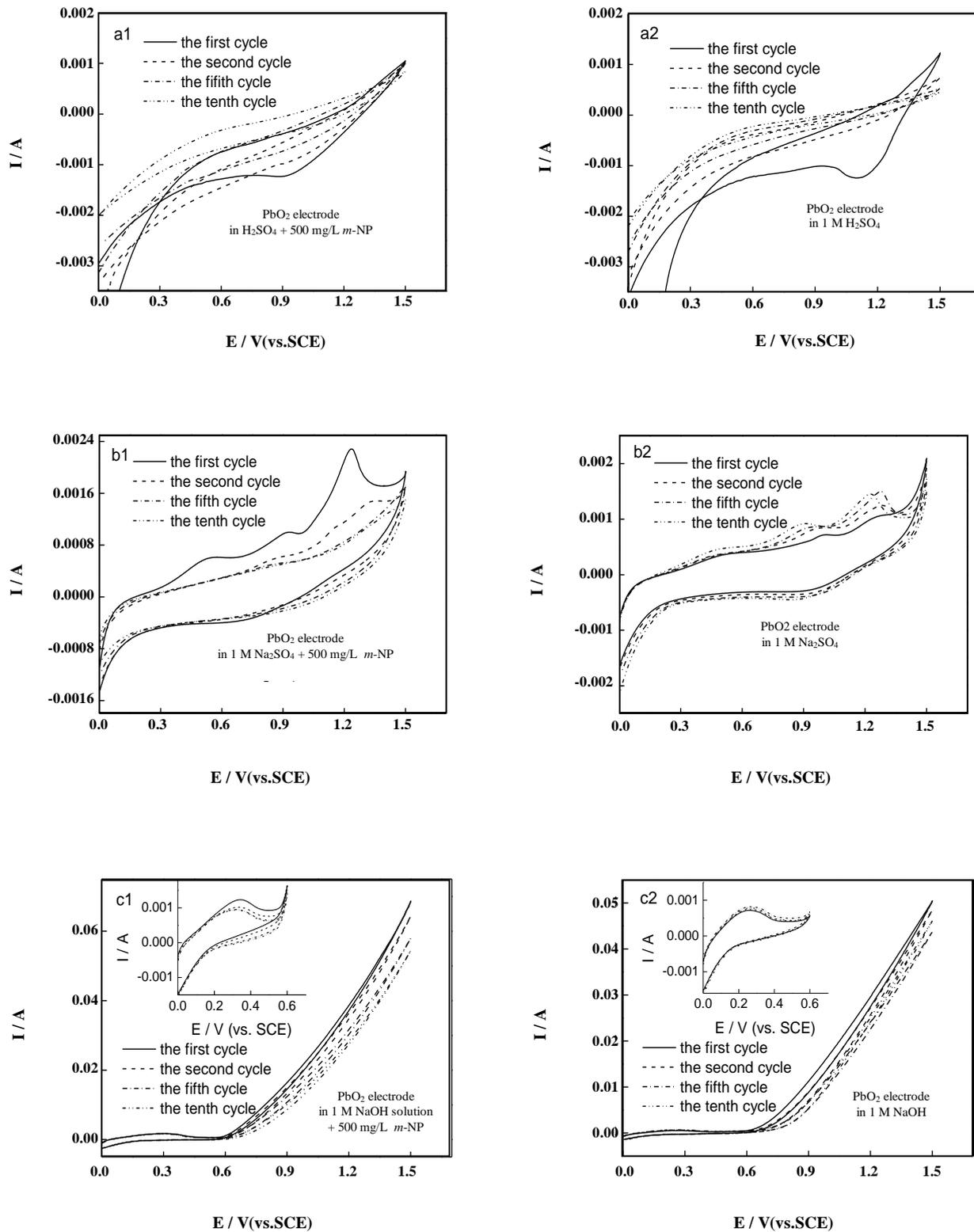


Fig. 3: Cyclic voltammograms of PbO₂ electrode in 1 mol/L H₂SO₄, Na₂SO₄, and NaOH solutions with (a1, b1, c1) and without (a2, b2, c2) 500 mg/L m-NP. Scan rate: 50 mV/s.

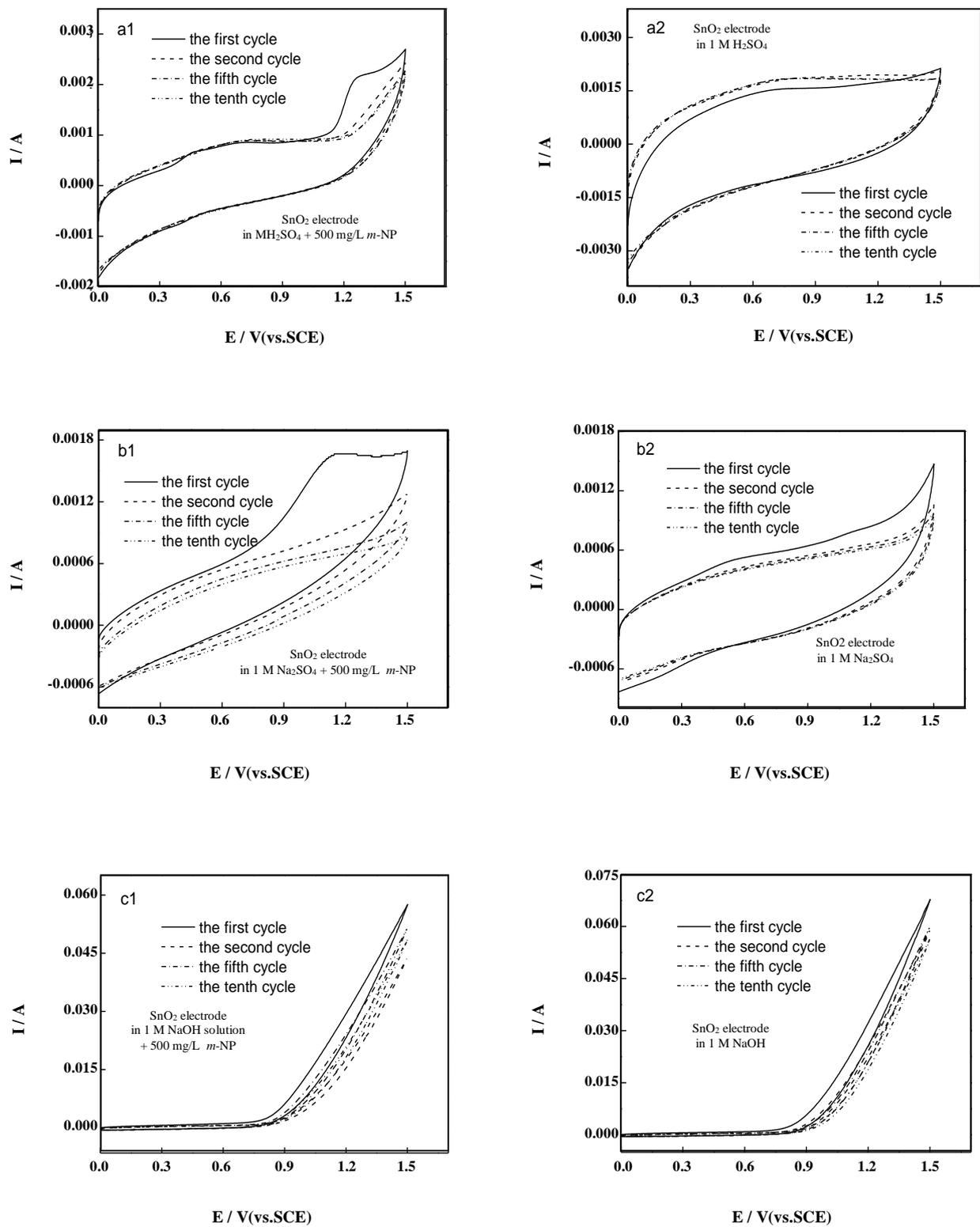


Fig. 4: Cyclic voltammograms of SnO_2 electrode in $1\text{ mol/L H}_2\text{SO}_4$, Na_2SO_4 , and NaOH solutions with (a1, b1, c1) and without (a2, b2, c2) $500\text{ mg/L } m\text{-NP}$. Scan rate: 50 mV/s .

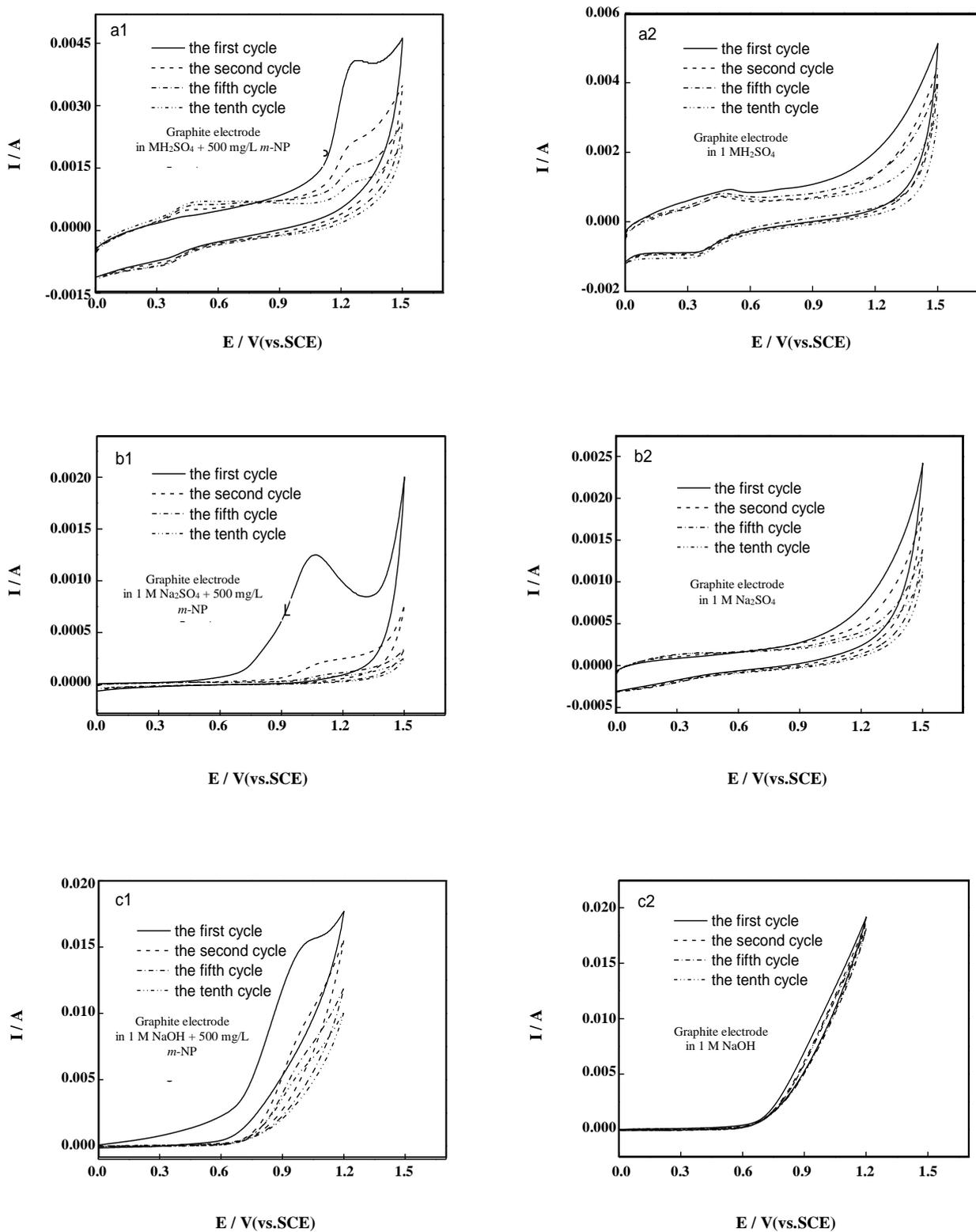


Fig. 5: Cyclic voltammograms of graphite electrode in 1 mol/L H_2SO_4 , Na_2SO_4 , and NaOH solution with (a1, b1, c1) and without (a2, b2, c2) 500 mg/L $m\text{-NP}$. Scan rate: 50 mV/s.

was very small, and the peak vanished almost after 10 scans. This means that the phenoxy radicals were indeed formed and these polymerized radicals resulted with a strongly adherent film on the surface of the electrode, which prevented the further oxidation of *m*-NP on the surface of the electrode. It also can be observed that the *m*-NP oxidation peak and oxygen evolution peak current is significantly decreased compared to the first cycle in the subsequent cycles in NaOH medium. It indicates that the electrode was also passivated in the alkaline medium, which was unlike glassy carbon electrodes. On the glassy carbon electrode, the oxidation of *m*-NP in NaOH solution did not lead to the passivation of the electrode. So, we deduced that the decrease of current on graphite electrode might be related to the bad corrosion resistance of graphite.

CONCLUSIONS

The electrochemical oxidation of *m*-NP on glassy carbon electrode, Pt electrode, PbO₂ electrode, SnO₂ electrode, and graphite electrode was investigated by cyclic voltammetry in acidic, neutral and alkaline media. The results show that both of the material of electrodes and pH value of media play a significant role in the oxidation of *m*-NP. Only on glassy carbon and graphite electrodes, the oxidation of *m*-NP occurred in all media, and the oxidation peaks of *m*-NP shifted towards lower potential values with the increase of pH value of the medium. In the alkaline medium, the *m*-NP could be directly oxidized only on glassy carbon electrode and graphite electrode, but anodic peaks were not well defined because the oxidation peak for *m*-NP occurred closer to oxygen evolution potential region. On Pt and SnO₂ electrodes, the *m*-NP was oxidized in H₂SO₄ and Na₂SO₄ solutions, while there was no any redox peak in the voltammograms obtained in NaOH solution. However, on PbO₂ electrode, the oxidation peak of *m*-NP only presented in the curves of Na₂SO₄ solution.

In all cyclic voltammetry curves, no corresponding reduction peak of *m*-NP was observed, implying that the oxidation of *m*-NP was totally irreversible electrode process under the experimental conditions. Additionally, passive films were formed on the surface of all electrodes after the electrochemical oxidation of *m*-NP except in the alkaline solution on the glassy carbon electrode.

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