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Polymer 42 (2001) 9665–9669

polymer

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Polypyrrole coatings on aluminum — synthesis and characterization

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Received 18 December 2000; received in revised form 15 May 2001; accepted 10 July 2001

Abstract

The electrodeposition of polypyrrole coatings on aluminum was carried out by cyclic voltammetry using oxalic acid as the electrolyte. The cyclic voltammograms show an anodic peak at around 0.0 V vs. SCE for very high scan rates (750 mV/s) at shorter cycles. With the increase in number of cycles (>10), the presence of this peak is no longer visible. This peak is related to the adsorption and oxidation of hydrogen. At shorter scan rates (50 mV/s), the length of time where the deposition of polypyrrole on the aluminum substrate takes place is much longer, and so the amount of polymer deposited in one cycle, is correspondingly more. The anodic peak at around 0.0 V vs. SCE was no longer visible after the first cycle in the cyclic voltammograms. The infrared spectroscopy of the coatings indicates that polypyrrole is in the doped form. The scanning electron micrographs show microspheroidal morphology of polypyrrole. © 2001 Published by Elsevier Science Ltd.

Keywords: Electrochemical deposition; Cyclic voltammetry; Polypyrrole

1. Introduction

In recent years, conducting polymers have taken a prominent place in the research world. They have potential applications in electronic displays [1], as electrode materials in batteries [2], as molecular electronic circuit elements [3], in restoration of data [4], as indicators of gasometers [5] and in biochemical analysis [6]. The conductivity of doped conducting polymers can be attributed to the delocalization of π-conjugated systems. Pyrrole is one of the important conducting polymers. Although polymers of pyrrole have been known for over 50 years, interest in these materials has greatly increased in the past decade because polypyrroles when doped become intrinsically electrically conductive.

The history of pyrrole dates back to 1916 [7] when it was prepared by the oxidation of pyrrole as powder called ‘pyrrole black’. In 1968 [8], it was noted that pyrrole could be electrochemically polymerized using a variety of oxidation agents to give a black conducting powder. Polypyrrole has a relatively high conductivity and environmental stability in the conducting state. For these reasons it has been an interesting material to study.

Polypyrrole can be synthesized both chemically [9] and electrochemically [10]. Aqueous electropolymerization has several advantages over the traditional coating techniques. It combines the formation of the polymer and its deposition on the substrate in one process. Because of this, a lot of work has been done in the synthesis of polypyrrole using the electrochemical technique. The nature of the working electrode plays an important role in the synthesis of polypyrrole. It is important that the working electrode does not oxidize concurrently with the monomer. For this reason polypyrrole was synthesized using an inert platinum or gold electrode [11]. But of late, polypyrrole has been synthesized on various substrates like iron, [12], steel [13], aluminum, brass, mild steel [14] and zinc. It has also been copolymerized extensively with polyaniline [15,16]. Polypyrrole has been doped with anions derived from oxalic acid [17] and hexacyanoferrate [18].

In this paper, we report the electrochemical polymerization of polypyrrole onto Al 2024 substrate in aqueous oxalic acid solution. Cyclic voltammetry is the technique used to electropolymerize polypyrrole.

2. Experimental

The electrochemical deposition of polypyrrole was carried out by using an EG and G Potentiostatic/Galvanostatic Model 273A. Cyclic voltammetry was used as the deposition technique. A one-compartment electrochemical cell was used to deposit the coatings. Two stainless steel rectangular sheets were used as the counter electrodes

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PII: S0032-3861(01)00529-8

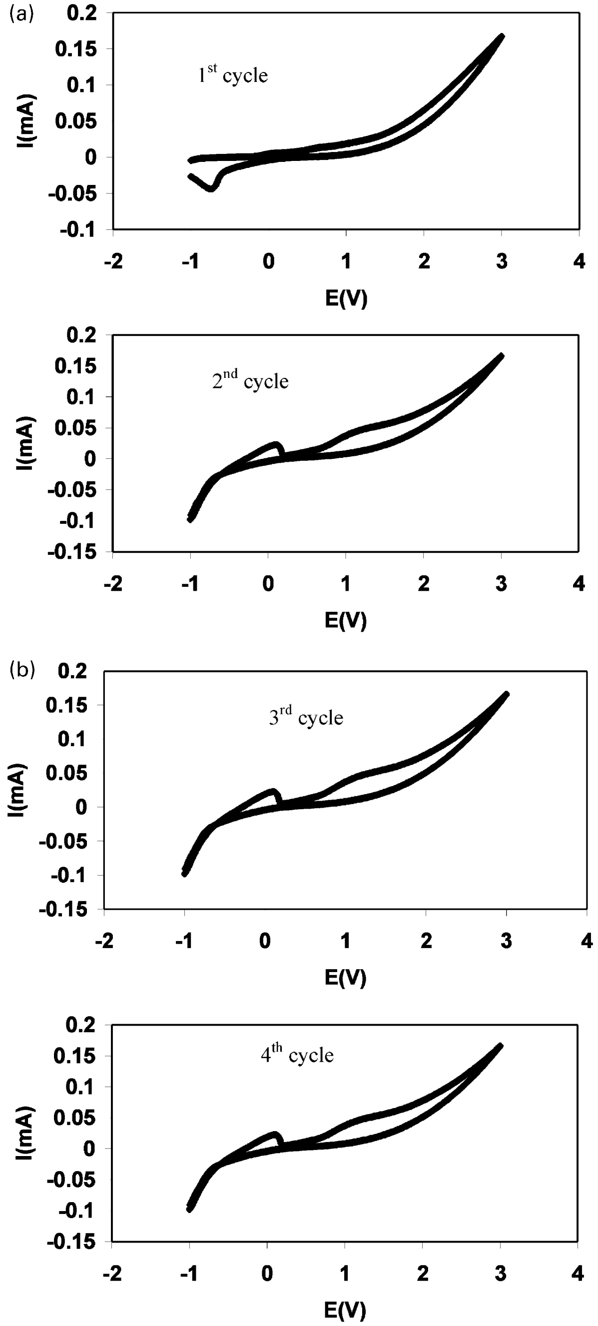


Fig. 1. Cyclic voltammograms of the polymerization of pyrrole (0.25 M) and oxalic acid (0.1 M) at 750 mV/s. (a) 1st and 2nd cycles, (b) 3rd and 4th cycles (working electrode; aluminum, counter electrodes; stainless steel, reference electrode; saturated calomel electrode).

(cathode) and a 2024 T3 bare aluminum alloy of dimensions $4 \times 1 \times 0.063''$ was used as the working electrode (anode). The aluminum samples were purchased from the Q-Panel Lab Products. The reference electrode was a saturated calomel electrode, SCE, which was purchased from the Fischer Scientific Company.

An aqueous solution of pyrrole (98%) and oxalic acid (98%) was prepared in deionized water. Pyrrole and oxalic acid were purchased from Aldrich Chemical Company. A 100 ml solution was used for each reaction. The concentrations of pyrrole and oxalic acid were kept constant at 0.25 and 0.1 M, respectively. Electrodeposition was carried out at scan rates of 50 and 750 mV/s, by varying the number of cycles (reaction time). All the reactions were monitored in the scan range −1.0–3.0 V vs. SCE. The pH of the solution was kept constant around 1.34. The current–potential (I–E) curves for the reactions were obtained for each scan rate and number of cycles. The aluminum samples were ultrasonically cleaned in acetone for 15 min before the reaction. The coated aluminum samples were washed with methanol and dried at room temperature.

The Reflection Absorption Infrared (RAIR) spectra of the polypyrrole coatings were obtained by using a Bio-Rad FTS-40 spectrometer. The angular specular reflectance attachment was set to an incident angle of 50°. The spectra was obtained using a resolution of 8 cm^{-1} and averaged over 256 scans for a scan range of 4000–400 cm^{-1}. A background spectrum of bare aluminum was subtracted from the acquired spectra in all cases. The surface structure and composition of the coatings were determined by scanning electron microscopy (SEM). The SEM micrographs were obtained by using a Jeol JSM-T220A Scanning Microscope.

3. Results and discussion

3.1. Cyclic voltammetry

Polypyrrole coatings were electrochemically deposited on aluminum substrate by cyclic voltammetry. Fig. 1(a) and (b), show the cyclic voltammograms obtained at a scan rate of 750 mV/s for the first four cycles. An anodic peak current is observed at around 0.0 V vs. SCE. This is

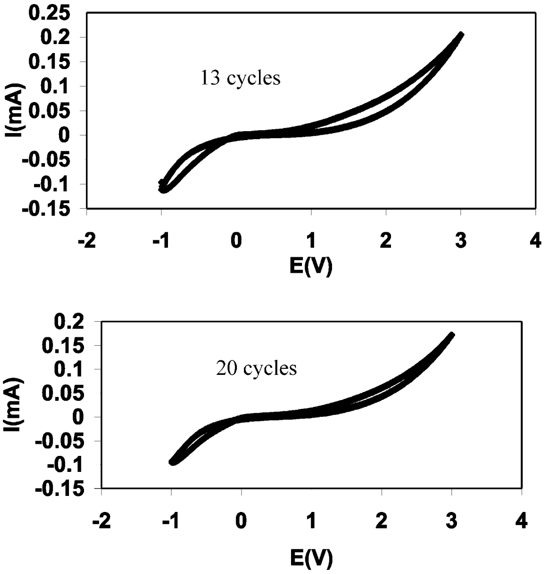


Fig. 2. Cyclic voltammograms of the polymerization of pyrrole (0.25 M) and oxalic acid (0.1 M) at 750 mV/s (working electrode; aluminum, counter electrodes; stainless steel, reference electrode; saturated calomel electrode).

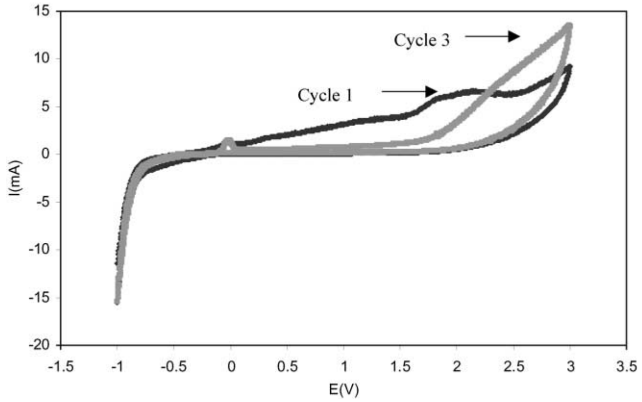


Fig. 3. Cyclic voltammograms of oxalic acid (0.25 M) at 20 mV/s for 1st and 3rd cycles (working electrode: aluminum, counter electrodes; stainless steel, reference electrode; saturated calomel electrode).

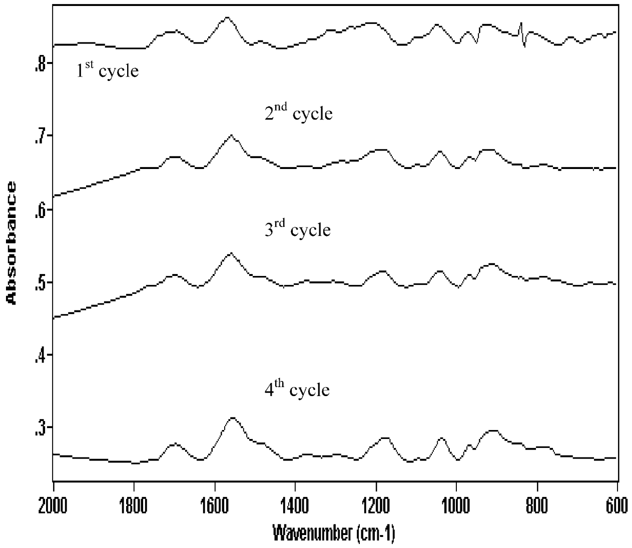


Fig. 5. Infrared spectra of the formation of polypyrrole at 750 mV/s.

the peak associated with the adsorption and oxidation of hydrogen (Eq. (4)). We believe that initially aluminum is oxidized to positive aluminum ions (Eq. (1)). Simultaneously oxalic acid dissociates to form the oxalate ions and positive hydrogen ions (Eq. (2)). These positive hydrogen ions and the electrons lost by the oxidation of aluminum combine to give hydrogen gas (Eq. (3)). The hydrogen gas, thus obtained adsorbs onto the working electrode and oxidizes to positive hydrogen ions. Also, from previous literature, it has been noted that adsorption of hydrogen also occurs at this point [19]. This is the reason for the peak around 0.0 V vs. SCE. There is no corresponding cathodic peak in the reverse scan implying that this process is irreversible. At this time, the oxalate ions and the positive aluminum electrons combine to form the amorphous passive layer, aluminum oxalate. There is another anodic peak current observed in the range of 0.5–1.0 V vs. SCE in the first cycle which becomes broader and shifts anodically from 1.0–1.5 V vs. SCE as the reaction is continued for two or more cycles. This peak is related to the oxidation of the monomer. There is a corresponding cathodic peak current at around −0.75 V, which is related to the reduction of the oxidized monomer in the first cycle. In the second

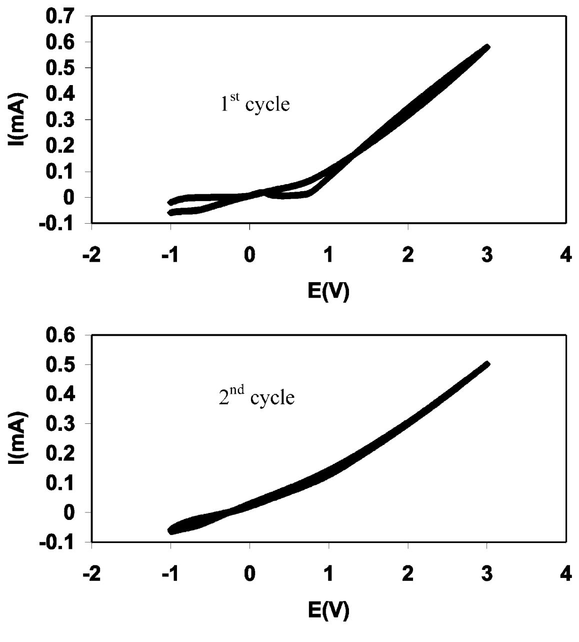


Fig. 4. Cyclic voltammograms of the polymerization of pyrrole (0.25 M) and oxalic acid (0.1 M) at 50 mV/s (1st and 2nd cycles) (working electrode; aluminum, counter electrodes; stainless steel, reference electrode; saturated calomel electrode).

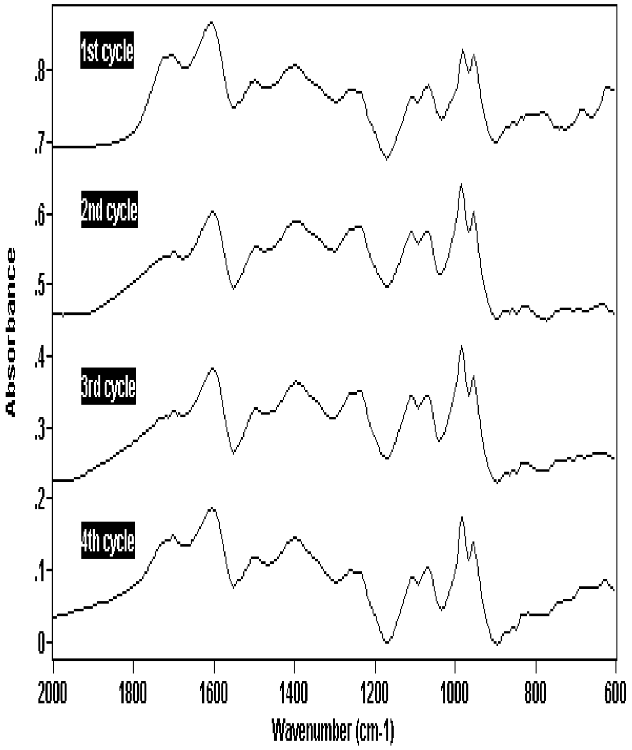
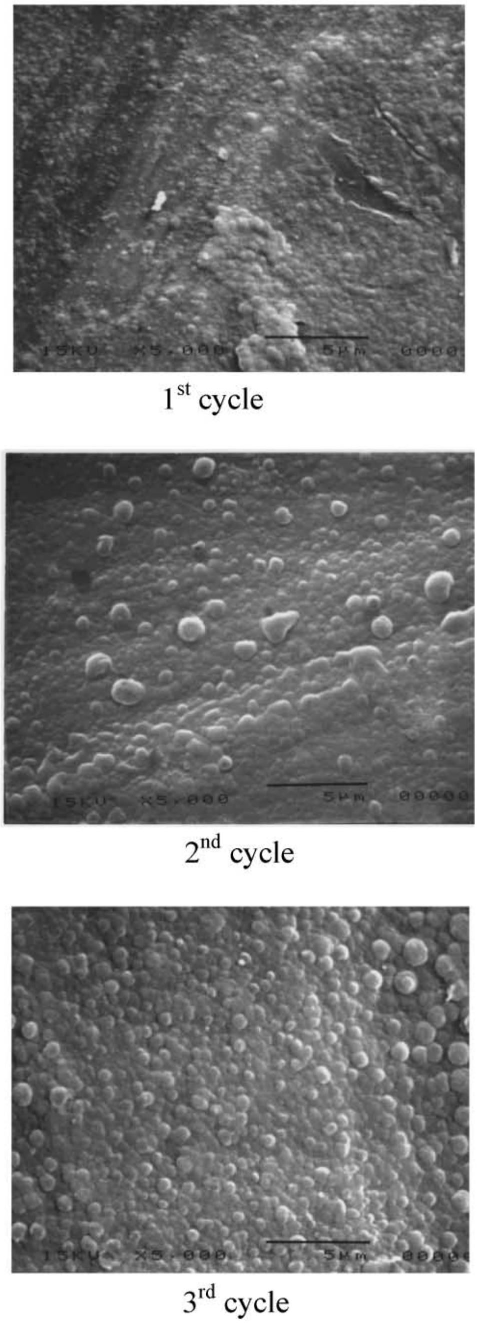


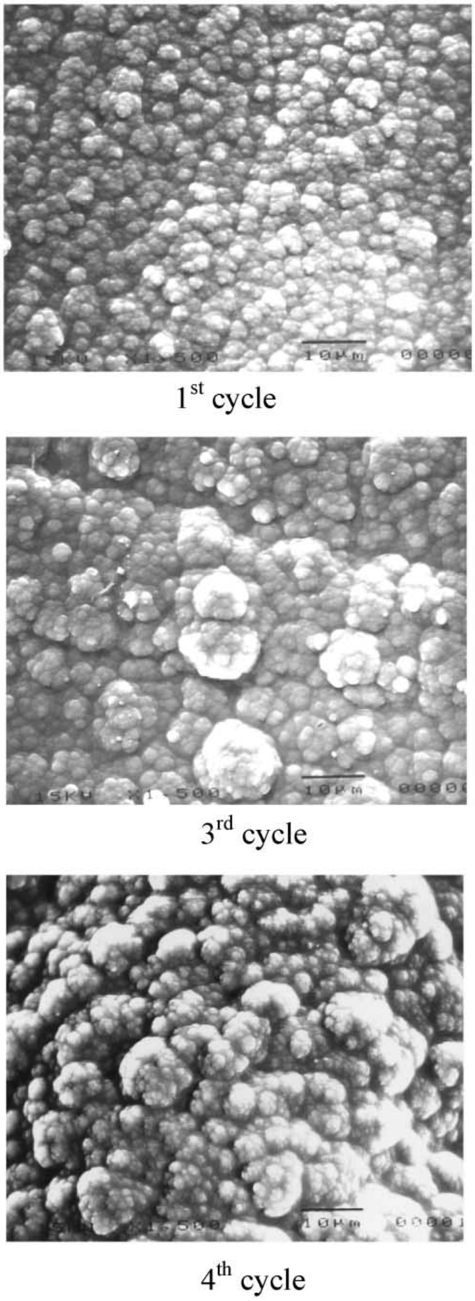
Fig. 6. Infrared spectra of the formation of polypyrrole at 50 mV/s.


1st cycle

2nd cycle

3rd cycle

Fig. 7. Scanning electron micrographs of the formation of polypyrrole at 750 mV/s.


1st cycle

3rd cycle

4th cycle

Fig. 8. Scanning electron micrographs of the formation of polypyrrole at 50 mV/s.

cycle there is no noticeable corresponding cathodic peak in the reverse scan implying that the reaction becomes completely irreversible. As the number of cycles are further increased (>10) all the anodic peak currents observed in the first few cycles are no longer visible, as can be seen from Fig. 2. The appearance of trace-crossing is observed in the cyclic voltammograms. The reason for the appearance of trace-crossing has not yet been clearly established [10]. The cyclic voltammograms showing the behavior of oxalic acid is shown in Fig. 3. It can be seen that the anodic peak at around 0.0 V vs. SCE is present. This suggests that the presence of this peak in the cyclic voltammograms is related to hydrogen and not to the monomer.

$$2\mathrm{Al} \Leftrightarrow 2\mathrm{Al}^{3+} + 6\mathrm{e}^- \tag{1}$$

$$\mathrm{H_2C_2O_4} \Leftrightarrow 2\mathrm{H}^+ + \mathrm{C_2O_4^{2-}} \tag{2}$$

$$2\mathrm{H}^+ + 2\mathrm{e}^- \Rightarrow \mathrm{H_2}\uparrow(\mathrm{g}) \tag{3}$$

$$\mathrm{H_2} \Rightarrow 2\mathrm{H}^+ + 2\mathrm{e}^- \tag{4}$$

$$2\mathrm{Al}^{3+} + 3\mathrm{C_2O_4^{2-}} \Rightarrow \mathrm{Al_2(C_2O_4)_3} \tag{5}$$

Since the current for the first cycle decreases with increase in scan rate, it can be said that this peak is not due to passivation. Fig. 4 shows the cyclic voltammograms for the polymerization of pyrrole at a scan rate of 50 mV/s for the first two cycles. But in this case the anodic peak current at around 0.0 V vs. SCE is visible only in the first cycle. This is because, at 50 mV/s, the length of time where the deposition of polypyrrole on the aluminum substrate takes place is much longer, and so the amount of polymer deposited in one cycle, is correspondingly more. At this point, trace-crossing appears in the cyclic voltammograms.

3.2. Infrared spectroscopy

The infrared spectra of the polypyrrole coatings were obtained by Reflection Absorption Infrared (RAIR) spectroscopy. Figs. 4 and 5 show the infrared spectra of the coatings deposited at 750 and 50 mV/s, respectively. The peaks in the range of 1580–1390 and 1105–1070 cm^{-1} are due to C=C and C=N in plane vibrations, respectively. The peak due to the pyrrole ring deformation is seen at around 1030 cm^{-1}. The peak seen at 1700 cm^{-1} is the C=O peak which is due to the dopant, in this case, the oxalate ions (Fig. 6).

3.3. Scanning electron microscopy

Fig. 7 shows the scanning electron micrographs of the formation of polypyrrole on aluminum substrate at a scan rate of 750 mV/s at a magnification of 5 K. It can be seen that as the number of cycles increase, the size of the microspheroidal grains, characteristic of polypyrrole also increase. The same trend can be observed for the formation of polypyrrole at a scan rate of 50 mV/s as shown in Fig. 8 at a magnification of 1.5 K. In both the cases, there is considerable increase in the formation of polypyrrole on the substrate as the number of cycles is increased.

4. Conclusions

The electrodeposition of polypyrrole on aluminum substrate was successfully carried out by using oxalic acid as electrolyte. The technique used for the synthesis of polypyrrole was cyclic voltammetry. The electrodeposition was carried out at scan rates of 750 and 50 mV/s. For the higher scan rate of 750 mV/s, an anodic peak due to the adsorption and oxidation of hydrogen is clearly observed in the cyclic voltammograms at around 0.0 V vs. SCE for short cycles. With the increase in number of cycles, trace-crossing appears in the cyclic voltammograms. At 50 mV/s, the length of time where the deposition of polypyrrole on the aluminum substrate takes place is much longer, and so the amount of polymer deposited in one cycle, is correspondingly more. The peak at 0.0 V vs. SCE due to the adsorption and oxidation of hydrogen is not seen in the second cycle. The infrared spectra suggest that polypyrrole is in doped form. The scanning electron micrographs reveal a microspheroidal structure of polypyrrole. They also indicate that in both the cases, there is considerable increase in the formation of polypyrrole on the substrate as the number of cycles is increased.

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