Effect of Modification on Electrochemical Chelation of Polyimide Films

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Abstract

Novel procedure of electrochemical chelation of polyimide films was developed. The kinetics of silver cation sorptions into the films during the chelation was found out. The effect of modification treatment of film surfaces on kinetics of electrochemical process was studied. The stabilization of ion-sorbed layer of films occurs in water-isopropanol solvents. Sorption of silver during electrochemical deposition is 0.75-1.5 mg per 100 μm of polyimide depending on modification solution. Thus, the most appropriate morphological modification with about 1.5 mg/100 μm take places in heterocyclic solvents. The resulting metallized polyimide films show good non-washing out adhesion of metal into gel-like structured surfacial layers of the film.

Introduction

Metallization of polyimide (PI) films is the most promising tendencies in current science and technology due to the possibilities to obtain constructs with specific physical and mechanical properties [1,2]. Physical methods of PI metallization (vacuum pulverization, electrochemical deposition and so on) do not provide the appropriate adhesion of metal on the PI surfaces due to poor adhesive properties between metal and PI. Moreover, such ways are quite expensive and require excessive energy. In these regards some methods of preliminary treatment of PI surface layers were developed [3,4]. Most of them include a few steps of aggressive physical treatment (laser ablation, UV-irradiation, electron or ion bombardments) or chemical ones, such as hydrolysis of the imide cycle in tough conditions (3-5 M alkali solutions); acid treatment of polyamate layers; or extensive cation exchange of alkali ions on Pd^{2+} ones. That can also include a final modifying treatment by tin chloride with the formation of such complex:

$$\begin{array}{c} O \\ \| \\ C-O \end{array} \left(\bigcirc^{-}\right) Pd^{2+}$$

with following electrochemical or chemical precipitation of copper cations onto modified surfaces The reduction of copper ions creates in PI films a metallic layer with its thickness of 30-35 μm.

Institute of Chemical Sciences (ICS) has developed a novel hydrolysis way of PI film modification in mild non-traumatic conditions [5]. Our last investigations [6-8] show that including chemical conversion of PI surface there is formation of well-developed mesoporous structures with pore diameter within 20-70 nm [8]. Modification of such porous layer leads to loosening of subsurface layer structure. Eventually, that strongly effects on depth of metal impregnation in PI films.

Sorption of silver cations by modified layer of PI films is a main step of the formation of electroconductive and reflective metal coating onto PI films. However, mechanism and kinetics of PI modification is still vague. A goal of this study is focused on the effect of morphological modification of PI films

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on their surface and subsurface structure. We studied kinetics of AgNO₃ sorption into the modified PI films after basic morphological changes of film surfaces. That plays a major role for the formation of metal layer onto PI matrix surfaces in the media of various solvents, such as keton and amide type solvents, including heterocyclic ones.

Experimental

Absorption kinetics of silver cations into a modified surface layer of PI films was carried out in 10^{-4}-10^{-2} M solutions of silver ions with its potentiometric control. Kapton 75HN and 100HN were used for electrochemical deposition of silver.

The films were modified in alcohol-aqueous solutions (stabilization I) and aqueous (stabilization II) solutions. Modification of films were carried out in heterocyclic, solutions, such as tetrahydrofuran (modification A); ketone solutions, such as acetone and diethylketone (modification B)

Ion-selective electrodes made of Ag₂S and silver wire, coated with AgCl were used. A standard AgCl electrode was as referent standard joined through a salt bridge. Background electrolyte and bridge ones were as solution of 0.1 N potassium nitrate.

The hydrolyzed films with size 1.5×4 cm (surface 12 sq.cm) were immersed into an electrochemical cell (volume 25 cm³) filled with silver nitrate. The solution was stirred gently at constant rate. The measurement of the potential of indicator electrode was recorded with digital pH-meter MERA-TRONIC 5170 (ELWRO) under 0.1 mV precision during 2-5 hs until fully absorption of Ag ions by the film [9].

Results and Discussion

Chemical chelation procedure developed at ICS could be described by such scheme:
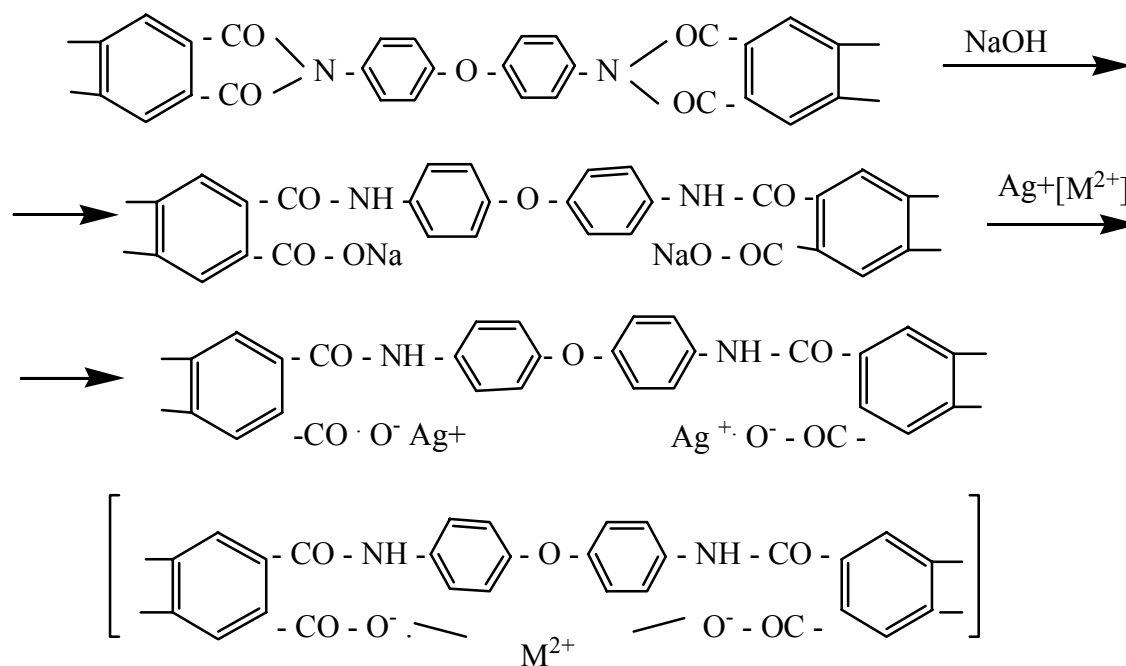
The main criterion of metal choice is to the formation of ligand complexes – metal/organic compound. Chelation kinetics is complicated process itself, which includes several step, such as:

1. shipment of ion to PI surface with following ion exchange at the interface of film and solution;
2. diffusion of chelating agent inside the film;
3. ion exchange inside the film (detail investigation of this process has been described earlier [12] with the use of model analog).

We suggest that a limiting step of the procedure is ion exchange rate inside film. Thus, the dependence of limiting reaction rate could be expressed by equation:

$$\partial C/\partial \tau = -KC, \text{ or } \partial(lnC) = K\partial \tau \qquad (1)$$

where, K- reaction rate constant; C – AgNO₃ concentration, that is referring to linear step of kinetic po-

tential. If there is a limitation of one of two first steps, that could be described:

$$C = C_0 exp(-K\tau) \quad (2)$$

where C_0 – initial concentration of AgNO$_3$; τ – sorption time; K – coefficient of rate constant at film-solution interface in the case of slowed reaction. By another words, K describes thickness of diffusion layer and ratio of film square to solution volume in the case of slowed diffusion.

Electrode potential measured in our experiments is strongly linked to silver cation concentration in solution by following equation:

$$E = E_o + \frac{RT}{nF} \ln C \quad (3)$$

or finally:

$$E = E_o + \frac{RT}{nF} \ln(C - K\tau) \quad (4)$$

Thus, potential-time plot at the both kinetic limitations should be linear [9]. To confirm that we studied a series of kinetics at both diffusive and reactive limitations with the change of the initial potential during silver ion sorption in the various solvents: A – heterocyclic type (Fig. 1); B – ketone (Fig. 2); and C – amide type (Fig. 3). As shown in Fig.1 the curves have following steps:

I – sharp drop of the potential at the initial time (a) due to chemical sorption of silver ions by PI film surface of modified active layers. The layers are a gel-like structure of potassium polyamate stabilized in water-alcohol (isopropanol) solutions;

II – linear decrease of potential (b) by lgC$_{Ag}$ as function of time. Some of them is divided by horizontal plot (d), which points out constant concentration of silver cations in the solution. There is a obvious slowing of chelation because of low ability of the cations for diffusion deep inside the modified layers;

III – stabilization of potential at the constant level according to degree of film saturation by the cations. We have described already [5] the details of this step regarding the accumulation of carboxyl groups in the modified layers with final stabilization at the maximal concentration of the groups. That was measured by so-called wet method [11].

Degree of film dissolution plays a major role for mechanism of chelation and strongly dependent on silver ion concentration. As known [6], solubility of the modified layer of PI films is extremely high, especially in aqueous solutions. To prevent it we chose
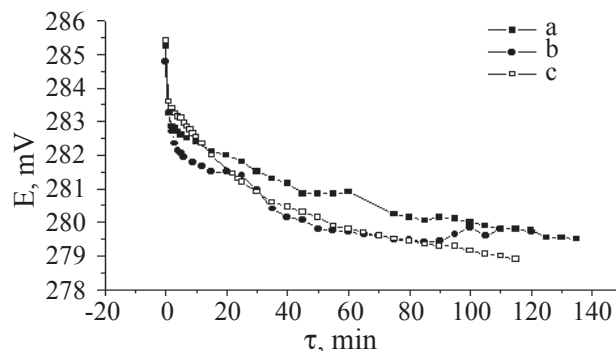

Fig. 1. Kinetics of chelation of PI films, modified by type A: a- stabilization II and b, c – stabilization I.
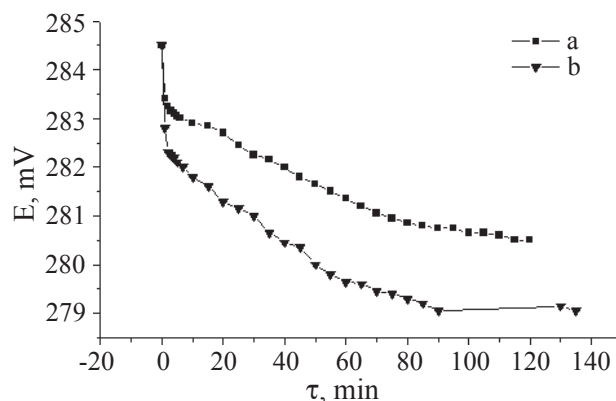

Fig. 2. Kinetics of chelation of PI films, modified by type B: a- stabilization II and b – stabilization I.
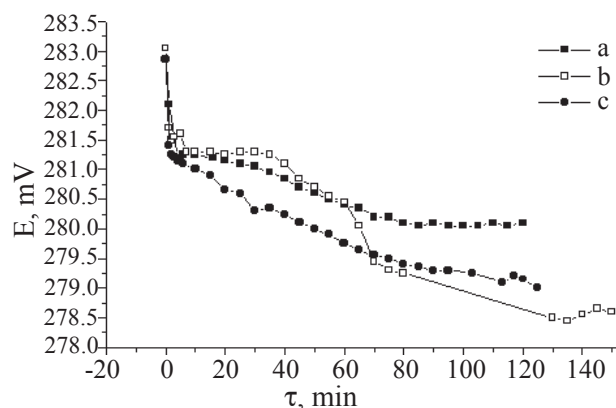

Fig. 3. Kinetics of chelation of PI films, modified by type C: a- stabilization II and b, c – stabilization I.

the optimal silver ion concentration 10^{-2} M, which is really close to fit conditions for electrochemical deposition of metals in the films. According to Table 1 the most appropriate morphological modification occurs in heterocyclic solvents.

Table shows calculated data of sorbed silver inside the modified PI films at various conditions and ways of surface stabilization.

It could be concluded comparing the results that

Table 1
Sorption of silver by modified PI film

Solvent	Satbilization method	Film weight addition (mg)	Sorbed Ag (mg)	Average Ag amount (mg)
Heterocyclic	isopropanol	0.45	5.5	5.82
		0.35	6.13	
	water	0.35	6.13	5.31
		0.25	6.05	
		0.20	5.17	
Ketone	isopropanol	0.70	5.15	5.15
		0.70	5.15	
	water	0.30	3.78	3.6
		0.10	3.4	
Amide	isopropanol	0.30	4.43	3.6
		0.20	2.80	
	water	0.30	3.83	5.10
		0.20	6.40	

the maximal silver sorption manifests in heterocyclic solvents with stabilization in alcohol aqueous solution. The minimal level occurs in ketone solvents with final water stabilization. Sorbed amount of silver does not wash out if the washing is gently carried out by alcohol-water mixture at the stabilization of PI films. Bicomponent solvent provides good enough washing out excess of hydrolytic alkali, besides alcohol does not dissolute modified layer stabilizing its gel-like structure. That was correlated with out IR-spectra data [13].

Acknowledgment

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