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Electrosynthesis of organic–inorganic nanocomposites

I. Zhitomirsky *

Department of Materials Science and Engineering, McMaster University, 1280 Main Street West,
Hamilton, Ont., Canada L8S 4L7

Abstract

Composite films containing nanoparticles of oxides/hydroxides of Al, Y and Zr in a polyethylenimine (PEI) matrix were prepared by novel electrochemical method based on cathodic electrosynthesis of inorganic nanoparticles and cataphoretic deposition of PEI. The PEI content in the films was varied in the range of 0–60 wt.% by variation of PEI concentration in solutions. Films of various thickness in the range of up to several microns were obtained by the variation of the deposition time. The mechanism of the deposition is discussed.

Keywords: Nanostructures; Polymer; Thin films; Precipitation; Thermal analysis

1. Introduction

The fabrication of organic–inorganic nanocomposites has been the subject of intense investigations [1–3]. Such composites combine the advantageous properties of inorganic materials with those of polymers, and exhibit important optical, electrical, magnetic, catalytic, mechanical and other functional properties.

There is an increasing interest in the development of nanostructured organic–inorganic composites by novel electrochemical methods. Cathodic electrosynthesis has been utilized for the fabrication of thin films and powders of individual oxides, complex oxide compounds and alloys [4–8]. Recently the possibility of cathodic electrosynthesis of composite materials containing inorganic nanoparticles and polymers has been demonstrated [8,9]. New electrochemical strategies [8–10] enable the formation of inorganic nanoparticles in situ in a polyelectrolyte matrix, preventing particle agglomeration. Recent studies showed the influence of polymers on the crystallinity and size of the inorganic nanoparticles formed by electrosynthesis in the polymer matrix [11,12]. New electrochemical methods provide the capabilities for the fabrication of fuel cells, superparamagnetic films, fiber reinforced composites and advanced coatings for biomedical implants [8–16].

PEI has many important properties utilized in biomedical, catalytic, electronic and other applications. Significant interest has been generated in the surface modification of materials using PEI. This paper, motivated by the importance of PEI for thin film applications, presents experimental results on the deposition of novel nanocomposites based on PEI and addresses the deposition mechanism.

2. Experimental procedures

Solutions of $ZrOCl_2 \cdot 8H_2O$ (Fluka), $Y(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich) and polyethylenimine (PEI, MW 70,000, Aldrich) in a mixed methanol–water (5% water) solvent were used for electrodeposition. Cathodic deposits were obtained by the galvanostatic method on Pt foils and carbon fibers (Lydall) at a current density of $5\,mA/cm^2$. The electrochemical cell for deposition included a cathodic substrate centered between two parallel platinum counterelectrodes. The electrolytic deposits were scraped from the Pt electrodes for X-ray diffraction (XRD) and thermogravimetric analysis (TG). The phase content was determined by XRD with a diffractometer (Nicolet I2) using monochromatic Cu Kα radiation at a scanning speed of 0.5°/min. TG analyses were carried out in air between room temperature and 1200 °C at a heating rate of 5 °C/min using a thermoanalyzer (Netzsch STA-409).

3. Experimental results

Fig. 1 compares the results of the TG analysis for the films prepared from the $Al(NO_3)_3$ solutions without additives and those containing 0.4 g/l PEI. Thermal analysis of the deposits prepared from the $Al(NO_3)_3$ solutions without additives revealed the total weight loss of 54.5 wt.% at 1200 °C. The weight loss below 400 °C can be attributed to the thermal dehydration of the deposits. The deposit prepared from the solution containing PEI showed weight loss of 64.1 wt.% below 500 °C, at higher temperatures the sample weight changed gradually, resulting in the total weight loss of 67.2 wt.% at 1200 °C. The sample prepared from the solution containing PEI showed higher weight loss compared to the sample prepared from the pure $Al(NO_3)_3$ solutions. The additional weight loss

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* Tel.: +1 905 525 9140x23914; fax: +1 905 528 9295.
E-mail address: zhitom@mcmaster.ca.

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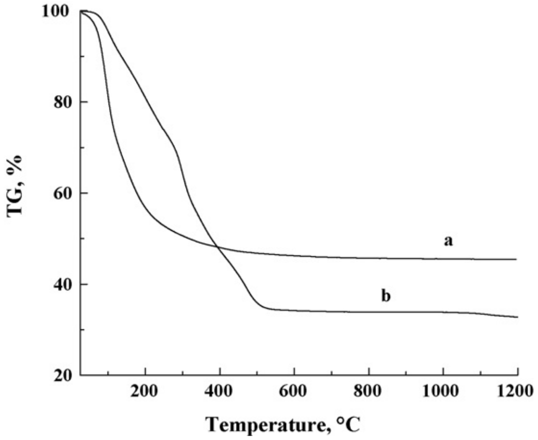

Fig. 1. TG data for the deposits prepared from the 5 mM $Al(NO_3)_3$ solutions without additives (a) and containing 0.4 g/l PEI (b) at a current density of 5 mA/cm^2.

can be attributed to burning out of the deposited PEI. From the TG data shown in Fig. 1 the amount of PEI in the composite films was found to be 27.9 wt.%.

TG studies (Fig. 2) of the samples prepared from the 5 mM $Y(NO_3)_3$ solutions, containing 0.4 and 0.8 g/l PEI showed the total weight loss of 52 and 62.4 wt.%, respectively. The total weight losses at 1200 °C for the deposits exceed the corresponding value of 48.6 wt.% for the deposits prepared from $Y(NO_3)_3$ solution without PEI. From the TG data shown in Fig. 2 it may be concluded that the deposition process resulted in the formation of composite films, containing different amounts of PEI.

The results given in Fig. 3 indicate that the deposit weight increases with deposition time at a constant current density. The weight increase was essentially linear, indicating a constant rate of deposition. Therefore the amount of the deposited material can be controlled by the variation of deposition time.

Fig. 4 shows the results of XRD study of the deposits prepared from 5 mM $Y(NO_3)_3$ solutions containing 0.4 g/l PEI. The films were essentially amorphous below 400 °C and exhibited a halo near $2\Theta \sim 30°$ (Fig. 4). Small peaks of Y_2O_3 appeared on X-ray diffraction pattern at 500 °C. On sintering the deposits at 600 °C, the X-ray diffraction pattern displayed the peaks of Y_2O_3 (JCPDS Index Card 25–1200). The results of XRD coupled with the results of TG study and deposition yield measurements indicate co-deposition of yttrium species and PEI and the formation of composite films.

The co-deposition of zirconia and PEI was performed from the solutions of various PEI concentration and the results of TG studies of the deposits were used for the calculation of the PEI content in the composite films. Fig. 5 shows the PEI content in zirconia–PEI deposits versus PEI concentration in the 5 mM $ZrOCl_2$ solutions used for electrodeposition. The increase in PEI concentration in the solutions resulted in increasing PEI content in the deposits. Obtained TG data indicates that the mass fraction of PEI in the deposits can be varied in the range of 0–60 wt.% by the variation of PEI concentration in the solutions.

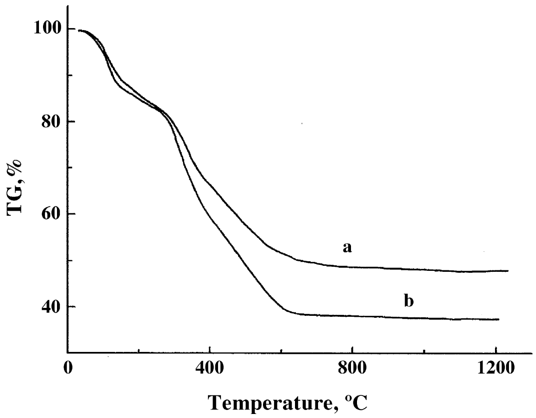

Fig. 2. TG data for the deposits prepared from 5 mM $Y(NO_3)_3$ solutions containing 0.4 g/l (a) and 0.8 g/l (b) PEI at a current density of 5 mA/cm^2.

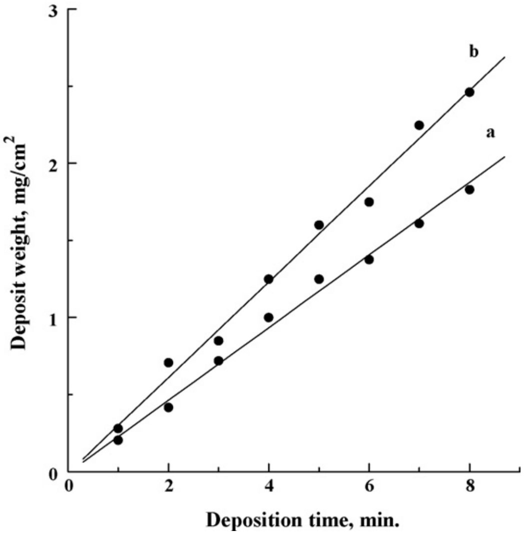

Fig. 3. Deposit weight versus deposition time for the deposit prepared from the 5 mM $Y(NO_3)_3$ solutions containing 0.4 g/l (a) and 0.8 g/l PEI (b) at a current density of 5 mA/cm^2.

SEM investigations revealed the formation of dense and uniform films. The film thickness was varied in the range of up to several microns by variation of deposition time. It is important to note that oxide/hydroxide films prepared by electrodeposition and other wet chemical methods exhibit cracking attributed to drying shrinkage when deposit thickness exceeds ~0.1 μm. The use of PEI with inherent binding properties enabled the formation of relatively thick, crack-free and adherent deposits.

4. Discussion

The experimental results indicate the possibility of the fabrication of composite films containing PEI and hydroxides/oxides of Al, Y and Zr. The mechanism of deposit formation is based on electrophoretic deposition of PEI and cathodic electrosynthesis of inorganic nanoparticles. Note, that PEI macromolecules have no charge and must be positively charged for the cataphoretic

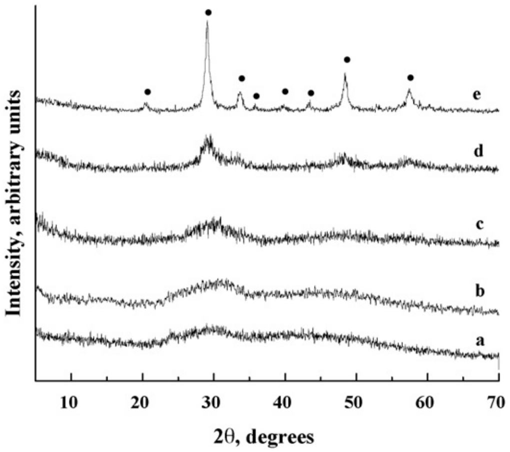

Fig. 4. X-ray diffraction patterns of deposits prepared from 5 mM $Y(NO_3)_3$ solutions containing 0.4 g/l PEI: as prepared (a) and after heat treatment at 300 (b), 400 (c), 500 (d) and 600 °C (e) ((●) Y_2O_3, JCPDS Index Card 25-1200).

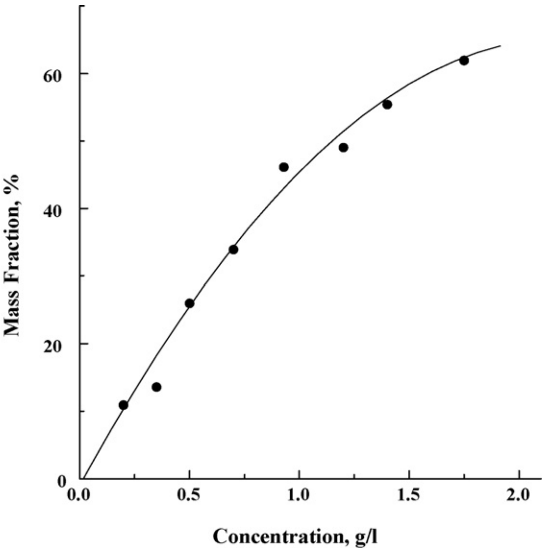

Fig. 5. Mass fraction of PEI in deposits versus PEI concentration in 5 mM $ZrOCl_2$ solutions.

deposition. It is suggested that PEI forms PEI–Me^{n+} (Me = Al^{3+}, Zr^{4+} and Y^{3+}) complexes [17–19], which behave as cationic polyelectrolytes in solutions. The complexation of metal ions by PEI occurs through intramolecualar formation of chelates, which form homogeneous solutions [18,19]. It is known that the drying of PEI–metal complex solutions results in the formation of amorphous solids that are generally insoluble in water due to crosslinking [18,19]. Therefore, the use of the solutions of PEI-metal ion complexes for electrodeposition offers a possibility of the formation of insoluble deposits.

It is known that the formation of PEI–Me^{n+} complexes is influenced by the pH. The solvated metal cations M^{z+} in solutions release protons to form acidic solutions:

$$M(H_2O)_n{}^{z+} \rightarrow M(H_2O)_{n-x}(OH)_x{}^{(z-x)+} + xH^+ \qquad (1)$$

As a result, PEI macromolecules can be partially protonated in the acidic solutions. Therefore, the charging of PEI can result from the formation PEI-Me^{n+} complexes or partial protonation of the PEI macromolecules. Due to the competitive bonding of H^+ and Me^{n+} to the PEI macromolecules at low pH, the M^{z+} ion binding capacity of PEI increases with increasing pH [17–19].

In the cathodic electrosynthesis method the bulk pH is usually low, whereas cathodic reactions result in significant pH increase at the electrode surface. Metal ions or complexes are hydrolyzed by electrogenerated base to form hydrated oxide or hydroxide deposits on the cathodic substrates [8]. Therefore the formation of composite films can be considered as a result of heterocoagulation of PEI–metal ion complexes or PEI macromolecules and inorganic particles formed at the electrode surface.

The experimental results presented in Fig. 5 indicate the fabrication of composite materials containing various amounts of PEI. The polymer content in the deposits can be varied by the variation of the polymer concentration in the solutions. The possibility of electrosynthesis of inorganic particles in situ in a polymer matrix holds a promise for the fabrication of non-agglomerated nanoparticles of controlled size [11,12]. Co-deposition of PEI and oxide/hydroxide films is also important for the fabrication of thick oxide films. In this case, the use of PEI as a binder with easy burnout properties is important for the crack prevention during the drying and sintering of the oxide films. The results of this work pave the way for the fabrication of thick films of complex oxide compounds, solid solutions and composites. Current research is focused on the use of PEI polychelates for the fabrication of thick films of yttria stabilized zirconia and ZrO_2–Al_2O_3 composites.

5. Conclusions

Composite films were obtained by the combined electrodeposition method based on electrosynthesis of inorganic nanoparticles and cataphoretic deposition of PEI. The method enables electrosynthesis of oxide/hydroxide particles of Al, Y and Zr in situ in a PEI matrix. The composition of the deposits can be varied by the variation of PEI concentration in the solutions. The deposition yield can be controlled by the variation of deposition time at a constant current density. The results pave the way for the fabrication of other organic–inorganic nanocomposites and thick oxide films.

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