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Electrodeposition of Organic-Inorganic Nanocomposites Materials

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Abstract

electrochemical deposition methods for the preparation of New organic-inorganic nanocomposite coatings were proposed. These methods are starts from the electrophoretic deposition (EPD) of ceramic nanoparticles and polymers. EPD is the motion that charged particles move towards the electrode in the applied electric field. Short processing time and process simplicity are the advantages of electrochemical deposition methods. Moreover, EPD methods for the fabrication of organic-inorganic of nanocomposites like ZnO films achieved non-agglomeration which is a promising method for the future industrial application. Electrode deposition achieved was by using 16-phosphonohexadecanoic acid (16PHA), octadecylphosphonic acid (ODPA), stearic acid (SA) and polyethylenimine (PEI) is used for dispersion.

The characterization can be performed by XRD, SEM, Cyclic voltammetry, impedance spectroscopy, potentiodynamic studies, FTIR, TGA, DTA etc.

For those organic-inorganic nanocomposites coatings, these various coatings are widely used in a great many aspects such as biomaterials, solar energy, aerospace, fuel cells, supercapacitors and quantum dots. These materials, combine the properties of organic and inorganic components and exhibit advanced properties, which broaden application areas and improve the applications' properties dramatically.

The article is trying to illustrate the new electrochemical deposition methods for the fabrication of organic-inorganic nanocomposites and its principle.

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Table of Contents

Electrodeposition of Organic-Inorganic Nanocomposites Materials
Abstract
Acknowledgementii
Chapter 1 Introduction 1
Chapter 2 Literature Review
2.1 Electrochemical Deposition
2.2 Particle interactions and suspension stability6
2.2.1 DLVO theory
2.2.2 Other interparticle forces
2.3 Deposition theories
2.3.1 Particle charging12
2.3.2 Aqueous suspensions13
2.3.3 Non-aqueous suspensions14
2.3.4 Additives for particle charging15
2.4 Solvents
2.5 Binders
2.6 Double layer and electrophoretic deposition kinetics
2.7 FRM materials and applications24
2.8 Co-deposition of organic-inorganic composite coatings by EPD

2.9 EPD of weak polyelectrolytes and electro-synthesis of inorganic
particles
2.10 EPD of weak polyelectrolytes and EPD of inorganic particles
2.11 Investigation of biomimetic adhesion
Chapter 3 Objectives
Chapter 4 Experimental Procedures
4.1 Materials
4.1.1 Materials purchased from commercial suppliers
4.1.2 Fabrication of materials by chemical precipitation
4.1.3 Hydrothermal synthesis of CeO ₂
4.2 Liquid-Liquid extraction
4.3 Coatings formation by electrodeposition methods
4.3.1 Experimental setups for electrodeposition
4.3.2 Preparation of solutions and suspensions for electrodeposition .46
4.3.3 Electrodeposition procedures
4.3.4Polymer-metal ion complex (PC) EPD47
4.5 Characterization of coatings
4.5.1 X-ray diffraction analysis
4.5.2 Scanning and transmission electron microscopy
4.5.3 Thermogravimetric and differential thermal analysis

4.5.4 Fourier-transform infrared spectroscopy (FTIR) 50
Chapter 5 Results and Discussion
5.1 Structural characterization of inorganic particles prepared by chemical
precipitation
5.1.1 X-ray diffraction analysis51
5.1.2 Transmission electron microscopy of inorganic particles53
5.1.3 The memory type flame retardant materials (FRM)
5.2 Particle extraction through liquid-liquid interface
5.2.1 Characterization of the inorganic particles after extraction
5.2.2 Mechanism of liquid extraction63
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles 66 Chapter 6 Investigation of LPEI 73 6.1 Electrodeposition of nanoparticles with polyethylenimine 73
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles 66 Chapter 6 Investigation of LPEI 73 6.1 Electrodeposition of nanoparticles with polyethylenimine 73 6.1.1 Mechanism of electrodeposition process 73
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles 66 Chapter 6 Investigation of LPEI 73 6.1 Electrodeposition of nanoparticles with polyethylenimine 73 6.1.1 Mechanism of electrodeposition process 73 6.1.2 SEM images of composite films 78
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles 66 Chapter 6 Investigation of LPEI 73 6.1 Electrodeposition of nanoparticles with polyethylenimine. 73 6.1.1 Mechanism of electrodeposition process 73 6.1.2 SEM images of composite films 78 6.1.3 Thermal properties of composites, prepared by EPD of LPEI
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles 66 Chapter 6 Investigation of LPEI 73 6.1 Electrodeposition of nanoparticles with polyethylenimine 73 6.1.1 Mechanism of electrodeposition process 73 6.1.2 SEM images of composite films 78 6.1.3 Thermal properties of composites, prepared by EPD of LPEI 82
5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles 66 Chapter 6 Investigation of LPEI 73 6.1 Electrodeposition of nanoparticles with polyethylenimine 73 6.1.1 Mechanism of electrodeposition process 73 6.1.2 SEM images of composite films 78 6.1.3 Thermal properties of composites, prepared by EPD of LPEI 82 Chapter 7 Anodic electrodeposition of alginate composites 87

7.2 Fabrication and characterization of particles for EPD	. 88
7.3 EPD of alginate composites and SEM studies	.91
Chapter 8 Conclusions	. 94
8.1 Conclusions related to FRM and EPD	. 94
8.2 Conclusions related to LPEI	. 94
8.3 Conclusions related to alginate	. 95
References	. 97

Chapter 1 Introduction

Organic-inorganic composite materials have attracted significant attention due to the possibility of combining the functional properties of organic and inorganic components[1]. Of particular interest is the fabrication of nanocomposite films, containing inorganic nanoparticles in a polyelectrolyte matrix[2]. Such composites exhibit valuable properties for electrochemical, biomedical, sensor, catalytic and energy storage applications. [3]The organic – inorganic composite films can also be used to modify surface of polymers and inorganic materials.[3] The organic-inorganic nanocomposites exhibit functional properties of the individual components and also new functional properties[3].

Organic-inorganic nanocomposite films are of particular interest for implant applications.[4] It is in this regard that the natural bone is a hierarchical nanocomposite made from organic materials and hydroxyapatite particles. In addition to this, the organic – inorganic materials have many applications in piezoelectric transducers and photovoltaic devices[5].

Another important application is flame retardant materials[6]. Flame retardant additives are used in many advanced composites to stop the fire. In modern society, polymers are key components in a large variety of products because of their outstanding physical properties[7]. However, for most of polymers, one severe problem is that they are highly flammable[8]. Flame retardant materials (FRM) are mandatory components for many important products such as black boxes of flight data recording, furniture, thermoplastics, ceiling linings as well as flame resistance fabrics[9]. Organic FRM have a lot of limitations including instability during processing time, high cost, and toxicity. Such FRM additive are harmful to humans and environment[6]. This problem can be addressed by the use of inorganic FRM, such as aluminum hydroxide and magnesium hydroxide[6]. The decomposition of such hydroxides results in the formation of non-toxic oxides and water, which are friendly to environment[7]. Therefore, the development and application of advanced hydroxides with higher water content and strong endothermic effect related to the dehydration is a promising direction for the design of advanced composites with FR properties[10].

Some technical problems are related to the development of methods for the fabrication of organic-inorganic composite materials[11]. The important task is to avoid agglomeration of inorganic nanoparticles and achieve their uniform distribution in a polymer matrix[3]. The major driving forces for agglomeration of particles is the reduction of surface area and condensation of OH groups on particle surface[12]. Agglomeration has a detrimental effect on the stability of suspensions used for colloidal processing and properties of composites[13].

This work was focused on the materials synthesis and fabrication of advanced nanocomposites using colloidal methods [13]. In this research, particle extraction through liquid-liquid interface (PELLI) techniques have been developed, which allowed direct particle transfer from a synthesis medium to device processing medium thus avoiding particle agglomeration related to conventional drying and re-dispersion strategies[14]. Various electrochemical strategies have been developed, which are based on electrophoretic co-deposition of organic and inorganic components, combined electrophoretic-electrolytic deposition method and polymer-mediated electrosynthesis[15]. The fundamental electrodeposition mechanisms were investigated and discussed[16]. Testing results provided an insight into the influence of material composition and processing methods on microstructure and properties of new organic-inorganic nanocomposites[13].

Chapter 2 Literature Review 2.1 Electrochemical Deposition

Electrochemical deposition is a promising method for the fabrication of organic-inorganic composite films and coatings.[3] There are two ways to achieve electrodeposition, electrophoretic deposition (EPD) and electrolytic deposition (ELD)[8]. EPD is based on the use of suspensions of ceramic particles. ELD starts from the solutions of metal salts and particles are electrochemically synthesized at the electrode[8]. Figure 2-1 shows the different range of thickness of films which were deposited by these methods. EPD is a significant tool for the fabrication of thick ceramic films. ELD enables the formation of thin nanostructured films[3].



Figure 2-1 Thickness of coating deposited using ELD and EPD

EPD and ELD are widely used in coating and other advanced applications. The EPD mechanism combines electrophoresis and deposition. Electrophoresis is the motion of charged particles towards the electrode in the applied electric field. The particles accumulate at the electrode surface and form the films during the deposition stage[3]. Figure 2-2 shows the schematic of EPD and ELD. It is worth to note that, EPD does not include the electrode reactions. The post-EPD processing step includes a suitable heat treatment which is used for eliminating deposit porosity[4]. The significance of EPD is not only based on its great diversity for various thin films and product shaping application[8]. EPD allows co-deposition of different materials and offers many advantages for surface modification compared with other techniques[3].

The advantages of EPD include short processing time, high deposition rate and process simplicity[8]. Moreover, uniform coating can be obtained on substrates of complex shape[11]. Composite films, containing different materials can be formed by EPD for various applications[3]. All these advantages contribute to versatile application of EPD techniques for the fabrication of thin films and coatings of organic and inorganic nanomaterials[3].



Figure 2-2 Schematic of cathodic electrophoretic deposition EPD and

electrolytic deposition ELD

In many experiments, electrolyte and polyelectrolyte play significant role in EPD of ceramic particles[3]. Several electrochemical strategies have been developed for the EPD of polymer-metal ion complexes, polyelectrolytes, as well as inorganic particles[3]. The deposition process is controlled by deposition parameters, bath composition as well as mass transport condition for organic and inorganic components[3].

2.2 Particle interactions and suspension stability

2.2.1 DLVO theory

The classical DLVO theory was developed by Derjaguin and Landau, Verwey and Overbeek[3]. This theory demonstrates that two interactions exist between colloidal particles, one is the Coulombic double-layer repulsion and another one is Van der Waals' attraction[3]. The classical DLVO theory contributes to the understanding of EPD and ELD deposition mechanisms[3].

For two isolated, identically charged particles, the total energy V_T is[3]:

$$V_T = V_A + V_R \tag{2.1}$$

 V_A is attractive energy of the London-Van der Waals' interaction between two spherical particles, which can be expressed by[3]:

$$V_A = -\frac{A}{6} \left(\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right)$$
(2.2)

In this case, A is the Hamaker constant and s = 2 + H/a, where H is the shortest distance between the two spheres and a is the particle radius[3]. When H \ll a, Eq. (2.2) could be simplified to:

$$V_A = -A \frac{a}{12H} \tag{2.3}$$

And the repulsive energy V_R could be describe as:

$$V_R = 2\pi\varepsilon\varepsilon_0 A\psi^2 \ln[1 + e^{-\kappa H}]$$
(2.4)

Where ε is the dielectric constant of the solvent, ε_0 is the vacuum dielectric permittivity, and ψ is defined as the surface potential, $\frac{1}{\kappa}$ is the Debye length[3]:

$$\kappa = \left(\frac{e_0^2 \Sigma n_i z_i^2}{\varepsilon \varepsilon_0 kT}\right)^{\frac{1}{2}} \tag{2.5}$$

In this case, e_o is the electron charge and k is the Boltzmann constant, T is the absolute temperature, n_i is the concentration of ions and z_i is valence[3]. The repulsion energy is directly related to the diffuse-layer on the particles[3].

The DLVO theory gives a description of the potential energy for pair interaction[3]. There will be an energy barrier to particle coagulation when the diffuse-layer repulsion is significantly higher than the van der Waals' attraction, and at this time, the total energy of this particle interaction will exhibit a maximum, as shown in Figure 2-3a[3].

The Debye length $(\frac{1}{\kappa})$ is is related to the thickness of the double layer, which is highly sensitive to the electrolyte concentration[3]. The DLVO theory revealed the influence of the electrolyte concentration on the coagulation, which decreased with the electrolyte ions valence for the ions with opposite charge to the charge of colloidal particles[3]. The potential energy peak also decreased with the increasing electrolyte concentration[3]. Flocculation that results from compressing the double layer also obeys the Hofmeister series[3]. While the ions are of the same charge, the flocculation values will increase in the order:

$$NH_4^+$$
, K^+ , Na^+ , Li^+ ;
 Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+}

Hence, a negatively charged sol could be flocculated by some large cations at a smaller concentration than by small cations of the same valency[3]. The value of the flocculation is in the range of 20 to 200 mM for monovalent ions, 0.3 to 3 mM for divalent ions, as well as 0.002-0.1 mM for trivalent ions[3]. Meanwhile, flocculation values can be influenced by sol concentration,

temperature, chemical nature of the sol as well as particle size of the colloid[3].





interparticle separation according to DLVO theory

2.2.2 Other interparticle forces

According to the DLVO theory, all the forces which have to be considered are Van der Waal's attraction and electrostatic repulsion[3]. But in real complex solution system, still exists some other forces which have to be taken into account[3]. The aggregation and flocculation of colloidal particles could be related to attractive forces between particles[4]. Those ions in EPD and ELD can also have influence the particles interactions. First, electric field could result in the aggregation of ceramic particles in the bulk of suspensions during EPD process[3]. Moreover, other forces like long-range attraction, polarization interaction, capillary interactions and electrohydrodynamic flows could also play roles in particle interactions[3].

It is still critical to understand that steric stabilization and structural forces may also influence the stability of the particle suspension[8]. Organic macromolecules can be adsorbed or bounded to the particle surface to enhance the steric mechanisms[4]. The adsorbed macromolecules could enhance the particle repulsion and stabilization[17]. The stabilization forces usually present as short-range forces. These forces also re-shape the potential which controls the particle-substrate interaction[3].

Polymer adsorption may result in particle flocculation or colloid stability. Steric repulsion relies on the thickness of the configuration of the polymer, the fraction of molecules adsorbed, the thickness of the adsorbed layer, and the firmness with which the polymer is anchored to the surface[8]. Neutral polymers or adsorbed polyelectrolytes might lead to the flocculation by charge neutralization or bridging flocculation. According to the previous work, attractions between polyelectrolytes and colloidal particles includes dipole-dipole interactions, electrostatic and hydrophobic interactions[3]. The interactions between two charged particles could be neutralized by grafted polyelectrolytes, which have been taken into research several years ago[3]. A long-range repulsion and short-range bridging attraction were considered in the salt-free solutions and the long-range repulsion has been demonstrated[3]. The non-adsorbing polymers could also influence the stabilization or flocculation of the colloidal particles[3]. It was found that non-adsorbed polymer would also result in depletion flocculation or stabilization[3].

It is very important to obtain well dispersed and stable suspensions in order to achieve the successful deposition[11]. There are several stabilization mechanisms such as steric, electrostatic, as well as electro-steric stabilization mechanisms[17]. It is important to avoid flocculation and enhance the stability of the suspensions[4]. The suspensions which contains particles with size equal or below 1µm may be more stable because of the Brownian motion of the particles. For the particles larger than 1µm, continuous hydrodynamic agitation will become necessary[17]. Flocculating suspensions would settle quickly and form low density, weakly adhering deposits. In contrast, deposition cannot be completed in a very stable suspensions because repulsive forces are higher than other forces[11]. According to the several models of EPD, it is necessary to obtain the suspensions which would be unstable in the vicinity of the electrodes. The formation of ions from electrolysis and discharge of the particles could lead to the local instability[3]. The flocculation near the electrode caused by these ions. Zeta potential (ξ) or electrophoretic mobility can be used to characterize the

suspensions[3].

2.3 Deposition theories

2.3.1 Particle charging

The charged particles in suspensions could move to the electrode under electric field. The particles are surrounded by counter ions which concentration is higher than the ions in the bulk solution[8]. It is called a double-layer. Generally, the particle and ions of opposite charge move to the opposite directions under electric field[4]. However, some ions are attracted by the particle and they move with the particle in the same direction. Thus, the net charge in the liquid sphere determined the speed of a particle, and these ions move with the central particle[11]. The potential at different surfaces is described by surface potential, stern potential, as well as zeta potential (ξ), as shown in Figure 2-4.



Figure 2-4 Schematic of a double layer which surrounding a charged particle and different potentials at the charged surface.

2.3.2 Aqueous suspensions

In aqueous solution, dissociation of surface groups and the adsorption as well as desorption can lead to the charge of the particles at the particle-solvent interface[3]. Oxide particles in water could combine with water molecules to form hydroxylated surfaces and then became negatively or positively charged, which will be depended on the pH of the suspensions:

$$M-OH + H^+ \Leftrightarrow M-OH_2^+$$
$$M-OH + 0H^- \Leftrightarrow M-0^- + H_2O$$

Colloidal stability is closely related to the zeta-potential of the colloidal

particles according to the DLVO theory[3]. In aqueous suspensions of ceramic oxide particles, zeta-potential changes with pH when hydrogen ions and hydroxide ions are potential-determined ions, shown as Figure 2-5. However, in more complex systems, containing colloidal particles together with metal ions and complexes, their behavior will be more complicated[3]. Even in some cases, it is difficult to find out the correlation between zeta-potential and colloidal stability[3].



Figure 2-5 Zeta-potential of ceramic particles versus pH of suspension

2.3.3 Non-aqueous suspensions

Generally, organic solvents are better than the water as a suspension medium for electrophoretic procedures because usually organic liquids have lower dielectric constant which gives a limitation on the charge of the particles[11]. As a result, lower dissociating power is needed[4]. However, due to some problems are greatly reduced like joule heating, electrolytic gas evolution and electrochemical attack of the electrodes, much higher field strengths must be used[3].

The pH is used to measure the alkalinity and acidity of suspension medium for aqueous media but pH is not useful for the non-aqueous solution[17].

It is important to select a suitable solvent for particle charging and dispersion[11]. Scientist discovered the effect of the dielectric constant of the suspending media and different charging modes could be resulted from different solvents[17]. Inorganic solvents or organic acids could work as proton donors. Otherwise, different surface characteristics could be influenced by different conditions during the experimental procedures for ceramic particles[4]. Electron transfer between particle and solvent in non-aqueous solution results in particle charging[17]. Charge transfer could also involve the adsorption and desorption of ions, instead of electron transfer[4].

2.3.4 Additives for particle charging

Many additives could be used for controlling particle charging when produce well-dispersed suspensions like phosphate ester, NH4OH,

I₂-H₂O-acetone, acids[11]. In the recent research, more and more attention have been put on the polymers which can be used to induce steric stabilization or depletion stabilization[3]. The steric stabilization could work in aqueous and non-aqueous media[8]. Polyelectrolytes could give steric stabilization and electrostatic to colloidal dispersion and are widely used as additives. Usually, polyelectrolytes can be divided into two groups: strong polyelectrolytes and weak polyelectrolytes[8]. For the strong polyelectrolytes, the degree of ionization is independent of the pH of the solution[18]. In contrast, for the weak polyelectrolytes, the degree of ionization is determined by the pH of the solution. For example, poly(ethylenimine)(PEI) is a kind of weak cationic polyelectrolyte because the increase in pH could decrease the charge of PEI[19]. On the contrary, poly(diallyl dimethylammonium chloride)(PDDA) is a strong polyelectrolyte. Both PDDA and PEI can be used to increase the stability of ceramic suspensions and work as additives for particles charging and electrodeposition for different materials[20].

2.4 Solvents

The solvents transfer ions in solutions (ELD) or ceramic particles in suspensions(EPD)[21]. In electrodeposition process, a solvent is supposed to

dissolve organic additives and inorganic salts[21]. There are two types of solvents which are used for electrodeposition: organic liquids (Table 2-1) and water[13]. In ELD process, water is necessary for cathodic reactions of base generations. Non-aqueous solvents can prevent the deposit from hydrating.

Solvent	Method	Deposited materials
	deposition	
Water	ELD	Al ₂ O ₃ -Cr ₂ O ₃ , ZnO
	EPD	Al ₂ O ₃
Dimethylformamide	ELD	Y ₂ O ₃ , TiO ₂
Methyl alcohol-water	ELD	TiO ₂ , RuO ₂ -TiO ₂
Ethyl alcohol-water	ELD	CeO ₂ , SnO ₂
	EPD	CaSiO ₃
Isopropyl alcohol	EPD	НА
Isopropyl alcohol ^a	ELD	YBa ₂ Cu ₃ O ₇ -X
Ethyl	EPD	MgO, Al ₂ O ₃
alcohol-acetylacetone		
Glacial acetic acid	EPD	Lead Zirconate Titanite
Ethyl alcohol	EPD	Al ₂ O ₃ , ZrO ₃
Dichloromethane	EPD	β-alumina

 Table 2-1 Examples of solvents used for electrodeposition

Acetone	EPD	Y ₂ O ₃ -stabilized ZrO ₂
Acetylacetone	EPD	Y ₂ O ₃ -stabilized ZrO ₂
Cyclohexanone	EPD	Y ₂ O ₃ -stabilized ZrO ₂
Methyl ethyl ketone	EPD	Al ₂ O ₃
Toluene-ethyl alcohol	EPD	Al ₂ O ₃

^a Solvent contained a small amount of water

It is well known that methanol can extract non-bridging hydroxo groups and free water[21]. And it is found that mixed ethyl alcohol-water and methyl alcohol-water solutions play an important role in reducing cracking and porosity in ELD process because the addition of alcohols to aqueous solutions can reduce the total dielectric constant of the solvent, and as the results, the solubility of the deposits has been reduced. Besides, repulsion between colloidal particles which formed near the electrode has relationship with the diffuse-layer charge on the particles[18]. The thickness of the double layer decreases with the decreasing dielectric constant of the solvent, which promoting particle coagulation[22].

In the EPD process, solvents should be inert with respect to the powder. Organic solvents are more suitable than the water as a suspension medium for EPD process[23]. Because the hydrolysis of water in water-based suspensions cause gas formation, which would result in pinholes and difficulties in the formation of uniform adherent films[19].

The charge on a colloidal particle can originate from solvents. Alcohols can work as proton donors for particle charging[24]. The mixture of solvents may also be useful for particle charging. The addition of alcohols to aqueous suspensions, containing titania can result in a shift of the isoelectric point (IEP) towards higher pH values, or the absence of IEP[3].

2.5 Binders

A binder works like a glue which can be added to suspensions or solutions to increase the strength and adherence of the deposited material as well as prevent cracking[25]. EPD of sub-micrometer particles gives advantages in the fabrication of uniform ceramic films with good sinterbility and dense packing. Micro-particles with high surface area promote deposit cracking, which threaten the stability of the films[26]. This kind of cracking problems could be avoided by binder materials. The optimal amount of binder depends on the particle surface area as well as particle size[25].

Different binders have been applied in non-aqueous EPD such as polyvinyl butyral (PVB), alkyd resin, nitrocellulose, as well as dewaxed shellac. In real experimental process, binder materials not only work as a binder, but also act as a dispersant[26]. The majority of water-soluble and dispersants is restricted especially compared with non-aqueous solvents. The low strength of water-soluble binder materials gives a limitation on their applicability. For example, polyvinyl alcohol is an important binder material for aqueous EPD[25].

For the polymer binders, they are commonly used in ceramic processing as additives, such as non-ionic types (polyacrylamide, polyvinyl butyral, polyvinyl alcohol, ethyl cellulose, etc.) The macromolecules of the polymer can adsorb onto the surface of ceramic particles[25]. The polymeric molecules move to the electrode and deposit on the cathodic or anodic substrates depending ontheir charge. The inherent binding properties of cationic polyelectrolytes such as PEI and PDDA, can be applied in EPD and particle charging[25].

The application of neutral polymers in ELD process is more difficult, because the formation of the ceramic particles is achieved near the electrode surface[26]. One significant discovery is the feasibility of electrochemical intercalation for charged polyelectrolytes into electrolytic deposits. By using cationic polyelectrolytes with inherent binding properties, the cracking problems in ELD could be avoided. Different organic-ceramic nanocomposite materials can be fabricated by electrodeposition. The polymers adsorb in the surface of ceramic particles and form the composite deposits[3].

The function of binders in EPD is multifunctional. Polymer binders can be used to increase the density of the deposits and avoid cracking. Moreover, binders can increase the stability of the suspensions of ceramic particles. In addition, binders could change viscosity of the suspension[8]. The amount of use of binder polymer is of great importance[4]. It depends on the polymer concentration in suspension and specific polymer-dispersant, polymer-solvent, polymer-particle, and particle-solvent interactions. It is necessary to use good solvents to get high polymer concentration[3]. However, when polymer's solubility in dispersion medium is low, it can be adsorbed on the surface of ceramic particles, which may result in bridging flocculation. On the contrary, it is important to achieve steric stabilization by using good solvents[4].

Metal alkoxides and hydroxides also can be used as binder materials. They can be formed near the cathode and then work as cementing materials to enhance the strength of deposits. The binder deposition depends on the amount of water in deposition bath[17].

2.6 Double layer and electrophoretic deposition kinetics

The EPD suspension is a complex system, each component of suspensions plays an important effect during the deposition. It is important to gain well dispersed and stable suspensions[27].

In suspension system, charged particles are forced to move toward an electrode under the electric field, which is called electrophoresis process. The charged particles in the suspensions are surrounded by counter ions, and the concentration of counter ions which near the particles is much higher and it will decrease as the distance from the surface increases[18]. The inhomogeneous distributions of ions which close to the particles formed the double layer[28].

Deposition rate is significant for deposit formation by EPD and control of the thickness of deposited film[19]. The deposition rate is also critical to achieve functionally graded materials. Many investigations were focused on the analysis of deposition yield and deposition mechanism[23]. During the study of the phenomena of EPD process in 1940, Hamaker discovered that the weight of deposits depends on the concentration of the suspension, surface area of deposit, electric field, as well as the time of deposition according to the following equation:

$$\frac{dY}{dt} = \mu ESC \tag{2.6}$$

where t is deposition time, Y is deposition yield, S is electrode surface area, μ is electrophoretic mobility (, C is solids concentration. This equation is known as Hamaker equation, which is a fundamental equation for kinetics of EPD. The equation (2.6) is based on a suggestion that each particle reaching the electrode is deposited[16]. Unfortunately, this equation ignored the change of solid concentration in suspension during deposition process. Another scientist proposed a kinetic equation incorporating changes of particle concentration in suspension in 1994[29]. This equation states that if dS are an infinitesimal area of depositing electrode on which dw weight of particles has been deposited in time dt, then we can get:

$$\int dw = \iint fudSC(t)dt = fu \iint dSC(t)dt$$
(2.7)

In which case, C(t) is the concentration of the particles in the suspension, u is the average velocity of the particles, f is the efficiency factor taking into account, which means that not all powder brought to the electrode by electrophoresis is also incorporated in the deposit ($f \le 1$). If all the particles reaching the electrode take part in the formation of the deposit, then f=1[30].

There are also two different theories of electrophoresis for polyelectrolytes and rigid particles for electrophoretic mobility, which can be defined as:

$$\mathbf{v} = \boldsymbol{\mu} \mathbf{E} \tag{2.8}$$

where v is velocity of the particle, E is electric field. In this equation, μ is electrophoretic mobility[8], which can be given by following equation for a rigid colloidal particle:

$$\mu = \frac{2\varepsilon\varepsilon_0\zeta}{3\eta}f(\kappa\alpha) \tag{2.9}$$

where η is the viscosity of the liquid. The function $f(\kappa \alpha)$ increases from

1 for $\kappa \alpha \ll 1$ to 1.5 $\kappa \alpha \gg 1$ to As for the particle size, it is much smaller than the Debye length, and electrophoretic mobility is described by Huckel equation[20]:

$$\mu = \frac{2\varepsilon\varepsilon_0\zeta}{3\eta} \tag{2.10}$$

In the contrast, if the particles size is much larger than the $1/\kappa$ like ceramic particles, the electrophoretic mobility can be described as the Smoluchowski equation[3]:

$$\mu = \frac{\varepsilon \varepsilon_0 \zeta}{\eta} \tag{2.11}$$

In this case, the electrophoretic mobility of a spherical polyelectrolyte, in which fixed are distributed at a uniform density ρ_{fix} , could be described by the following equation[3]:

$$\mu = \frac{\rho_{fix}}{\eta \lambda^2} \left[1 + \frac{2}{3} \left(\frac{\lambda}{\kappa} \right)^2 \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa} \right]$$
(2.12)

Where $\lambda = (\frac{\gamma}{\eta})^{0.5}$, γ is the prictional coefficient of the polyelectrolyte.

In equation (2.12) for electrophoretic mobility the charge density was used instead of zeta potential, because the concept of zeta potential was developed for rigid particles[4].

2.7 FRM materials and applications

FRM are used to slow the fire or even stop the fire. FRM are the mandatory

components of many important product, such as black boxes of flight data recorders, thermal plastics, ceiling linings, curtains in cinemas, electronics, fibers, wood furniture etc[10].

Polymer materials are widely used in our daily life due to their excellent chemical stability, mechanical properties, low weight and easy processing. However, polymers are also known for their high flammability[31]. The combustion process is usually accompanied by the production of corrosive or toxic gases as well as smoke[8]. Therefore, improving the flame-retardant properties of polymers is the main challenge to promote their application in most fields[7].

At present, the demand for safety is getting higher. Polymers are highly reactive to fire, but modified polymers have good flame retardant properties[32]. Recently various flame retardant additives, such as halogenated additives, were phased out due to their proven or suspected adverse environmental effects[12]. As the results, the common challenge is to develop effective and environmentally friendly flame retardant systems for polymer materials[6].

Inorganic FRM are typical new environmentally friendly FRM and Al(OH)₃ is a typical example of inorganic FRM. This kind of inorganic FRM can be decomposed to non-toxic oxides and water under high temperature:

$$Al(OH)_3 \rightarrow Al_2O_3 + H_2O \tag{2.13}$$

25

But the thermal properties of this kinds of inorganic FRM must be improved. For the thermogravimetric analysis (TGA) of $Al(OH)_3$, shows mass loss of 35% related to water release[12]. It is critical to develop advanced inorganic FRM with higher water release[33].

2.8 Co-deposition of organic-inorganic composite coatings by EPD

Recently, more and more scientists have put their attention on the organic-inorganic composite materials because of their advanced properties combining properties of the organic and inorganic materials[1]. The fabrication of nanocomposite films containing inorganic nanoparticle in the polyelectrolyte matrix is so-called co-deposition, which is based on self-assembly[34]. This method is based on the adsorption of oppositely charged inorganic nanoparticles and polyelectrolytes[22]. The co-deposition of organic and inorganic nanomaterials can be achieved at room temperature, which can avoid the sintering-related problems[35]. This method be also used to fabricate layer-by-layer of polyelectrolyte multilayers as well as polyelectrolyte capsules. EPD is an alternative way for the synthesis of composite coatings.

layer-by-layer self-assembly[36]. Scientists are now focused on the electrochemical strategies, which include the EPD or electrosynthesis of inorganic particles and the EPD of polyelectrolytes or polymer-metal ion complexes[37]. In order to decrease the electrostatic repulsion of the polyelectrolyte molecules at the electrode and achieve co-deposition of polyelectrolytes and ceramic particles, a variety of electrochemical strategies were developed[38]. It is very promising to use polyelectrolytes for the fabrication the advanced organic-inorganic nanocomposites by EPD[39].

In addition to polyelectrolytes, polymer-metal ion complexes could offer another important method to synthesis composites[40]. Polymer-metal complexes are formed from polymer ligand and the metal ions which are attached to the polymer ligand by a coordinate bond[41]. It is discovered that the polymer chelate is formed when metal ions were added to the solutions of the polymer, such as polyethyleneimine (PEI)[42]. The use of polymer-metal ion complexes and polyelectrolytes give the way for fabricating advanced nanostructured organic-inorganic composite materials by combining EPD and electrosynthesis of inorganic particles[35].

2.9 EPD of weak polyelectrolytes and electro-synthesis of inorganic particles

It is important to keep the nanoparticles non-agglomerated and well-dispersed. Nanoparticles can be prepared by electrosynthesis in a polymer matrix of cationic polyelectrolytes or polymer-metal ion complex in order to avoid agglomeration[43]. The pH near the cathode is high because of the electrolysis of water, which results in the formation of colloidal particles by ELD and these particles coagulated on the electrode[44]. The charge of weak polyelectrolytes such as polyethyleneimine(PEI) would reduce with the increasing of pH[45]. As a result, the pH increase near cathode enables charge neutralization and deposition of weak cationic polyelectrolytes[46]. Electrodeposition of composite films can be achieved by combining EPD of polyelectrolytes with electrosynthesis of inorganic particles[44].

In many investigations, composite deposits were obtained containing nanoparticles of Co, Mn, Ce, Zr, Fe, Al, Cu, Mg, Zn oxides or hydroxides in a PEI matrix[47]. The electrophoretic deposition of Mn-PEI complex has been applied for the deposition of nanocomposites with Mn₃O₄ particles, which provides the significant advantages for the fabrication of electrode materials for supercapacitors[48].

The mechanism of deposition has been widely studied. As proposed, the PEI
could get a positive charge due to complex formation with metal ions including Co^{2+} , Mn^{2+} as well as Ni²⁺. Then, the polymer-metal ion complexes will move to the electrode under electric field[47]. These complexes could participate in cathodic reactions to form nanoparticles of metal oxides[49]. It was suggested that free metal ions in solutions, which are not complexed with PEI, could contribute the electrosynthesis of the inorganic species[50].

2.10 EPD of weak polyelectrolytes and EPD of inorganic particles

Both inorganic particles and polyelectrolytes could be electrophoretically deposited to form composite coatings[51]. The manipulation of the pH value in the suspension provides the possibility to control the solubility and the charge of the polymers[43]. As a weak polyelectrolyte, PEI can be deposited on the cathode due to its pH is responsible charge and solubility properties[49]. PEI is only soluble when it is in the acid solution and protonated[47]. PEI can be deposited at the cathode to form a film when it is neutralized by the electrogenerated base:

$$\text{PEI-}H^+ + OH^- \to PEI + H_2O \tag{2.14}$$

A variety of studies have been focused on the electrophoretic co-deposition of PEI and nanoparticles[49]. It is proved that PEI can promote the EPD of the latex nanoparticles, which are uniformly distributed in the PEI film.

2.11 Investigation of biomimetic adhesion

It is critical to understand adhesion for chemical modification of bulk material surfaces in modern biological, chemical as well as materials sciences[52]. Many approaches have been widely studied for the functional modification of material surfaces such as self-assembled monolayer (SAM) formation, Langmuir-Blodgett deposition, functionalized silanes, layer-by-layer assembly etc. And these approaches still have different limitations for widely real use[13].



Figure 2-6 Photograph of mussels attached to a rock surface

In recent research, a newly surface modification method has been developed according to an article publish on the Science by Phillip and his colleagues, which inspiration comes from the adhesive proteins secreted by mussels for attachment to wet surfaces (Figure 2-6)[53]. Mussels can attach to almost all kinds of inorganic and organic surfaces. Mussels have perfected the art of adhering tenaciously, opportunistically and quickly to all manner of slippery and wet surfaces due to their wave-swept habits [54]. In addition to the modification of a large variety of materials, the resultant surface can react further, and thus the extent for applications widens significantly[44]. According to the investigations of footprints of mussels on smooth substrates, scientists have discovered that a unique group of proteins could help mussels achieve adhesion, including Mytilus foot protein 5(Mfp-5), of which 30% of the residues in the sequence are 3,4-dihydroxyphenyl-L-alanine (DOPA), which compound contains catechol, and 15 percent are lysine, an amino acid with a side-chain ending in a primary amine group. DOPA might come from the mussel adhesion (Figure 2-7), which not only play an role in the reactions resulting in bulk solidification of the adhesive, but forms strong noncovalent and covalent interactions with substrates[47]. These catechol family compounds such as DOPA act as binders for adhesive inorganic surfaces, which including the electro-polymerization of dopamine on conducting electrodes in EPD process[47].



Figure 2-7 Chemical structure of DOPA



Figure 2-8 Chemical structure of Dopamine

It is critical for accomplishing adhesion to many materials that the catechol (DOPA) and amine (lysine) groups are co-existence, Messersmith and his colleagues combined two compounds in their use of dopamine, which is a catechol family (1,2-dihydroxybenzene) compound with a mainly amine functional group (Figure 2-8) work as an alternative to natural adhesive[48]. According to Messersmith and his colleagues' study, for further functional use, the structural mimic of Mfp-5 is a powerful building block for spontaneous deposition of this polymer film forming on materials surfaces, which can be deposited easily[8].

This kinds of coating can be formed on almost every kinds of material surfaces,

for example : noble metals (Pt, Au, Pd and Ag), metals with native oxide surfaces (NiTi shape-memory alloy, stainless steel as well as Cu), oxides (TiO₂, Nb₂O₅, Al₂O₃, crystalline SiO₂(quartz), non-crystalline SiO₂), semiconductors (Si₃N₄ and GaAs), Ceramics (hydroxyapatite and glass) as well as synthetic polymers (polyurethanes, polyetheretherketone, polydimethylsiloxane, polyethyleneterephthalate, polycarbonates, polyethylene, polystyrene).

Besides, the polydopamine film can also work as an perfect stage for further reactions, which could result in tailoring of the coatings for different functional purposes[42]. For example, the metal-binding ability of catechol present in the polydopamine film was applies to deposit adherent and uniform metal coatings onto substrates[47]. In addition, polydopamine films could also provide support to different reactions with organic agents for the application of functional organic ad-layers[48].

Chapter 3 Objectives

The long-term objective of this investigation was the development of advanced electrochemical and colloidal methods for the fabrication of organic-inorganic composites for flame-retardant, energy storage and other applications. The long-term objective of this investigation was based on the short term objectives:

Synthesis of inorganic nanoparticles by chemical precipitation and hydrothermal methods and investigation of the influence of processing conditions on particle crystallinity and morphology

Development of PELLI method and advanced extractors for agglomerate-free processing of inorganic materials, analysis of the extraction mechanisms and influence of the anchoring groups of the extractors on the extraction efficiency.

Development of dispersing agents with enhanced adsorption on inorganic particles for EPD and analysis of the adsorption mechanisms.

Development of techniques of electrodeposition of polymers and composites using EPD of weak cationic polyelectrolytes or polymer-metal ion complexes

Characterization of microstructure and properties of the composites.

Chapter 4 Experimental Procedures

4.1 Materials

4.1.1 Materials purchased from commercial suppliers

The materials listed in the following Table 4-1 were purchased from industrial suppliers and were used for the fabrication of coatings.

Materials	Supplier	Purity and Other
		specification
Cerium nitrate	Sigma-Aldrich	≫ 98%
Zinc nitrate	Sigma-Aldrich	»» 97%
Copper nitrate	Sigma-Aldrich	»» 97%
Aluminium nitrate	Sigma-Aldrich	» 98%
Titanyl sulfate	Sigma-Aldrich	
Magnesium chloride	Sigma-Aldrich	» 98%
Zirconyl chloride	Sigma-Aldrich	
Manganese chloride	Sigma-Aldrich	» 98%
Nickel chloride	Sigma-Aldrich	» 98%
Iron chloride	Sigma-Aldrich	» 98%

Table 4-1 Materials purchased from commercial suppliers

Potassium hydroxide	Caledon	Meet ACS specifications
Sodium hydroxide	Caledon	Meet ACS specifications
Bufexamac	Sigma-Aldrich	» 99%
Octanohydroxamic acid	Sigma-Aldrich	» 99%
16-phosphonohexadecanoic acid	Sigma-Aldrich	≫ 99%
Octadecyl phosphonic acid	Sigma-Aldrich	≫ 99%
Stearic acid	Sigma-Aldrich	≫ 99%
Octyl gallate	Sigma-Aldrich	≫ 99%
Alginic acid sodium salt	Sigma-Aldrich	≫ 99%
1-Pyrenecarboxaldehyde	Sigma-Aldrich	≫ 99%
Lauryl gallate	Sigma-Aldrich	≫ 99%
Undecanal	Sigma-Aldrich	≫ 97%
Decanal	Sigma-Aldrich	» 97%
linear polyethylenimine	Polyscience.Inc.	≫ 99%
Stearyl Gallate	TCI	» 97%
Hexadecylamine	Sigma-Aldrich	» 98%
1-butanol	Sigma-Aldrich	≫ 99.8%

4.1.2 Fabrication of materials by chemical precipitation

ZnO, Cu(OH)₂, TiO₂, Al(OH)₃, Mg(OH)₂, ZrO(OH)₂ and MgAlZr(OH)_x

complex hydroxide were prepared by following chemical reactions:

$$\operatorname{Zn}(\operatorname{NO}_3)_2 + 2KOH \to ZnO + H_2O + 2KNO_3 \tag{4.1}$$

Reaction (4.1) happened at pH ~ 8 under 80°C

$$Cu(NO_3)_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaNO_3$$
(4.2)

$$TiOSO_4 + 2NaOH \rightarrow TiO(OH)_2 + Na_2SO_4 \tag{4.3}$$

$$\text{TiO}(\text{OH})_2 \to TiO_2 + H_2O \tag{4.4}$$

$$Mg(NO_3)_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaNO_3$$
(4.5)

$$Al(NO_3)_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaNO_3$$

$$(4.6)$$

$$ZrOCl_2 + 2NaOH \rightarrow ZrO(OH)_2 + NaCl$$
(4.7)

*Reactions (4.2) and (4.3) occur when the pH equals 6. Reaction (4.5) can be achieved when the pH equals 9.5. Reactions (4.6) and (4.7) could be completed when the pH is around 7.



Figure 4-1 ZnO precipitate synthesized by s chemical precipitation method



Figure 4-2 Cu(OH)₂ precipitate synthesized by a chemical method



Figure 4-3 AlMgZr(OH) $_x$ complex hydroxide synthesized by a chemical

precipitation method

4.1.3 Hydrothermal synthesis of CeO₂

We used a hydrothermal method for the synthesis of CeO₂ inorganic particles, the hydrothermal chemical reaction is following:

$$4Ce(NO_3)_3 + O_2 + 12NaOH \rightarrow 4CeO_2 + 6H_2O + 12NaNO_3$$
(4.8)

This reaction happened at 100 °C for 24 hours.



Figure 4-4 CeO₂ inorganic particles synthesized by the hydrothermal



method

Figure 4-5 Hydrothermal furnace



Figure 4-6 Image of hydrothermal autoclave reactor

4.2 Liquid-Liquid extraction

Particles extraction through liquid-liquid interface (PELLI) has attracted attention for colloidal processing of ceramic particles and surface modification. PELLI provides a special environment for controlled synthesis of non-agglomerated nanostructured oxides and hydroxides, such as Cu(OH)₂, CeO₂, ZnO, TiO₂, etc. PELLI also provides an easy access for organic surfactants to the inorganic particles and help them to form the modified particles. PELLI allows particle transfer from aqueous synthesis medium to the processing medium, such as organic solvent phase.

The development of PELLI has been motivated by the need of avoiding the formation of agglomerates. In many processing technologies, the particles

synthesized in aqueous solution are transfered to organic solvents for the preparation of coatings and devices through drying and re-dispersion, which would result in agglomeration because of the reduction of surface area and condensation of surface OH groups.

In contrast, PELLI provides a direct way for particles transfer from the synthesis aqueous solution to organic processing medium. The non-aqueous suspensions of transferred particles can be used for manufacturing of nanostructured composite coatings. Various organic molecules were used as extractors, such as 16-phosphonohexadecanoic acid (16pha), Octadecyl phosphonic acid (ODPA), Stearic acid (SA), Octanohydroxamic acid (OHA), Bufexamax (BF), Stearic acid (SA), Octyl gallate (OG), Lauryl gallate (LG), Undecanal, Decanal, Stearyl Gallate (SG), as well as Hexadecylamine (HDA) which were dissolved in 1-butanol in different proportions by ultrasonication (Figure 4-7). Then inorganic particles extracted to the organic solvent were separated from the aqueous phase.



Figure 4-7 Ultrasonicator device

4.3 Coatings formation by electrodeposition methods

4.3.1 Experimental setups for electrodeposition

Electrodeposition was used for the fabrication of inorganic and inorganic-organic composite films. A schematic of the setup of the electrochemical cell for the deposition is shown in Figure 4-8. This cell included cathodic or anodic substrate (15-30cm²) which were centred between two

parallel platinum (Pt) counter electrodes. The distance between the electrodes was 15mm. The volume of deposition bath was 300 mL and the electrophoresis power supply EPS 601(Amersham Biosciences) or EPS 2A200 (Amersham Biosciences) was used to provide the DC electric field for electrodeposition in a constant voltage mode or a constant current density (galvanostatic)



Figure 4-8 A schematic of the setup of the deposition cell



Figure 4-9 Electrophoresis power supply EPS 601 (Amersham



Biosciences)

Figure 4-10 Electrophoresis power supply EPS 2A200 (Amersham

Biosciences)

4.3.2 Preparation of solutions and suspensions for electrodeposition

 40g L^{-1} ZnO/CeO₂/Cu(OH)₂/Al(OH)₃ hydroxides suspension in water were prepared for EPD. Different dispersants, such as 16pha, ODPA, SA, OHA, BF, SG etc. were added to form well-dispersed and stable suspensions. The concentration of dispersants were in the range of 0-1.0 g L⁻¹. Different polymers were added to the suspensions.

4.3.3 Electrodeposition procedures

Ceramic and organic-inorganic composite deposits were prepared on various conductive cathodic substrates under galvanostatic or constant voltage conditions. The substrates materials including stainless steel AISI 304 foil ($50 \times 50 \times 0.1$ mm) or Pt foil ($50 \times 50 \times 0.1$ mm).

1 g LPEI was protonated and dissolved in 100 mL water using 2 mL of acetic acid to form LPEI-H⁺ solutions for EPD. The suspensions for EPD of LPEI-Mn₃O₄, LPEI-ZnO, LPEI-halloysite, and LPEI-AMZ contained 1 g L⁻¹ LPEI-H⁺ and 0.5-2 g L⁻¹ of the inorganic components in a mixed water-ethanol (20% water) or water-ethanol-1-butanol (20% water, 20% 1-butanol) solvents. Alcohol solvents offered an advantage of reduced gas evolution. However, water was 46 necessary for OH⁻ generation. Anodic electrodeposition was performed using alginic acid sodium salts solutions, as it is described below.

In order to get uniform coatings, the voltage in the range of 0-30 V was used for the constant voltage deposition. The current density is in the range of 0-0.064 A/m^2 was used for the constant current deposition. The deposition time was varied in the range of 0-5 min to form deposits of different thicknesses. Obtained films were dried in the air at room temperature.

4.3.4Polymer-metal ion complex (PC) EPD

Polymer-metal ion complex (PC)-EPD method has been developed for the fabrication of nanocomposites. The method was based on the use of LPEI-metal ion complexes for EPD and the electrosynthesis of metal oxides and hydroxides in the LPEI matrix. It was found that PC-EPD can be used for the fabrication of electrodes for energy storage devices.

Polymer-mediated electrosynthesis was performed at constant current densities of 1-5 mA cm⁻².

In the LPEI-mediated electrosynthesis method, 1 g LPEI was dissolved in 100 mL of aqueous solutions, containing 1.19 g NiCl₂·6H₂O or 0.63 g MnCl₂·4H₂O to form LPEI-Ni²⁺ or LPEI-Mn²⁺ solutions. The solutions for LPEI-mediated electrosynthesis contained 1 g L^{-1} LPEI and 5 mM NiCl₂ or MnCl₂ in water-ethanol (20% water) solvent.

In order to get uniform coatings, the voltage in the range of 0-30 V was used for the constant voltage deposition. The deposition time was varied in the range of 0-5min to get deposits of different thicknesses. Obtained films were dried in the air at room temperature.

4.5 Characterization of coatings

4.5.1 X-ray diffraction analysis

X-ray diffractometry is commonly used to determine the phase content in minerals and materials. Besides, it is also important for the measurement of crystal orientation, crystal size, internal stresses, lattice parameters etc.

In this work, the phase content of the deposits was determined by XRD with a diffractometer (Nicolet I2), using monochromatized Cu K α radiation at a scanning speed of 0.5°/min. The studies were performed on powder samples prepared by chemical precipitation or hydrothermal synthesis.

4.5.2 Scanning and transmission electron microscopy

The microstructure and surface morphology of the deposited coatings were studied by scanning electron microscopy (SEM) using a JEOL JSM-7000F scanning electron microscope. The transmission electron microscopy (TEM) investigations were performed using a Philips CM12 microscope and a JEOL 2010 FEG high resolution transmission electron microscope.

4.5.3 Thermogravimetric and differential thermal analysis

Thermogravimetric analysis (TG) is an analytical technique which is used to determine materials' thermal stability and fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is usually carried out in air or in an inert atmosphere, and the weight is recorded as a function of increasing temperature of the sample.

Differential thermal analysis (DTA) can be used to monitor the energy released or absorbed via phase transformations and chemical reactions during the heating process. This is performed by recording the temperature difference between the specimen and the reference.

In this work, DTA and TGA were both carried out using the deposits which

were removed from the stainless-steel electrodes after deposition and dried in air at room temperature. The thermo-analyzer (Netzsch STA-409) was operated in air between room temperature and 1200°C at a heating rate of 5°C/min.

4.5.4 Fourier-transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique used to obtain absorption or emission infrared spectra of solids, liquids or gases. The FTIR spectrometer also collects high spectral resolution data over a wide spectral range.

In this work, the studies were performed on different powder samples. For the preparation of powder samples, the deposits were removed from the stainless-steel electrodes and dried in air at room temperature for 24 hours before FTIR analysis. In another case the powder samples contained the inorganic-organic particles after the Liquid-Liquid extraction.

Chapter 5 Results and Discussion

5.1 Structural characterization of inorganic particles prepared by chemical precipitation

5.1.1 X-ray diffraction analysis

Figure 5-1 to Figure 5-3 show the X-ray diffraction patterns of the as-prepared powders after they were dried in the air. The X-ray diffraction pattern of CeO₂ showed peaks matching JCPDS file 34-0394. The XRD data for ZnO showed peaks corresponding to JCPDS file 36-1451. The X-ray diffraction pattern of Cu(OH)₂ showed peaks matching JCPDS file 13-0420. TiO₂, Al(OH)₃, Mg(OH)₂, ZrO(OH)₂ were amorphous.



Figure 5-1 X-ray diffraction pattern of as-precipitated CeO₂ (▼- peaks

corresponding to JCPDS file 34-0394)



Figure 5-2 X-ray diffraction pattern of as-precipitated ZnO (▼- peaks

corresponding to JCPDS file 36-1451)



Figure 5-3 X-ray diffraction pattern of as-precipitated Cu(OH)₂ (▼-

peaks corresponding to JCPDS file 13-0420)

5.1.2 Transmission electron microscopy of inorganic particles

Figure 4 and Figure 5 show the TEM images of CeO₂ and ZnO. The TEM studies revealed fibrous morphology of the CeO₂ powders. Drying resulted in partial agglomeration of the powders. The length of the fibers was about 0.5 μ m and diameter about 20-30 mn. The size of ZnO particles was about 1-4 μ m Cu(OH)₂, TiO₂, Al(OH)₃, Mg(OH)₂, ZrO(OH)₂ and MgAlZr(OH)_x particles were highly agglomerated after drying.



Figure 5-4 TEM images of CeO₂



Figure 5-5 TEM images of ZnO

5.1.3 The memory type flame retardant materials (FRM)

The memory type FRM is a new type of flame retardant materials.. Usually inorganic FRM of hydroxide type are decomposed at elevated temperatures to release water and cannot be used again[32].

The new memory type FRM is a kind of FRM which can recover after the use. They can adsorb water and reconstruct their internal structure and FRM properties and can be used again.

The figure 5-6 shows the X-ray diffraction of original memory type FRM and the same FRM decomposed at 500 $\,^{\circ}C$ and reconstructed.



Figure 5-6 X-ray diffraction of (A) original FRM and (B) FRM after decomposition at 500°C and reconstruction (▼-peaks of hydrotalcite)

The XRD graphs are highly similar to each other which indicates that the internal structure of the memory type FRM has been recovered after decomposition.

The Figure 5-7 shows the thermogravimetric (TGA) and differential thermal (DTA) analysis of original FRM and recovered FRM. TGA data showed that the original FRM exhibited 45% mass loss due to water release under high temperature while the recovered FRM showed a similar behavior with 45% mass loss at high temperature. The DTA data showed that the original FRM has an endothermic peak at the 400 °C while the recovered FRM also has an endothermic peak at the 400 °C peak. Both DTA graphs are highly similar to each other. All these data indicated that the recovered FRM has same good FR properties as original FRM.



Figure 5-7 Thermogravimetric (TGA) and differential thermal (DTA) analysis

of (A) original FRM and (B) recovered FRM, (a-TGA, b-DTA)

5.2 Particle extraction through liquid-liquid interface

5.2.1 Characterization f the inorganic particles after extraction

The application of particle extraction through liquid-liquid interface (PELLI) to the extraction of oxides and hydroxides is a relatively new area, which has generated tremendous interest for many novel applications in nanotechnology[13]. PELLI provides an easy access for organic surfactants to the inorganic particles and help them to form the surface modified particles[14]. PELLI allows particle transfer from aqueous synthesis medium to the processing medium, such as organic solvent phase[13].

The development of PELLI has been motivated by the need of avoiding the formation of agglomerated particles. In many processing technologies, the particles often synthesized in aqueous solution and must be transferred to organic solvents for the preparation of coatings and devices through drying and re-dispersion, which would result in agglomeration because of the reduction of surface area and condensation of surface OH groups[26]. Of particular importance is the use of PELLI for the agglomerate-free processing of inorganic nanoparticles and fabrication of advanced nanocomposites with improved mixing of the individual components[11]. A number of strategies have been developed to extract oxide and hydroxide particles. In general, PELLI methods rely on the synthesis of nanoparticles in aqueous/organic phase or at the LLI, surface modification at the LLI and particle transfer to an organic phase. Conceptually new extractors and extraction mechanisms have been developed[38]. Such extractors offer advantages of strong adsorption on particle surface and high extraction efficiency. In the bottom-up strategy, the particles are extracted from an underneath aqueous synthesis medium of higher density into a 1-butanol phase, which was used as a top receiving liquid of lower density[27].

Figures 5-8 - 5-14 show extraction of different particles with different extractors. In this work different extractors were used, such as 16-phosphonohexadecanoic acid (16pha), Octadecyl phosphonic acid (ODPA),

Stearic acid (SA), Octanohydroxamic acid (OHA), Bufemax (BF), decyl phosphonic acid (DPA), Stearic acid (SA), Octyl gallate (OG), Lauryl gallate (LG), Undecanal, Decanal, Stearyl Gallate (SG), as well as Hexadecyl amine.



Figure 5-8 a) AlMgZr complex hydroxide extracted by 16pha, b)

AlMgZr complex hydroxide extracted by DPA, c) AlMgZr complex



hydroxide extracted by OHA

Figure 5-9 a) Cu(OH)₂ extracted by BF, b) Cu(OH)₂ extracted by LG,

c) Cu(OH)2 extracted by OHA



Figure 5-10 a) as-precipitated CeO₂ inorganic particles, b) CeO₂ extracted by 16pha, c) CeO₂ extracted by ODPA, d) CeO₂ extracted by SA in high concentration, e) CeO₂ extracted by SA in low concentration



Figure 5-11a) CeO₂ inorganic particles, b) CeO₂ extracted by OHA.



arrow shows LLI

Figure 5-12 a) ZnO inorganic particles, b) ZnO extracted by 16pha,

c) ZnO extracted by ODPA, d) SA for mass ratio of extractor 1:3, e) SA



for mass ratio of extractor 1:1

Figure 5-13 a) ZnO inorganic particles, b) ZnO extracted by OHA



Figure 5-14 a) ZnO extracted by LG, b) ZnO extracted by SG



Figure 5-15 PELLI and solid gel formation for (a)TiO₂, (b) Al(OH)₃, (c) CeO₂ and (d) ZnO (L-liquid, LS-liquid suspension, SG-solid gel) using undecanal

The procedures for the aqueous precipitation of titania, $Al(OH)_3$, CeO_2 and ZnO were described in previous chapters. The addition of undecanal to the aqueous suspensions of as-precipitated inorganic particles resulted in their extraction to the undecanal phase. The volume ratio of immiscible water and undecanal was 5:1. The concentration of the inorganic particles in water was in the range of 0.5-4 gL⁻¹.

The approach, developed in this investigation can be used for the

development of other materials and composites with advanced functionality. Titania was successfully extracted from an aqueous synthesis medium to the undecanal phase. In contrast, interesting gelling behavior was observed for particles of other materials. It was found that CeO₂, Al(OH)₃ and ZnO acted as inorganic gelators for undecanal. In the case of CeO_2 and $Al(OH)_3$ we observed liquid-solid extraction, which resulted in separation of a liquid aqueous phase and a solid undecanal-inorganic particle phase. The liquid-solid strategy is promising for the extraction of particles from the synthesis medium because the solid phase can easily be separated from the liquid phase and then dissolved in ethanol. This strategy represents a promising and unexplored route in the particle extraction from the synthesis medium. In the case of ZnO a single solid phase was formed, which included ZnO particles and molecules of undecanal and water. The results indicate that novel organic-inorganic hybrid gels can be formed by the use of inorganic particles as gelators. The gel formation can be controlled by variation of composition of the inorganic phases. Advanced physical and chemical properties of gels are important for various applications, such as drug delivery, tissue engineering, template materials synthesis and separations[55][56]. In contrast to organic gels, the use of functional inorganic particles as gelators paves the way for novel applications of organic-inorganic gels. New gels with advanced functionality can contain magnetic, catalytic, fluorescent, redox-active,

flame-retardant and other functional inorganic nanoparticles.

5.2.2 Mechanism of liquid extraction

The use of organic solvents for EPD provides advantages especially compared to water, due to the elimination of problems related to gas evolution at the electrode[13]. Therefore, the particles synthesized in aqueous solutions must be transferred to an organic solvent using PELLI.



Figure 5-16Chemical structures of (A) 16PHA, (B) ODPA and (C) SA



Figure 5-17 adsorption mechanisms, involving metal (M) atoms on the particle surface and (a–d) phosphonic acid group of ODPA or (e, f)

carboxylic acid group of SA: (a,b, e) bridging, (c, d, f) chelation

Figure 5-16 showed chemical structure of the organic additives, which were used in this investigation, including 16pha, ODPA, SA. These additives have similar structures, which containing acetate groups, phosphate groups, as well as hydrocarbon chains. The adsorption can be based on either bridging (Figure 5-17 (a, b and e)) or chelation (Fig5-17 (c, d and f)) mechanisms[57].



Figure 5-18 Chemical structure of undecanal

Figure 5-18 shows a chemical structure of undecanal, which includes an aldehyde group and an alkyl group. The use of undecanal was inspired by strong aldehyde-metal oxides interactions, which were observed in experiments on adsorption of acetaldehyde[58] from a gas phase on TiO₂, CeO₂ and Al₂O₃. Undecanal is a water-immiscible liquid. The PELLI strategy, developed in this investigation was conceptually different from previous works[59], because the use of extractor molecules was avoided. In this strategy, undecanal was used not only as a particle receiving medium, but also as a vehicle for particle phase transfer. This eliminates the need in extractor removal from an organic phase after extraction.
There are two different mechanism for extraction. For the usual extractors, during the extraction process, organic molecules accumulated at the liquid-liquid interface with the hydrophilic groups exposed to water and hydrophobic hydrocarbon chains extending into the 1-butanol phase [57]. Such an accumulation and orientation of the molecules facilitated their adsorption on inorganic particles at the liquid-liquid interface, as well as the particle transfer from water to the 1-butanol phase (Figure 5-22 A-C) [57]. For another solid extraction, interesting gelling behavior was observed for particles of other materials. It was found that CeO₂, Al(OH)₃ and ZnO acted as inorganic gelators for undecanal. In the case of CeO_2 and $Al(OH)_3$ we observed liquid-solid extraction, which resulted in separation of a liquid aqueous phase and a solid undecanal-inorganic particle phase. The liquid-solid strategy is promising for the extraction of particles from the synthesis medium because the solid phase can easily be separated from the liquid phase and then dissolved in ethanol. This strategy represents a promising and unexplored route in the particle extraction from the synthesis medium. In the case of ZnO a single solid phase was formed, which included ZnO particles and molecules of undecanal and water. The results indicate that novel organic-inorganic hybrid gels can be formed using inorganic particles as gelators. The gel formation can be controlled by variation of composition of the inorganic phases. Advanced physical and chemical properties of gels are important for various applications, such as drug delivery, tissue engineering, template materials synthesis and separations[55][56]. In contrast to organic gels, the use of functional inorganic particles as gelators paves the way for novel applications of organic-inorganic gels(Figure 5-15).



Figure 5-22 Schematic of PELLI method: (A) particles, precipitated in aqueous phase, (B) transfer through liquid-liquid interface, (C) formation of a stable suspension of particles in n-butanol

5.3 Fourier-transform infrared spectroscopy (FTIR) analysis of extracted particles

The adsorption of organic additives on oxide particles was confirmed by FTIR studies of the extracted particles. Figure 5-23 to Figure 5-25 compares FTIR spectra of as-received extractor molecules and extracted particles. The absorptions at 2848 and 2914 cm^{-1} in the spectrum of 16PHA, 2848 and 2912

 cm^{-1} in the spectrum of ODPA, 2848, 2950 and 2912 cm^{-1} in the spectrum of SA were attributed to CH₂ symmetric and asymmetric stretching[16], respectively. Similar absorptions were observed in the spectra of extracted CeO₂ and ZnO particles, which all indicated that extracted particles contained adsorbed 16PHA, ODPA and SA.



Figure 5-23 FTIR spectra for pure 16pha, CeO2 extracted by 16pha,







Figure 5-24 FTIR spectra for pure ODPA, CeO2 extracted by ODPA,

ZnO extracted by ODPA, respectively

Figure 5-25 FTIR spectra for pure SA, CeO2 extracted by SA, ZnO

extracted by SA, respectively

The feasibility of particle extraction with 16pha indicates that molecules containing two hydrophilic end groups (HTH) molecules could be used as extractors in addition to head-tail (HT) surfactants for PELLI[57]. Therefore, the search for extractors should be focused on molecules of other types with advanced functionality that can advance PELLI applications. Hence, we employed 16pha not only as an extractor for PELLI, but also as a dispersing and charging agent for EP. With this conceptually new approach, the particles extracted into the organic phase using 16pha as an extractor, were electrophoretically deposited from the organic phase by also using 16pha as a dispersing and charging agent. The formation of stable suspensions of charged non-agglomerated particles is important for EPD, where organic solvents provide advantages due to the reduced gas evolution at the electrode[57].

The particles extracted with 16pha had enhanced suspension stability in the 1-butanol phase, compared to the same particles extracted using ODPA and SA. It is reasonable to suggest that 16pha adsorption occurs via bonding of the PO_3H_2 groups whereas dissociated COOH end groups impart a negative charge to the particles and facilitate their electrostatic dispersion. However, the dispersion is also attributed to the steric effect. EPD experiments confirmed that CeO₂ and ZnO particles extracted with 16pha were negatively charged and deposited on the anode surface[57].

Due to the similar peaks in each line, it is reasonable to suggest that all the materials have similar groups, which also means the inorganic particles are well combined with extractor molecules.



Figure 5-26 FTIR spectra for pure OHA, OHA with CeO₂, OHA with





Figure 5-27 FTIR spectra for pure BF, BF with CeO₂, BF with ZnO, BF

with Cu(OH)₂, respectively

The adsorption of organic additives on oxide particles was confirmed by

FTIR studies of the extracted particles. Figure 5-26 to Figure 5-27 compares FTIR spectra of as-received extractor molecules and extracted particles. The absorptions at 2844, 2914, 2943 and 2956 cm⁻¹ in the spectrum of OHA, 2873,2929 and 2958 cm⁻¹ in the spectrum of BF were attributed to CH_2 symmetric and asymmetric stretching, respectively. Each composite has similar peak with its extractor, which shows the inorganic particles are well combined with different extractor.



Figure 5-28 .FTIR spectra for (a) DPA and (b) AMZ extracted using

DPA

The DPA adsorption was confirmed by the results of FTIR studies (Figure 5-28). The FTIR spectra of powder samples of extracted AMZ showed

absorptions at 2848, 2918 and 2956 cm⁻¹, which were attributed to asymmetric and symmetric vibrations of CH₂ groups[57]. Such adsorptions were not observed in the spectrum of pure AMZ. However, the FTIR spectrum of as-received DPA powder showed similar absorptions.

Chapter 6 Investigation of LPEI

6.1 Electrodeposition of nanoparticles with polyethylenimine

6.1.1 Mechanism of electrodeposition process

Polyethylenimines have many applications in synthesis, colloidal processing, dispersion and surface modification of materials. Branched polyethylenimines (BPEIs) are water-soluble liquids, whereas linear polyethylenimines (LPEIs) are water-insoluble solids[60]. LPEIs contain secondary amino groups, while BPEIs have primary, secondary and tertiary amines. The amino groups of BPEIs and LPEIs can be protonated in acidic solutions and the protonated polymers exhibit properties of cationic polyelectrolytes in aqueous solutions at low pH values. The cationic properties of BPEIs have been utilized for electrophoretic deposition of materials. BPEIs showed strong adsorption on inorganic surfaces, which is beneficial for particle dispersion and surface modification[60].

Although BPEIs have attracted significant research interest, their thin film applications are limited due to high solubility of BPEIs in water. Another difficulty is related to protonation of BPEI molecules. The pH of aqueous BPEI solutions is typically about 11 and at this pH the BPEI molecules are electrically neutral. The protonation of BPEIs requires significant amounts of acids, which contaminate solutions as well as dispersions of colloidal particles, containing BPEIs[61]. In contrast, LPEIs can easily be protonated. The deprotonated LPEIs are used for thin film applications, due their insolubility in water, film-forming and binding properties. The electro-kinetic and chemical properties of the LPEI macromolecules can be modified by the formation of LPEI-metal ion complexes[62].

BPEIs and LPEIs are attractive materials for biomedical applications, such as biosensors, biomedical implants, drug and gene delivery. Many applications are based on the remarkable ability of LPEIs to form complexes with various inorganic and organic materials[63]. LPEIs are increasingly being explored as gene carriers. Many investigations focused on the analysis of LPEI-DNA complex formation. In contrast to other polyelectrolytes, LPEI offers benefits of stronger transfection efficiencies and improved protection of DNA[61]. It was found that LPEIs have enhanced gene expression and lower toxicity, compared to BPEIs. Enhanced biocompatibility was achieved in LPEI-DNA-metal ion complexes. LPEI-cyclodextrin (CD) complexes have been developed for drug delivery[64]. Enhanced complex formation was observed at high pH above pK_a (8.9) of LPEI.

Many applications of LPEI are based on the use of thin films. In a previous investigation we found that LPEI films can be deposited by electrophoretic deposition (EPD). Two methods were used for the electrodeposition of

74

organic-inorganic composites based on the use of LPEI[65].

The method based on EPD of PEI and FRM particles, which prepared by chemical precipitation and extraction are following the process:

Cathodic electrodeposition of polyethylenimine (PEI):

Protonation and dissolution:

$$PEI+H^+ \to PEI - H^+ \tag{6.1}$$

Local pH increase at the cathode surface:

$$2H_20 + 2e^- \to H_2 + 20H^- \tag{6.2}$$

Deprotonation (charge neutralization) and formation of insoluble PEI films:

$$PEI - H^+ + OH^- \rightarrow PEI + H_2O \tag{6.3}$$

While PEI-H⁺ is adsorbed on particles and charged particles are co-deposited with PEI.



Figure 6-1 Mechanisms of electrodeposition of organic-inorganic composites:
(a) EPD, involving electrophoresis of particles, containing adsorbed LPEI-H⁺,
(b) PC-EPD, involving electrophoresis of LPEI-metal ion complexes and particle synthesis in electrode reactions.

Figure 6-1 shows schematics of colloidal-electrodeposition mechanisms used in this investigation for the deposition of organic-inorganic composites. The protonated LPEI-H⁺ was used for EPD of inorganic particles. In this method, LPEI-H⁺ adsorbed on the particles and provided their charging and dispersion. The deposition process involved cataphoresis of charged particles, containing adsorbed LPEI-H⁺. The LPEI-H⁺ discharge and deposit formation were governed by chemical reactions. In the PC-EPD method, LPEI was dissolved in metal (M) salt solutions to form LPEI-M²⁺ complexes. It is known that PEIs exhibit the remarkable ability to form complexes with metal ions[65] and such complexes show properties of polyelectrolytes in solutions[66]. The PC-EPD mechanism (Figure 6-1(a)) was based on cataphoresis of LPEI-M²⁺, cathodic electrosynthesis of metal oxide or hydroxide particles, charge neutralization and film formation at the cathode surface:

$$LPEI-M^{z+} + zOH^{-} \rightarrow LPEI + MO_{z/2} + (z/2)H_2O$$
(6.4)

$$LPEI-M^{z+} + zOH^{-} \rightarrow LPEI + M(OH)_{z}$$
(6.5)

PC-EPD method resulted in electrosynthesis of metal oxide or hydroxide nanoparticles in LPEI matrix. In contrast to chemical precipitation method, which requires the use of alkali for pH adjustment, the PC-EPD method involved electrogenerated OH⁻ species for the synthesis of inorganic particles. PC-EPD is conceptually different from electrosynthesis-EPD method, which is based on the use of strong polyelectrolytes, such as poly(diallyl dimethylammonium chloride) (PDDA) with pH-independent charge[56]. Electrosynthesis-EPD is limited to the synthesis of oxides and hydroxides with relatively low isoelectric points. It involves independent electromigration of metal ions and polyelectrolytes, electrosynthesis and electrostatic heterocoagulation of the inorganic and organic components at the electrode surface[20].

PC-EPD method is different from the polymer-mediated electrosynthesis,

based on the use of branched PEIs, which are soluble in water and do not form films by EPD in aqueous solutions[8]. The development of PC-EPD method was inspired by interesting electrosynthesis phenomena, such as influence of polymers on crystallinity, functional properties and size of particles, which were observed in electrosynthesis-EPD experiments, involving the use of PDDA[67-68]. Moreover, it was found that weak polyelectrolytes, containing amino groups facilitate room temperature crystallization of functional inorganic materials in the polymer microcapsules[66]. Electrosynthesis-EPD method showed that polymers with amino groups can promote room temperature crystallization of particles synthesized in the polymer matrix. Therefore, LPEI is a promising material for the development of the PC-EPD method[67].

6.1.2 SEM images of composite films

Previous investigations showed that EPD of pure LPEI resulted in the formation of dense films. The addition of oxide particles to the LPEI-H+ solution resulted in changes of film microstructure. The increase in the particle concentration in suspension resulted in increasing particle concentration in films. Figure 6-2 shows SEM images of films, prepared by EPD from 1 g L⁻¹ LPEI-H⁺ solutions, containing 2 g L⁻¹ of Mn₃O₄, ZnO, halloysite nanotubes and AMZ.

The SEM images show porous films, containing oxide or hydroxide particles. The porosity is mainly attributed to particle packing. Some larger pores can result from H_2 evolution in electrode reaction (6.2). The EPD method allowed the fabrication of films with thickness of up to 30 µm. Mn₃O₄ and ZnO are advanced materials for energy storage, sensor and electronic applications[69-70].



Figure 6-2 SEM images of composite films, prepared from 1 g L⁻¹

LPEI-H⁺ solutions, containing 2 g L⁻¹ (A) Mn₃O₄, (B) ZnO, (C) halloysite

and (D) AMZ

The ability of LPEI to form complexes with metal ions allowed the development of PC-EPD method, which represents another promising avenue for the fabrication of composites. Prof-of concept studies were focused on the fabrication of nanocomposites using LPEI-Ni²⁺ and LPEI-Mn²⁺ complexes in

solutions9[71]. Figure 6-4 shows SEM images of the films prepared by this method. The films were relatively dense and uniform. However, very small pores were observed in the films prepared from LPEI-Mn²⁺ solutions. Such pores can result form H₂ evolution during electrodeposition. The method resulted in the development of crack-free films with thickness of 1-2 µm. The thickness of the films, prepared by the PC-EPD method was lower, compared to the thickness of the film prepared by EPD. It is important to note that PC-EPD involves synthesis of inorganic particles. The growth of the insulating and relatively dense films can limit charge transfer and electrosynthesis yield, resulting in lower final film thickness[72]. X-ray diffraction studies (Figure 6-3) (CuKa and CoKa radiations) did not show diffraction peaks for deposits prepared using LPEI-Mn²⁺ solutions. In contrast, the deposits prepared using LPEI-Ni²⁺ solutions showed broad peaks of Ni (OH)₂. Such X-ray diffraction data can result from very small particle size and fully or partially amorphous nature of the inorganic phases[73].



Figure 6-3 X-ray diffraction patterns (CoKa radiation) of deposits,

prepared from (a) 5 mM MnCl₂ and (b) 5 mM NiCl₂ solutions, containing 0.5

g L⁻¹ LPEI.



Figure 6-4 SEM images of deposits, prepared from (a) 5 mM MnCl₂ and

(b) 5 mM NiCl₂ solutions, containing 0.5 g L⁻¹ LPEI.

6.1.3 Thermal properties of composites, prepared by EPD of LPEI and LPEI complexes

Halloysite is a promising material for drug delivery, corrosion protection and flame-retardant applications[32]. The AMZ is an advanced memory-type flame-retardant material. In contrast to other hydroxide materials, the thermally dehydrated AMZ shows unique ability to reconstruct its original composition and flame-retardant properties by adsorption of water[74]. The flame-retardant properties of halloysite and AMZ are attributed to endothermic process of dehydration. The thermal decomposition of halloysite and AMZ resulted in mass loss of 18 and 45%, respectively, which was related to dehydration (Figure 6-5, Figure 6-6). The composite materials showed additional mass loss, related to burning out LPEI. The films, prepared from 1 g L^{-1} LPEI-H⁺ solutions, containing 2 g L^{-1} of halloysite nanotubes and AMZ showed mass loss of 48 and 63%, respectively.



Figure 6-5 TGA data for (a) as-received halloysite and (b) a deposit,

prepared from 1 g L-1 LPEI-H⁺ solution, containing 2 g L-1 halloysite.



Figure 6-6 TGA data for (a) as-received AMZ and (b) a deposit,

prepared from 1 g L⁻¹ LPEI-H⁺ solution, containing 2 g L⁻¹ AMZ.

It is known that the size of the particles in the films, prepared by electrosynthesis from pure metal salt solutions is typically lower than the size of the particles in the films deposited by EPD from colloidal suspensions[75]. The

polymer matrix can potentially limit the size of the electrosynthesized particles. Metal oxide or hydroxide films, prepared by electrosynthesis or other wet chemical methods usually exhibit cracks attributed to drying shrinkage, especially for the films with thickness above 0.1 μ m[76]. LPEI acted as a binder, preventing cracks in the films formed by PC-EPD method. The formation of organic-inorganic composites by PC-EPD was confirmed by TGA studies (Figure 6-7). The deposits showed mass loss attributed to burning out of LPEI and dehydration[77]. The deposit, prepared from LPEI-Mn²⁺ solutions showed several steps in mass loss , the total mass loss at 1000°C was about 59%. Therefore, the Ni(OH)₂ content in the composite was ~ 51%. Ni(OH)₂ is an important charge storage material for applications in batteries[78].



Figure 6-7 TGA data for deposits, prepared from (a) 5 mM MnCl₂ and

(b) 5 mM NiCl₂ solutions, containing 0.5 g L⁻¹ LPEI.



Figure 6-8 FTIR spectra of (a) LPEI, (b) CD, (c) Hb, (d) deposit prepared from aqueous 1 g L⁻¹ LPEI-H⁺ solution, containing 1 g L⁻¹ Hb, (e) deposit, prepared from 1 g L⁻¹ LPEI solution in 5mM MnCl₂ solution,

containing 1 g L⁻¹ CD.

Figure 6-8compares the FTIR spectra of LPEI, cyclodextrin (CD) and hemoglobin (Hb) with spectra of the LPEI-Hb and LPEI-CD composite films. The FTIR spectrum of Hb shows absorptions at 1645 and 1535 cm⁻¹, which are attributed to amide I band and amide II band[79], respectively. Similar absorptions were observed in the spectrum of the composite LPEI-Hb films in addition to peaks of LPEI. The FTIR spectrum of CD showed a broad peak centered at 1018 cm⁻¹ due to C–O–C vibrations[80]. A similar absorption was observed in the spectrum of the deposit prepared from LPEI-Mn²⁺ solutions, containing CD. The shift of this peak to 1031 cm⁻¹ can result from the polypseudorotaxane formation. The results of FTIR studies confirmed that Hb and CD were incorporated into the LPEI films. In this investigation Hb was used as a model protein for the development of a deposition mechanism. It is expected that a similar approach can be used for the deposition of other proteins and enzymes for diverse applications in biomedical implants and biosensors. CD is a unique carrier[81-83] of various functional organic molecules, therefore CD can facilitate their incorporation of into the LPEI films.

Chapter 7 Anodic electrodeposition of alginate composites

7.1 Electrodeposition of alginate

Alginic acid sodium salt (AlgNa) was used as an anionic polymer for the deposition of composites by anodic EPD. The deposition mechanism involved dissociation of AlgNa to form anionic Alg⁻ species:

$$AlgNa \rightarrow Alg^{-} + Na^{+}$$
(7.1)

Electrophoretic transport of the anionic Alg⁻ species resulted in their accumulation at the anode surface. The electrochemical decomposition of water resulted in a local pH decrease at the anode surface:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (7.2)

The following reaction resulted in charge neutralization and formation of anodic films of water insoluble alginic acid AlgH

$$Alg^- + H^+ \rightarrow AlgH$$
 (7.3)

Electrodeposition of AlgH can be performed form aqueous or mixed ethanol-water solutions (60% ethanol). The use of the mixed solvent offered the advantages of reduced gas evolution, which allowed for the reduction of porosity related to gas evolution and formation of dense deposits. The use of the mixed solvent was necessary for the deposition of composite coatings, because relatively high voltages of 50-100 V were necessary for the particle transport.

7.2 Fabrication and characterization of particles for EPD

TiO(OH)₂ particles were prepared by precipitation from TiOSO₄ solutions at pH=7. X-ray studies showed that as precipitated material was amorphous. The particles were extracted to the 1-butanol solvent using lauryl gallate as an extractor. Figure 7-1 shows TG and DTA data for the powder sample.



Figure 7-1. (a) TG and (b) DTA data for TiO(OH)₂.

88

The TG data showed two steps in mass loss, attributed to dehydration. Significant reduction of mass loss was observed below 220°C, an additional step in mass loss was observed in the range 550-650°C. The total mass loss at 1000°C was 35% of the initial sample mass. The DTA data revealed an endothermic peak at 120°C related to dehydration. Therefore, TiO(OH)₂ is a promising FRM material for the fabrication of organic-inorganic composites. The FRM properties of TiO(OH)₂ are related to water release and endothermic effect. The analysis of TG data indicated that TiO(OH)₂ contained adsorbed water. Therefore, the water release resulted from the liberation of adsorbed water and decomposition of TiO(OH)₂.

CaAl double hydroxide was another promising FRM material. The X-ray diffraction studies of as-precipitated CaAl double hydroxide showed crystallinity of this material. Figure 7-2 shows X-ray diffraction pattern of the as-prepared material with Ca:Al atomic ratio of 3:2. The major peaks corresponded to Ca₃Al₂(OH)₁₂ phase (JCPDS file 01-084-1353), however small peaks of hydrated Ca₄Al₂(CO₃)(OH)₁₂ (JCPDS file 04—011-4223) were also observed. The adsorption of CO₂ from air promoted the formation of this phase. The CaAl double hydroxide material was studied by TG and DTA (Figure 7-3). The TA studies showed the total mass loss of about 48% at 1000°C. However, the mass loss was observed mainly below 400°C. This mass loss was attributed to dehydration. The DTA data showed an endotherm at 220°C, which corresponded to mass loss related to dehydration. Therefore, CaAl

double hydroxide is another promising material for FRM applications due to significant water release related to dehydration and strong endothermic effect. The CaAl double hydroxide material was used for the formation of composite coatings by EPD.



Figure 7-2. X-ray diffraction pattern of CaAl double hydroxide (▼- peaks

corresponding to JCPDS file 01-084-1353).



Figure 7-3 (a) TG and (b) DTA data for CaAl double hydroxide.

7.3 EPD of alginate composites and SEM studies

In this investigation sodium alginate coatings, containing various inorganic materials were prepared by EPD. Alginate was used as a charging and dispersing agent for the EPD of inorganic particles. The use of alginate allowed the fabrication of stable suspensions for EPD. Alginate adsorbed on the particles and allowed for their electrosteric dispersion. SEM studies showed FRM particles in the alginate matrix. Therefore, SEM studies confirmed the formation of composite coatings, containing FRM. Figures 7-4, 7-5 and 7-6 show SEM images of composites, containing TiO(OH)₂, CaAl double hydroxide and AMZ, respectively. It is suggested that similar approach can be used for deposition of alginate coatings, containing other FRM. Moreover, anodic EPD can be used for co-deposition of other anionic polymers containing FRM additives.



Figure 7-4 SEM image of a composite coating, prepared from 1 g L⁻¹ alginate

solution, containing 1 g L^{-1} TiO(OH)₂.



Figure 7-5 SEM image of a composite coating, prepared from 1 g L⁻¹ alginate



solution, containing 1 g L⁻¹ CaAl double hydroxide.

Figure 7-6 SEM image of a composite coating, prepared from 1 g L⁻¹ alginate

solution, containing 1 g L⁻¹ AMZ.

Chapter 8 Conclusions

8.1 Conclusions related to FRM and EPD

In this work, author developed chemical precipitation methods for FRM particles and also developed PELLI for the extraction of non-agglomerated FRM particles. Various extractor molecules were tested.

The EPD method has been developed for co-deposition of PEI or alginate with inorganic materials, which showed promising properties for FRM and other applications.

8.2 Conclusions related to LPEI

The pH-dependent charge and solubility, unique binding and complex-forming properties of LPEI play a vital role in EPD and PC-EPD methods. Cathodic EPD has been developed for the fabrication of composite films containing Mn₃O₄ and ZnO nanoparticles, as well as advanced flame retardant materials, such as halloysite nanotubes and memory-type AMZ in the matrix of the water insoluble LPEI. Liquid-liquid extraction method has been developed for the agglomerate-free processing of AMZ particles. Efficient extraction was achieved using DPA as an extractor. A conceptually new PC-EPD method has been developed, which is based on the use of LPEI-metal ion complexes. PC-EPD method allowed the fabrication of LPEI-Ni(OH)₂ and PLEI-MnOx nanocomposites. The composites showed valuable flame retardant and charge storage properties. The unique film forming and chemical properties of LPEI allowed the development of electrochemical strategies for the fabrication of organic composites by cathodic EPD and PC-EPD. Hb was used as a model protein for the fabrication of LPEI-Hb. The extension of these studies can result in the development of new composites, containing other proteins and enzymes for application in biomedical implants and biosensors. Another important finding was the possibility of the fabrication of composites, containing CD, which is a unique carrier of various functional organic molecules. EPD and PC-EPD are versatile methods, which allow the deposition of novel PLEI based composites containing various functional materials.

8.3 Conclusions related to alginate

Anodic EPD was developed for the deposition of composite coatings, containing advanced FRM in an alginate matrix. Alginate was used as a charging and dispersing agent for the FRM nanoparticles. TiO(OH)₂, CaAl double hydroxide and AMZ are promising FRM materials for the fabrication of organic-inorganic composites. The FRM properties of TiO(OH)₂, CaAl double hydroxide and AMZ are related to significant water release and related endothermic effects. A similar approach can be used for the deposition of other anionic polymers, containing FRM additives.

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107

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