

Electrochemical Deposition of Organoceramic Materials

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Electrochemical methods are increasingly being used for the preparation of thin films of metals, ceramic materials and polymers. In the last few years organoceramic materials have emerged as new promising materials for future technologies. These materials exhibit interesting mechanical, thermal, electrical, optical and magnetic properties whose applications have motivated the development of novel processing techniques. Electrodeposition allows room temperature processing of organoceramic films based on magnetic, ferroelectric, piezoelectric, optoelectronic and other functional materials. The rapidly increasing scientific interest in electrodeposition of organoceramic materials has opened new opportunities in development of advanced thin films for novel applications.

Various electrochemical strategies were developed for cathodic electrodeposition of organoceramic films. Cathodic electrodeposition of ceramic materials can be performed by electrophoretic (EPD) or electrolytic (ELD) deposition. The important finding was the feasibility of electrochemical intercalation of cationic polyelectrolytes poly(diallyldimethylammonium chloride) (PDDA) and polyethyleneimine (PEI) into ceramic deposits prepared using ELD and EPD. Organoceramic films based on oxides or hydroxides of Zr, Ce, Gd, Fe, Ni, Cr, Y, Cu, Co, La were obtained on various conductive substrates. By varying the current density, concentrations of polymers, ceramic particles and electrolytes, the amount of the deposited material and its composition could be controlled. Deposition rate was evaluated at different experimental conditions. Films in the range of thickness up to 10 μm were prepared as monolayers or laminates of different materials.

The deposits were studied by thermogravimetric analysis (TG), X-ray diffraction and scanning electron microscopy (SEM). TG results indicate that film composition could be controlled by variation of the polyelectrolyte concentration in solutions used for deposition. The amount of an organic phase in organoceramic deposits was found to be in the range 0-70 wt%. The deposit weight was also traced as a function of polyelectrolyte concentration in solutions. It was established that the increase of polyelectrolyte concentration near the electrode surface prevents electrosynthesis of colloidal particles. As a result the efficiency of electrodeposition of both organic and inorganic phases decreases.

A mechanism of electrochemical intercalation of the cationic polymers into ceramic deposits prepared using EPD and ELD is discussed. A model has been developed based on electrostatic attraction of oppositely charged colloidal particles and polyelectrolytes. SEM observations indicate formation of thin films of uniform thickness. The uniformity of the deposits prepared by electrodeposition results from insulating properties of the deposited materials and electric field dependence of the deposition rate.

Electrodeposition could be used for intercalation of ceramic particles into growing polymer films to form organoceramic deposits. In contrast to cationic polyelectrolytes, polyvinyl alcohol (PVA) is a neutral polymer. Therefore, EPD cannot be used to deposit a layer of pure PVA. Cathodic electrodeposition was performed from PVA solutions containing small amounts of boric acid or borax. The method used for PVA deposition is based on a local pH increase and formation

of borate ions $\text{B}(\text{OH})_4^-$ near the cathode, followed by crosslinking of PVA molecules by the borate ions and PVA gelling. Deposit yields obtained at various concentrations of boric acid and borax were compared. Electrode reactions are not directly involved in deposit formation and electrochemical deposition of PVA is not a Faradaic process. However, experimental data presented in indicate that deposit weight increases proportionally with deposition time and current density. Adherent deposits of uniform thickness were obtained on various conducting substrates. Deposit thickness was controlled by variation of deposition time or current density. SEM observations indicate that uniform and adherent deposits were obtained at low current densities (up to 0.3 mA/cm^2). PVA films obtained at current density of 0.1-0.3 mA/cm^2 were transparent, uniform and adhered well to the substrates. Films up to several microns thick could be deposited.

EPD and ELD of ceramic particles were used for intercalation of ceramic particles into the growing PVA film. Multilayer polymer-ceramic films were prepared by alternative electrodeposition of PVA and EPD or ELD of conductive ceramic layers. ELD is an important technique for deposition of nanostructured materials. EPD has the advantage of higher deposition rate. The stoichiometry of EPD deposits is controlled by the composition of powders used for deposition.

Organoceramic materials obtained in this way combine the advantageous properties of ceramics with those of polymers within a composite material. Possible applications of the prepared materials are discussed.