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A novel approach to PZT coatings for conformal sensors

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Original Article

Abstract

Lead zirconate titanate (PZT) is placed as the most suitable piezoelectric material for underwater acoustic sensor applications and none of the other materials match up to its performance. Currently, the trend in technology is shifting towards developing flexible large area sensors conformal to the platform on which it has to be deployed or fitted. The flexible polymeric piezomaterials such as PVDF, copolymers of PVDF currently lacks acceptability due to their inferior piezoelectric properties when compared to that of PZT. In this work, an attempt is made to develop PZT thin films on flexible substrates using electrolytic deposition (ELD) technique for conformal sensor applications. PZT is deposited as films on various flexible substrates such as carbon fibers, thin metal foils (titanium, stainless steel) using the electrodeposition technique. The effect of different key parameters like electrolyte medium (aqueous and non-aqueous), current density (10 to 40 mA/cm^2), time of deposition (1 to 10 minutes), sintering temperature (300 to 500°C) and heating time (15 minutes to 1 hour) are described and the results of characterisation using techniques such as SEM (Scanning Electron Microscopy), EDAX (Energy dispersive X ray spectroscopy), XRD (X ray diffraction) and dielectric studies are reported.

***Keywords**: Lead zrconate titanate, tlectrolytic deposition, piezoelectricity, sintering.*

Introduction

The most widely used underwater detection technique (Reactions 1, 2) is based on the transmission of sound energy of various frequencies, receiving and processing it to get the details of target of interest. Acoustic energy is commonly used for underwater detection due to its ease of transmission in water and piezoelectric materials are primarily used for underwater electroacoustic transducers which convert electrical energy into acoustic energy or vice versa. Piezoelectric ceramics have been used extensively in underwater acoustic transducers, and PZT has been the most important family in piezoelectric ceramics because of their excellent piezoelectric properties, high Curie points, high mechanical strength etc.

The traditional PZT sensors being hard and brittle, requires the host structure to be planar and smooth, in order to ensure a robust and seamless fitting for an accurate measurement. However, in many cases the structural surfaces are curved, where the conformability of the ceramic sensor and the host structure is very poor, and extra modifications are required to fit the sensors. Conformal sensors are a new class of sensors which can be adhered on to planar/non planar structures with equal ease. In this particular work, it is tried to obtain PZT as thin/ thick films on flexible substrates in order to develop conformal

PZT sensors for underwater acoustic applications. In this paper, electrolytic deposition (ELD) is used to obtain PZT films for conformal sensor applications. Electrodeposition (Reactions 3 -7) is defined as the method of depositing a material on to a conducting surface from a suspension or solution in the presence of an electric field. The method of electrodeposition is favoured due to its many advantages over other methods like sol-gel, sputtering etc. It provides uniform deposits over flat as well as on curved shapes and also on selected areas of a substrate. It offers rigid control of film thickness and stoichiometry of the deposit, does not require very high initial investment cost and can be converted from laboratory to manufacturing scale very easily. Fig. 1 shows the schematic set up for electrolytic deposition.

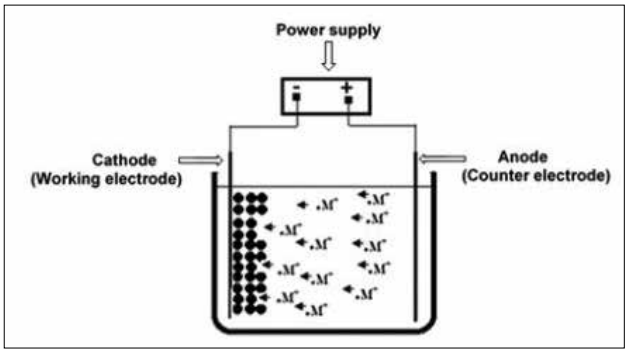

Fig.1. Schematic set up for electrolytic deposition

In this paper optimization of process parameters such as (i) current density (ii) time of deposition (iii) sintering temperature and time (iv) influence of medium/electrolyte for electrolytic deposition of PZT was carried out. Moreover, deposition of PZT on various metal foils (titanium and stainless steel)and carbon fibre mats were also described.Further, characterization of the deposits was carried out using techniques like SEM (Scanning Electron Microscopy), EDAX (Energy dispersive X ray spectroscopy) and XRD (X ray diffraction) and Dielectric studies using Impedance Analyser.

Material and methods

Substrates

Metal foils obtained from Alfa aesar *viz.* (i) Stainless steel (SS) (ii) Titanium and (iii) carbon fiber mat were used as substrates for deposition. Surface preparation of metal foils were, done using emery papers of different grades (80, 180, 320, 800) cleaned and wiped with acetone to get a mirrorfinish.

Electrolytic deposition

Various aqueous electrolytes were prepared by dissolving AR grade salts of lead nitrate $Pb(NO_3)_2$ (Alfa aesar), Zirconium chloride hydrate $ZrOCl_2$. $8H_2O$ (Sigma Aldrich), Titanium tetrachloride $TiCl_4$ (Merck) and H_2O_2 (Acros Organics) in distilled water in the ratio 1:0.52:0.48:10. Similarly non-aqueous electrolyte was prepared by dissolving the AR grade salts of lead nitrate Pb $(NO_3)_2$ (Alfa aesar), Zirconium chloride hexa hydrate $ZrOCl_2.8H_2O$ (Sigma Aldrich), Titanium tetrachloride $TiCl_4$ (Merck) in DMSO (Dimethylsulphoxide, Alfa Aesar). Studies were performed using aqueous and non-aqueous electrolyte solutions. Depositions were done by making the substrate of interest as cathode and platinum foil as anode.

Characterisation

The microstructure of the films and their composition were studied using a scanning electron microscope (Jeol, model JSM-6390LA) equipped with EDAX (Energy dispersive X ray spectroscopy). The structure or phase analysis was done using X-ray diffraction (XRD) studies using Bruker AXS D8 Advance model instrument. The dielectric studies were done using a Precision impedance analyser (Wayne Kerr 6500 B) instrument.

Results and discussion

Optimisation of ELD process parameters

In this study, optimisation of process parameters such as (i) current density, (ii) time of deposition for electrolytic deposition of PZT were studied in aqueous electrolytes and expertimental setup are given in Fig. 2. The deposition of PZT obtained at various current densities *viz.* (i) 10mA/cm^2 (ii) 15mA/cm^2 (iii) 20mA/cm^2, (iv) 25mA/cm^2 (v) 30m A/cm^2 (vi) 40m A/cm^2 are given in Fig 3. It can be seen from the figure that maximum deposit was obtained at a current density of 15 mA/cm^2. Ren

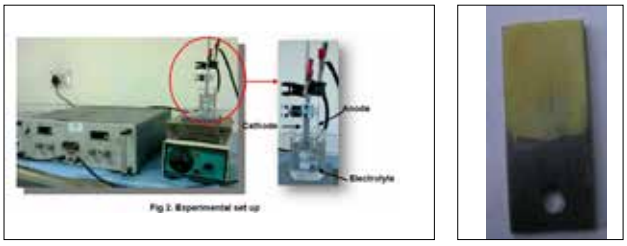

Fig. 2. (a) Experimental setup, (b) PZT deposition after sintering

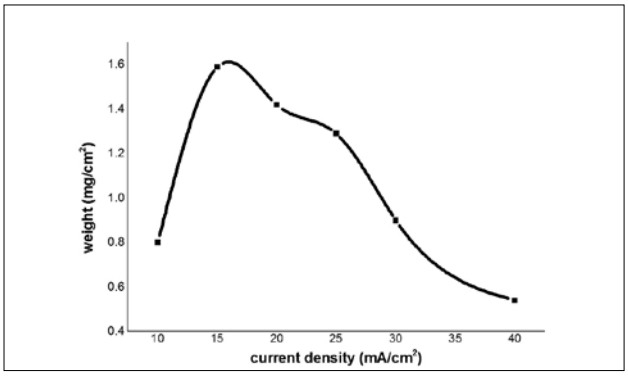

Fig. 3. Variation of deposit weight with current density

et al. (2008) obtained an optimum value of 20-30 mA/cm^2 for current density for PZT thin film deposition by electrochemical reduction in an electrolyte containing only constituent salts. The shift in optimum current density in this experiment may be probably due to the formation of peroxocomplexes as it contains hydrogen peroxide.

Fig. 4 shows the PZT coating obtained on SS at a current density of 15 mA/cm^2 for different durations. It can be seen that the deposit weight increased up to 5 minutes and further increase caused the deposit not attaching the substrate and deposit weight remained almost constant.

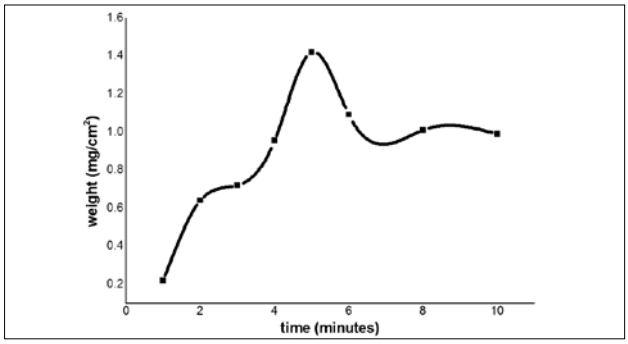

Fig. 4. Variation of deposit weight with time

Optimisation of temperature and time for sintering of PZT deposits

Since the deposition obtained (green deposit) is amorphous, heat treatment or sintering is necessary to crystallise the deposit to perovskite piezoelectric PZT material. Sintering increases the bonding between the substrate and coating by removing impurities present in the deposit. X-ray Diffraction (XRD) analysis was performed to ascertain crystal structure of the deposit. Studies were performed for non aqueous depositions at different temperatures such as (i) 300°C (ii) 400°C, (iii) 450°C, (iv) 500°C (Fig. 5). For the deposits sintered at 500ºC, peaks were obtained at 2θ values: 21.522, 30.671, 37.96, 44.338, 50.06, and 54.687 which can be identified as the characteristic

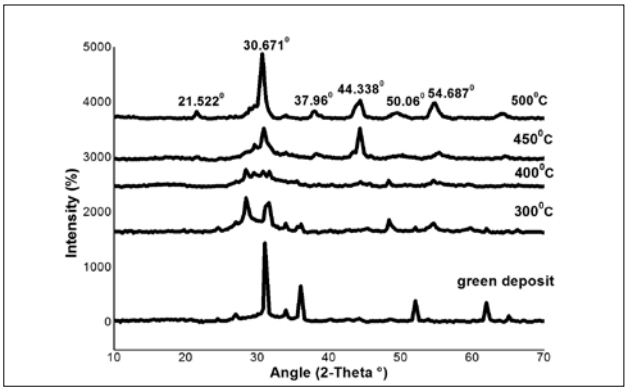

Fig. 5. Sintering done at different temperatures for a constant time of 1 hour

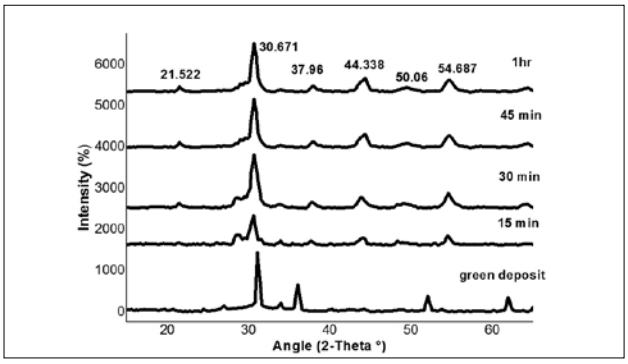

Fig. 6. Sintering at 500°C for different time intervals

peaks for a perovskite PZT structure and hence the sintering temperature was optimised as 500°C.

Further in order to optimise the heating duration experiments were performed for different durations *viz.* (i) 15 minutes (ii) 30 minutes (iii) 45 minutes (iv) 1 hour (Fig. 6). It has been found that a minimum time heating time of 45 minutes at 500°C results in good perovskite structure for the deposit.Further increase in sintering time does not have any significant effect on the structure of the PZT deposit.

Microstructure characterisation of PZT coatings on different substrates

Two principal types of electrolytes were studied namely aqueous and DMSO based non-aqueous systems. Aqueous electrodeposition is the commonly used technique, as the highly polar water dissolves a large variety of salts and hence gives electrolyte solutions of low resistivity. However, aqueous electrolytes also have certain limitations. The adsorbed water in green deposits can cause shrinkage and cracking during sintering. In this work, non-aqueous deposition was found to give better results than aqueous deposition. Fig. 7 shows the

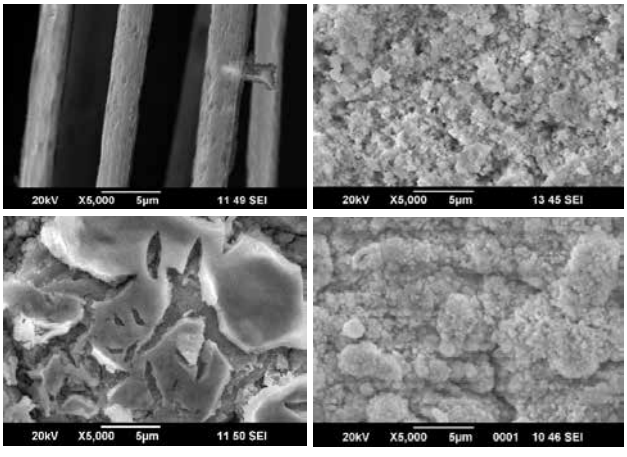

Fig. 7. SEM images of PZT deposits on (a) carbon fibers (aqueous deposition), (b) Titanium foil (non-aqueous deposition), (c) SS foil (non-aqueous deposition) and (d) SS foil (aqueous deposition)

SEM images of PZT deposition developed on (a) carbon fibers using aqueous electrolyte, (b) on titanium foil using DMSO based non-aqueous electrolyte, (c) on SS using aqueous electrolyte and (d) on SS using a DMSO based non aqueous electrolyte system.

It can be seen from the micrographs that a good coating were formed on titanium foil and SS foil in non-aqueous medium. However, the film formed on SS foil using an aqueous electrolyte showed non uniform morphology. Aqueous deposits also showed surface cracks and poor adhesion to the substrate. This can be due to the high conductivity of the electrolyte aqueous medium resulting in many electro active species. The reaction mechanism (9) of PZT electrolytic deposition is as follows:

Base generation

In case of non-aqueous electrolytes, water of hydration in the salts are used for base generation.

$$2H_2O + 2e^- \longleftrightarrow H_2 + 2OH^- \quad (1)$$

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^- \quad (2)$$

$$O_2 + 2H_2O + 4e^- \longleftrightarrow 4OH^- \quad (3)$$

Dissociation of salt

$$Pb(NO_3)_2 \longrightarrow Pb^{2+} + 2NO_3^- \quad (4)$$

$$ZrOCl_2.nH_2O \longrightarrow ZrO^{2+} + 2Cl^- + nH_2O \quad (5)$$

$$TiCl_4 \longrightarrow Ti^{4+} + Cl^- \quad (6)$$

The deposition process hereafter is different for both aqueous and non-aqueous systems. In aqueous electrolytes, due to the instability of titanium salts in water, hydrogen peroxide is used so that stable peroxocomplexes are obtained which are then deposited as hydrated mixed oxides at cathode. The aqueous deposition process is shown below:

$$Pb^{2+} + H_2O_2 + (n-2)H_2O \longrightarrow PbO_2(OH)_{n-2}^{(2-n)+} + nH^+ \quad (7)$$

$$PbO_2(OH)_{n-2}^{(2-n)+} + mOH^- + kH_2O \longrightarrow PbO_2(H_2O)_x \quad (8)$$

$$ZrO^{2+} + H_2O_2 + (n-2)H_2O \longrightarrow ZrO_3(OH)_{n-2}^{(2-n)+} + nH \quad (9)$$

$$ZrO_3(OH)_{n-2}^{(2-n)+} + mOH^- + kH_2O \longrightarrow ZrO_3(H_2O)_y \quad (10)$$

$$Ti^{4+} + H_2O_2 + (n-2)H_2O \longrightarrow TiO_2(OH)_{n-2}^{(4-n)+} + nH^+ \quad (11)$$

$$TiO_2(OH)_{n-2}^{(4-n)+} + mOH^- + kH_2O \longrightarrow TiO_3(H_2O_z \quad (12)$$

Decomposition of the peroxo hydrated deposit during sintering result in PZT film.

$$PbO_2(H_2O)_x + ZrO_3(H_2O)_y + TiO_3(H_2O)_z PbZrTiO_3 + \longrightarrow (x+y+z)\,H_2O + 5/2\,O_2 \quad (13)$$

In the case of non-aqueous electrolytes, all the metal ions such as Pb^{2+}, Zr^{4+} and Ti^{4+} are deposited at the electrode as their respective hydroxides which are then converted to their respective oxides during sintering.The non-aqueous deposition mechanism is shown below:

$$Pb^{2+} + 2OH^- \longrightarrow Pb(OH)_2 \quad (14)$$

$$ZrO^{2+} + H_2O \longrightarrow Zr(OH)_2^{2+} \quad (15)$$

$$Zr(OH)_2^{2+} + 2OH^- \longrightarrow Zr(OH)_4 \quad (16)$$

$$Ti^{4+} + 4OH^- \longrightarrow Ti(OH)_4 \quad (17)$$

Dehydration and formation of a complex oxide,

$$Pb(OH)_2 + Zr(OH)_4 + Ti(OH)_4 \longrightarrow PbZrTiO_3 + 5H_2O + O_2 \quad (18)$$

In DMSO the base generation is limited and occurs only from the water of hydration present in constituent salts. In addition, insoluble reduction products of trace H_2O, O_2 and CO_2 precipitate on the electrode (10). Therefore, the mechanism of formation of peroxocomplex is not present in the case of non-aqueous electrodeposition. It seems that in aqueous electrodeposition, super hydrated mixed oxides resulted from the peroxocomplexes on heating has a tendency to crack due to the escape of adsorbed water.

Dielectric studies of the PZT deposits

Fig. 8 shows the impedance plot of PZT deposit. The dielectric studies were performed using a Precision Impedance Analyser (Wayne Kerr 6500 B) instrument and the measurements of impedance values were done in the frequency range of interest 1kHz to 1MHz. PZT samples deposited on titanium with a thickness of 100 μm were used for the measurement and the dielectric constant values were calculated. The dielectric constant values showed a decreasing trend with increase in frequency from 1kHz to 1MHz.

In this study the method of electrolytic deposition has been successfully utilised for the fabrication of thin film PZT on flexible substrates such as carbon fibers, tianium foils, stainless steel foils which in turn can be utilised to develop flexible or conformal forms of piezoelectric PZT for futuristic underwater sensor applications. The process of PZT deposition has been extensively studied by optimising

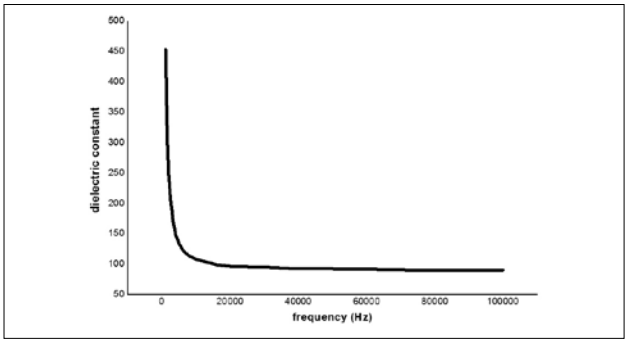

Fig. 8. Dielectric constant vs. frequency plot

process parameters current density and time of deposition. Deposition at different current densities (i) 10 mA/cm^2 (ii) 15 mA/cm^2(iii) 20 mA/cm^2 (iv) 25 mA/cm^2 (v) 30 mA/cm^2 (vi) 40 mA/cm^2 and time intervals (1 to 10 minutes) were carried out and optimised as 15 mA/cm^2 for 5 minutes. The studies on the effect of temperature (i) 300°C (ii) 400°C, (iii) 450°C, (iv) 500°C and time of heating (i) 15 minutes (ii) 30 minutes (iii) 45 minutes (v) 1 hour has been done and found that sintering at a temperature at 500°C for a minimum time of 45 minutes is necessary to obtain a perovskite structure for the eletrodeposited PZT. The microstructure, adhesion of the PZT film to the substrate and their dielectric properties were also studied.

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