EXECUTIVE SUMMARY

Adaptive structures mimic the ability of biological structures (e.g., bone) to redistribute their structural mass in response to dynamic service loads and damaging effects. The adaptive features yield enhanced levels of structural efficiency and safety in dynamic service environments.

The project developed a theoretical basis for modeling and design of adaptive structures, validated the fundamental principles governing the structural performance of adaptive systems, and undertook developments and material and system levels toward development of inherently adaptive structures.

Adaptive phenomena are guided and driven by mechanical energy, noting that redistribution of structural substance strives to match the distribution of mass to the distribution of mechanical energy within the structural system. The adaptive mechanism involves conversion of mechanical to electrical energy using piezoelectric effect. Redistribution of mass occurs electrochemically in the context of a solid electrolyte, which is guided and driven by piezo-induced electric potential and charge, respectively.

Theoretical modeling of the adaptive phenomena confirmed that: (i) the piezoelectric effect can, within the geometric and mechanical constraints of actual structural systems, generate sufficient electric potential and charge (through harvesting the available mechanical energy) to enable electrochemical mass transport within solid electrolyte; and (ii) the redistribution of mass in dynamic service environments can alter structural attributes within viable time frames to yield enhanced structural efficiency for altered service environments.

The fundamental principles governing adaptive phenomena were validated through demonstration of piezo-induced electrolytic phenomena in solid electrolytes, and by verifying gains in mechanical performance associated with such phenomena. Substantial efforts were devoted to enhancement of the functional (piezoelectric and solid electrolyte) constituents rendering self-healing effects. Major gains in processability, functional attributes and thermomechanical performance of functional constituents were achieved.

Various system configurations were devised and verified for incorporation of functional constituents rendering adaptive effects into structural systems. Processing methodologies were developed for integration of structural and functional elements, and the occurrence of adaptive phenomena within integrated systems was verified.

Adaptive phenomena are guided and driven by piezoelectric effect, which harvests the mechanical energy of structural systems to enable electrochemical phenomena rendering adapting effects. The effectiveness and rate of adaptive phenomena are governed by the efficiency of the piezoelectric constituent in converting mechanical to electrical energy. Major opportunities exist to achieve enhanced piezoelectric effects through development of piezoelectric nanocomposites. The project took preliminary steps to verify the benefits of nanostructured piezoelectric composites. Another area of improvement would involve solid electrolytes, which could benefit from enhanced levels of thermomechanical performance and ion-conductivity. The project initiated efforts toward development of solid nanocomposite electrolytes with enhanced performance characteristics.
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CHAPTER 1
INTRODUCTION

Developments in advanced composite materials and structures are increasingly lowering the weight and enhancing the performance of diverse aerospace systems. The adaptive composite materials which are subject of this research promise significant benefits in terms of the reliability, survivability, life-cycle economy and weight of future aerospace systems.\textsuperscript{1} The adaptive mechanism effectively mobilizes material resources to optimize structural performance in light of altered service environments or damaging effects, mitigate catastrophic damage growth, and greatly benefits the reliability, efficiency, longevity and maintenance requirements of structural materials. The adaptive phenomena would be activated upon changes in stress distribution within the material system, caused by changes in service environment or by damaging effects. This section briefly reviews the prevalent damage phenomena in composites, and introduces the adaptive principles which mitigate catastrophic damage propagation.

Under load and environmental effects, damage initiates and accumulates in composites in the form of matrix, interface, inter-laminar and fiber cracks (Figure 1). The growth process of fatigue damage in composite laminates is, for example, depicted in Figure 2.\textsuperscript{2} This process starts with the development of homogeneous, non-interactive matrix cracks in individual plies, which grow into inter-laminar cracks. Damage eventually localizes in zones of high crack density and interaction, where failure occurs by a catastrophic sequence of fiber ruptures. Various damaging phenomena (impact, temperature cycles, fatigue, etc.) all contribute to the crack development process, with their cumulative effects governing to the failure of composites. Figure 3, for example, depicts the matrix, inter-laminar and fiber cracks which typically develop in laminated composites under impact loads. Any source of local stress rise in composites, including bonded or mechanical joints (Figure 4) and concentrated forces, accentuate the localization of damage, and accelerate the failure process.

![Figure 1. Basic Modes of Crack Development in Composites.](image-url)
While the processes of damage accumulation and failure are more complex in composites than in homogeneous materials, they are both characterized by the concentration of damage in critical zones where catastrophic failure initiates. In both cases, the fate of structural system is determined by a very small fraction of its volume (where damage localizes), rendering the bulk of material resources available elsewhere largely under-utilized. Concentration of stress and strain energy is a defining attribute of the local zones of damage concentration within structural systems. Our adaptive mechanism makes constructive use of the destructive energy concentrated at such critical zones to effectively mobilize the material resources available elsewhere against catastrophic failure. Composites embodying such adaptive principles can assume different system configurations. An example where functional constituents rendering adaptive effects are introduced as a hybrid fiber coating is presented in Figure 5. Figure 5(a) depicts a catastrophic sequence of fiber rupture in a conventional composite. Through introduction of a hybrid fiber coating, our approach provides the composite with the inherent capability (see Figure 5(b)) to
transport structural substance towards and deposit it at the critical zone of stress concentration in order to mitigate the catastrophic sequence of fiber rupture.

Figures 5(c)-(e) present a more detailed view of the hybrid coating which provides the adaptive mechanism introduced in Figure 5(b). The adaptive phenomenon involves electrochemical processes guided and driven by the gradient buildup of strain energy in damaged composite structures. The piezoelectric effect is used to convert the (gradient) strain energy into electrical energy, which in turn drives electrochemical phenomena in solid electrolyte to transport structural substance towards the damaged zone where strain energy concentrates. The constituents rendering adaptive effect (piezoelectric ceramic and solid electrolyte with dissolved metal salt) are applied in Figures 5(c)-(e) as a layered coating onto reinforcing fibers; other system configurations are also possible. The local nature of damage (as well as the statistical distribution of fiber strength) cause early rupture of some reinforcing fibers in composites. Figure 5(c) shows the perturbation in stress state upon fracture of a fiber. Tensile stress drops to zero at the point of fiber fracture, and it builds up along the two fiber segments by interfacial shear. The load of fractured fiber would be transferred to adjoining fibers, yielding a local rise in stress and thus strain energy. In conventional composites (see Figure 5(a)), this local phenomenon prompts catastrophic failure of the system. The adaptive phenomenon depicted in Figures 5(b)-(e) enables the composite to realize its full potential through concentration of structural substance at critical zones where strain energy concentrates. Given the unpredictable nature of critical damage locations, one needs to build the capability into composites for dynamic transfer of structural substance in response to evolving stress gradients. For this purpose, a hybrid coating comprising piezoelectric and solid electrolyte (with dissolved metal salt) constituents is applied onto reinforcing fibers (see Figure 5(d)). The local rise in stress and strain energy prompts the piezoelectric effect, which guides and drives electrochemical transport of mass to critically stressed areas (Figure 5(e)).
The adaptive mechanism depicted in Figure 5 would function satisfactorily if: (i) the piezo-induced electric potential is sufficient to stimulate the electrolysis phenomenon; (ii) conversion of mechanical to electrical energy generates sufficient power for transport of substance at viable rates; and (iii) electrodeposition can occur within solid electrolytes to render viable strengthening effects. An integrated analytical/experimental research was undertaken in order to validate these fundamental principles towards development of adaptive structural materials.

The adaptive mechanisms introduced above mimic those occurring in biological life. Bone, for example, employs a simple but powerful control mechanism to reconfigure its structure in order to remove stress gradients for optimum performance. The adaptive phenomenon in bone is guided by the electrical potential gradient generated in bone under stress gradient (Figure 6a); this piezoelectric effect guides transport of bone substance towards areas experiencing higher levels of compressive stress. The transport process thus seeks to eliminate stress gradient and promote an optimum structural performance with structural substance concentrated along compressive stress paths. A classic experiment conducted to demonstrate the advantages of this phenomenon (Figure 6b) involved removal of a part of the ulna of pigs; the resulting stress gradient (under eccentric loading) more than doubled the peak stress on the radius during walking. An explosive redistribution of structural substance followed with the objective of eliminating stress gradient (eccentricity of loading). In three months, stress was lowered to within 10% of the original level. Indeed, a fairly simple method of control is observed to restore optimum structural performance after the system experiences a major damaging effect.
The research reported herein focused on validation of the fundamental principles of adaptive structural materials, and development of processing techniques to integrate the functional constituents rendering adaptive effects into a hybrid coating system. The following objectives were accomplished in the project.

1. Theoretical modeling and analytical validation of adaptive composites embodying our principles.
2. Experimental verification of the electrostripping, ionic transport and electrodeposition phenomena in mechanically viable solid electrolytes, and assessment of the gains in mechanical performance associated with electrodeposition in solid electrolytes.
3. Experimental validation of piezo-driven electrolysis in mechanically viable solid electrolytes.
4. Processing of system constituents as hybrid coating, and preliminary experimental evaluation of integrated systems embodying the adaptive principles.
CHAPTER 2
THEORETICAL MODELING AND ANALYTICAL VERIFICATION OF ADAPTIVE COMPOSITES

2.1 Introduction

Cracking and fiber rupture (Figure 1), as key manifestations of damage in composites, bring about local concentration of stress and thus further growth of damage zone. Our approach builds the capability into composites to transport structural substance towards damage zones in order to strengthen these zones and mitigate damage propagation. This adaptive phenomenon occurs upon development of stress gradient within the composite structure, and strives (through transport of structural substance) to restore a normalized stress distribution.

2.2 Stress Analysis within the Damage Zone of Composites

Stress rise at damaged areas (Figure 7a) is the phenomenon that guides and drives the adaptive mechanism. The expression for stress ($\sigma$) as a function of the distance from crack tip ($r$) is as follows:\textsuperscript{3}

$$\sigma = \frac{K_c}{(2\pi r)^{1/2}}$$

where, $K_c$ is the critical stress intensity factor.

The above expression provides the basis to identify a damage zone in the vicinity of the crack tip, defined as the zone where concentrated stress exceeds a threshold level ($\sigma_D$) corresponding to damage (e.g., debonding) initiation. The size of damage zone ($r_D$) can be expressed as follows (see Figure 7b):\textsuperscript{3}

$$r_D = \frac{K_c^2}{(2\pi \sigma_D^2)}$$

In the case of carbon fiber reinforced epoxy laminate $[0/90]_4s$, a typical critical stress intensity factor ($K_c$) is equal to 13 MPa.m\textsuperscript{1/2} and a typical tensile strength is 6.38 MPa.\textsuperscript{4} For a damage threshold stress that is 75 % of ultimate tensile strength, the above expression yields a damage zone size ($r_D$) of 0.12 mm. The damage zone (Figure 7b) responsible for damage growth leading to catastrophic failure is thus relatively small. In other words, the faith of a damaged composite is decided by a very small fraction of its volume. Our approach mitigates catastrophic damage growth by strengthening the damage zone. For this purpose, structural substance is transported towards and deposited within the damage zone to render strengthening effects which mitigate damage growth.
The ratio of fiber clear spacing to fiber diameter \( \frac{s}{d} = \left( \frac{P}{V_f} \right)^{1/2} - 1 \), for hexagonal arrays of fibers \( P = 0.91 \) and fiber volume fraction \( V_f \) of 0.75, would be 0.15. With a fiber diameter of 10 micron, this translates into clear and center-to-center fiber spacing of 1 and 11 micron, respectively. Hence, a damage zone of 0.12 mm dimension would encompass 11 fibers within each laminate.

### 2.3 Theoretical Modeling of the Piezo-Driven Adaptive Phenomena

Composites embodying our adaptive principles may incorporate carbon fibers which have received a hybrid coating comprising piezoelectric and solid electrolyte layers (Figure 8). The solid electrolyte layer would incorporate close to 15 % by weight of metal (associated with a dissolved salt); electrostripping of this metal from outside the damage zone, and its transport into and electrodeposition within the damage zone constitute the adaptive effect which mitigates damage propagation and catastrophic failure of damaged composite.

The piezo-driven electrolysis would be possible if: (1) piezo-induced voltage would be sufficient to overcome the activation and polarization over-potentials at anode and cathode and also the i.R drop within solid electrolyte; and (2) piezo-induced power would be sufficient for electrochemical mass transport at viable rates. Theoretical models addressing these issues are presented below.

The piezo-induced electric voltage \( V \) is proportional to the stress gradient generated in piezoceramic \( S_p \) along the fiber:
\[ V = g_{31} S_p t \]

where, \( g_{31} \) is the piezoelectric stress constant, and \( t \) is the thickness of piezoelectric layer. The elastic modulus \( (E_p) \) of piezoceramics is typically a fraction of the elastic modulus \( (P_f) \) of reinforcing fibers. This implies that the stress gradient within the piezoceramic coating would be a fraction \( (E_p/E_f) \) of the stress gradient \( (S_f) \) along the fiber:

\[ S_p = S_f \cdot (E_p/E_f) \]

Assuming that fibers outside the critical (damaged) area are subjected to a fraction \( (\alpha) \) of their ultimate tensile strength \( (S_u) \), and that fibers within damaged area approach their ultimate tensile strength, the stress gradient along a fiber would be:

\[ S_f = (1-\alpha).S_u \]

The piezo-induced voltage \( (V) \) can thus be expressed as follows:

\[ V = g_{31} (E_p/E_f) \cdot (1-\alpha).S_u t \]

Current transfer through the solid electrolyte is by ionic transport (Figure5e); this process involves electrostripping, ionic transport, and electrodeposition of metal, and concentrates metallic substance in critically stressed areas. The piezoelectric effect converts the mechanical energy input of external loads to electrical energy. The charge produced \( (Q) \) per unit area \( (A) \) can be calculated as follows:

\[ Q/A = d_{31} S_p \]

where, \( S_p \) is the stress gradient in piezoceramic, and \( d_{31} \) is the piezo strain constant.

If \( 2(l) \) refers to the fiber length along which local stress rise occurs, the area over which piezo-induced charge would be produced would be: \( 2\pi \cdot (l) \cdot (d) \). The piezo-induced charge generated by each application of stress to each individual fiber is thus:

\[ Q = 2\pi \cdot (l) \cdot (d) \cdot d_{31} \cdot (E_p/E_f) \cdot (1-\alpha).S_u \]

The calculations presented earlier assumed a mean ionic transport distance \( (l) \) of 2 mm; to be consistent, we assume that the length of fiber \( (2l) \) to be charged (by piezoelectric effect) in response to local stress rise (damage) is 4 mm. The area over which piezo-induced charge would be produced (for 15 micron fiber diameter) would be \( 1.88 \times 10^{-7} \text{ m}^2 \). The piezo-induced charge generated by each application of stress to each individual fiber is thus \( 7.6 \times 10^{-8} \text{ coulombs} \).

Since 1 mole of electrons carries a charge of 1 faraday, or 96,485 coulombs, the moles of electron \( (\text{moles}) \) transported by the charge generated by each application of stress can be expressed as follows:

\[ \text{moles} = 2\pi \cdot (l) \cdot (d) \cdot d_{31} \cdot (E_p/E_f) \cdot (1-\alpha).S_u / (96,485) \]
For metallic ions with $n$ electronic units of charge and atomic mass of $m$, the actual mass ($M$) transported per fiber for each application of stress can be calculated as follows:

$$M = 2\pi (l).d_31.(E_p/Ep) (1-\alpha).S_u.m / (96,485 n)$$

### 2.4 Analytical Verification of the Adaptive Phenomena

In order to provide analytical support for the adaptive principles, we assumed that the piezoelectric and solid electrolyte layers of the hybrid fiber coating (Figure 8) are 0.5 and 1 micron thick, respectively, with an original fiber diameter of 10 micron. We further assumed that the metal to be transported to damage zone is nickel (which is amenable to electrolysis). Nickel offers yield strength and elastic modulus of about 350 MPa and 207 GPa, respectively. The tensile strength and elastic modulus of carbon fibers are about 2700 MPa and 380 GPa respectively; they rupture at a strain of about 0.00711. The adaptive phenomenon electrodeposits a layer of nickel onto the carbon fiber coating; this electrodeposited nickel may actually assume a nano-structured configuration with mechanical properties which surpass those of bulk nickel introduced above. This analysis is, however, conducted using the conservative bulk properties of nickel. The electrodeposited nickel would yield as fiber approaches its rupture strain; it thus develops a stress of 350 MPa. In order to add 20 % to the rupture strength of a carbon fiber, $1.08\times10^{-7}$ g of nickel should be deposited within the 0.12 mm fiber length segment within damage zone (Figure 9). With 15 % weight fraction of nickel in the solid electrolyte layer of 1 micron thickness, one would need nickel from the solid electrolyte coating within a 17 mm length segment of the fiber to effectively strengthen the fiber length occurring within the damage zone (Figure 9).

The average carbon fiber stress within and outside the damage zone (where electrodeposition and electrostripping, respectively, take place) are 638 and 57 MPa, respectively; a fiber stress difference of 581 MPa thus drives the electrolysis process within solid electrolyte. The piezoelectric coating is considered to offer mechanical performance attributes and piezoelectric coefficients which partially reflect on recent developments in the field of nano-structured piezoceramics. An elastic modulus of about 130 GPa was assumed for the piezoelectric layer, which is 40 % that of carbon fiber. The stress difference of 581 MPa within fiber thus translates into 232 MPa stress gradient within the piezoceramic coating. The potential difference (voltage) generated by the piezoelectric layer of 0.5 micron thickness (considering a $g_{31}$ coefficient of 0.2 V/m.N/m$^2$) would be close to 23 V, which is more than sufficient to overcome the over-potentials at cathode/electrolyte and electrolyte/anode interfaces and also the friction potential loss within solid electrolyte. The charge generated with each application of stress to the piezoelectric layer (over the 17 mm length segment of fiber) is $10^6$ coulombs (for a $d_{31}$ piezoelectric coefficient of $8\times10^{-9}$ C.N). This charge can transport $3\times10^{11}$ g of nickel for electrodeposition within the damage zone. Hence, in order to transport a total of $1.08\times10^{-7}$ g of nickel to damage zone (to render the targeted fiber strengthening effect), one needs 1,080 applications of stress. If we assume that stresses are applied at a frequency of 10 Hz, the targeted strengthening (adaptive) effect would be completed over a period of 108 seconds (1.8 minutes). This period can be substantially reduced by implementing recent developments in nano-structured piezoelectric materials which offer orders of magnitude gains in piezoelectric response over today’s bulk piezoelectric materials. These developments are briefly introduced in the following.
The above calculations provide key analytical support for the hypothesis that piezo-driven electrolysis within solid electrolyte can provide a viable basis for development of adaptive composite materials. Introduction of a hybrid coating onto carbon fibers yields, with a relatively small weight penalty, the desired adaptive effect which can be completed within a relatively short time period.

2.5 Enhancement of the Adaptive Phenomenon with Piezoelectric Nanotubes: An Analytical Assessment

The adaptive phenomenon relies on piezoelectric effect to convert the destructive mechanical energy concentrated within damage zones into electrical energy, which in turn drives (and guides) the adaptive process. Figure 10 depicts this phenomenon for a piezoelectric fiber coating subjected to stress gradient. The analytical and experimental work conducted in the research concluded that the piezoelectric effect generates excess electric potential (E) to ensure the occurrence of electrochemical phenomena which render adaptive effects. The piezo-induced charge (D) is the rate-limiting factor which determines the rate of self-adaptation. With conventional piezoelectric ceramics, typical examples analyses presented above indicated that the adaptive process would occur over a time span of few minutes. Acceleration of this process is highly desired; recent developments in piezoelectric nano-tubes provide the basis to substantially enhance the rate of electrochemical mass transport and thus speed of self-adaptation.

Figure 9. Length Segments of Carbon Fiber Subjected to Electrostripping and Electrodeposition.
Figure 10. Piezo-Induced Potential and Charge for Piezoelectric Coating on a Fiber under Stress Gradient.

The piezo-induced charge ($D$), which defines the rate of self-adaptation, is proportional to the surface area ($A$) of piezo-ceramics. Our approach towards elevating the piezo-induced charge (and thus the rate of self-adaptation) relies on development of fiber coating systems comprising piezoelectric nano-tubes\textsuperscript{17,19,20} embedded in a ceramic matrix. This approach increases the piezoelectric surface area ($A$) by orders of magnitude over that in bulk piezoelectric materials. For a fiber diameter of $d$, a fiber length segment of $l$, and a piezoelectric coating thickness of $t$, the bulk and the nano-tube reinforced piezoelectric coatings provide the following surface areas ($A$):

**Bulk Piezo-Ceramic:**

$$A = \pi (d + t).l$$

**Nano-Tube Reinforced Piezo-Composite:**

$$A = \pi (d + t).l.(4t.V_f/d_f)$$

where, $V_f$ and $d_f$ are the nano-tube volume fraction and diameter, respectively.

The nano-tube reinforced piezo-composites magnify the piezoelectric surface area (and charge) over that of bulk piezo-ceramic by a factor of $4t.V_f/d_f$. For a piezoelectric nano-fiber diameter of 40 nm and volume fraction ($V_f$) of 30 %, and for a piezoelectric coating thickness of 1 micron, the nano-tube reinforced piezoelectric provides 3000 times the piezo-induced charge of the bulk piezo-ceramic coating. Hence, piezoelectric nano-composite coatings offer the potential to increase the rate of self-adaptation by orders of magnitude; this would add greatly to the value of adaptive composites in critical aerospace applications.
CHAPTER 3

EXPERIMENTAL VERIFICATION OF THE OCCURRENCE AND THE IMPLICATIONS OF ELECTROLYSIS PHENOMENA WITHIN SOLID ELECTROLYTES

3.1 Introduction

The envisioned adaptive principles rely on piezo-driven electrolysis within a solid electrolyte to transport structural substance towards (and deposit it at) highly stressed areas. This phenomenon would be guided and driven by stress gradients which develop within the damage zones of structural systems. Tests were conducted in the research program to verify: (i) the occurrence of electrostripping, ionic transport and electrodeposition phenomena in solid electrolytes; and (ii) the gains in mechanical performance associated with electrodeposition in solid electrolytes.

Electrochemical phenomena have been traditionally realized in the context of liquid electrolytes. The growing demand for solid-state batteries and fuel cells, on the other hand, have prompted major development efforts in the field of solid electrolytes. Solid electrolytes cover a host of polymer and ceramic materials; the research reported herein focused on solid polymer electrolytes.

3.2 Selection and Processing of Solid Electrolytes

3.2.1 Introduction to Solid Polymer Electrolytes

The ability to dissolve salts is not limited to liquid solvents. The existence of polar groups in polymers is a common feature; it may thus be expected that some polymers will have the potential to dissolve salts and form stable ion-polymer complexes. A salt dissolves in a solid polymer only if the associated energy and entropy changes produce an overall reduction in free energy of the system. This arises when the interaction between ionic species and the coordinating groups on polymer chain compensates for the loss of salt lattice energy. Transfer of electric current through solid electrolytes incorporating dissolved salts can then occur through ionic transport. Ions are transported in a polymer electrolyte by a combination of ionic motion coupled with the local motion of polymer segments (Figure 11). Ion-conducting polymers exhibit three key characteristics: (i) atoms or groups of atoms with sufficient electron donor power to form coordinate bonds with cations; (ii) low barriers to bond rotation so that segmental motion of polymer chains occurs readily; and (iii) a suitable distance between coordinating centers facilitating the formation of multiple intra-polymer ion bonds.

(a) Segmental Motion of Polymer Chain by Bond Rotation   (b) Transfer of Cation between Polymer Chains

Figure 11. Schematic Presentation of the Cation Transport Process in a PEO-Based Polymer Electrolyte.
Solid state batteries and fuel cells employ solid electrolytes simply as fast ion conductors. The adaptive phenomenon which is subject of this research, however, requires simultaneous occurrence of electrostripping, ionic transport and electrodeposition within solid electrolytes. Furthermore, the mechanical performance of solid electrolytes is of utmost importance in their incorporation into high-performance composites. Selection of a mechanically viable class of solid electrolytes, and validation of complete electrolysis phenomena (electrostripping, ionic transport and electrodeposition) within this solid electrolyte thus constitute critical steps in development of adaptive composites.

A comprehensive literature review followed by a sequential laboratory evaluation of potentially viable solid electrolytes provided the basis for selection, processing and characterization of solid electrolytes for use in adaptive composites.

3.2.2 Preliminary Selection of Solid Polymer Electrolyte: PAN-BASED Polymer

Materials

Poly(acrylonitrile) (PAN, \(M_w = 86,200\)), ethylene carbonate (EC, 98 %), propylene carbonate (PC, 99 %), copper (II) trifluoromethanesulfonate (CuTf, 98 %), copper powder (3 micron, dendritic, 99.7 %), acetonitrile (99.93 %+, HPLC grade), and silica (99.8 %, fumed) were purchased from Aldrich, and were used without any further purification. The use of copper slat in this investigation implies that copper is the metal to be ionically transported and electrodeposited to render adaptive effects. Copper is a preliminary selection for validating the fundamental principles of adaptive composites. A variety of metals (nickel, etc.) can replace copper in the process; optimum selection of the metal rendering adaptive effect will be subject of follow-up investigations after thorough validation of the fundamental principles of the approach.

Preparation of Solid Electrolyte without Copper Filler

PAN (1.06 g or 20 mole %), EC (3.6 g or 41 mole %) and CuTf (1.8 g or 5 mole %) were weighed into a ceramic crucible and mixed well before adding PC (3.4 g or 34 mole %). PC was then added, and the blend was stirred until thorough dissolution and a mixture of uniform light blue color was obtained. The mixture was then heated to 120°C and maintained at this temperature for 45 minutes (using a temperature-programmed oven with heating rate of 20°C/min, and total heating duration of 51 minutes). The mixture was then allowed to cool down to room temperature, and was then vacuum dried for 24 hours, and further dried at 60 °C under vacuum for 2 hours. The end product was light green in color, and it was pressed to yield the test specimen.

Preparation of Solid Electrolyte with Copper Filler

The copper salt dissolved in solid electrolyte can act as the source of metallic ion to be transported and deposited for adaptive effects. In addition, one can add copper fillers to raise the quantity of metal available to render adaptive effects. In order to prepare the PAN-based solid electrolyte incorporating copper filler, first PAN, EC and CuTf were weighed in a ceramic crucible, and mixed well before adding PC. PC was then added, and the mix was magnetically stirred until thorough dissolution (a uniform mixture) was achieved after about 1 hour. Different amounts of copper particles were then added to the
mix and magnetically stirred until a mixture with uniform light brown/blue color was obtained; the intensity of brown color depended on the dosage of copper filler. The mixture incorporated 0.5 g of water for 5 % filler content or 1 g of copper for 10 % filler content. The remaining steps in synthesis and pressing of solid electrolyte specimens with copper filler were similar to those taken for the specimen without filler.

**Preparation of Solid Electrolyte with Inorganic (Silica) Filler**

Inorganic filler was added to the solid electrolyte in order to assess the potential to enhance the physical attributes of solid electrolytes with fillers. In order to prepare the PAN-based solid electrolyte with inorganic filler, first PAN, EC and CuTf were weighed in a ceramic crucible, and mixed well before adding PC. PC was then added to the mixture and magnetically stirred until thorough dissolution was achieved after about 1 hour; acetonitrile was added subsequently and stirred until a uniform mixture was obtained. Different amounts of silica powder (5 and 10 % by total weight) were added to the blend, and magnetically stirred until a uniform light blue mixture was obtained (the blue color and its consistency varied depending on the amount of silica added). The remaining steps in synthesis and pressing of solid electrolyte specimens with silica filler were similar to those implemented for the specimen without filler.

### 3.2.3 Final Selection of Solid Polymer Electrolyte: PVDF-HFP

The approach presented above involved enhancement of the physical attributes of solid electrolyte through introduction of fillers; an alternative approach would select new solid electrolytes with high inherent mechanical characteristics which also offer high levels of ionic conductivity. Based on a comprehensive literature review, we selected poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) to provide a desirable balance of ionic conductivity and mechanical attributes. Because of the high density of fluorine groups, PVDF-HFP has a high coordinating ability with many metal ions; this leads to relatively high levels of ionic conductivity. Fluorine can further form H-bonds which provide the system with pseudo cross-linking and thus enhanced physical attributes.

**Materials**

The materials used for preparation of PVDF-HFP solid electrolyte included poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (pellets, crystalline thermoplastic copolymer, 15 % HFP average Mw ~ 400,000), ethylene carbonate (EC, 98 %), propylene carbonate (PC, 99 %), copper (II) trifluoromethanesulfonate (CuTf, 98 %), and tetrahydrofuran (THF, 99.9 +% HPLC grade, inhibitor free). All materials were purchased from Aldrich, and were used without any further purification. The electrodes were made of stainless steel shims (thickness of 0.005 cm) purchased from McMaster and used after cutting to the required size and shape.

Three different solid electrolytes were prepared by varying the composition of copper salt, EC and PC while keeping the PVDF percentage constant.
Preparation of PVDF-HFP Solid Electrolyte with 3% Copper Ion Concentration

PVDF-HFP was dissolved in THF (30% by weight, 3g) at moderately elevated temperature (60 °C). Subsequently, CuTf (1.8084 g), EC (3.5224 g) and PC (1.7865 g) were added to the mix (70% by weight at CuTf:EC:PC ratio of 1.0:8.0:3.5), and dissolved until a uniform solution was obtained. The solution was cast on a Petri dish, and left at room temperature until all the THF was evaporated. A blue green color sheet was obtained, which was cut into pieces for use in electrochemical experiments.

Preparation of PVDF-HFP Solid Electrolyte with 6% Copper Ion Concentration

PVDF-HFP was dissolved in THF (30% by weight, 3 g) at moderately elevated temperature (60 °C). The amount of CuTf was increased to 3.6168 g, and the amounts of plasticizers were reduced: EC (1.7612 g) and PC (0.89325 g), with the total percentage kept at 70%. The remaining processing steps were similar to those explained above for the 3% case.

Preparation of PVDF-HFP Solid Electrolyte with 9% Copper Ion Concentration

PVDF-HFP was dissolved in THF (30% by weight, 3 g) at moderately elevated temperature (60 °C). The amount of CuTf was increased to 5.452 g, the amounts of plasticizers were reduced: EC (1.174 g) and PC (0.5955 g), with the total percentage kept at 70%. The remaining processing steps were similar to those explained above for the 3% case.

3.3 Experimental Verification of Electrolysis Phenomena within Solid Electrolytes

3.3.1 Preliminary Electrolysis Tests with PAN-Based Solid Polymer Electrolyte

Experimental Procedures

Three different electrolysis experiments were performed on solid electrolyte specimens with no copper filler:

i. The anode (positive terminal) was copper sheet, and the cathode was aluminum sheet. Both sheets were weighed before the experiment. The solid electrolyte specimen was tightly sandwiched between the two electrodes, and a constant voltage (15 V) was applied for a period of 15 hours as shown in Figure 12(a).

ii. The anode was a copper strip, and the cathode was a stainless steel wire. These electrodes were inserted into the solid electrolyte specimen, and a constant voltage was applied between the two electrodes for about 24 hours as shown in Figure 12(b).

iii. Same as (i) except that the anode was an aluminum sheet (Figure 12©). For each experiment, after passing current, the anode and cathode were weighed, and microscopic images were taken in order to verify occurrence of electrostripping and electrodeposition phenomena.

The solid electrolyte with copper filler was tightly sandwiched between two aluminum electrodes as shown Figure 12©, and a constant voltage was applied for a period of three days. After three days, the electrodes were weighed and microscopic images of anode and cathode sides were taken.
(a) Solid Electrolyte Sandwiched Between Copper Sheet (Anode) and Aluminum Sheet (Cathode)

(b) Copper Strip (Anode) and Stainless Steel Wire (Cathode) Inserted into Solid Electrolyte

(c) Solid Electrolyte Sandwiched Between Two Aluminum Sheets (Cathode & Anode)

Figure 12. Experimental Set-Ups for Verification of the Occurrence of Electrostripping, Ionic Transport and Electrodeposition Phenomena within Solid Electrolyte.

Figure 13 presents pictures of the experimental set-up. The solid electrolyte sandwiched between cathode and anode is depicted in Figure 12(a) (for test conditions of Figures 12(a) and 12(c)). Figure 13(b) presents a close view of the experiment with inserted electrodes (for test condition of Figure 12(b)). The constant-voltage power supply used in experiments is shown in Figure 12(c).
(a) Solid Electrolyte Sandwiched Between Electrodes

(b) Solid Electrolyte with inserted Electrodes

(c) Constant-Voltage Power Supply

Figure 13. Pictures of Electrolysis Experiments with Solid Electrolytes.
PAN-based solid polymer electrolytes with fumed silica filler were made into pellets. These pellets were sandwiched between stainless steel electrodes as shown in Figure 14(a). The electrodes/electrolyte assembly was clamped in a Teflon cell with plastic backing plates (Figure 14(b)). A constant potential of 4 V was applied to electrodes for a period of fifteen hours. Subsequently, the solid electrolyte was examined under optic microscope.

![Image](image.png)

(a) Test Set-Up       (b) Solid Electrolyte Electrolysis Cell

Figure 14. Electrolysis Set-Up with Solid Electrolyte Cell.

Test Results and Discussion

PAN-Based Solid Electrolyte without Metallic Filler

(i) Electrolysis with Copper Sheet as Anode and Aluminum Sheet as Cathode

When copper sheet was used as anode, it was noted that copper dissolved after electrolysis (resulting in 20% weight loss of the copper electrode), and color on the anodic surface changed to yellow-brown (Figure 15(a)). The cathode surface of the solid electrolyte turned black, and it was adhered to the aluminum sheet; after separation of the aluminum sheet from anode, deposited copper was found to be the cause of adhesion of the solid electrolyte to aluminum sheet (Figure 15(b)). These observations confirm that electrostripping and electrodeposition phenomena can occur in the context of a solid electrolyte.
Figure 15. Consequences of Electrostripping and Electrodeposition within Solid Electrolyte.

(ii) Electrolysis with Inserted Electrodes

Figure 16 shows a cross-section of the solid electrolyte specimen after the application of constant voltage. Near the inserted copper electrode at anode, indications of copper dissolution were observed, and the weight of copper electrode was lowered by about 13 % as a result of electrostripping. The stainless steel electrode at cathode was adhered to the solid electrolyte matrix, and indications of copper deposition were noted around the cathode.
(iii) Electrolysis with Aluminum Sheets at Anode and Cathode

Since the solid electrolyte has some copper salt dissolved in it, in spite of the fact that no copper electrode (or filler) was used in this case, indications of electrodeposition of copper was observed to occur on the aluminum sheet at cathode (Figure 17), with some evidence of degradation of aluminum noted at cathode.

**Figure 17. Deposition of Copper on Aluminum Sheet at Cathode.**

**PAN-Based Solid Electrolyte With 5 % Metallic Filler**

Metallic fillers were added to the PAN-based solid electrolyte to complement the dissolved metal salt as the source of metal for electrolysis processes which render adaptive effects. In the case of solid electrolytes with metallic filler, both electrodes were aluminum and thus dispersed copper fillers were (besides the dissolve copper salt) the only source of copper for electrostripping and electrodeposition phenomena. Figure 18(a) shows the aluminum sheet surface at cathode after application of constant voltage. Electrodeposition of copper on aluminum sheet at cathode is apparent in Figure 18(a). Microscopic images of the aluminum sheet surface at cathode prior to and after application of constant
voltage, presented in Figure 18(b), provide further evidence for electrodeposition of copper at cathode. Finally, the solid electrolyte at anode showed light blue areas (see Figure 18(c)) which could be attributed to the occurrence of electrostripping of copper fillers.

(a) General Views of Aluminum Sheet Surfaces at Cathode Prior to and After Electrodeposition

(b) Microscopic Images of the Aluminum Sheet Surface at Cathode

(c) Indications of Electrostripping within Solid Electrolyte at Anode

Figure 18. Electrodeposition of Copper on Aluminum Sheet Electrode at Cathode for PAN-Based Solid Electrolyte with 5 % Copper Filler.

PAN-Based Solid Electrolyte Specimens with 10 % Metallic Filler

Strong evidences of electrostripping and electrodeposition were also obvious in the case of solid electrolytes with 10 % copper filler. Figure 19(a) shows images of the aluminum sheet surface at cathode where substantial electrodepositoin took place, resulting in a 7 % weight gain. It is interesting to note
that, with metallic fillers acting as the source of copper for electrolysis, the appearance of electrode surface at anode (Figure 19(b)) is different from that for the case where the electrode itself was the source of copper for electrodeposition (Figure 19(a) (right)). Figure 19© shows surfaces of the solid electrolyte with copper filler at anode and cathode, with obvious indications of copper electrodeposition at cathode.

Figure 19. Aluminum Sheet Surfaces at Cathode and Anode After Electrolysis with Solid Electrolyte Incorporating 10 % Copper Filler.
**PAN-Based Solid Electrolyte with 5% Inorganic Filler**

Transport of copper cations towards cathode and their deposition as copper metal at cathode constitute the key objectives of this experiment, which are fundamental to the process of self-adaptation in the new class of composite materials which are under development in this project. Figure 20 is a schematic presentation of the PAN-Based/Cu salt/Fumed Silica sandwiched between two stainless steel electrodes. Prior to application of voltage, copper ions are complexed to the cyano groups of PAN. When voltage is applied, copper ions migrate towards the cathode and get reduced at the cathode.

![Schematic Diagram](image)

*Figure 20. Schematic Presentation of PAN Sandwiched Between Steel Electrodes Prior to and After Application of Voltage.*

After application of constant voltage, the stainless steel electrodes were detached from the solid electrolyte. Dissolution of metal was observed at anode, and copper deposition was observed at cathode. The electrode at cathode was also noted to be adhered to the solid electrolyte; this was not the case at the anode. The solid electrolyte surface prior to electrolysis is presented in Figure 21(a); Figures 21(b) and 21(c) present the anode and cathode interfaces of the solid electrolyte after electrolysis; electrodeposition of copper at cathode is apparent in Figure 21(c). The microscopic images of anode and cathode interfaces presented in Figure 22 further confirm this visual observation; the copper metal deposited at cathode interface is shown in Figure 22(b).
The solid electrolyte samples were sectioned and observed under microscope after the electrolysis process (Figure 23). Areas near cathode (Figure 23(b)) showed a darker and denser texture due to deposition of copper metal, when compared with areas near anode (Figure 23(a)).
PAN-Based Solid Electrolyte with 10 % Inorganic Filler

The observations with 10 % fumed silica in PAN-based solid electrolyte were similar to those presented above for 5 % microsilica. Microscopic images of both planar (Figure 23) and side (Figure 24) views of anode and cathode interfaces provided clear evidence of copper electrodeposition at cathode. These results further confirm the occurrence of electrostripping, ionic transport and electrodeposition in the context of solid electrolytes, and indicate that the incorporation of inorganic fillers for gains in mechanical performance does not interfere with these electrolytic phenomena occurring in filled solid electrolytes.

Figure 23. Microscopic Images of Sectioned Solid Electrolyte with 5 % Inorganic Filler after Electrolysis.

Figure 24. Microscopic Images of Planar Views of Anode and Cathode Interfaces for the PAN-Based Solid Electrolyte with 10 % Inorganic Filler.
3.3.2 Final Electrolysis Tests with PVDF-HFP Solid Polymer Electrolyte

Experimental Procedures

PVDF-HFP-CuTf/EC/PC specimens containing different amounts of copper salt were sandwiched between stainless steel electrodes as shown in Figure 26. The electrodes/electrolyte assembly was clamped in a Teflon cell with plastic backing plates (Figure 26(b)) to ensure adequate contacts between the electrodes and the polymer sheet. The weights of electrodes and the polymer sheet were measured prior to electrolysis. A constant potential of 4 V was applied to electrodes for a period of fifteen hours. Subsequently, the solid electrolyte was examined under optical microscope.
Test Results and Discussion

The primary goal of the experimental effort reported herein was to prove the feasibility of electrolysis (electrostripping, ionic transport and electrodeposition) occurring in the context of a mechanically viable solid electrolyte. Prior to the application of voltage, copper ions are complexed to the fluorine atoms in PVDF-HFP. When voltage is applied, due to polarity differences, two ends of the positively charged copper ions will be attracted to the negatively charged cathode. Copper ions migrate from one site to the other, and get reduced at the cathode where they deposit as copper. Since the most common coordination number of copper is four, each copper ion will bind with four fluorine atoms as shown in Figure 27. The maximum molar ratio between copper ion and polymer should thus be 2:1. This ratio guides our efforts to increase the concentration of copper ions in PVDF-HFP.

![Figure 27. Binding of Copper via Fluorine Atoms](image)

PVDF-HFP Solid Electrolyte With 3 % Metal Ion Concentration

After application of a constant voltage of 4 V, the stainless steel electrodes were detached from the solid electrolyte and observed. Figure 28(a) presents the surface of solid electrolyte prior to electrolysis, and Figures 28(b) and 28(c) show the cathodic and anodic surfaces of the solid electrolyte after electrolysis. Copper deposition was quite obvious at cathode, and dissolution of metal was observed at anode. We also observed that the cathode was adhered to the solid electrolyte; no such adherence was observed at anode. Unlike our previous studies with poly(acrylonitrile) and poly(ethylene oxide) solid electrolytes, the extent of electrodeposition was quite large with PVDF-HFP, yielding an obvious metallic appearance at cathode. This confirms that PVDF-HFP has a higher ionic conductivity than those of solid electrolytes investigated earlier. In addition, the superior mechanical attributes and stability of PVDF-HFP facilitates its handling and experimentation.

![Figure 28. Visual Appearances of PVDF-HFP Solid Electrolyte Containing 3 % Copper.](image)
Microscopic images of the solid electrolyte prior to and after electrolysis (anode and cathode interfaces) are presented in Figure 29. Microscopic images confirm the visual observations; the copper metal deposited at the cathode interface is shown in Figure 29©, while anode interface (Figure 29b) shows clear areas resulting from removal of copper.

Figure 29. Microscopic Images of PVDF-HFP Polymer Containing 3 % Copper.

PVDF-HFP Solid Electrolyte With 6 % and 9 % Metal Ion Concentrations

Copper ions at 6 % and 9 % concentrations could be conveniently dissolved in PVDF-HFP solid electrolyte without any major change in ionic conductivity. The electrolysis results with 6 % and 9 % copper ion concentrations (see Figures 30 and 31, respectively) were similar to those with 3 % copper ion. Deposition of copper was observed at the cathode interface, with no deposition detected at the anode interface. Adherence of the stainless steel electrode to solid electrolyte was also observed at the cathode interface. A higher copper ion concentration implies a larger metallic reservoir for use in the adaptive process; successful development of the solid electrolyte system with 9 % copper concentration is thus an important accomplishment in our project.
Figure 30. Microscopic Images of PVDF-HFP Solid Electrolyte With 6 % Copper.

Figure 31. Microscopic Images of PVDF-HFP Solid Electrolyte With 9 % Copper.

3.4 Assessment of the Mechanical Consequences of Electrolysis within Solid Electrolyte

Mechanical (hardness) tests (Figure 32) were performed following the ASTM D 2240 procedures for PVDF-HFP solid electrolytes with different copper concentrations (3 % and 6 %). After electrolysis, the polymer sample was detached from electrodes, and hardness of cathode and anode interfaces were measured separately. The hardness tests were performed at three different locations on each surface.

Hardness measurements provided a basis to assess the mechanical performance of PVDF-HFP polymer prior to and after electrolysis. The hardness test data are summarized in Figure 32. Hardness, as a measure of mechanical attributes, is observed to increase markedly at cathode after electrolysis. This
finding provides further evidence for the viability of our approach which relies on electrolysis phenomena within solid electrolytes to transport mass towards (and deposit it at) sites of stress rise (cathode) to render adaptive effects. The gains in mechanical properties associated with electrolytic mass transport (through the solid electrolyte) to cathode confirms that the process can actually render adaptive effects. The data presented in Figure 33 suggest that the concentration of copper ions in solid electrolyte influences the gains in mechanical performance at cathode after electrolytic mass transport.

![Figure 32. Hardness Test Set-Up](image)

![Figure 33. Hardness Test Results (ASTM D 2240).](image)

### 3.5 Evaluation of Ionic vs. Electronic Transport Phenomena in PVDF-HFP Solid Electrolyte

Solid electrolytes generally transfer electric current by a combination of ionic and electronic transport phenomena. While electronic transport is sustainable, ionic transport could be limited by the finite quantity of metals available to be ionized (and transported). Without metallic electrodes, solid electrolyte would rely only on the dissolved metal salt as the source of metal for ionic transport. Long-term polarization experiments, conducted here, allows us distinguish between ionic and electronic transport phenomena.

Polarization tests were conducted by connections the ammeter between the power supply and the solid electrolyte cell. A bias voltage of 15 V was applied between electrodes of the cell, with current measured versus time.

In the polarization tests conducted in the research reported herein, the time-history of electric current was measured under a constant bias voltage over a period of 6 hours. Figure 34 presents the current time-history for PVDF-HFP systems containing different copper cation concentrations (3 % & 6 %). The PVDF-HFP systems are observed to experience a drop in current flow over time. This suggests that they rely largely on ionic (in lieu of electronic) transport of electric current, which favors use of PVDF-HFP in adaptive composites.

The predominance of ionic (versus electronic) conductivity ensures that the electrical energy (resulting from transformation of mechanical energy by piezoelectric effect) is used efficiently to transport mass (in lieu of electrons) to render adaptive effects. It should also be noted that the relatively small fraction of electronic transport has a role to play in the system. Eventual reduction of metal cations for deposition of
metal requires electrons; the electronic fraction of current transfer ensures greater availability of electrons not only at but also near the cathode interface, thereby broadening the volume within damage zone where electrodeposition (and thus adaptation) occurs.

Figure 34. Current-Time Curves for PVDF-HFP’s with Different Copper Concentrations.
CHAPTER 4

EXPERIMENTAL VALIDATION OF PIEZO-DRIVEN ELECTROLYSIS WITHIN SOLID ELECTROLYTE

4.1 Introduction

The adaptive composite materials which are subject of this research rely on the mechanical energy concentrated in critical zones within the structure to guide and drive the electrochemical processes which render adaptive effects. Piezoelectric effect is employed to convert mechanical energy to electrical energy; piezo-induced potential guides the electrochemical mass transport towards critical (highly stressed) areas, and piezo-induced charge drives this mass transport phenomenon.

The experimental program presented in previous chapter verified the electrochemical mass transport phenomenon within solid electrolytes, and the mechanical implications of this phenomenon using direct electric power supply. The experimental work presented in this chapter is concerned with verifying the electrolysis phenomena driven by piezoelectric effect in solid electrolyte.

Piezoelectricity is the ability of certain crystalline materials to develop an electric charge in response to mechanical stress. While stress causes only a proportional strain in ordinary solids, it can also generate an electric charge in piezoelectric materials. Figure 35(a) presents examples of piezo-induced electric charge generation under uniform stress. In the context of adaptive composites (Figure 5), a piezoelectric coating would be applied onto carbon fibers; the stress gradient along fiber would then generate the piezo-induced potential and charge, which guide and drive the self-adaptation phenomenon. This unconventional manifestation of the piezoelectric effect, which is schematically presented in Figure 34b, was successfully verified in our research.

The piezo-induced potential guides the adaptive effect in the sense that it turns zones of stress concentration into cathode towards which electrolytic mass transport would occur. The piezo-induced charge drives the adaptive effect in the sense that it governs the rate of mass transport towards cathode. Piezoelectric coefficients governing generation of electric potential and charge under stress are briefly introduced below.

Piezoelectric materials possess anisotropic properties. Consequently, the electrical response of the material is dependent upon the direction of external mechanical loads. In order to define the electromechanical properties relative to prescribed body-fixed axis frames, conventions have been developed for
piezoelectric plate-like geometries (see Figure 36(a)). Piezoelectric coefficients are defined with two subscripts; the first one identifies the axis of electric field while the second one corresponds to mechanical stress. Expressions for piezo-induced electric charge (D) and potential (E) and for a stress system that is relevant to our application are depicted in Figure 36(b), where $d_{31}$ and $g_{31}$ are the relevant piezoelectric coefficients. For piezo-driven electrolysis to actually take place in solid electrolyte it is essential that: (i) the piezo-induced potential (E) is sufficient to overcome the activation and polarization over-potentials at anode and cathode, and also the i.R drop within the solid electrolyte; and (ii) piezo-induced charge is sufficient for electrochemical mass transport at viable rates.

![Figure 36. Some Fundamental Piezoelectric Principles.](image)

**Figure 36. Some Fundamental Piezoelectric Principles.**

Piezoelectric effects are commonly encountered in biological matter (e.g., bone, horn, tendon, starch); among man-made materials, some ceramics (e.g., PZT and BaTiO$_3$) and polymers (e.g., PVDF) exhibit pronounced piezoelectricity.$^{14-16}$ The $d_{31}$ piezoelectric coefficients of PZT, BaTiO$_3$ and PVDF are 110, 78 and 23 pC/N, respectively, the corresponding $g_{31}$ coefficients are 10, 5 and 216 mV.m/N, respectively. Piezoelectric materials play central roles in growing efforts towards incorporation of functional qualities into structural systems. They are thus subject of intense research and development efforts, which have led to substantial rise in piezoelectric coefficients. For example, PZT and ZnO nano-tubes developed recently can yield composites with piezoelectric responses which are five orders of magnitude greater than those observed in traditional (bulk) piezoelectric materials.$^{17}$ These recent developments will be used in our follow-up research to pronounce and greatly expedite the adaptive effects in composites. The work summarized below validated piezo-induced electrolysis within solid electrolyte using conventional piezoelectric materials. Bulk piezo-ceramics as well as PZT fiber reinforced composite were used with similar outcomes. The results produced with PZT fiber reinforced composite with $d_{31}$ coefficient of 233 pC/N are summarized below.

### 4.2 Experimental Program

In order to validate piezo-induced electrolysis within solid electrolyte, PVDF-HFP specimens with different copper (salt) concentrations were prepared as described earlier. The solid electrolyte specimens were sandwiched between two stainless steel electrodes. Piezoelectric (PZT fiber reinforced composite) sheets were then subjected to repeated stress application, and the piezo-induced voltage was applied between the electrodes. Current was measured at pico amp precision (between the piezoelectric setup and electrodes). The basic elements of the test set-up are depicted in Figure 37(a), with the actual test set-up
shown in Figure 37(b). The current flowing through the solid electrolyte was found to be 20 µA; a load frequency of 3Hz was used in this experiment which lasted 18 hours.

The piezoelectric effect employed in the setup of Figure 36 to drive electrolysis phenomena within solid electrolyte is activated through application of uniform stress to the piezoelectric element (see Figure 37(a)); our application, however, mobilizes the piezoelectric effect under stress gradient (Figure 37(b)). The final system configuration is depicted in Figure 38(c), where piezo-induced electric potential and charge under stress gradient are employed to guide and drive electrolytic mass transport phenomena which render adaptive effects. The proposed use of piezoelectric effect under stress gradient (Figure 37(b)) is unconventional, noting that piezoelectricity is generally employed under uniform stress. Experiments were thus conducted in order to verify the effect under stress gradient. Figure 39 presents the experimental set-up used to verify the piezoelectric effect under stress gradient.

![Experimental Set-Up for Validation of Piezo-Induced Electrolysis within Solid Electrolyte.](image)

(a) Schematic Presentation
(b) Test Set-Up

Figure 37. Experimental Set-Up for Validation of Piezo-Induced Electrolysis within Solid Electrolyte.

(a) Schematic Presentation
(b) Test Set-Up

Figure 38. Piezoelectric Effects under Uniform and Gradient Stress Conditions.
4.3 Test Results

The experimental results provided clear evidence of metal deposition at cathode interface under piezo-driven electrolysis in solid electrolyte. As shown in Figure 40, the cathode interface of PVDF-HFP solid electrolyte showed obvious signs of metal deposition. The particular test specimen presented in Figure 39 was made of PVDF-HFP with 6% metal concentration. It is important to reiterate that the electrolytic mass transport towards and its deposition at cathode interface in Figure 40 occurred without any direct application of electric potential but by application of stress, with piezoelectric effect transforming the mechanical energy to electrical energy for guiding and driving electrolytic mass transport in solid electrolyte. After piezo-driven electrolysis, the solid electrolyte adhered to the electrode at cathode; clear evidence of electrodeposition was also noted when surfaces of anode and cathode (stainless steel) sheets were compared (Figure 41).
Experimental results for piezoelectric elements subjected to stress gradient confirmed that the piezoelectric coefficient, $g_{33}$, which relates piezo-induced potential to applied stress under uniform stress ($s$) condition of Figure 37(a) ($E=g_{33}.s.t$), is also equally applicable to gradient stress condition of Figure 37b for relating piezo-induced potential to the difference in stress ($\Delta s$): $E=g_{33}.\Delta s.t$. 
CHAPTER 5

DEVELOPMENT OF DIFFERENT CONSTITUENTS OF THE ADAPTIVE COMPOSITE MATERIALS

5.1 Introduction

The functional (piezoelectric and solid electrolyte) constituents that render adaptive effects are introduced into composite materials as a hybrid fiber coating system (see Figure 5). As a first step towards preparation of this hybrid coating system, processes for application of piezoelectric and solid electrolyte coatings were developed. Experiments were also conducted to validate piezo-driven electrolysis phenomena in the context of solid electrolyte coatings.

5.2 Development and Characterization of Piezoelectric Polymer Coating

Piezoelectric polymer coatings were developed in this research through ionic self-assembly;\(^\text{18}\) this process relies on electrostatic attraction forces for layer-by-layer deposition of coatings with excellent molecular-level uniformity and precise structural control. Ionic self-assembly is a simple, low-cost and environmentally friendly process, which involves layer-by-layer adsorption of polyanions and polycations from aqueous solutions (Figure 42(a)). The process can incorporate charge colloidal (metal or ceramic) nano-particles as replacement for one or both polyions (Figure 42(b)).

![Figure 42](image-url)

(a) Polcation/Polyanion Nano-Layers  
(b) Polyion/Colloid Nano-layers

Figure 42. Ionic Self-Assembly of Nano-Structured Coatings.\(^\text{18}\)

We used ionic self-assembly to deposit nano-layered (sodium 4-styrenesulfonate)/poly(diallyldimethylammonium chloride) (PSS/PDDA) piezoelectric coating. The chemical structures of PSS and PDDA are depicted in Figure 43(a). The deposition process on carbon substrate involved: (i) pretreatment of substrate with a 30:70 mixture of 30 % hydrogen peroxide and concentrated sulfuric acid followed by rinsing with acetone and alcohol to assume negative charge; and (ii) alternate immersion in 1 % PDDA (v/v) aqueous solution and in 2 mg/ml solution of PSS at pH 6-7 to achieve a coating thickness of 0.2 micron. Figure 43(b) shows a schematic diagram of the set-up used for measurement of piezoelectric coefficient. The conductive substrate formed one electrode, and a metal test weight, which made contact with the opposite side of the deposited coating, was used as the other electrode. By dropping the weight onto the film from a known height and measuring the resulting charge with an electrometer, the \(d_{33}\) piezoelectric coefficient may be determined. The experiment was carried out under quasi-static conditions. According to hydrostatic equations, the piezoelectric coefficient charge constant
The piezoelectric coefficient $d_{33}$ resulting from direct piezoelectric effect and measured by the normal load method can be calculated as: 
\[
d_{33} = \frac{Q}{F} = \frac{C_0 V}{F},
\]
in which $Q$ is the induced charge in the coating within the electrode area for an applied force $F$; and $C_0$ is the capacitance of the standard capacitor used in the set-up (Figure 43(b)). The normal load tests indicated that the ionically self-assembled PSS/PDDA multi-layer system (as deposited) provided a piezoelectric coefficient $d_{33}$ of about 7.0 pC/N without any electric field poling treatment. This experiment successfully demonstrated that piezoelectric coatings can be deposited by ionic self assembly, which is amenable to implementation in the context of fiber coating systems.

\[
\begin{array}{c}
\text{PSS} \\
\text{FDDA}
\end{array}
\]

(a) Constituents

(b) Test Set-Up

Figure 43. The Piezoelectric Coating Constituents and Test Set-Up.

### 5.3 Development and Characterization of Piezoelectric Ceramic Coatings

Piezoceramic coatings were processed by two alternative techniques: (i) sol-gel; and (ii) layer-by-layer self-assembly. These processing techniques and the piezoelectric attributes of the resulting coating systems are reviewed below.

#### 5.3.1 Sol-Gel Processing and Characterization of Piezoceramic Coating

**Materials**

2-methoxy ethanol (99.3 % ACS reagent grade) and lead (II) acetate trihydrate were purchased from Aldrich. Zirconium n-propoxide 70 % (w/w) and titanium (IV) isopropoxide 97 % were purchased from Alfa Aesar. Copper sheet was purchased from McMaster, and was used after cleaning with distilled water. All chemicals were used as received, without further purification.

**Procedure for Preparation of Complex Alkoxide Sol**

1 M metal organic solution was synthesized by dissolving lead acetate trihydrate, titanium isopropoxide and zirconium n-propoxide in methoxyethanol and 5 % (by volume) propanoic acid. Methoxyethanol (boiling point 125 °C) was used as solvent to facilitate dehydration by boiling. Lead acetate trihydrate (18.9665 g) was added to 50 mL of methoxyethanol. Lead acetate was dissolved by boiling at 125 °C for 30 minutes to remove water. During this time, the solution needs to be stirred continuously to facilitate dissolution. The dehydrated solution was immediately cooled to 90 °C; this was followed by the addition of zirconium n-propoxide (16.378 g) and titanium isopropoxide (14.194 g) in 50 mL of methoxyethanol. The solution was heated to boiling point (125 °C) in order to promote complex formation and elimination of
alkylacetates which were by-products of the reaction. Subsequently, 5 mL of proponol was added, and the solution was diluted 100 mL by adding methoxyethanol.

Coating of PZT on Copper Sheet

The copper sheet was cleaned, dried and weighed. The sol prepared following the above procedure was cast on copper sheet by immersing the sheet in and removing it from the sol at controlled speed, and allowing the excess sol to drip from copper sheet. The coating was then treated (baked) at 300 °C for 15 minutes, and then annealed at 600 °C for one minute. This heat treatment will produce the piezoceramic coating composition PbZr_{0.5}Ti_{0.5}O_{3} (PZT- Lead zirconate titanate). The casting, baking and annealing procedure was repeated 20 times to reach a coating thickness of 4 µm for experimental evaluation of piezoelectricity; the repetition of the process would not be necessary in eventual application of the piezoceramic coating on fibers. Figures 43 and 44 present the visual appearance and microscopic images of the copper sheet surface prior to and after application of the piezoceramic coating.

![Figure 44. Visual Images of the Copper Sheet Substrate and Piezoceramic Coating.](image)

![Figure 45. Microscopic Images of the Surfaces of Copper Sheet Substrate and Piezoceramic Coating.](image)
Poling of Piezoceramic Coating

In order to prepare the coated specimen for performance of piezoelectric tests, the coating was removed from one face of the copper sheet. The exposed copper surface would act as an electrode during poling and also in subsequent measurement of the piezoelectric response. A second copper sheet was pressed against the top surface of PZT coating, making sure that the two copper sheets do not short during voltage application. This second copper sheet constituted the second electrode for voltage application. In order to pole the piezo-ceramic coating (see Figure 46), it was subjected (via the two electrodes) to an external voltage 12 V for 15 minutes at room temperature. This voltage was selected based on a thorough literature review which concluded that 2 V of potential should be applied for each micron of coating thickness during poling. After 15 minutes, the PZT coated copper sheet was detached from the set-up and used in subsequent measurement of piezoelectric response.

![Figure 46. Schematics of the Set-Up Used for Poling of the Piezoceramic Coating.](Image)

Measurement of Piezoelectric Response

The piezoceramic coated copper sheet was sandwiched between metal sheets, and was subjected to repeated stress applications as shown in Figure 47. This set-up applied a uniform stress normal to the coating surface, and measured the piezo-induced potential. A stress of 2.5 MPa generated an output potential of 0.25 V; the $g_{33}$ piezoelectric coefficient of the PZT coating system was thus:

$$g_{33} = \frac{\text{Potential} / \text{Thickness}}{\text{Stress}} = \frac{0.25 / 4 \times 10^{-6}}{2.5 \times 10^6} = 25 \times 10^{-3} \frac{V}{m^2}$$

The measured value of $g_{33}$ coefficient is within the range of values reported for PZT piezoceramics. This confirms successful application of piezoceramic coating by the sol-gel technique.

![Figure 47. Experimental Set-Up for Measurement of Piezoelectric Response.](Image)
5.3.2 Establishment of the Layer-By-Layer Self-Assembly Process for Piezoceramic Coatings

Introduction

Theoretical models of adaptive composites, presented earlier, clearly highlighted the advantages of nano-engineered piezoelectric coatings in terms of the rate and the extent of adaptive effects. The research reported herein took preliminary steps, outlined below, towards application of the layer-by-layer self-assembly technique towards processing of nano-structured piezoceramic materials.

Piezoelectric ZnO nano-particles were the primary building blocks of the nano-structured piezoelectric coating processed so far in the project. The nano-structured multi-layer coating comprised 5 nm diameter zinc oxide particles (ZnO) and poly(diallyldimethylammonium chloride) (PDDA), which were applied on a copper sheet substrate via sequential electrostatic adsorption of ZnO and PDDA from dilute solutions. The ferroelectric nature of ZnO makes it a piezoelectric material, and nano-particles of ZnO with very high specific surface area promise very high levels of piezo-induced charge. Figure 48 makes a schematic presentation of the process. Surface charge is a primary requirement in the layer-by-layer self-assembly process employed here; the copper substrate was thus immersed in a 1 mM ethanolic solution of MUA in order to develop sufficient (negative) surface charge. The charged substrate was then immersed in PDDA polyelectrolyte solution (with fixed positively charge functional groups along the polymer backbone), which would be adsorbed onto the surface (Figure 48(a)). After removing the substrate from solution and rinsing it with water, it was immersed in a suspension containing negatively charged colloidal ZnO (Figure 47b). The colloidal particles would then be adsorbed onto the positively charged surface, where they ionically bond to cationic polymer molecules. By repeating this simple two-step process, multilayer coatings with alternating layers of PDDA polymer and ZnO nano-particles can be formed (Figures 48(c) & 48(d)). The self-assembly process may be followed by heat treatment in order to burn-off the polymer constituent and consolidate the coating into an all-ceramic system of high elastic modulus, which exhibits pronounced piezoelectric response due to the high surface area of nano-structured ZnO.

Figure 48. Layer-By-Layer Self-Assembly of Multilayer PDDA/ZnO Nano-Structured Piezoceramic Coating.

Materials

Poly(diallyldimethylammonium chloride) ($M_w = 400,000-500,000$, 20 wt % in water, PDDA), 11-mercatoundecanoic acid (MUA), ethanol, Sodium chloride (NaCl, ACS reagent), hydrochloric acid and sodium hydroxide (NaOH, pellets, 97 +%, ACS reagent) were purchased from Aldrich. Nayacol® DP5370 colloidal zinc oxide (ZnO) was purchased from Nyacol Nano Technologies, Ashland, MA. This
was a dispersion of ZnO (30 %) in water at pH 9.5, with particle size of 50-90 nm. All materials were used as purchased. Copper sheet with thickness of 0.01 cm was purchased from McMaster, and was chemically etched before use as substrate for depositions.

**Self-Assembly of Multilayer PDDA/ZnO**

The copper sheet was first cleaned by immersion in a 1 mM ethanolic solution of MUA. In was then rinsed with ethanol and then by distilled water. Due to the covalent bond formation between copper and S-atoms of thiol molecules, a monolayer of MUA form on copper sheet. The MUA coated copper sheet is negatively charged due to the carboxylate functional groups; it was thus first immersed in positively charged 0.5 wt % PDDA solution in water at pH 4.2 (containing 0.5 M NaCl to increase the coating thickness) for 5 minutes, and then rinsed very well. Due to the electrostatic attraction between polyelectrolyte and copper, a monolayer of PDDA would be deposited on copper, reversing the surface charge. The substrate was then immersed in a suspension of 30 % ZnO at pH 9.5 for 5 minutes, and rinsed extensively with distilled water. Immersion in ZnO suspension allows negatively charged ZnO nano-particles to assemble on the positively charged PDDA monolayer, yielding a bilayer of PDDA and ZnO. Repetition of the dipping and rinsing process generates a multilayer of polymer/nano-particle (PDDA/ZnO) with targeted thickness. Figure 49 presents microscopic images of the copper sheet surface prior to and after application of the nano-structured piezoelectric coating.

![Microscopic Images of Copper Sheet Substrate and Nano-Structured Piezoelectric Coating](image)

*Figure 49. Microscopic Images of Copper Sheet Substrate and Nano-Structured Piezoelectric Coating*
Introduction

Zinc oxide (ZnO) is a versatile smart material that has applications in catalysts, sensors, piezoelectric transducers, transparent conductors, and surface acoustic wave devices. The non-central symmetry and the tetrahedral coordinated ZnO₄ unit in ZnO result in anisotropic piezoelectric properties. Structurally, the wurtzite structured ZnO crystal is described schematically as a number of alternating planes comprising four-fold coordinated O²⁻ and Zn²⁺ ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged Zn and negatively charged O polar surfaces, resulting in a normal dipole moment and spontaneous polarization as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO±(0001) is an exception, which is atomically flat, stable, and without reconstruction. In particular, ZnO films oriented along the c-axis have been used as surface acoustic wave devices because of their large piezoelectric coefficient. Past investigations have shown that the most preferred orientation of ZnO for large piezoelectric effect is dependent on the firing temperature of the ZnO film. Many studies suggested that preheating to 300 °C before firing gives the highest degree of crystal orientation (002). Previous studies also suggest that the peak intensity increases with post-heating up to 500 °C, with a unique peak intensity pointing at preferred grain growth along (002) plane (Figure 50). The (002) peak intensity, however, rapidly decreases above 600 °C, where other peaks appear. Therefore, preheating to 300 °C followed by post-heating at 500 °C yields the preferred crystal orientations for piezoelectric response. Furthermore, unlike other ferroelectric materials (PVDF, PZT, etc.), ZnO has the advantage that it does not require electro-thermal poling because of its self-poling capability.

Figure 50. Increase of Peak Intensity 002 Plane with Heating Temperature.
The techniques commonly used for deposition of ZnO include sol-gel, r.f. magnetron sputtering, vacuum sublimation, spray pyrolysis, evaporation, and chemical vapor deposition. Here we use electrostatic self-assembly and sol-gel processes for fabrication.

5.4.1 Sol Gel Processing of Piezoelectric ZnO

Materials

2-methoxy ethanol (99.3 % ACS reagent grade), zinc(II) acetate dehydrate (ZnAc, Zn(CH₃COO)₂·2H₂O) and monoethanol amine (MEA) were purchased from Aldrich. Copper and stainless steel sheets were purchased from McMaster and used after cleaning with distilled water and sonication. All the chemicals were used as received without further purification.

Procedure for Preparation of Complex Zinc Acetate (ZnAc) Sol

ZnAc was first dissolved in a 2-methoxyethanol-MEA solution at room temperature. The molar ratio of MEA to ZnAc was kept at 1.0, and the concentration of ZnAc was 0.75 mol L⁻¹. The resultant solution was stirred at 60 °C for 30 minutes to yield a clear and homogeneous solution, which served as coating solution. The gel film was fabricated by dipping the substrate in the coating solution and withdrawing it out from the solution at a slow rate. Substrate was left for excess solution to drip off, and the post-deposition heat treatment followed as described below.

Post-Deposition Heat Treatment and Firing of ZnO

After dip coating of each ZnAc layer, the substrate containing the coating was baked at 300 °C for 10 minutes. After repeating the dipping and baking steps several times, the coating was fired at 500 °C for 10 minutes. Baking removes all the solvent water, and enables formation of a dense coating. Firing under selected conditions not only forms a dense coating, but also yields the preferred crystal structure with greatest piezoelectric response. The baking and firing temperatures and durations were determined based on a literature review. Figure 51 shows the flow chart for preparation of piezoelectric ZnO coating films.
Figure 51. The Flow Chart for Preparation of Piezoelectric ZnO Coatings.

Figure 52 shows the visual appearance of the copper sheet prior to (Figure 52(a)) and after (Figure 52(b) and (c)) coating with ZnO. Microscopic images of the uncoated and coated sheets (prior to and after firing) are presented in Figure 53. Figures 54 and 55 show the visual appearances and microscopic images of the stainless steel sheet before and after coating with ZnO and subsequent heat treatment.
Figure 52. Visual Appearance of Copper Sheet; (a) Before Coating, (b) After Coating with ZnO and baking and (c) After Firing the ZnO Coating.

Figure 53. Microscopic Images of Copper Sheet; (a) Before Coating (b) After Coating with ZnO and Subsequent Baking and (c) After Firing the ZnO Coating.

Figure 54. Visual Appearance of Stainless Steel Sheet; (a) Before Coating (b) After Coating with ZnO and Subsequent Baking and (c) After Firing the ZnO Coating.
Experimental Evaluation of Piezoelectric Response

The piezoelectric response of ZnO coating was assessed without any poling of the coating. The experiment involved measurement of output voltage as the piezoelectric coating was subjected to repeated stress application (Figure 56). An oscilloscope was used for measurement of the output voltage. On one face of the metal sheet, the coating was removed; an uncoated copper or stainless steel sheet was placed on the opposite (coated) face of the sheet, with ZnO coating preventing any direct contact between the two metal sheets which act as electrodes on opposite faces of the ZnO coating. This set-up was sandwiched between two rubber sheets, and was subjected to repeated stress application in a servo-controlled hydraulic test system. As noted earlier, the piezoelectric response monitored with an oscilloscope. The test set-up is shown in Figures 56 and 57. The ZnO coating exhibited a desirable piezoelectric response, with output voltage approaching 0.5 volt (which is competitive against poled PZT coating); the 5 micron thick coating did not exhibit any signs of cracking or deterioration during the test.

Figure 55. Microscopic Images of Stainless Steel Sheet; (a) Before Coating (b) After Coating and Subsequent Baking and (c) After Firing the ZnO Coating.

Figure 56. Schematic Presentation of the Test Set-Up for Measurement of Piezoelectric Response.
5.4.2 Electrophoretic Deposition of Piezoelectric ZnO Coating

Introduction

The electrophoretic deposition process was employed for relatively high-throughput deposition of ZnO nanoparticles. Electrophoresis offers simple, economical and versatile means of assembling charged nanoparticles (and also nanosheets and nanotubes/nanofibers) on an electrode from stable colloidal suspensions using a dc electric field. Compared with alternative deposition techniques, electrophoretic deposition provides for precise control of thickness and morphology of deposits by varying electrochemical parameters; moreover, uniform and dense deposits can be deposited on electrodes of complex geometry at a high rate of deposition. Electrophoretic deposition through aqueous media offers important environmental and cost advantages when compared with deposition through non-aqueous media.

ZnO is well known as an amphoteric oxide which can be easily dissolved in both acids and bases. ZnO is hydrated to form Zn\(^{2+}\) cation at acidic pHs of <6.3, and it forms hydroxide layers in water at basic pHs, where Zn(OH)\(_2\) is in equilibrium with the Zn\(^{2+}\), Zn(OH)\(^+\), Zn(OH)\(_3^-\), and Zn(OH)\(_4^{2-}\) species. At pH >12, the latter two zincate ions become the dominant species in solution. In this study, the pH range of 7-11 was chosen to prepare the suspension; the ZnO particle is usually negatively charged in this pH range. In this study, the cationic polyelectrolyte poly(ethylene imine) (PEI) was used to provide the ZnO particles with a positive charge potential and good dispersion in aqueous media. PEI has imido (-NH) groups that readily adsorb protons in the solution; PEI becomes positively charged through to the following reaction:
The protonation of PEI is reported to occur at pH ≤ 10.8. Here, probably because of the formation of zinc hydroxide, PEI will absorb more protons that remain in the suspension, which causes the ZnO particles to have a positive charge over a large pH range. This facilitates cathodic electrodeposition of ZnO.

**Experimental Program**

**Materials**

Nyacol® DP5370 colloidal zinc oxide (30% dispersion in water, 50-90 nm diameter, pH 9.5) was obtained from Nyacol Nanotechnologies Inc., Ashland, MA. Cationic polyelectrolyte, polyethyleneimine (PEI, -(CH$_2$-CH$_2$-NH-)$_n$, $M_w = 90,000$) was purchased from Alfa Aesar. All chemicals were used as purchased. The hydrochloric acid used for pH adjustments was purchased from Aldrich. Substrates (copper, stainless steel and carbon steel) were purchased from McMaster. The substrates were rinsed, sonicated in water, and dried before depositions. Platinum-clad, expanded mesh niobium electrode, with 3 µm of Pt clad on both sides, was purchased from Larry King, NY.

**Methods**

**Preparation of the Suspension for Electrodeposition**

PEI (2% of the total weight) was dissolved in water by ultrasonication. Colloidal ZnO (5% of the total weight) was added to the mixture, and ultrasonicated for 10 minutes in order to break the agglomerates. The mixture was subsequently stirred for 12 hours until a uniform dispersion was obtained, ensuring achievement of equilibrium polymer absorption. The pH of solution was then adjusted to 10 with dilute HCl.

**Electrolytic Cell and Electrode Cleaning**

All electrodeposition processes were carried out in an open polypropylene support containing different compartments for electrodes. The electrodes were clamped in polypropylene molds, and placed on a container of colloidal suspension. Two electrodes, platinum (platinum-clad niobium mesh) anode and stainless steel or copper cathode, was placed parallel to each other at 1 cm spacing. The dimensions of cathode and anode were 28 × 20 mm and 50 x 50 mm, respectively. Before initiating the electrodeposition process, cathode was sonicated with distilled water, ethanol, and acetone, and was then dried and subjected to ozone cleaning. All electrodeposition processes were conducted in the galvanostatic mode using a constant voltage/current DC power supply. A constant cell current was applied (~10 mA) between the electrodes as shown in Figure 58. The electrolytic suspension was not stirred, and its temperature was maintained at 298 K. After each electrodeposition trial, the ZnO coated stainless steel or copper sheet was removed from the supporting cell, rinsed several times with distilled water to eliminate the residual components of suspension, and dried in an open atmosphere up to a constant weight. The resulting ZnO deposits were further dried overnight in air at room temperature. The weight of electrodeposited ZnO was then determined as the mass gain of cathode after electrodeposition.
Figure 58. (a) Experimental Set-Up for Electrophoretic Deposition of ZnO Nanoparticles and (b) Enlarged View of Electrophoresis Cell.

Sintering of ZnO Coating

The deposited and dried ZnO coating was first baked in oven at 300ºC for 10 minutes in air. It was then fired at 500ºC for one hour in a furnace, and allowed to cool down to room temperature. The weight of the coated sheet was measured at this stage.

Characterization techniques

The surface morphology and thickness of the ZnO deposit were investigated by scanning electron microscopy (SEM) with a Jeol T 300 microscope. For measurement of thickness, samples were cut and
mounted onto a holder, and their cross-section was observed. Thickness of the deposited film can also be estimated indirectly using the weight gain of electrode upon electrodeposition.

**Evaluation of the Piezoelectric Properties of ZnO Coatings**

As a first step to verify the piezoelectric response of the ZnO deposit, it was subjected to repeated stress application, and the voltage output was measured by an oscilloscope.

Unlike previous cases, we did not need to remove the coating from one face of the substrate sheet; this is because electrodeposition was performed only on one face of the sheet. An uncoated stainless steel sheet was used as one electrode, with the metallic substrate sheet acting as the other electrode. The zinc oxide coating was covered with a piece of stainless steel sheet in such a way that there was no direct contact between the substrate and the stainless steel sheet, with the coating acting as an insulator between the two sheets. This set-up was sandwiched between two rubber sheets, and then metal sheets; the whole assembly was tightly wrapped with tape. This set-up was subjected to repeated stress application in a servo-controlled hydraulic system, with the piezoelectric response monitored using an oscilloscope. The test set-up is shown in Figures 59 and 60.

![Schematic Presentation of the Test Set-Up for Measurement of Piezoelectric Response.](image)

*Figure 59. Schematic Presentation of the Test Set-Up for Measurement of Piezoelectric Response.*
Figure 60. (a) Experimental Test Set-Up for Measurement of Piezoelectric Response and (b) Enlarge View of the MTS Machine Showing the Piezo Sample.

Experimental Results

After deposition of ZnO, the surface appearance of stainless sheet changed as shown in Figure 61.
Figure 61. Visual Appearance of Stainless Steel Sheet (a) Before, (b) After Coating with ZnO and Baking at 300 ºC and (c) Firing at 500 ºC for One Hour.

Scanning electron microscopic images (Figure 5) show complete coverage of the surface by electrodeposited ZnO. The effect of sintering, that is fusion of ZnO nanoparticles, is apparent in Figure 62.
Figure 63. Scanning Electro Micrographs of (a) Uncoated Stainless Steel Surface, (b) Zno Coated Surface and (c) ZnO Coated Surface After Baking and Sintering.

A scanning electron microscopic image of the cross-section of the stainless steel sheet with ZnO coating is shown in Figure 64, such images were used to measure the thickness of the deposit. This thickness was close to 20 µm.

Figure 64. SEM Images of ZnO Coated Surface Cross-sectional View ZnO Coated Surface

Piezoelectric Response

The ZnO coating deposited on stainless steel sheet exhibited a very promising piezoelectric response, with output voltage approaching 1 volt, without any damage to the 20 micron thick coating. This output
voltage, which was obtained without any need for poling, was comparable with commercially available PVDF piezoelectric polymer sheet of 500 micron thickness under similar stress application conditions.

5.5 Efforts towards Development of Thermally Stable Solid Electrolytes

Introduction

Efforts towards development of solid electrolytes with enhanced ion conductivity have focused on new polymeric matrices or modification of existing polyether-salt complexes. Introducing of nano-sized inorganic fillers has emerged as a successful approach. Clay is inorganic filler used in this approach, which offers intercalating properties. An intercalating polymer within a layered clay host provides a polymer electrolyte nanocomposite with tremendous interfacial area which reduces the crystallinity of polyether chains, leading to enhanced ion conductivity. Furthermore, the mechanical properties and thermal resistance of the semi-crystalline poly (ethylene oxide) (PEO)-based electrolyte used in this process can also be improved in the presence of clay. Incorporation of the appropriate quantity of clay can drastically increase the ionic conductivity of solid polymer electrolytes. The clay mineral can dissolve metal cations because silicate layers of clay play the role of a Lewis base to complex with the metal cations. However, the effect of polymer intercalation with clay on enhancement of ionic conductivity is not clearly understood.

Experimental Program

Materials

PEO with a weight-average molecular weight ($M_w$) of 200,000 was purchased from Aldrich. Dimethyldioctadecylammoniumchloride (DDAC) and sodium montmorillonite (sodium form of natural clay) were purchased from Aldrich. DDAC was used to modify the clay, and the structure is illustrated in Figure 65.

![Figure 65. Structure of DDAC.](https://example.com/figure65)

Preparation of Mineral Clay-DDAC-Modified Clay

The cation-exchange capacity of sodium montmorillonite was 1.15 meq/g. The sodium montmorillonite clay (1 g) and 50 mL of distilled water were placed in a 100-mL beaker, and 1 g of dimethyldioctadecylammonium chloride (DDAC) was added to the solution. The mixture was stirred
vigorously for 8 h, filtered, and then washed three times with 100 mL of hot water to remove NaCl. After washing with ethanol (50 mL) to remove residual ammonium salt, the modified clay was dried in a vacuum oven at 60 °C for 24 h.

**Preparation of Solid Polymer Electrolyte (SPE)**

Desired amounts of PEO, vacuum-dried CuTf salt, and clay in dry acetonitrile were mixed to form PEO/clay/CuTf nanocomposites of various compositions. Following continuous stirring for 24 h at 80°C, these solutions were maintained at 50 °C for an additional 24 h to facilitate initial dissolution. Further drying was carried out under vacuum at 70 °C.

Processing of this solid electrolyte nanocomposite with metal salts and plactiziers, and experimental evaluation of ionic conductivity, mechanical performance and thermal resistance are in progress.

### 5.6 Development of Nanostructured Conductive Coatings of Carbon Nanotube/Polymer Nanocomposites through Electrophoretic Deposition

**Introduction to Electrolytic and Electrophoretic Deposition Techniques**

Electrochemical methods are increasingly used for the preparation of thin films and coatings. Recently, electrodeposition of metals attracted renewed attention, due its adoption for processing of advanced microelectronic components. Electrodeposition is also broadly investigated for processing of polymer films. Major progress has been made in electrochemical deposition of ceramic materials. Electrodeposition is also being recognized as an effective technique for fabrication of organoceramic films. It is generally viewed that electrolytic and electrophoretic deposition techniques (Figure 66) will play major roles as major techniques for processing of nanocomposites. Our approach uses the electrophoretic deposition process to develop a thin, highly conductive coating comprising carbon nanotubes and a binder.

![Figure 66. Schematics of Electrolytic and Electrophoretic Deposition Techniques.](image-url)
Solvents Used in Electrophoretic Deposition (EPD)

Solvents used in EPD should be inert with respect to the suspended material. Organic liquids are superior to water as a suspension medium for EPD. The use of water-based suspensions causes gas formation from hydrolysis of water, preventing the deposition of a uniform adherent layer and yielding pinholes. A variety of non-aqueous organic solvents are commonly used to prepare suspensions for EPD. The charge on a colloidal particle could originate from solvents. Alcohols are known to behave as proton donors and are important for particle charging.

Binders in Electrophoretic Deposition

A binder is added to suspensions or solutions in order to increase the adherence and strength of the deposited material and prevent cracking. EPD of nano-sized particles offers advantages in the fabrication of uniform ceramic coatings with dense packing and good sinterability. However, the use of fine particles initiates deposit cracking, which could be prevented by proper use of a binder. The optimal amount of binder depends on particle size and particle surface area.

The most common binders used in electrophoretic deposition are non-ionic-type polymers (polyvinyl alcohol, polyvinyl butyral, ethyl cellulose, polyacrylamide, etc). The polymeric molecules adsorb onto the surfaces of ceramic particles. Positively charged ceramic particles provide for electrophoretic transport of the polymer molecules to form deposits on cathodic substrates. Cationic polyelectrolytes with inherent binding properties, such as poly(dimethyl diallyl ammonium chloride) (PDDA) or polyethylenimine (PEI), could be used for particle charging and EPD.

A suspension for electrophoretic deposition is a complex system, in which each component has a substantial effect on deposition efficiency. It is very important to obtain well-dispersed and stable suspensions. In general, suspensions can be dispersed by electrostatic, steric, or electrosteric stabilization mechanisms. Ceramic particles must be electrically charged to permit forming by EPD. In aqueous media, the charge at the particle–solvent interface could originate from adsorption or desorption of ions, or dissociation of surface groups. Surfaces of oxide particles dispersed in water tend to coordinate water molecules to form hydroxylated surfaces. The surfaces may become positively or negatively charged, depending on pH.

Organic macromolecules could be utilized to induce steric stabilization, where the macromolecules are attached to the particle surface, or they can induce depletion stabilization where the macromolecules are free in suspension. Steric stabilization is effective in both aqueous and non-aqueous media. Polyelectrolytes are widely used additives that can impart electrostatic and steric stabilization to a colloidal dispersion. The polyelectrolytes can be categorized into two groups: strong polyelectrolytes for which the degree of ionization is independent of the solution pH, and weak polyelectrolytes for which the degree of ionization is determined by the solution pH. PEI is an example of weak cationic polyelectrolytes. An increase in pH decreases the charge of PEI. In contrast, PDDA, because of the quaternary ammonium group, is an example of strong polycations, and the degree of dissociation of the ionic groups is nearly pH-independent over a wide pH range. The adsorption of polyelectrolytes on ceramic particles depends on pH, polyelectrolyte charge density, particle charge, and ionic strength. PEI and PDDA were used to stabilize ceramic suspensions. Moreover, considerable shift of the particle
isoelectric point was reported. Adding a suitable amount of PEI can reverse the surface charge of silica particles.

Important factors to consider when selecting a binder–dispersant–solvent system are: chemical compatibility of components, solubility of binder and additives, particle charge, viscosity, and electric resistivity of the suspension.

Rapid and Controlled Processing of Highly Conductive Coatings Incorporating Carbon Nanotubes

Carbon nanotubes (CNTs) are cylinder-shaped macromolecules with a radius as small as few nanometers, which can be grown up to 20 cm in length. The walls of these tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. They are capped at their ends by one half of a fullerene-like molecule. In the most general case, a CNT is composed of a concentric arrangement of many cylinders (Figure 67). Such multi-walled nanotubes (MWCNTs) can reach diameters of up to 100 nm.

![Figure 67. Structure of Multi-Walled Carbon Nanotube.](image)

Carbon nanotubes (CNTs) can offer high levels of electric conductivity; depending on the tube diameter and angle of roll with respect to the graphite structure, CNTs exhibit metallic conductivity. Nanotubes can be either electrically conductive or semiconductive, depending on their helicity, leading to nanoscale wires and electrical components. Then can exhibit electrical conductivity levels comparable to that of copper, thermal conductivity levels as high as diamond, strength levels that are 100 times greater than that of steel at one-sixth the weight, and tremendous strain capacities.

Carbon nanotubes are uniquely suitable as lightweight electrically and thermally conductive materials. However, due to their tendency to agglomerate into bundles and also because of their relatively weak adhesion to other materials, their processing into useful products presents a challenge. The intermolecular forces of attraction between adjacent nanotubes, that leads to their agglomeration, are based on a π-bond.
stacking phenomenon (the π-stacking mechanism). Because there can be hundreds of π-stacking sites between two CNTs, intermolecular forces are stronger than those found between two relatively small hydrocarbon molecules. When nanotubes are made to slide along their length, however, resistance is lower than what is normally found in entangled polymeric molecules. Hence, nanotubes are normally in the form of bundles, which have to be processed and/or functionalized into dispersed materials. This is especially true if the nanotubes are going to be used to reinforce polymeric materials. If other properties of nanotubes are desired, such as their excellent electrical and thermal properties, then a partial level of dispersion might be adequate. Solvents and additives with relatively strong specific intermolecular forces are reportedly required along with the application of ultrasound to facilitate dispersion of CNT.

A major barrier for developing CNT-based devices is the insolubility of CNT in all solvents. The challenge of solubilizing CNT has been addressed through their covalent modification or noncovalent functionalization. The low dispersability stems from the tendency of as-prepared CNT to assemble into bundles or ropes that contain hundreds of well-aligned CNT arranged in a close-packed triangular lattice, due to van der Waals attraction. The ropes with lengths in micrometer range further entangle into networks. A recent calculation suggests that the typical inter-tube attraction is on the order of 36 kT for every nanometer of overlap between adjacent tubes, leading to a cohesive energy of a few thousands of kT per micrometer-long tubes. Unlike the case of classical colloids, the attraction is short-ranged and decays to a negligible value over a distance of a few nanometers.

Current approaches to dispersion and exfoliation of bundled CNT into individual tubes include covalent modifications, π-π interactions, surfactant adsorption, and more. Most of these methods are designed to reduce the short-range attraction between adjacent nanotubes via introduction of a repulsive interaction of similar strength. Consequently, these treatments often lead to modification of the structural, electronic, and mechanical properties of nanotubes. The challenge is to disperse these nanotubes without altering their unique properties. In particular, “wrapping” of CNT in polymeric chains has shown promise for improving their solubility without impairing their physical properties. This approach to preparation of well dispersed nanotube suspensions is shown in Figure 68. CNT’s held by strong, short-range inter-tube attraction (Figure 68(a)) form ropes and bundles (Figure 68(b)). Gentle sonication causes exfoliation of ropes into individual tubes (Figure 68(c)). The exfoliated tubes may be stabilized in liquid media, and aggregation may be prevented by introduction of relatively weak repulsion at a large distance between nanotubes, such as osmotic (steric) repulsion among the tails of tethered polymers in good solvents, or electrostatic repulsion by charge ends of tethered polymers.
Figure 68. Schematic Presentation of the Concept: (a) Curve Showing Total Interaction Energy Vs Separation Distance for Two Nanotube, (b) Nanotubes in a Solvent (Due to van der waals Attractions CNT’s Tend To Aggregate in Solvent, (c) Sonication Leads to Exfoliation and Temporary Dispersions and (d) Selective Tethering of Polymers on Nanotube Walls Stabilizes the Exfoliated Tubes and Prevents Re-Aggregation.

Our approach to dispersion of carbon nanotubes involves first dispersion of CNT in an organic solvent such as tetrahydrofuran (THF) by sonication, and then capping the nanotube walls with tetra octyl ammonium bromide (TOAB). This approach to preparation of well-dispersed nanotube suspensions is shown in Figure 69. Carbon nanotubes held by strong, short-range intertube attraction form ropes and bundles (Figure 69(b)). Gentle sonication causes exfoliation of ropes into individual tubes (Figure 69(a)). The exfoliated tubes may be stabilized in liquid media, and aggregation may be prevented by introduction of relatively weak repulsion at a large distance between tubes, such as osmotic (steric) repulsion among the tails of tethered polymers in good solvents, or electrostatic repulsion by charged ends of tethered polymers. In our case, by introducing TOAB to nanotubes, long-chain octyl groups of TOAB were bound to nanotube walls (hydrophobic interactions), giving an overall negative charge to nanotube surfaces. These overall negative charges on nanotube surfaces create electrostatic repulsions between individual capped nanotubes, allowing nanotubes to be separated from each other and forming a stable suspension.
Figure 69. Scanning Electron Micrographs of Surfaces of Carbon Nanotubes Dispersed in THF With: (a) The Aid of a Dispersing Agent/Binder; and (b) Without The Aid of a Polymer Dispersing Agent/Binder. The Better Definition of the Rope Structure in (a) Indicates a Higher Electrical Conductivity on the Nanotube Surface. (Figures were adapted from Journal of Minerals & Materials Characterization & Engineering, Vol. 3, No.2, pp 73-80, 2004)

What are the advantages of carbon nanotube over conducting particles for development of conductive coatings? Since conduction is by electrical charge percolation from particle to particle through the coating, the coatings must be filled with high loading levels (>>5 %) of the conductive media to reach significant electrical conductivity. The high loading levels damage some mechanical (and optical) properties. With carbon nanotube, however, composites reach the electrical percolation threshold at loading levels of only 0.04 wt. %, and can yield improvements in various physical and mechanical properties.

Experimental Program

Materials

Multi-Walled carbon nanotubes (MWNT) with “bamboo” structure ((MWNT-B, processed via chemical vapor deposition (CVD), purity>95 %, outer diameter = 30±10 nm, length = 1-5 µm) were purchased from NanoLab (Boston, MA) (Figure 70). Tetraoctyl ammonium bromide (TOAB) and tetrahydrofuran (THF), methanol and 5 % nafion solution in low aliphatic alcohol were purchased from Aldrich. All the chemicals were used as purchased with out any further treatment.
Solubilization of MWNT in Organic Solvents

Purified MWNTs synthesized by electric arc method (from NanoLab) were solubilized by mixing with tetraoctylammonium bromide (TOAB) in THF (10 mg MWNT and 0.13 g TOAB in 25 ml THF). Sonication of the mixture for 20-30 minutes yields a stable dark suspension. This suspension was centrifuged at 10,000 rpm for approximately 10 minutes. The clear supernatant liquid containing unbound TOAB was discarded. This procedure was repeated and the final centrifugate, after removing the solvent, was dried. The repeated washing and centrifuging procedure allowed us to discard any unbound TOAB from the MWNT material. The dried material consisting of TOAB bound MWNT was readily suspendable in organic solvents. Typically, TOAB-bound MWNT was re-suspended in 25 ml THF and sonicated for 10-15 minutes. Based on weight gain, capping of 1 mg of TOAB per 10 mg of MWNT is estimated. The quaternary ammonium salt, TOAB allows solubilization by binding to the MWNT through hydrophobic interactions of its alkyl chains.

Electrophoretic Deposition of MWNT Nanocomposite Film on Electrode Surfaces

The electrophoretic deposition process was carried out in a 30 mL beaker containing 10 mL of TOAB-capped MWNT in THF. Two aluminum sheets 1 x 5 cm were used as electrodes; they were kept parallel to each other as close as possible in the beaker as shown in the Figure 71.

When a dc voltage of ~50 V was applied (100 V was applied for one minute initially to start the deposition process), capped CNT’s slowly moved from the suspension towards the positively charged electrode. Continuous application of dc voltage resulted in the deposition of CNT nanocomposite film on the electrode surface; the thickness of deposited CNT films could be increased by increasing the time of electrophoretic deposition.
Characterization Techniques

The surface morphology and thickness of the films were studied by scanning electron microscopy (SEM) with a Jeol T 300 microscope. For thickness studies, samples were cut and mounted onto a holder, and the cross-section was observed under scanning electron microscope.

Experimental Results

Nanotube walls are very hydrophobic and, due to van der walls forces, usually tend to aggregate. Upon introduction of TOAB to nanotubes, the long-chain octyl groups of TOAB can bind to nanotube walls (hydrophobic interactions) giving an overall negative charge to nanotube surfaces (Figure 72).

Figure 72. Tetraoctylammonium Bromide Capped MWNT (Note: For Figure Clarity Nanotubes are Drawn Larger than the Polymer)
Due to charge repulsions, modified nanotubes will not aggregate, and will easily solubilize and redisperse in organic solvents. Figure 73 shows carbon nanotubes in THF before and after capping with TOAB; a uniform and stable dispersion of carbon nanotubes is obtained.

![Carbon Nanotubes in THF](image)

*Figure 73. Carbon Nanotube Suspension in THF; (a) Nanotubes in THF and (b) TOAB-Capped Nanotubes in THF*

Capping with tetraoctyl ammonium groups thus allowed electrophoretic deposition of nanotubes. When DC voltage was applied, the negatively charged nanotubes migrated towards and deposited at anode. Figure 74 shows the visual appearance of cathode and anode surfaces after continuous application of electric field.

![Electrophoretic Deposition](image)

*Figure 74. Visual Appearance of Electrodes after Electrophoretic Deposition.*
Formation of a black-colored coating on the anode surface indicates that the nanotube deposition was successful. Scanning electron microscopic (SEM) images of the cross-section further confirmed success of electrophoretic deposition (Figure 75). SEM images can also be used to estimate the deposited thickness. The estimated thickness was 25 microns after an electrophoretic deposition period of 5 hours.

Alternative Approaches to Preparation of MWNT Suspension

**MWNT-Nafion in Methanol**

5 mg of MWNT was added to 10 mL of nafion (0.5 %)/methanol (9 mL methanol + 1 mL of 5 % nafion solution), and sonicated for one hour until a uniform dispersion was obtained. The structure of nafions is depicted in Figure 76.

Application of Nanotube Coatings on Alumina Substrates

The alumina substrate was first rinsed with ethanol and dried under the fume hood. Films were cast by pouring the sonicated mixtures onto alumina substrates. The solvent formed a wet film, which was allowed to dry inside the fume hood for at least 24 hours. The partially dried film was then vacuum-dried for at least one hour at 50-60 °C.
Conductivity Measurements

In-plane conductivities were measured by the standard four-point van der Pauw method. Due to its convenience, this method is widely used in the semiconductor industry to determine the resistivity of thin samples. As originally devised by Vander Pauw, one uses an arbitrarily shaped thin plate sample containing four very small ohmic contacts placed on its periphery, preferably at the corners of the plate. A schematic of the rectangular Van der Pauw configuration is shown in Figure 70. All specimens were dried with compressed air before conductivity experiments. Following the procedures outlined in Figure 9, the two characteristic resistances $R_A$ and $R_B$ were measured by contacting the four corners of the rectangular coated sheet as shown in Figure 10. Voltage is supplied between points 3 and 4 and the resulting current flowing between points 1 and 2 is measured with a precision pico-ammeter. The characteristic resistance $R_A$ can then be calculated using the equation presented in Figure 77. Similarly, $R_B$ can be calculated by supplying an external voltage between points 1 and 4, with measurement of the resulting current flowing between 2 and 3. Using $R_A$ and $R_B$ and thickness of the coating, the resistivity of the coating can be calculated. Inverse of resistivity gives the electrical conductivity of the coating. Figure 72 shows the experimental set up used for conductivity measurements.

Figure 77. Schematic of a Van der Pauw Configuration Used for Determination of the Two Characteristic Resistances $R_A$ and $R_B$.

Figure 78. Electric Connections at Four Corners.
Experimental Results

Figure 80 shows the solubilization process for nanotubes; as shown in Figure 73(a), due to strong inter-tube attractions, nanotubes will aggregate and settle down in THF. Figure 73(b) shows that sonication yields only partial dispersion by exfoliation of nanotubes. Upon addition of TOAB, due to charge repulsions, nanotubes will not aggregate and form a uniform dispersion in organic solvents (Figure 73(c)).

Figure 80. Dispersions of Carbon Nanotubes

Formation of an overall negative charge on modified nanotube walls enables their electrophoretic deposition. When a DC voltage is applied to the suspension, the negatively charged nanotubes migrate towards anode, and deposit on the anode. Figure 81 shows the visual appearance of cathode and anode surfaces after application of electric field.
Formation of the dark coating on anode surface suggests that electrophoretic deposition of nanotubes was successful. Scanning electron microscopic (SEM) images of cross-sections further confirmed the deposition. SEM image can also be used to assess the deposited thickness, which was estimated at 25 microns after 5 hours of electrodeposition.

For the purpose of conductivity measurements, nanotube coatings should be deposited on a non-conducting or semi-conducting substrate; we used the solvent-evaporation casting method to apply the nanotube coatings on alumina substrates. The nanotube suspension in nafion/methanol seems to particularly suit the solvent evaporation casting technique. Figure 82 shows the visual appearance of alumina substrate prior to and after casting and solvent-evaporation of nanotube suspension.
Resistance can be calculated based on the measured values of current using the equations given in Figure 77. Resistivity of carbon nanotube coating can be calculated from the following equation:

\[ \rho = R \times d \]

where, \( \rho \) is resistivity, \( R \) is Resistance, and \( d \) is thickness of the coating. The calculated value of resistivity is 0.045 \( \Omega \text{cm} \). Conductivity can be estimated from the following equation:

\[ \text{Conductivity} = \frac{1}{\rho} \]

The estimated conductivity of nanotube coating was 22 S/cm for the 1 micron thick coating. No detectable conductivity was obtained for the uncoated substrate. This measured value of conductivity is 100 times greater than the conductivity values previously obtained for polyaniline coatings. The process can be conveniently adapted towards application of ultra-thin conductive coatings.

5.7 Development of Nanostructured Rectifier Titania Coatings through Electrophoretic Deposition

Introduction to Electrodeposition of Titania

The rectifier ensures that transport of mass to sites of stress concentration is not reversed due to reversed (cyclic) loading conditions. The rectifier developed in this investigation comprises modified titania nanoparticles processed into a thin coating via electrophoretic deposition. The uniformity and integrity of nanostructured titania coatings was confirmed through scanning electron microscopy.

Thin titania coatings are considered here as rectifier layers to be applied on piezoelectric coatings. The electrolytic suspension used for electrodeposition of rectifier coating contains nanocrystalline TiO\(_2\) particles at pH = 1.5. This pH value is well below the pH for zero charge of TiO\(_2\) (pH = 6.2), and thus the particles are expected to be positively charged by adsorbed protons. On the other hand, when TIP is dissolved in absolute EtOH and H\(_2\)O is added, a yellow solution is obtained due to the formation of peroxtitanium complexes, which prevent condensation of Ti cations. In the electrolytic suspension at pH 1.5, these complexes are also positively charged and their main components are dinuclear species. The existence of positive charges also impedes the adsorption of such titanium soluble species on the TiO\(_2\) electrodeposits.

Electrolysis was carried out by applying a constant cell voltage higher than 2.0 V between the electrodes, trying to induce two parallel electrodeposition processes (cathodic and electrophoretic) on the Al cathode. At these high cell voltages, both processes also compete with the fast electrogeneration of OH\(^-\) from the reduction of dissolved oxygen, and/or the depletion of protons by their reduction to hydrogen gas. Hence, when the positively charged peroxtitanium complex reaches the vicinity of the cathode, where pH is basic due to the presence of electrogenerated OH\(^-\) ions, it reacts with the precipitation of an insoluble peroxtitanium hydrate, TiO\(_3\)(H\(_2\)O)\(_x\) (1 < x < 2). In addition, the positively charged TiO\(_2\) nanoparticles move electrophoretically towards the cathode, being codeposited with the above-mentioned peroxtitanium hydrate. Electrodeposited TiO\(_2\) films thus obtained were white, as expected when no peroxo species are present (at least not in any significant proportion). This point was confirmed by the
high stability of the films when treated with strong acidic solution (HNO₃ or HCl) at room temperature. It can then be inferred that during the electrolytic process, the insoluble TiO₃(H₂O), decomposes, probably by cathodic reduction, and for this reason it is not present in the final TiO₂ electrodeposit. It is noteworthy that the yellow color of the suspension faded away as the electrodeposition process took place, while the pH of solution remained practically constant throughout the electrolysis process (near 1.5), indicating that all the soluble peroxo species were consumed in the process.

Materials

Titanium dioxide P25 (TiO₂ P25, 80 % anatase, 20 % rutile) was kindly supplied by Degussa. Tetraisopropyl orthotitanate (TIP) was purchased from Alfa Aesar. Nitric acid (HNO₃, 52.5 %), absolute ethanol (EtOH) and concentrated hydrogen peroxide (H₂O₂, 30 wt % in H₂O) were purchased from Aldrich. These chemicals were used without further purification. All solutions were prepared using distilled water.

Experimental Methods

Preparation of the Suspension for Electrodeposition

Several procedures were attempted to prepare a stable electrolytic suspension until an effective approach was identified. In this approach, 0.375 g TiO₂ P25 (4.70 mmol) was ultrasonically dispersed in 25 mL of H₂O for 2 min, and 360 µL of HNO₃ (4.71 mmol) was added afterwards. Subsequently, 209 µL TIP (0.680 mmol) was dissolved in a mixture of 25 mL of EtOH and 70 µL of concentrated H₂O₂ (0.680 mmol). The solution of TIP was added drop-wise to the suspension of TiO₂ P25, and the resulting suspension was homogenized by sonication for 10 min. The electrolytic medium thus obtained has a pH of 1.5, being stable at 298 K for more than 10 hours without separation of the TiO₂ powder.

Electrolytic Cell and Electrode Cleaning

The electrodeposition processes were carried out in an open, polypropylene support containing different compartments for electrodes. Electrodes were clamped in the polypropylene mold, and the mold was placed on a container of the suspension. Two electrodes, platinum (platinum-coated niobium mesh) anode and aluminum cathode, were placed parallel to each other at 1 cm spacing. The dimensions of cathode and anode were 2.8 cm length × 2 cm width and 5 cm x 5 cm, respectively. Before initiating the electrodeposition process, cathode was polished with a SiC paper and then sonicated sequentially with distilled water, ethanol, acetone and Milli-Q water; it was subsequently dried and then subjected to ozone cleaning. All electrolysis experiments were conducted in the potentiostatic mode using a constant voltage/current DC power supply. A constant cell voltage of 3.5 V was applied between the electrodes as shown in Figure 83. The electrolytic suspension was not stirred, and its temperature was maintained at 298 K. After each electrodeposition trial, the coated aluminium foil was removed from the cell, rinsed several times with Milli-Q water to eliminate the residual components of suspension, and dried in an open atmosphere to a constant weight. The weight of electrodeposited TiO₂ was then determined as the mass difference between the coated and uncoated cathode.
Characterization Techniques

The surface morphology and thickness of the films were studied by scanning electron microscopy (SEM) using a Jeol T 300 SEM. For thickness studies, samples were cut and mounted onto a holder, and cross-sections were observed under SEM. Thickness of the deposited film may also be estimated from weight gain after deposition.

Characterization of Rectifier Properties

Titania coatings were covered with a piece of aluminum sheet, avoiding direct contact with the substrate aluminum sheet. The substrate will act as one electrode, and the aluminum piece that covers titania coating acts as the other electrode. One sheet was connected directly to the power supply, and the other was connected through a pico-ammeter as shown in Figures 84 and 85. A constant voltage was applied across the thickness, and current flow though the setup was measured using a pico-ammeter. The alligator clips were then switched and current flow through the thickness was measured in the opposite direction.
Figure 84. Schematic Drawing of the Rectifier Film Experimental Setup

Figure 85. Experimental Setup for Measurement of the Rectifier Properties of Titania Coating

Experimental Results

The surface appearance of the aluminum sheet changed after electrophoretic deposition of titania nanoparticles (Figure 86). Cross-sectional SEM images (Figure 87(a)) were used to estimate the thickness of the electrodeposited titania coating. The film thickness was found to be about 45 μm. Planar SEM imaged (Figure 80(b)) confirmed complete coverage of the surface with electrodeposited titania nanoparticles.
Figure 86. Visual Appearance of Aluminum Sheets Before and After Electrophoretic Deposition of Titania Nanoparticles
Application of a constant voltage of 20 V across the thickness of titania coating generated 3.5 nA current in one direction; in the opposite direction, the generated current was close to zero. This confirms that the titania coating provides rectifying attributes. The relatively thick (45 micron) titania coating, however, has a relatively high electrical resistance in the conductive direction.
CHAPTER 6

INTEGRATION OF THE PIEZOELECTRIC AND SOLID ELECTROLYTE CONSTITUENTS OF ADAPTIVE COMPOSITE MATERIALS

6.1 Initial Trials of Integration of the Piezoelectric and Solid Electrolyte Constituents

6.1.1 Integrated Structure with Piezo PVDF and PVDF-HFP Solid Polymer Electrolyte Coating

Introduction

Experimental studies were conducted in order to validate the possibility of developing an integrated piezoelectric/solid electrolyte coating system within which the piezo-driven electrolytic phenomena can occur to render adaptive effects by enhancing the mechanical attributes of highly stressed areas. For this purpose, first the piezoceramic PZT coating was applied on a copper sheet substrate following the procedures outlined above. A solid electrolyte PVDF-HFP, with 9% copper (salt) concentration, was then applied onto the piezo-coated substrate. Piezo-driven electric mass transport in this hybrid coating was then investigated through local application of stress on the hybrid coating system.

Materials

The raw materials used for development of solid electrolyte coating system included poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (pellets, 15% HFP, average $M_w \sim 400,000$), ethylene carbonate (EC, 98%), propylene carbonate (PC, 99%), copper (II) trifluoromethanesulfonate (CuTf, 98%), and tetrahydrofuran (THF, 99.9+% HPLC grade, inhibitor free). All materials were purchased from Aldrich, and were used in as-received condition. Piezoelectric polymer sheet, AIRMAR PiezoLEX™ PVDF (Polyvinylidene Fluoride) was purchased from AIRMAR Technology Corporation, New Hampshire.

Experimental

Application of Solid Electrolyte Coating on the Piezo-Coated Substrate

A copper sheet substrate was first subjected to sol-gel processing for application of the piezoceramic PZT coating, as described above (see Figure 43). The materials and procedures used for application of the solid electrolyte coating are reviewed below.

The raw materials used for development of the solid electrolyte coating system included poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (pellets, 15% HFP, average $M_w \sim 400,000$), ethylene carbonate (EC, 98%), propylene carbonate (PC, 99%), copper (II) trifluoromethanesulfonate (CuTf, 98%), and tetrahydrofuran (THF, 99.9+% HPLC grade, inhibitor free). All materials were purchased from Aldrich, and were used as purchased.

PVDF-HFP was dissolved in THF (30% by weight, 3 g) at moderately elevated temperature (60 °C). EC, PC and CuTf were then added, and dissolved well until a uniform solution was obtained. Subsequently, the proportion of CuTf was increased (final weight of 5.452 g), and the amounts of plasticizers reduced as follows: EC (final weight of 1.174 g) and PC (final weight of 0.5955 g); the total percentage of EC, PC and CuTf was maintained at 70%. All materials were dissolved in THF/PVDF-HFP until a uniform solution was obtained, comprising the solid electrolyte with 9% concentration of copper ions.
The THF solution containing CuTf, EC and PC was cast onto the piezo-coated substrate, and the THF solution was allowed to evaporate; this casting and drying process was repeated to form a uniform coating of solid electrolyte. Figure 49a shows the system comprising the copper sheet substrate with hybrid piezoelectric/solid electrolyte coating system.

In order to verify piezo-driven mass transport within solid electrolyte (under stress gradient), the coated sheet was subjected to local stress application at a frequency of 3 Hz over a period of 24 hours. As shown in Figure 49b, there appeared a visual distinction between the stressed and unstressed areas, which could be attributed to the electrolytic transport of copper from the unstressed zone to the stressed where they were deposited (which is the phenomena used in our approach to render adaptive effects). This visual observation was further confirmed by conducting hardness tests (ASTM D 2240) at unstressed and stressed areas. The average hardness values were 39 and 65 shore A (ASTM D 2240) for unstressed and stressed areas, respectively. This finding confirms the ability of the integrated piezoelectric/solid electrolyte system to yield piezo-driven mass transport phenomena which cause mechanical strengthening of the highly stressed areas. The final system configuration (Figure 88) would apply this hybrid coating system onto the reinforcing fibers used in composites.

![Image](Unstressed Stressed 5 mm)

**Figure 88. Piezo-Driven Electrolytic Mass Transport in Integrated Piezoelectric/Solid Electrolyte Coating Subjected to Stress Gradient.**

6.1.2 Integrated Wire Embedded System with Piezoelectric and Solid Electrolyte Coatings

*Introduction*

Hybrid piezoelectric/solid electrolyte coatings were applied on a metal wire, which was introduced as reinforcement within a polymer matrix. Introduction of damaging effects which cause local stress rise was shown, under stress application, to prompt electrolytic mass transport towards damaged area where signs of mechanical strengthening effects were detected. Alternatively, the piezoelectric and solid electrolyte constituents rendering adaptive effects were introduced within a biomimetic cellular structure with mimics not only the adaptive features but also the structure of bone. Under repeated application of stress gradient, this biomimetic structure exhibited signs of mass transport from unstressed towards highly...
stressed areas. The lessons learned from both the hybrid fiber coating and the cellular implementations of the adaptive principles are now being used to enhance both these architectures for development of adaptive structures.

**Materials**

2-methoxy ethanol (99.3 % ACS reagent grade), lead (II) acetate trihydrate, were purchased from Aldrich. Zirconium n-propoxide 70 % (w/w) and titanium (IV) isopropoxide 97 % were purchased from Alfa Aesar. Copper sheet and copper wire were purchased from McMaster and used used after cleaning with distilled water. All the chemicals were used as without further purification.

**Experimental**

**Synthesis of Piezoelectric Coating on Copper Wire via Sol-Gel Processing**

**Procedure for Preparation of Complex Alkoxide Sol**

1 M metal organic solution was synthesized by dissolving lead acetate trihydrate, titanium isopropoxide and zirconium n-propoxide in methoxyethanol and 5 % (by volume) propanoal. Methoxyethanol (boiling point 125 ºC) was used as the solvent to facilitate dehydration by boiling. Lead acetate trihydrate (18.9665 g) was added to 50 mL of methoxyethanol. Lead acetate was dissolved by boiling at 125 ºC for 30 minutes for removal of water. (During this time the solution needs to be stirred all the time to facilitate dissolution). Then dehydrated solution was immediately cooled to 90 ºC and added zirconium n-propoxide (16.378 g) and titanium isopropoxide (14.194 g) in 50 mL of methoxyethanol. Then the solution was raised to the boiling point (125 ºC) to promote complexation and the elimination of alkylacetates, which were by-products of the reaction. Then added 5 mL of propanol and solution was diluted 100 mL by adding methoxyethanol.

**Coating of PZT on Copper Wire**

Copper wire was cleaned, dried and weighed. The prepared sol was cast on copper wire by immersing the wire in sol and letting the excess sol drop from the copper wire (Figure 89). Then coating was baked at 300 ºC for 15 minutes, and annealed at 600 ºC for one minute. This process forms a film composition of PbZr_{0.5}Ti_{0.5}O_{3} (PZT- Lead zirconate titanate). This casting, baking and annealing procedure was repeated 20 times to build a relatively thick piezoceramic coating (with 6 µm thickness) on the copper wire.
Poling of the PZT Coating on Copper Wire

The PZT coating was removed from one end of the wire, with the exposed copper surface acting as an electrode during poling and measurement of piezoelectric response. The coated part of the copper wire was wrapped with a copper shim in such a way that copper sheet and exposed copper did not short during voltage application. The wrapped copper sheet acts as the outside electrode for voltage application during poling. For the purpose of poling the piezo-ceramic coating, as shown in Figure 90, the coated copper wire was connected to a constant-voltage power supply the through two electrodes (the wrapping copper shim and the exposed end of the wire), and was subjected to an external voltage of 12 V for ~15 minutes at room temperature. This voltage was selected based on the past experience reported in the literature, suggesting that 2 V should be applied for each micron of PZT thickness.
As a first step to verify the piezoelectric response of the PZT coating applied on copper wire, the coated wire was wrapped in a copper shim (as done during poling), and was sandwiched between two rubber sheets. This set-up was subjected to repeated stress application in a servo-controlled hydraulic test system, with the piezoelectric response monitored with an oscilloscope (see Figures 91 and 92). The PZT coating on wire exhibited a desirable piezoelectric response, with output voltage approaching 1 volt without any damage to the 7 µm thick coating.
Measurement of Piezoelectric Response under Extension

We also measured the piezoelectric response of PZT coated wire by pulling the wire with constant stress. PZT coated copper wire was attached to the load cell through a constant force spring of 20 LB capacity as shown in Figure 93. The PZT coated wire was wrapped with a copper shim which acts as an electrode during voltage measurement, with the open end of copper wire acting as the other electrode. Cyclic stress was applied, and the output voltage was measured with an oscilloscope (Figure 94).
After measurement of piezoelectric response, a solid electrolyte coating was applied on the PZT-coated wire, and the wire was embedded in polymer matrix in order to verify the adaptive effect in the context of an axially loaded wire reinforced polymer.

**Synthesis of Solid Electrolyte Coating on the PZT-Coated Copper Wire**

The raw materials used for development of solid electrolyte coating system included poly(vinylidine fluoride-co-hexafluoropropylene) (PVDF-HFP) (pellets, 15 % HFP, average $M_w \sim 400,000$), ethylene carbonate (EC, 98 %), propylene carbonate (PC, 99 %), copper (II) trifluoromethanesulfonate (CuTf, 98 %), and tetrahydrofuran (THF, 99.9 +% HPLC grade, inhibitor free). All materials were purchased from Aldrich, and were used in as-received condition.

PVDF-HFP was dissolved in THF (30 % by weight, 3 g) at moderately elevated temperature (60 °C). EC, PC and CuTf were then added, and dissolved well until a uniform solution was obtained. Subsequently, the proportion of CuTf was increased (final weight of 5.452 g), and the amount of plasticizers was reduced as follows: EC to final weight of 1.174 g, and PC to final weight of 0.5955 g, while keeping the total percentage of EC, PC and CuTf at 70 %. All materials were dissolved in THF/PVDF-HFP until a uniform solution was obtained, comprising the solid electrolyte with 9.5 % copper ions.

The PZT-coated copper wire was immersed in a THF solution containing CuTf, EC and PC, and was then removed with THF allowed to evaporate. This dip coating procedure was repeated several times until a relatively thick coating of few micron thicknesses was developed. Figure 95 shows the dip coating procedure.
Figure 95. Dip Coating of Solid electrolyte; (a) PVDF-HFP Polymer Solution Containing Copper Ions; and (b) After Immersion of PZT Coated Copper Wire in Polymer Solution for Coating.

Embedment of the Wire with Hybrid Coating in Polymer Matrix

The copper wire with Piezoelectric and solid electrolyte coatings was embedded in an epoxy matrix through casting within a Teflon mold. The wire with hybrid coating was fixed at mid-height of the mold. The mold had received a spray of release agent (Chemlease 88 purchased from ADTECH) with time allowed for the solvent to evaporate. The epoxy mixture was prepared by thoroughly mixing Tech Coat Resin (EC-428) (100 g) with hardener (EC-428) (8.5 g). Epoxy resin-hardener mixture was cast in the two part mold containing the wire. (Figure 96), and left for 24 hours for curing. The specimen was then removed from the mold for experimental evaluation.
Figure 96. Various Stages of the Fabrication of PZT-Solid Electrolyte Coated Wire Embedded in Epoxy Resin; (a) Teflon Mold, (b) Wire Inserted Teflon Mold, (c) Epoxy Resin Filled Teflon Mold  and (d) Wire Reinforced Epoxy Specimen After Removing from the Mold.

Stress Application on Wire Reinforced Epoxy

The specimen was prepared for mechanical testing using the set-up schematically presented in Figure 97. This set-up subjects the coating to stress gradient (with peak stress occurring at the notch); the adaptive effect is anticipated to transport mass towards the notch (where stress concentration occurs), causing strengthening of the highly stressed notch area.

A 2 mm notch was cut on either side of the wire reinforced epoxy specimen as shown in Figure 98(a). Then wire embedded specimen was clamped between two stainless steel plates as support (Figures 98(b) and 98(c)). The specimen was then sandwiched between two steel plates, with compression springs (three springs each having 85 lb capacity) fixed on top plate.
Figure 97. Schematic Presentation of the Test Set-Up.

(a) Wire Embedded Specimen
(b) Compression Springs
(c) Wire with Hybrid PZT/Solid Electrolyte Coating

Figure 98. (a) Wire Reinforced Epoxy System after Making 2 mm Notches on Both Sides of the Specimen, (b) Specimen Clamped Between two Stainless Steel Plates and (c) Whole Compression Set-Up with Compression Springs for Repeated Load Applications.

The wire reinforced epoxy specimen was placed within a servo-controlled hydraulic loading system, and repeated loads of 250 N peak level was applied as shown in Figure 99.
Figure 99. (a) Test Set-UP for Application Stress, and (b) Enlarged View of the Wire Reinforced Epoxy Specimen Under Compression Springs.

Experimental Results

Figures 100 and 101 present the visual and microscopic images of the copper wire before and after coating with PZT and subsequent annealing. Figure 100 presents the visual appearance of the copper wire coated with PZT prior to (Figure 100(a)) and after (Figure 100(b)) coating with solid electrolyte.

Figure 100. Visual Appearance of Copper Wire (a) Before and (b) After Coating with PZT.
The piezoelectric response of PZT coating was confirmed under axial load, with a peak output voltage of 0.3 V recorded under both tension and compression.

The composite specimen comprising the wire with hybrid coating embedded within epoxy matrix is shown in Figure 103(a) (prior to application of the notch). Figure 103(b) shows the visual appearance of the notched specimen just before repeated stress application.
After stress application, the wire reinforced epoxy specimen was cut along the axis of load application (across on thickness) adjacent to the PZT/solid electrolyte-coated copper wire (Figure 104). Each half was investigated visually and under microscope for signs of mass transport towards the highly stressed notch area. Figures 104(a) and 104(b) show visual appearances of the cross-section of wire reinforced epoxy specimen. Microscopic images of the cut specimen are depicted in Figure 98.
Figure 104 (c) Close View of Cut Section of the Wire Reinforced Epoxy Specimen.

Deposition of Substance
6.1.3 Alternative Approach to Integration of Piezoelectric and Solid Electrolyte Coatings

The work presented so far focused on incorporation of the functional constituents rendering adaptive effects (primarily piezoelectric and solid electrolyte materials) as a fiber coating system. Alternatively, the functional constituents can be introduced into the foam (core) system of sandwich composites, as shown in Figure 106.

![Figure 106. Adaptive Sandwich Composite with Functional Constituents Introduced Within the Foam Core.]

**Synthesis of Piezoelectric Coating on Aluminum Foam by Sol-Gel Process**

**Materials**

The chemicals used for alkoxide sol preparation were the same as described earlier. Substrate aluminum foams (40 pores per inch) were purchased from ERG. These foams were made from alloy 6101-F with a 6-8% density. Synthesis of the Alkoxide sol followed the procedures describe earlier in this report.

**Experimental**

Coating of PZT on Aluminum Foam
The aluminum foam was cleaned, dried and weighed. The prepared PZT sol was cast on aluminum foam by immersing the foam in sol, and letting the excess sol drop from the foam (Figure 107(a) & (b)). The coated aluminum foam was then baked at 300 ºC for 15 minutes, and annealed at 600 ºC for one minute. This process forms a film with composition of PbZr$_{0.5}$Ti$_{0.5}$O$_3$ (PZT- Lead zirconate titanate) on aluminum foam surfaces. The casting, baking and annealing procedure was repeated 20 times to build a relatively thick piezoceramic coating (with 6 µm thickness) on the aluminum foam.

Poling of the PZT Coating on Aluminum Foam

The PZT coating was removed from one side of the foam to expose the aluminum surface over a small surface area. The PZT-coated aluminum foam was sandwiched between copper shims (Figure 108(d)). These copper shims are placed in such a way that they do not short during voltage application; they act as electrodes during poling. Rubber sheets were placed on top and bottom sides of the foam away from the copper shim. The foam was then tightly wrapped with tape to provide good contacts between the electrode and PZT coating, and also between the other electrode and exposed aluminum surface. For the purpose of poling, the piezoceramic coated, aluminum foam was connected to a constant-voltage power supply through two copper electrodes (placed on top and bottom of the PZT-coated foam), as shown in Figures 108(c) and 108(d), and was subjected to an external voltage of 12 V for ~15 minutes at room temperature. This voltage was selected based on the past experience reported in the literature, suggesting that 2 V should be applied for each micron of PZT thickness.

Figure 108. Sol-Gel PZT Coating and Subsequent Poling.
(a) PZT Alkoxide Sol, (b) Immersion of Aluminum Foam in PZT Sol for Coating, (c) Experimental Set-Up for Poling the Piezo-Ceramic Coating on Aluminum Foam and (d) Close View of the PZT Coated Aluminum Foam Sandwiched Between Copper Electrodes.
Casting of Solid Electrolyte on PZT-Coated Aluminum Foam

Solid polymer electrolyte (PVDF-HFP, 30 % by total weight) containing copper salt (CuTf) and plasticizers (EC & PC) was prepared in THF as described earlier in this report. The PZT-coated aluminum foam was dipped in the THF/PVDF-HFP/CuTf/EC/PC solution, and was then removed and allowed the THF to evaporate. This dip coating procedure was repeated several times until a relatively thick coating (few micron thicknesses) was developed. Figure 109 shows the dip coating procedure. Once the desired thickness was reached, the foam was dried in oven at 60 ºC for one hour in order to remove THF via evaporation.

Gradient Stress Application on PZT/Solid Electrolyte-Coated Aluminum Foam

The PZT/solid electrolyte-coated aluminum foam was sandwiched between two rubber sheets and metal plates. Repeated stress was applied only on half of the foam, with the other half remaining unstressed during the test (Figure 111). The foam density was measured prior to gradient stress application.

Figure 109. (a) Solid Electrolyte Solution, and (b) Immersion of Aluminum Foam in Solid Electrolyte Mixture for Coating.

Figure 111. Test Set-Up for Application of Stress Gradient (a) Just Before Stress Application and (b) During Stress Application.
Investigation of Mass Transport under Stress Gradient

After application of stress gradient, the foam was cut into two (stressed and unstressed) halves. The two halves were investigated under microscope in order to detect any indication of electrolytic mass transport towards the stressed half. The density and surface hardness of each half were also measured.

Mechanical Test

Hardness tests were conducted on the PZT/solid electrolyte coated foam (Figure 112) before and after repeated stress applications. After stress application, each half of the foam was also subjected to hardness tests.

Experimental Results

Figure 113 shows the visual appearance of the aluminum foam before (Figure 113(a)) and after (Figure 113(b)) coating with PZT and annealing. Microscopic images of the uncoated and coated foams (prior to and after coating and firing) are presented in Figure 114.
Figure 113. Visual Appearance of Aluminum Foam (a) Before and (b) After Application of Piezoelectric Coating, Followed by Annealing.

Figure 114. Microscopic Images of (a) Bare Aluminum Foam and (b) After PZT Coating and Annealing.

Figures 115 and 116 present the cut halves of aluminum foam with hybrid PZT/solid electrolyte coating.

Figure 115. Visual Appearance (Cut-Section View) of the Cut Halves of PZT/Solid Electrolyte-Coated Foam (a) Stressed Half and (b) Unstressed Half.
Density of the PZT/solid electrolyte-coated aluminum foam prior to stress gradient application was 1.0022 g/cm\(^3\). The density of the stressed half of the foam after stress application was 1.0039 g/cm\(^3\), and that of the unstressed half of foam 1.0003 g/cm\(^3\). Hence, the density of the unstressed half of the foam was lowered while that of the stressed half was raised. This early indication supports the adaptive features of the system. On-going improvements of this system emphasize use of piezoelectric coatings that do not require poling, noting that the complex geometry of the coating applied on an open-cell substrate complicates the poling process.

The hardness test data generated in this investigation were not conclusive. The device utilized here was not capable of measuring the hardness value of a thin coating while mitigating the effects of substrate. The measured values of hardness did not show any difference between the stressed and unstressed halves of the coated foam.

6.2 More Successful Studies of Mass Transport Under Stress Gradient of Different Integrated Systems with Piezoelectric and Solid Electrolyte Constituents

Several integrated systems embodying piezoelectric and solid electrolyte constituents were evaluated experimentally. The integrated systems employ the piezoelectric effect in a non-conventional way, relying on stress gradient to generate piezo-induced potential and charge on the same face of piezoelectric coatings/sheets. More conclusive experimental evidence was generated for successful integration of the functional (piezoelectric and solid electrolyte) constituents rendering adaptive effects in the context of a cellular structure. Convincing experimental observations were made of electrolytic transport of mass toward and its deposition at locations subjected to elevated compressive stress. System architectures other than cellular structures were also investigated further. Initial steps were taken toward development of an energy-based theoretical framework for design of adaptive composites. This approach acknowledges the prevalence of energy criteria in determining damage growth and catastrophic failure of composites.
6.2.1 Integrated System Comprising 1-3 Piezoelectric Composite and Solid Polymer Electrolyte Materials

**Piezoelectric Composite**

Piezoelectric composites are manufactured by Smart Material Corporation, and are typically used for ultrasonic and acoustic control applications. The 1-3 piezoelectric composite used in this investigation contains piezoelectric fibers embedded in a polymer matrix and aligned along the thickness of the composite. Figure 117 shows this arrangement of fibers within the piezoelectric composites, where the active fibers can be either rectangular (80 microns with 120-micron spacing) or round (70 micron diameter with 50 micron spaces) in cross-section.

![Figure 117. 1-3 Composites by Smart Materials Corporation; (a) Rectangular Fibers and (b) Round Fibers.](image)

The 1-3 notation refers to the connectivity pattern for this particular arrangement of fibers and the surrounding matrix material. Specifically, the piezo-ceramic constituent is continuous in one direction, i.e. through the thickness, while the matrix material is connected in all three orthogonal directions. Once the piezoceramic fibers have been formed, the remaining space is filled with a polymer matrix material that protects the brittle fibers from accidental breakage. Metal electrodes are then bonded to the ends of the fibers, and are first used to polarize the piezoceramic at an elevated temperature, and then to collect the piezo-induced charge from the composite.

**Solid Electrolyte**

The materials used in the preparation of solid electrolytes include poly(vinylidine fluoride-co-hexafluoropropylene) (PVDF-HFP), copper (II) trifluoromethanesulfonate (CuTf, 98 %), propylene carbonate (PC, 99 %), ethylene carbonate (EC, 98 %) and tetrahydrofuran (THF, 99.9 +% HPLC grade, inhibitor free). All chemicals were purchased from Aldrich and used without any further purification.

PVDF-HFP was dissolved in THF (30 % by weight, 3 g) at moderately elevated temperature (60 °C). Subsequently, CuTf (1.8084 g), EC (3.5224 g) and PC (1.7865 g) were added to the mix (70 % by weight at CuTf:EC:PC ratio of 1.0:8.0:3.5) and dissolved until a uniform solution was obtained.

**Experimental**
Evaluation of the Piezoelectric Properties of 1-3 Composite

The piezoelectric composite was sandwiched between two copper sheets (electrodes), which were connected to the oscilloscope probe during voltage measurements. This setup was sandwiched between two rubber sheets to protect the piezo-composite from damage during stress application. This assembly was tightly wrapped and placed on the bottom plate of a servovalve-controlled hydraulic loading system (Figure 118). Repeated stress was applied, and voltage output was observed. Under 500 N load application, the measured voltage was 14.2 V, which confirms the strong piezoelectric response of the composite. The structural qualities of toughness and strength, complemented with strong piezoelectric effect are the distinguishing features of the piezoelectric composite sheet.

![Oscilloscope](image)

Figure 118. Experimental Set-Up for Measurement of Piezoelectric Response

Application of Solid Polymer Electrolyte Coating to the Piezoelectric Composite

The electrode (gold plating) was removed from the cathode (negative) face of the piezoelectric composite by etching. The surface was then cleaned well with distilled water and then ethanol, and dried in air. Figure 119 shows the surface appearance of the 1-3 composite before (a) and after (b) removal of the electrode.
Figure 119. Surface Appearance of 1-3 Composite (a) With Electrode and (b) After Removal of the Electrode

The PVDF-HFP/CuTf/EC/PC solution (in THF) was cast on the cathode face of the piezoelectric composite (care was taken to avoid dripping of the solid electrolyte coating onto the anode face). The solid electrolyte coating was left in air for solvent to evaporate. This process was repeated until a uniform coating of solid electrolyte with targeted thickness was obtained. This coating was allowed to dry overnight for complete removal of the solvent (Figure 120).

Figure 120. Surface Appearance of 1-3 Composite with Solid Electrolyte Coating.

Local Stress Application and Evaluation of Mass Transport under Stress Gradient: First Trial

The integrated system comprising solid electrolyte applied on one face of the piezoelectric composite sheet was sandwiched between two protective rubber sheets. Local stress was applied at the center of the integrated specimen (as shown in the Figure 112) on solid electrolyte coating side. After one week of stress application specimen was detached from the set-up and observed under the microscope for movement of material.
Figure 121. Local Stress Application on the Integrated System.

Figure 122(a) shows the surface appearance of the integrated specimen after an extended period of repeated stress application. The composite specimen was sectioned (using water jet) along perpendicular centerlines (Figure 122(b)). Water jet cutting was employed to minimize any effect on the specimen. The cut surfaces (cross-sectional views) were investigated under SEM and light microscopes to detect mass transport under stress gradient.

Figure 123 shows the light micrographs of the loaded and unloaded ends of the sectioned specimens, and Figures 124 and 125 show enlarged views of the sections near loaded area. While a denser structure is observed towards the stressed face, this first-trial effort did not provide a solid evidence for copper deposition under stress gradient. A second trial with refined loading condition was subsequently implemented, as discussed below.
Figure 123. Cross-sectional View (a) Loaded Area of the Specimen and (b) Unloaded Area.

Figure 124. Cross-sectional Views of the Integrated Specimen at the Loaded End.
Local Stress Application and Evaluation of Mass Transport under Stress Gradient: Second Trial

A specimen similar to that introduced above was produced, comprising piezoelectric composite sheet and solid polymer electrolyte coating. The test set-up was also similar to that introduced above, except that the specimen was placed in upside-down position (with load applied onto the piezoelectric sheet in lieu of the solid electrolyte).

As a first step, an oscilloscope was used to measure the piezo-induced potential gradient which develops in the system under the applied stress gradient (see Figure 126). The measured value of electric potential developed between loaded and unloaded areas of the piezoelectric composite sheet (on the same cathode face) was 2 V. This electric potential is sufficient for the piezoelectric effect to drive electrolytic mass transport within solid electrolyte.
The integrated system comprising the piezoelectric composite sheet with solid electrolyte coating was then subjected to repeated local stress application. Observation of the specimen prior to and after loading provided the first solid evidence that copper deposition can occur within integrated systems, driven by potential gradient on the same face of piezoelectric sheet. Figure 127 shows the visual appearance of the solid electrolyte coating prior to and after local stress application. Copper deposition towards the edges away from the area of load application was observed. The microscopic images of deposited copper are depicted in Figure 128.

Figure 127. Visual Appearance of the Solid Polymer Electrolyte Prior to and After Repeated Load Application at the Center.

Figure 128. Microscopic Image of Solid Polymer Electrolyte after Stress Application.
6.2.2 Integrated Cellular Foam with Hybrid Piezoelectric/Solid Electrolyte Coating

In this experiment, the cellular structure was subjected to stress gradient and electrolytic transport of mass toward and its deposition at stressed area was confirmed through microstructural observations. Given the significance of this finding, replicated tests were conducted to ensure the validity.

Materials

Zinc oxide (ZnO) nanoparticles were purchased from Inframat Advanced Meterials. Polyethyleneimine, branched, M.W. 70,000 (PEI, 30 % by weight) was purchased from Alfa-Aesar. A 2.5” X 2.5” cylindrical platinum-clad niobium anode was designed by Larry King Corporation. A 1” x 1.25”x 1.25” block of 40 PPI, Duocel Aluminum Foam (6101-T6) alloy, 6-8 % density, purchased from ERG Materials and Aerospace Corporation, Oakland, CA. The cellular structures served as cathode during electrophoretic deposition.

Experimental
Preparation of the Suspension for Electrodeposition

5 % w/v ZnO and 2 % w/v PEI were added to the required amount of distilled water and sonicated for 10 minutes. The pH of the solution was then adjusted to 10, and the solution was stirred overnight at room temperature. A homogeneous white solution was obtained. During deposition solution was checked everyday for separation of solid as well pH of the solution.

Electrophoretic Deposition of ZnO on Cellular Substrates

Cylindrical platinum-clad niobium expanded mesh was used as anode, and aluminum or copper foam was used as cathode (Figures 129 and 130) where deposition takes place. The cathode and anode were fit into a specially designed propylene mold to hold the electrodes at 1.5 cm spacing, as shown in Figures 129(a) and (b). For foams, a constant current of 50 mA was applied over extended periods of time until a 50 micron thickness of ZnO coating formed on the foam.
Figure 129. (a) Anode, Cathode and Deposition Solution for Electrophoretic Deposition and (b) Electrophoretic Deposition Set-up.

Figure 130. (a) Enlarged View of Electrophoretic Cell for ZnO Deposition and (b) Top-View of the ZnO Deposition Cell
Baking and Firing of ZnO Coating

Preheating of the ZnO coating to 300 °C prior to firing gives the highest degree of crystal orientation (002) which exhibits pronounced piezoelectric effect; the peak intensity also increases with post-heating up to 500 °C, with a unique peak intensity pointing at preferred grain growth along (002) plane (Figure 122). The (002) peak intensity, however, rapidly decreases above 600 °C, where other peaks appear. Therefore, preheating to 300 °C followed by post-heating for one hour at 500 °C yields the preferred crystal orientations for piezoelectric response. Furthermore, unlike other ferroelectric materials (PVDF and PZT), ZnO has the advantage that it does not require electro-thermal poling because of its self-poling capability. This is a major advantage in our application where piezoelectric coatings can assume complex geometries.

![Figure 131. Heat Treatment Temperature on the Peak Intensity Corresponding to 002 Plane (favoring piezoelectricity).](image)

Once the desired thickness of ZnO was deposited, the coated woven metal fabric was dried with a flow of nitrogen gas, and then left overnight to dry in air at room temperature. The coating was subsequently baked at 300 °C for 10 minutes, followed by firing at 500 °C for one hour. Baking removes all the solvent water, and enables formation of a dense coating. Firing under the selected condition not only forms a dense coating, but also yields the most preferred crystal structure for pronounced piezoelectric response.

Casting of Solid Polymer Electrolyte on Cellular Substrates

The solid polymer electrolyte (PVDF-HFP, 30 % by total weight) containing copper salt (CuTf) and plasticizers (EC and PC) was prepared in THF as explained earlier. The ZnO-coated aluminum foam was dipped in the THF/PVDF-HFP/CuTf/EC/PC solution, and was then removed and allowed for THF to evaporate. This dip-coating procedure was repeated several times until a relatively thick coating (of few micron thicknesses) was developed. Figure 124 shows the dip coating procedure. Once the desired
thickness was achieved, the foam was dried in oven at 60 ºC for one hour for thorough removal THF by evaporation. After drying, the weight of specimen was recorded.

Figure 132. (a) Solid Electrolyte Solution and (b) Immersion of Aluminum Foam in Solid Electrolyte Solution for Coating.

Introduction of the Integrated System and Loading Condition
A refined version of the foam system with hybrid functional coatings was fabricated. The aluminum foam first received the (nanostructured piezoelectric) ZnO coating through electrophoretic deposition. Subsequently, a solid electrolyte coating was applied onto the ZnO coating. The specimen was subjected to compressive stress application on on-half of its area. Figure 133 shows the visual appearance of the foam after coating with different functional layers, and also after repeated stress application. The loading set-up is depicted in Figure 134.

Figure 133. Application of Functional Coatings Onto Aluminum Foam.
Measurement of Piezo-Induced Potential Gradient under Stress Gradient

In order to measure the piezo-induced potential gradient (under the applied stress gradient), after ZnO coating and sintering, conductive silver paint was applied to the two halves of the foam, preventing any contact between the conductive coating on the two halves (Figure 135). This silver paint on each half acts as an electrode; they were connected to an oscilloscope probe with wires. Repeated compressive loading was applied onto one-half of the foam specimen, and the potential difference between loaded and unloaded halves were measured (Figure 136). A similar specimen was performed using bare aluminum foam without the piezoelectric ZnO coating (Figure 137). The specimen with piezoelectric (ZnO) coating exhibited a potential difference of 4 V between loaded and unloaded areas; no similar potential difference was observed in the case of the bare (uncoated) aluminum foam.
Investigation of Mass Transport within Coated Foam under Stress Gradient

After application of stress gradient on the coated aluminum foam, it was sectioned (perpendicular to load application axis) by water jet cutting (Figure 138). The cut surfaces of the foam were investigated under microscope to detect any indications of mass transport towards stressed areas. Microscopic images of the loaded and unloaded areas of the foam with hybrid functional coating are depicted in Figure 139. After
stress application, the bulk densities of the loaded and unloaded areas were 0.512 and 0.482, respectively. Further refinement of this system is currently in progress.

![Diagram of foam sectioning configuration with hybrid functional coating](image)

**Figure 138.** Sectioning Configuration of the Foam With Hybrid Functional Coating After Load Application on Half of Its Surface Area.

![Light micrographs of cut slices of foam](image)

**Figure 139.** Light Micrographs of Cut Slices of the Foam (a) Loaded Area and (b) Unloaded Area.

Figures 140 through 143 present scanning electron microscope (SEM) images obtained from different sections of the foam. Under compressive stress gradient, the unloaded segment of foam could act as cathode (due to piezoelectric effect); mass transport towards and deposition within the unloaded region of
the cellular structure are thus expected. Further evaluation of the cellular structure after repeated application of stress gradient is currently in progress. The images captured so far could feasibly point at a denser microstructure in the unloaded region which supports cathodic deposition of matter within this region.

*Figure 140. SEM Micrograph (top view) at the Upper Region of the Foam.*

*Figure 141. SEM Micrograph (Top View) of the 2nd Layer (from top) of the Foam*
SECOND TRIAL - INTEGRATED CELLULAR FOAM ARCHITECTURE: FURTHER VALIDATION WITH DIFFERENT FOAM GEOMETRY

Relatively thin (6 mm thickness) aluminum foam was used as the scaffold for application of the functional coatings. First, piezoelectric ZnO coating was applied through electrophoretic deposition and sintering, and then the solid electrolyte was cast on the ZnO coating. The resulting foam with hybrid functional coatings was subjected to stress gradient through repeated load application at the edge of the specimen.

Materials

Materials used were same as above except for foam dimension. Same Duocel aluminum foam (6101-T6 alloy), 6-8 % density, 2” x 0.25” x 1” block of 40 PPI, was purchased from ERG Materials and Aerospace Corporation, Oakland, CA.
**Experimental**

Electrophoretic deposition of ZnO on cellular substrate followed by baking and firing was same as described earlier. Figure 144(a)- (c) show the visual appearance of the cellular substrate before and after application of the nanostructured ZnO coating.

**Evaluation of Piezoelectric Response**

After application of ZnO coating and subsequent baking and sintering, and before application of solid polymer electrolyte, we checked the piezoelectric response of the system. This was accomplished by sandwiching the piezo-coated foam with two stainless steel electrodes connected to an oscilloscope. A small load was applied to the sandwiched foam, and the output voltage was monitored on the oscilloscope. After making sure that there is a piezoelectric response, a solid electrolyte topcoat was applied on the ZnO coating.

**Casting of Solid Electrolyte on ZnO-Coated, Sintered Aluminum Foam**

The solid polymer electrolyte (PVDF-HFP, 30 % by total weight) containing copper salt (CuTf) and plasticizers (EC and PC) was prepared in THF, as explained in earlier reports. The ZnO-coated aluminum foam was dipped in the THF/PVDF-HFP/CuTf/EC/PC solution, and was then removed and allowed for THF to evaporate. This dip-coating procedure was repeated several times until a relatively thick coating (of few micron thicknesses) was developed. Once the desired thickness was achieved, the foam was dried overnight at room temperature for thorough removal of THF by evaporation. Figure 144(d) shows the visual appearance of the foam with solid electrolyte topcoat on piezoelectric coating.

*Figure 144. Visual Appearance of the Aluminum Foam; (a) prior to any coating, (b) After Coating with ZnO, (c) After Baking and Sintering of ZnO Coating, and (d) After Applying Solid Electrolyte Coating (PVDF-HFP Containing Copper Ions).*
**Application of Stress Gradient**

The aluminum foam with hybrid piezoelectric ZnO-solid electrolyte coating was sandwiched between rubber sheets and metal plates to prevent damage to foam during load application. Repeated compressive stress was applied near a corner on the foam surface, with the remainder of the foam left unstressed (Figure 145).

*Figure 145. Local Application of Stress on the Foam.*

**Investigation of Mass Transport under Stress Gradient**

After dynamic application of stress gradient for an extended period of time, the foam was removed from the test setup and observed for copper deposition at the stressed area. This experiment was quite successful; after load application, copper deposition around the stressed was obvious, with no signs of copper deposition detected away from the stressed area (Figure 146).
For further confirmation, the tested foam was observed under microscope. Figures 147 through 149 are the micrographs of the foam surfaces after repeated load applications. Microscopic images confirmed the visual observations, providing further indications of copper deposition at the stressed areas. It should be noted that the bottom side of the foam (away from the surface) was supported on a flat surface, and thus received relatively uniform stress; no copper transport and deposition was observed on this uniformly stressed (bottom) face. These results confirm that the stressed area acts as cathode (negative electrode), and attracts the positively charged copper cations. More importantly, the results indicate that the piezo-induced potential is sufficiently large to overcome frictional (ohmic) and interfacial (electrode) resistances, and that piezo-induced charge is adequate for transport and deposition of a detectable mass of copper.
Figure 147. Light Micrographs of the Stressed Area of Foam Surface.
Figure 148. Light Micrographs of the Unstressed Area of Foam Surface.

Figure 149. Light Micrographs of the (Uniformly Stressed) Bottom Face of the Foam.
THIRD TRIAL- INTEGRATED CELLULAR FOAM ARCHITECTURE: FURTHER VALIDATION WITH DIFFERENT FOAM GEOMETRY

The experiment on cellular structure subjected to stress gradient was repeated with a different foam size (1.25” x 1.25” x 1”). The sequence of sample preparation was as before, comprising: (i) electrophoretic deposition of ZnO; (ii) baking and firing of ZnO; (iii) experimental verification of piezoelectric response; (iv) application of solid polymer electrolyte via solvent evaporation; and (v) dynamic application of stress gradient. Figure 150 shows the visual appearance of the aluminum foam at different stages of the process. Figure 151 shows the foam subjected to local stress application.

Figure 150. Visual Appearance of the Aluminum Foam at Different Stages of Processing.
Figure 151. **Two Views of the Cellular Structure Subjected to Local Stress Application.**

Figure 152 shows the visual appearance of the foam prior to and after local stress application. Deposition of copper in the vicinity of the stressed corner is obvious, further confirming that the integrated cellular implementation of our inherently adaptive principles is functional.

![Visual Appearance of the Foam](image)

(a) Before Stress Application

(b) After Stress Application

Figure 152. **Visual Appearance of the Foam (a) Just Before and (b) Just after Repeated Application of Local Stress (near bottom-left corner).**
The two foam test data presented above further validate the potential for integration of active elements in the context of inherently adaptive systems. The above structures are, however, precursor systems, and further improvements are needed in the following areas: (i) the nanostructured piezoceramic coating requires further refinement to exhibit enhanced mechanical integrity (for long-term operation under severe loading conditions) and magnified piezo-induced charge (for acceleration of the inherently adaptive phenomena); (ii) the solid polymer electrolyte needs to be refined to exhibit enhanced thermo-mechanical performance; and (iii) the system efficiency may be improved through introduction of a thin-film rectifier at the interface of piezoelectric and solid electrolyte layers.

6.2.3 Validation of Inherently Adaptive Principles in the Context of Integrated Composites

Introduction

First-generation composite comprising woven metal (copper) fiber reinforcement with a nanostructured piezoelectric coating was used as reinforcement in a solid polymer electrolyte matrix. The composite comprised two layers of woven metal fiber reinforcement, and was subjected to repeated flexural loading. The resulting bending moment generated tensile and compressive stresses in the two layers. The piezoelectric effect would generate potential difference between the two layers. Microstructural investigations were conducted in order to identify electrolytic mass transport within the solid polymer electrolyte matrix towards cathode (tensile fibers).

Materials

Zinc oxide (ZnO) nanoparticles were purchased from InfraMat Advanced Materials. Polyethyleneimine, branched, \( M_w = 70,000 \) (PEI, 30 % by weight in water) was purchased from Alfa-Aesar. The raw materials used for development of solid electrolyte coating included poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (pellets, 15 % HFP, average \( M_w \sim 400,000 \)), ethylene carbonate (EC, 98 %), propylene carbonate (PC, 99 %), copper (II) trifluoromethanesulfonate (CuTf, 98 %), and tetrahydrofuran (THF, 99.9 +% HPLC grade, inhibitor free). All the materials used for synthesis of solid electrolyte coating were purchased from Aldrich, and were used in as-received condition.

Experimental Program

Electrophoretic Deposition of Nanostructured Piezoelectric Coating on Woven Metal Fabric-Preparation of Electrodes

A 5” x 7” niobium-clad platinum anode was designed by Larry King Corporation, New York. For the cathode, woven copper fibers of 100 X 100 mesh with 0.0045” wire diameter were purchased from McMaster Carr. The woven metal fabric was cut into 5” x 12” pieces, and rinsed with ethanol and water prior to electrophoretic deposition.

Preparation of the Suspension for Electrodeposition
5 % (w/v) ZnO and 2 % (w/v) PEI were added to required amount of distilled water and sonicated for 10 minutes. The pH of solution was then adjusted to 10, and the solution was stirred overnight at room temperature. A homogeneous solution with white color was obtained.

**Electrophoretic Deposition of ZnO**

The cathode and anode were fit into a specially designed propylene cell to hold the electrodes at 1.5 cm spacing (Figure 153). The woven copper fabric was connected to cathode, and a platinum-clad sheet was connected to anode. A constant current of 266 mA (0.67 mA/cm²) was applied between electrodes for an extended time period, as shown in Figure 1. Unlike our previous effort, in order to ensure uniformity of deposition on a larger surface area, the electrodes were placed horizontally, with the woven copper fabric (cathode) placed on top (Figure 154) to overcome any non-uniformity of deposition due to sedimentation. All these precautions were taken to obtain a uniform piezoelectric ZnO coating. Once the desired thickness of ZnO deposition was achieved, the coated metal fabric was taken out of the electrophoretic bath, washed well with water, and dried under a flow of nitrogen. The coated mesh had grey color. ZnO/PEI solutions were refreshed every 24 hours during electrophoretic deposition in order to assure the uniformity of piezoelectric coating thickness.

![Connections to the Power Supply](image1.png)

![Copper Mesh- Cathode](image2.png)

![Platinum Electrode -Anode](image3.png)

![Polypropylene Cell](image4.png)

**Figure 153. Enlarged View of the Polypropylene Electrophoretic Cell.**
Baking and Firing of ZnO Coating

Preheating of the ZnO coating to 300 °C prior to firing gives the highest degree of crystal orientation (002) which exhibits pronounced piezoelectric effect; the peak intensity also increases with post-heating up to 500 °C, with a unique peak intensity pointing at preferred grain growth along (002) plane (Figure 155). The (002) peak intensity, however, rapidly decreases above 600 °C, where other peaks appear. Therefore, preheating to 300°C followed by post-heating for one hour at 500 °C yields the preferred crystal orientations for piezoelectric response. Furthermore, unlike other ferroelectric materials (PVDF and PZT), ZnO has the advantage that it does not require electro-thermal poling because of its self-poling capability. This is a major advantage in our application where piezoelectric coatings can assume complex geometries.
Once the desired thickness of ZnO was deposited, the coated woven metal fabric was dried with a flow of nitrogen gas, and then left overnight to dry in air at room temperature. The coating was subsequently baked at 300 °C for 10 minutes, followed by firing at 500 °C for one hour. Baking removes all the solvent water, and enables formation of a dense coating. Firing under the selected condition not only forms a dense coating, but also yields the most preferred crystal structure for pronounced piezoelectric response.

Characterization Techniques

The surface morphology and thickness of piezoelectric coatings were investigated through scanning electron microscopy (SEM) with a Jeol T 300 microscope. For thickness measurement, samples were cut and mounted onto a holder, and their cross-sections were observed. Thickness of the deposited piezoelectric coating can also be estimated from weight of the sheet before and after electrophoretic deposition.

Preparation and Application of Solid Polymer Electrolyte

PVDF-HFP was dissolved in THF (30 % by weight, 3 g) at moderately elevated temperature (60 °C). Subsequently, CuTf (1.8084 g), EC (3.5224 g) and PC (1.7865 g) were added to the mix (70 % by weight at CuTf:EC:PC ratio of 1.0:8.0:3.5), and dissolved until a uniform solution was obtained.

The metal fabric with piezoelectric ZnO coating was cut into 1” x 7” pieces and placed within a Teflon mold; the dissolved solid polymer electrolyte solution was then poured on to the mold and left overnight for THF to evaporate (Figure 156). Subsequently, the solid electrolyte/ZnO coated metal fabrics were taken out of the mold, and placed parallel to each other with a separation of 3 mm. This set-up was fixed within the mold, and more solid electrolyte solution was poured, and left overnight for THF to evaporate. The final composite (Figure 157) with two layers of woven metal fabric reinforcement had a total thickness 10 mm.

Figure 156. Experimental Set-up for Casting the Solid Polymer Electrolyte onto Woven Metal Fabric Reinforcement.
Figure 157. Schematic Presentation of the Layers Constituting the Composite.

Figure 158. Final Appearance of the Polymer Composite Comprising Solid polymer Electrolyte Matrix with Piezo-Coated Woven Metal Fabric Reinforcement.

For the fabrication of sandwiched composite for initial load estimation, was done similarly except plain copper mesh (there was no ZnO coating) was used. Two pieces of (each 1” x 7”) copper mesh sandwiched between solid electrolyte layers as similar to previous case. Schematic diagram of the hybrid composite is shown in Figure 159.

Figure 159. Schematic Diagram Showing the Different Layers of Sandwiched Composite used for Initial Load Estimation Studies

Preliminary Assessment of the Composite Flexural Performance

Flexure tests were performed using mechanical test device as shown in Figure 160. Sandwiched specimen was placed on the steel mold as shown in Figure 160. The flexural load and deflection data were acquired during the test. Figure 161 depicts the resulting flexural load-deflection curve for the composite made with uncoated woven metal fabrics.
Figure 160. (a) Mechanical Test Set-up for Flexure Test (b) Closer View of Specimen Just Prior to the Test and (c) Closer View Just After the Flexure Test.

Figure 161. Load Deflection Curve for the Sandwiched Composite

Cross-sectional analyses were conducted considering the woven metal fabric comprises copper fibers of 110 micron diameter with center-to-center spacing of 150 micron. The specimen width was 25.4 mm, and the spacing of top and bottom woven metal fabrics was 3 mm. Cross-sectional flexural analysis indicated that, at the peak flexural load of 18 N (Figure 154) over a span of 162.5 mm, the copper fibers developed a stress of 158 MPa, which is close to the ultimate tensile strength of copper. This result indicates that the composite is performing satisfactorily in flexure, mobilizing the tensile and compressive load-carrying capacity of its (woven metal fabric) reinforcement.
Experimental Evaluation of the Functional Attributes of the Composite

Tests were conducted in order to investigate electrolytic mass transport (driven by the piezoelectric effect) in the composite with piezo-coated reinforcement. Tests were conducted under repeated flexural loading. As a first step, the composite was subjected to flexural loading (Figure 162) in order to determine its elastic loading limit. This step enabled selection of a safe level of flexural load (and deflection) for repeated application to the composite. The composite specimen was clamped between end rubber grips, over a 6.5” span (Figure 163). Repeated flexural deformation was applied at mid-span with a frequency of 78 cycles per minute. After testing, multiple cross-sections of the composite specimen were subjected to microstructural studies for observation of electrolytic mass transport.

Figure 162. Test Set-Up for Assessment of Elastic Load and Deflection Limits.

Figure 163. Test Set-Up for Repeated Application of Flexural Deflection.
After repeated application of flexural deflections, the composite specimen was sectioned following the configuration of Figure 164 (by water-jet cutting). The cross-sections were observed under both scanning electron and optic microscopes in order to detect any mass transport driven by piezoelectric effect under (flexural) stress gradient. The oppositely stressed (and thus charged) woven metal fabrics act as electrodes in this electrolysis process.

Figure 164. Sectioning Configuration of Composite Specimens after Repeated Flexural Loading.

Results of Microstructural Investigations

Figure 165 shows the visual appearance of the woven metal fabric before and after application (and subsequent firing) of piezoelectric ZnO coating.

Figure 165. (a) Visual Appearance of Woven Metal Fabric Prior to and (b) After Application (and Sintering) of Piezoceramic Coating.

Figure 166 shows the Scanning Electron Microscope (SEM) images of uncoated and (piezoelectric) ZnO-coated woven metal fabrics.

Figure 166 shows the Scanning Electron Microscope (SEM) images of uncoated and (piezoelectric) ZnO-coated woven metal fabrics.
Figure 166. SEM Micrographs of Uncoated and ZnO-Coated Fabrics at (a) Lower and (b) Higher Magnifications.

Figure 167 shows more SEM micrographs of the ZnO-coated and uncoated woven copper fabrics.

Figure 167. SEM Micrographs of (a) Cross-sectional View of ZnO-Coated (after Firing) Woven Copper Fabric (b) Cross-sectional View of Uncoated Copper Fabric (c) Cross-sectional View of ZnO-Coated Fabric at Lower Magnification and (d) Top View of Uncoated Copper Fabric.
Figures 168(a) and (b) present the visual appearance of the composite prior to and after repeated flexural load application, respectively. The composite experienced a marked color change within the contact zone under flexural loading.

Figure 168. (a) Visual Appearance of the Composite Prior to and (b) After Repeated Flexural Load Application.

Figure 169 shows the optic microscopy images (cross-sectional views) of tensile segment (lower face at midspan) of the composite; the corresponding images for the compressive segment (upper face at midspan) are presented in Figure 162.
The tension zone (near lower face at midspan) of composite appears to have developed a denser microstructure of darker color (Figure 170). This observation may indicate that the tension fibers (with
piezoelectric coating) act as cathode within the solid polymer electrolyte; the dense and dark region may have thus been formed as a result of the electrolytic transport and cathodic deposition of metal cations.

At support, due to the change in direction of bending moment, the top fibers develop tensile stresses and the bottom fibers act in compression. The darker and seemingly denser region again form in the vicinity of tensile fibers which are now located at top (see Figures 171 and 172). This observation provides further support for the possibility of piezo-driven mass transport and deposition occurring with the composite.

Figure 170. Several Cross-Sectional Images Taken at Different Locations of Compression (Lower) Side of Composite Specimen at Support.
6.3 Summary

A refined foam system incorporating the primary functional constituents rendering inherently adaptive effects (piezoelectric and solid electrolyte coatings) was tested under stress gradient. Microstructural (as well as visual) observations produced convincing evidence that electrolytic mass transport and deposition occurred within this integrated system. These phenomena are more pronounced in the integrated foam than other integrated systems. A polymer composite incorporating metal mesh reinforcement with functional (piezoelectric and ion-conducting) coatings was also tested, which produced only preliminary evidence of electrolytic mass transport under stress gradient.
CHAPTER 7

CONCLUSIONS AND ASSESSMENT OF TECHNICAL FEASIBILITY

7.1 Conclusions

Analytical and experimental studies were conducted to validate the fundamental principles of the new adaptive composites. Processing methodologies were also developed for integrating the functional constituents rendering adaptive effects into composites. The key conclusions of the project are as follows:

1. Theoretical modeling and analytical investigation of adaptive composite materials embodying our principles validated that piezo-driven electrolytic mass transport in solid electrolyte provides a viable basis for development of adaptive composites which are inherently capable of strengthening damage zones within a short time period to mitigate catastrophic propagation of damage. The functional constituents rendering adaptive effects can be introduced as fiber coatings with minimal weight penalties; the gains in reliability associated with adaptive effects can actually yield more efficient structural designs of reduced weight.

2. Experimental investigation of selected solid polymer electrolytes verified that electrolytic mass transport (i.e., electrostripping, ionic transport, and electrodeposition) can take place within mechanically viable solid electrolytes, and can yield marked gains in mechanical performance near cathode interface where electrodeposition occurs.

3. Experimental studies confirmed that the piezoelectric effect can generate sufficient electric potential and charge to guide and drive electrolytic transport of mass in solid electrolyte, which render adaptive effects by enhancing mechanical attributes through electrodeposition.

4. Low-cost and high throughput technique was developed for fabrication of piezoelectric ZnO coatings. Experiments confirmed the ZnO coating without poling has comparable voltage output to PZT.

5. The self-poling nature of piezoelectric ZnO coatings facilitates introduction of the piezoelectric effect in the context of biomimetic cellular structures. Processing techniques for application of hybrid piezoelectric ZnO/solid electrolyte coatings onto cellular substrates were developed.

6. The most convincing evidence generated so far is for a cellular substrate which has received a hybrid piezoelectric/solid electrolyte coating. Under stress gradient, electrolytic mass transport toward and its deposition at the loaded (highly stressed) area was confirmed visually and through microscopic observations.

7.2 Assessment of Technical Feasibility

The integrated analytical/experimental efforts undertaken in the project validated the fundamental principles of adaptive structural materials, and established the processing methodologies for integration of the functional constituents rendering adaptive effects into high-performance composites. These constituents are integrated into composites as thin fiber coatings. There are broad selections of key functional constituents available, and diverse processing methodologies can be employed for their application as fiber coating. The diversity of materials and processing techniques promises that
composites with effective adaptive qualities can be designed and processed to meet the stringent performance requirements in aerospace applications. Recent developments in nano-structured piezoelectric materials and also in nano-composite solid electrolytes are expected to greatly enhance the adaptive phenomena validated in the research, and will receive due consideration in follow-up research and development efforts. The processing methodologies established for application of hybrid functional fiber coatings rendering adaptive effects indicate that: (i) low-cost, abundantly available and environmentally friendly raw materials can be employed towards application of the hybrid fiber coating; and (ii) soft-solution (environmentally friendly) processing techniques with minimal energy and cost implications suit application of the functional fiber coating.

In short, the outcomes of the research project reported herein validated the technical viability of adaptive structural materials embodying our principles, and suggested that such materials can be developed at viable cost and with minor weight and environmental penalties to meet the stringent performance requirements of aerospace applications.
CHAPTER 8

REFERENCES


CHAPTER 9

FOLLOW-ON EFFORTS

Adaptive structural systems mimic the distribution of mechanical energy within structural systems to produce an optimum distribution of structural mass, with mass concentration varying in accordance with mechanical energy (and stress) distribution. Conversion of mechanical energy to electric energy via the piezoelectric effect is the primary phenomenon which guides and drives the adaptive phenomena. Piezoelectric effect essentially converts the mechanical to electrical energy at a certain degree of efficiency. Development of piezoelectric materials with improved elastic modulus and strain capacity (and high energy conversion efficiency) would be critical to successful implementation of the concept of adaptive structural systems. Such systems would, due to their high elastic modulus, attract increased levels of mechanical energy; their high strain capacity also enables them to absorb increased levels of strain (mechanical) energy. The increased level of mechanical energy absorption together with enhanced energy conversion efficiency would enhance the ability of the piezoelectric constituent to guide and drive adaptive phenomena within structural systems. The project established a sound basis for use of piezoelectric nanocomposites toward achieving the enhancements in piezoelectricity which are essential for successful development of adaptive structures.

The piezoelectric effect is partly reversible during unloading. The subsequent reversion of electric energy output would thus partially nullify the adaptive trend of mass transport toward areas of mechanical energy concentration. Development of ultrathin rectifiers which prevent reversion of mass transport during unloading would thus enhance the efficiency of adaptive effects. The project took preliminary steps toward development of nanostructured ultrathin rectifier interlayers to be applied between the piezoelectric and solid electrolyte layers. This approach provides a viable basis for enhancement of the efficiency of piezoelectric effect and thus the rate and extent of self-adaptation.

The adaptive phenomena involve electrolytic mass transport and electrodeposition within a solid electrolyte. The project used a variety of solid polymer electrolytes, and demonstrated the potential to improve the thermomechanical performance and ion conductivity of solid polymer electrolytes through introduction of nanoparticles and nanosheets. Efforts in this direction should be continued focusing on introduction of solid ceramic electrolytes in the context of polymer nanocomposites with a desirable balance of mechanical performance and heat resistance.

The project developed models for adaptive phenomena, which provide the basis to account for adaptive features in design of structural systems. Further refinement of the theoretical models would be needed for development of reliable methodologies to incorporate adaptive features into design of structural systems. One would also need to assess the gains in system reliability resulting from the introduction of adaptive features, which would lower the safety factors in structural design, resulting in reduced weight of structural systems without compromising their safety and serviceability.

The project devised and verified various system architectures (e.g., composites and cellular structures) within which the functional constituents rendering adaptive effects could be incorporated. The system architectures developed in the project should be further refined and optimized for aerospace applications.
SUMMARY

The project focused on modeling and experimental verification of adaptive structural systems which are inherently capable of redistributing structural mass for optimum performance in dynamic service environments. The adaptive features involve harvesting of mechanical energy to drive electrochemical phenomena within all-solid systems which tune mass distribution to the distribution of mechanical energy within the system. This effect concentrates mass in areas of mechanical energy concentration, thereby making effective use of structural substance for load resistance.

Theoretical models were developed for structural systems embodying adaptive features, and were used successfully to verify the effectiveness of adaptive phenomena in enhancing structural performance. The functional elements rendering adaptive effects within structural systems are: (i) piezoelectric constituents responsible for harvesting of mechanical energy to generate electrical energy; and (ii) solid electrolytes within which electrochemical mass transport (driven by the harvested electrical energy) enables dynamic mass redistribution. Theoretical analyses confirmed that, within the geometric and mechanical constraints of actual structural systems, adequate electrical energy can be generated through conversion of mechanical energy by piezoelectric effect to cause viable gains in structural performance within acceptable time frames.

The fundamental principles of adaptive structures were verified through performance of experiments which successfully verified: (i) electrolytic mass transport within solid electrolytes using electrical energy which results from harvesting of mechanical energy through piezoelectric effect; and (ii) gains in structural performance resulting from piezo-driven electrolytic mass transport within solid electrolytes.

Various structural configurations were devised for incorporation of functional (piezoelectric and solid electrolyte) constituents rendering adaptive effects into structural systems. Selected structures were designed and manufactured, and their adaptive features were verified experimentally. This experimental verification of self-healing structures involved improvements in the functional and thermomechanical performance of piezoelectric and solid electrolyte materials.

Adaptive structures can benefit from further improvement of piezoelectric and solid electrolyte materials. The potential to achieve such improvements via development of functional nanocomposites was demonstrated. Developments in functional (piezoelectric and solid electrolyte) nanocomposites would directly benefit the rate and extent of self-adaptation which can be introduced into structural systems subjected to dynamic service environments.

Inherently adaptive structural systems can provide the basis for development of a new generation of aerospace structures with enhanced levels of efficiency for optimum performance in dynamic service environments. Adaptive structures are also more survivable because they can optimally mobilize available structural resources to mitigate catastrophic failure under extreme loading and exposure conditions. These structures are also more reliable because they can, through mass redistribution, mitigate the effects of manufacturing defects, and thus lower the variability in structural performance.
Adaptive structures mimic the ability of biological structures (e.g., bone) to redistribute their structural mass in response to dynamic service loads and damaging effects. The adaptive features yield enhanced levels of structural efficiency and safety in dynamic service environments.

The project developed a theoretical basis for modeling and design of adaptive structures, validated the fundamental principles governing the structural performance of adaptive systems, and undertook developments and material and system levels toward development of inherently adaptive structures.

Adaptive phenomena are guided and driven by mechanical energy, noting that redistribution of structural substance strives to match the distribution of mass to the distribution of mechanical energy within the structural system. Adaptive structures are thus inherently capable of tuning their structure performance to service environment in order to make optimal use of their structural mass under dynamic loading conditions.

Theoretical models were developed for adaptive structures, and were used to verify that harvesting of mechanical energy to drive adaptive phenomena is feasible, and that viable rates and extents of adaptive effects can be realized using the principles considered in this investigation.

The fundamental principles of adaptive structures were verified through generating experimental support for harvesting of mechanical energy to redistribute mass within all-solid systems via electrochemical phenomena, and by verifying the structural changes associated with the redistribution of mass.

Different structural systems incorporating functional constituents responsible for adaptive effects were designed and manufactured, and the occurrence of adaptive phenomena in response to gradient dynamic stress conditions was verified experimentally.

Functional materials which harvest mechanical energy and enable electrochemical mass transport are key to successful development of inherently adaptive structural systems. Concepts were developed for enhancement of these functional constituents through developments in the field of nanotechnology. The potential to achieve higher functional and thermomechanical attributes through introduction of functional constituents in the context of nanocomposites were demonstrated.