March 29, 2012

Dear Students, Colleagues and Guests:

The National Society of Black Engineers (NSBE) serves as a sounding board and resource for minority engineering students around the world, and we are proud that you decided to showcase your research in the 2012 Technical Research Exhibition. With more than 35,000 members globally, our mission is to increase the number of culturally responsible Black engineers who excel academically, succeed professionally, and positively impact the community. Academic excellence is our first priority.

As National Academic Excellence Chair my goal is to promote research and technical excellence, and to understand the academic needs of our students. These proceedings are proof that NSBE is a one-stop-shop for academically gifted and technically savvy students. I invite you to attend the oral presentations and poster session to learn about the research your fellow members are conducting around the world.

Thank you for helping us see our mission realized.

Yours in NSBE,

Jasmine Keene
National Society of Black Engineers (NSBE)
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A Clean and Efficient Synthesis of Diaryl Ethers Under Solvent-Free Conditions

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Diaryl ethers are common among pharmaceutically valuable compounds. Consequently, the preparation of diaryl ethers has received considerable attention in recent years. We report a significantly improved procedure for the preparation of diaryl-ethers from phenols and aryl halides via Nucleophilic Aromatic Substitution (SNAr). This methodology utilizes commercially available solid base (KF/Alumina) under solvent-free conditions at ambient temperature or with microwave heating. This novel procedure offers improvements over traditional SNAr procedures and alternate strategies (i.e. Ullman and Pd catalyzed couplings) in terms of cost, reaction time, temperature, substrate scope, and ease of product isolation. Electronically favorable substrates react at room temperature within hours and unfavorable substrates can be induced by brief microwave irradiation. Products are recovered by simple filtration. This simple efficient process offers a useful tool for modern drug discovery given the pharmaceutically relevant nature of the diaryl ether functionality.

An Experimental Approach to the Understanding and Mitigation of Jet Noise

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The goal of this study was to gain an understanding of how the dynamics of a turbulent jet plume correlates to its far-field acoustic signature. We investigated the pressure, velocity and acoustic fields of a transonic jet. Measurements were carried out at Syracuse University's large scale anechoic chamber and jet facility. Test conditions were comprised of a 2-inch axisymmetric Mach 0.6 (~204m/s) jet. In order to understand how active flow control can be used for purposes of jet noise reduction, system characterization of the jets response to localized perturbations of the developing shear-layer at the jet lip were performed. Simultaneous near-field hydrodynamic pressure and far-field acoustic data were acquired at 40 kHz, alongside 10 kHz Time Resolved Particle Image Velocimetry (TR-PIV) measurements in the r-z plane. Cross correlations were performed exploring how both near-field Fourier filtered pressure and low dimensional Proper Orthogonal Decomposition (POD) modes relate to the far-field acoustics. Of interest are those signatures which exhibit the strongest correlation with the far-field, and subsequently how these structures can be controlled. The goal was to investigate how flow-induced perturbations of the developing shear layer might bring insight into how one may alter the flow such that the far-field acoustic signature is mitigated. The TR-PIV measurements will prove to be a powerful tool in being able to track the propagation of physical structures for both the controlled and uncontrolled jet.
Analyzing Android Testing Systems

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The Android operating system is one of the most popular mobile platforms. Its user friendly interface and wide distribution on phones and networks have made it easy for everyone to get their hands on at least a smart phone. In addition to many wanting an Android phone, many programmers want to develop for the platform. During or after the development of the application, a programmer may want to test their application. One way in particular is to test their application via Graphical User Interface (GUI) manipulation. The GUITAR testing harness is an example.

GUITAR is a testing software, developed by Associate Professor Atif Memon and students at the University of Maryland, for model based GUI testing. The software contains a ripper (collects application-specific information), model converters (transforms ripper information into graphical models), test case generators (finds potential sequences to execute as test cases), and replayer (used test case execution). GUITAR currently is available for UNO, SWT, iPhone, Android, and WebGuitar.

Programmers can test their applications by tweaking the existing workflow to include desired application apk. Although many people use Android GUITAR, one question that stands out is its effectiveness of testing the developer’s code. This research evaluates the effectiveness of Android GUITAR by looking at two properties: code coverage and fault-seeding and then compares it to similar Android testing systems.

Characterization of fracture properties of D2 and A2 tool steels using Nanoindenter

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The concept of fracture has continued to evolve into a vast subject ever since its fundamental concepts were pioneered by Griffith, Irwin, Inglis and Orowan. Evidently, more fracture phenomena has emerged which has challenged researchers to develop more sophisticated tools as to provide further insight in areas of materials failure behavior. In recent times, different mechanical characterization techniques have been used successfully to explain the mechanism associated with fracture and the removal of material at very small scale (nano- and micro levels) during high-speed grinding and dynamic wear in machine tools. While A2 and D2 tool steel are known for their high wear resistance, and fracture toughness, the study of their material properties on a nano scale could mean possible reduction with minimal errors in their use in tool steel fabrication. This could also ensure improvement in their usage for machining activities which has seen tremendous growth in the early part of last century.

Cube-corner indenter was used in this experiment because it substantially reduces the cracking threshold in the test of fracture toughness. A sharp indenter like the cube-corner tip which has an included angle of 35.26 between the axis of symmetry and a face, when used for fracture properties
characterization, generates radical crack at fewer indentation loads than Vickers or Berkovich indenters. Vickers and Berkovich indenter has relatively large face angles of 65.27 and 68 respectively; using them for this test will likely cause deformation by expanding cavity model than slip-line theory thus generating a higher compressive force which is undesirable in fracture toughness test. In this study, nanoindentation technique is used to characterize important property in fracture- fracture toughness $K_{IC}$, in tool steels materials (A2 and D2) heated to austenitizing temperature and then quenched (1) In open air, (2) In water (10C).

### Computational Study of Direct Bonded Copper (DBC) Substrates

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Silicon Carbide based power electronic devices have become popular in the microelectronics industry due to their applications at high temperatures. Direct Bonded Copper (DBC) substrate, a ceramic based conductor trace, often used in such devices. Different Coefficient of Thermal Expansion (CTE) of the substrate materials are responsible for stresses at the interface of different materials. These thermal stresses result in delamination at the bond interface when subjected to high temperature fluctuations.

Among different ceramic materials, Alumina (Al2O3) and Aluminum Nitride (AlN) are good candidates for substrates. The combination of substrate thickness and dimpling effects are determinant factors to be incorporated in the studies using computational analyses.

A computational model was developed and finite element analyses were performed to understand the behavior of the substrates at high temperature fluctuations. Cyclic temperature fluctuations was applied from -40C to +200C in the substrate. The temperature fluctuations resulted in fatigue stresses and eventually fatigue failure occurred by delamination. Inclusions such as void, impurities, micro crack from fabrication process are responsible for crack initiation in the substrate due to fatigue stress state.

### Data Fusion of Ultrasonic Testing with Finite Element Analysis

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Computational methods fused with of high quality Ultrasonic C-Scan data adds to the body of knowledge in the field of Nondestructive Testing. This fusion allows for a quantitative approach to analyze ultrasonic tested specimen. The success of this analysis relies on the ability to generate high quality C-scan data to create accurate CAD data models. The generation of high quality scans will produce vital analysis information such as material properties, thickness, voids, surface inclusions and other critical deformities, all which will be used to generate a CAD analysis. With the ultrasonic data generated, a finite element analysis can be utilized to further evaluate tested specimen. The analysis will provide an assessment of the integrity of the specimen without destructive testing. This technique has been applied to an aluminum block sample with known defects.
The project is intended to 1) cultivate cells in three dimensions and create several different internal architectures for nutrient distribution. 2) Conduct cell viability assays to achieve best cellular viability while obtaining a successful scaffold structure and 3) characterize the mechanical properties of PEGDA infused with cells, in room and body temperature, and for different internal architectures. Cells if cultivated on their own will only grow in two dimensions, and that is why the purpose of our project will be to construct scaffolds on which cells can be cultivated. We decided to use Polyethylene glycol diacrylate as the basic material for building the scaffold. Polyethylene (glycol) diacrylate (PEGDA) is a synthetic, hydrophilic starting material which forms hydrogels in the presence of photo initiator and UV light. The PEGDA will act as an extracellular matrix for the cells to grow in three dimensions. To provide the cells in the center of the matrix with nutrients, we will construct channels in the PEGDA through which nutrients can go in and waste products go out. We are going to introduce cells to the mixture and carefully control the concentrations of the photo initiator, PEGDA and the intensity of the UV light as all of these can be toxic to the cells until we find the ideal concentrations for maximum cell viability. The structure will also need to have enough mechanical strength to maintain its integrity in certain conditions like stretching and compression so we will be doing tests using an actuator and a custom designed tensile stage to measure the characteristics of the PEGDA mold under compression and tension scenarios. To keep the cells alive during this, we will be carrying out the tests in an incubator to provide the cells with an environment resembling human body conditions. Our areas of concern are the necessary presence of toxic photoinitiator to successfully cure PEGDA specimens and the frictional force present in the bearing of the custom-designed tensile-tester stage. In order to overcome these difficulties we will be carefully studying the relationship between photoinitiator concentration and cell viability to minimize its harmful effects and we will optimize the tensile-tester design to minimize friction.

Developing an In Situ Remediation Technique for Mercury Contaminated Soils

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While metal mercury (Hg) was widely used historically for multiple industrial applications, the negative and sometimes fatal health effects have caused the use of mercury in industry to be sharply reduced. These effects have necessitated the remediation of mercury waste in soil. While Hg vapor pressure is relatively low because it is a liquid at room temperature, it is higher than most metals. It also reacts readily with sulfur to form mercuric sulfide which is its more stable form. These properties were used to adapt a potential treatment method for contaminated areas that could be done with limited
disturbance to the soil. To test the efficiency of mercury uptake by sulfur, an energy dispersive x-ray fluorescence instrument was used to analyze Hg sand samples that were taken from a closed 24.5 cm diameter x 24.5 cm length glass bell jar that initially contained a sulfur treatment rod in the middle of a homogenous mixture of Hg and sand. The extracted samples were taken at various points on the surface of the system and at different depths. After a few weeks, the sand closer to the treatment rod was higher in Hg than the outer region. This suggests that the Hg was being drawn inward by the sulfur treatment rod. However, after several months when equilibrium was apparently reached, the sand closer to the treatment rod had the lowest Hg concentrations and the sand furthest from the treatment rod had the highest. This implies that sand further away from the treatment rod was not affected as significantly as sand closer to the treatment rod. Further work will be done to determine how other conditions such as temperature and distance would optimize uptake of mercury and to gauge the sphere of influence of the treatment rod.

**Duty Cycling in Wireless Sensor Networks: Experimental Analysis of an Energy-efficient Randomized Scheme on Crossbow TelosB Sensor Nodes**

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In wireless sensor networks, switching sensor nodes between active and dormant state according to a duty cycling scheme is used to prolong the network lifetime and allow for battery recharging in energy harvesting devices. Randomized schemes are adopted due to their simplicity and limited communication overhead. Operations performed by sensor nodes when switching between active and dormant states consume time and energy, thus reducing the overall efficiency of the scheme. A recently proposed Markov chain-based randomized scheme aims to improve the efficiency, while not affecting connection delay and duration. In this paper, we present a TinyOS based system to validate the Markov chain-based scheme on Crossbow (MEMSIC) TelosB sensor nodes. We introduce the architecture of the experimental testbed and describe the experiments used to analyze the performance of the randomized scheme on TelosBs in terms of energy efficiency, connection delay and connection duration. We predict the expected experimental results and state the activities and outcomes of the research project.

**Dynamic Registration for Dental Robotics**

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Computer-Aided Design and Computer-Aided Manufacturing (CAD/CAM) technology is an important developing field in dentistry. These specialized CAD/CAM computer programs are used prior to surgery to determine implant placement and create customized dental prosthesis for various dental restoration procedures. The inaccuracies in the current non-automated methods for dental implants may lead to dental implant failure due to improper positioning of the implant. Our objective is to develop an autonomous robotic arm that completes the dental implant placement and crowning preparation
procedures with higher accuracy than the current manual methods. The previous work from the Bionic's Lab "Dental Robotics" project executed implant placement procedures on static dental models fastened to a mounting plate using a robotic arm [Denso VM-B01G] with a dental tool attached. The current goal is to extend this application to work for moving dental models using dynamic registration. Dynamic Registration is a method to implement real-time indexing between two devices by using a passive robotic arm [Microscribe MX] as a feedback mechanism to maintain a desired registration. The robotic arm will execute the procedure while using the real time feedback from the passive arm to insure accurate implant placement. Our objective is to define and experimentally verify an algorithm to implement the dynamic registration for motion tracking between the tip of the dental drill and the site of the implant location. Further developments will account for integrating dynamic registration with the current operation procedure and then improving the accuracy of the procedure using post-operative scanning to verify the implant placement.

Elevated Carotenoid Production by Overexpressing the Non- Mevalonate Biosynthetic Pathway Enzymes in Chlamydomonas Reinhardtii

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In this work, we explored the non-mevalonate pathway in Chlamydomonas Reinhardtii for the production of an elevated levels of carotenoids (a class photo oxidative compounds known for their therapeutic and biofuel applications). The model organism we are using is the C. Reinhardtii. Even though industrially, Dunaliella Salina has proven to be more applicable, on the research front C. Reinhardtii is more attractive because of the amount of information available on it. The nuclear, chloroplast and mitochondrial genomes have all been sequenced and hence provide a useful basis for genetically engineering this algae.

My method is to assemble cassettes for the genes of interest by the use of homologous recombination in Saccharomyces cerevisiae. To do this, the DNA assembler method in yeast was used and the bacteria DH5α is used in amplifying the assembled plasmid. This is then transferred into the algae by biolistic particle delivery system. We test for the production of carotenoid metabolites with Liquid Chromatography-Mass Spectroscopy(LC-MS). In order to test the level of transcription, RT-PCR was used to determine the mRNA level. Preliminary results show a higher amount of carotenoid in the engineered algae.

Examination of the Effects of Individual Differences on Performance for the Development of Human Performance Moderators

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Technological devices have emerged in areas of education, health care, entertainment and more recently, military applications. From a military perspective, the ultimate goal for these highly
sophisticated devices is to assist soldiers in operational effectiveness across the evolving spectrums of missions, environments, and threats. Since mission success is often dependent on the interaction between the soldier and the device, it is critical for designers to concentrate efforts on understanding that unique interaction. An underlying factor in this understanding is enhancing the overall usability of the human-machine system. Usability is defined as how “user-friendly” a device is or how well the design of the device allows users to meet their intended goals. Factors that affect usability include task requirements, cognitive constraints, cultural factors and the environment. Although there are previous usability studies, there has been little research exploring how socio-cultural factors influence usability.

The purpose of this research is to analyze how the influence of specific cognitive variables, (self-efficacy and computer anxiety), affect performance of a navigational task within a military representative population. These findings are beneficial to the enhancement of human performance modeling through the provision of realistic, valid and accurate information. This granular knowledge will aid in Soldier/Commander decision making through increasing cultural awareness which will ultimately heighten reliability for performance assessment.

Examining Variability in the Mechanical Properties of Parts Manufactured in Polyjet Direct 3D Printing

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Additive Manufacturing (AM) is a layer-by-layer manufacturing process for rapidly fabricating parts and elaborate structures. Polyjet Direct 3D Printing is an AM process in which layers are created by photopolymers and cured with an ultraviolet light. To improve the consistency and reliability of these polymeric materials, their variability and sensitivity to a set of inherent building parameters must be thoroughly understood. This study examines variability in the accuracy and precision of the Tensile Strength and Tensile Modulus of parts printed in an Objet Connex 350 using a Verowhite material. Mechanical properties were measured using an American Society of Testing and Manufacturing (ASTM) standard tensile test procedure. Design of Experiments was conducted using a Full-Factorial Design with three parameters to analyze their effects on the specimen’s material properties. The experiments were carried out varying the in-build plane part orientation (X-Y), the out-of-build plane part orientation (Z), and the distance between specimens (Part Spacing). Initial results showed that Part Spacing had the largest effect on the Tensile Strength, but the three parameters produced no statistically significant effects on the Tensile Modulus. Orienting specimen in the X and Z axes with minimal Part Spacing resulted in the highest Tensile Strength and Modulus. Whereas, orienting specimen in the Y and Z axes, at the farthest Part Spacing led to the lowest mechanical properties. This study will be concluded by relating the experimental results to the kinetics of the printing process. This research has a practical application in engineering design by aiding in the development of mechanical systems, determining material characteristics, and ensuring part reliability in Polyjet Direct 3D Printing.
Experimental Investigation of Cryogenic Cooling and Minimum Quantity Lubrication Strategies for End Milling of Advanced Aerospace Materials (Titanium Alloy - Ti-6Al-4V)

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Cryogenic cooling (Liquid Nitrogen, LN2) and Minimum Quantity Lubrication (MQL) are emerging and environmentally-conducive cooling and lubrication strategies for improving the machinability of advanced aerospace materials. This paper presents the results of the investigation of the individual and combined effects of LN2 and MQL, and conventional (emulsion) cooling on cutting forces, surface roughness, and surface integrity during endmilling of titanium alloy (Ti-6Al-4V) used in aerospace manufacturing. Endmilling experiments were conducted on Cincinnati Milacron, Sabre 750 vertical machining center equipped with Acramatic 2100 controller. Four and Five-flute 0.5 inch diameter endmills with varying corner radii uncoated and coated with TiAlN were used. Cutting force components were acquired using a Kistler 9272 4-component dynamometer which were fed into a Kistler type 5010 dual amplifier and then passed through a low-pass filter to get rid of unwanted noise from the endmilling process. These filtered signals were passed through a Tektronix TDS 420A digitizing oscilloscope where they were digitized. The digitized signals were transferred to a Pentium PC for further processing and analysis. The result shows that cryogenic cooling and the combination of cryogenic cooling and Minimum Quantity Lubrication (MQL) significantly improve the machinability of titanium alloys (Ti-6Al-4V) over conventional cooling, and thus improve the quality of machined parts. The results and optimum cooling/lubrication strategy for machining titanium alloys (Ti-6Al-4V) are presented.

Exploring Effective Techniques to Fabricate Thin Film Cells Composed of CZTS (Cu2ZnSnS4): A Literature Review

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Our research covers some of the various methods of fabricating and characterizing thin film solar cells using (Cu2ZnSnS4) CZTS as the absorber material. The methods discussed for fabricating thin films are the solution gel method. The techniques used for characterizing CZTS thin films are the use of a scanning electron microscope, (SEM), and X-ray Diffraction device, (XRD). There are several other methods, but the selected methods will be discussed as far as their purpose, how they work, and the results for using that method or device. CZTS thin films are discussed as a whole, including their characteristics concerning solar cells and why research should continue in order to increase these cells efficiency ratings. Future studies are underway in the research and development of fabrication and characterization of thin film CZTS solar cells.
Fabrication and Characterization of Silver Nanowire Based On-Chip Capacitor for the Integrated Power Circuit

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Designed and fabricated on-chip capacitor based upon silver (Ag) nanowires (NWs) for use in power circuit. Vertical arrays of Ag NWs with a high surface to volume ratio as electrodes were fabricated on silicon dioxide/ silicon substrates by electrodeposition using anodized aluminum oxide (AAO) nanoporous templates. Bismuth ferric oxide (BFO) thin films were deposited as a dielectric material between the electrodes by electrodeposition. Capacitance from measurements and simulation are 1.4nF/mm$^2$ and 0.7nF/mm$^2$ at 1 MHz, respectively.

Factors Affecting Ultrafine Particle and PM2.5 Emissions from Heated Cooking Oil

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Cooking appliances such as electric or gas stoves, and heated oils emit a large number of particles which contaminate the air. The fumes given off during cooking with oils produce a great number of airborne particles. These particles contribute to increasing the level of human exposure to both ultrafine particles (UFP) and fine particulate matter (PM2.5). Exposure to UFP and PM2.5 has been associated with health effects including respiratory disease, cardiovascular disease, and cancer.

This study focuses on characterizing emission rates for several cooking oils and their impact on indoor air quality. This research project hopes to demonstrate the dependence of oil type, temperature, surface area, additives and other factors on particle emissions and resulting particle exposures to humans during frying. We will investigate these factors under a range of cooking temperatures. The particle mass emission and particle size distribution will be determined with the use of a TSI (St. Paul, MN) Model 3007 Condensation Particles Counter (CPC), and an MSP (Shoreview, MN) Model 100XP Wide Range Particle Spectrometer (WPS). We also aim to validate computation fluid dynamics (CFD) model for estimating human exposure from cooking in a residence.

Finite Element Modeling of a Back Grinding Process for Through Silicon Vias (TSV) Wafers

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The optimization of the grinding parameters for silicon wafers is necessary in order to maximize the reliability of electronic packages. This poster describes the work performed to simulate a back grinding process for Through Silicon Via (TSV) wafers using the commercial finite element code ABAQUS. The grinding of a TSV wafer with a thickness of 120 µm mounted on a backing tape was simulated. The wafer was thinned to a thickness of 115.5 µm, by simulating the grinding with a diamond particle cutting through successive silicon and copper layers. The computed residual stresses induced in the wafer were
compared with experimental values, and the plastic deformation in the simulated ground surface was compared with literature data and showed good correlation. The numerical model developed can be used to better understand the local grinding parameters in the TSV wafers and the effect of the copper vias on the wafer properties.

**Healing Efficiency of a PCL/Epoxy System: Mitigating Corrosion on Metal Surfaces**

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Metallic corrosion has been a major problem in American industry and has lead to billions of dollars in expenses on corrosion reparation. There is a demand for mitigating corrosion in various industries such as: infrastructures, transportation, and utilities. Inspired by biological systems that have healing characteristics, self-healing polymeric coatings have been introduced as a solution for reducing corrosion. Various self-healing material methods have been studied for their ability to recover from load bearing damage. Although there are benefits to their self-healing capabilities, there are challenges that limit their use in practical applications. The purpose of this study is to target healing variables (healing time and healing temperature) that allow for optimal healing results. The approach that is used in this study encompasses a biphasic coating comprised of electrospun poly-caprolactone (PCL) fibers and an epoxy matrix that meet the advantages of being low on cost and provides for a toughening matrix thermoset. Electrospinning and spin-coating processes were used to coat the self-healing system. Two coating thicknesses were tested (10 and 15 minute electrospun PCL fibers). Mechanical damage was induced onto the biphasic coating, and self healing variables were tested (healing times: 10, 30, and 60 minutes) at a fixed temperature (80 °C) for observation of optimal healing efficiency. Structural and condition experimental variables were tested to observe their self-healing characteristics. The results revealed that the coating system was able to self-heal in the given healing times. Our findings suggest that using smaller time intervals in future testing may disclose more accurate readings in the ability of the coating system to heal rapidly. Additional stability and uniformity in damaging methods can eliminate variability in testing results. Detailed understanding of variable properties will assist with future design techniques for fine tuning of this system for larger scale application.

**Influences of Non-Traditional Insulation Materials on Quench Propagation in REBa2Cu3O7-δ Coated Conductor Based Superconducting Coil**

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For a REBa2Cu3O7-δ (REBCO) coated conductor (CC) based high temperature superconducting (HTS) magnet, effective quench detection and protection is paramountly needed to maintain coil integrity. A “quench” is said to occur when a disturbance, such as a Lorentz force-induced movement of a CC winding wire, generates enough heat to cause a growing resistive normal zone within a superconducting CC winding wire. A normal zone heat grows when the Joule heating from the resistive region outgrows the heat dissipation. As a result, quench behavior can be profoundly affected on a micro-scale by conductor...
architecture and material properties of the constituent components, including the insulation material. In this study, the effects of material properties of a thermally conducting dielectric insulator on quench propagation within a HTS coil are investigated via a 2-D/3-D mixed-dimensional REBCO multilayer tape model implemented with COMSOL, a commercial finite element analysis software. The difficulties in modeling the high aspect ratio thin constituent layers of a REBCO CC with finite element analysis are tackled by approximating the thin layers as 2-D surfaces or contact resistance type boundary conditions, which are also used to couple the 2-D and 3-D physics. Here, the effects on multi-dimensional quench propagation and key quench protection parameters such as peak voltage, peak temperature and its gradient, are studied.

This work was supported by Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, OH

Is The Climate Really Changing? Visible Signs of Climate Change in Idaho

AYODEJI B. AROGUNDAYE, RUSSELL J. QUALLS
Department of Biological and Agricultural Engineering, University of Idaho

With so many on-going debates around the world on the possibility of climate change, one is sometimes tempted on what to believe. In this study, we present some visible signs of climate change as observed from the historical trends of snow water equivalent measured from snow telemetry stations (SNOTEL) in Idaho. Undoubtedly, snow accumulation and melt are the most profound of all the seasonal changes occurring over snowmelt-dominated regions of the world; several studies have also indicated that snowpacks are highly subject to changes associated with climate variability and change. Hence, one way to ascertain if the climate is warming or changing is to look at snow water equivalent, which happens to be the amount of water contained within the snowpack, and the historical trends of this common snowpack measurement. To achieve the objective of this study, snow water equivalent measured over a period of 60 years (1950 to 2010) from several SNOTEL stations located in the northern and southern parts of Idaho were used. Results from the various observations and analysis indicate a declining trend in snow water equivalent which is an indication of a warming climate in Idaho over the time period examined.

Localized siRNA Delivery with Lipid-Coated Modified Polyethylenimine

MORGAN GILES
Boston University

Coronary heart disease, the number one cause of death in the United States, is due to plaque build-up in the arteries. Plaque accumulation in arteries causes occlusion of blood flow which can lead to heart attack or stroke. This accumulation, called atherosclerosis, is partially due to an inflammatory response by the vascular cell adhesion molecule 1 (VCAM-1). By targeting VCAM-1, disorders associated with VCAM-1 expression can potentially be reduced. Small-interfering RNA (siRNA) provides a highly specific treatment for disabling VCAM-1 expressing cells. Unfortunately, unpackaged siRNA degrades rapidly in circulation and requires a delivery vehicle for effective treatment. The most commonly studied vehicles for siRNA delivery are viral vectors. However, viral vectors limit the size of genetic material that
can be delivered and are immunogenic. Alternative methods for gene delivery are non-viral vectors because they are more versatile, less immunogenic and are capable of delivering various sizes of nucleic acids or liposomes. Polyethylenimine, a non-viral polymer, has high transfection efficiency but is rapidly cleared from circulation and has a high cytotoxicity due to its high positive charge. Liposomes are biocompatible, non-toxic and have a long half-life in circulation but release rates are uncontrollable. Combining the properties of PEI and liposomes allows for an optimal vehicle for transfection. In this project, PEI is acetylated to reduce its positive charge and cytotoxicity. The modified PEI-siRNA polyplex is coated with pH-sensitive lipids, which facilitate polyplex release from the endosome into the cell cytoplasm. The pH-triggered release of the PEI-siRNA particle from endosomes, efficiency of siRNA transfection and successful suppression of VCAM-1 was tested and compared with unmodified PEI-based polyplexes. Through successful suppression of VCAM-1, the occurrence of atherosclerotic plaque can be reduced. The use of modified PEI for siRNA transfection can be applied to other types of arterial injury and cancer tumor suppression.

Micro Solar Thermal Power Harvesting Using Thermoelectric Generator

EMMANUEL OGBONNAYA, DR. LELAND WEISS
Department of Mechanical Engineering, Louisiana Tech University

The use of a thermoelectric generator (TEG) in generating useful power from solar thermal energy is demonstrated. This device represents a portable and autonomous power generation system operating from solar power, capable of powering micro/nano systems. The TEG was integrated with a micro solar thermal collector plate to enhance the thermal radiation absorption capacity of the hot side of the TEG. Solar thermal collectors were fabricated on copper substrate. Electro-chemical deposition techniques were used to deposit the selective absorber coating consisting of a black nickel-tin bimetallic layer. The selective coating significantly improved the ability of the collector to transform incident solar radiation into thermal energy. This is demonstrated by the improved output power of 9.15 mW from the TEG with a selective absorber plate as compared to a baseline setup without a selective coating where only 2.01 mW was generated. The overall area of the collector was 16 cm².

Molecularly Sensitive Contrast Agents for Early Cancer Detection

ZACHARY CRISS, KIMBERLY HOMAN, CAROLYN BAYER, GEOFFREY LUKE, STANISLAV EMELEIANOV
Department of Biomedical Engineering, University of Texas at Austin

In 2011 over 500,000 lives were taken due to cancer, the second leading cause of death after heart disease. Early detection of cancer can significantly improve survival rates and dramatically reduce the chance of metastasis (the spreading of cancer cells from the primary tumor to distant organs). Therefore, there is an urgent need to develop biomedical imaging strategies that can molecularly target and detect cancer in early stages. A new technique receiving intense interest from researchers for the detection and imaging of cancer is photoacoustic (PA) imaging. PA imaging uses light to interrogate tissue and can receive ultrasound signals from the tissue corresponding to the optical absorption properties of the tissue.
Recently, gold nanoparticles (AuNPs) have been introduced as contrast agents for PA imaging. These AuNPs can provide an avenue to image the molecular signature of cancer non-invasively using PA imaging. Furthermore, it was recently reported that the PA signal of a nanoparticle can be significantly increased by adding a silica layer to the particle. To make these particles molecularly sensitive, a method of conjugating antibodies to silica coated nanoparticles is needed. Therefore, we present the directional conjugation of antibodies to the surface of silica-coated nanoparticles (SiNPs) for the purpose of molecularly detecting cancer. The conjugation method was confirmed by testing the affinity of the molecularly targeted SiNPs for A431 melanoma cells in vitro. Specifically, after directionally conjugating the antibody to epidermal growth factor receptor to the surface of silica coated gold nanoparticles, darkfield microscopy confirmed their uptake in A431 cells in comparison to controls. Therefore, the molecularly sensitive SiNPs we synthesized have the potential to be used as a highly sensitive contrast agent that can non-invasively detect the early molecular onset of cancer using PA imaging.

**Nanoparticles and B7-H4: Superparamagnetic iron-oxide nanoparticles target cancer-expressing protein B7H4**

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Department of Obstetrics and Gynecology, University of Pennsylvania

Superparamagnetic iron-oxide nanoparticles (SPIONs) have remarkable properties, including inductive heating triggered by magnetic fields, contrast agent for MRI, nanometer size, and biocompatibility. These properties can be exploited for improved prognosis of ovarian cancer by targeting the immunosuppressive protein, B7-H4. B7-H4 negatively regulates T-cell function, and is overexpressed by tumor-associated macrophages (TAMs) that promote ovarian tumor growth by various mechanisms, including secretion of tumor growth factors. We hypothesize we can detect B7-H4+ TAMs by MRI and destroy them by thermoablation using anti-B7-H4-coated SPIONs. The Scholler lab has developed novel biotinylated recombinant antibodies directed against B7-H4 called biobodies. Our goal was to assemble streptavidin-coated SPIONs attached to anti-B7-H4 biobodies. Unclear was whether these biobody-linked streptavidin-coated SPIONs could be assembled and whether they would successfully target B7-H4. To study this, we cultured B7-H4+ cells, assembled streptavidin-coated SPIONs attached to anti-B7-H4 biobodies, and tested for B7-H4/SPION attachment in vitro. We found that the SPIONs can be streptavidin-coated and that biobodies attach to the streptavidin on the SPIONs. Furthermore, the B7-H4/SPIONs attach to the B7-H4+ cells. Our findings thus indicate that the B7-H4/SPIONs we produced are functional and therefore should be able to target B7-H4. Once this is confirmed with flow cytometry and/or an MRI test, these SPIONs can be used in vivo. We propose that targeting B7-H4 with these SPIONs could promote thermoablation of TAMs and improve MRI detection, advancing the fields of targeted immunotherapy and imaging for ovarian cancer.
Non Equilibrium Plasma Reforming of Hydrocarbon Fuels Without CO₂ Emission

FELA ODEYEMI
Department of Mechanical Engineering and Mechanics, Drexel University

With non-equilibrium plasma, an alternative process of extracting energy from fossil fuels (coal, biomass, hydrocarbons etc) without the emission of CO2 is possible. Apart from CO and CO2, there exist carbon oxides which can be polymerized to form chemically and thermodynamically stable substances. These carbon oxides are known as carbon suboxides (C3O2). This article describes a novel process of extracting the chemical energy from fossil fuels without the emission of CO2 while producing hydrogen and carbon suboxide (a reddish, brown polymer) which is an important constituent of organic fertilizers. This approach has the capability of avoiding the drawbacks associated with combustion of fossil fuels such as CO2 emissions. The conversion process of a hydrocarbon feedstock (butane) as well as the analyses of the byproduct of the conversion process with electron dispersive X-ray spectroscopy is discussed. Thermodynamic calculation of energy efficiencies of conversion of readily available hydrocarbon feed stocks such as biomass; natural gas and low quality coal (lignite and peat) into hydrogen and carbon suboxide resulted in energy efficiency of 60% - 75% in comparison to energy efficiency of producing syngas (100%).

Off-Chip Photomultiplier-based Continuous Flow Photometer 'Channelscope™' System for the Detection of Programmed Immuno-agglomerates in Fabrica

ANDRE STEVENSON
Department of Biomedical Engineering, Vanderbilt University

Increased knowledge in molecular detection of diseases has reaped an incredible tool for diagnosing and monitoring sickness in the body. Point of Care technology has produced portable easy-to-use devices such as blood glucose machines, food pathogen screening tests, and infectious disease test strips where the patient receives rapid and accurate results characterizing their medical condition. Though detection of molecules has been greatly beneficial, the ability to rapidly detect specific antigen molecules at sub-picomolar concentrations, in a single portable device has been difficult to achieve. Antibody based recognition remains one of the most promising strategies in detecting pathogens in the body. The ability to conjugate antibody (Ab) onto the surface of semiconducting nanocrystals, such as quantum dots (QDs), has yielded a promising method in detecting antigen, which in turn corresponds to detecting specific disease. QD's are conjugated with antibody and when placed in a saline solution with specific antigen, the QD-Ab constructs rapidly self assemble into aggregates due to antibody – antigen bridging. These micron-sized QD agglomerates are much larger than the un-conjugated QDs. Our goal was to detect agglomerates via a microfluidic device, and determine a photovoltaic difference between those micron-sized particles and their precursor QD-Ab constructs. Samples were pumped through a 70 μm microfluidic channel constructed from standard soft lithography methods, and fluorescent detection was achieved via the Channelscope TM, an instrument built at Vanderbilt University used to convert
fluorescence in a microfluidic device into an easily interpretable voltic signal. The fluorescent intensity of QD agglomerates is statistically greater than the fluorescent intensity of un-conjugated QD nanoconstructs, which is an integral first step in detecting antigen biomarkers via a microfluidic device. This technology has the simultaneous multiplexing ability to detect for numerous antigens and diseases based on the variety of antibody that can be conjugated to the QD surface.

### Power Interference Analysis of a Transcutaneous Multiband Inductive Link that uses a Figure-8 Pulse Harmonic Modulation Data Transmission System

DAVID TORIBIO  
Department of Electrical and Computer Engineering, Utah State University

An analysis of the power interference in a pulse harmonic modulated (PHM), low power, wideband data communication system that uses a near field transcutaneous multiband inductive link is presented. Including both features, a multiband inductive link and a PHM data transmission system, in near field transcutaneous communication systems can lead to an optimization of data rate, data transmitter power consumption and power efficiency. The system was modeled using Verilog Analog Mixed Signal (Verilog AMS). The system model employs a multiband inductive link that utilizes Figure-8 coils in order to minimize the cross coupling coefficients between the data and the power link. The separation between the transmitter and the receiver coils was modeled to be 10mm. It was determined that an increase in power amplitude leads to an increase of modulation of the data received signal by the power carrier. It was also determined that there is a directly proportional relationship between the power amplitude and the comparator reference voltage needed to minimize the bit error rate (BER) of the system. Verilog AMS was found convenient to model this system since the multiband inductive link could be modeled using simple differential equations as opposed to complex transfer functions as would have been the case if a more abstract tool had been used for the analysis such as MATLAB.

### Predicting the performance of II-IV based thin film photovoltaic cells during Elemental Vapor Transport at Atmospheric Pressures (EVTAP) via process modeling

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This project focuses on a fundamental investigation into the impact of stoichiometric variations on the doping of II-IV compounds such as Cadmium telluride (CdTe), deposited in polycrystalline form. The main experimental tool is a vapor deposition apparatus, which will be used to deposit CdTe films under various growth conditions (Cd/Te ratio; the films will also be extrinsically doped with impurities such as antimony (Sb)). Performance of the apparatus can be modeled with that of the process modeling software CHEMCAD. This model will predict the degree of re-sublimation onto photovoltaic cell substrates based on changes in the stoichiometric ratio between Cd/Te and substrate temperature. Ultimately, these investigations will develop a better understanding of the fundamental aspects that impact the development
of CdTe photovoltaic cells and reveal optimal aspects that will increase the efficiency of solar cells to over 20%. This will lead to the widespread usage of thin-film photovoltaic cells for electricity generation due to their low manufacturing costs.

Rheological and micro-Raman time-series characterization of enzyme sol-gel solution toward morphological control of electrospun fibres

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Rheological and micro-Raman time-series characterizations were used to investigate the chemical evolutionary changes of sol-gel mixtures for electrospinning fibres to immobilize an enzyme (tyrosinase). Oscillatory rheological measurements agreed with the expected structural transitions associated with reacting sol-gel systems. The electrospinning sols exhibited shear-thinning behaviour typical of a power law model. Diameter distributions of ultrafine (200-300 nm) fibres produced at early and late times within the reaction window of approximately one hour from initial mixing of sol solutions with and without enzyme showed much smaller deviations than expected. The enzyme dramatically increased magnitudes of both elastic and viscous moduli but had no significant impact on final fibre diameters, suggesting that the shear-thinning behavior of both sol-gel mixtures is dominant in the fibre elongation process. The time course and scale for the electrospinning batch fabrication show strong correlations between the magnitudes in rheological property changes over time and the chemical functional group evolution obtained from micro-Raman time-series analysis of the reacting sol-gel systems.

Keywords: Electrospinning; Rheology; Sol-gel chemistry; Ultrafine fibres; Nanofibres; Micro-Raman; Plateau modulus

Self-folding Polymers Enable Microfluidics with a Twist

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An important feature of many living systems, such as leaves and tissues, is that they contain curved microfluidic networks for precise chemical transport in three dimensions (3D). Here we describe the self-folding of polymeric films into intricate 3D microfluidic channels and investigate their utility as bio-inspired synthetic vasculature for in vitro tissue culture models. We first characterize our self-folding mechanism, whereby initially planar SU-8 films spontaneously self-fold into curved geometries due to stress gradients that arise from differential photo-crosslinking and solvent conditioning. These films reversibly curve and flatten upon film de-solvation and re-solvation. We show how film curvature can be controlled and we achieve wafer-scale assembly of micropatterned geometries including helices, polyhedra and corrugated sheets. We then integrate polydimethylsiloxane (PDMS) channels with these SU-8 films to achieve curved, self-assembling microfluidic devices. We demonstrate localized 3D
chemical delivery of biochemicals to discrete regions of cells (1) cultured on the curved SU-8/PDMS surfaces and (2) cultured in a thick, surrounding hydrogel. Our self-assembly strategy is compatible with planar microfabrication technique. Thus, dissimilar materials, functional optoelectronic modules and more complex microfluidic architectures can be incorporated to extend planar microfluidics to curved architectures and to enable the self-assembly of 3D reconfigurable metamaterials and vascularized tissue scaffolds.


Separation of Single Stranded DNA by Steady and Pulsed Electroosmotic Flows in a Microchannel

PARAMESWARA SUBRAMANIAN

The enhancement of mass transfer and separation of ssDNA by a novel technique through steady and pulsatile electroosmotic flows in a microfluidic chip is studied in this work. The ssDNA separated with both steady and pulsed flows. The separation increased at certain voltage-frequency combinations of the pulsatile flows as compared to that of steady flows. This study achieves the initial goal of proof-of-concept of microscale separation through electroosmotic flows and aims towards a larger purpose of building a hand-held lab-on-a-chip device that could be used to analyze various biomolecules at remote locations.

Rapid prototyping was used to make a positive relief on a silicon wafer to mold a T-shaped pattern onto polydimethyl siloxane (PDMS). A mixture of 10mer and 50mer ssDNA with equal volumes was used in this research to visualize the separations. The 10mer ssDNA, prelabeled with Alexa fluor 488 at its 5’ end was observed to separate from the 50mer ssDNA prelabeled with Alexa fluor 405 at its 5’ in the microchip when subjected to steady and pulsed electric field. The observations were visualized using a fluorescent microscope and analyzed in MATLAB. The peak-to-peak separation distance between the two labels exhibits a complex dependence on the electrical double layer, the microchannel dimensions, pulse frequencies and amplitudes. Simplified mathematical models were developed to predict velocity, concentration and overall mass transfer profiles of oscillatory electroosmotic flow to help provide further insight on understanding the dependence of these parameters to the separation process.
Social Media and Disaster Response

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The use of social media in regards to disaster preparedness and response has become a new phenomenon in society. An increasing amount of response agencies are now creating accounts on an array of social media platforms such as YouTube, Facebook, Twitter and all other forms of online databases such as Google and Yahoo to relay safety information, and hazard advisories all in a timely manner. The purpose and anticipated result of this project is to raise awareness of the benefits; saving lives, and reducing costs both financial, and economically that can come from using social media in response to disaster preparedness and response, which I believe in confidently will result in more and more agencies choosing this method of action.

Sorption of Methylparaben in Treatment of Household Greywater in a Membrane Bioreactor

ANNIE MBRIDE
Department of Chemical Engineering, University of Texas at Austin

As the demand for water resources increases worldwide and existing sources become stressed, the need to identify alternative water sources has become apparent. Greywater, household wastewater generated from sinks, washing machines, tubs and showers, represents a possible source for a variety of applications including industrial reuse, groundwater recharge, lawn irrigation and drinking water. The necessary treatment prior to reuse depends on the application, but typically removal of organic matter, particles, and dissolved constituents will be required. Membrane bioreactors (MBRs) are frequently used to treat greywater because they will achieve reduction of organic matter concentrations through biodegradation as well as pathogen removal via filtration.

In addition to removing bulk constituents present at mg/L concentrations, it is often necessary to remove trace concentrations (µg/L) of potentially toxic compounds. The overall objective of this research was to investigate the removal of one such trace contaminant, methylparaben (MP), in MBRs treating a synthetic greywater. Removal of MP in the MBR may occur through biodegradation and/or sorption to bacteria growing on the organic matter present in the synthetic greywater. This poster focuses on the evaluation of MP sorption in the MBR. A series of sorption experiments were conducted to quantify the extent of MP sorption to the bacteria. The results of the experiments indicated that less than one percent of the influent MP was removed via sorption.
Surface Characterization of a Silica Nanospring-mat Functionalized with ZnO/Ag Nanocomposites

BLAISE-ALEXIS FOUETIO KENGNE
Department of Physics, University of Idaho

The ultra high surface area of silica nanosprings, in conjunction with a variety of functionalization possibilities, makes them a novel and unique platform for many applications including catalysis, biomedical devices, and chemical sensing/detection. In this study, mats of SiO2 nanosprings coated with a thin layer of ZnO and decorated with Ag nanoparticles were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Ultra-violet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS). The characterization results show that the top surface of the samples is highly crystalline and composed of metallic Ag, Ag2O and ZnO. The coating of a nanospring is about 40 nm thick and the average size of the Ag nanoparticles 10 nm.

The Analysis of Titanium Implant Surface Coatings

PIAGET J. FRANCOIS
Bioengineering Department, University of Pittsburgh

Implant composition and surface coatings affect the structural and functional connection between living bone and the surface of a load-bearing artificial implant, a property called osteointegration. An optimal implant should induce controlled, guided, and accelerated wound healing by providing an interfacial matrix with a composition and structure characteristic of a bone, i.e. be biomimetic. Osteointegration is critical for long term success of the implant because it will prevent aseptic loosening of the implant. The rate, quantity, and quality of bone responses, such as osteointegration, are related to the surface properties of the implant. The stability of the coating influences the dissolution kinetics, the coating thickness influences attachment to the substrate, and corrosive properties and the biological activity of the coating influence inflammation. Manufacturers of a new calcium phosphate brushite coating, “Coating A” claim that it is easier to apply to the implant, exhibits good bonding and dissolution, and is faster at enhancing the activity of osteoblasts. The objective of this project was to test the manufacturer’s claim by comparing Coating A to the standard coating by considering these factors: 1) how fast the coating dissolves using Micro CT analysis, 2) the effects of the coating on osteoblast and osteoclast activity, 3) and the extent of the foreign body reaction by histochemistry and microscopy. Results show that Coating A is dissolving faster than the standard coating which is enhancing bone formation and is more likely to prevent aseptic loosening and does not create an abnormal foreign body reaction.
The Microwave Drying of Molecular Sieve for Joint Chemical Agent Detector Technologies: Phase 1 Regeneration

RICHARD A. NEGRI
Department of Civil Engineering, Morgan State University

Beginning in the year 2011, the Secretary of Defense has agreed to cut military funding by tens of billions of dollars that he and his generals believe that our nation can do without. The Joint Chemical Agent Detection (JCAD) Program provides a capability to the Joint Warfighter that ensures that he or she is not exposed to any Toxic Industrial Chemicals (TICs) and/or Chemical Warfare Agents (CWAs) in their vapor form. The Molecular Sieve is an essential component of current JCAD technologies which adsorb samples of TICs and/or CWAs during sampling that could possibly be contaminating any environment. However, these sieve components are extremely susceptible to moisture which expedite expiration, and are expensive to replace. By implementing a recycling program that regenerates expired molecular sieve for re-use in Joint Chemical Agent Detector technologies a greater cost-savings can be achieved, given the aforementioned military spending cuts. The purpose of this research is to investigate the ability to use a household microwave to dry expired molecular sieve as a part of a regeneration process which may garner more efficiencies as oppose to more industrial methods of regeneration. Experimental research shows that for a 12-14 g sample of expired molecular sieve material, microwaving at 1000 Watts for 5 minutes will return the sample back to its original dry weight without changing its physical characteristics or abilities as a desiccant, with an associated energy cost of $0.01.

Thorium 229 Isomer, Search for the Half-Life

DEONTE L. THOMAS
Department of Physics and Dual-Degree Engineering Program, Morehouse College

The first excited state of 229 Th has the lowest energy of any known nuclear excitation, which has been indirectly determined to be 7.6 eV ± 0.5 eV. 229Th is produced by the alpha decay of 233U; this was discovered by the Kroger and Reich in using high resolution germanium detectors. My group, which studies low energy physics, has taken an exotic approach to search for the half life of 229Th. The setup involves a vacuum chamber pumped down to the order of 4 – 6 × 10^{-6} Torr. The chamber contains a 233U source electroplated on an aluminum plate and allows 229Th recoils to escape following the alpha decay of the source. The 233U source faces two parabolic shaped wire mesh grids, one behind the other. The back grid is biased positive to ~5000 V to allow alpha particles of heavy ions to travel behind the grid and deflect only the low energy ions backward through a collimator towards a micro channel plate (MCP) detector, which can amplify a signal from a single internal conversion electron by a factor of 10^7. Usually, MCPs have an efficiency that is proportional to the open area of the exposed surface of the detector ~ 60%. The MCP was biased to about 3300 volts to attract the low energy electrons reflected off the catcher plate, that we want to observe. Utilizing state of the art data acquisition systems we are able to gate the detector signal and graphically visualize the decay curve of the electrons. The half life of the 229Th has not yet been observed, but there would be many life changing applications to the
discovery. One of the most important discoveries would be a nuclear optical clock and the enabling to search for a new fine structure changing in time.

**Use of Amazon Cloud Computing Elastic Cloud 2 and San Francisco Stae University's Center for Computing Life Sciences**

CORLISS D. N. ATTERBERRY  
Department of Computer Science, San Francisco State University

Amazon Cloud Computing has been used at SFSU CCLS (http://cs.sfsu.edu/ccls/index.html) for a variety of projects ranging from bioinformatics to testing. The cloud computing is a complimentary high performance resource (HPC) which is supported with a grant from Amazon for the Elastic Cloud 2 (EC2).

Several benefits motivated us to use Amazon EC2. Amongst them are low start up costs, flexible and ease of provision instant type(s) and operating systems. Other features include security and network access, large variety of ways to configure project instances, and ability to choose from preconfigured cloud systems or configuring a personalized group. Some of the applications CCLS use EC2 with are BLAST bioinformatics program, optimizing machine learning algorithms and using it for Quality Assurance (Software testing).

The purpose of this oral research presentation is to continue the research on improvements with the use of EC2. It will reflect the use of tutorials to apply EC2 and the results of using simple applications. The presentation will also have an evaluation of the ease of use and performance improvements. The benefit of the research will aid in more comprehension about the technology of cloud computing in an educational scientific setting.

The proposed research will be conducted from February to mid March of 2012. It will be conducted within the SFSU Computer Science Department with Dr. Dragutin Petkovic, other faculty, students and myself. This abstract is being submitted for the Technical Research Exhibition competition at the 2012 NSBE National Convention

**Zebra Mussels: A nuisance or A Valuable Asset to Aquatic Systems?**

THEODORE D. WILLIAMS  
Engineering & Computer Science, Syracuse University

This study investigates the quantity of total mercury (THg) being temporarily and permanently sequestered from different sampling areas in the Seneca River and Harbor Brook of the Onondaga Lake. Temporary THg concentrations were as high as 0.63 µg/m2 and 749.2 µg/m2 in zebra mussels’ tissues in Onondaga Lake and the Seneca River respectively. Zebra mussels (Dreissena polymorpha) are a group of invasive species that are also known as effective filter feeders. These mussels have been acknowledged as valuable monitoring organisms and accumulators of heavy metals (Voets et al. 2009). Zebra mussels (5-25mm length) were collected between 2009 and 2010 from the highly mercury contaminated
Onondaga Lake and the channelized Seneca River that flows from west to east before merging with the Onondaga Lake and flowing north.

Zebra Mussels’ shells were digested by volume, because the dry mass method used for the thermal spectrometry analysis was undetected. The shells were prepared for a non-sediment based mercury leaching procedure for 14, 30, 90 and 120 days to evaluate the retention rate of THg after zebra mussels’ death and shell deposition.

Based on extreme laboratory conditions, the minimal retention rate of THg in zebra mussels’ shells providing permanent sequestration was 92.9 percent. This rate can be used to calculate the load of total mercury being permanently sequestrated in many different locations, including the Seneca River and Onondaga Lake, where THg concentration in zebra mussels’ shells ranges from 2.35 µg/m2 to 27.9 µg/m2 and .0028 µg/m2 to 0.039 µg/m2 respectively.
Dynamic Registration for Dental Robotics

ARIEL ANDERS
Bionics Lab, Computer Engineering Department, University of California, Santa Cruz
School of Dentistry, University of Washington

ABSTRACT

Computer-Aided Design and Computer-Aided Manufacturing (CAD/CAM) technology is an important developing field in dentistry. These specialized CAD/CAM computer programs are used prior to surgery to determine implant placement and create customized dental prosthesis for various dental restoration procedures. The inaccuracies in the current non-automated methods for dental implants may lead to dental implant failure due to improper positioning of the implant. Our objective is to develop an autonomous robotic arm that completes the dental implant placement and crowning preparation procedures with higher accuracy than the current manual methods. The previous work from the Bionic's Lab "Dental Robotics" project executed implant placement procedures on static dental models fastened to a mounting plate using a robotic arm [Denso VM-B01G] with a dental tool attached. The current goal is to extend this application to work for moving dental models using dynamic registration. Dynamic Registration is a method to implement real-time indexing between two devices by using a passive robotic arm [Microscribe MX] as a feedback mechanism to maintain a desired registration. The robotic arm will execute the procedure while using the real time feedback from the passive arm to insure accurate implant placement. Our objective is to define and experimentally verify an algorithm to implement the dynamic registration for motion tracking between the tip of the dental drill and the site of the implant location. Further developments will account for integrating dynamic registration with the current operation procedure and then improving the accuracy of the procedure using post-operative scanning to verify the implant placement.

1. INTRODUCTION

1.1 Motivation and Background

The inaccuracies in the current non-automated methods for dental implants may lead to dental implant failure due to improper positioning of the implant. The Bionics Lab "Dental Robotics" project's objective is to develop an autonomous robotic arm to complete the dental implant placement procedures with higher accuracy than the current manual methods. In our previous research, we were able to conduct dental implant placement procedures. The active robotic arm would move autonomously on a prepared surgical plan trajectory while holding the dental tool to mill the jaw and conduct the procedure. Our goal is to conduct these same procedures on non-fixed dynamic models that would mimic a human's motion during the operation. Although there are other methods for motion control, our goal is to use a mechanical system to sense the patient's movement using Dynamic Registration for high accuracy and quick response time. The passive robotic arm used in our procedures, Microscribe MX, is highly precise 3D digitizer with accuracy up to 0.002 inches (Immersion Corporation, 2006). Additionally the straightforward direct kinematic equations do not require high computational power; once a control algorithm is developed and thoroughly tested, we plan to implement the procedure using embedded systems; this could increase the accuracy through real-time feedback and real-time response.
1.2 Previous Work

The project uses two six-degrees-of-freedom manipulating robotic arms: one that is active and another that is passive. The active arm has servo-motor actuators in each joint and can move itself, whereas the passive arm simply has optical encoders and can be moved by an outside force. The servomotors and optical encoders in these robotic arms give them the ability to detect the angle of each joint at any given period. These joint angles are used to find the location of the tip of the robotic arm, the "end effector", using a process called "Direct Kinematics". This is a key component in our algorithm we developed to implement the "Dynamic Registration".

Figure 1: SolidWorks generated model of the Denso Vm-B01G[2]

2. PROCEDURE IMPLEMENTATION

2.1 Table of Equipment

This table shows the equipment used in the Dental Robotics experiment at the Bionics Lab:

<table>
<thead>
<tr>
<th>Denso VM60B1G</th>
<th>Mechanical Grippers</th>
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<tbody>
<tr>
<td>6-degree of freedom active robotic arm (Denso Wave Incorporated, 205)</td>
<td>Schunk PTAP70 Parallel plate mechanical grippers with jaws by RADIR These mechanical grippers are able to slide open and closed to firmly grasp an object, such as the dental tool</td>
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<th>Microscribe MX</th>
<th>Implant Kit</th>
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<td>3D digitizer &amp; Passive robotic Arm (Immersion Corporation, 2006)</td>
<td>Nobel Care Osseo Set 200</td>
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<th>Software</th>
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<td>Wincaps III (CAM)</td>
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<td>Visual Studio</td>
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<tr>
<td></td>
</tr>
</tbody>
</table>

Figure 2: Table of Equipment.
2.2 Procedure Methods
The dynamic registration procedure will work as follows:
- If a movement is detected by the passive robotic arm
- The robot stops the procedure
- An altered treatment plan based off the new location is computed (Matlab)
- The plan is uploaded directly to the robot's memory using network interfacing software (ORiN)
- The robot executes the treatment plan (altered) until complete or a movement is detected.

3. SOFTWARE IMPLEMENTATION
To conduct the proposed procedure, the active robotic arm is in an infinite loop program to move to a position variable 'P0'. This position variable is constantly being updated by the PC using a Visual Studio Program and ORIN's CAO dynamic link library. The Visual Studio program is polling data from the passive robotic arm every millisecond; once it has received data from the passive robotic arm, it computes the active robotic arm's corrected position and updates the Position variable 'P0'. The corrected position is computed in Matlab using direct kinematic techniques.

![Software implementation model](image)

This diagram shows how the visual studio program acts like a shell between the passive robotic arm, active robotic arm, and Matlab; the flow of the program is shown in the light blue lines, however the implementation is done through visual studio indicated by the bold black lines.

4. DIRECT KINEMATICS FOR THE DENSO VM-B01G
The Denavit-Hartenberg Parameters for the Denso VM-B01G are shown in the figure below. There are 24 parameter values: four for each of the six different joints (including the joint angle). Additionally, there are six coordinate frames attached to each link denoted by the x and z axis that follow from the previous diagram of the DH values.
There are many approaches for finding the transformation matrix between each joint of a manipulating robotic arm. The approach the Bionics Lab use is the "Modified Denavit-Hartenberg" approach that is outlined in Robert Craig's Introduction to Robotics book[1].

Table 1: Denavit-Hartenberg Parameters for the Denso VM-B01G

<table>
<thead>
<tr>
<th>Link Number</th>
<th>Link Twist</th>
<th>Link Length</th>
<th>Link Offset</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>475mm</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>180mm</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>520mm</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>-90</td>
<td>-100mm</td>
<td>590</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>-90</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Each row of the DH table creates the following homogeneous transformation matrices:

\[
D_0 \ T \ \cdot \ \ D_1 \ T \ \cdot \ \ D_2 \ T \ \cdot \ \ D_3 \ T \ \cdot \ \ D_4 \ T \ \cdot \ \ D_5 \ T \ \cdot \ \ D_6 \ T
\]

Then, the transformation from the base 0 frame to the end effector frame 6 is found by using the following equation:

\[
D_0 \ T \ D_1 \ T \ D_2 \ T D_3 \ T D_4 \ T D_5 \ T D_6 \ T = D_0 \ T
\]  

(1)

[1]
Similarly, the transformation matrix $T_{M0}$ for the passive robotic arm, Microscribe MX, is found using this method using equation 1.

Using the process of Direct Kinematics, we are able to define the transformation from the base of the robotic arms to their end effectors based off joint angles. For the following discussion, we will define the transformation from the base to the end effector for the Denso, the active robotic arm, to be $T_{D0}$ and the Microscribe MX, the passive robotic arm, to be $T_{M0}$.

5 DYNAMIC REGISTRATION ALGORITHM

The setup for a procedure with dynamic registration is shown in the following picture. The dental jaw is not attached to the mounting plate, instead it's attached to the passive robotic arm. Previously, the active robotic arm just held the dental tool with the dental jaw firmly attached to the mounting plate.

5.1 Step 1: Finding Static Homogenous Transformation Matrices

The first step is to define homogenous transformation matrices for the equipment used in the experiment that stay constant throughout the procedure. This refers to the transformation from the active robotic arm to the passive robotic arm and the "tool transformations" for both robotic arms. One tool transformation is the transformation from the active robotic arm's end effector to the tip of the dental tool; the other is the passive robotic arm's end effector to the location of the implant site.

5.1.1 Denso to Microscribe Transformation

![Denso to Microscribe Transformation](image)

Figure 6: Denso to Microscribe Transformation.
The Denso (Active robotic arm) and Microscribe Mx (passive robotic arm) are mounted on the table with their relative coordinate systems in the same orientation; hence, the homogenous transformation matrix describing the relationship consists of only translation.

1. From the base of the Denso to the base of the Microscribe, the distance to the is $D_0 P_{M_0}$.

2. Since there is no rotation between the two coordinate systems, the rotation matrix between base of the Denso to the base of the Microscribe, the identity matrix:

$$ R_{D_0 M_0} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} $$

3. Thus, the transformation matrix from the Microscribe End Effector to the desired implant location with respect to the Microscribe end effector is:

$$ D_0 T_{M_0} = \begin{bmatrix} 1 & 0 & 0 & P_x \\ 0 & 1 & 0 & P_y \\ 0 & 0 & 1 & P_z \\ 0 & 0 & 0 & 1 \end{bmatrix} $$  \hspace{0.5cm} (2)

5.1.2 Passive Robotic Arm to Desired Implant Location

1. From the tip of the Microscribe, the distance to the desired implant location is: $M_6 P_{\text{implantLoc}}$

2. Since there is no rotation between the two coordinate systems, the rotation matrix between the Microscribe's end effector and the desired implant location with respect to the Microscribe's end effector is the identity matrix:

$$ R_{\text{implantLoc}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} $$

3. The transformation matrix from the Microscribe End Effector to the desired implant location with respect to the Microscribe end effector is:

$$ M_6 T_{\text{implantLoc}} = \begin{bmatrix} 1 & 0 & 0 & P_x \\ 0 & 1 & 0 & P_y \\ 0 & 0 & 1 & P_z \\ 0 & 0 & 0 & 1 \end{bmatrix} $$  \hspace{0.5cm} (3)
5.2 Active Robotic Arm to the Dental Tool Tip

![Diagram of Active Robotic Arm to the Dental Tool Tip]

Figure 8: Active Robotic Arm to the Dental Tool Tip

1. From the tip of the active robotic arm the distance to the dental tool tip is: $D_6 P_{tool}$

2. The rotation between the active robotic arm's end effector to the tool tip is: $D_6 R_{tool}$

3. Then, the transformation from the active robotic arm's end effector to the tip of the tool is given:

$$
D_6^{implantLoc} T = \begin{bmatrix}
D_6 P_{tool} & D_6 R_{tool}
\end{bmatrix}
$$

(4)

These matrices are calculated using the Denso's internal functions for tool calibration.

5.3 Step 2: Finding the Corrected Position Transformation Matrix

The key concept for dynamic registration is to obtain a constant configuration between the tip of the dental tool and the dental implants.

By connecting the passive robotic arm to the dental implant model, we can manually move the dental implant to simulate a patient's sudden undesired movement and know the new configuration of the tip of the dental implant. The movement is detected in the change of the non-static homogenous transformation matrix of the passive robotic arm $M_{implantLoc}^0 T \Rightarrow M_{implantLoc}^0 T^*$ where * indicates the new orientation.

It follows that the active robotic arm needs to also move to retain the initial configuration.

$$
D_0^T \Rightarrow D_0^T_{next} \quad D_6^T \Rightarrow D_6^T_{next}
$$

To find $D_6^T_{next}$ we can set up and solve the following set of equations:

Finding the desired implant location with respect to the base of the Denso:

$$
D_0^{implantLoc} T = D_0^T_{implantLoc} T \star M_0^{implantLoc} T
$$

(5)

$$
D_0^{implantLoc} T = D_0^T_{tool} T \star M_{tool}^{implantLoc} T
$$

(6)

Equating equation 11 and 12 for $D_0^{implantLoc} T$:
\[
D_0 T^* M_0 T = D_0 T^* \text{tool} M_0 T^* \text{implantLoc} T
\] (7)

Then, we can solve for
\[
D_0 T^* = D_0 T^* M_0 T^* (\text{tool} M_0 T^* \text{implantLoc})^{-1}
\] (8)

When jaw moves to new location it is changes the homogenous transfer matrix for the passive robotic arm:
\[
M_0 T^* \text{implantLoc} \Rightarrow M_0 T^* \text{implantLoc}
\]

The position the active robotic arm needs to move to can be solved from Equation 13:
\[
D_0 T_{next} = D_0 T^* M_0 T^* (\text{tool} M_0 T^* \text{implantLoc})^{-1}
\] (9)

Once we have found the transformation for the active robotics' arm next position we can abstract the a position and fixed axis rotation.

\[
D_0 T_{next} = \begin{bmatrix}
 r_{11} & r_{12} & r_{13} & P_{next_x} \\
 r_{11} & r_{12} & r_{13} & P_{next_y} \\
 r_{11} & r_{12} & r_{13} & P_{next_z} \\
 0 & 0 & 0 & 1
\end{bmatrix}
\] (10)

The next configuration of the robot's tool can be found by the translation:
\[
D_0 P_{tool_{next}} = \begin{bmatrix}
 P_{next_x} \\
 P_{next_y} \\
 P_{next_z}
\end{bmatrix}
\]

The orientation can be found using the X-Y-Z inverse matrix solution for fixed angles[1]

\[
R_{next_y} = \text{Atan2}(-r_{31}, \sqrt{r_{11}^2 + r_{21}^2})
\] (11)

\[
R_{next_z} = \text{Atan2}(\frac{r_{21}}{\cos(R_{next_y})}, \frac{r_{11}}{\cos(R_{next_y})})
\] (12)

\[
R_{next_x} = \text{Atan2}(\frac{r_{32}}{\cos(R_{next_y})}, \frac{r_{33}}{\cos(R_{next_y})})
\] (13)

These six values define the corrected Position variable for the active robotic arm:

\[
\text{NextPosition} = \begin{bmatrix}
 P_{next_x} \\
 P_{next_y} \\
 P_{next_z} \\
 R_{next_x} \\
 R_{next_y} \\
 R_{next_z}
\end{bmatrix}
\]

By constantly updating and moving the active robotic arm to the next position we can implement the dynamic registration algorithm.
6 RESULTS
Using this workflow, we were able to successfully implement the motion tracking between the tip of the dental tool and the dental jaw model. The active robotic arm does in fact follow the passive robotic arm to achieve a constant orientation between both devices, however; the constant orientation has a static error of one to two millimeters. However, when both robotic arms are moving the error increases as well. Due to safety concerns, the active robotic arm's internal speed is set up to fifty percent of its maximum capacity. Additionally, the passive robotic arm outputs data at its minimum update period of two milliseconds and causes a significant delay in the motion tracking inhibiting real-time data streaming. The following graph shows data collected during a reference tracking experiment.
In these diagrams the active robotic arm, shown in red, clearly trails the passive robotic arm, shown in blue. However, when the passive robotic arm is not changing position, the passive robotic arm catches up and decreases this offset.

7 CONCLUSION

The inaccuracy in our current design is a limitation of our equipment. The error in the motion tracking of both devices is constant, indicating that there is an initial calibration error that could be solved using more precise grippers to hold the dental drill and the dental jaw. Additionally, the minimum update period of our feedback device is 2ms accounting for lag within the procedure.

Further developments will work on improving the accuracy of the current design along with intelligent trajectory planning. The dental tool follows the dental jaw; however, based on the orientation of the jaw, a sophisticated trajectory may be needed to safely move the dental tool to achieve its desired registration. After improving the accuracy of the current design, we plan to use postoperative scanning to verify and improve the quality of the procedures.
ACKNOWLEDGEMENTS

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REFERENCES


Is Climate Really Changing? Visible Signs of Climate Change in Idaho

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ABSTRACT

With so many on-going debates around the world regarding climate change, it is confusing what to believe. In this study, we present some visible signs of climate change as observed from the historical trends of snow water equivalent measured from snow telemetry stations (SNOTEL) in Idaho. Undoubtedly, snow accumulation and melt are the most profound of all the seasonal changes occurring over snowmelt-dominated regions of the world; several studies have also indicated that snowpacks are highly subject to changes associated with climate variability and change. Hence, one way to ascertain if the climate is warming or changing is to look at snow water equivalent, which is to be the amount of water contained within the snowpack, and the historical trends of this common snowpack measurement. To achieve the objective of this study, snow water equivalent measured over a period of 60 years (1950 to 2010) from several SNOTEL stations located in the northern and southern parts of Idaho were used. Results from the various observations and analysis indicate a declining trend in snow water equivalent which is an indication of a warming climate in Idaho over the time period examined.

1.0 INTRODUCTION

Different views on climate change have left many people in the dark not knowing which of the views to believe. While it has been established in several scientific journals that climate is changing owing to some notable signs all over the world, other school of thoughts have also viewed the issue of climate change as nothing but political. Many in this school of thoughts hold the view that there are insufficient evidences to suggest that the climate is changing or the globe warming. These divergent views have further created a lot of misconceptions in the minds of people as to the truth about climate change, leading many to question the reality of climate change. One of the ways to know if the climate is changing is to look at the various seasonal changes in our immediate environment that could easily be impacted by climate change.

The fact that the climate is changing have long been established in the literature. According to the World Meteorological Association as stated in Cayan et al. (2008), “since the start of the 20th century, the global average surface temperature has risen between 0.6°C and 0.7°C. But this rise has not been continuous. Since 1976, the global average temperature has risen sharply, at 0.18°C per decade. In the northern and southern hemispheres, the 1990s were the warmest decade with an average of 0.38°C and 0.23°C above the 30-year mean, respectively”. Increases in land surface temperatures are widespread as indicated by various climate records (Brunetti et al., 2000; Regonda., 2005, Webber et al., 1994). Likewise at the regional scales, the winter and spring temperatures have witnessed an upward swing in western North America during the twentieth century (Folland et al., 2001; Mote et al., 2005; Barnette et al., 2004; Stewart et al., 2005).
This warming trend across the western United States and the world is likely to continue according to the Intergovernmental Panel on Climate Change (IPCC) Forth Assessment Report (2008) which forecasts global temperatures to rise by an additional 1.8 to 4.0°C by 2090 (Day, 2009). The thoughts in some quarters that the increasing trend in temperature was totally due to natural variability from key ocean-atmosphere indices, among which are El Nino Southern Oscillation (ENSO) and Pacific Decadal Oscillation (PDO) have been observed to be untrue. Undoubtedly, natural variability in regional air temperatures resulting from key ocean-atmospheric indices, including Pacific Decadal Oscillation (PDO) and North Pacific Index (NPI) partially explain these temperature changes (Day, 2009) and sometimes influences the declining trend in snowpack accumulation, however, Mote (2006) explained that natural variability such as NPI can only account for about half of the trends in the Pacific North West since midcentury. Furthermore, it is reported in the literature that the observed increasing trend in temperature was unchanged even after the removal of these indices’ signals from the overall trend (Day, 2009; Mote et al., 2008; Mote, 2006, Stewart et al., 2005; Feng and Hu, 2007).

As reported by Regonda et al. (2005), increasing regional warming trends modify the hydrologic cycle through changes in snowpack accumulation and a shift in winter precipitation from snow towards rain as already being seen in the western part of the United States (Robinson, 1999; Van Kirk and Naman, 2008, Mote, 2006); in addition, seasonal timing of streamflow is also affected (Dettinger et al., 2004). Undoubtedly, snow accumulation and melt are the most profound of all the seasonal changes occurring over snowmelt-dominated regions of the world; several studies have also indicated that snowpacks are highly subject to changes associated with climate variability and change. Hence, one way to ascertain if the climate is warming or changing is to look at snow water equivalent. Several studies have been conducted on the observed declining snowpack trends in the western United States (Cayan, 1996, Day, 2009, Regonda, 2005; Hamlet et al., 2005; Mote, 2003; Mote, 2006), and many of the studies have attributed these trends to increased warming associated with climate change. In fact, a large reduction in mountain snowpack has been listed to be the most significant impact of a general warming (Barnett et al., 2005), and any response to regional warming is most likely to be detectable at lower elevations (Mote et al., 2008). This study attempts to examine the historical snow water equivalent dataset recorded in snow course stations in southern and northern Idaho with the aim of ascertaining if climate is really changing or not. The study further aims to answer these questions: (i) Are there any observed changes in SWE trends in Idaho to suggest a warming climate (ii) Are these trends associated with climate warming?

2.0 STUDY AREA
This study was carried out in Idaho using thirty eight snow course stations located in the southern and northern parts of the state (Figure 1). Idaho is located in the Pacific Northwest (PNW) region of the United States of America, a region whose water supply is dominated by snowmelt runoff. The region has been identified to be very vulnerable to the impacts of climate change owing to the fact that a snow dominated area is easily affected by the anthropogenic forcings of temperature and precipitation. Idaho, being a state within the PNW, is chosen for this study because of the fact that snowpack is the major source of water supply in the state, and anything that impacts the snowpack also impacts the water resources and the lives of people in the state.

3.0 DATA AND METHOD
Spring snowpack accumulation is a regional climate indicator (Changnon et al., 1991) and an important predictor of summer streamflow (Mote et al., 2005). Starting in the 1930s, conventional
methods including the use of snow courses began to be used to obtaining point measurements of snow water equivalent (Dressler et al., 2006). These manual methods worked well in providing historical records of snow water equivalent; however, measurements of the snow water equivalent are conducted at monthly intervals. The low spatial and temporal resolution of the data coupled with the labor intensiveness of data collection from these snow courses were significant drawbacks to the usefulness of the conventional methods. Installation of an automated network of snow telemetry (SNOTEL) sites began in 1963 with the aim of supplementing, and to some extent, replacing the manually operated snow courses as elucidated in Serreze et al. (1999). Real time data of snow water equivalent can be collected from these SNOTEL stations.

In this study, data from snow-course surveys conducted by the National Resource Conservation Service (NRSC) were used to investigate the trends in SWE. The snow course data covering a period of sixty years (1950 to 2010) were obtained from NRSC website (http://www.wcc.nrcs.usda.gov/snotel/Idaho/idaho.html). The main dataset used from these snow courses for the purpose of this study is the snow water equivalent. An optimal date for analysis is 1 April because it is representative of peak SWE in many regions (Regonda et al., 2005; Cayan, 1996), it is the most frequent observation date and it is widely used for streamflow forecasting (Mote et al., 2005). Thirty eight snow course stations were selected for this study (twelve from northern Idaho and twenty six from southern Idaho) (Figure 1). The stations were chosen across various elevations with the aim of providing a relatively uniform spatial sample and also maximizing elevation coverage (Table 1). In addition, observations from 1 April are the primary data used in this study. Trends are examined at each snow course location using linear regression.

4.0 RESULTS AND DISCUSSION

4.1 Observed Patterns of SWE

Snow course stations were chosen at different elevations in order to fully appreciate the spatial and temporal pattern in snow water equivalent. Similar patterns and trends were observed in the snow water equivalent plots (Figure 2), with the largest values occurring about the same time among all the stations in the fifty-year period examined. 1 April SWE shows a declining trend in most of the snow course stations examined, with the exception of two of the thirty eight snow course stations which exhibit an increasing trend. Specifically, SWE decreased at all twelve of the snow course stations examined in northern Idaho, while twenty four out of the twenty six stations in southern Idaho also show a declining trend. The mean of 1 April SWE measured in southern and northern snow course stations also indicates declining trends (Figure 3). Furthermore, as shown in Figure 4, the mean SWE measured at different elevations were plotted against their respective elevations for twelve snow courses in northern Idaho with the view to understanding the pattern of precipitation deposition. It was observed that high-elevation locations recorded greater amount of precipitation compared to the lower-elevation locations corroborating the fact that snow increases with elevation. However, regarding losses of snowpack, low-elevation stations recorded greater loses.

4.2 Trends in accumulated snowpack

Spring snow accumulation has been demonstrated to serve as a regional climate indicator (Changnon et al., 1991). Figure 5 maps trend SWE for 1st of April in four of the twelve snow course stations in northern Idaho used for this study, and Figure 6 also the trends in SWE recorded in four of the twenty six
snow course stations in southern Idaho. However, it cannot be concluded that the observed trend is due to a warming climate until the influences of precipitation and temperature are separated.

Certainly, both precipitation and temperature influences the trend in snowpack accumulation (Cayan et al., 1991; Mote et al, 2008; Regonda et al., 2005), however, Mote (2003) explained that one of the ways to separate the influences of temperature and precipitation is to examine the SWE trends as a function of elevation. According to Mote (2003), changes in SWE associated with precipitation should be nearly uniform with altitude while changes associated with temperature should be much greater at lower elevation, since at lower elevation a moderate change in temperature can significantly alter the fraction of precipitation that falls as snow.

As explained by Mote et al. (2005), the clearest signature of warming-induced changes in snowpack is that trends become increasingly positive with increasing elevation. Plots of SWE as a function of elevation are shown in Figure 7 with a view to examining the percentage changes in the trend of SWE. The largest decline and negative trend in SWE (46%) was observed at the lowest elevation station (975m) and the trend become less negative with increasing elevation. The various percentage changes in trends of SWE as observed at the different elevation stations also indicate that lower elevations are more sensitive to changes in surrounding environment, especially air temperature (Day, 2009) since they exist at an elevation which is presently experiencing a shift across the critical temperature mean 0°C during the snow accumulation period at which precipitation changes from snow to rain. It is evident that trends depend on elevation going by the fact that the trend becomes less negative with increasing elevation; a strong indication of response to warming of the region. These results further indicate that low elevation snowpack is much more sensitive to temperature than high elevation snowpack (Mote, 2003; Mote et al. 2006; Mote et al. 2008).

4.3 Trends in Snow ablation

Observed melt-out dates of snow in a basin located in western Wyoming (Figure 8) that drains across the Snake River plain of southern Idaho, also shows a declining trend. The basin is important in that it represents an important water resource for agriculture, power generation, as well as municipal, commercial, and industrial uses, in Idaho. Figure 9 also shows the snow covered area as at April 22 of two different years. Figure 10 is a plot of the melt-out dates of snow (1981 to 2011) as observed from remotely sensed MODIS images. The plot shows a declining trend in the melt-out dates of snow in the basin.

5.0 CONCLUSION

The results from this study can be summarized into the following points
1. Snow water equivalent (SWE) measurements in April shows a general decreasing trend which indicates a reduction in snowpack.
2. Strong dependence of trends of SWE on elevation in Idaho suggests that the trend is primarily due to a warming climate. Largest losses in snowpack are observed at lower elevations and smallest losses are observed at higher elevations, even though higher elevations receive greater amount of precipitation compared to lower elevations.
REFERENCES


Nanoparticles and B7-H4
Superparamagnetic iron-oxide nanoparticles target cancer-expressing protein B7H4

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ABSTRACT

Superparamagnetic iron-oxide nanoparticles (SPIONs) have remarkable properties, including inductive heating triggered by magnetic fields, contrast agent for MRI, nanometer size, and biocompatibility. These properties can be exploited for improved prognosis of ovarian cancer by targeting the immunosuppressive protein, B7-H4. B7-H4 negatively regulates T-cell function, and is over expressed by tumor-associated macrophages (TAMs) that promote ovarian tumor growth by various mechanisms, including secretion of tumor growth factors. We hypothesize we can detect B7-H4+ TAMs by MRI and destroy them by thermoablation using anti-B7-H4-coated SPIONs. The Scholler lab has developed novel biotinylated recombinant antibodies directed against B7-H4 called biobodies. Our goal was to assemble streptavidin-coated SPIONs attached to anti-B7-H4 biobodies. Unclear was whether these biobody-linked streptavidin-coated SPIONs could be assembled and whether they would successfully target B7-H4. To study this, we cultured B7-H4+ cells, assembled streptavidin-coated SPIONs attached to anti-B7-H4 biobodies, and tested for B7-H4/SPION attachment in vitro. We found that the SPIONs can be streptavidin-coated and that biobodies attach to the streptavidin on the SPIONs. Furthermore, the B7-H4/SPIONs attach to the B7-H4+ cells. Our findings thus indicate that the B7-H4/SPIONs we produced are functional and therefore should be able to target B7-H4. Once this is confirmed with flow cytometry and/or an MRI test, these SPIONs can be used in vivo. We propose that targeting B7-H4 with these SPIONs could promote thermoablation of TAMs and improve MRI detection, advancing the fields of targeted immunotherapy and imaging for ovarian cancer.

BACKGROUND

The use of superparamagnetic iron-oxide nanoparticles (SPIONs) has powerful potential biomedical applications, including magnetic resonance imaging, hyperthermia, drug delivery, cell and tissue targeting and transfection (Gupta et al, 2007). Importantly for in vivo use, SPIONs are thought to be nontoxic and biocompatible (Kievit & Zhang, 2011). Furthermore, SPIONs have magnetic properties that can be exploited for magnetic resonance imaging (MRI) (Kievit & Zhang, 2011). The surface of the SPIONs can be coated with various targeting agents, which allows for specific localization of the particles (Kievit & Zhang, 2011). In addition, magnetic particles produce heat when subjected to an altering magnetic field (Johansenn et al, 2005). Therefore, magnetic nanoparticles can promote tumor cell death by increasing the temperature of the tumor microenvironment. For these reasons, SPIONs represent a promising therapeutic tool for cancer. Targeted with specific antibodies, the SPIONs can specifically
attach to cancer cells as well as to the cells of the tumor microenvironment, making targeted therapeutics and imaging possible.

B7-H4, also known as B7-S1 or B7x, is an immunosuppressive molecule of the adaptive immune system (Zou & Chen, 2008). B7-H4 is a member of the B7 family, and B7 molecules are known to both stimulate and inhibit T-cell function specifically (Choi et al, 2003). Although a soluble form exists, B7-H4 is usually expressed on antigen-presenting cells (APC) including tumor-associated macrophages (TAMS), and lipo-polysaccharide activated B-cells (Durbaka et al, 2003). In addition, B7-H4 is described as being expressed by tumor cells in many cancers, including ovarian, breast, urinary, and lung cancer (Yi & Chen, 2009). (Salceda et al, 2005). TAMs play an important role in tumor cell proliferation. Once activated by a cancer cell, TAMs secrete growth factors, proteolytic enzymes, cytokines, and inflammatory mediators (Shih & Yuan, 2003). In some cancers like ovarian cancer, TAMs secrete B7-H4 and disrupt tumor-associated antigen (TAA)-specific T-cell immunity (Zang et al, 2003). Therefore, B7-H4 is likely to contribute to tumor immunity down-regulation due to the inhibition of T-cell proliferation inhibition, cytokine secretion, and apoptosis while enhancing cell cycle arrest and tumor outgrowth (Yi & Chen, 2009). The connection between ovarian cancer and B7-H4 is especially strong. One study found up to 85% of ovarian cancer tissues expressing B7-H4 (Choi et al, 2003). Blocking expression of B7-H4 has been proven to disable T-cell suppression (Kryczek, 2007). Still more research is needed to better understand the potential of B7-H4 as a molecular target for tumor immunotherapy.

Therefore, targeting TAMs expressing B7-H4 can open new therapeutic avenues, and SPIONs have unique properties to assist in this targeting. Targeting SPIONs to B7-H4-expressing cells requires the use of an anti-B7-H4 affinity reagent. The Scholler lab has developed two novel recombinant antibodies (scFv) directed against B7H4 called biobodies (Bb) (Scholler et al, 2006). The scFv are secreted directly biotinylated by yeast. Biotin has a high affinity for streptavidin, and therefore biotinylated biobodies should bind strongly to streptavidin-coated surfaces. We rationalize this biobody-SPION assembly method will result in anti-B7-H4-targeted SPIONs.

**MATERIALS AND METHODS**

1. **Biobody Production**

   The biobody production involved yeast growth, induction of biobody secretion, and validation.

   1a. **Growth of yeast secreting Biobodies.** The biobodies are secreted by galactose-dependent yeast. Two anti-B7-H4 biobodies were generated by the Scholler lab, #26 and #56. To grow the yeast, growth medium containing 75ml SD-CAA (minimal media), 3.75ml 20X glucose and 0.75ml 100X streptomycin was added to 1.5ml of yeasts 26 and 56 each and incubated at 30°C for 24 hours. Yeast culture were then centrifuged at 10,000rpm for 10 minutes and the supernatant drained.

   1b. **Induction of Biobody Secretion.** To induce biobody secretion the pellet was re-suspended in 75 ml YEP-GR (yeast extract/bactopeptone supplemented with galactose and raffinose), 7.5ml 10X GRD, 0.75ml 100X TRP, and 0.75ml 100X streptomycin. Yeast culture was incubated at 20°C for 4 days. The culture was centrifuged for 5 minutes at 3000rpm and 4°C. The yeast supernatant that contains the biobodies was harvested and stored at 4°C.

   1c. **Validation of Biobody Presence in yeast supernatant.** Before the biobodies were used for experimentation, the presence of biobodies was measured in yeast supernatant by an ELISA assay. The ELISA procedure involved a streptavidin-coated plate washed with PBST (0.05%Tween-20 PBS) three times. A 2-fold dilution of the yeast supernatant was carried out eight times, and 50ul of each sample was
added to a well. The plate was incubated and shaken at room temperature for 1 hour, then washed 3 times with PBS. Because biobodies are tagged with V5, 50ul of 1:1000 dilution of anti-V5-HRP was added to each well, and incubated at room temperature for 30 minutes to detect the biobodies attached to the streptavidin-coated wells. The plate was washed with PBS 3 times again, and finally 50ul of TMB was added to develop the reaction. 50ul of HCl were finally added to stop the reaction. The plate was read in the Gen5 BioTek Absorbance Microplate Reader at 450nm.

2. Streptavidin-coated SPION Assembly and Validation

2a. Assembly of Streptavidin-coated SPIONs. The SPIONs assembly began with cobalt-iron-oxide nanoparticles (CoFe2O4) covered with oleic acid. These SPIONs (suspended in hexane) were set in the hood overnight to dry out. The SPIONs were made water-soluble by adding PEG rich-phospholipids, including methyl ester (-OMe) and amines (-NH2). To make a 1:10 iron to phospholipid weight-weight concentration and a 1:10 amine to methyl ester concentration, 0.5ml CHCl3, 450ul of 10mg/ml methyl ester, 20ul of 25mg/ml, were added to 0.5mg iron. The solution was then kept at room temperature for three days to allow for assembly. To separate phospholipids-coated SPIONs from leftover uncoated particles, the solutions were then run in a 0.6% agarose gel made with 0.6g agarose in 100ml of PBS. Then, to further filter desired SPIONs, a sucrose density gradient fractionation was executed by layering 10.5ml of varying concentrations (5-80%) of sucrose solutions, and centrifuging the SPIONs at 24,000rpm for 18 hours at 4°C. The visible brown SPIONs were then extracted from the sucrose solution with the matching density, and dialyzed in 5ml overnight. Traut’s reagent was added to replace the amines with sulphydryl groups. 1mg of the reagent was mixed with 0.5ml SPIONs, 25ul of 20X borate buffer, and 5ul of 0.5M EDTA. After incubation at room temperature for an hour, the SPIONs were centrifuged in a 10K filter tube at 3,000rpm. Maleimide streptavidin was added to attach to the sulphydryl groups on the SPIONs. 0.5ml of maleimide streptavidin was added to 0.5ml of SPIONs. After incubating for 12 hours at room temperature, the SPIONs were washed four times with PBS in a 100K filter tube at centrifuge speed 3,000 rpm.

2b. Validation of Streptavidin-coated SPION Assembly. Several reagents were added to the SPIONs in order to attach streptavidin. To ensure each reagent bound to the SPIONs, several different tests were performed. To ensure amines were attached to the SPIONs, a TNBSA assay was executed following the TNBSA protocol. For the control, 50ul of each butylamine dilution (2-fold) was added to 25ul of 0.01 TNBSA, 25ul of 10% SDS, and 12.5ul of 1M HCl. For the SPION samples, 50ul of SPIONs samples (25, 10, and 5ul of SPIONs with 10X borate buffer) were added to 25ul of 0.01% TNBSA, 25ul of 10% SDS, and 12.5ul of 1M HCl. Ellman’s reagent was used to verify sulphydride groups attached to the amine groups. Ellman’s Reagent was used to verify the sulphydrides were present on the nanoparticles. 250ul of each sample was added to 50ul of 4mg/ml Ellman’s Reagent solution with 2.5ml of 20X borate buffer with 1mM EDTA. After incubation at room temperature for 15 minutes, the absorbance was measured on the Nanodrop at 412nm.

To ensure streptavidin attached to the SPIONs, a biotin-binding assay was executed using biotin fluorescein (B4F). A 2-fold dilution of an original 1:1000 dilution of B4F was performed. To 50ul of each diluted solution, 100ul of 1:10 SPIONs, 1:100 SPIONs, and PBS were added to wells in a black plate. After an hour of incubation in the dark and using the Gen5 BioTek Absorbance Microplate Reader, the absorbance was measured at 494nm.

A ferrozine assay was performed to quantify the concentration of iron before and after streptavidin-coating. Amine-SPION samples contained 5ul, 10ul and 20ul of SPIONs. First, each sample was
incubated in 70°C until solvent dried out. Then 200ul of 1:1 NaCl was added to each tube and incubated at 60°C for 4 hours in order to separate the particles since SPIONs are acid-sensitive. Following ferrozine assay protocol, 25ul of ammonium acetate, 50ul of 200mg/ml ascorbate solution, and 50ul of ferrozine were added to 25ul of each sample. The absorbance was measured on the Gen5 BioTek Absorbance Microplate Reader at 570nm. The same protocol was carried out for streptavidin-coated SPION samples.

3. Biobody attachment to Streptavidin-coated SPIONs

To gauge attachment of anti-B7-H4-Bb to streptavidin-coated SPIONs, 100ul of Bb (yeast supernatant) was added to 0,1,5,10 and 20ul of SPIONs, adding PBS to reach a total volume of 115ul. To neutralize pH, 2.5ul of 10M NaOH was added to the stock solution (500ul) of Bb. Each solution was incubated at room temperature for one hour to allow attachment to occur. An ELISA was then performed to ensure attachment. Into a streptavidin-coated plate, a 3-fold serial dilution in PBST was performed starting with a 1:10 dilution of each sample. After one hour of shaking at room temperature, 50ul of 1:1000 anti-V5-HRP in PBST was added. After shaking at room temperature for 30 minutes, the solutions were washed by centrifugation with PBST at 3000 rpm 3 times. Development was carried out using 50ml of TMB solution. To halt the reaction, 50ul of 1M HCl was added. The absorbance was measured at 450nm using the Gen5 BioTek Absorbance Microplate Reader.

4. Cell Culture Methods

4a. B7-H4-Expressing Cell Lines. B7-H4+ cells were required for B7-H4 targeting. SKBR3 is a human breast cancer cell line previously described as expressing B7-H4 (Salceda et al, 2005). Similarly, the Epstein-Barr virus-transformed B cells (EBVB) also expresses B7-H4 (Park et al, 2009).

4b. Cell Growth. A large cell population was required for testing, and therefore cell culture was needed. The freezer-stock of SKBR3 cells was placed in a 37°C water bath and immediately removed once thawed. To suspend the cells, 10mL of RPMI media was slowly added to the cell pellet, and centrifuged at 12,000 rpm for 5 minutes. The supernatant was drained, and the pellet was re-suspended in 5mL of RPMI. The cells incubated horizontally in a cell culture flask at 37°C to allow cells to stick to the flask and replicate. Cells were lifted every three to four days, which involved draining media, adding 0.5ml trypsin to lift the cells off of the flask, incubating for a few minutes at 37°C to ensure trypsin lifts all cells, adding 5ml of RPMI media, and re-suspending cells. Cells were counted often to monitor cell growth so that cell count was maintained between 0.1 and 2 million. The cells were counted on a hemacytometer using a 1:1 cell solution to trypan blue dye volume.

EVVB was cultured by adding 5ml of media (2%BME in RPMI). Splitting these cells involved centrifuging at 12,000rpm for 5 minutes, removing supernatant, re-suspending cells in 5ml of new media, and incubating at 37°C until the next splitting event.

5. Flow Cytometry Analysis

Flow cytometry was carried out for both cell lines to test B7-H4 expression. Seven samples were produced: five controls and two test samples. The controls included non-labeled cells, cells labeled with isotype Ab, cells labeled with commercial anti-B7-H4 Ab, cells incubated in SPIONs, and cells incubated with non targeted SPIONs or with SPIONS targeted with a non-relevant biobody (Bb137) (Zhao et al, 2011). The two test samples included cells incubated with SPIIONS targeted with anti-B7-H4 #26 or with anti-B7-H4 #56. SPION samples were assembled as follows: 5ul of iron-oxide were added to 0.5ml of PBS (with .05% BSA) and placed on a magnetic block for 10 minutes to wash and separate the beads.
Then, 0.5ml of the yeast containing the anti-B7-H4 or the control biobodies were added to each tube, along with 2.5ul 10M NaOH and 1:1000 B4F in PBS. After 30 minutes of incubation in the dark (because of the light-sensitive B4F), tubes were placed on the magnetic block. The supernatant was drained and 0.5ml of PBS was added and vortexed. This washing occurs 3 times, and finally the SPIONs were re-suspended in 0.5ml of FACS (1:50 FBS in PBS) buffer. 0.5ml of FACS was added to tubes three control samples as well, and then all tubes receive approximately 100,000 cells, which had been centrifuged at 10,000 rmps for 15 seconds and drained of supernatant. The reagents for the control samples were added as well. After refrigeration for 30 minutes, the samples were centrifuged for 15 seconds at 10,000 rpm. The supernatant was drained and the washing was repeated. 0.5ml of FACS was added, and each sample was ready to be evaluated in the flow cytometer.

RESULTS

Characterization of PEG-coated SPIONs

To verify that phospholipids, specifically amines and methyl esters, were added, the SPIONs were run through an agarose gel (see Figure 1). Triplicate samples of phospholipid-coated SPIONs (lanes1-3) were compared to one sample of the original CoFe$_2$O$_4$ SPIONs (lane 4). As expected, the phospholipid-coated SPIONs remain at the top of the gel because their larger size inhibits them from moving down the gel. In comparison, the smaller uncoated SPIONs in lane 4 move through the gel.

![Figure 1: Amine-coated SPION Agarose Gel.](image)

Ferrozine assays were performed to quantify the iron concentration in the SPIONs solutions. The iron concentration was calculated to be 199.3ug/ml. The ZetaSizer calculated the SPIONs coated with amines to have an average radius of 21.22nm. In addition, a TNBSA assay involving the SPIONs with amines was evaluated. Using butylamine as a standard, it was calculated that these SPIONs have amine concentrations around 10.5nmol/ml.

Validation of streptavidin coating on SPIONs

To ensure sulphhydride groups attached to the amines, the absorbance of samples using Ellman’s reagent was measured on the Nanodrop at 494nm. The absorbance values shifted from 0.005 with buffer and the reagent to 0.016 with the nanoparticles and the reagent. Ellman’s reagent produces a yellow-colored product when it reacts with a free sulphhydride group. The increase in absorbance values shows that the nanoparticles have sulphhydride groups attached.
Biotin binding assays were used to confirm streptavidin coating of the nanoparticles and to pinpoint the streptavidin saturation point. Figure 2 shows a non-linear curve on the fluorescence versus B4F concentration graph validates that there is B4F binding, which means there is streptavidin on the particles. In addition, a breaking point can be evaluated by calculating the intercept of the two linear portions of the curve. The breaking point is the concentration at which the streptavidin is saturated. This information revealed how much biobody needs to be added to fully cover the nanoparticles.

Validation of Biobody Production and Biobody-SPION Attachment

An ELISA on a streptavidin-coated plate was performed to test biobody secretion. The yeast supernatants for #26 and #56 both secreted biobodies. The biobody-SPIONs were also analyzed by an ELISA on a streptavidin-coated plate. The results confirm that biobodies attached to the streptavidin-coated SPIONs. (data not shown)

Identification of B7-H4 expressing cells

SKBR3 and EBVB cells were tested for B7-H4 expression using a commercially available antibody. In our hands, SKBR3 did not express B7-H4 but EBVB cells did.

Anti-B7-H4 targeted SPIONs bind to B7-H4 expressing Cells.

Seven samples were created, including four controls and three test samples. The controls included non-labelled cells, cells incubated with a control isotype antibody, with a commercially purchased Ab-B7-H4, and with non targeted SPIONs or with SPIONs targeted with Bb137. None of the negative controls bound to the cells (figure 3, red line). The cells incubated with SPIONs (figure 3, blue line) and the test samples, including cells incubated with SPIONs targeted with Bb26 (green) and or withBb56 (orange), bound to the B7-H4 expressing cells. The results demonstrate that anti-B7-H4 Bb-coated SPIONs specifically targeted B7-H4+ cells.
DISCUSSION

The biomedical applications of SPIONS are promising, including MRI detection and thermoablation. In order to generate a proof of concept for such applications, we used streptavidin-coated SPIONs coated with anti-B7-H4 biobodies. In this paper, we report preliminary findings supporting the successful coating of B7-H4 antibody fragments onto streptavidin-coated SPIONs. SPIONs were first coated with streptavidin by adding amines, converting these amines to sulfhydride groups, and adding maleimide streptavidin for attachment to the sulfhydride groups. A biotin-binding assay confirmed that streptavidin-coated SPIONs could be assembled. Furthermore, ELISA results proved that biobodies could be attached to streptavidin-coated SPIONs. Finally, flow cytometry validated functional attachment of the B7H4 targeted SPIONs to EBVB cells.

More research needs to be done in order to maximize accuracy and efficiency of this targeting method. First, several variables can be changed in the assembly of the SPIONs that might make targeting more efficient. The percentage of amines (we used 10%) could be increased, which will ultimately increase the amount of streptavidin on the SPIONs. Alternatively, sulfhydride groups could be added to the streptavidin and maleimide added to the phospholipids to see the effects of that change. Furthermore, targeting B7-H4 should be attempted in vivo in a tumor microenvironment with B7-H4 expressing macrophages.

Figure 3: Binding of Anti-B7-H4 targeted SPIONs to B7-H4 expressing cells. B7-H4+ EBVB cells were incubated with SPIONs targeted with anti-B7-H4 #26 (green) or with anti-B7-H4 #56 (orange). As negative controls, EBVB cells were incubated with non targeted SPIONs (blue), or SPIONs targeted with control Bb137 (red).
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Exploring Effective Techniques to Fabricate Thin Film Cells Composed of CZTS (Cu₂ZnSnS₄): A Literature Review

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ABSTRACT

Our research covers some of the various methods of fabricating and characterizing thin film solar cells using (Cu₂ZnSnS₄) CZTS as the absorber material. The methods discussed for fabricating thin films are the solution gel method. The techniques used for characterizing CZTS thin films are the use of a scanning electron microscope, (SEM), and X-ray Diffraction device, (XRD). There are several other methods, but the selected methods will be discussed as far as their purpose, how they work, and the results for using that method or device. CZTS thin films are discussed as a whole, including their characteristics concerning solar cells and why research should continue in order to increase these cells efficiency ratings. Future studies are underway in the research and development of fabrication and characterization of thin film CZTS solar cells.

Keywords
CZTS, Thin Film Solar Cells, SEM, Sol-gel, XRD, Magnetron Sputtering

INTRODUCTION

Sunlight by far is the most abundant form of non-carbon energy. Harnessing sunlight for the use of electricity is still a very expensive process. To see the use of solar power become more widespread there needs to be a dramatic drop in costs. Besides the expense of fabricating solar cells, the cost alone for materials is high. Table 1 shows some of the drawbacks with current photovoltaic, PV, materials (1).

Table 1: Drawbacks of current PV materials

<table>
<thead>
<tr>
<th>PV Material</th>
<th>Drawback</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>Requires thick layers which increases cost</td>
</tr>
<tr>
<td>a-Si</td>
<td>Low mobility, stability problems</td>
</tr>
<tr>
<td>GaAs</td>
<td>Arsenic toxicity, substrate cost</td>
</tr>
<tr>
<td>CIGS</td>
<td>Indium scarcity/cost</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium toxicity, tellurium scarcity/cost</td>
</tr>
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The PV industry is already a billion dollar industry. There has been a steady and rapid decline in the cost of thin-film modules (2). Figure 1 shows the best research-cell efficiencies and from the graph one can see that the highest thin-film cell, copper indium gallium (di)selenide, (CIGS), has an efficiency of 20.3% followed by cadmium telluride, (CdTe), 17.3%, amorphous silicon, (a-Si), 12.5%, and under emerging PV CZTS with 10.1% (3). Though the use non-toxic, inexpensive, and abundant materials, the cost of fabricating solar cells could be driven down to a more market appealing cost.
CZTS Background
CZTS solar cells are a new area of thin-film growth in the development of solar cells. CZTS is abbreviated as copper, zinc, tin, and sulfur. CZTS are becoming a popular alternative because of their abundant, low cost, non-toxic properties. The abundance of Cu, Zn, Sn, and S in the earth’s crust are 55, 70, 2.0, 260 ppm, respectively (4).

The more common silicon based solar cells are efficient however from Table 1, they require thick layers and have stability problems. Other common solar cells contain elements such as cadmium, arsenic, gallium, and indium which are rare and toxic elements which drive up the cost to produce cells. To be an efficient solar cell, from Figure 3 (5), it must first be within the optical band-gap...
energy levels of 1.2 – 1.5eV. CZTS has a direct band gap of 1.4-1.5eV and an absorption coefficient of the order of the 10^4 cm^-1 (4).

The CZTS make-up contains: copper (II) acetate monohydrate, zinc (II) acetate dihydrate, and tin (II) chloride dihydrate dissolved in a solvent and stabilizer and then goes through a sulfurization process. Min Yen Yeh reported using the following CZTS precursors: copper (II) chloride, zinc (II) chloride, tin (IV) chloride, and thiourea in a mixture and dissolved in deionized water containing 30 vol% ethanol (6). The important thing to note about the CZTS chemical make-up is that the compound is not stoichiometric but copper poor and zinc rich to improve the conversion efficiency. Figure 4 show that CZTS forms a crystal lattice structure. The CZTS solar cells prepared in vacuum causes their preparation processes to be expensive and complicated. IBM holds the record for the highest conversion efficiency and prepared their CZTS solar cell without a vacuum using a solution-gel method.

As seen in Figure 5 (7): a typical thin film device structure is composed of 4 layers:
1. A ZnO film which is the window layer;  
2. A CdS film which is the buffer layer;  
3. CIGS, CZTS for the purpose of this research, film which is the absorber layer;  
4. A Mo film which is the back contact.

This stack creates the $pn$ junction necessary for a solar cell to work. The $n$-type half of the device is actually composed of two layers, a ‘buffer’ layer of CdS which is very thin (~50 nm) and a thicker ‘window’ layer of ZnO. Electrical contact is made with the top of the device by addition of a transparent conducting oxide and metallic contact grid. The absorber layer is fabricated on a Mo-coated substrate, which provides mechanical strength and electrical contact to the back of the film (7). CZTS is the $p$-type half of the device and this is the layer where the incident light is absorbed and the excitation of electrons occurs. The interface of the $pn$ junction is where the flow of electrons occurs. There are several ways to fabricate and characterize thin film solar cells. Each way has its own benefits and its drawbacks. For this research, fabrication methods are focused on the sol-gel method. For characterizing thin films, the focus covers the use of a SEM, and XRD.

**Fabrication with Sol-gel**

Sol-gel or solution-gel is one of the least expensive approaches for fabricating a thin film solar cell. The greatest benefit is the equipment is relatively inexpensive and simple to operate, and doesn’t require the use of a clean room. The sol-gel method is based on hydrolysis and polycondensation reactions. Usually, oxyhydrate precursors can be deposited by the sol-gel method and oxides are obtained by annealing in air. (8) Sulfur is the oxide usually obtained through the annealing in air; however, thiourea has been used as a source for sulfur. (6) After a recipe has been created the solution has a gel like consistency. This gel is spin-coated onto a substrate and then goes through a sulfurization process. Spin-coating spreads the gel evenly across a substrate. The properties of the coating all vary depending on spin speed, acceleration, spin time, and exhaust volume. The quality of the wafer sample will also vary depending on the surrounding environment, i.e. pressure, humidity, temperature, and whether or not the process was performed in a clean room. The drawback with this method is it is difficult to duplicate the same procedure because of so many outside variables. Spin coating can also cause air pockets in the solution which directly affects the efficiency of the cell, although when the cell is heated through the sulfurization process it helps to reduce air pockets and possible cracks in the film, although it may not completely remove them. As stated before, CZTS is not stoichiometric meaning that the chemical make-
up of this compound does not have a one-to-one ratio and this can cause problems during the fabrication process. A finished cell may not actually contain CZTS. To verify whether the absorber layer is in fact CZTS, there are characterization tools that can determine the properties of the absorber layer.

**Characterizing with a SEM**

A SEM, allows the user to magnify the cell to see the physical structure of the cell. From the image created, the user can determine where modifications can be made in the fabrication process to fabricate a better cell. The SEM used, Hitachi 3700 VP-SEM, is capable of magnifying an image up to 300,000x normal magnification. This is possible because of the devices electron beam. As electrons are projected towards the target and bounce off to the collectors, a detailed image can be made. Figure 6 shows a two CZTS samples magnified at 200,000x normal magnification from the top view. When characterizing with an SEM, the top view will give a good view of grain size and how compact the grains are. The cross-sectional view image, shown in Figure 7, will give a good view of the layers thickness and the bonding of each layer. A current struggle with the fabrication of CZTS cells are in the grain sizes and how compact they are. From the SEM top view in Figure 6, the grain samples were either small and compact or large with many voids. Small grain sizes of CZTS cause short diffusion length of carriers. (11) Tanaka reported that the efficiency of polycrystalline solar cells increases with the increasing grain size in the absorber layer, and therefore, the larger grains are required for the fabrication of high efficiency solar cells. Higher temperature treatment of CZTS films showed increased crystallinity and grain size. To improve crystallinity and to grow larger grains, higher temperature annealing in the precursors are necessary. (8)

![Figure 6: CZTS under magnification by a SEM, top view.](image)

![Figure 7: CZTS under magnification by a SEM, cross-sectional view.](image)

**Characterizing with a XRD**

A XRD, X-Ray Diffraction, device yields the atomic structure of a given material. This is important since the CZTS compound is not stoichiometric, during the recipe process of making the compound, the
researcher may actually not come up with the correct compound. The way XRD does this is, as X-rays are projected toward the cell, and then picked up by the detector, a unique pattern is created. Based on the pattern and intensities of the waves detected a chemical makeup can be determined. From the results the researcher can determine what part of the recipe they would need to alter in order to come up with the CZTS compound. Figure 8 shows the output of a CZTS cell. The large spikes indicate when a wave reflected off a large grain and a definite signature of the compound can be picked up.

![Figure 8: XRD plot of a CZTS cell.](image)

The CZTS sample used in Figure 8 elected to use a sulfur powder to anneal the CZT sample. From Figure 8 the existence of S and MoS peaks suggest too much sulfur was added and CZTS peaks show stannite structure. (9)

**RESULTS**

The results of a CZTS cell vary greatly as there has yet to have been fabricated a high efficient marketable CZTS solar cell. Because CZTS cells offer a band-gap level very similar to that of silicon based cells, in theory, a CZTS cell should offer similar efficiency ratings. When choosing to go with the less expensive of the fabrication methods, sol-gel, the efficiency of the cell will undoubtedly be less than that of the more expensive methods of fabrication. The use of a clean room will improve efficiency of the cells as well as the least number of variables to factor in, the more likely to get a more consistent cell. The clean room will help to keep other particles from becoming part of the solution during the recipe process or the fabrication process. Having a vacuum will also eliminate the air pockets that could occur during the fabrication process in the sol-gel method.

**DISCUSSION**

When creating a solar cell there are certain characteristics to look for in the cells that would determine how efficient the cell will perform. IBM has fabricated the most efficient CZTS cell with an efficiency of 9.6% (10), now 10.1% via Figure 1. An ideal CZTS thin film cell will have large compact grains. From the SEM image in Figure 6, there are two CZTS samples. The sample on the left have very compact grains; however, the grains are very small. The sample on the right has large grains, but there are black voids in between the grains. This is the current struggle with CZTS cells. During the sulfurization process when going through the recipe, the cells are annealed at a high temperature >500 °C (4) (10) which causes the grains to grow. If the cells are annealed for too long then the chemical make starts to alter and is no longer CZTS. The crystal structure of CZTS is analogous to that of the chalcopyrite type semiconductor.
of CIGS, which is presently considered as the most promising absorber layer material in terms of efficiency in thin films. (11) Other areas that could be the cause of the low efficiency in the solar cells could reside in the window layer of the cell. The window layer acts as the top contact for the cell. The transmittance of the window layer should allow ~85% in the visible and near infrared region which would not be the cause of the low efficiency but a high resistivity of the window layer could account for some of the loss in efficiency. If the carriers cannot propagate through the window layer because of high resistivity this would lead to low efficiency. (11) When the cells are able to achieve a market acceptable efficiency, the cells could end up replacing silicon based cells because of the fact they are more cost effective to fabricate.

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The Analysis of Titanium Implant Surface Coatings

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ABSTRACT

The purpose of the project is to analyze the histomorphology of the bone-implant interface to determine whether a new biomimetic coating for titanium implants is as good as or better than the standard coating, BONIT matrix. The samples collected were small bone fragments of rabbit distal femur with calcium phosphate coated titanium implants imbedded in the tissue. To quantify the presence of osteointegration, Micro-Ct data was collected to measure bone contact volume at the implant surface. To maintain the integrity of the harvested tissue for further histological evaluation the titanium implant was dissolved using an electrochemical process developed in the lab. Once the implant was removed, the sample was re-imbedded using plastic technovit to conserve the biological structure of calcified bone in order to investigate the molecular mechanisms evoked by wear debris or degradation products derived from biodegradable polymers or metal alloys. After re-imbedding, the samples were evaluated using classic histological staining. These stains were analyzed with light microscopy and axiovision to observe the quality of tissue at the interface. Under analysis, the new coating seemed to show increased dissolution kinetics temporally thereby enhancing resorption around the implant interface for osseointegration. However, with the amount of data collected we could not prove or disprove the proficiency of the new coating because osteoblast and osteoclast activity appeared to be normal and low macrophage count showed little inflammation occurred in both coating types.

INTRODUCTION

Implant composition and surface coatings affect the structural and functional connection between living bone and the surface of a load-bearing artificial implant, a property called osteointegration. An optimal implant should induce controlled, guided, and accelerated wound healing by providing an interfacial matrix with a composition and structure characteristic of a bone [1]. Osteointegration is critical for long term success of the implant because it will prevent aseptic loosening of the implant. The rate, quantity, and quality of bone responses, such as osteointegration, are related to the surface properties of the implant [2]. Surface properties that play a major role are: chemical and physical properties, ionic composition, hydrophilicity, and roughness. Titanium is hydrophilic which is favorable in vivo and the calcium phosphate coating “increases the saturation of body fluids and results in the precipitation of a biological apatite onto the surface of the implant which serves as a matrix for osteogenic cell attachment and growth” [2]. Results from an in vitro study on the effects of brushite coated surfaces on osteoblastic activity show that the brushite coated titanium alloy surfaces supported the function of osteoblasts and the expression of extracellular matrix, supporting the idea that brushite coatings could enhance osteointegration in vivo [5].
Metallic implants are widely used as biomaterials, however their surface modifications vary. Surface topography influences osteoblastic proliferation, differentiation, and extracellular matrix protein expression [3]. Calcium phosphate coatings can be applied by many different methods, each with respective pros and cons and qualities that have varying effects on surface topography. The widely used Sol-Gel method is less porous and shows better biological performance, while other methods like plasma spraying produces thick, inhomogeneous coats [3]. Regardless of the method used for application, calcium phosphate coatings have certain characteristics that influence the efficacy of the implant. The stability of the coating influences the dissolution kinetics, the coating thickness influences attachment and adhesion to the substrate, and corrosive properties and the biological activity of the coating influence inflammation and other immune responses [3].

Some surface modifications other than calcium phosphate are nitride coatings, surface hardening by nitrogen ion implantation, and oxidizing agents [3]. However, calcium phosphate in its various forms such as hydroxyapatite, brushite, and β-tricalcium phosphate, has been proven to be effective in osteointegration.

In order to study the effects of coating A on a titanium implant, rabbits received these implants in their distal femur, and the tissue samples were explanted and imbedded using the Technovit 9100 technique because this method allows for the conservation of the biological structure of calcified bone. This is important in order to investigate the “molecular mechanisms evoked by debris or degradation products derived from biodegradable polymers or metal alloys” [4]. Possible problems at the implant interface could be aseptic loosening, implant migration, acute inflammation, and a foreign body reaction. To prove the coating A is as good as or better than BONIT matrix we would want to analyze the implant-tissue interface for signs of a foreign body capsule around the implant or any signs of the aforementioned possible problems, and we are looking to observe normal bone growth and resorption.

**PROJECT OBJECTIVE**

In this project we are analyzing a new composition and application method of biomimetic coatings on titanium implants, specifically the calcium phosphate coating brushite (CaHPO$_4$ - 2H$_2$O). The new coating will be referred to as “Coating A,” and it is thought to have certain advantages over the commonly accepted coating, BONIT matrix distributed by the DOT Company. The manufacturers of Coating A claim that it is easier to apply to the implant, exhibits good bonding and dissolution, and is faster at enhancing the activity of osteoblasts. We will be testing this claim by comparing the 2 surface coatings using histology and X-ray micro tomography.

**MATERIALS AND METHODS**

*Sample Acquisition*

The rabbit animal model, received implants in the distal femur, although blind during the study, implant type 1 with the BONIT coating was inserted into the left femur, and implant type 2 with Coating A was implanted in the right femur. These animals were then sacrificed at the time intervals of 4 weeks and 8 weeks. The implant and surrounding tissue was harvested and frozen. Micro tomography was performed on the frozen samples to get a three dimensional image of the sample. This was used to assess the bone contact volume around the implant. Once this had taken place the tissue samples were fixed in formalin and imbedded in Technovit 9100.

*Micro-CT analysis*
Using the program Contact 3, the picture data from the micro-CT were imported to analyze the volume of bone in contact with the implant. To allow the program to distinguish between bone and implant, the brightness threshold for bone was 65 and the brightness threshold for the implant was 160. With these settings the computer executed a program that outputted the 4 sets of data: voxels within 300µm outside the implant, voxels within 300µm outside the implant which are recognized as bone, volume of the implant, volume of the convex cover. Using these outputs the percentage of bone within the perimeter area was calculated.

\[
\% \text{ bone within the perimeter area} = \frac{100}{\text{number of perimeter voxel}} \times \text{voxels recognized as bone}
\]

Electrochemistry

To maintain the integrity of the harvested tissue for histological evaluation, the titanium implant had to be explanted from the tissue by electrochemical dissolution.

**Materials:** Bio-Rad Power Pac HC Power Supply, Magnetic stirring plate and stirring bar, continuous flow pump capable of pumping at least two lines simultaneously, 10%NaCl solution (1L), 3.175 diameter copper wire, open-top glass rectangular staining vessel, silver slurry solution, clear nail coating, epoxy, sandpaper, pliers, metal pin tool.

**Methods:** A polished 10 cm piece of copper wire was attached to the titanium of the implant using the silver slurry at the connection. Once the silver slurry had dried for an hour, epoxy was applied to the back of the copper wire to adhere it to the Technovit block, the epoxy was allowed to set overnight. The clear nail coating was used to coat all of the metal surfaces on the probe except the titanium.

For the dissolution system, the open-top glass vessel was filled with 10% NaCl, the solution with the magnetic stirring system was stirred rigorously. Using the pump, the 1L reservoir of 10% NaCl was connected to the open glass vessel, creating an inlet tube and outlet tube for both reservoirs. For the pair of cables plugged into the Bio-Rad PowerPac, the negative lead (red) was attached to the end of the copper wire, and the positive lead (black) to the cathode. The amperage on the machine was set to 70mA and the voltage to 10V. Dissolution continued until the Bio-Rad PowerPac no longer detected the load.

When the probe was finished it was rinsed with distilled water, the copper wire was detached, the epoxy was cleaned off and the sample was set out to dry for at least 24 hours.

Re-imbedding

**Materials:** Technovit stock solutions A and B, vacuum chamber, -4°C temperature refrigerator, plastic molds.

**Methods:** Tissue must be fixed and preinfiltrated prior to polymerization steps. For polymerization 45 mL of stock solution A and 5 mL of stock solution B was combined in a graduated cylinder. The tissue samples were placed into the mold and the Technovit was poured onto the tissue, but before closing the mold, the samples were set in a vacuum chamber for at least ten minutes. Then the mold was closed and the imbedded sample was kept in a -4°C refrigerator for 3 days to allow for slow and accurate polymerization.

**Sectioning (adapted TESA film method)**

**Materials:** microtome, TESA film, clamp box, 30% ethanol, paint thinner
Method: 30% alcohol was rubbed on the block and a small strip of TESA film was pressed across the block. Sectioning with the TESA film attached was done slowly to avoid making cracks in the sample. Once the section was firmly on the tape, the tape was placed across the cassette box with the tissue facing into the box and the box was closed with the lid. The entire box was incubated in paint thinner overnight. Then histological staining could proceed as normal.

Staining [4]

Classical Stains:
1. Masson Goldner’s Trichrome: Samples are first placed in Weigert’s haematoxylin (Chroma, Münster, Germany) for 4 min, briefly differentiated in 4% HCl–ethanol and washed in tap water for 10 min. Sections are then incubated in a solution of Ponceau de xylidine/acid fuchsine O (both from Chroma) in 0.5% acetic acid for 5 min, rinsed in 1% acetic acid and incubated in tungsten–phosphoric acid/orange G solution (both from Chroma) for 2 min. Sections are again rinsed in 1% acetic acid for 30 s, followed by incubation in light green SF (Merck) for 5 min and a further wash in 1% acetic acid. Samples are then dehydrated in a graded series of ethanol and mounted with Eukitt.
2. Toluidine Blue: Rehydrated sections are incubated in 0.1% toluidine blue O (Sigma, Taufkirchen, Germany) for 20 s, washed in distilled water, dehydrated in a graded series of ethanol and mounted in Eukitt.

Enzyme-based histochemical Stains:
1. Tartrate-resistant acidic phosphatase (TRAP) stain. Rehydrated sections are first placed in 0.2 M acetate buffer (pH 5.0) for 20 min and then in freshly prepared TRAP staining solution containing naphthol-AS-MX phosphate sodium salt as enzyme substrate and Fast Red TR salt as azo dye in 0.2 M acetate buffer (all from Sigma) for 120 min. After staining, the sections are washed in distilled water and mounted with Aquatex.

Immunohistochemical Stain:
1. MAC 387. The rehydrated sections are first washed in TBS, then treated with Proteinase K solution in Tris-HCl (pH 8.0) for 20 min at 37°C then washed with TBS again. Then the endogenous peroxidases are removed in 30 min treatment with 3% H2O2, followed by another TBS wash. After 30 min incubation in normal goat serum, the primary antibody MAC 387 is placed on the sections for 60 min at 37°C. After a TBS wash, the secondary antibody AK goat anti mouse x peroxidase En Vision is added for 30 min. The sections are then developed with DAB for 15 min and counterstained with DAPI for 2 min. Finally the sections are rinsed with distilled water and mounted with an Aquatex medium.

Microscopy and Photo-documentation
All microphotographs were taken using a Zeiss axioskop 40 combined with a Zeiss AxioCam Mrc digital 380 camera and Zeiss AxioVision software.

RESULTS

Micro-CT data

<table>
<thead>
<tr>
<th>TiAl6V4 + CaP Type 1**</th>
<th>TiAl6V4 + CaP Type 2**</th>
</tr>
</thead>
</table>

Table 1. Average percentage of bone around the implant in a 300 µm perimeter
** Conducted as a blind study: Titanium implant type 1 has the BONIT matrix coating from the DOT Company consisting of 2 layers, the inner layer being composed of hydroxyapatite, and the outer layer composed of brushite with each component representing 50% of the composition. Titanium implant type 2 has coating A with 95% brushite and 5% hydroxyapatite.

** Table 2. Average percentage of bone around the implant in a 300 µm perimeter by week  

<table>
<thead>
<tr>
<th></th>
<th>4 weeks</th>
<th>8 weeks</th>
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<tr>
<td>TiAl6V4 + CaP Typ 1</td>
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<td>TiAl6V4 + CaP Typ 1</td>
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<tr>
<td>TiAl6V4 + CaP Typ 2</td>
<td>77.77%</td>
<td>TiAl6V4 + CaP Typ 2</td>
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** Table 3. Quantitative analysis of tissue samples  

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<th>Osteoclasts</th>
<th>Osteoblasts</th>
<th>Fibrous Capsule</th>
<th>Macrophage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deru 1 – Li 4 weeks- Type 1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
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<tr>
<td>Deru 1 – Re 4 weeks- Type 2</td>
<td>0</td>
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<td>Deru 3 – Li 8 weeks- Type 1</td>
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</tbody>
</table>

** Table 3 Key  

<table>
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<th>Osteoclasts</th>
<th>Osteoblasts</th>
<th>Fibrous Capsule</th>
<th>Macrophage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 = Normal</td>
<td>1 = Slightly Above Normal</td>
<td>2 = Much Above Normal</td>
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</tbody>
</table>

** Note for Fibrous capsule- 2 would indicate a fibrous capsule that is a sign of a foreign body reaction, but 1 indicates that there is fibrous tissue that is transitioning to bone instead of scar tissue referred to as osteoid, the un-mineralized bone matrix.

** Photo-documentation  

Figure 1. TRAP stain: 4 weeks- type 1. Osteoclasts are red dots.
Figure 2. Masson Goldner stain: 4 weeks- type 1. Fibrous tissue in pink

Figure 3. MAC 387 stain: 8 weeks- type 1. No positively stained macrophages

Figure 4. MAC 387: Positive control spleen

Figure 5. Toluidine Blue Stain: 8 weeks- type 2. Normal Osteoblastic activity and no signs of fibrous tissue
DISCUSSION

Bone Contact Volume

It is very important for an implant coating to promote osteointegration to prevent aseptic loosening of the implant in vivo. The Micro-CT data shows the percentage of bone in contact with the implant in a 300 µm region around the implant surface. This data allows for the analysis of bone growth around the implant up to the time of sacrifice of the animal. A higher percentage of bone in contact with the implant would suggest that osteointegration at the implant interface is also higher.

The data suggests that coating A, present on implant type 2, is promoting quicker bone formation because at 4 weeks there is a higher percentage of bone in contact with the implant surface than on the BONIT matrix coating on implant type 1. However these effects seem to be temporal because by week 8, there is no significant difference in the percentage of bone in contact with implant between implant type 1 and implant type 2.

Due to the observation of increased bone volume by week 4, it can be assumed that coating A is dissolving faster than the BONIT matrix coating which is enhancing bone formation.

Electrochemical Dissolution

In order to preserve the tissue-implant interface, electrochemical dissolution was used to dissolve the titanium implant. There was an alteration to the method because unlike prior samples, these Technovit blocks were very small and did not have an exposed edge of titanium. Therefore an electric drill was used to drill through the Technovit in order to expose the implant. The copper wire was made into a conical shape to fit into the whole made by the drill.

This method proved to be a success, because in most cases the titanium dissolved completely and it allowed the tissue sections to come out more intact while also preserving the tissue adjacent to the former implant.

TESA Film method of histological analysis

The TESA film method of histological analysis created certain advantages for the analysis of the tissue samples. While microtoming the sections, the adhesive property of the film allowed for the section to avoid having wrinkles and folds, as normally occurs when microtoming. Also while staining; the tissue was not subject to falling off of the slide or coiling onto itself. By the end of the histological process the tissue samples on TESA film were less folded and deformed than the more common method without TESA film which allowed for a better qualitative view of the samples.

Although the TESA method produced an overall better result for the tissue samples, there were also some disadvantages to this method. Since the film is fragile, it would bend up and coil easily causing cracks in the sample during microtoming and staining steps. Some of the cracking was reduced when the cassette method was adopted. Also removing the excess adhesive on the tape requires 20 hours in a paint thinner solution before any staining can be done, and even with the extra precaution the TESA film seemed to cause a high amount of background staining. As this is a new technique, managing the cassettes between steps of the staining procedures was cumbersome and time consuming.

Conclusion

Current evidence suggest that Coating A is dissolving faster than the BONIT matrix coating on the titanium implant surface in vivo, which is enhancing bone formation and increasing osteointegration at a faster rate. This finding is most likely attributed to the higher brushite content in Coating A. However the effects of dissolution are only temporal because the data shows a significant difference in bone contact volume between type 1 and type 2 implants at week 4, but by week 8 the difference becomes marginal.
Histological findings show that neither coating created a significant foreign body reaction because none of the samples showed fibrous tissue capsules at the tissue-implant interface and since all of the samples showed negative results for the macrophage stain it can be concluded that little to no inflammation occurred. Also there was little difference in the activity of osteoblasts or osteoclasts near the interface amongst the two surface coating types.

Although the trend from this data shows that Coating A is exhibiting good bonding and dissolution, in order to prove the Coating A is better than the BONIT matrix coating at enhancing osteoblastic activity and osteointegration, more data would need to be collected.

REFERENCES


Healing Efficiency of a PCL/Epoxy System: Mitigating Corrosion on Metal Surfaces

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ABSTRACT

Metallic corrosion has been a major problem in American industry and has lead to billions of dollars in expenses on corrosion reparation. There is a demand for mitigating corrosion in various industries such as: infrastructures, transportation, and utilities. Inspired by biological systems that have healing characteristics, self-healing polymeric coatings have been introduced as a solution for reducing corrosion. Various self-healing material methods have been studied for their ability to recover from load bearing damage. Although there are benefits to their self-healing capabilities, there are challenges that limit their use in practical applications. The purpose of this study is to target healing variables (healing time and healing temperature) that allow for optimal healing results. The approach that is used in this study encompasses a biphasic coating comprised of electrospun poly-caprolactone (PCL) fibers and an epoxy matrix that meet the advantages of being low on cost and provides for a toughening matrix thermoset. Electrospinning and spin-coating processes were used to coat the self-healing system. Two coating thicknesses were tested (10 and 15 minute electrospun PCL fibers). Mechanical damage was induced onto the biphasic coating, and self healing variables were tested (healing times: 10, 30, and 60 minutes) at a fixed temperature (80 °C) for observation of optimal healing efficiency. Structural and condition experimental variables were tested to observe their self-healing characteristics. The results revealed that the coating system was able to self-heal in the given healing times. Our findings suggest that using smaller time intervals in future testing may disclose more accurate readings in the ability of the coating system to heal rapidly. Additional stability and uniformity in damaging methods can eliminate variability in testing results. Detailed understanding of variable properties will assist with future design techniques for fine tuning of this system for larger scale application.

1. INTRODUCTION

Corrosion has been a major problem in industry, costing millions of dollars each year in reparation. It is estimated that the cost of corrosion in the U.S alone is $276 billion dollars a year (CC Technologies, 2006). Humid environments accelerate the amount of corrosion, particularly on outdoor metal surfaces. The corrosion then compromises the surface of the metal, causing rusting and mechanical damage. These damages compromise the structure of the metal surfaces. Inspired by the healing mechanism of biological systems, polymers are introduced as self-healing coatings to help alleviate corroding metal surfaces. These self-healing materials have the ability to affectively restore the properties of the material after thermal or mechanical damage.

Several studies have shown different techniques that incorporate self-healing materials that can repair damage. An approach first introduced by the University of Illinois of Champaign (UIUC) involves the mechanism of healing agents (monomers) being released by microcapsules that rupture as a result of crack propagation. The healing agent polymerizes in the presence of a catalyst and re-bonds the crack
This autonomic system contains unterminated chain ends that are designed to polymerize only when there is crack propagation.

While these studies have shown the ability for this system to self-heal, there have been technical concerns that include but are not limited healing agent stability, release of healing agent from microcapsules and unevenness of healing agent distribution (Brochu, Craig, & Reichert, 2011).

Other self-healing techniques include highly cross-linked reversible reactions that have the ability to chemically mend cracks and rebind deformations on the polymer (Yoshie, Watanabe, Araki, & Ishida, 2010). This self-healing technique uses a thermally reversible Diels-Alder reaction. This reaction favors cross-linking when cooled and decrosslinking when heated. At 60°C, at what is considered the forward reaction of the Diel-Alder (DA) reaction, this network of polymer is cross-linked. At a temperature of 145°C, the reverse reaction of DA reproduces decrosslinking of the maleimide furan polymer network. (Yoshie, Watanabe, Araki, & Ishida, 2010).

Self-healing coatings are currently looking to integrate self-healing sensing control. Damage is detected using electro-optical sensing. The key to these ideas are to control healing so that all reparations can be monitored based on continuous sensor data. These designs are improving the face of self-healing materials (Hurley & Huston, 2011). In addition, hydrophobic materials that mimic naturally occurring hydrophobicity have been investigated. It is the hopes that the incorporation of this characteristic can repel water thus mitigating corrosion on metal surfaces. Cathodic protection can prevent water absorption thus slowing down metal oxidation (Self-Healing Superhydrophobic Coatings For Corrison Protecton, 2006).

The technique used for this study combines electrospun poly(caprolactone) (PCL) fibers and an epoxy matrix as the barrier. PCL is a biodegradable polymer that has been used in several different types of biomedical applications including drug delivery, scaffolds, suture and vascular graft development (Pires, et al., 2005). Its chemical and physical properties allow for its wide range of use and compatibility in biological settings. With its particular influence from biological reparative system behavior, PCL can be applied to coatings as a self-healing composite in polymer coatings. Polymeric coatings are introduced in this application to alleviate the problem of corrosion. PCL is also a hydrophobic polymer and with its self-healing capabilities, its incorporation into a self-healing material to alleviate corrosion is, thus appropriate. PCL fibers serve as the healing agent of this coating system, where healing can be activated by an increase of temperature.

An epoxy thermoset is also incorporated into this self-healing coating system. The desired properties for typical coatings, for example, adhesion to substrate, and hardness, make the thermoset epoxy ideal for this study. The simple means of producing this epoxy has been explored and previously reported (Xie & Rousseau, 2009). This thermoset epoxy has been selected for this coating system. The epoxy system was tailored and temperatures were easily controlled using different ratios of aromatic diepoxide and aliphatic diepoxide. The epoxy thermoset also has a high stiffness which makes it ideal for this application.

Studies by Luo have shown that the concept of shape-memory assisted self-healing coatings are effective in providing for corrosion resistance to metal surfaces by. The current understanding of self-healing polymer coatings, allows us to investigate the effects of self-healing parameters that account for the most ideal ways to self heal. The aim of this study is to investigate the effects of self-healing parameters and how they account for optimal self-healing. There are a variety of parameters that affect the self-healing characteristics that include: coating thickness, healing time and healing temperature. There are structural variables that include fiber diameter, coating thickness and weight fraction. Condition
variables include healing temperatures and healing time. In particular, coating thickness will be examined, aiming to account for any variability in self-healing efficiency for the crack damaged surface.

2. MATERIALS AND METHODS

Polyolcaprolactone, polyester, is the polymer used for the self-healing agent in this experiment. Polyolcaprolactone has several chemical and physical properties that make it an ideal polymer for its application in self-healing coatings. It is biodegradable, biocompatible, and have melting and glass transitioning temperatures that allow for its mend ability in this particular application. At a melting point around (60°C), PCL becomes (malleable) and in this transition stage, the polymer is able to self-heal. The self healing mechanism occurs by triggering an increase in temperature. When heat is applied, the damaged surface of the coating matrix is able to bring the crack to close proximity while the fibers diffuse to re-bond the crack/damage surfaces together (Luo, 2010).

Epoxy, composed of neopentyl glycol diglycidyl (NGDE), diglycidyl ether of bisphenol-A (DGEBA) and Jeffamine. Previous protocols are followed to optimize the molar ratio of each component of the epoxy (1:1:1) (Xie & Rousseau, 2009).

Figure 1. Molecular structure of PCL/Epoxy System

The materials selected for this study, (PCL/Epoxy) as a self-healing coating, once cured onto the surface provides for good adhesion and has been previously studied to show characteristics of shape memory properties (Xie & Rousseau, 2009).

2.1. Synthesis of PCL solution

The polymer solution is composed of 2g of PCL and a solvent volume ratio of 8 mL of chloroform and 2 mL of dimethyl formaldehyde (DMF). The mixture was stirred until the mixture was transparent and homogeneous. The mixture was poured into a glass syringe in preparation for electrospinning.
2.2. Synthesis of Epoxy

DGEBA was first melted in the oven at a temperature of 70 °C and placed in a glass bottle. The NGDE and Jeffamine were then added proportionally to the amount of DGEBA that was placed in the glass bottle so that the mol ratio for the three components is (1:1:1). Once the solution was stirred and homogeneous, the solution was poured into a syringe to prepare for spin-coating.

2.3. Coating with PCL/Epoxy System

Electrospinning is used to layer metal substrates with PCL fibers. The electrostatic forces cause tension, stretching to form microfibers. Figure 1 illustrates the electrospinning setup for the placement of PCL fibers onto the metal surface substrate. For the purpose of this study the electrospinning parameter voltage was kept at 14kv for all coated samples. At this voltage the diameter of the fibers are most homogeneous and the flow at which the fibers were mounting on the metal substrate was stable (no clogging). The metal substrates dimensions measured 3 x 3 cm. When metal substrates are completely coated, they were left to dry for 24 hours to ensure the PCL fibers were not wet and the PCL fibers have adhered to the surface.

Experimental Setup: Electrospinning Conditions

![Diagram of Electrospinning Setup]

Electrospinning Parameters
- Flow Rate: 1 ml/hr
- Voltage: 14 kv
- Distance to tip: 15 cm

Polymer Solution: 2 g of PCL, Chlorform/DMF (8:2 volume ratio)

Figure 2. Electrospinning Conditions. A high voltage (14kv) DC power supply was used to mount the PCL fibers onto the surface of the metal substrate. The white surface on the plate is indicative of PCL fibers successfully coating the metal substrate.

2.3.1. Coating Thickness

The coating thicknesses on the surface of the metal substrates are accounted for by the running time of electrospinning. Previous experiments have shown that the coating thickness of the PCL fibers has a linear correlation to the electrospinning time (Luo). This structural variable will be examined for the remainder of the experiment to explore potential effects of coating thickness/amount of healing agent in
healing efficiency. The run time for electrospinning was 10 and 15 minutes. The coating thickness for 10 minutes of electrospinning is approximately 100 µm, for 15 minutes 150 µm.

2.3.2. Spin-Coating
The epoxy coating is done using a spin-coater. With a set rotation system speed,(set forth in preliminary studies) the epoxy solution is placed in a syringe and attached to the spin-coater. It takes approximately 1.5 mL of epoxy solution to wet the PCL fibers on the metal substrate surface. When the samples are coated with the PCL/Epoxy coating, the samples are left to cure for 48 hours and 24 hours at 40 ºC.

2.3.3. Weight fraction of PCL fibers and PCL/Epoxy
The weight fraction of PCL fibers on the surface is calculated using the equation $W_f$ is the fraction of the PCL fibers on the surface, $W_m$ is the weight of the metal substrate and $W_c$ accounts for the mass of the PCL and epoxy coating combined. Understanding the relationship of how weight fraction of PCL fibers on the surface can assist with the correlation of PCL fibers and self-healing efficiency.

$$\frac{W_f - W_m}{W_c - W_m}$$

Equation 1. Equation for weight fraction of fibers on the metal substrate surface

2.4. PCL Fiber Analysis
Scanning Electron Microscopy was used to exam the fibers to observe for homogeneity when electrospinning. Preliminary studies have selected to maintain fiber diameters around 1 µm. For the purpose of maintaining all other parameters consistent, 1µm was replicated for this experiment.

Using Image Processing and Analysis in Java (Image J), fiber diameter was measured for electrospun PCL fibers at 12 kV and 14 kV. A comparison of fiber size was done to observe, which would result in fibers closest to the desired diameter.

2.5. Characterization of Thermal Properties of the PCL/Epoxy System
Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were conducted to ensure melting($T_m$) and crystallization ($T_c$) temperatures were as anticipated $T_m$ approximately 60°C, $T_c$ 25°C. (Luo).

2.6. Water Absorption of PCL/Epoxy
Tests were also conducted to observe for any absorption of water by the coating. For this section of the experiment, the coating was placed in a vile filled with distilled water. Absorption was measured by placing samples on a scale to determine the mass after each specified time. Samples were weighted for 144 hours.

2.7. Damaging Technique
Using a razor blade and a diagonal cut (1.5cm) was made across the coating using a secured parallel clamp to ensure straight cut damaged to the coating system. The razor blade damage is made to account for real-life damages that may occur to this coating so that, self-healing abilities can evaluated.

The damaged samples will then be placed in a NaCl (5 wt%) solution to mimic corrosive environments. The samples were left in solution for 5 days and removed.
2.8. Self Healing Method and Evaluation of Corrosion

Understanding the temperature at which self-healing occurs (60˚C) and for future testing temperature ranging from 60-100 degree can be tested. In consideration of this experiment the healing temperature was set to 80 degrees.

Test Groups

The control groups for the experiment are the coated not self healed coating. These samples were not placed in the oven at 80˚C for any of the three healing times specified in Table 1 (10, 30 and 60 minutes). The other tested samples were healed by placement in the oven at 80 ˚C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>10 minute</th>
<th>30 minute</th>
<th>60 minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Not Self-healed)</td>
<td>X</td>
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<td>X</td>
</tr>
<tr>
<td>Self-Healed</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 1. Experimental Setup for Testing. Healing Time is also accounted for in this experiment for 10 minute and 15 minute electrospun coatings

The mean corrosion of the corroded area around the damage was measured by scanning the sample using Canon Scan 800F and measuring the area of corrosion using Image J. The mean corrosion creepage is calculated using the following formula where A, indicates the area and L is the length of the damaged area.

\[ C = \frac{A}{2L} \]

Equation 2. Mean corrosion creepage equation.

Used to calculate the corrosion surround the damaged crack area

3. RESULTS

Analysis of PCL fiber and corrosion resistance was completed in this study. Coating thickness, the structural variable and healing time a condition variable were the primary factors to take note of in this study.

3.1. Weight fraction of PCL fibers

The observed weight fraction allows for the analysis to correlation of healing agent to self-healing efficiency for the PCL/Epoxy system. Weight fraction of PCL fibers were measured and results revealed comparable amounts of PCL fibers on the surface of the metal substrate for ten and fifteen minutes of electrospinning.

Table 2 indicates the amount of PCL fibers in weight grams on the surface of the metal substrate.
3.2. Fiber Diameter Analysis

Using Image Processing and Analysis in Java (Image J), pixels were measured and converted to centimeters (cm). Image J permits the measurement of the SEM imaged fibers using a straight segmented line to measure across the diameter of each fiber. The fiber measurement of the diameter is given in pixels and converted to centimeters (cm). Figures below show SEM images of electrospun PCL fibers. The electrospun 14 kv PCL fibers are, on average thinner in diameter than the 12 kv electrospun PCL fibers. The samples were coated using 14kv for the remainder of the experiment. Under SEM images, these fibers were observed to be homogeneous.

![E-spun at 12kv](image1)

![E-spun at 14kv](image2)

Avg. Fiber Diameter= 1.5109 ± .9845 µm

Avg. Fiber Diameter= 1.0725 ± .4908 µm

Figure 3. Fiber diameter analysis of electrospun PCL fibers. 14kv was observed to be similar to preliminary studies thus was selected for the fixed voltage for all samples

3.3. Characterization of Thermal Properties

Characterization of thermal properties Retesting for these temperatures, proved to be comparable to previous testing. Table 4 indicates the values determined for the \( T_m \) and \( T_c \) for the PCL fibers. Similarly TGA and DSC test were also done for the PCL/Epoxy coating. Transition temperatures (\( T_m \) and \( T_c \) for the PCL/Epoxy coating were 52.72 °C and 21.02°C respectively.

**Table 2. Weight fraction for 10 and 15 minute electrospun PCL/Epoxy system**

<table>
<thead>
<tr>
<th>Weight Fraction of PCL fibers (grams)</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 minute coating of PCL/Epoxy</td>
<td>0.0898</td>
<td>0.0831</td>
</tr>
<tr>
<td>15 minute coating of PCL/Epoxy</td>
<td>0.0708</td>
<td>0.0871</td>
</tr>
</tbody>
</table>
Figure 4. TGA and DSC analysis. The graph on the left indicates the TGA analysis and DSC to right. According to preliminary the temperatures indicated are in close proximity to expected temperatures

Table 4. Melting and Crystallization temperatures for the electrospun PCL fibers

<table>
<thead>
<tr>
<th>PCL Fibers (Thermal Properties)</th>
<th>Transition Temperature</th>
<th>heat energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$</td>
<td>54.84 °C</td>
<td>54.03 J/g</td>
</tr>
<tr>
<td>$T_c$</td>
<td>27.98 °C</td>
<td>46.65 J/g</td>
</tr>
</tbody>
</table>

Figure 5. TGA and DSC Analysis of PCL/Epoxy System. Both TGA and DSC temperatures show that the melting and crystallization temperatures to the healing agent PCL fibers
Table 5. TGA and DSC melting and crystallization temperatures for the PCL/Epoxy System

<table>
<thead>
<tr>
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<td>46.65 J/g</td>
</tr>
</tbody>
</table>

TGA and DSC analysis also allow for the investigation of residue curing. Residue curing occurs during heating and may give a misinterpretation of self-healing temperatures. The samples tested did not show evident signs of residue cure.

3.4. Water Absorbency of PCL/Epoxy System

There is an increase of water absorption with increase of healing agent, suggesting a correlation among the two variables. Recordings of water absorbency are unstable which may factor into surface evaporation upon removal of submerged sample from the distilled water.

3.5. Corrosion Resistance Tests

There is an increase of water absorption with increase of healing agent, suggesting a correlation among the two variables. Recordings of water absorbency are unstable which may factor into surface evaporation upon removal of submerged sample from the distilled water.
7 indicated that the samples that underwent the self healing procedure showed less Mean Corrosion Creepage indicating that the PCL/Epoxy system is affective in alleviating corrosion.

![Graph 10 Minute Coating of PCL/Epoxy](image1)

Figure 7. Ten minute PCL/Epoxy system. Results show that healed surfaces were less prone to corrosion in comparison to damaged unhealed surfaces. There is a variance of time of 10, 20 and 30 minutes. The variation of time show no distinct influence on resistance to corrosion.

![Graph 15 Minute Coating of PCL/Epoxy](image2)

Figure 8. Fifteen minute PCL/Epoxy system. Results vary more this thicker coating in comparison to 10 minute coatings. No defined behavior.
Table 6. Results of measured mean corrosion creepage for ten minute PCL/Epoxy System. Corrosion for healed coatings were distinctly smaller than the damaged unhealed samples

<table>
<thead>
<tr>
<th>Healing Time (min)</th>
<th>Damaged</th>
<th>Healed</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.46 ± 0.3</td>
<td>0.10 ± 0.0</td>
</tr>
<tr>
<td>30</td>
<td>0.24 ± 0.1</td>
<td>0.10 ± 0.1</td>
</tr>
<tr>
<td>60</td>
<td>0.26 ± 0.3</td>
<td>0.03 ± 0.0</td>
</tr>
</tbody>
</table>

The measured perimeter surrounding the crack (damaged area) for the unhealed coating surface has a larger perimeter of corroded surface than the healed surface. The PCL/Epoxy coating thus shows effectively in its ability to alleviate corrosion around damaged cracks on the surface. A comparable test was done on 15 minute coated samples; an inconsistency compared to the 10 minute coating is very evident. Variability in crack dimension is accounted for in this end result, indicating that thickness of the coating system influences the corroded area. Thicker coatings and variability in healing time resulted in similar results for corrosion area for both damaged and healed cracked surfaces.

Table 7. Mean corrosion creepage for fifteen minute PCL/Epoxy System. There is no distinct behavior relationship between the healed and damaged samples. Variation may be due to thickness and incomplete penetration to the PCL/Epoxy system

<table>
<thead>
<tr>
<th>Healing Time (min)</th>
<th>Damaged</th>
<th>Healed</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.50 ± 0.4</td>
<td>0.14 ± 0.1</td>
</tr>
<tr>
<td>30</td>
<td>0.14 ± 0.1</td>
<td>0.1464 ± 0.2</td>
</tr>
<tr>
<td>60</td>
<td>0.15 ± 0.0</td>
<td>0.2119 ± 0.0</td>
</tr>
</tbody>
</table>

4. DISCUSSION

Evaluation of characteristic of the PCL/Epoxy system proved to be similar to preliminary studies conducted where specifically melting temperatures for PCL and the PCL/Epoxy were ≈ 60˚C (Luo). The understanding and importance of thermal properties to be similar in the beginning step, provide for little variation as other variables such as coat thickness and heal time come into play. Figure 3 illustrates the homogeneity of fiber diameter. We are not yet certain if fiber diameter directly affects the ability for this healing agent to be more or less effective.

The knowledge of variables such as fiber diameter, coating thickness, healing time and healing temperature propose a variety of ways this system can be manipulated by. Figure 7 and 8 illustrate the behavior of healing thickness and there were no evident consistent relationships with the amount of healing agent. With larger thicknesses, creating a clean damaged cut becomes more difficult due to the
surface of the PCL/Epoxy System. Thus the means of damage must be stabilized to ensure identical damaged surfaces for all samples.

Suggestions for experimenting with healing the samples in water, also create for a real-life situation, and can evaluate the ability of the coating system to heal while submerged in a corrosive environment. For this experiment samples were submerged for 5 days and then removed from the NaCl solution. More corrosive activity could have occurred which could in turn increase the amount corroded surface. Increasing the length of time of submersion may influence mean corrosion creepage but for restrictions to this project, five days was found to be adequate enough to start recording mean corrosion creepage.

CONCLUSION

Healing time of the PCL/Epoxy coating system may be a minimal factor in efficiency of preventing corrosion. The variability in the mean corrosion creepage for the ten and fifteen minute electrospun coated samples may be due the method of damage to the coated system with a razor blade. Based on the healing times that were tested (10, 30 and 60) minutes, one might infer that shorter healing times should be tested to decipher if shorter healing periods can account for equivalent healing capabilities.

The application of this coating material can perhaps be used in larger metal surfaces for coating ships and aircraft. Different coating techniques, such as spraying or dip-coating would provide for more efficient means for covering surfaces of this magnitude.

Future development in the stability and uniformity in the technique used to create damaged area (cracks) can eliminate variable areas for corrosion to occur. The knowledge of these structural and condition variables can allow for further fine-tuning to create possible novel material in this current design strategy. Continued work will assure the appropriate chemical and physical properties are most ideal for durability and efficiency.

REFERENCES


Non Equilibrium plasma reforming of hydrocarbon fuels without carbon dioxide emission

FELA ODEYEMI, MIKHAIL PEKKER, ALEXANDER RABINOVICH, ALEXANDER FRIDMAN

A.J Drexel Plasma Institute, Drexel University, Philadelphia PA

INTRODUCTION

With non-equilibrium plasma, an alternative process of extracting energy from fossil fuels (coal, biomass, hydrocarbons etc) without the emission of CO₂ is possible. Apart from CO and CO₂, there exist carbon oxides which can be polymerized to form chemically and thermodynamically stable substances. These carbon oxides are known as carbon suboxides (C₃O₂). This article describes a novel process of extracting the chemical energy from fossil fuels without the emission of CO₂ while producing hydrogen and carbon suboxide (a reddish, brown polymer) which is an important constituent of organic fertilizers. This approach has the capability of avoiding the drawbacks associated with combustion of fossil fuels. Carbon suboxide (C₃O₂) is a foul-smelling lachrymatory non-toxic gas. It has linear symmetric structure that can be represented as O=C=C=C=O. The suboxide is stable at -78°C; at 25°C it polymerizes to form a highly colored solid material with a polycyclic six member lactone structure. Carbon suboxide is typically produced by thermal dehydration of malonic acid CH₂(COOH)₂ in the presence of P₂O₁₀ (a drying agent)[1]. The carbon suboxide is the acid anhydride of malonic acid, and it slowly reacts with water to produce that acid. It can be stored (compared to CO) at a pressure of a few Torr, but under standard conditions C₃O₂ forms a yellow, red, or brown polymer (C₃O₂)n (ruby-red above 100°C, violet at 400°C, and it decomposes into carbon at 500°C)[2].

EXPERIMENTAL

A non-equilibrium plasma discharge (dielectric barrier discharge) is better suited for low temperature gaseous hydrocarbon oxidation reactions due to its low temperature and low power requirement. Low temperature plasma assisted oxidation of hydrocarbon experiments were conducted in a Dielectric barrier discharge (DBD) reactor with butane (C₄H₁₀) as the hydrocarbon feedstock mixed with air. The DBD reactor consists of a 4 feet long quartz tube with 22 mm internal diameter (ID). The quartz tube functions as a dielectric barrier. Inside the quartz tube is an 80cm long stainless steel electrode, the stainless steel electrode serves as the high voltage electrode. The high voltage electrode was held in place inside the quartz tube with the aid of a silicone stopper at the inlet of the quartz tube and a ceramic holder at the inner center of the reactor. The uniform distance between the high voltage electrode and the quartz inner wall will ensure the uniformity of the propagation of the plasma discharge from the high voltage electrode to the inner wall of the quartz tube. A copper mesh is wrapped around the outer surface of the quartz tube to align with the stainless steel electrode, spanning 40cm in length. The copper mesh serves as the ground electrode. Butane gas and air were mixed before entering the DBD reactor. The gas mixture was delivered to the reactor via ¼” tubes and fed directly into the reactor through an aperture within the stainless steel electrodes. Butane and Air flow rates were each controlled with Omega FMA-2605A series mass flow controllers according to the desired oxygen to carbon ratio. A variable alternating current (A.C) power supply was used to generate the DBD plasma. The power supply has an operational frequency of 50Hz – 1.66 kHz and a maximum peak to peak voltage range of 20 kV– 34 kV. The cylindrical DBD reactor was placed in a temperature controlled Carbolite STF 16/610 furnace. In order to accelerate the rate of
deposition of solid products produced from the plasma assisted oxidation of butane (C₄H₁₀), a water-cooled heat exchanger made from 1/16” copper tubing, (wound into a spiral shape) was inserted inside the post plasma region of the DBD reactor. Typical experiments involves the treatment of butane-air mixture with DBD for 150 minutes after which butane and air flows are shut off and the deposit dried up in the reactor via the heat from the furnace.

**RESULTS AND DISCUSSION**

The low temperature oxidation experiments were conducted in the DBD plasma reactor with butane (C₄H₁₀) and air as the reacting gases. The experiments were conducted at atmospheric pressure conditions. The temperature around the external region of the DBD reactor was constantly monitored with the aid of thermocouples connected to temperature readers. Glass slides (19”x19”) were placed within the post plasma region of the DBD reactor to collect solid deposits for analyses and characterization.

Solid deposits start to form within moments of butane-air reaction in the presence of plasma. The deposits formed within the post plasma region of the reactor usually appear reddish brown at temperatures between 150C - 400C and carbon black at temperatures greater than 500C. The reddish – brown deposits collected after 150 minutes of plasma treatment at low temperatures (150C - 400C) appear wet and sticky. This is attributed to some water produced during the butane - oxidation reaction. The gas produced at the post plasma region of the DBD reactor as well as the reddish brown deposits were observed to be characterized by a pungent smell and lachrymatory. The reddish brown deposits collected on the glass slides inside the reactor were dried (using the heat from a furnace) and analyzed for its chemical structure via energy-dispersive x-ray spectroscopy (EDX)[3].

To ensure the accuracy of the characterization results, the Energy-dispersive X-ray spectroscopy device was tested for its accuracy by performing elemental analysis tests on a known sample – Caprolactam (C₆H₁₁NO) - placed on gold with respect to the Carbon: Oxygen ratio. The Carbon:Oxygen atomic ratio result came out to be 5.5~6.5:1; this confirmed the accuracy of the SEM-EDX feedback. Elemental analysis tests were carried out on the solid deposit samples collected during the plasma assisted butane oxidation experiments. The Carbon: Oxygen ratio of the sample analyzed was in the range 1.5~1.8: 1 (Table 1) and this ratio corresponds to that of carbon suboxide C₃O₂ (Carbon: Oxygen = 1.5)

**Table 8: Atomic balance of a tested sample showing the carbon: Oxygen ratio**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atoms (%)</th>
<th>Atoms (%)</th>
<th>Atoms (%)</th>
<th>Atoms (%)</th>
<th>Atoms (%)</th>
<th>Atoms (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>53.69</td>
<td>50.55</td>
<td>51.43</td>
<td>51.64</td>
<td>52.7</td>
<td>51.74</td>
</tr>
<tr>
<td>N</td>
<td>12.77</td>
<td>15.78</td>
<td>14.18</td>
<td>10.61</td>
<td>14.66</td>
<td>14.65</td>
</tr>
<tr>
<td>O</td>
<td>33.54</td>
<td>33.67</td>
<td>34.39</td>
<td>35.41</td>
<td>32.51</td>
<td>33.61</td>
</tr>
<tr>
<td>C:O ratio</td>
<td>1.60</td>
<td>1.50</td>
<td>1.50</td>
<td>1.46</td>
<td>1.62</td>
<td>1.54</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Experimental testing of non-thermal plasma reforming of butane in DBD reactor confirms carbon suboxides production. Elemental analysis (carried out with EDX spectroscopy) of the produced deposits suggests that C:O ratio in the analyzed sample is 1.5 and this corresponds to the C:O ratio of carbon suboxide \((C_3O_2)_n\). Further work will be focused on establishing the optimal regimes for carbon suboxide and hydrogen production using different hydrocarbon feed stocks at different O/C ratios, temperature, plasma power and reagents flow rates.

ACKNOWLEDGEMENT

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REFERENCES


Micro Solar Thermal Power Harvesting using Thermoelectric Generator

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Research Advisor: Dr. Leland Weiss

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ABSTRACT

The use of a thermoelectric generator (TEG) in generating useful power from solar thermal energy is demonstrated. This device represents a portable and autonomous power generation system operating from solar power, capable of powering micro/nano systems. The TEG was integrated with a micro solar thermal collector plate to enhance the thermal radiation absorption capacity of the hot side of the TEG. Solar thermal collectors were fabricated on copper substrate. Electro-chemical deposition techniques were used to deposit the selective absorber coating consisting of a black nickel-tin bimetallic layer. The selective coating significantly improved the ability of the collector to transform incident solar radiation into thermal energy. This is demonstrated by the improved output power of 9.15 mW from the TEG with a selective absorber plate as compared to a baseline setup without a selective coating where only 2.01 mW was generated. The overall area of the collector was 16 cm².

INTRODUCTION

Energy demands across the world have been on a rapid rise recently due to population growth and industrialization. It is obvious that traditional fossil fuels are under increasing demand and there is a need to examine alternate energy sources to augment these energy sources for power generation. More over with advancements in the development and commercialization of Micro/Nano Electro-Mechanical Systems (MEMS/NEMS) and devices, there is need and opportunity to develop portable and autonomous power generation systems that will ensure such systems and devices are adequately powered even in remote locations. The sun represents one such alternative energy source, which is presently underutilized. Solar energy is a renewable and sustainable energy source. It has a promising potential to meet both the present and future world energy needs. More so, solar energy can be harvested and used on-site without requiring connection to a power grid. The portable and self sufficient characteristics of solar energy make it a viable alternative in energy harvesting particularly for micro/nano devices.

Solar energy is available in most parts of the world. Further, it is free and in abundant supply in many locations. The power of the sun received on the earth surface is approximately 1.8 X 10¹¹ MW [1]. This is significantly higher than commercial energy sources currently available. Direct solar energy harvesting in modern power generation typically involves either photovoltaic systems or large-scale solar thermal energy installations. Photovoltaic systems rely on the direct conversion of light energy from the sun into electrical energy using solar cells. Photovoltaics, though not very efficient (usually ≤ 20%), are very scalable. Therefore, they are widely utilized both in macro and micro power generation. By contrast, solar thermal installations harvest the heat energy of the sun. The heat is then used to drive other mechanical systems for power production. Large scale solar thermal application is well established with thermal efficiencies greater than 80% [2]. By comparison, there is relatively little literature on micro solar thermal energy.
Thermoelectric generators, TEG, represent one method of utilizing solar thermal energy on the smaller scale [3, 4]. Other small scale thermal devices utilizing solar heat as input energy have also been demonstrated [5, 6]. A thermoelectric generator is a mechanism that converts heat into electric power. This technology is based on the Seebeck effect. The Seebeck effect describes a phenomenon in which a temperature difference between two dissimilar electrical conductors or semiconductors produces a voltage difference between the two materials. One of the primary considerations for thermoelectric power generation is the temperature gradient across the device. Increased output is generated by increased temperature gradient.

Solar energy is a low temperature energy source on the earth’s surface. Hence, it is not readily used for energy generation purposes. Solar radiation flux rarely exceeds 1 kW/m² and the total radiation in a day is typically below 7 kWh/m², even in very hot regions of the world [1]. This means that large collection areas are required to produce significant output power. Alternatively, the use of concentrating devices can be applied to increase the amount of harvested energy as is done in large, mega-Watt scale solar thermal applications. The use of concentrating devices adds to the complexity of micro scale designs, however. More so, the size constraint of a micro device limits the collection area of the plate. Because of these limitations, this paper examines a selective absorber coating that has been developed to increase solar thermal energy harvesting in flat plate collectors for TEG use. The selective absorber coating maximizes absorption in the solar radiation spectrum while minimizing re-radiation losses in the infrared region. We previously reported the fabrication of a micro solar thermal collector utilizing a selective absorber coating [7]. In this work, we demonstrate the integration of the micro collector plate with a TEG. In this manner the collector plate is used to enhance absorption of incident solar radiation thereby increasing the hot side temperature of the TEG. Overall, the output power from the TEG is improved by the increased temperature gradient resulting from the micro collector plate.

The Solar Thermal Collector, STC, is a special kind of heat exchanger that transforms solar radiation energy into internal energy of the transport medium [8]. In this work, the STC serves as a major component of the solar energy harvesting system. Solar radiation that is incident on the STC is absorbed and transformed into heat. This absorbed thermal energy then serves as input energy for the TEG. STCs are typically made of good thermal conductors like copper or aluminum, though they can also be made of plastic for very low temperature applications like swimming pool heating [9]. The surface of the collector is generally coated with black paint or a selective absorber to increase thermal absorption. However, black paint, or surfaces that are perfect absorbers (in the solar radiation range, 0.3 – 2.5 µm), also have high emissive values in the infra-red range (> 2.5 µm). By contrast, so-called “selective” absorber surfaces absorb all incident radiation but show reduced emission in the infra-red region. Hence, advanced absorber substrates are typically covered with a coating that strongly absorbs in the solar radiation wavelength range in order to obtain high values of absorptivity, while yielding reduced emittance in the infrared region [2].

Fabrication of selective absorbers has focused mainly on electrochemical deposition technique. This is largely due to the cost effective nature of this technique and the relative simplicity of the technique itself [1]. Sputtering, CVD, chemical oxidation, sol gel, and painting are among other techniques for preparing the selective absorber coating [10]. Black chromium has been reported as the most widely and successful material used to prepare selective absorbers [1]. However, due to the toxicity of the plating bath and high energy consumption, other materials have been investigated [11]. Black nickel-tin selective coating has shown promising potential as a highly effective selective absorber structure [11, 12]. The electrolyte used in preparing the nickel-tin selective surface is less hazardous and operates at about a
neutral pH. We previously reported the use of this technique in fabricating a MEMs-based solar thermal collector on a copper substrate [7].

In this present work, a solar thermal collector fabricated on copper substrate is integrated with a TEG. An improved energy harvesting capability is shown with the advanced selective collector plate based on its ability to transform incident radiation into thermal energy. Overall, the output power from the TEG is improved by the increased temperature gradient resulting from the micro collector plate.

**EXPERIMENTAL METHODS**

**Fabrication**

Two different collector plates were examined. Copper substrate was used for each STC fabricated and characterized in these experiments. The collector served to enhance the hot side temperature of the TEG. This way solar thermal energy was harvested for practical power applications via a TEG. Copper has been selected due to its excellent thermal conductivity. More so, copper is cheap and readily available. The high thermal conductivity ensured the absorbed heat was readily conducted through the plate and reached the back side where it served to increase the hot side temperature of the TEG. Furthermore, the high resistance of copper to corrosion has made it very useful in solar thermal collector applications [13]. The same dimensions and overall sizes were maintained for each collector studied to facilitate comparison when tested. Each collector plate had an overall size of 40 mm by 40 mm. This overall size was to allow for easy integration with an off-the-shelf acquired thermoelectric generator (TEG), which had similar dimensions.

First, bare polished copper was used as a collector plate. This allowed for the characterization of a baseline collector without modification. The thickness of the copper plate was 210 µm. The second type of collector plate was created using a nickel-tin selective absorber coating formed atop a copper substrate. The two collector plates allowed for comparison of the solar thermal radiation harvesting performance of bare copper and a selective absorber flat plate collector. The creation of a collector plate with a selective coating allowed for enhanced absorption and low re-radiation losses from the collector surface. Two fabrication steps were required to create the selective absorber coating. Chemical electrodeposition technique was used for both fabrication steps. The first step involved the fabrication of a nickel under coat layer from a Watt-type warm bath [14]. The nickel layer served as a thermally transparent layer and increased heat conduction to the base substrate. This was followed by the fabrication of a thin layer of a nickel-tin selective absorber coating from a near-neutral electrolyte at room temperature [12]. The electrodeposition condition for each step is shown in tables 1 and 2. Each step has been reported in detail previously [7].

<table>
<thead>
<tr>
<th>Table 1. Electrodeposition Conditions for Nickel Layer [14].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bath composition (g/l)</strong></td>
</tr>
<tr>
<td>Nickel Sulfate-6-Hydrate 250</td>
</tr>
<tr>
<td>Nickel Chloride-6-Hydrate 45</td>
</tr>
<tr>
<td>Boric Acid 30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Electrodeposition Conditions for Nickel-Tin Selective Absorber [12].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bath composition (g/l)</strong></td>
</tr>
<tr>
<td>Nickel Chloride 100</td>
</tr>
<tr>
<td>Searous chloride 25</td>
</tr>
<tr>
<td>Ammonium bifluoride 25</td>
</tr>
<tr>
<td>Diethanolamine</td>
</tr>
</tbody>
</table>

The deposition of a thin layer of selective nickel-tin coating produced a selective collector plate ready for testing. Figure 1 (a) shows the bare copper substrate while the polished nickel layer is shown in figure 1 (b). The black selective nickel-tin coating is shown in Figure 1 (c). The schematic of the procedure is shown in figure 2. The thermal collectors were then integrated with a TEG by coupling the plate to the hot
side of the TEG. The assembled device was then exposed to solar radiation to characterize the ability of the plate in increasing the hot side temperature of the TEG thereby leading to increased energy harvesting. The next section describes the test setup.

**TEST SETUP**

As a practical step in solar energy harvesting, the absorber plate was coupled to the hot side of a TEG for useful energy generation. The TEG as earlier mentioned operates on the Seebeck effect, which is a phenomenon in which a temperature difference between two dissimilar electrical conductors or semiconductors produces a voltage difference between the two materials. A commercially available power generation module from Custom Thermoelectric® (1261G-7L31-04CQ) was used as the TEG. The overall size of the TEG (40 mm length by 40 mm width) fitted well with the solar absorber plate. The back (cold) side of the TEG was coupled to a heat sink to ensure continuous cooling of the cold side, as this ensured heat could be readily rejected by the TEG cold side. A Custom Thermoelectric® water block WBA-1.62-0.55-CU-01 was used as the heat exchanger device. The surface area of the water block was 40 mm by 40 mm. Thermal grease was applied between the heat sink and the TEG, as well as between the TEG and collector. OmegaTherm® 201 thermal paste was used. The thermal paste also ensured good contacts between the surfaces. To further ensure the device was well clamped together, an acrylic frame was fabricated and used to clamp the device together using screws. Figure 3 shows the heat sink and TEG, while figure 4 shows the device assembly. A MityFlex® 913 Variable speed pump was used to drive water through the heat exchanger block. The heat sink ensured continuous pull of heat energy away from the device cold side until steady state was reached.

In this investigation, a solar simulator has been used for the experimental analysis. All tests were carried out by exposing the assembled device to incident radiation from the simulator. A Sun System® SS-2 MH 400 halogen lamp was used as the simulator in these tests. A Hukseflux® SR11 pyranometer was used to validate the intensity of the radiation from the simulator lamp. A pyranometer is used to measure broadband solar irradiance on a planar surface. It is a sensor that is designed to measure the solar radiation flux density from a field of view of 180 degrees. Different heights from the lamp were evaluated...
in order to select flux density that closely approximated available real life flux density. A z-stage laboratory jack was used in adjusting the height of the test setup from the lamp.

As it has been previously noted, radiation flux even in hot regions of the world rarely exceeds 1000 W/m². With this in mind, simulated solar radiation intensity was maintained below this incident value. An intensity of ~700 W/m² was selected. Based on pyranometer output, this intensity of output was obtained at a distance of 6.5 inches from the lamp. The lamp was allowed to operate until stable conditions were reached for each test setup.

Temperature profiles of the hot and cold sides of the TEG were monitored throughout the experiment. Omega® K-type thermocouples were used for these temperature measurements. Similarly, the voltage output from the TEG as well as the radiation intensity as monitored by the pyranometer was monitored simultaneously throughout the experiment. The thermocouples, TEG output and pyranometer were linked to a computer using National Instruments® cDAQ-9174 data logger. Figure 5 shows the setup for the TEG analysis.

Initial tests were conducted using a bare polished copper plate coupled to the TEG. This provided a baseline for all future comparisons. Voltage output from the TEG was monitored until steady state was achieved. Following the baseline analysis, the selective absorber plate coupled with a TEG was also analyzed. This followed the same procedure as the baseline copper substrate. Each test was carried out several times in order to produce results that were both reliable and repeatable.

RESULTS

The radiation flux, Q, to each device was 700 W/m² of simulated solar radiation over a cross sectional area, A of 0.0016 m² (0.04 m x 0.04 m). Hence, the power, P available as useful input to the device is given by

\[ P = QA = 700 \frac{W}{m^2} \times 0.0016 \ m^2 = 1.12 \ W \]  

(1)

With the input power set at this value (1.12 W); we evaluated the performance of the device in harnessing this available power.

At this stage of this work, the collector plate had no top cover and so convection losses from the plate surface lowered the useful output of the plate. More so, with the large heat sink coupled to the device, the
The overall operating temperature of the device was significantly reduced. The cold side temperature, $T_C$, of the TEG was maintained at 25 C while the maximum temperature obtained at the hot side, $T_H$, was 32 C. Thermoelectric generators generally operate at very low efficiencies particularly in lower temperatures ranges. First, we evaluated the maximum efficiency $\eta_{\text{max}}$ expected from the TEG given the material properties and the operating temperature of the device. The maximum efficiency expected would be

$$\eta_{\text{max}} = \frac{T_H - T_C}{T_H} \sqrt{1 + \frac{Z^2}{1 + \frac{T_H}{T_C}}}$$

(2)

The figure of merit $Z$ is given by

$$Z = \frac{s^2}{k}$$

(3)

For an average temperature $T$ of the 300 K (27 C), typical BiTe material properties indicate $s = 2.01 \times 10^{-4}$ V/K, Resistivity $\rho = 1/\sigma = 1 \times 10^{-3}$ ohm cm and $k = 1.5 \times 10^{-2}$ W/cm K. This resulted in an expected $ZT$ value of 0.808 based on Equation 3. Hence, for operating temperatures of 32 C as $T_H$ and 25 C as $T_C$, the maximum efficiency expected from equation (2) is given by

$$\eta_{\text{max}} = \frac{T_H - T_C}{T_H} \sqrt{1 + \frac{Z^2}{1 + \frac{T_H}{T_C}}} = 0.02872 \text{ or } 2.87\%$$

(4)

Thus, it is expected that the maximum power output from the device given the above parameters is

$$P_{\text{max}} = 1.12 \ W \times .02872 = 32.17 \text{ mW}$$

(5)

These expected output values help establish the true operation and capabilities of the solar thermal collectors. First, the baseline copper substrate was tested. The voltage output from the TEG assembly was monitored over time until steady state was reached. The result showed the output voltage from the bare copper collector assembly stagnated at 0.06 V. This test represented a baseline operating point. Following the baseline characterization, the device with a selective surface collector was tested to characterize the effect of the coating on the thermal absorption of the substrate. As in the baseline analysis, the output voltage was also monitored until steady state was achieved. The result shows a faster rise in the slope of the voltage profile signifying increased heat absorption and heating of the TEG via the collector plate. The result is shown in Figure 6. The output voltage stagnated at 0.129 V. This is significantly higher than baseline values. The increased output voltage results from the enhanced heat absorption capability of the selective absorber surface. Hence, the overall input energy into the TEG was enhanced leading to better output voltage.

To verify the output power of the device, the TEG resistance value was interpolated from the manufacturer’s given chart. At an average temperature of 28.5 C, the resistance, $R$, was 1.8325 ohms. The output power is calculated as $P = \frac{V^2}{R}$. The graph of the power output over time until steady state was reached is shown in figure 7. As shown in the figure, the power output of the device when bare copper was used as collector plate was 2 mW while the output with a selective absorber plate was 9.1 mW. The results indicated an increase in power output of 4.5X through the use of the collector with a selective absorber coating.
Further, the useful power output demonstrates the ability of the collectors in harvesting solar radiation. The maximum theoretical power expected from the TEG (32.17 mW) was compared to the experimental results. The ratio of the expected power and the actual output power characterizes the efficiency of this device, operating from solar thermal energy as input. For the baseline collector plate, the output power was 2.01 mW, representing 6.24 % of power input. By contrast, the device with selective absorber plate showed an average of 9.15 mW of harvested power, representing 28.44 % of theoretical maximum. The use of selective absorber coating has significantly improved the ability of the solar collector substrate to harness the heat of the incoming radiation. This heat energy served as useful input to the thermoelectric device for portable autonomous power generation.

Further work is underway to enhance the operating temperature of the device by reducing convection losses from the collector plate through the use of cover glass. At higher operating temperature, the power output from the device will be increased. Continuing work is also underway to scale up the design for use with a larger collector surface area. In this manner, more solar radiation can be harnessed and utilized in generating useful power output.

**CONCLUSION**

In this work, the use of a TEG in generating useful power from solar thermal energy has been demonstrated. The TEG was integrated with a solar collector plate to enhance temperature gradient via the thermal radiation absorption capacity of the device. Solar thermal collectors were fabricated on copper substrate. Two types of collector plates were examined: a bare copper plate and a selective absorber coating on copper plate. An electro-chemical deposition technique was used to deposit a selective absorber coating consisting of black nickel-tin bimetallic layer. The selective coating significantly improved the ability of the collector to transform incident solar radiation into thermal energy. This was demonstrated by the improved output power of 9.15 mW from the TEG utilizing the selective absorber plate as compared to the base copper plate setup (2.01 mW). The device was produced on a scale that is portable and generates autonomous power useful for powering micro/nano devices. Future work to improve the performance of the system through heat loss reduction is underway. This will include a top glass cover on the collector plate.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>STC</th>
<th>Solar Thermal Collector</th>
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</thead>
<tbody>
<tr>
<td>TEG</td>
<td>Thermoelectric Generator</td>
</tr>
<tr>
<td>Q</td>
<td>Solar Radiation flux</td>
</tr>
<tr>
<td>A</td>
<td>Collector plate area</td>
</tr>
</tbody>
</table>
\[\begin{align*}
P &= \text{Power input} \\
P_2 &= \text{Power output} \\
T_C &= \text{Temperature on cold side of TEG} \\
T_H &= \text{Temperature on hot side of the TEG} \\
\eta &= \text{Efficiency} \\
T &= \frac{T_H + T_C}{2} = \text{Average temperature} \\
\sigma &= \text{Electrical conductivity} \\
s &= \text{Seebeck coefficient} \\
k &= \text{Thermal conductivity} \\
\rho &= \text{Resistivity} \\
Z &= \text{Figure of merit}
\end{align*}\]

**ACKNOWLEDGEMENT**

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**REFERENCES**

Rheological and Micro-raman Time-series Characterization of Enzyme Sol-gel Solution toward Morphological Control of Electrospun Fibres

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ABSTRACT

Rheological and micro-Raman time-series characterizations were used to investigate the chemical evolutionary changes of silica sol-gel mixtures for electrospinning fibres to immobilize an enzyme (tyrosinase). Oscillatory rheological measurements agreed with the expected structural transitions associated with reacting sol-gel systems. The electrospinning sols exhibited shear-thinning behaviour typical of a power law model. Diameter distributions of ultra-fine (200-300 nm) fibres produced at early and late times within the reaction window of approximately one hour from initial mixing of sol solutions with and without enzyme showed much smaller deviations than expected. The enzyme dramatically increased magnitudes of both elastic and viscous moduli but had no significant impact on final fibre diameters, suggesting that the shear-thinning behavior of both sol-gel mixtures is dominant in the fibre elongation process. The time course and scale for the electrospinning batch fabrication show strong correlations between the magnitudes in rheological property changes over time and the chemical functional group evolution obtained from micro-Raman time-series analysis of the reacting sol-gel systems.

Keywords: Electrospinning; Rheology; Sol-gel chemistry; Ultrafine fibres; Nanofibres; Micro-Raman; Plateau modulus

1. INTRODUCTION

Electrospinning is a remarkably simple and highly versatile technique used in the production of a variety of one-dimensional (1D) nanostructured materials with diameters ranging from a few hundred to tens of nanometers, within a short time [1-4]. It is a process that relies on electric charges (from an applied electric field) to deform a droplet of a fluid solution that is then ejected from a nozzle tip into ultra-fine fibres [5]. Electrospun nanofibres have unique properties such as high surface area, potential for surface functionalization and modification, low weight, and high permeability making them suitable for diverse applications [2,6]. These numerous applications include filtration, wound healing, tissue engineering scaffolds, drug delivery, sensors, energy storage/conversion devices, composite materials for reinforcements, sound absorption, heavy metal adsorption, protective clothing, catalyst and enzyme carriers, etc. [2,7].

The last decade has presented significant and promising research in the use of electrospun nano-ultra-fine fibres as biocatalyst/enzyme carriers [8-12]. A novel research area in the fabrication of ultrafine fibres is the synthesis of hybrid/composite biocatalytic nano-ultrafine fibres using the combination of sol-gel chemistry with electrospinning to produce a very high surface area platform for immobilizing active enzymes in what is virtually a one-step fabrication method that does not require the complexities of designing surface chemistry approaches for anchoring enzymes to a pre-existing high surface area substrate while retaining sufficient enzyme activity for applications such as detection and
remediation [10,12]. Electrospinning with the enzyme already in the sol-gel solution presents several advantages compared to other conventional biocatalyst immobilization techniques, which are mostly physical and chemical methods. These advantages include bio-compatible/bio-friendly properties—due to the use of non-toxic reagents during the fabrication of the fibres and the biomolecular immobilization process occurring at ambient temperatures; the potentially easy of addition of fibre porosity; the potential for reusability of enzyme-laden fibres that do not need to be recovered from free solution; low or no enzyme loss and leakage due to the immobilization on and/or within the fibres; and the inexpensive nature of electrospinning by comparison to many other techniques [10,12].

However, there remains the significant challenge of rapid gelation, which makes electrospinning silica fibres in batches on a lab-scale difficult. The cross-linking reactions that transform the silica precursor sol into its much denser gel create the necessary three-dimensional molecular network to make the solid, sometimes porous fibre mat as the desired end product, which also renders electrospinning impossible at some point in the convention batch process. Oriero et al. [12] produced a delaying effect on this rapid gel formation in the electrospinning process by adding a protic solvent (100 mM acetic acid) into the recipe during preparation of the enzyme-sol precursor. This provided a suitably long window of time to electrospin sufficient number of fibres for research purposes. The mechanism of this delaying effect is based on the formation of hydrogen bonds with reacting silanol groups in order to inhibit the cross-linking reactions (i.e., silanization) for a time [13].

The designed delay in gelation opens a now practical time window for electrospinning with silica sol-gel chemistry; however, process still has the inherent potential for time-variant fibre morphology, specifically fibre diameter and—more important to future interests—por formation targeted toward increasing active and accessible surface area for maximizing enzyme utilization. The fundamental factor is believed to be the changing viscosity of the electrospinning solution [1,3,5], or viscoelasticity, to be more broadly correct to the specific case of sol-gel electrospinning. The time-dependent viscoelastic behaviour of the reacting fibres under formation has significant and at some times critical influence on fibre stability, final fibre diameter, and even pore formation. Detailed rheological characterization of the enzyme sol-gel system within the electrospinning time window will be required to understand the reasons for a particular fabrication outcome with respect to fibre mat morphology in terms of average diameter changes throughout a continuously-deposited fibre mat.

The present work attempts to assess the influence of evolving rheological and chemical properties of electrospinning silica sol-gel mixtures, with and without an active enzyme additive, on the final fibre diameters within randomly-deposited layers during the course of the time window expanded by the judicious use of acetic acid [12]. Batches of fibre samples are characterized by scanning electron microscopy (SEM) to quantify fibre diameter distributions. Sol-gel mixtures are tested for elastic and viscous moduli by rheometry and for chemical functionality by micro-Raman spectroscopy over the same time window for electrospinning ultrafine fibre mats. The combined information is directed toward fine-tuning the electrospinning time against the desired fibre diameter and may also help toward optimum processing conditions for production scale-up, conversion from batch to continuous or semi-continuous electrospinning, better substrate coverage and uniformity, and ultimately for maximizing active and accessible fibre mat surface area for enzyme utilization in chemical detection and conversion processes.

For the production of porous fibres, merely targeting an increase in surface area does not necessarily mean it will be accessible for enzyme loading and activity or for enzyme-substrate processes to occur without substantial diffusion limitations on practical improvements. Smaller fibre diameters provide greater specific surface area externally but exhibit a tradeoff in decreasing their superficial volume within
which a porous network may be housed. The interplay between various electrospinning conditions and pore formation processes further complicates the situation, where the time window for consistent fibre diameter may not be over the same range or begin at the same time from initial solution mixing as the best time window for pore formation of a particular pore size distribution that would be beneficial for effective enzyme immobilization. A constant loading of the pore-forming agent D-fructose—as implemented in other studies [9,12]—is included in these formulations as a fixed starting basis with the future plan of continuing parametric investigations toward optimizing pore formation for increased active enzyme loading. The present findings represent the initial steps in a larger investigation to improve enzyme-fibre material and structure.

2. MATERIALS AND METHODS

Mushroom tyrosinase (polyphenol oxidase C. 1.14. 18.1) with a specific activity of 1460 units/mg was obtained from Worthington Biochemical Corporation (Lakewood, NJ). Poly(vinyl alcohol) (130,000 mol. wt., degree of saponification 86.7–88.7%) and tetramethyl orthosilicate (TMOS, 99%) were purchased from Sigma Aldrich Chemical Company, Inc. D-fructose was obtained from Fisher Scientific (Fairlawn, NJ). Sodium phosphate monobasic monohydrate crystals and sodium phosphate dibasic anhydrous (for preparation of sodium phosphate buffer, pH 6.8) and acetic acid were purchased from Mallinckrodt (Baker, NJ). The buffer solution pH was determined with a Dwyer PH0-1 pH meter (Dwyer Instruments, Inc., Michigan City, IN). Gluteraldehyde (50% solution) was obtained from Polysciences, Inc. (Warrington, PA) while hydrochloric acid was purchased from EMD chemicals (Gibbstown, NJ). Indium-tin oxide (ITO)-glass plates (coated on one surface) were obtained from Delta Technologies (Stillwater, MN). An Advance Infusion System series 1200 syringe pump was obtained from Cellpoint Scientific Inc., Gaithersburg. Syringes (1 mL and 3 mL) and steel needles (27G 1 ¼-in.) were obtained from Becton, Dickinson (Franklin Lakes, NJ).

2.1. Preparation of enzyme sol-gel solution

The preparation of the enzyme (tyrosinase) sol-gel precursor solution for electrospinning was accomplished by an approach similar to that of Patel et al [10] with some modifications to make electrospinning of a sol-gel simpler and improve the stability of the fibre mat in aqueous environment. A mixture of TMOS (0.76 g silica precursor), water (0.18 g for a H2O:TMOS mole ratio of 2) and HCl (30 µL of 40 mM stock as catalyst to speed up the hydrolysis reaction) were added with continuous stirring to form the hydrolyzed silica sol. Thereafter, the reaction mixture was heated to a temperature of 60°C for 30 minutes. The resulting sol was allowed to cool and the pore-forming material (500 µL of 50% w/v aqueous D-fructose) was added with continuous stirring. PVA (700 µL of 10% w/v) was added next to the mixture with continuous stirring. A cross-linker, gluteraldehyde, (200 µL of 90:1 mole ratio gluteraldehyde:HCl) [14] was introduced to improve the mechanical stability of the fibre mat to be used in aqueous environments as reusable enzyme-immobilizing and potentially enzyme-encapsulating (within the pores) fibres. The addition of PVA, D-fructose and gluteraldehyde made the sol highly viscous, thereby facilitating electrospinning into fibres rather than electrospraying into droplets.

Fifteen µL of 100 mM acetic acid were added to the electrospinning solution to delay gelation and provide a short but feasible time window for electrospinning. Tyrosinase enzyme (300 µL) in buffer solution (6 mg/mL) was introduced into the above sol with continuous stirring for about 4-6 minutes before the mixture was electrospun into fibres. A second electrospinning sol was similarly
prepared, adding 15 µL of 100 mM of acetic acid, but without the enzyme, viz., silicate-fructose-PVA-gluteraldehyde.

2.2. Rheological characterization of the electrospinning enzyme sol mixture

Dynamic rheological measurements (oscillatory test/frequency sweep) were performed on the electrospinning sols with and without enzyme for analysis of elastic (storage) modulus \( (G') \), viscous (loss) modulus \( (G'') \), loss tangent or \( \tan(\delta) \), complex modulus \( (G^* = G' + iG'') \), or complex viscosity \( (G^* = \eta^*/\omega) \), and steady-state shear flow over the sol-gel reaction time applicable for comparison to the electrospinning time window. Data obtained regarding these rheological parameters are important in understanding the sol-gel transition, the viscoelasticity of the sol and enzyme-sol in comparison, how these relate to fibre diameters and distributions, and any correlation between these parameters and the effective electrospinning conditions for maximizing accessible surface area for nonwoven fibre networks and random mats. Rheological measurements were performed using a Bohlin CVO rheometer with parallel plate geometry (40-mm aluminum plates, 0.8-mm gap between the plates) at 25°C and with an applied oscillatory strain across a frequency range of 1-100 Hz; in addition, time-dependent studies were performed at a controlled frequency of 1 Hz for up to one hour, equivalent to the longest feasible electrospinning duration of roughly one hour.

2.3. Electrospinning fibres from enzyme sol mixture

Approximately 1 mL of the silicate-fructose-PVA-tyrosinase sol was introduced into a 3-mL syringe and placed in a syringe pump. The electrospinning setup [12] is similar to the one used by Jabal et al [15]; a syringe pump was used to control the sol flow rate at 10 µL/min and thus the droplet size undergoing electrodynamic distortion from a 10-kV source during production. The syringe containing the enzyme-sol mixture was subjected to an electric field of 100 kV/m from the tip of the needle to the collecting electrode. The grounded collector plate (ITO-glass plate 25×18×1.1 mm³, surface conductivity 0.010-0.014 S/m) was placed at a distance of 10 cm from the needle tip. At the controlled flow rate, a continuous fluid jet resulting in the formation of ultrafine fibres randomly deposited onto the ITO plate as a white, nonwoven mat containing the enzyme tyrosinase [10]. Fibre mats without enzyme were produced in identical fashion. After the electrospinning process, the fibre mats were soaked in water for two hours to attempt leaching of fructose from the fibres.

2.4. Morphological characterization of electrospun fibres

Average fibre diameters of electrospun fibres from electrospinning sol (with and without enzyme) within the allowable time window (up to 70 min) for electrospinning were imaged using SEM (Zeiss Supra 35 VP field emission-SEM, Center for Electron Microscopy and Microanalysis, University of Idaho). The fibre mats, electrospun onto ITO-glass plates, were sputtered with a thin layer of Au/Pd nanoparticles and then exposed to the electron beam. Thereafter, high resolution (1280×1024 pixels) tif images were obtained for fibre diameter measurements using the ImageJ software (NIH) of 10 fibres per sample, 5 samples per group, where a total of four groups, or sample types, consisting of fibres with and without enzyme electrospun over early and late time windows, resulting in a sample-type distribution of 50 fibres represented by histogram. To ensure that a fibre within a given micrograph was not measured twice, a straight line was drawn along the image diagonal (using the line tool of the ImageJ software) and the fibres crossing this diagonal were labeled and measured.
2.5. Porosity and surface area measurements of electrospun fibres

The Brunauer-Emmet-Teller (BET) surface area and pore volume of the electrospun fibres were determined by N2 adsorption-desorption isotherm measurements using a Micromeritics Tristar II 3020 physisorption analyser. Before measurement, the samples were degassed at 423 K and 500 mTorr for 3 h. Surface area, pore volume and diameter were calculated using the accompanying software from Micromeritics.

2.6. Micro-Raman time-series spectra analysis of electrospinning solution

Micro-Raman time-series spectra were acquired from samples of the reacting sols using a WITec alpha 300R scanning confocal Raman microscope (WITec GmbH, Ulm, Germany). Specifically, spectroscopic analysis was performed to monitor the real-time formation of siloxane via TMOS hydrolysis and condensation, the effects of acetic acid solvent-delay on gel formation and to make a connection as regards the timescale involved in electrospinning ultrafine fibres. Droplets of the electrospinning mixture was placed on a glass slide where a Nikon 20× objective (NA = 0.4, WD = 3.8 mm) was used to focus the Raman excitation source (100 mW, 532 nm Nd:YAG laser) at the center of the droplet. Upon focusing, the sample was irradiated at a constant attenuated incident power of 8 mW for 75 minutes to prevent the thermal destruction of the sample during the study.

The Raman scattered light was collected in the backscattering configuration and detected using a UHTS-300 spectrometer (WITec). A diffraction grating of 600 lines/mm was employed giving a spectral coverage of 200 to 3800 rel. cm⁻¹. The integration time of the EM-CCD array detector was set to 5 seconds, as the effective sampling rate of the reacting mixture, which resulted in 900 collected spectra for the 75-minute time-series duration. Raman spectral data were processed and analyzed using the WITec Project software. Fluorescence baseline correction was performed using a third-order polynomial followed by the application of a three-point moving average filter to eliminate most of the perturbing baseline. Following baseline correction, all spectra were scaled by the spectral average intensity. This procedure helped to mitigate the influence of the large refractive index change on the intensities of the Raman bands over the course of the sol-gel reaction (clear-to-opaque liquid-to-solid material quality evolution). Of course, this procedure assumes that the refractive index change affects all bands equally.

Three Raman bands known to correspond to functional groups of interest (siloxane, silanol and methyl groups) were subjected to non-linear, least-squares curve-fitting procedure to estimate the amplitude changes of the Raman bands over the duration of the reaction, that is, in each of the 900 spectra per experiment. The band shapes were assumed to have a Gaussian profile, which is sufficient for the present study. When necessary, a five-point moving average filter was used to smooth all spectral bands prior to curve fitting. Plotting the estimated amplitudes of selected bands against time elucidates the timescale of the major chemical features evolving in the sol-gel system.

3. RESULTS AND DISCUSSION

3.1. Time-dependent rheology and frequency sweep test

The typical log-log plots of elastic modulus (G'), viscous modulus (G'') and loss tangent (tanδ) with frequency (figures 1-2) and semi-log plots of complex modulus (G*= G' + iG''), G', and G'' values with sol-gel reaction time (figures 3-4) were generated from the two types of rheological experiments conducted. (G* may be thought of as an overall measure or index for general resistance to stress.) Data obtained from shear flow analysis was fitted using the power-law fluid model (Ostwald-de Waele two-
parameter model) [15-16]:. The exponential factor n is the power-law index or flow behaviour index, σ is the shear stress, K is the flow consistency index, is the shear rate. Power-law index values are less than one for both electrospinning sols (0.47 without enzyme and 0.72 with enzyme) (figure 5), reflecting a non-Newtonian, shear-thinning behaviour: decreasing viscosity with increasing shear rate. The different quantitative behaviour with and without enzyme are affected in part by the general fluid properties of greater total fraction of dissolved and/or dispersed solids content (fructose + PVA + sol particles ± enzyme) and the fact that the enzyme is a higher molecular weight constituent being added, rather than a clear and specific physicochemical property of the enzyme alone. Shear-thinning behaviour of the reacting sol mixtures occurs mostly due to the reduction in the rate of cross-linking of the three-dimensional poly-silicate network structure as the shear rate increases resulting in a decrease in viscosity as well as slowing the emergence of the elastic behavior.

Log-log plots of $G'$ and $G''$ v. frequency for sol mixtures with (figure 1) and without (figure 2) enzymes showed similar characteristics with $G'$ being dominant over $G''$ ($G' > G''$) from low to high frequency (1-100 Hz), typical of time-dependent viscoelastic materials like this polymer/reacting sol-gel solution. The characteristic features of viscoelastic fluids are observed in their oscillatory responses (figures 1-2): high phase angles (23° and 24° from tan(δ) values 0.4245 and 0.4452, respectively) at low frequency (near 0 Hz, when the fluid is at rest), and generally lower phase angles at high frequencies. The loss tangent, as tangent of the ratio $G''/G'$, is a standard measure of the energy dissipation capacity of a material under cyclic stress compared to its elasticity [16-18]. Figures 1 and 2 also suggest that the sol-gel mixtures rapidly evolve into more solid-like behaving fluids, as expected with its gelation. Clearly, the sol mixture with enzyme is more capable of resisting stress by flow and elastic deformation than the sol without the enzyme.

Figure 1. Frequency-dependent behaviour of the enzyme sol mixture based on $G'$, $G''$ and tan(δ).
The most significant feature is the presence of a rubbery or plateau region where the so-called plateau modulus \( G_p' \) can be determined as an index of the cross-link density in the network structure of the sol-gel mixture [19]. The cross-link density is a determinant of the rigidity of the gel. \( G_p' \) can be calculated as

\[
G_p' = \frac{cRT}{M_e}
\]

(1)

where \( c = \) concentration, \( R = \) gas constant, \( T = \) absolute temperature, \( M_e = \) Molar mass between cross-links [16,19]. Values for \( G_p' \) can be extrapolated from where \( G' \) appears to have a flat or horizontal plateau (nearly zero slope), made more apparent on log-log scales. Within the plateau vicinity, \( G'' \) decreases with increasing frequency towards a minimum before rising again. Hence, \( G_p' \) is determined as that value of \( G' \) when \( G'' \) is a minimum and thus can also be easily deduced from \( \tan(\delta) \) [16]. Larger values of \( G_p' \) are then associated with greater gel strength [19]. Extrapolated \( G_p' \) is almost an order of magnitude higher for the electrospinning sol with enzyme (1378 Pa) than without enzyme (163.2 Pa). It should be noted that eq. 1 is not quantitatively rigorous unless the frequency state of this sol-gel is indeed behaving as an ideal rubbery solid. Though contradicted by the data, it is a fair approximation where the storage modulus is much greater than the loss modulus. The addition of enzyme clearly has a significant impact on and will affect the electrospinning process accordingly. Under the same applied electric field, it will be more difficult to electrospin the enzyme-sol, which can decrease the deposition rate and increase the fiber diameter but will also stabilize fluid jetting against breakup. This suggests that future experiments may be able to reduce the amount of PVA used in electrospinning with enzyme.

Figure 3 is the semi-log plot of \( G^*, G' \) and \( G'' \) data for both electrospinning sol mixtures (with and without enzyme) as measured over approximately 6 minutes of reaction time, showing rapid, exponential
increases in viscosity and elasticity. The elastic moduli over this early time window increase more quickly than the viscous moduli, and both properties are greater with the addition of enzyme. Data acquired at later times in the rheological scans exhibit regular, smooth trends only for up to roughly 15 minutes (Original data are reported in the supplementary data section figures S1 and S2). After more than 15-20 min into the time-series measurements, rheology data become increasingly irregular or erratic with time for both sol types, and this is attributed to significant chemical structural changes in the evolving sol-gel, where the act of measuring rheology is in direct physical competition with the cross-linking process. From this observation, there is reason to suspect some characteristic shift in the electrospinning process and the final fibre quality between fibres produced at early and late times within a given batch. Fibre production rate is likely slower and the diameter and perhaps distribution would be increased.

Figure 3. Comparison of time-dependent behaviour of $G'$, $G''$ and $G''$ for sol mixtures with and without enzyme.

It should be noted that the fairly rapid increase in viscoelastic resistance may also substantially influences the frequency-dependent studies illustrated by figures 1-2 while the increase in shear-thinning with higher frequency will somewhat compensate with respect to the magnitudes observed in figure 3 for constant shear at 1 Hz. Whether the net effect has a dominate bias over the results of figures 1-2 or is essentially self-canceling is very difficult to determine in a reacting system.

Figure 4 shows the time-dependent data for both source mixtures as smoothed by a weighted-residual method (KaleidaGraph 4.1.1, Synergy Software) to display the average trend in rheological properties for convenience, without the inherent “noise” at later times for the reacting sol-gel. Both figures 3 and 4 display similar, generally-increasing trends in all parameters, with liquid-like behavior dominating initially ($G'' > G'$, figure 3) and solid-like behaviour dominating at later times (figure 4) as expected for the gelling silica [16,18-21]. Similar to the frequency sweep measurements, the magnitudes of $G'$, $G''$, and $G''$ for the enzyme-sol mixture are higher at all times than the sol without enzyme. There is also a
qualitative different in the significantly higher rate of increase elasticity for the enzyme-gel material becoming obvious after 1500 s (figure 4). The elastic modulus may even decrease slightly over a few minutes of the testing for the gel without enzyme. This may indicate that the enzyme has a significant structural impact on the growing gel network and a potentially stronger fibre product, though this hypothesis will need some carefully-designed mechanical measurement on the fibres as a future study.

Figure 4. Time-dependent rheological measurements for sol mixtures over approximately one hour plotted from a weighted-residual method to smooth increasingly scattered data at late times.

Figure 5. Shear stress with shear rate showing power-law fitted parameters for both electrospinning sol mixtures (a) with tyrosinase and (b) without enzyme.
3.2. SEM results

The average diameter (mean ± standard deviation, figure 6) of the fibres reflects the structural evolution of a sol-gel system as expected generally from the rheology results. Fibres from the early time window (zero up to ~25 min) have diameters about 60 nm smaller than those collected within the late time window (from 25 min up to ~1 h). The relatively large standard deviations suggest significant diameter fluctuations throughout the electrospinning process. Even so, it is rather surprising in light of the rheology results that there is not a greater deviation in diameters from early to late times. One would expect that the increasing viscosity and cross-link density would translate into increasing fibre diameters, but the shear-thinning quality, which would be substantial under the very rapid elongation regime of electrospinning the fluid into fibers, must be dominating the fluid-flow process in this regard, maintaining a roughly constant fiber diameter even within the early time regime where both viscosity and elasticity are increasing most rapidly. Furthermore, the enzyme-containing fibres are not statistically larger in diameter than their enzyme-lacking counterparts. Again, in spite of being unexpected on first consideration of the rheology measurements (figures 1-4), this finding agrees with the relative insensitivity of electrospun fibre diameter to the fairly drastic increases in viscous and elastic moduli over time.

![Average fiber diameter plots](image)

Figure 6. Frequency distribution plots of the diameters of various sample groups of electrospun fibres indicate fairly broad ranges, consisting of 50 measurements per plot.
Figure 7. SEM micrograph of electrospun fibres with enzyme within the early time window.

Figure 8. SEM micrograph showing labeled fibres with enzyme electrospun within the late time window, whose diameter were measured along diagonal of the micrograph using ImageJ software (Java based imaging program developed by the NIH).
3.3. Porosity and surface area measurements of electrospun fibres

The N2 adsorption-desorption isotherm (figure 9) of the electrospun fibres is typical of a type IV isotherm with type H3 hysteresis loop (i.e., presence of a steep adsorption branch at relative pressures of unity and a sloping desorption branch at intermediate relative pressures) [22]. This hysteresis loop is associated with capillary condensation in pores with diameters of 2-50 nm, though the hysteresis is obviously very small. Type H3 hysteresis loops are also typically indicative of pores with open slit-shaped capillaries with parallel walls [22]. The average pore diameter (BJH pore diameter) of the electrospun fibres was 8.4 nm for the enzyme samples, 7.2 nm without enzyme (not shown). Though this pore size range is likely too small to avoid diffusion limitations for practical use as designed for enzymes, it suggests that the non-surfactant template method of pore formation in the silica sol-gel electrospinning process using D-fructose worked to some limited extent. The much lower than expected BET surface area of 2.9 m²/g may indicate that the fructose has not been sufficient leached out of the pores by simply soaking in water for only two hours; for nanoporous material, we would expect something less than but of the same order are activated carbon, depending of course on the extent of porosity. Therefore, a new method may be needed to remove more fructose without damaging the fibre mats before use, which will be pursued in the future.

![Figure 9](image)

**Figure 9.** N2 Adsorption-desorption isotherm of electrospun fibres at 77 K.

3.4. Micro-Raman time series spectra analysis of electrospinning solution

Figure 10 shows the processed (i.e., baseline corrected, etc.) Raman spectrum acquired from the electrospinning enzyme-containing sol mixture after reacting 25 min. This is comparable to the electrospinning time (viz., post mixing). Figure 10 shows that the Raman spectral bands for three chemically-reacting species associated with the sol-gel process were identified (i.e., normal modes of siloxane, silanol Si-O bond and methyl group) and their intensities were monitored during the time-series
acquisition. Figure 11(a, b and c) display snap-shots in the time-dependent peak intensities of these functional groups (CH$_3$ symmetric, Si-O antisymmetric and Si-O-Si symmetric stretching modes, respectively) at ten-minute intervals, as the reaction progresses [23-26]. Additional bands were labeled to illustrate a few points. For example, the intensities of the antisymmetric stretching modes of CH$_3$ and CH$_2$ at wavenumber 2945 cm$^{-1}$ (figure 10) remain steady in addition to the CH$_3$ antisymmetric deformation at wavenumber 1460 cm$^{-1}$ [26]. PVA, fructose and gluteraldehyde all possess CH$_3$ and CH$_2$ groups whose Raman modes overlap within these regions. The symmetric carbonyl (C=O) stretch at 1655 cm$^{-1}$ is explained by the formation of the ester functional group due to gluteraldehyde-PVA cross-linking reaction. The broad peak observed over 3000-3500 cm$^{-1}$ reflects the inevitable presence of water in the mixture by the OH groups (Si-OH inclusive).

![Figure 10](image.png)

**Figure 10.** Raman spectra of electrospinning enzyme-sol mixture in arbitrary units of intensity versus relative wavenumber.

Raman modes can be monitored for changes in peak intensity as a qualitative and relative measure of concentration for particular chemical functional groups according to their vibrational states, where the Raman events occur frequently enough to remain above the practical detection limit of the instrument under specific operating parameters. Figure 11(a) displays the time-dependent decrease in peak intensities of the CH$_3$ group (CH$_3$ symmetric stretching mode at wavenumber 2843 cm$^{-1}$), which originates from the precursor material TMOS and undergoes conversion to methanol (a significant percentage is lost via evaporation). This decrease is associated with the hydrolysis and condensation reactions. Figure 11(b)
also presents a gradual time-dependent reduction in peak intensities associated with the Si-O bond from silanol. Si-O bonds are formed both in hydrolysis and condensation, which later progress into the formation of siloxane bonds [13,27]. Figure 11(c) shows a steady time-dependent increase in Si-O-Si bonds; the product of the cross-linking and condensation reactions, which are responsible for gel formation.

Figure 11. Time-series analysis of peak intensities of (a) CH$_3$ symmetric, (b) Si-O antisymmetric, (c) Si-O-Si symmetric Raman modes from TMOS disappearing as the sol-gel conversion proceeds and (d) normalized peak mode intensity trends with time of the three main chemical functional groups in the sol mixture from TMOS reacting into a siloxane gel.

Figure 11(d) is a convenient compilation of the time-dependent peak intensities of these functional groups as the reaction progresses. A decline in the band intensities of the Si-O moiety and CH$_3$ group are observed, while that of Si-O-Si increases during the process. The structural evolution of the sol into a gel is quite obvious, and the key time-series data as compiled in figure 11(d) allow direct comparison to rheological behavior with time. Due to the different drying conditions and material configurations between electrospinning fibers, reaction in the rheometer and under the Raman microscope system, it is difficult to conclude that the coincidence of the crossing of the Raman time-series intensities at ca. 30 min
is quantitatively meaningful with respect to the obvious difference in fiber diameters spun before and after the 25 min mark. Intensities less than zero (not shown) are an inherent anomaly of background subtraction errors and have no physical meaning in an absolute sense; the negative-going drift with time of the methyl peak curve is indicative of the Raman mode disappearing into the background where the peak-fitting method becomes invalid. At ~50 minutes, the amplitude of the Si-O band surpassed the detection threshold of the spectrometer inhibiting the implementation of peak-fitting procedures. In the interest of continuity, the Si-O band profile was extrapolated empirically from 50 to 78 minutes using a 3rd-order polynomial.

The acetic acid delaying effect on gelation appears in both rheometry and Raman spectrometry as a gradual but steady effect. While the downward trends in Raman peak intensities for the methyl and silanol moieties are obvious and expected (figure 11d), a more unusual feature is the gradual but clear collapse of the siloxane band (that is, the silica gel) beginning at ~67 min, which might seem counter-intuitive on first consideration. This behaviour was consistent across several experimental runs. This apparent weakening of the siloxane Raman mode probably reflects the tipping point in the physical/structural transition from a transparent suspension of the sol into the highly-scattering translucent-to-opaque solid. From this time onward in the process, sufficient cross-linking of interconnected Si-O-Si bonds are already being formed in addition to the very low peak intensities of CH₃ and Si-O groups (indicating increased magnitude of condensation/poly-condensation and cross-linking reactions). These transitions are also in line with the fact that electrospinning fails at ~1 h (similar time range of rheology results) due to hard gelation overcoming the electric field.

4. CONCLUSION

The optimum time window range for electrospinning the tyrosinase-encapsulating porous silica gel fibres with relatively high surface area was identified to be within ~25 minutes after preparing the sol mixture, which yields smaller fibre diameters due to lower cross-link densities at the time of spinning. The acetic acid delaying effect on silica gelation appears in both rheometry and Raman spectrometry as a gradual but steady effect. Fibres produced after 25 minutes from mixing are larger by 60 nm on average than the early time fibres. With the current formulations, the practical time window for producing sol-gel fibres is restricted to an hour due to hard gelation halting the electrojetting process. In order to determine a more specific optimum time window, the balance between production rate, or amount (e.g., fibre mat thickness and collector substrate dimensions), and required specific surface area, or fiber diameter (and porosity), must be set.

The shear-thinning quality of sol mixtures with and without enzyme appears to dominate in the electrospinning process rather than the elastic and/or viscous moduli values regarding fibre diameter, since there is no statistically-meaningful difference in fibre diameters of both types. The larger plateau modulus and higher viscosity of the enzyme-containing sol-gel system support the possibility of reducing the amount of PVA required to maintain stable electrospinning, which should reduce the final fibre diameter to increase accessible surface area in the mats. There is some hint from elasticity data in the late time window range that the additional of the enzyme may in some way increase the final fibre strength without impacting fibre diameter.

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