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**COLLABORATIVE RESEARCH AND DEVELOPMENT
(CR&D)**

**Delivery Order 0066: Nano-bio Material Integration into Proximity
Sensors**

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Universal Technology Corporation

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Final Report**

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14. ABSTRACT This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 6 October 2006 through 01 February 2008. Integration of novel nanocomposite and bio-derived materials into fabricated micro-scale test-beds such that the feasibility and processing limitations of the materials as the active component in proximity sensors can be evaluated. The effort included material characterization (impedance spectroscopy, thermal analysis, mechanical evaluation), material processing (thin film deposition, solution processing), device design and fabrication, test-fixture design and construction, and determination of device performance.						
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January 2007

Major Activities:

SAXS Liquid Cell

A custom sample cell and mount were designed to house liquids for testing in the small angle X-ray (SAXS) system. This cell design works in conjunction with the SAXS vacuum extension couplings that were previously created for use with this X-ray system. The components were designed using the Rhinoceros[®] CAD software, and CNC machined from Delrin[®] plastic.

Laponite Experiments

Impedance spectroscopy temperature variable measurements were finished this month for two Laponite samples provided by Dr. Peter Mirau. This data set was conducted to correlate his NMR measurements with those provided by the impedance spectrometer. The idea is to use NMR's microscopic-based measurement information to corroborate local mobility and dipole relaxation behavior with the indicative responses detectable in the impedance measurements.

Laponite Impedance Modeling

Modeling software was employed to fit a generalized impedance complex-valued analytical equation to the measured data. The model parameterizes the response of the material in the frequency domain (0.01Hz-1MHz) and across a range of temperatures (0°C–150°C).

Laponite Elemental Analysis

A chemical analysis of elemental components: Na, P, Br, Cl, Li, was requested for the Laponite samples used in the impedance spectroscopy measurements.

Novocontrol Quatro RTD Temperature Sensor Repair

The primary instrument used for temperature controlled impedance measurements is Novocontrol's Quatro with the Alpha impedance analyzer. At cryogenic temperatures it was found to have a faulty temperature sensor. A replacement PT-100 RTD sensor and a conference call from Germany allowed us to successfully replace the damaged element and recover full functionality of the Quatro system.

Investigation of TSDC Capability

The thermally stimulated depolarization current (TSDC) measurement technique is possible with the Novocontrol Quatro system. It, however, requires a hardware and software upgrade, including a special TSDC sample cell, and the WinTSDC software package for controlling polarization/thermal parameters and evaluating time domain spectroscopy.

Tasks/Milestones:

Complete data set and model fit of the Laponite. Combining NMR's microscopic analysis with impedance spectroscopy's macroscopic measurement technique. The results will be published.

February 2007**Major Activities:***SAXS Liquid Cell*

Re-machined this design (completed last month) to improve the seal around the Kapton windows.

Quote for TSDC Novocontrol Upgrade

The thermally stimulated depolarization current (TSDC) measurement technique is possible with the Novocontrol Quatro system. It, however, requires a hardware and software upgrade, including a special TSDC sample cell, and the WinTSDC software package for controlling polarization/thermal parameters and evaluating time domain spectroscopy. The quote received was \$48,369.50.

Laponite Impedance Modeling

Impedance modeling was completed for the collaboration with Peter Mirau. This allowed the investigation and correlation of impedance and NMR measurement techniques for Laponite pressed nanoclay powder. This effort applied these techniques to the investigation of the dynamic relaxations and charge transport mechanisms and characteristics present in this material.

Capillary Sample Cell Design

Designed and machined a cell made of Delrin to allow 1mm capillary tubes to be quickly inserted and help in an Intec X-ray fixture. This small sample holder was designed for Hilmar Koerner to aid his experiments at the Brookhaven National Laboratory.

X-Ray Intensity Transformation Software

Wrote a simple Window's application to perform X-ray background intensity subtraction and normalization of raw X-ray intensity versus 2θ data. The user interface makes quick and efficient use of the common drag-n-drop operation, which enables automated application of the transform to many sequential files.

Tasks/Milestones:

Completed modeling/analysis of the Laponite samples.

March 2007

Major Activities:

Impedance Spectroscopy Modeling of CP2 Polyimide

Worked with Mike Arlen (AFRL/MLBP, Univ. of Akron) to perform low temperature impedance/dielectric spectroscopy measurements ($10^{-1} - 10^6$ Hz). The results have been modeled using techniques developed in house.

Continued the Design of the Nanocomposite Processing (NCP) System

The ongoing design that will enable in situ impedance spectroscopy of nanocomposite materials and electric field directed morphology actuation has continued this month. Some of the activities include creating a desktop surface for the system chassis; drilling panel holes for conduit, indicators, and controls; and working on the rear flange electrical feed throughs.

Shipping Procedure for Transporting the NCP System to WPAFB

Identified the appropriate paperwork and resources required to ship the NCP system from Cincinnati (i.e., its current location) to WPAFB. The transport is expected to happen the week of April 16th.

Custom Design of an Electrode Attachment for the Mini-Tensometer Unit

To facilitate in situ conductivity measurements of shape recovery materials during applied stress conditions, a design was drawn (Figure 1) up to allow electrodes to be fastened to the existing mini-tensometer system. Next month the design will be constructed.

Tasks/Milestones:

Major work was completed on the NCP system and towards shipping it on base.

Activities for Next Month:

Ship the nanocomposite process control system from Cincinnati to WPAFB.

Begin the electrical wiring, software control development, and testing.

Machine and test the electrode holder for the mini-tensometer.

Finish the impedance modeling of the CP2 sample.

Start organizing presentations for the talks that will be given at the University of Cincinnati and WPAFB in late May.

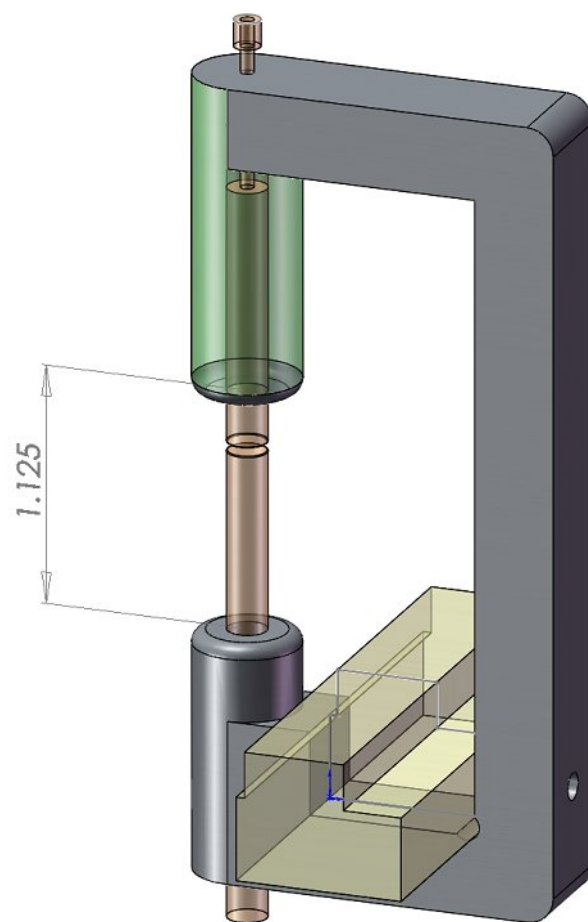


Figure 1. Electrode attachment drawing for the mini-tensometer.

April 2007

Major Activities:

Impedance Spectroscopy Modeling of CP2 Polyimide

Worked with Mike Arlen (AFRL/MLBP, Univ. of Akron) to perform high temperature impedance/dielectric spectroscopy measurements ($10^{-1} - 10^6$ Hz, 190 – 225 °C). Impedance modeling has been completed for this temperature range (Figure 1).

Continued the Design of the Nanocomposite Processing (NCP) System

Primary mechanical and hydraulic design and construction has finished and the electrical wiring is scheduled for next month. The unit has been shipped from its prior location at Anza, Inc., Cincinnati, OH, to its final location at WPAFB. This marks a considerable milestone in progress towards completion of this anticipated material processing system (Figure 2).

Machined a Custom Electrode Cell for Specialized Conductivity Measurements

To facilitate in situ conductivity measurements of shape recovery materials during applied stress conditions, a design was drawn (Figure 3) up to allow electrodes to be fastened to the existing mini-tensometer system. This design has been machined and is ready for initial testing.

3D Spectral Impedance Data Visualization

Added a 3D graphing module to the current software that has been designed to fit complex nonlinear least squares models to measured impedance data (Figure 4). Also, another modeling element (Havriliak-Negami) was added to extend the software capabilities to capture the presences of a 4th relaxation process.

Tasks/Milestones:

Major work was completed on the NCP system and it was successfully shipped to WPAFB.

High temperature impedance modeling was completed for the CP2 sample.

The specialized conductivity cell was constructed.

May 2007

Major Activities:

Impedance Spectroscopy Modeling of CP2 Polyimide

Performed an in-depth comparison of the polyimide impedance/dielectric measurement data obtained from our equipment with that of our collaborator, Zoubeida Ounaies (Texas A&M University).

Presentations at WPAFB/MLBP Branch and the University of Cincinnati

Gave a 40 minute presentation covering the progress and goals of the research I am involved in. This talk was given to graduate students at the University of Cincinnati and also to the MLBP branch at WPAFB.

Modifications to the Electrode Cell for Tensometer Conductivity Measurements

To facilitate in situ conductivity measurements of shape recovery materials during applied stress conditions, a design was drawn up to allow electrodes to be fastened to the existing mini-tensometer system. This design has been modified to provide improved mounting to the tensometer.

3D Spectral Impedance Data Visualization

Finished the 3D graphing module add-on for the CNLS modeling software that is currently used to fit complex-valued models to measured impedance data.

Dielectric Polymer Nanocomposite Workshop

Attended the dielectric polymer materials workshop hosted by Rich Vaia and Mike Arlen (AFRL/WPAFB).

Tasks/Milestones:

A detailed research presentation was delivered successfully in two venues.

Corroboration of CP2 dielectric data was successful.

The tensometer conductivity cell was modified as needed and tested this month.

June 2007

Major Activities:

Impedance Spectroscopy Modeling of CP2 Polyimide

Performed more comparisons of the polyimide impedance/dielectric measurement data obtained from our equipment with that of our collaborator, Zoubeida Ounaies (Texas A&M University).

Vice Sample Cell Design for X-Ray Measurements

Designed a sample cell with a vice-like grip that can be mounted to optical benches and stages. This was used to streamline the repetitive setup of numerous X-ray experiments performed at the Brookhaven National Laboratory this month.

Automatic Model Compensation Due To Sample Geometry Modifications

Added code to the CNLS modeling software to automatically adjust modeling parameters when the user changes sample geometry values associated with the impedance measurements.

Design of a Test-Bed for Performing Conductivity Measurements of Au Nanoliquids

A test-bed design was started this month which will be used to investigate the conductivity of Au nanoparticle liquids. The cell will utilize an existing fabricated 4-pt conductivity sensor, facilitate convenient attachment of measurement cables through a strain-relief fastener, and provide measurement points consisting of spring-loaded probes in a “bed-of-nails” type of arrangement.

Nanocomposite Process Control System Progress

The electrical power was connected and tested (120, 220Vac). The main power relay coil required a reverse catch diode to counteract the inductive “kick-back” when the relay demagnetizes. When the power is suddenly removed from the relay coil (during power down) the diode provides a current path to safely discharge the coil preventing the coil current and voltage from otherwise damaging system components.

Tasks/Milestones:

The sample cell design used at Brookhaven was successful.

The electrical power was successfully tested and the main power relay issue was resolved.

June 2007

Major Activities:

CP2 Polyimide Publication

Worked with Mike Arlen (AFRL/MLBP, Univ. of Akron) to start drafting a publication to describe the impedance results for the CP2 polyimide system.

Continued the Design of the Nanocomposite Processing (NCP) System

The power input, emergency stop, and electronic actuation circuits were wired and successfully tested this month. A custom circuit has yet to be designed to control the front panel indicators. The National Instruments computer interface components have been installed, but still need testing. The peripheral components including, solenoid valves, heater, vacuum pump, control valve, thermocouples, and impedance sensors also still need to be wired.

4-Point Conductivity Measurement Cell Design for Gold Nanoliquids

A 4-point measurements cell was designed and fabricated to enable conductivity measurements of Au nanoparticle liquid samples. The cell will be tested next month.

Low-Frequency Pressed Nanoclay Impedance Measurements

The pressed nanoclay powder systems were revisited to better understand potential sources of error in the low-frequency portion of the impedance spectra. In particular, the large amplitude responses have raised concern about whether there are nonlinearities the root cause. Spectra were taken repetitively for 10 hours to verify measurement stability and consistency for pressed nanoclays. The results showed that there is some suppression of the complex permittivity with time, which worsens at lower frequencies.

Tasks/Milestones:

Major portions of the electrical control panel for the NCP system have been completed this month.

A specialized 4-pt conductivity cell was constructed.

August 2007

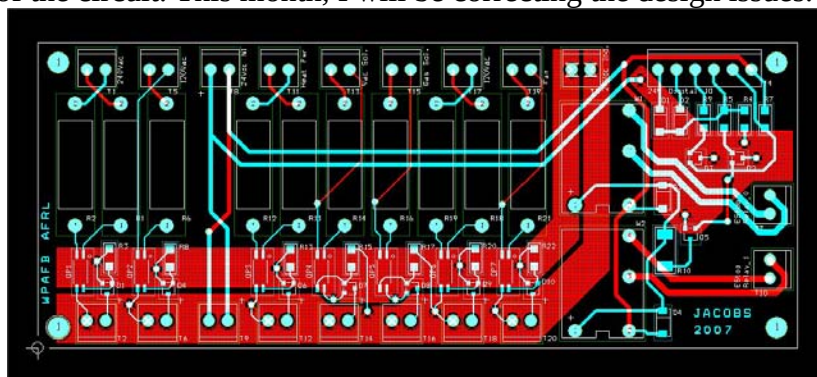
Major Activities:

CP2 Polyimide Publication

Continuing work on drafting a publication to describe the impedance results for the CP2 polyimide system. I'm collaborating with graduate students at Texas A&M University to complete the experimental work for the publication.

Nanocomposite Processing (NCP) System

A circuit design and printed circuit board was designed to control the front panel indicators. This is required to allow the low-voltage front panel indicators to be controlled by higher voltage sources. For example, the heater power operates at 240Vac, when the heater is on the 24Vdc operated LED indicator must turn on to show its operational state. This task is done using optocouplers to isolate and drive the indicators using a separate 24Vdc power supply. In addition, this circuit design also provides some hardware redundant logic to prevent the simultaneous operation of the solenoids that control vacuum and pressure to the vessel. Finally, the circuit also allows E-stop functionality to be remotely actuated by way of a digital signal, allowing the E-stop to be utilized from a computer interface and also a mechanical pushbutton interface. The design fell short of its intention due to an assumption of how the solid state relays operate on the high-voltage input side of the circuit. This month, I will be correcting the design issues.



4-Point Conductivity Measurement Cell Measurements for Gold Nanoliquids

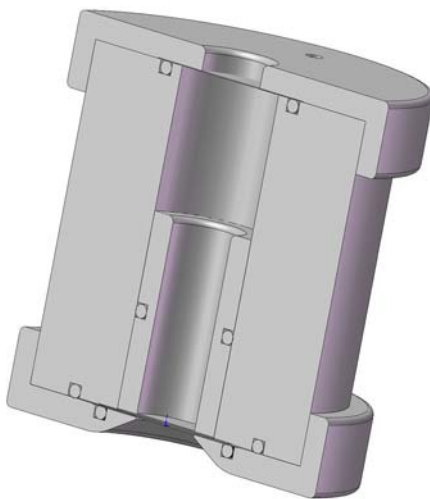
The 4-point measurements cell designed last month has undergone some testing this month. More verification is required to identify whether the geometry of the 4-point sensor will be adequate for the materials being measured. This evaluation will continue through next month.

Low-Frequency Pressed Nanoclay Impedance Measurements

The pressed nanoclay powder systems were revisited to better understand potential sources of error in the low-frequency portion of the impedance spectra. Discussions with Enis Tuncer have revealed some ideas concerning the difficulties of measuring porous material systems. He also provided some code for testing the linearity of impedance measurements.

Electrochemical In-Situ X-Ray Cell

A new design has begun to enable in situ X-ray measurements of lithium intercalation batteries. This cell is more technical than many of the previous. There will be more to describe next month when it is completed.



Tasks/Milestones:

There was a minor setback due to the unexpected behavior of the SSR devices. The PCB will need to be reworked this month.

The electrochemical test cell design was nearly completed. It will be constructed next month.

September 2007

Major Activities:

Nanocomposite Processing (NCP) System (Version 2)

Revisions were required for the circuit design and printed circuit board fabricated last month to control the front panel indicators. Comparator circuits were added to compensate for the non-zero input voltages produced by leakage through the snubber networks on the outputs of the solid state relay devices. This design monitors these output voltages and the previous design produced an improper response in the presence of these non-zero leakage voltages. The new design accounts for this behavior and should now respond appropriately.

The control panel wiring has been completed this month. Once the front panel PCB is installed all major electrical systems will be ready for rigorous testing; and software design and integration can proceed.

Electrochemical In-Situ X-Ray Cell

A new design to enable in situ X-ray measurements of lithium intercalated batteries has been completed. This cell is more technical than many of the previous and has required much more time to design and construct. This cell design has undergone initial testing and some design improvements will be necessary in the next revision. Some of these improvements will include a smaller internal size to accommodate smaller test samples, changes to enable easier assembly, and deterministic mechanical pressure when assembled.

Tasks/Milestones:

The front panel design/PCB has been reworked this month. This design should be robust enough to handle the identified input signal uncertainty.

Electrical wiring for the NCP system was completed this month (all *major* wiring, that is)!

The in situ X-ray electrochemical test cell design was completed. Design changes have been identified through testing.

October 2007

Major Activities:

Nanocomposite Processing (NCP) System

The NCP system hardware including instrumentation, sensors, system wiring, and complete testing was finished this month. Piping was modified to allow the addition of a pressure transducer which replaced the nonfunctioning pressure sensor built into the electronic pressure regulator. LabVIEW control software is being written to enable automated use of the system for experimentation. Such experiments will include the online monitoring of clay/epoxy nanocomposites using in situ impedance spectroscopy, and the morphology actuation of these materials using large external electric fields. The software will enable the user to explore the processing space (temperature and pressure) to aid the optimization of processing cycles for improved material products.

A Novocontrol Alpha-A impedance analyzer is in the process of being purchased. This will be dedicated for use by the NCP system and will enable in situ measurements to be made during processing. It will be remotely controlled by the LabVIEW control software by way of the IEEE-488.2 (GPIB) interface.

Laponite NMR/Impedance Spectroscopy Paper Revisions

Several additions to the draft of “*The Structure and Dynamics of Surfactant Interfaces in Organically Modified Clays*” (Mirau, Serres, Jacobs, and Vaia) were added to show that impedance-based measurements provided complimentary material related information and supported the basic NMR results as well as provided characteristics regarding microstructure and charge mobility.

Tasks/Milestones:

The front panel design/PCB reworked last month was installed and tested successfully.

All hardware aspects of the NCP construction were completed and the system was successfully tested.

November 2007

Major Activities:

Nanocomposite Processing (NCP) System

LabVIEW control software has been the main focus for development this month. Most of the control software has been architected which will allow simple temperature and pressure control. Electric field actuation, impedance sensor multiplexing, and the Novocontrol impedance analyzer interface still needs developed. Most of the effort this month has been in developing the PID control loops for the temperature and pressure control. Temperature control has been problematic due to the large thermal mass associated with the insulated and pressurized vessel. The system does not cool down efficiently; therefore we may want to look into implementing a method for platen cooling (probably in future work).

A high voltage multiplexer circuit was designed to allow impedance sensing and electric fields to be applied to samples in the NCP chamber in an interleaved fashion, since it is not feasible to apply them at the same time. The design has been created, and it will be constructed during this next month.

A Novocontrol Alpha-A impedance analyzer is about to be shipped. This will be dedicated for use by the NCP system and will enable in situ measurements to be made during processing. It will be remotely controlled by the LabVIEW control software by way of the IEEE-488.2 (GPIB) interface.

Tasks/Milestones:

Impedance sensor/electric field multiplexer circuit was designed.
Closed loop heat and temperature control is functional.

December 2007

Major Activities:

Nanocomposite Processing (NCP) System

A high voltage multiplexer circuit was designed to allow impedance sensing and electric fields to be applied to samples in the NCP chamber in an interleaved fashion, since it is not feasible to apply them at the same time. The design was created last month and the printed circuit board was created this month.

A simple epoxy sample was successfully created to test the processing capabilities of the NCP system.

A pre-owned Novocontrol Alpha-A impedance analyzer was received. This system was determined to need an upgrade before it will be applicable to our analysis needs. In the mean time we will use our other Novocontrol impedance analyzer. Fortunately, we can arrange the equipment to enable the required measurements.

Tasks/Milestones:

Impedance sensor/electric field multiplexer circuit PCB was fabricated.

Epoxy sample was successfully processed.

January 2008

Major Activities:

Nanocomposite Processing (NCP) System

The high-voltage multiplexer design was constructed, installed, and successfully tested. This is the final component for the NCP system and marks the end of the design and construction. All that remains is to finish the supervisory control software.

Wrote more LabVIEW software to interface the Alpha-A impedance analyzer necessary for automating measurements. This addition provides digital switching and control of relays to facilitate multiplexing several in situ impedance sensors using a single channel analyzer.

A quote for upgrading the pre-owned Novocontrol Alpha-S impedance analyzer to the latest Alpha-ANB model was received. This system upgrade is required before it will be applicable to the needs of the NCP system. In the mean time we will use our other Novocontrol impedance analyzer. Fortunately, we can arrange the equipment to enable the required measurements.

Tasks/Milestones:

Total completion of the nanocomposite material processing system with in situ impedance morphology monitoring and electric field actuation.