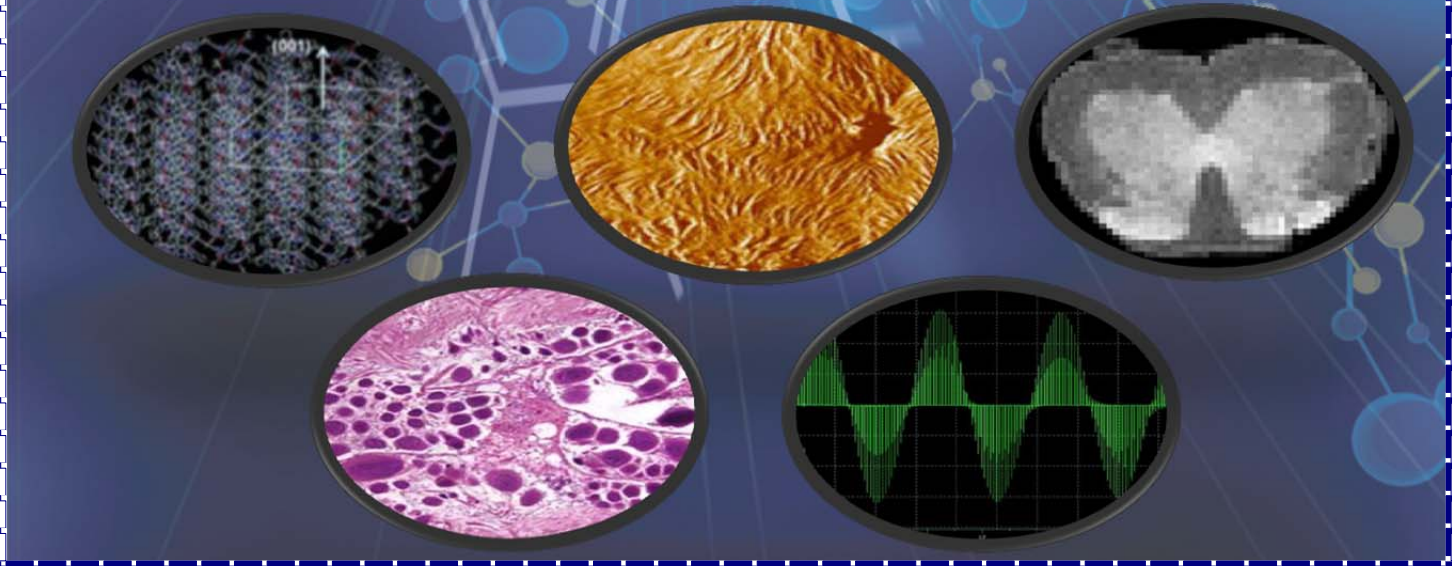
# 2014 Departmental Research Day

## Department
## of
## Chemical & Biomedical Engineering
## FAMU-FSU College of Engineering

**National High Magnetic Field Laboratory**
**1800 E. Paul Dirac Drive, Tallahassee, FL**

**9:00 am – 2 pm, Friday April 25, 2014**



# Schedule of Events

| | |
|---|---|
| 08:00 | Poster and Presentation Setup |
| 09:00 | Poster Session 1 – Odd posters |
| 10:00 | Keynote Speaker – Dr. Jim Zheng, ECE |
| 10:50 | Break |
| 11:00 | Oral Graduate Student Session |
| 13:00 | Lunch & Poster Session 2 – Even posters |
| 14:00 | Adjournment & Cleanup |

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# Welcome!

*On behalf of the Department of Chemical & Biomedical Engineering at the FAMU-FSU College of Engineering, I wish to extend to you our sincerest welcome to the Annual Departmental Research Day. This yearly event allows our graduate students, undergraduates and postdoctoral fellows to put their research efforts on display. We are proud of the work performed by our students and trainees, and this event gives them the opportunity to defend their research and discuss it among peers and faculty in an informal setting. These kinds of exchanges are critical to the education of our students but also provide a forum or scientific review and critique. As such, this event helps not only our students and trainees to mature but also helps their engineering and scientific work to mature.*

*Representing some of the superior research performed at the FAMU-FSU College of Engineering, this year's keynote speaker is Dr. Jim Zheng, Sprint Eminent Scholar Chair in Electrical & Computer Engineering Professor and courtesy professor in Chemical & Biomedical Engineering. We thank Dr. Zheng for sharing some of his research and participating in this day.*

*We also greatly appreciate the support of the sponsors of this event. And we look forward to a day of fruitful discussions, conversations and networking among students, fellows and faculty.*

*With Regards,*

*Samuel C. Grant, PhD*

*CBE Graduate Coordinator*

# List of Graduate Student Oral Presentations

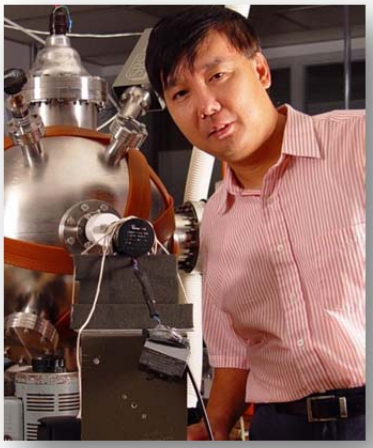
| Presentation Time | |
|---|---|
| 11:00-11:30 | **Robert Wandell,** *Organic Synthesis with Continuous Flow Water Film Pulsed Plasma Discharge* |
| 11:30-12:00 | **Jifeng Sun,** *First-Principles Study of Electronic and Optical Properties in a New Semiconducting Oxytelluride $Ba_2OTe$* |
| 12:00-12:30 | **Sarah Leonard,** *Solid-State NMR Constraints on Molecular Organization within MAX8 Designer Peptide Nanofibers* |
| 12:30-13:00 | **Yijun Liu,** *Analysis of Human Mesenchymal Stem Cell Metabolic Heterogeneity during Expansion* |

# List of Graduate Student Poster Presentations

**Poster Number**

1. **Xuejian Chen**, *Effect of Length of 1-alkene on Melt Memory of Crystallization Above the Equilibrium Melting Temperature of Random Ethylene Copolymers*
2. **Lianyang Dong**, *High Quality $FeSb_2$ Single Crystal Growth by a Self-flux Method*
3. **Oyidia Elendu**, *Electroless Cu-Ni-Mo Catalyst for the Low Pressure Hydrogenolysis of Glycerol to Propan-1,2-diol*
4. **Chris Golding**, *Using Geometrical Shapes to Predict Anisotropic Diffusion in Muscle Fibers*
5. **Danting Huang**, *Solid State NMR Evidence for Antiparallel β-Sheet Structure within Toxic Oligomers Of Alzheimer's β-Amyloid Peptide*
6. **Ben Hudson**, *Water-soluble Rada16-I Peptide Species within Rada16-I Designer Nanofiber Hydrogels*
7. **Hamed Janani**, *Melt Miscibility of Blends of Isotactic Polypropylene and Homogeneous Iso-propylene-1-hexene* Copolymers
8. **Jose Muniz**, *A Quadrature Saddle RF Coil Design for* In Vivo *Ultra-High Field MR Applications*
9. **Onyekachi Oparaji**, *Structural Characterization of Solid Polymer Electrolyte Materials*
10. **Ang-Chen Tsai**, *Actin-mediated Contractility in Three-dimensional Aggregates of Human Mesenchymal Stem Cells*
11. **Sébastien Sart**, *Extracellular Matrices derived from Pluripotent Stem Cell Aggregates for Tissue Development*
12. **Junfei Xia**, *Self-Assembly of Live Cell and Asymmetric PLGA Microdisk for Drug Delivery*
13. **Yuanwei Yan**, *Cryopreservation of Pluripotent Stem Cell-derived Neural Progenitor Aggregates Labeled with Iron Oxide Particles for MRI Analysis*
14. **Guang Yang**, *Designing Composite Polymer Electrolyte Interfaces for Stable Electrodes*
15. **Xiaoshi Zhang**, *FTIR Analysis of the Effect of Chlorine on Polymorphism of Precision Halogen Substituted Polyethylene*
16. **Maxwell Zimmerman**, *Rationalizing Solid-State NMR Constraints of Amyloid-β(1-42) Oligomers*

# Keynote Speaker



## Dr. Jim P. Zheng, Ph.D.

Sprint Eminent Scholar Chair
Professor, Electrical & Computer Engineering
Center for Aero-Propulsion, Mechatronics & Energy (AME)
Center for Advanced Power Systems (CAPS)

**Education**
P h.D. in Electrical Engineering, State University of New York at Buffalo
M.S. in Electrical Engineering, State University of New York at Buffalo
B.S. in Physics, Fudan University, China

# High Energy Density Lithium-ion Capacitors using Carbon-Carbon Electrodes

The energy density of conventional electric double-layer capacitors is about 6-7 Wh/kg and due to the limited specific capacitance and cell voltage, and a large amount of electrolyte which is required to build a layer of charge of the double-layer. The energy density theory guide clearly shows that the energy density of double-layer capacitors is ultimately limited by how many ions are available in the electrolyte or the salt concentration in the electrolyte.

We demonstrate a lithium-ion capacitor, which is capable of achieving high energy density over 20 Wh/kg, long cycle life and high power density. The lithium-ion capacitor consists of a battery electrode with lithium intercalated hard carbon anode and a double-layer activated carbon cathode electrode with the open-circuit potential at or near the maximum potential when the cell is fully charged. The stabilized lithium metal powder was applied onto the surface of prefabricated hard carbon anode electrodes.

**Short Biography:** Dr. Jim P. Zheng is Sprint Eminent Scholar Chair and Professor at the Department of Electrical and Computer Engineering of Florida State University. He obtained his Ph.D. degree from the State University of New York at Buffalo in 1990. He has worked at US Army Research Laboratory for about 5 years. He has published more than 200 articles in scholarly journals and conference proceedings. He has won numerous research grants from many governmental agencies such as NSF, DOE, DOD, and NASA totaling more than $14 M.

## ORGANIC SYNTHESIS WITH CONTINUOUS FLOW WATER FILM PULSED PLASMA DISCHARGE

Robert J. Wandell, Kevin Hsieh, and Bruce R. Locke
*Department of Chemical and Biomedical Engineering, Florida State University, 2525 Pottsdamer Street Tallahassee, FL 32310 USA*

Stefan Bresch and Igor V. Alabugin
*Department of Chemistry and Biochemistry,*
*Florida State University, Tallahassee, FL 32306 USA*

Plasma discharges generated by moderate frequency, low energy pulses in a flowing carrier gas with liquid water have been shown capable of producing hydrogen peroxide at moderately high energy yields. The leading hypothesis for the success of this production method is that free elections produced by the plasma in the gas phase dissociate vaporized water molecules into hydroxyl radicals and hydrogen. The hydroxyl radicals rapidly react to form hydrogen peroxide, which is sequestered into the liquid phase. Many reactor designs have been explored with various gas-liquid contact schemes in order to enhance the overall efficiency of this process. Recently, a continuously flowing, liquid film, pulsed plasma reactor has been developed in our laboratory which has a number of significant benefits over the previously explored configurations. Using this novel reactor configuration in conjunction with inspiration and techniques developed from work with pure water, the main objective of our current research is to explore the synthesis of organic compounds with soft oxidation by hydroxyl radicle attack. To do so, small amounts of organic solvent are vaporized into the plasma where they undergo electron attack and oxidation by hydroxyl radicals formed from water to generate more useful chemical species. Results with n-hexane and cyclohexane show that alcohol, aldehyde, and ketone products can be successfully generated. A significant amount of hydrogen peroxide is also generated in conjunction with the oxygenated products. It has also been found that selectivity of the reaction products is affected by variation of the water flow rate, organic to water ratio, and choice of parent compound. In this presentation we will report on recent experiments in our laboratory which utilize this continuously flowing water film reactor for the chemical synthesis of organic compounds and will focus on how the choice of organic parent compound can affect the distribution and selectivity of reaction products.

1. R. J. Wandell, S. Bresch, K. Hsieh, I. V. Alabugin, and B. R. Locke, “Formation of Alcohols and Carbonyl Compounds from Hexane and Cyclohexane with Water in a Liquid Film Plasma Reactor”, IEEE Trans. Plasma Sci., in-press.

* Work supported by the National Science Foundation grant CBET 1236225

## FIRST-PRINCIPLES STUDY OF ELECTRONIC AND OPTICAL PROPERTIES IN A NEW SEMICONDUCTING OXYTELLURIDE $Ba_2OTe$

Jifeng Sun, Daniel Ramirez, Jeffrey Whalen, Theo Siegrist
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*National High Magnetic Field Laboratory, Florida State University*
*1800 E Paul Dirac Dr, Tallahassee, FL 32310*

A first-principles study has been performed to investigate the electronic and optical properties of a new semiconducting material, $Ba_2OTe$. In order to compare and get the right band-gap, we employed both the traditional PBE type GGA functional and Modified Becke-Johnson (MBJ) potential implemented in the full potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT). Our band structure calculations show a direct band gap with 1.9 ev (PBE) and 2.6 eV (MBJ) at Γ point, respectively, which is formed by Ba-d states in the conduction band and Te-p states in the valence band. The dielectric tensors are derived within the random phase approximation (RPA). The results of the dielectric function, absorption coefficient, and reflectivity are all along both x and z directions. The optical band gap calculated (2.6 eV) agree well with the experimental value (~3 eV).

## SOLID-STATE NMR CONSTRAINTS ON MOLECULAR ORGANIZATION WITHIN MAX8 DESIGNER PEPTIDE NANOFIBERS

Sarah R. Leonard[1,2], Maxwell I. Zimmerman[1,2], Xiaodong Pang[3], Huan-Xiang Zhou[3], Anant K. Paravastu[1,2]

[1]*Department of Chemical and Biomedical Engineering, Florida State University, 2525 Pottsdamer Street, Tallahassee, FL 32310 USA*

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[3]*Department of Physics and Institute of Molecular Biophysics, Florida State University, Tallahassee, FL 32306*

MAX8, a designer peptide known to undergo self-assembly following changes in temperature, pH, and ionic strength, has demonstrated utility for tissue engineering and drug delivery. Here, we report evidence from solid-state NMR spectroscopy that supports the presence of the hypothesized β-hairpin conformation and constrains the arrangement of MAX8 molecules within nanofibers. Specifically, $^{13}$C-$^{13}$C 2-dimensional correlation spectroscopy indicates spatial proximity between V3 and K17 residues, and $^{13}$C-$^{13}$C dipolar coupling measurements reveal proximity between the V3 and V18 backbone carbonyls. Moreover, isotopic dilution of labeled MAX8 nanofibers did not result in a loss of the $^{13}$C-$^{13}$C dipolar couplings, showing that these couplings are primarily intramolecular. Additional MAX8 samples were synthesized to differentiate between two possible arrangements of MAX8 molecules: 1) the "syn" configuration, with all β-hairpin hinges aligned along the same edge of the β-sheet, and 2) the "anti" configuration, with alternating β-hairpin hinges aligned along opposite edges of the β-sheet. $^{13}$C-$^{13}$C dipolar coupling measurements indicate weak interactions between neighboring V5 backbone carbonyls, consistent with the syn configuration. Intermolecular $^{15}$N-$^{13}$C dipole-dipole couplings indicate spatial proximity between the V5 backbone carbonyl and the V16 backbone nitrogen, also consistent with the syn configuration. A lack of contact between the V3 and T12 residues with $^{13}$C-$^{13}$C 2-dimensional correlation spectroscopy is indicative of a syn-parallel between-sheet conformation with all β-hairpin hinges aligned along the same edge of the stacked β-sheet. Combined, these results led to the development of an all-atom molecular model of MAX8 nanofibers consistent with current NMR experimental constraints.

## ANALYSIS OF HUMAN MESENCHYMAL STEM CELL METABOLIC HETEROGENEITY DURING EXPANSION

Yijun Liu[1], Nathalie Muñoz[2], Teng Ma[1], Timothy M. Logan[2]
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Human mesenchymal stem cells (hMSCs) are a primary cell source in cell therapy for a wide range of diseases. However, bone marrow derived hMSCs are intrinsically heterogeneous and comprise subpopulations that differ in their proliferation, multi-potency, and functional properties. The conventional cell culture techniques used in producing hMSC for clinical studies lead to a gradual loss of the multipotent subset and cellular senescence. Understanding hMSC metabolism is important in designing an approachable strategy for hMSC expansion while maintaining their therapeutic potency. In this study, a GC-MS-based metabolic profiling approach was employed to analyzing the fate of the 13C labeled glucose and the label incorporation in the major intracellular metabolites involved in glycolysis and TCA cycle in (1) hMSC clonal population, (2) hMSC in passaging. The results revealed distinct global metabolic profiles for hMSC clonal and passing subsets with the most significant differences involving citrate, malate, fumarate, lactate, and branched chain aminoacid. In hMSC clonal population, enhanced glycolysis coupling to TCA cycle was observed. For HD-hMSC, enhanced oxidative phosphorylation was found to be associated with increased senescent population under expansion. Together, the results revealed hMSCs population heterogeneity is associated with metabolic heterogeneity, with more active glycolytic activities in hMSC clonogenic population and more active oxidative phosphorylation in hMSCs passaging population. Thus, defining hMSC metabolic heterogeneity during expansion plays an important role in determining the optimal conditions for hMSC in order to better preserve hMSCs clonogenic subset.

# EFFECT OF LENGTH OF 1-ALKENE ON MELT MEMORY OF CRYSTALLIZATION ABOVE THE EQUILIBRIUM MELTING TEMPERATURE OF RANDOM ETHYLENE COPOLYMERS

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Model random ethylene copolymers with ethyl branches are known to exhibit strong melt memory of crystallization even above their equilibrium melting temperatures. Seeds remain in the melt at high temperatures lowering the change in free energy barrier for nucleation, and hence increasing the crystallization rate. The seeds are molten ethylene sequences from the initial crystallites that remain in close proximity due to restrictions to diffuse and reach the initial copolymer random melt topology. We found that erasing memory of the prior sequence selection in ethylene 1-butene copolymers requires temperatures ~ 25 degrees above the equilibrium melting. The ethylene 1-butene data are contrasted in the present work with data of 1-alkene ethylene copolymers with longer branches. The effect of branch length in melt diffusion is correlated with the range of melt temperatures where seeds survive and, hence, with the strength of melt memory. Narrowly distributed, metallocene catalyzed, ethylene copolymers with 1-butene, 1-hexene, 1-octene or 1-decene comonomer are analyzed in a range of comonomer content from 0.6 to 12.6 mol%, and Mw ~ $10^5$ g/mol. Independently of branch length, the critical temperature of the melt to reach a homogeneous copolymer melt state ($T_{critical}$) shows a bell-shape with increasing comonomer content. $T_{critical}$ reaches its maximum at ~1.5 mol% and the equilibrium melting at 0 and ~4.5 mol% branches. Moreover, the nominal $T_{critical}$, and strength of melt memory, defined as ($T_{critical}$ - $T_m^o$), decrease up to 20 °C with increasing branch length. We attribute the decrease in strength of melt memory with increasing branch length to less restricted topological ties, loops and knots in the inter-lamellar region of the semicrystalline structure, which are aided by faster melt diffusion of copolymers with longer branches. Data on ethylene 1-octene copolymers with a small content of long chain branches support that the limit of branch length to decrease strength of melt memory is reached at the critical entanglement length (~1,300 g/mol).

# HIGH QUALITY $FeSb_2$ SINGLE CRYSTAL GROWTH BY SELF-FLUX METHOD

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**Introduction**

$FeSb_2$ has been characterized as an example of a strongly correlated Kondo insulator-like material with 3*d* ions.[1-3] Similar to FeSi, heavy fermion states were discovered in $FeSb_2$ by doping-induced metallization.[4] In 2007, Bentien et al. reported a colossal Seebeck coefficient of -45000 mV/K at 10K in single crystal $FeSb_2$ which leads to a record-large thermoelectric power factor.[5] If the mean free path of the dominant phonons could be reduced without substantially reducing the thermoelectric power factor, $FeSb_2$-based materials may turn out to be ideally suited to build a future solid-state cooling device at cryogenic temperatures, making, for example, superconducting microelectronic devices more feasible.[5]

**Synthesis method**

The inter-metallic compound $FeSb_2$ was prepared by self-flux method from mixtures of the pure elements Fe powder (>99.99%), and Sb metal grains (>99.99%) with a molar Fe: Sb ratio of 1:10, thus employing Sb as both reactant and flux medium. Excess Sb metal was separated by centrifuge after reaction. The products consist of well-shaped, silvery-gray, crystals with size up to 5 millimeters.

**Results**

The lattice parameters at the room temperature (around 300K) were measured by using X-calibur ™2 single crystal diffractometer from Oxford Instruments. The structure was refined from single-crystal X-ray data showing $FeSb_2$ compound crystallizing in orthorhombic space group *Pnnm* (#58) with $Z$=2. Its lattice constants are $a$=5.8328 Å , b=6.5376 Å and $c$=3.1973 Å. The resistivity of $FeSb_2$ decreases with increasing temperature which is clearly semiconducting, and a large decrease in resistivity of more than six orders of magnitude was observed in the temperature range from 0 to 150 K.

**Conclusions and future works**

High quality bulk single crystals of $FeSb_2$ were successfully synthesized by using self flux method. The resistivity of $FeSb_2$ indicated a semiconductor behavior, and it is weakly dependent on temperature in the range 10-30K.

Future works will include band structure calculation, magnetic property study, evaluation of thermoelectric performance (Seebeck coefficient, thermal conductivity and carrier concentration study) and both Fe-site and Sb-site doping.

**References**

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2 C. Petrovic, Y. Lee, T. Vogt, N. Dj. Lazarov, S. L. Bud'ko, and P. C. Canfield, Phys. Rev. B **72**, 045103 (2005).
3 A. Perucchi, L. Degiorgi, Rongwei Hu, C. Petrovic, and V. F. Mitrovic, Eur. Phys. J. B **54**, 175 (2006).
4 A. Bentien, G. K. H. Madsen, S. Johnsen, and B. B. Iversen, Phys. Rev. B **74**, 205105 (2006).
5 A. Bentien, S. Johnsen, G.K.H. Madsen, B.B. Iversen, and F. Steglich, Europhysics Letters **80** 17008 (2007).

# ELECTROLESS Cu-Ni-Mo CATALYST FOR THE LOW PRESSURE HYDROGENOLYSIS OF GLYCEROL TO PROPAN-1,2-DIOL

Oyidia Elendu

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Glycerol is a valuable by-product of biodiesel production, which can be used as a feedstock for the production of many other chemicals of industrial importance. One of these, propan-1,2-diol can be obtained from glycerol through hydrogenolysis over metal catalysts under high temperature and pressure. Different metals have shown different activities and selectivities towards this reaction, and Ni/Cu bimetallic catalysts have shown great promise in terms of cost and good hydrogenolytic activity towards this reaction.

Here, a low pressure technique for the hydrogenolysis of glycerol to propan-1, 2-diol is being investigated in stages. The first step involves the development of Cu-Ni-Mo/$Al_2O_3$ prepared by electroless deposition method. Deposition times, optimal metal loading, pH and temperature ranges for the supported metal catalysts will be investigated and the characterization of active catalyst using XRD, TEM SEM and EDAX will be done. Detailed microstructural and texture characterization of the Cu-Ni-Mo/$Al_2O_3$ catalysts, and their correlation with glycerol hydrogenolytic activity will also be investigated.

# USING GEOMETRICAL SHAPES TO PREDICT ANISOTROPIC DIFFUSION IN MUSCLE FIBERS

Chris Golding[†], Dr. Locke[†] and Dr. Kinsey[‡]

[†]Florida State University, Department of Chemical and Biomedical Engineering
[‡] University of North Carolina, Wilmington, Department of Biology and Marine Biology

Muscle fibers are one of the few cells that have multiple nuclei. These nuclei are thought to be distributed non-randomly to facilitate uniform muscle growth. Nuclei are recruited from satellite cells when growth of the muscle occurs beyond some critical myonuclear domain size. The location and orientation related to other nuclei has not been shown to be a product of diffusion and currently has not been investigated.

The current method to determine the size of the myonuclear domains uses a 2-dimensional method of a slice of fibers (closest volume to nuclei multiplied the depth of the slice). With the advancement of imaging techniques a 3-dimension can be developed for an entire muscle fiber. The 3-dimensional analysis determines the total volume of each individual myonuclear domain as the volume closest to that nucleus (nearest neighbor approach) by imaging the entire fiber.

Using the same image as the nearest neighbor approach, a new method has been developed to attempt to analyze the orientation as well as size of the myonuclear domains. Each nucleus will have an ellipsoid placed around it as a representation of its myonuclear domain. The size of the myonuclear domain will be expanded and analysis of the total coverage and overlap of the muscle fiber will be analyzed.

# SOLID STATE NMR EVIDENCE FOR ANTIPARALLEL β-SHEET STRUCTURE WITHIN TOXIC OLIGOMERS OF ALZHEIMER'S β-AMYLOID PEPTIDE

Danting Huang,[*] Maxwell I. Zimmerman,[*] Patricia K. Martin,[+] Jeremy Nix,[+] Terrone L. Rosenberry[+] and Anant K. Paravastu[*]

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Significant genetic, pathological, and biochemical evidence link Alzheimer's Disease (AD) to the aggregation (self-assembly) of the β-amyloid peptide (Aβ). It is known that complex aggregation pathways produce a variety of aggregated Aβ structures, eventually producing amyloid fibrils (filamentous protein nanostructures) that deposit into plaques in the brain. The latest evidence suggests that smaller oligomeric Aβ aggregates, composed of 2-50 molecules, may be the primary toxic species in AD. Sodium dodecylsulfate (SDS) ionic lipids can stabilize oligomers of the 42 amino acid form of Aβ, to produce 150 kDa oligomers that exhibit biophysical and neuronal toxicity profiles similar to *in vivo* derived oligomers. Our group has previously reported the primary difference between this oligomer and fibril structure lies in arrangement of β-strands within β-sheets. Here, we report new highly specific constraints on β-strand organization within these oligomers.

Aβ42 oligomers with $^{13}C$ isotopic labels at E11, Q13, H15, L17, I32, M35, G37 and V40 were prepared as described [1]. The oligomer secondary and tertiary structural characterization was performed by 2D fpRFDR, 2D DARR and 2D CHHC solid state NMR experiments. Molecular models for Aβ42 oligomers were established using molecular simulation based on the experimental constraints obtained from NMR measurements.

The 2D fpRFDR NMR spectra exhibited I32, M35, G37 and V40 peak positions which are consistent of β-strand conformation. Intermolecular contacts between I32/V40, M35/G37 were observed from 2D DARR experiments and 2D CHHC experiments. Based on these constraints, we produced four different all-atom molecular models were built.

Our results indicated that in the 150kDa Aβ42 oligomer, each molecule has a conformation consisting of two β-strands separated by non-β-strand or 'turn' region, and molecules are organized into anti-parallel β-sheets as proposed in our hypothesized model.

1. Tay, W. M., D. Huang, T.L. Rosenberry and A.K. Paravastu "The Alzheimer's Amyloid-beta(1-42) Peptide Forms Off-Pathway Oligomers and Fibrils that are Distinguished Structurally by Intermolecular Organization." *J. Mol. Biol.* **425:** 2494-2508 (2013).

# WATER-SOLUBLE RADA16-I PEPTIDE SPECIES WITHIN RADA16-I DESIGNER NANOFIBER HYDROGELS

Ben Hudson, Anant Paravastu

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The designer peptide RADA16-I (RADARADARADARADA) can form nanofiber matrices with important biomedical applications (1,5,6). Peptide self-assembly into nanofibers occurs at physiological conditions after peptide is dissolved in an aqueous solvent (e.g., pH 5 phosphate buffer). Once fully self-assembled, the peptide/solvent solution takes the form of a hydrogel. The peptide concentrations necessary for matrix formation depend on pH and buffer concentration, but in practical applications the gel will be more than 99% $H_2O$ (less than 10 mg/mL RADA16-I). The resulting RADA16-I hydrogel has been used extensively in 3-dimensional cell culture (3), as well as animal models which have used the gel as a scaffold to promote the repair of neuronal tissue following a traumatic brain injury (2,4). These studies have shown no detectable immune response due to RADA16-I.

Using high resolution magic angle (HRMAS) NMR spectroscopy, we have observed a signal from water-soluble RADA16-I peptide within a nanofiber system. The immediate results of these experiments have yielded a proton ($^1$H) spectrum showing several mobile species in solution. We consider this result significant, as it is the first time these mobile species have been observed. Mobile peptide may play a role of nanofiber self-healing, which is the spontaneous re-growth of nanofibers fragmented by sonication (6). While sonication has been used in the past in order to fragment the nanofiber matrix and allow for reassembly (1), though the $^1$H spectrum we have acquired does not appear to be significantly affected by it. This suggests the components observed in the proton spectrum may not be key components in the structure of the nanofiber matrix. Up to this point, no one has succeeded in identifying the self-assembly and self-healing mechanisms of RADA16-I nanofibers. We believe the possible identification of mobile species in the RADA16-I nanofiber matrix will shed new light on the processes involved and eventually allow for the development of an accurate mechanistic model of a RADA16-I nanofiber system.

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# MELT MISCIBILITY OF BLENDS OF ISOTACTIC POLYPROPYLENE AND HOMOGENEOUS ISO-PROPYLENE-1-HEXENE COPOLYMERS

Hamed Janani, Rufina G. Alamo

Department of Chemical & Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University, Tallahassee, FL 32308

The miscibility of blends of isotactic polypropylene and propylene-1-hexene (PH) copolymers with 11 and 21 mol% of 1-hexene (PH11 and PH21, respectively) has been studied theoretically and using DSC, DMA, and AFM techniques. Using experimental PVT data, the solubility parameter approach leads to a critical difference in 1-hexene content for melt miscibility of 17 mass% (~11 mol%) at 200 °C and 0.1 MPa. The theoretical window for miscibility is in close agreement with thermal properties of the blends. The glass transition (Tg) of miscible blends (iPP/PH11 and PH11/PH21) decreases proportionally to the content of PH having the lowest Tg, while immiscible blends (iPP/PH21) display invariable Tg with blend composition. The same trend was extracted from the analysis of the β-relaxation by dynamic mechanical analysis. Room temperature AFM images of blends quenched from 200 °C into liquid nitrogen confirm phase segregation of iPP/PH21 in domains of 1–5 microns, while the AFM images of iPP/PH11 and PH11/PH21 lack any obvious signature of phase separation prior to crystallization.

# A QUADRATURE SADDLE RF COIL DESIGN FOR IN VIVO ULTRA-HIGH FIELD MR APPLICATIONS

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Quadrature RF configurations for MRI can enhance the measured signal-to-noise ratio (*SNR*) from an increase in coil elements and a reduction in sampled thermal noise, improve the $B_1$ homogeneity (*i.e.*, over linear surface coils) and reduce the specific absorption rate. Alongside sensitivity enhancements provided from ultra-high magnetic fields, the quadrature surface coil provides a localized field of view for *in vivo* MRI applications, including magnetic resonance microcopy, magnetic resonance spectroscopy (MRS) and ultra-fast imaging sequences such as echo-planar imaging (EPI) and spatiotemporally encoding (SPEN). A surface quadrature coil's performance for *in vivo* rodent imaging at 21.1 T (900 MHz Larmor frequency) will be evaluated and applied to SPEN and spectrally selective MRS.

Built on a 3.57-cm fiberglass epoxy former (see Fig. 1), the coil can accommodate a 350-g Sprague Dawley rat and achieve isolation (via capacitive decoupling) below -20 dB ($S_{21}$ measurement). Coil performance is validated in terms of the $B_1$ homogeneity (flip maps) and image *SNR*, especially when compared to similarly sized linear surface (factor of $\sqrt{2}$ improvement) and birdcage (factor of 2 improvement) configurations. *In vivo* applications at the National High Magnetic Field Laboratory (NHMFL) include high resolution imaging through $T_2$-weighted RARE (15 minute acquisition time) and both ultrafast single-shot SPEN (12 ms acquisition time) and longitudinal relaxation enhancement (LRE) MRS sequences (5 $mm^3$ voxel) on stroke induced rats treated with stem cell therapy.

# STRUCTURAL CHARACTERIZATION OF SOLID POLYMER ELECTROLYTE MATERIALS

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An ideal electrolyte material for a solid-state battery would have an ionic conductivity $\geq 10^{-4}$ S/cm, be a flexible solid and capable of binding effectively with inorganic components in a heterogeneous electrode. Poly (ethylene oxide – *b* – styrene) copolymer (SEO) in lamellar morphology satisfies the design requirement. A detailed knowledge of the mechanical properties of SEO would aid in predicting how battery cycling induces stresses, causes battery degradation/fading and model lithium battery performance as a result of stresses. The work presented here describes an easy method of making solid – form electrolyte material and determination of the structural properties of SEO using modern techniques. Also parametric studies of the measured structural properties with temperature would be described.

# EXTRACELLULAR MATRICES DERIVED FROM PLURIPOTENT STEM CELL AGGREGATES FOR TISSUE DEVELOPMENT

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Pluripotent stem cells (PSCs) secrete large amounts of endogenous extracellular matrices (ECMs), which play an important role in regulating PSC self-renewal, lineage commitment, and tissue morphogenesis. ECMs derived from PSCs have broader signaling capacity compared to somatic ECMs and contain the unique signaling networks that regulate the self-renewal and lineage specification during tissue development. In this study, ECMs from undifferentiated PSC aggregates or differentiated embryoid bodies at different developmental stages and lineage specifications were decellularized and their capacities to direct PSC (include mouse embryonic stem cells and human induced pluripotent stem cells) proliferation and differentiation were characterized. The results demonstrate that the PSC-derived ECMs were able to influence PSC proliferation and differentiation by direct interactions with the cells and by influencing the signaling functions of the regulatory macromolecules. Proteomic analysis by liquid chromatography–mass spectrometry (LC-MS) indicated the shared and distinct proteins in ECMs derived from undifferentiated and different types of differentiated aggregates. To enhance the stability of PSC-derived ECMs, ECMs were crosslinked by a natural cross-linker which increased the stiffness of ECMs. The effect of biomechanical properties of ECMs on neural differentiation was also evaluated. Taken together, the PSC-derived ECMs have the potential to direct lineage- and development-specific cellular responses for in vitro applications or in vivo cell delivery.

# ACTIN-MEDIATED CONTRACTILITY IN THREE-DIMENSIONAL AGGREGATES OF HUMAN MESENCHYMAL STEM CELLS

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## Introduction

Human mesenchymal stem cells (hMSCs) are an important cell source for therapeutic applications because of their ability of self-renewal and multilineage potential. A major challenge is to maintain the functions of the culture expanded hMSCs. Prior studies have shown hMSC 3D aggregation improved a range of biological properties, including multilineage potential, secretion of therapeutic factors, and resistance against ischemic condition. In this study, the results suggest that reorganization of actin cortical network during cell aggregation plays a prominent role in mediating hMSC aggregate assembly, contraction, and transition from liquid to solid state.

## Materials and Methods

HMSCs from monolayer culture were trypsinized and added in each well of an ultra-low attachment 96-well plate with round-bottom for overnight. Suspended single hMSCs spontaneously self-assembled into one aggregate per well. The aggregates were cultured and tracked individually up to 7 days with changing media every two days. Actin modulators: Cytochalasin D (cytoD), lysophosphatidic acid (LPA), Y-27632, were added into culture media.

## Results and Conclusions:

The addition of actin polymerization inhibitor, CytoD, disrupted hMSC aggregation, indicating that actin is required in hMSC aggregation. Treatments with CytoD or Y-27632 after hMSC aggregation prevent cell contraction, but can not increase cell viability, suggesting that actin-mediated contractility is the major force on compaction but not the primary factor leading to cell death. HMSC aggregates have fusion and spreading behavior, whereas CytoD treated aggregates don't, showing actin changes viscoelastic behavior. LPA treatment aggregates have the similar properties as the control. Further, we found the cell death is induced by apoptosis.

# SELF-ASSEMBLY OF LIVE CELL AND ASYMMETRIC PLGA MICRODISK FOR DRUG DELIVERY

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Assembly of live cells with biodegradable materials attracts great interests over the recent years. The conventional methods, however, are unsatisfactory due to high cost, high complexity and long processing time. In this study, we present a quick and highly efficient method for assembling live cells with microfabricated asymmetric PLGA microdisks and demonstrate its potential application for drug delivery. The microdisks are fabricated through a technique called microcontact printing, which can create asymmetric structure of printed materials. The fabricated microdisks consist of a cell binding layer and a drug loading layer where different layers are crosslinked by covalent bond thus possessing high stability. The single cell-microdisk complexes are formed spontaneously by simply mixing cells with microdisks in a chamber. Moreover, this self-assembly process allows control of the number of microdisks per cell by adjusting the initial ratio of cells and microdisks. This method holds potential application in drug delivery in two aspects: 1. Deliver drug molecules to the binding cell due to local high concentration; 2. Function as a drug carrier and achieve long term drug release. In this study we use K562 leukemia cell line as the model cell line.

# CRYOPRESERVATION OF PLURIPOTENT STEM-CELL-DERIVED NEURAL PROGENITOR AGGREGATES LABELED WITH IRON OXIDE PARTICLES FOR MRI ANALYSIS

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Clinical applications of neural progenitor cells (NPCs) require large quantities of cells which can be obtained through pluripotent stem cell (PSC) expansion, differentiation, and cryopreservation. Magnetic resonance imaging (MRI) provides an effective approach to track the labeled NPCs for neural transplantation and neurological disorder treatments. However, labeling the cryopreserved NPCs after thaw can be limited by the inefficient intracellular labeling and variations in labeling efficiency. Therefore, cryopreservation of the pre-labeled NPCs can offer the uniform cell population and operational convenience for the following in vivo transplantation. In this study, the feasibility of cryopreserving PSC-derived NPC aggregates labeled with micron-sized particles of iron oxide (MPIO) was investigated. The NPC aggregates were derived from embryoid body formation and were labeled with different concentration of MPIO in the range of 0 to 100 μg Fe per mL. The MPIO-labeled cell survival, proliferation, cytoskeleton distribution, cytotoxicity, the level of oxidative stress, and neural differentiation were evaluated before and after cryopreservation. The results indicated that intracellular MPIO incorporation was retained after cryopreservation (70-80% labeling efficiency), which did not significantly affect the cell recovery, proliferation, cytotoxicity and neural lineage commitment. The labeled cells maintained similar pattern of cytoskeleton distribution and the expression level of oxidative stress compared to non-labeled cells. MRI analysis showed comparable detectability for the MPIO-labeled cells before and after cryopreservation indicated by T2 and T2* relaxation rates. These findings indicate the feasibility of cryopreserving MPIO-labeled PSC-derived NPC aggregates for potential large scale banking toward various in vitro and in vivo studies.

# DESIGNING COMPOSITE POLYMER ELECTROLYTE INTERFACES FOR STABLE ELECTRODES

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Polymer electrolytes are promising materials for high energy density rechargeable batteries. However, typical polymer electrolytes are not electrochemically stable at the charging voltage of advanced positive electrode materials, which is above 4 V. The initial goal of this project is to understand polymer electrolyte oxidation and design advanced composite electrolytes to prevent such oxidation. The polymer electrolyte used in this study comprises poly(ethylene oxide) (PEO) and lithium bis(trifluoromethanesulfonyl) imide salt (LiTFSI). We have chosen an inert metal electrode (gold) to measure PEO + LiTFSI electrochemical stability in the absence of reversible electrochemical reactions. Gold nanoparticles (AuNPs) have been used as probes in a heterogeneous electrode for the following reasons: AuNPs have large surface-to-volume ratio to provide sufficient contact area and signal; they are non-reactive with LiTFSI and PEO; surface modification is facile. The AuNP + PEO + LiTFSI composites are characterized using X-ray Diffraction (XRD) and small angle X-ray diffraction (SAXS). The electrochemical properties of AuNP + PEO + LiTFSI are studied using impedance spectroscopy and cyclic voltammetry. The effect of the AuNP/polymer interface composition on electrode stability will be presented.

# FTIR ANALYSIS OF THE EFFECT OF CHLORINE ON POLYMORPHISM OF PRECISION HALOGEN SUBSTITUTED POLYETHYLENE

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Polyethylenes with halogen substitution at a precise distance along the methylene backbone are unique models to study the effect of nano-structured chain-defects on folding and crystallization of polymers. Prior work has shown that the halogen is accommodated in the crystal disrupting the unit cell symmetry and crystallization proportionally to the halogen's size. Packing of the Chlorine units in the crystallites of polyethylene with Chlorine substitution on every $15^{th}$ backbone carbon was found to undergo a transition which is kinetically controlled within one degree of undercooling. On crystallization from the melt at temperatures < 53 °C the chains pack in an all-trans planar conformation (Form I) with layered crystalline chlorines that present some longitudinal disorder as demonstrated by FTIR. The crystals formed at higher temperatures pack in a non-planar herringbone-like structure (Form II) with a TGGT….TG'G'T backbone conformation around the substitution, while conserving the trans packing of the methylene sequence. The analysis of the FTIR spectra for the rocking-twisting progression in a broad range of crystallization temperatures is extended here to a series of polyethylenes with Cl substitution every $9^{th}$, $19^{th}$ and $21^{st}$ carbons. The FTIR dispersion curves are analyzed in reference to the behavior of n-alkanes with length equivalent to the length of methylene sequence between Chlorines. The unique polymorphic transition found in the system with Chlorines between 15 carbons, is also found in all members of the series, making the planar and non-planar packing with respect to undercooling a general feature of crystallization of polyethylenes with Chlorine substitution. The polymorphic transition temperatures and temperature range of coexistence of

# RATIONALIZING SOLID-STATE NMR CONSTRAINTS OF AMYLOID-β(1-42) OLIGOMERS

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Overwhelming genetic, pathological, and biochemical evidence link Alzheimer's Disease progression and neurotoxicity to the self-assembly of the Amyloid-β (Aβ) peptide, though little is known of the Aβ self-assembly process. In fact, recent studies of Aβ toxicity indicate that smaller oligomeric species are more toxic than their fibril counterparts.[1] A large hindrance to the understanding of Aβ self-assembly lies in the incomplete structural knowledge of Aβ molecular assemblies. While Aβ fibril structures are not well known, even less is known of the smaller oligomeric species. Previously conducted solid-state NMR studies of Aβ fibril structures reveal a characteristic in-register parallel β-sheet arrangement.[2] In contrast, recent solid-state NMR evidence indicates that Aβ(1-42) oligomers are not characterized by this in-register parallel β-sheet arrangement.[3] This data, however, is not sufficient to fully characterize the tertiary or quaternary structure of Aβ(1-42) oligomers. Here, it is shown that an Aβ(1-42) oligomer species adopts an antiparallel β-sheet arrangement approximately spanning residues 30 to 42. In order to rationalize the observed solid-state NMR constraints, it has been hypothesized that Aβ(1-42) oligomers are characterized by stacked β-sheets with domain swapping between two β-strand regions of the Aβ peptide. Based on this hypothesis, four all-atom molecular models have been developed and further speculation is provided regarding the higher level organization of stacked β-sheets into complete oligomeric structures.

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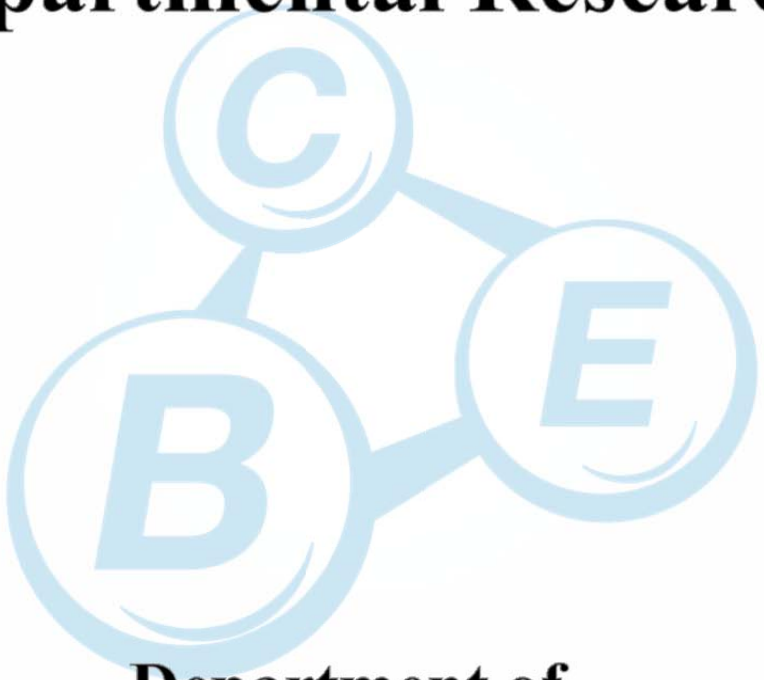


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