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www.chbe.gatech.edu/mesd

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Notes from the Chair

Dear Division members,

I am happy to report to you that the Division is in excellent shape. Our financial status is strong and our activity level continues to be exemplary within the society. Much of the success of the division is of course due to the efforts of the many volunteers that organize the annual meeting sessions, keep up the website, create the newsletters, monitor the books and generally keep the well oiled machine running. The past year is no exception, and we have been fortunate to have had two tireless individuals contribute amazing energy to the division, Alon McCormick, the past Division chair, and Brian Mitchell, who is Program chair for the 2006 meeting and will take over as Chair next year. The efforts of both of these Division officers go well beyond their duties and I am fortunate to have them to rely on in executing the normal business of the division. The theme of this preamble and the foundation of the Division is volunteerism, so I encourage all of you to become involved in Division activities to any extent that you are able. In order to further foster the important principle of volunteerism and to thank those of you who have provided service to the Division, we are planning two "experiments" or events for next year's annual meeting. The first is to convene a public business meeting that so that all division members can participate in division activities. The second is to plan a Division reception to honor division awardees and all of you who have provided such essential service to the Division. I look forward to seeing you in November.

Jeff Koberstein
MESD Chair

Bob Sylvester of DuPont (right) presents the 2005 Charles M.A. Stine Award to Nitash Balsara (left) of the University of California-Berkeley.

Application Deadline Rapidly Approaches for 2006 Charles M.A. Stine Award

The deadline for this year's Charles M. A. Stine Award in Materials Engineering and Sciences is **February 15th**. The award is given to recognize outstanding contributions by members of the AIChE to the scientific, technological, educational, or service areas of Materials Engineering and Science. The $1500 award is sponsored by E.I duPont de Nemours and Company and is to be presented at the AIChE Annual Banquet. Selection criteria include:

1. Nominations must be submitted by members of the Materials Engineering and Sciences Division; however, the only requirement for the nominee is that he/she must be an AIChE member.
2. Applications must be received no later than Feb 15th
3. The award can be given to an individual or a team
4. Is given for significant discoveries, important research, development of new products or processes, outstanding service to the materials community, education concepts, or initiation of new materials and management.

Additional information, including previous winners of this award, can be found on the AIChE website at www.aiche.org/awards. Under the "Select Award Category", click on Division Awards; the Stine Award is listed under MESD. If interested please contact Dennis W Hess:

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2005 Fall Annual Meeting Highlights

MESD once again offered a large and varied program of sessions at the 2005 AIChE Annual Meeting. This year, the meeting was held October 30 – November 4 in Cincinnati, OH. A total of 59 sessions were offered by MESD, of which they were primary sponsor for 52. Programming areas again included Polymers, Biomaterials, Ceramics and Electronic Materials, as well as special sessions like the Stine Award Plenary Session.

At the Plenary Session, the Charles M.A. Stine Award Lecture was presented by Nitash Balsara of the University of California-Berkeley, the transcript for which appears earlier in this newsletter. Other lectures at the Plenary Session were presented by Eric W. Kaler,
Nicholas L. Abbott, Bradley F. Chmelka, and Eray S. Aydil.

The MESD Executive Committee Meeting was held Tuesday afternoon. Newly-elected officers were introduced: Paula Hammond, 2nd Vice Chair; Tom Keuch and Buddy Ratner (Directors). Several topics were discussed, including creating travel awards for graduate student presenters at the Annual Meeting, and increasing division membership. Alon McCormick, outgoing MESD Chair, announced his intentions to update the division by-laws and create an officer's handbook. Minutes of all Executive Committee meetings will be made available on the MESD website.

A total of 61 posters, ten of them from international contributors, were presented at the MESD Poster Session on Monday evening. The event was chaired by Alex Chang and Yossef Elabd. As in recent years, awards were presented to outstanding posters, as determined by a panel of five judges. First Prize went to Benita Comeau (Co-authors: Clifford L. Henderson and Benjamin Katz) of the Georgia Institute of Technology for her poster on "Material and Process Approaches to the Fabrication of Hierarchically Structured Tissue Engineering Scaffolds." Rhutesh K. Shah of the University of Texas Austin (Co-author: Donald R. Paul) received a Second Place Prize for his poster entitled "Polyolefin-Organoclay Nanocomposites: Properties, Morphology, and Applications." There was a tie for Third Place between Luis F. Hakim of the University of Colorado Boulder (Co-authors: Guodong Zhan, Steven M. George, and Alan W. Weimer) "Conformal Coating of Ceramic Nanoparticles Via Atomic Layer Deposition," and Sowmitri Tarimala of Texas Tech University (Co-authors: Chih-yuan Wu and Lenore L. Dai) "Pickering Emulsions - a Paradigm Shift."

Session Chair Alex Chang (L) presented MESD Poster Session Awards to Rhutesh Shah (2nd), Benita Comeau (1st), Luis F. Hakim (T3rd) and Sowmitri Tarimala (T3rd, not pictured).

Next year's Annual Meeting will be held in San Francisco. Keep your eyes open for the upcoming Call for Abstracts, and plan early!

Congratulations to our newly elected officers:

Second Vice Chair: Paula T Hammond
Directors with terms ending 2007:
Buddy Ratner and Tom Keuche

Upcoming Meetings and Events
Stine Application Deadline February 15th

AIChE has its annual spring meeting April 23rd -27th
For a detailed program list goto www.aiche.org

Nanostructured Polymer Electrolytes

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INTRODUCTION

Rechargeable Li ion batteries for all electric vehicle (EV) applications require high energy density with good cyclability and electrode stability.[i] Batteries that employ Li anodes suffer from failures due to side reactions and dendrite growth on the Li electrodes. Recent theoretical work indicates that dendrite growth can be stopped if the shear modulus of current polymer electrolytes can be increased to ~ 1 GPa without a significant decrease in the ionic conductivity.[ii,iii] This high modulus requirement essentially renders most rubbery polymer electrolytes incompatible with the electrode material, as the elastic moduli of typical rubbery polymers are ~ 1 MPa. Several studies have shown that cation transport is intimately coupled to segmental motion of the polymer chains.[iv,v] High ionic conductivity is obtained in soft polymers such as rubbery poly(ethylene oxide) (PEO) because rapid segmental motion needed for ion transport also decreases the rigidity of the polymer.[vi] There is, thus, a clear need to develop a new methodology for decoupling the electrical and mechanical properties of polymer electrolytes. Glassy polymers such as polystyrene (PS) offer very high modulus (~3 GPa) but are poor ion conductors. In order to combine high ionic conductivity with a high elastic modulus we have employed a polymer electrolyte which is a PS-*b*-PEO copolymer (SEO) doped with (LiTFSI) lithium bis(trifluoromethylsulfonyl)imide, $Li[N(SO_2CF_3)_2]$. The idea is to use a nanostructured polymer electrolyte where the major phase (PS) provides a rigid framework with nanostructured ionically conducting channels (PEO). Prevailing thought is that network morphologies are essential for ion transport. To the contrary, our experiments demonstrate that non-network morphologies can be effective ion transporters.

EXPERIMENTAL

A series of PS-*b*-PEO diblock copolymers, with varying molecular weights and EO volume fractions, were synthesized using high vacuum anionic polymerization. The number averaged molecular weight and the polydispersity index (PDI) of the PS block was obtained using gel permeation chromatography measurements using a Waters 2690 separations module and a Viscotek triple detector system calibrated with polystyrene standards. The volume fraction of each block was determined using ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The data shown here is for a specific SEO copolymer where the molecular weights (number averaged) of the PS and PEO blocks are 36 and 25 kg/mol, respectively, and the PEO volume fraction in the copolymer is 0.38. Polymer electrolytes were prepared by blending a SEO/benzene solution with the necessary amount of a 10 wt% solution of $LiN[SO_2CF_3]_2$ in THF in an argon glove box. The concentration of salt in the polymer electrolyte is indicated by *r*, = [LiTFSI]/[EO]. The solution was freeze-dried in a glove box compatible desiccator for one week to remove all solvent. Polymer electrolyte samples were pressed into pellets using Teflon spacers to control the thickness and the area. All sample preparation and characterization steps are conducted in a dry box or with dry box integrity. AC impedance spectroscopy measurements were made using a homemade test cell on thermo-stated pressed samples in the glove box, and a Solartron 1260 Frequency Response Analyzer machine connected to a Solartron 1296 Dielectric Interface. Rheological measurements were performed using an ARES rheometer from Rheometric Scientific Inc. with parallel plate geometry. Approximately 1 mm thick samples were placed between 8 mm plates for SEO, and 50 mm plates for PEO, in a closed oven with an N_2 atmosphere.

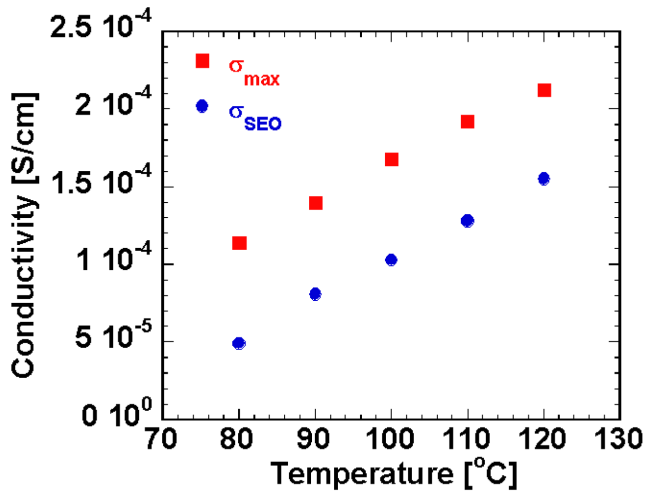

Figure 1. Conductivity of SEO diblock in comparison with PEO (M.W. ~ 20K) at $r \cong 0.020$, as a function of the temperature. The maximum theoretical conductivity (σ_{max}) is $0.38*\sigma_{PEO}$.

RESULTS AND DISCUSSION

The bulk ionic conductivity of these polymer electrolytes is measured by using AC impedance spectroscopy. PEO doped with LiTFSI serves as the benchmark for the SEO based electrolytes. If all of the PEO channels in our nanostructured electrolyte provided conducting pathways for the ions, then the maximum value of the conductivity of our doped SEO sample, σ_{max} would be ϕ_{PEO} (σ_{PEO}), where ϕ_{PEO} is the volume fraction of the conducting domains (PEO). As shown in Figure 1, results indicate that the conductivity values are approximately ½ of the maximum conductivity, over a wide temperature range. The conductivity results are very promising with values on the order of 10^{-5} S/cm at 80 °C. Figure 2 shows a typical TEM of a thin section of the SEO copolymer without the salt. The TEM shows the presence of a weakly ordered lamellar morphology. The SAXS data (not shown here) indicate that the there is no significant morphological change upon the addition of the salt. Hence, the TEM and the SAXS data rule out the possibility of an interpenetrating network phase in the composite electrolyte.

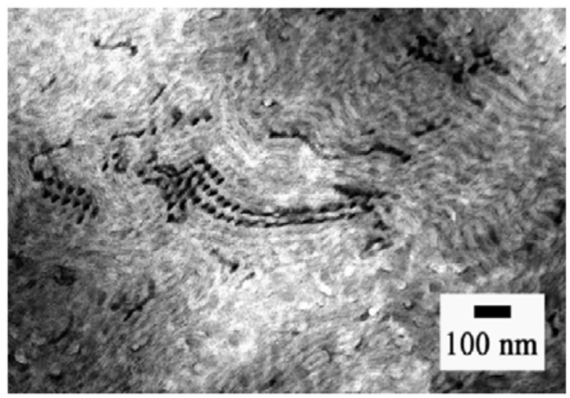

Figure 2. Transmission electron micrograph of the pure SEO copolymer showing a perforated lamellar morphology. The PEO phase is darkened by RuO_4 staining.

The volume fraction of the PS phase in the SEO copolymer is 0.68, implying that the mechanical properties of the SEO based polymer electrolyte should reflect the high rigidity expected from glassy PS. The glass transition temperature (T_g) of PS in the SEO copolymer is ~ 100 °C (Data not shown), which ensures high rigidity well above the room temperature. Figure 3 shows the rheological behavior of the polymer electrolyte in comparison with the PEO homopolymer at 80 °C.

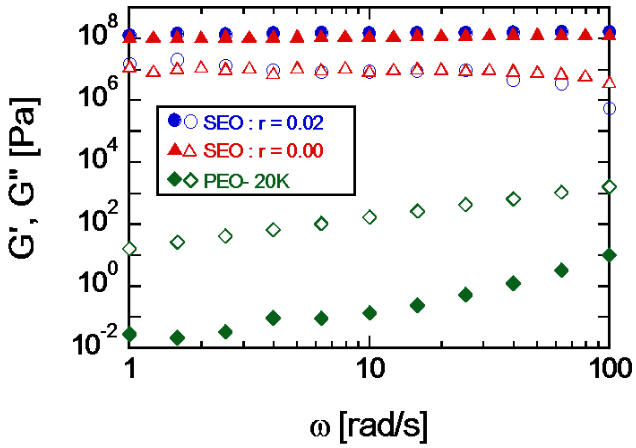

Figure 3. Rheological measurements on SEO (triangles), SEO/salt with r = 0.020 (circles), and PEO (Mw~20K) (squares) samples at 80ºC. Storage/elastic modulus $G'(\omega)$ is shown with filled symbols, and the loss modulus $G''(\omega)$ is shown with the hollow symbols

The frequency-independence of the moduli and the fact that G' is an order of magnitude larger than G" indicate that our composite electrolytes are, to a good approximation, elastic solids. The data in Figure 3 also confirm that the addition of small amounts of salt has no detrimental effect on the mechanical properties of our material. The value of G' obtained from our SEO electrolytes is 100 times larger than the plateau modulus of pure PEO[vii] and several orders of magnitude larger than that of the PEO homopolymer used in this study (molecular weight of the PEO homopolymer is similar to that of the PEO block in the SEO copolymer). By adding the PS block to the PEO chain, we have increased the shear modulus by several orders of magnitude while reducing the ionic conductivity by only a factor of about four.

By showing that network phases are not necessary to obtain ionic conductivity, we have introduced the possibility of using a wide variety of morphologies for designing ionically conducting polymers. No special processing is needed to create percolating conducting pathways in these materials; they are formed entirely by quiescent self-assembly. We hope that the proposed strategy will yield polymer membranes with high ionic conductivity that are important for applications such as solid-state batteries and fuel cells.

ACKNOWLEDGEMENTS

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MESD Officers