

## CPP 51: Poster: Charged Soft Matter, Polyelectrolytes, Ionic Liquids

Time: Wednesday 18:30–21:00

Location: P3

CPP 51.1 Wed 18:30 P3

**In situ small angle X-ray scattering investigation of solid-state polymer electrolyte for lithium-ion batteries** — ●GILLES MÖHL<sup>1</sup>, EZZELDIN METWALLI<sup>1</sup>, BERNHARD SPRINGER<sup>1</sup>, RUNE JOHNSEN<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — <sup>2</sup>TU Denmark, Department of Energy Conversion and Storage, Roskilde, DK-4000

Many present problems regarding the safety of liquid electrolytes in lithium-ion batteries may potentially be overcome by the use of solid-state polymer electrolytes. Polystyrene-block-polyethylene oxide PS-b-PEO diblock copolymer (DBC) electrolyte have been recently investigated as a membrane for Li-ion battery. The performance of these DBC electrolytes strongly depends on its morphology, serving highly oriented PEO domains as pathways for lithium ions migration. Thus, in situ structural investigation of these Li-ion doped DBCs systems during (dis)charge cycling in an operating battery is essential. A capillary-based micro-battery cell allowing simultaneous structural and electrical evaluation has previously been reported [1]. The current in situ small-angle X-ray scattering (SAXS) study of the solid-state polymer electrolytes using a modified version of the micro-battery cell provides a deeper insight into the possible structural modification and thus, on the involved conduction mechanisms during battery operation.

[1] R.E. Johnsen, P. Norby, *J. Appl. Cryst.* 2013, 46, 1537.

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**In situ SANS investigation of block copolymer electrolyte under lithium stripping/plating cycling** — ●BERNHARD SPRINGER<sup>1</sup>, EZZELDIN METWALLI<sup>1</sup>, ROBERT CUBITT<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — <sup>2</sup>ILL, 6 rue Jules Horowitz, 38042 Grenoble, France

Due to safety concerns, solid-state electrolytes have recently garnered a great interest to replace liquid electrolytes. The conductivity and morphology of the solid-state lithium-salt containing polystyrene-block-polyethylene oxide (dPS-b-PEO) diblock copolymer (DBC) electrolyte are investigated during lithium metal stripping/plating cycling at different temperatures. The in situ small angle neutron scattering (SANS) measurements were performed on electrolytes, which are sandwiched between two thin lithium electrodes. Cylindrical morphology with interpenetrated nano-domains of both, the PS and PEO/Li-ion is observed. During cycling, the morphology of the system showed nearly no changes for temperatures up to 35°C, indicating good intrinsic stability. At higher temperatures > 50°C, a slight change in the inter-domain spacing indicates only a slight change in morphology. Interestingly, the level of domain alignment is significantly enhanced. The possible migration of the lithium ions during the galvanostatic cycling seems to open pathways between the two electrodes so that at high enough temperatures the domain re-orientation is favored. Our results imply that possible dendrite formation is highly suppressed for the employed solid-state electrolyte.

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**Charge transport in monomeric vs. polymerized ionic liquids** — ●FELIX WIELAND<sup>1</sup>, WOLF HILLER<sup>2</sup>, ALEXEI SOKOLOV<sup>3</sup>, ROLAND BÖHMER<sup>1</sup>, and CATALIN GAINARU<sup>1</sup> — <sup>1</sup>Fakultät Physik, Technische Universität Dortmund, D-44221 Dortmund, Germany — <sup>2</sup>Fakultät für Chemie und Chemische Biologie, Technische Universität Dortmund, D-44221 Dortmund, Germany — <sup>3</sup>Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA

Polymerized ionic liquids have been recently receiving the attention of scientific community as potential candidates for energy-storage materials in industrial applications [1] but also as testing ground for polymer research in general. In this work we analyze the variation of charge dynamics in monomeric, oligomeric, and long-chain ionic melts by means of dielectric spectroscopy, rheology, and field-gradient nuclear magnetic resonance. In this respect the length of the positively charged backbone is systematically increased while the type of anions and their concentration are kept invariant. Surprisingly, indications of a clear decoupling between the dynamics corresponding to positive and negative charges occur already for oligomeric chains comprising two to three monomeric units only. Our investigation aims at describing the

evolution of transport parameters with the degree of polymerization and also at providing a general picture of the conductivity mechanism in ionic and polymerized ionic liquids [2].

[1] Fan, F. et al. *Macromolecules* 48 (13), 4461-4470 (2015). [2] Gainaru, C. et al. *J. Phys. Chem. B* 120 (42), 11074-11083 (2016).

CPP 51.4 Wed 18:30 P3

**Effect of weakly/strongly interacting cation mixtures on LCST-LLPS in protein solutions** — ●OLGA MATSARSKAIA<sup>1</sup>, NIRZARI ANN<sup>1</sup>, FELIX ROOSEN-RUNGE<sup>2</sup>, JOHANNES MÖLLER<sup>3</sup>, FAJUN ZHANG<sup>1</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — <sup>2</sup>Institut Laue-Langevin, Grenoble, France — <sup>3</sup>ESRF, Grenoble, France

In the presence of trivalent cations, negatively charged globular proteins show a rich phase behaviour including reentrant condensation, crystallisation, clustering [1] and lower critical solution temperature metastable liquid-liquid phase separation (LCST-LLPS) [2]. Here, we present a systematic study of the influence of mixtures of varying ratios of Ho<sup>3+</sup>/La<sup>3+</sup>. Small-angle X-ray scattering (SAXS) data reveal that the interaction between BSA and the small cation Ho<sup>3+</sup> is very strong, while the large La<sup>3+</sup> interacts only weakly, which can be partly attributed to cation size effects. Using a combination of temperature-dependent UV-Vis as well as  $\zeta$  potential measurements, we furthermore show that an increasing Ho<sup>3+</sup>/La<sup>3+</sup> ratio systematically shifts the LCST to lower values. Our findings imply that cation size and other cation-specific effects can be a sensitive tool to fine-tune protein-protein interactions and phase behaviour in solution.

[1] Zhang *et al.* *Pure & Appl. Chem.* 2014, 86, 191-202; [2] Matsarskaia *et al.* *JPCB* 2016, 120, 7731-7736.

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**Solvent isotope effect on protein phase behavior in aqueous protein solutions** — ●MICHAL K. BRAUN<sup>1</sup>, MARCELL WOLF<sup>1</sup>, OLGA MATSARSKAIA<sup>1</sup>, STEFANO DA VELA<sup>1</sup>, FELIX ROOSEN-RUNGE<sup>2</sup>, MICHAEL SZTUCKI<sup>3</sup>, ROLAND ROTH<sup>4</sup>, FAJUN ZHANG<sup>1</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — <sup>2</sup>ILL, Grenoble, France — <sup>3</sup>ESRF, Grenoble, France — <sup>4</sup>Institut für Theoretische Physik, Universität Tübingen

Knowledge about interactions and phase behavior of proteins in aqueous solutions is crucial in fields like protein crystallization, drug design and treatment of diseases. For many spectroscopic techniques in protein science D<sub>2</sub>O is commonly used instead of H<sub>2</sub>O in order to improve the signal. Here we present our finding of a strong solvent isotope effect on the protein phase behavior and the effective interactions in solutions of bovine serum albumin (BSA) with trivalent salts [1]. At intermediate salt concentrations the phase diagram exhibits a regime where condensation occurs [2]. This regime is significantly broadened when H<sub>2</sub>O is replaced by D<sub>2</sub>O. The lower critical solution temperature of liquid-liquid phase separation decreases significantly when D<sub>2</sub>O is added to the solvent. Small angle x-ray scattering (SAXS) data shows that the reduced second virial coefficient is lower in D<sub>2</sub>O than in H<sub>2</sub>O. Both the macroscopic observations as well as the microscopic results consistently show that the attraction between the protein molecules increases when H<sub>2</sub>O is replaced by D<sub>2</sub>O.

[1] Braun *et al.*, *in preparation*

[2] Zhang *et al.*, *Pure Appl. Chem.*, **86**, 191, 2014

CPP 51.6 Wed 18:30 P3

**Morphology of lithium-ion containing block copolymer electrolytes for rechargeable lithium-ion batteries** — ●YINONG ZHANG, EZZELDIN METWALLI, BERNHARD SPRINGER, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching

Block copolymers (BC) electrolytes have been recently investigated as solid-state membranes for lithium-ion batteries. Nanostructured BC electrolyte contains both, the ionic conducting as well as the high-tensile polymer domains, enabling both, high ionic conductivity and improved mechanical stability. Since the diffusion path of the lithium ions only follows the percolation path of the ionic conducting domain, the morphology of the BC electrolyte is an essential parameter. Theoretical studies have recently reported that the BC electrolyte phase diagrams significantly deviate from the conventional BC phase dia-

grams due to electrostatic interactions between polar chains and the alkali metal-ions. The morphology of ion-containing BC electrolyte was investigated using SEM and SAXS. In the current study, morphological deviation compared with that of the conventional BC phase diagrams in consistent with the theoretical studies is experimentally proved. Conductivity measurements of the Li-salt containing BC hybrid films were examined for different morphologies using impedance spectroscopy.

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**Nanoporous titania/silica hybrid electrodes for lithium-ion batteries** — ●KEJIE ZHANG, EZZELDIN METWALLI, THOMAS KAPS, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching

Light-weight, high energy density, stable and flexible solid-state lithium ion micro-batteries are of great importance due to its applications for miniature medical devices such as capsule endoscopes, implantable heart pumps and biosensors. The sol-gel template method synthesized nanostructured hybrid flexible thin film electrodes of titania (TiO<sub>2</sub>) with silica (SiO<sub>2</sub>) are expected to inherit titania's high charge/discharge rate, stability and good cyclability with silica's high gravimetric capacity and low potential. Different ratio of TiO<sub>2</sub>/SiO<sub>2</sub> porous electrodes were prepared using different ratios of precursors and different weight ratio of polystyrene-block-polyethylene oxide (PS-*b*-PEO) diblock copolymer (DBC) guiding template. Here, lithium salt doped DBC is sandwiched between a developed TiO<sub>2</sub>/SiO<sub>2</sub> anode and typical lithium cobalt dioxide cathode. Charge/discharge cycling capacity and impedance measurements after each cycle were acquired to characterize the stability, cyclability and capacity development of the assembled lithium-ion microbatteries. Small and wide angle X-ray scattering (SAXS/WAXS) were used for determination of the structures of free-standing TiO<sub>2</sub>/SiO<sub>2</sub> nanoporous hybrid electrodes. The structure-property correlation of these hybrid electrodes are discussed.

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**Specific Ion Effects on the Interfacial Structure and Foam Properties of Polystyrene Sulfonate Solutions** — ●FELIX SCHULZE-ZACHAU and BJÖRN BRAUNSCHWEIG — Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany

Poly(sodium 4-styrenesulfonate) (NaPSS, 70 kDa) modified air/water interfaces were investigated with tensiometry, ellipsometry and vibrational SFG spectroscopy. Specific ion effects of K<sup>+</sup>, Ca<sup>2+</sup> and Nd<sup>3+</sup> on the interfacial structure and adsorption properties of 20 mM NaPSS were studied. For a better understanding of the behavior in the bulk phase, turbidity measurements were performed. In order to relate the molecular structure of NaPSS in the bulk and at the interface to macroscopic foam properties, foams of these mixtures were analyzed with respect to their stability and structure. SFG spectra reveal charge screening with increasing ionic strength which is more effective for higher charged ions and linked with high foam stability. For Ca<sup>2+</sup> ions, a change in the intensity ratio of CH<sub>2</sub>/CH<sub>3</sub> vibrational bands can be related to a change in molecular structure at low salt concentrations. Structural changes in the foams can be linked to this change of molecular structure as we observe a bimodal bubble size distribution which

is connected with poor foam stability. With increasing ionic strength, a decrease in surface tension and an increase of adsorbate thickness as well as foam stability is observed. The reason for that is charge screening and formation of aggregates which stabilize the foam bubbles and give rise to small mean bubble sizes.

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**Scaling laws and solution rheology of semiflexible polyelectrolyte carboxymethyl cellulose: influence of electrostatic and hydrophobic interactions** — ●CARLOS LOPEZ<sup>1</sup>, PETER GRAHAM<sup>2</sup>, RALPH COLBY<sup>3</sup>, and JOAO CABRAL<sup>1</sup> — <sup>1</sup>Department of Chemical Engineering, Imperial College London, London SW7 2AZ, United Kingdom — <sup>2</sup>Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington L63 3JW, United Kingdom — <sup>3</sup>Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

We investigate the conformation and rheology of sodium carboxymethyl cellulose (NaCMC) solutions. Scaling laws for the overlap and entanglement concentrations are established in salt free, NaCl and NaOH solutions. NaCl screens electrostatic interactions but not hydrophobic ones, while NaOH screens both. In salt free and NaCl solution, a highly substituted sample displays typical polyelectrolyte and neutral polymer in good solvent behaviour respectively. The viscosities in NaOH solutions are similar to those in NaCl. Less substituted samples display hydrophobic behaviour in salt free and NaCl solution, becoming thixotropic gels at high concentrations. However, the viscosities in NaOH are identical to those of the more substituted sample due to solubilisation of unsubstituted cellulose patches.

By varying the ionic strength and pH of aqueous solutions, it is possible to tune the polymer-solvent interactions for NaCMC samples. This allows us to separate the effects of entanglements, electrostatic and hydrophobic interactions on the solution rheology of NaCMC.

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**Annealing in polyelectrolyte multilayers: influence of entanglements** — PETER NESTLER, MALTE PASSVOGEL, ANNKATRIN SILL, ●AMIR AZINFAR, and CHRISTIANE A. HELM — Inst. of Physics, Greifswald University, Germany

Polyelectrolyte multilayer films were assembled by the layer-by-layer (LbL) technique using poly(styrene sulfonate) PSS as polyanion and poly (diallyldimethylammonium) (PDADMA) as polycation. The first compartment of the film is built with protonated PSS, the second compartment with deuterated PSSd. The films were annealed in 1 M NaCl and the time dependent intermixing recorded with neutron reflectivity. If the layers are adsorbed from 0.1 M NaCl, the largest diffusion constant is found for  $M_w(\text{PDADMA}) = 45$  kDa. If  $M_w(\text{PDADMA})$  was lower, so was the diffusion constant. If  $M_w(\text{PDADMA})$  was higher, then the diffusion constant dropped by two orders of magnitude. These findings suggest the diffusion of PDADMA/PSS complexes. The largest diffusion constant was obtained if the salt concentration of the preparation solution was decreased (0.03 M, 0.005 M). At low salt concentrations, less polyelectrolyte adsorbs with each deposition step, and fewer entanglements occur. These results suggest that polycation/polyanion complex formation and polymer entanglements influence the diffusion constant within polyelectrolyte multilayers.