CPP 20: Interfaces and Thin Films I

Time: Tuesday 11:30–13:00 Location: H38

Invited Talk CPP 20.1 Tue 11:30 H38

Tailored polymer thin films enabled by initiated chemical vapor deposition (iCVD): From fundamentals to functional applications — •Stefan Schröder — Christian-Albrechts-Universität zu Kiel, Kiel, Germany

Functional polymer thin films are of great interest in vast application fields ranging from electronic devices to biomedical interfaces. Device miniaturization and the consequent need for new polymer films on the nanoscale demand precise thickness control and defect free films. Solvent-free initiated chemical vapor deposition (iCVD) meets these demands, because it circumvents de-wetting and surface tension effects encountered in conventional solution-based polymer thin film fabrication. The process provides conformal polymer coatings on the nanoscale on large-area substrates as well as complex geometries. In addition, it enables deposition on delicate substrates like flexible organic substrates, copy paper and biomedical patches at room temperature. This talk demonstrates the versatility of the iCVD process and highlights recent results from fundamental studies based on density functional theory (DFT) on the underlying reaction processes up to the application of iCVD films in sensors, biomedicine and electronic devices.

CPP 20.2 Tue 12:00 H38

Highly Electrically Conductive PEDOT:PSS films via Layer-by-Layer Electrostatic Self-Assembly — •Muhammad Khurram, Sven Neuber, Annekatrin Sill, and Christiane A. Helm — muhammad.khurram@uni-greifswald.de

Electrically conductive films of Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS) are usually formed by spin coating of aqueous dispersions with PEDOT:PSS nanoparticles. The adsorption conditions are investigated using dip coating and a flow cell with different flow rates. Multilayer films are formed by sequential adsorption of oppositely charged macromolecules. PEDOT:PSS serves as polyanion, and PDADMA is the polycation. In dip coating, the first layer consists of approximately 70 nm thick monolayer of PEDOT:PSS nanoparticles. Subsequent PDADMA/PEDOT:PSS bilayers have a low, constant thickness (9.5 nm). Using the flow cell (0.2 mL/min) for film preparation also resulted in a constant PDADMA/PEDOT:PSS bilayer thickness (7.5 nm). PEDOT:PSS nanoparticle monolayers could also be observed with the flow cell, but only if the washing step after PEDOT:PSS adsorption was omitted. The films prepared by flow cell showed the highest conductivity (230 kS/m) and the lowest roughness (2 - 4 nm). We propose that the adsorption in a flow cell leads to a nearly flat orientation of the PEDOT molecules, increasing charge carriers' mobility. We also find that the relative humidity strongly influences the volume density and mobility of the charge carriers

CPP 20.3 Tue 12:15 H38

DFT Study of Catalyst-Ionomer Interactions in Hydrogen Fuel Cells — •Johanna Weidelt[1], Fabian Tipp[1], Tobias Binninger[1], and Michael Eikerling[1,2] — [1]Theory and Computation of Energy Materials (IET-3), Institute of Energy Technologies, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — [2]Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

Proton exchange membrane fuel cells (PEMFCs) are promising devices for electricity generation from hydrogen. High efficiencies at low temperatures are achieved with platinum (Pt) as catalyst and Nafion as ionomer material. Because of the environmental persistence of the perfluorinated Nafion chains, fluorine-free ionomer materials are searched that maintain PEMFC performance and durability. To this end, the influence of the ionomer on the catalysis of the oxygen reduction reaction (ORR) in the cathode catalyst layer must be considered. Previous studies suggested that interactions between ionomer and Pt surface can compete with the adsorption of oxygenated ORR intermediates and negatively affect the catalytic activity. In this talk, we present a computational study investigating the competitive adsorption of ionomer species and reaction intermediates at a Pt(111) surface using grand-canonical density functional theory simulations. The Pt-adsorbate interaction strength was evaluated and surface phase diagrams were derived from adsorption energies calculated in implicit water environment under constant electrode potential.

CPP 20.4 Tue 12:30 H38

Dynamical and morphological changes of polyethylenimine thin films in relation to its CO2 absorption performance — •Maximilian Brückner[1], Martin Tress[1], Soma Ahmadi[2], and Shiwang Cheng[2] — [1]Peter Debye Institute for Soft Matter Research, Physics Department, Leipzig University, Germany — [2]Department of Chemical Engineering and Materials Science, Michigan State University, United States

Chemical reactions between carbon dioxide (CO2) and amine have been extensively characterized, however, their influence on the dynamics of polyamines remains largely unexplored. In this work, we compare the dynamics of polyethylenimine (PEI) before and after CO2 absorption through broadband dielectric spectroscopy (BDS). The molecular processes of bulk PEI are very different from those of thin film PEI, highlighting an interesting interface and nano-confinement effect. Detailed analyses show CO2 absorption slows down the PEI dynamics, which is consistent with an elevated glass transition temperature of PEI upon CO2 absorption. Further aspects of thin-film-preparation, namely the impact of molecular weight, film thickness, used solvent and plasma treatment of the substrate on surface roughness were investigated by atomic force microscopy and reveal pronounced de-wetting which did not occur in high-molecular-weight PEI on plasma-treated surfaces. The observed changes in dynamics and morphology are likely to reduce the performance of large-scale CO2 capture devices based on low-molecular weight PEI in porous silica, thus suggesting modifications of this approach.

CPP 20.5 Tue 12:45 H38

Thermo-Responsive Surface Structure and Wetting of Polymer Brushes with Octadecyl Side Chains — •Billura Shakhayeva[1], Franziska Neuhaus[1], Luciana Buonaiuto[2], Sander Reuvekamp[2], Sissi de Beer[2], Frieder Mugele[2], and Björn Braunschweig[1] — [1]University of Münster, Institute of Physical Chemistry, Münster (Germany) — [2]University of Twente, Physics of Complex Fluids, Enschede (The Netherlands)

Polymers are extensively studied as coatings due to their ability to respond to environmental changes, such as temperature or humidity variations, which greatly influence their wettability. This study investigates the effect of temperature on the molecular structure of poly-octadecylmethylacrylate (P18MA) brushes and their wetting behavior with hexadecane. Vibrational sum-frequency generation (SFG) spectroscopy was used to examine the molecular structure at the brush surface, both in air and in contact with hexadecane, by recording in situ SFG spectra near the three-phase contact line. The SFG spectra showed strong CH stretching bands of the octadecyl side chains at the air interface, indicating partial chain ordering that varies with temperature. For brushes in air, a phase transition at 311 K was identified as the surface melting temperature, 3 K higher than the bulk melting point. In the presence of hexadecane, surface melting occurred at 309 K, likely due to liquid penetration. Optical microscopy also revealed halo formation around the drop, suggesting local brush swelling. Below the surface melting point, the contact angle gradually decreased, while crossing the melting point enhanced hexadecane spreading.