

| Time | Wednesday, 21.10. | Thursday, 22.10. | Friday, 23.10. | |
|-------|---|--|---|----------------------------------|
| 8:30 | | 8:30 – 9:30 U. Tallarek: Morphology-transport relationships for disordered porous media | 8:30 – 9:00 C. Hugenschmidt: Water and Ionic Liquid Loaded Silica Gel Characterized by Positron Lifetime Spectroscopy | |
| 9:00 | | | 9:00 – 9:30 A. Wagner: The radiation source ELBE | |
| 9:30 | | 9:30 – 10:30 C. Kübel: Electron tomographic techniques to study the 3D morphology of porous solids | 9:30 – 11:15 Visit of ELBE radiation facility | |
| 10:00 | | | | |
| 10:30 | | | | |
| 11:00 | | 12:00 – 13:00 Registration / Lunch | 10:30 – 11:15 Coffee / Poster | 11:15 – 11:45 Coffee / Poster |
| 11:30 | | | 11:15 – 12:15 R. Zaleski: Porosimetry using Positron Annihilation | |
| 12:00 | 12:15 – 13:30 Lunch | | 11:45 – 12:15 H. Uhlig: Characterization of bimodal silica-gel with Positron-Annihilation-Lifetime-Spectroscopy | |
| 12:30 | 13:00 – 13:15 Opening: Prof. Dr. Ulrich Schramm | 12:15 – 13:30 Lunch | 12:15 – 12:30 D. Enke: Summary and Closing | |
| 13:00 | | | 12:30 – 13:30 Lunch Departure | |
| 13:30 | 13:15 – 14:15 C. Reichenbach: LN2 Sorption | 13:30 -14:30 M. Kraatz: Advanced porous low-k films for microelectronics | | |
| 14:00 | 14:15 – 15:15 S. Mascotto: Small-angle scattering methods for the study of porosity in nanoporous materials | | 14:30 – 15:30 J. Matysik: 129-Xenon-NMR | |
| 14:30 | | | | |
| 15:00 | 15:15 – 16:00 Coffee / Poster | 15:30 – 16:15 Coffee / Poster | | |
| 15:30 | | | | |
| 16:00 | 16:00 – 17:00 M. Rückriem: Theory and Applications of Mercury Intrusion | 16:15 – 17:00 T. Hyodo: A simple shape-free model for (large) pore size estimation with positron annihilation lifetime spectroscopy (PALS) and its application to silica-aerogel | | |
| 16:30 | | | | |
| 17:00 | 17:00 – 18:00 by R. Valiullin NMR Cryoporometry: From fundamentals to application | 17:15 Evening Event: Bus transfer to City of Dresden 22:30 Bus return to HZDR via Hotel Arcade | | |
| 18:00 | 18:00 – 21:00 Get-together Meeting | | | |

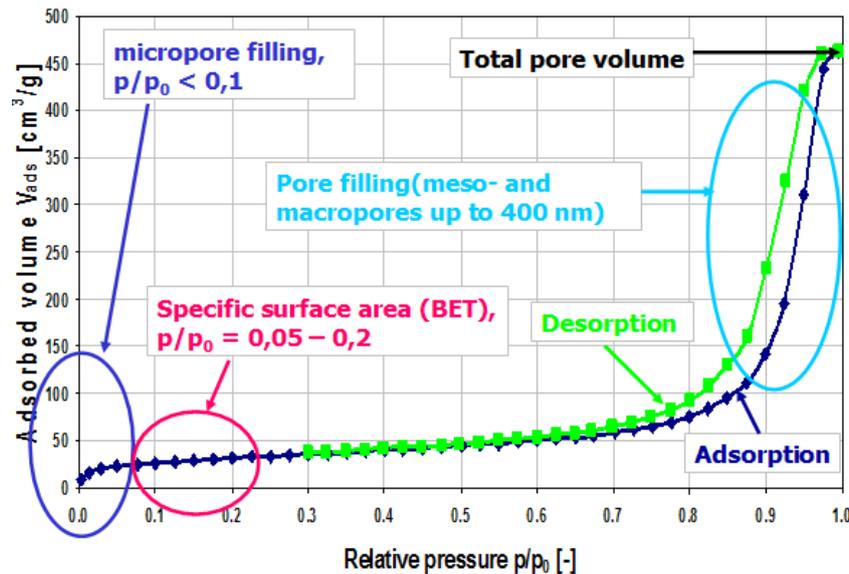
Abstracts of oral presentations

Characterization of Porous Solids by Gas Adsorption

Discussion of the new IUPAC Report

C. Reichenbach, Quantachrome GmbH & Co. KG, Odelzhausen/Deutschland
christian.reichenbach@quantachrome.de

Physisorption of gasses provides a precise and comprehensive measure of textural properties of porous solids and fine powders. Specific surface areas, pore volumes, pore size distributions and even characteristics of the surface chemistry can be deduced from physisorption isotherms (see Figure).



Technical and theoretical considerations on that important technique have been described and discussed in a technical report, published by the IUPAC (International Union of Pure and Applied Chemistry). The recommendations in the 1985 report have been broadly followed and referred to by the scientific and industrial community. Over the past 30 years major advances have been made in the development of nanoporous materials. Their characterization has required the development of high resolution experimental protocols and novel procedures based on density functional theory and molecular simulation. These new procedures, terms and concepts have necessitated the updating and extension of the 1985 recommendations which were just released (2015).

In this tutorial we will recall the basic concepts of physical adsorption of gases with special reference to the recent recommendations of the just released IUPAC report.

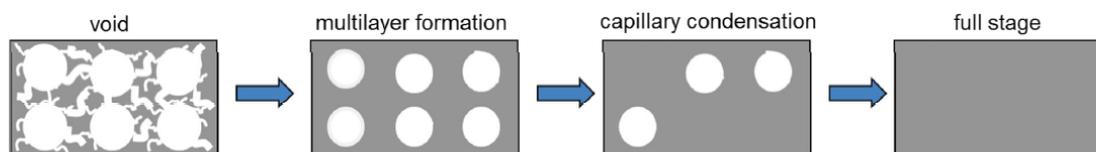
Small-angle scattering methods for the study of porosity in nanoporous materials

Simone Mascotto

Institute of Inorganic and Applied Chemistry, University of Hamburg

Martin-Luther-King Platz, 6 - 20146 Hamburg

Since the discovery of the M41S mesoporous silicas, the design of novel nanoporous materials evolved very fast providing systems with improved catalysis, sensing or separation properties. However, the material characterization, with special regards to porosity, became much more challenging due to the higher complexity of these systems. Standard characterization methods, e.g. gas physisorption, are in many cases not enough for clear understanding of porosity features and therefore more advanced approaches are required.



Scheme 1: Pore filling of porous material from the point of view of a photon/neutron during contrast matching conditions: Only the void pores contribute to the scattering.

One possible solution is the combination of gas physisorption with small-angle scattering of X-ray or neutrons. The so called in situ SAXS/SANS-Physisorption experiment revealed to be an useful and elegant method especially for the investigation of structures with complex and disordered pore networks. In principle, during the adsorption of specific adsorptives, which have the same electron density as the material matrix, only the void pores will contribute to the X-ray/neutron scattering (Scheme 1). In this way, the pore filling process can be precisely monitored and the accessibility of the porous network determined. Moreover, the porous properties of the system (e.g. free surface area and pore sizes) can be independently obtained by the SAXS/SANS curves at different filling grades applying case related analysis approaches.

In the present tutorial, after a short introduction on the basic principles of small-angle scattering, different applications of the in situ SAXS/SANS-Physisorption experiment will be presented. These case studies will deal with the porosity investigation in porous silica, organosilica and carbon materials.]

Theory and Applications of Mercury Intrusion Porosimetry

Michael Rückriem, Jürgen Adolphs

Porotec GmbH, Niederhofheimer Str. 55a, 65719 Hofheim, Germany

Phone: +49 171 2140968, e-mail: michael.rueckriem@porotec.de

web-site: <http://www.porotec.de/>

The characterization of pore size and porosity is a key factor in numerous applications. It is important to use a well described measurement process and to be aware of possible shortcomings and problems of the applied technique for quality control and research and development purposes.

Mercury intrusion porosimetry (MIP) measures pore sizes between 900 μm and 4 nm. This is one of the reasons, why it is so widely used for the characterization of porous materials. However, mercury intrusion porosimetry also has some limitations.

The presentation will provide a brief overview on the historical development, general theoretical aspects of the technique and explain why and when one has to be careful with the interpretation of data.

Specifically sample preparation, contact angle, surface tension, equilibration times, compressibility and thermal effects will be discussed. All these parameters can either cause problems with respect to the interpretation of the data.

Modern pore network data analysis will be shown and complement the traditional data analysis.

Examples will demonstrate how the intrusion and extrusion behavior can be interpreted and analyzed.

Various references to national and international standard testing-procedures and round robin results will be discussed.

NMR Cryoporometry: From fundamentals to application

Daria Kondrashova, Rustem Valiullin

University of Leipzig, Faculty of Physics and Earth Sciences, Leipzig, Germany

NMR cryoporometry is a sub-class of the thermoporometry methods developed for structural characterization of porous solids. It exploits the occurrence of the size-dependent solid-liquid and liquid-solid transition temperatures in confined spaces. Despite a relatively high resolution in the determination of the pore sizes which it may provide, this method has not found widespread applications. In part, this was caused by the fact that in-depth quantitative analyses of the thermoporometry data were often impeded by the lack of the respective theoretical models allowing for assumption-free descriptions of solid-liquid equilibria under confinements. Recently, we have developed a microscopic lattice model which allowed to gain deeper insight into the physics of the freezing and melting transitions for fluids confined in mesoporous materials with arbitrary pore geometries. By comparing its predictions to the experimental results obtained for mesoporous solids with ideal pore structures, we show that the model reproduces the key findings obtained in the thermoporometry experiments, including the shifted transition temperatures, irreversibility between freezing and melting, and strong impact of the pore structure. As the next step, we have applied the model to disordered materials. In this way, we provide conditions and recipes for the most reliable characterization of disordered porous solids using the thermoporometry methods. *NMR Cryoporometry: From fundamentals to application*

Morphology-Transport Relationships for Disordered Porous Media:

From Materials Science to Technical Catalysis

Prof. Dr. Ulrich Tallarek

Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany
(tallarek@staff.uni-marburg.de)

The discovery of morphology-transport relationships for disordered materials belongs to the major challenges in adsorption, separation, and catalysis. Because these fundamental relationships can be neither inferred from visual inspection nor from two-dimensional simulations, the three-dimensional physical reconstruction and/or computer-generation, together with a detailed morphological analysis and three-dimensional modeling of relevant transport phenomena, provides the only direct as well as the most realistic approach to understand and optimize current and future support structures.

In this presentation I will provide a brief summary of these challenges and present our latest progress at the following levels: (i) Computer-generation of bulk and confined packed beds allows the systematic investigation of individual parameters, such as the particle size distribution, bed porosity, and the effect of the macroscopic confinement [1]. These studies are complemented by the physical reconstruction of real packed and monolithic beds, which demonstrate numerous features coupled with the packing process or monolith synthesis that are under the control of the experimentalist [2]. (ii) Once the computer-generated and/or physically reconstructed packed-bed and monolith morphologies are available, they are analyzed with statistical methods to derive appropriate and unique structural descriptors for mass transport (effective diffusion coefficients, hydrodynamic longitudinal and transverse dispersion coefficients) [2,3]. Spatial tessellation schemes (for packings) and chord length distributions (for monoliths) proved to be particularly useful in this regard and allowed us to deduce correlations between the degree of local as well as packing-scale heterogeneities and effective diffusion and hydrodynamic dispersion. Because they are based on fundamental morphology-transport relationships, derived structural descriptors show potential for refining theoretical framework describing mass transport in any support. (iii) Three-dimensional transport simulations are performed on a dedicated high-performance computing platform, which enables us to quantify relevant transport processes from the pore scale up to the column (confinement) scale, including adsorption and reaction at the solid-liquid interface [4].

The combination and correlation of information gained with steps (i)–(iii) delivers morphology-transport relationships, arriving at a realistic global picture through carefully decoupled levels of methodologies, validated approaches, as well as length scales behind structural heterogeneities and mass transport regimes.

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Electron tomographic techniques to study the 3D morphology of porous solids

Dr. Christian Kübel

Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Over the last 15 years, electron tomographic techniques have been established as a powerful set of tools to directly image complex structures with high spatial resolution to accurately characterize the 3D structure of nanomaterials. Electron tomography has been successfully employed in such diverse areas as the analysis of tissue, whole cells and cellular ultrastructure in life science applications and in materials sciences from catalysis and quantum dots to semiconductors, block copolymers and polymer composites to highlight just a few application areas. Two principle approaches are used in electron tomography: 1) slice&view based techniques in a focused ion beam (FIB) system for the analysis of 'large' volumes around $100\,000\ \mu\text{m}^3$ with a few ten nanometer resolution and 2) transmission electron microscopy (TEM) based tomography of volumes typically less than a μm^3 with (sub)nanometer resolution. Both tomographic approaches provide a direct real space representation of the structural features of a material in 3D and can be quantitatively interpreted to describe the morphology of a material.

This presentation will provide a brief introduction to electron microscopy and the different imaging modes available and then focus on a basic theoretical background and practical aspects of both FIB slice&view and (S)TEM tomography. Finally image segmentation and data quantification will be discussed. The different steps will be illustrated by application examples.

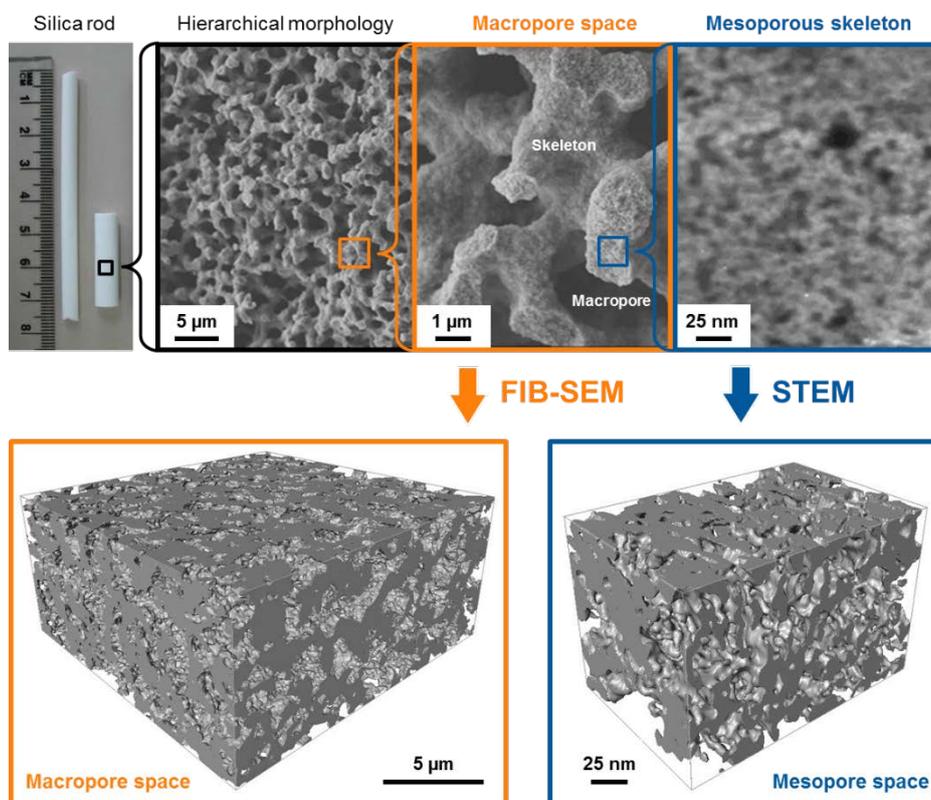


Fig. 1: Characterization of hierarchical structure combining FIB-SEM and HAADF-STEM tomographic techniques to build a 3D model [based on D. Stoeckel et al, Langmuir (2014) 30, 9022-9027].

Positron Porosimetry: Advantages and Issues

R. Zaleski*

*Maria Curie-Skłodowska University, Institute of Physics, Department of Nuclear Methods,
pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland*

*email: radek@zaleski.umcs.pl

Positron porosimetry is based on two relationships: first one is between the lifetime of ortho-positronium (o-Ps) and the size of free volume, where o-Ps annihilates; the second one – between the o-Ps intensity and the free volume concentration. The o-Ps lifetimes and intensities in a porous material are obtained from positron annihilation lifetime spectroscopy (PALS). Whereas, the relationships are calculated using the quantum mechanical models. Frequently used models are the Extended Tao-Eldrup (ETE) model [1] or the Rectangular Tao-Eldrup (RTE) model [2] coupled with the model giving the intensity-concentration relationship [3].

Positron porosimetry has several advantages over classic gas adsorption techniques. Compared to them, positron porosimetry allows to characterize much smaller free volumes, i.e. not only mesopores, but also micropores and even intermolecular spaces. The measurements can be carried out in almost every conditions, e.g. low or high temperature and pressure. Moreover, an *in situ* monitoring of processes taking place inside pores is possible, e.g. adsorption and desorption.

Still, positron porosimetry requires development. There are several effects causing distortion of the results. One of them is o-Ps migration, which is observed in materials having interconnected pores of different size. The migration can be reduced by shortening the o-Ps lifetime in an oxygen atmosphere. However, o-Ps quenching by oxygen has to be taken into account to obtain quantitative results from measurements in presence of the gas. The appropriate amendment to the model was developed basing on the measurements carried out at various oxygen or air pressures. Despite the positive results of described previously method, total elimination of o-Ps migration is not possible. Thus, knowledge of this phenomenon is necessary for reliable pore size determination. The migration is not only an obstacle but it can extend the positron porosimetry capabilities, e.g. difficult to determine size of holes in a pore wall can be estimated from the o-Ps migration probability at various temperatures.

It is also desirable to develop the models used in positron porosimetry. Both the ETE and the RTE models base on the assumptions, which allowed to simplify the required calculations but they are somewhat unrealistic. The progress in numerical methods makes difficulties in calculations obsolete. Therefore, more realistic model can be used.

Several examples illustrating above basic research problems as well as application research will be presented.

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Positron annihilation lifetime spectroscopy study of advanced porous low-k films for microelectronics

M. Kraatz¹, A. Clausner¹, M. Gall¹, E. Zschech¹, M. Butterling², W. Anwand³,
A. Wagner³, R. Krause-Rehberg², K. Pakbaz⁴

¹*Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany*

²*Department of Physics, Martin Luther University Halle-Wittenberg, Halle, Germany*

³*Institute of Radiation Physics, Helmholtz-Zentrum, Dresden-Rossendorf, Dresden, Germany*

⁴*SBA Materials, Inc., Albuquerque, New Mexico, USA*

ABSTRACT

In microelectronics, the insulation between on-chip interconnects is of great concern. As chip dimensions shrink, the capacitances between interconnects increase and in turn also the signal delay increases. The increase in transistor speed is limited by the signal speed in interconnects. To address this limitation, materials with low permittivity (dielectric constant or k-value) are used as insulation, so-called low-k materials. One approach is the use of organosilicate glasses as low-k material. Organosilicate glasses incorporate methyl groups into the glass matrix, which open up volume in the matrix and decrease the density with so-called cage structures by almost maintaining mechanical properties. The dielectric constant of organosilicate glass is about 3, compared to about 4 for conventionally used silicon dioxide. The only viable approach to lower the dielectric constant below 2.2, a critical value for microelectronics industry, is to introduce pores into the material. To measure the pore size of porous organosilicate glass, positron annihilation lifetime spectroscopy was performed on material with self-assembled pores. In principle, the lifetime of the ortho-positronium that is formed after positrons penetrate the thin film determines the size of the pores. Traveling through larger pores, collisions with pore walls is less frequent and pick-off annihilation by exchanging a wall material electron and forming para-positronium takes a longer time. We have measured material ranging in upper limits in porosity from 25% to 50% and corresponding k-values ranging from 2.4 to 1.8, including a reference material with $k = 3.0$ without porosity. We have measured 4 lifetime components, the largest induced by the pores and three small ones not related to the pores such as open volume in the glass matrix. The average pore size was determined to be 3.5 ± 0.5 nm. No pore size dependence on k-value indicates good process control of the pore fabrication.

¹²⁹Xenon NMR

Julia Hollenbach, Jörg Matysik

*Institut für Analytische Chemie, Universität Leipzig, Linnéstr. 3, D-04103 Leipzig
joerg.matysik@uni-leipzig.de*

Over the last two decades, ¹²⁹Xe-gas NMR has become a well-known method to probe porous materials, as the chemical shift of the gas is highly sensitive towards the surrounding.¹ Thus, this non-destructive technique is suitable to characterize pore structure and the interconnectivity as well as the dynamical behavior of a fluid inside the pore space.

Based on the pioneer work of ITO and FRAISSARD², there have been established Chemical Shift/Pore Size correlations for various silica based materials.^{1,3} Research has been extended to other classes of compounds such as Metal Organic Frameworks (MOFs), polymers and composite materials, i.e. Zeolitic Imidazolate Frameworks (ZIFs) and Al₂O₃ based systems. Here ¹²⁹Xe-gas NMR was also used to study the gas migration and pore interconnectivity in those materials and the effect of modification on the surface of the pores.^{4,5}

This seminar presentation provides an overview on the application of ¹²⁹Xe-MR for probing the structure as well as exchange and dynamics in porous media. Therefore, the NMR-related features and hardware requirements are discussed at first before common experimental techniques and their application examples are introduced.

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A simple shape-free model for (large) pore size estimation with positron annihilation lifetime spectroscopy (PALS) and its application to silica-aerogel

T. Hyodo* and K. Wada

Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0003, Japan

Positronium (Ps) is a hydrogen-like bound state consisting of an electron and a positron. Since the spin of the electron and the positron is $1/2$, the total spin of the Ps is either 1 or 0. The former is the triplet state, called *ortho*-positronium (*o*-Ps), while the latter is the singlet state, called *para*-positronium (*p*-Ps). Because of conservation laws, *o*-Ps self-annihilates into 3γ with a lifetime of 142 ns in vacuum, while *p*-Ps annihilates into 2γ with a lifetime of 125 ps in vacuum.

The annihilation lifetime of the *o*-Ps in materials is much shorter than 142 ns because of the "Pickoff" annihilation, where the positron in the *o*-Ps annihilates into 2γ with an electron of the materials with whom total-spin-singlet state is possible. Quantum mechanically, the overlap of the positron part of the Ps wave function with the wave function of the material electrons determines the pickoff annihilation rate. When *o*-Ps is trapped in a pore the probability of the pickoff annihilation is reduced and its lifetime becomes longer. This is the basis for the pore size estimation by the positron annihilation lifetime spectroscopy (PALS).

The *o*-Ps lifetime in a small pore is related to the pore size in the Tao-Eldrup model [1], which assumes the overlap of the tail of the Ps wave function with the wall of the spherical pore causes the pickoff annihilation. For larger pores Dull et al. developed a model assuming a rectangular pores and including the effect of the excited state occupied by Ps [2].

Recently we developed a shape-free model for the PALS analysis of the size of large pores [3]. It is based on a classical picture: the pick off annihilation rate is expressed by the rate of the collision of the Ps with the pore wall multiplied with the annihilation rate per collision. If we adjust a parameter so that the function smoothly touch the Tao-Eldrup model with the effect of the self-annihilation included, the function agrees surprisingly well with the model by Dull et al. [2]. The present model is pore-shape free because it is a function of the mean-free-distance of the pore system. In the case where it is appropriate to assume a shape for the pore, the mean-free-distance is easily converted into a characteristic parameter of the shape.

We applied the present model to the free volume in three different kinds of silica aerogel. The macroscopic specific gravity of each sample estimated from the results and the specific surface area measured with BET agrees with the value directly measured.

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* Corresponding author, email address: toshio.hyodo@kek.jp

Nanometer Size Pores in Ionic Liquid Loaded Silica Gel Characterized by Positron Lifetime Spectroscopy

Christian Herold¹, Hubert Ceeh¹, Thomas Gigh¹, Markus Reiner¹, Marco Haumann², Andreas Schönweiz², and Christoph Hugenschmidt¹

¹ Heinz Maier-Leibnitz Zentrum (MLZ) and Physik Department E21, Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany

² Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander Universität, Erlangen-Nürnberg, Germany

Corresponding author: e-mail hugen@frm2.tum.de, Phone: +49-89-289-14609, Fax: +49-89-289-11695

We present studies on the free volume of silica gel dependent on water absorption and on loading with a different amount of the Ionic Liquid (IL) [C₂MIM][NTf₂] using Positron Lifetime Spectroscopy (PLS). The found two long lifetime components (~2 ns and 10-20 ns) are attributed to the annihilation of ortho-positronium (o-Ps) in micropores of different size. The application of a semi-empirical quantum mechanical model allowed us to correlate the measured o-Ps lifetimes to the absolute mean size of the micropores by approximation with a spherical shape. The mean diameter of the pores in the pure silica gel could hence be determined to 1.72(6) nm. IL loading with up to 70 vol% lead to the formation of smaller voids with a mean diameter of 1.28(4) nm according to a reduction of the mean pore volume by about 60%. In addition, the accumulation of H₂O molecules from the surrounding air inside the pores

Characterisation of bimodal silica-gel with Positron-Annihilation-Lifetime-Spectroscopy

H. Uhlig¹⁾, S. Zieger²⁾, C. Bluhm²⁾, R. Krause-Rehberg²⁾, D. Enke³⁾

¹⁾University of Leipzig, Institut für Nichtklassische Chemie, ²⁾MLU Halle/ Wittenberg, Institute of Physics, ³⁾University of Leipzig, Institute of Chemical Technology

The pore system of hierarchically structured porous materials is usually characterized by physisorption methods and mercury intrusion. However, these methods have some limitations. In the case of low temperature nitrogen adsorption it is often very difficult to characterize amorphous micro- and meso porous materials and to obtain a “real” pore size distribution. Furthermore, problems like pore blocking, bubbling effects or insufficient filling of the pores with condensed adsorptive may occur [1]. Very high pressures (up to 4000 bar) are necessary to detect small meso pores with mercury intrusion. This can lead to changes in the pore structure during the measurement. Additionally, only pores with openings larger than 3.9 nm can be considered. Finally, a closed porosity cannot be detected by both methods. In this context Positron-Annihilation-Lifetime-Spectroscopy (PALS) is recognized as an alternative method to characterize porous materials.

In this study the results of the characterization of hierarchical silica-gel samples with nitrogen adsorption and PALS are compared [2]. The hierarchical silica-gel samples were synthesized by pseudomorphic transformation of a meso porous silica gel with CTAOH according to Einicke [3] and Uhlig [4]. A set of 8 samples was synthesized using different volumes of 0.07 M CTAOH (5 - 42 ml/g) to obtain hierarchical pore systems with controlled proportions of 15 nm pores of the initial silica-gel and 4 nm

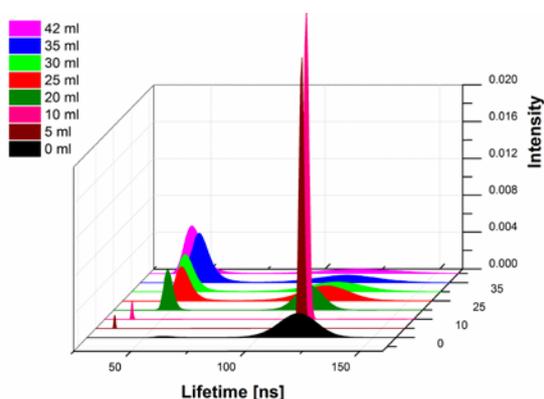


Figure 1 Lifetime spectra of hierarchical silica gels [7]

pores formed by the MCM-41 phase. The results of the PALS measurements clearly indicate the hierarchical pore structure of the materials. Two individual pore systems can be detected with a good resolution (Figure 1). The peak area of the signals can be calculated and compared with the pore volumes determined by nitrogen adsorption. In some cases, strong differences in the total peak areas were observed. Threw a standardization of the total area to 1 comparable peak areas could be calculated. The results in Figure 2 (left) show a correlation between the pore volume determined by nitrogen adsorption and the peak area calculated from PALS. With increasing amount of CTAOH solution (increase of MCM-41-volume) the pore volume of the starting material (15 nm pores) decreases. The drop of the values measured by PALS is not as steep as from nitrogen adsorption. This can be seen as an indication of the formation of a closed porosity by the pseudomorphic transformation.

Figure 2 (right) shows a comparison between the pore volume from nitrogen adsorption and the calculated peak areas of the formed MCM-41-phase. A very good correlation was observed in this case. All pores of the MCM-41-phase seem to be accessible for nitrogen.

In summary, PALS measurements enable a complementary characterisation of pore systems in the micro and meso pore range. Hierarchically structured porous materials can be studied and the individual pore systems are well separated. The observed correlation between intensities respectively peak areas from PALS and pore volumes determined by nitrogen adsorption for the different pore classes allows via calibration the direct estimation of the pore volumes by PALS and the quantification of a potential closed porosity.

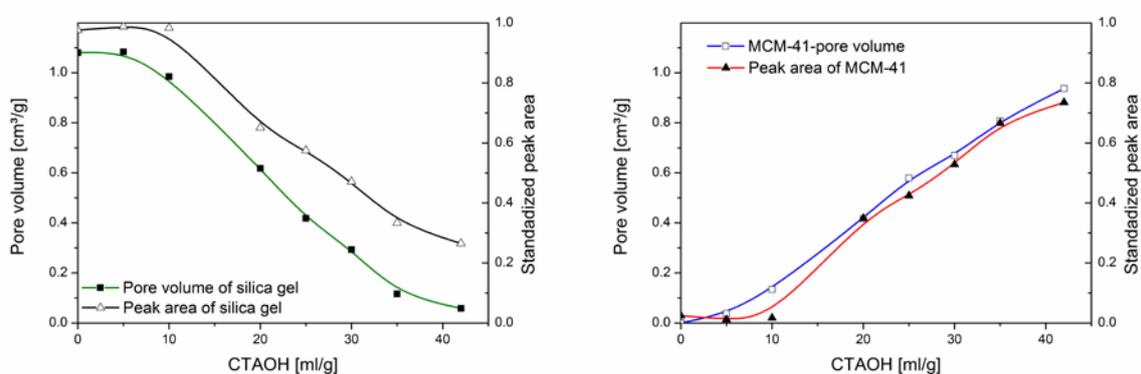


Figure 2 Comparison between the calculates pore volume of the starting pore system with 15 nm (left) and the MCM-41 pore volume (right) obtained from nitrogen adsorption with the calculated peak area obtained from PALS

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Poster presentations

1. **Nanostructured Magnéli Phases**; Giuliana Beck, Universität Giessen
2. **Microwave-assisted Synthesis of Microporous Zn(II)- and Co(II)-Imidazolate-4-amide-5-imidate Frameworks**; Karsten Behrens, Universität Potsdam, Potsdam, Germany; Igor. A. Baburin, Technische Universität Dresden, Germany; Stefano Leoni, Cardiff University, United Kingdom; Jens Weber, Hochschule Zittau/Görlitz, Germany; Hans-Jürgen Holdt, Universität Potsdam, Germany,
3. **Investigation of Nanodiamonds by Positron Annihilation spectroscopy**; Gulidova Lyudmila, Laptev Roman, Mikhaylov Andrey, Bordulev Iurii, Tomsk Polytechnic University, Institute of Physics and Technology, General Physics Department, Tomsk, Russia
4. **Study of porosity in a SiOCH low-k material by slow positron beam with secondary electron tagging for positron annihilation lifetime spectroscopy**; N. Djourelou¹, M. Lépinay², H. Marinov³; 1 Extreme Light Infrastructure - Nuclear Physics, Horia Hulubei National Institute for Physics and Nuclear Engineering, 30 Reactorului Street, P.O. Box MG-6, 077125 Magurele, Ilfov county, ROMANIA; 2 STMicroelectronics, 850, rue Jean Monnet, Crolles Cedex, France; 3 INRNE-BAS, 72 Tzarigradsko chaussee Blvd, 1784 Sofia, Bulgaria
5. **Preparation of carbon monoliths with adjustable porosities and structural characterization by an advanced evaluation method of wide angle X-ray scattering data**; M. Loeh¹, F. Badaczewski¹, S. Hintner², J. Metz², B. M. Smarsly¹; 1 Department of Chemistry, Justus Liebig University, Giessen, 35390, Germany, 2 Schunk Kohlenstofftechnik GmbH, 35452 Germany
6. **High Impact Polypropylene: Morphology generation during homo-stage**; Miguel Plata, Michael Bartke, Martin Luther University, Germany; Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands
7. **Challenges of determining the porosity in different classes of materials -micro-/meso-/macroporosity in organosilicas and carbons** Malina Bilo, Mateusz Rogaczewski, Tamás Simon, Felix J. Brieler and Michael Fröba Institute of Inorganic and Applied Chemistry, University Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany
8. **Understanding Transport in Pore Spaces with Complex Pore Geometries**; Daniel Schneider, Rustem Valiullin, Jörg Kärger; Faculty of Physics and Earth Sciences, University of Leipzig, Leipzig, Germany
9. **Mono-energetic Positron Source (MePS) – a large-scale facility for Porosimetry at ELBE**; T. T. Trinh^{1,2}, M. O. Liedke¹, W. Anwand¹, A. Wagner¹, R. Krause-Rehberg³, M. Jungmann³, M. Butterling¹, T. E. Cowan^{1,2}; 1 Helmholtz-Zentrum Dresden-Rossendorf, Germany; 2 Technische Universität Dresden, Germany; 3 Martin-Luther Universität Halle-Wittenberg, Germany
10. **Positron-based spectroscopy methods at ELI-NP**; Victor Leca, Andreea Oprisa, and Nikolay Djourelou; Extreme Light Infrastructure-Nuclear Physics, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Street, Bucharest-Magurele, Romania
11. **Pulse stretching of a linac-based slow-positron beam for pore size analysis**; K. Wada¹, M. Maekawa², I. Mochizuki¹, and T. Hyodo¹; 1 Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-

0003, Japan; 2 Quantum Beam Science Center, Sector of Nuclear Science Research, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

12. **A simple function for pore-size estimation with PALS analysis;** K. Wada* and T. Hyodo; Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0003, Japan
13. **Soft-Templated Mesoporous CsTaWO₆ for Photocatalytic Hydrogen Production;** Tobias Weller, Roland Marschall; Institute of Physical Chemistry, Justus-Liebig-University Giessen, 35392 Giessen, Germany
14. **Porosimetry with Positrons;** S. Zieger, C. Bluhm, E. Hirschmann, R. Krause-Rehberg; Institut für Physik, MLU Halle-Wittenberg, Halle (Saale) 06099, Germany

Nanostructured Magnéli Phases

Giuliana Beck, Universität Giessen

The stoichiometric, suboxidic Ti_nO_{2n-1} Magnéli phases are interesting for many industrial applications because of their high stability, low costs and good conducting properties. As electrode material in batteries or in catalysis Ti_4O_7 is of special interest. It combines a high chemical and mechanical stability with an electron conductivity comparable to graphite.

The combination of Ti_4O_7 with a photo catalytically active material like Fe_2O_3 or $ZnFe_2O_4$ may result in highly efficient photoelectrodes based on sustainable and abundantly available elements. Key point is a high surface area to enable the deposition of sufficient photocatalyst and still remain high interfaces for reactions.

Therefore my PhD thesis is concerned with the synthesis of nanostructured and porous Ti_4O_7 . To archive this, TiO_2 needs to be reduced under very well controlled conditions. On my poster I would like to present my recent results on the synthesis of mesoporous TiO_2 monoliths with controllable macropore size and their H_2 -reduction to phase pure Ti_4O_7 .

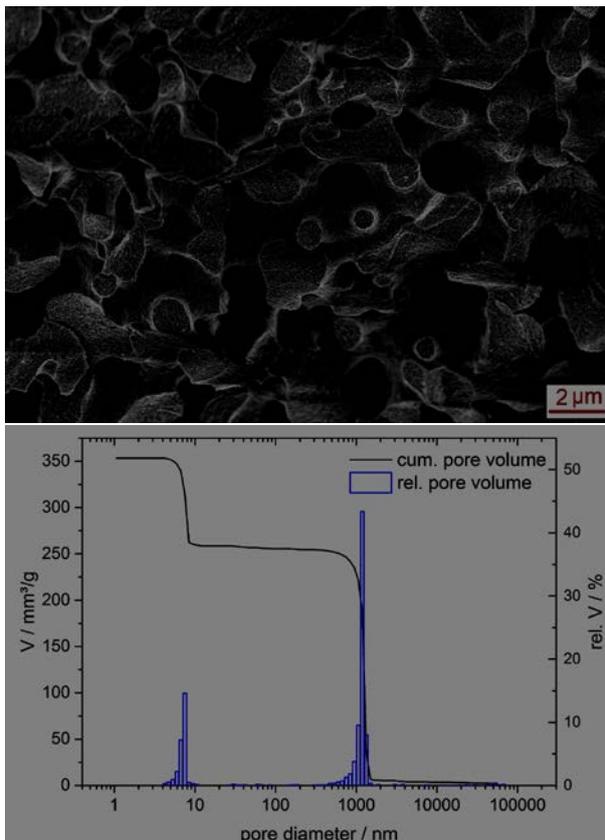


Figure 1: SEM image of a mesoporous TiO_2 monolith and its pore size distribution obtained by mercury intrusion porosimetry.

Microwave-assisted Synthesis of Microporous Zn(II)- and Co(II)-Imidazolate-4-amide-5-imidate Frameworks

Karsten Behrens, Universität Potsdam, Potsdam, Germany; Igor. A. Baburin, Technische Universität Dresden, Dresden, Germany; Stefano Leoni, Cardiff University, Cardiff, United Kingdom; Jens Weber, Hochschule Zittau/Görlitz, Germany; Hans-Jürgen Holdt, Universität Potsdam, Potsdam, Germany

Metal-organic frameworks (MOFs) have been traditionally prepared by the solvothermal/hydrothermal methods with temperatures from room temperature up to 200 °C and reaction durations from hours to days. Also alternate techniques for MOFs synthesis were established, e.g. solvent-free synthesis and ultrasonic or microwave (MW) method.^[1]

In recent years we developed an isostructural series of imidazolate frameworks, named as IFP (Imidazolate Framework Potsdam). Based on a 2-substituted 4,5-dicyanoimidazole precursor, the cyano groups convert under solvothermal conditions *in situ* into amide- imidate groups and formed with transition metals (Zn, Co) imidazolate frameworks with 1D hexagonal channels (Figure 1).^[2]

Herein, we represent the synthesis of IFPs under MW-assisted conditions. For assembly, the time duration of these materials can be minimized from days to under one hour when reactions are done and the resultant materials are formed also in higher yields. Co(II)-imidazolate frameworks, namely IFP-11 (R=Cl), -12 (R = Br) and -13 (R=Et) we achieved exclusively under MW conditions.^[3]

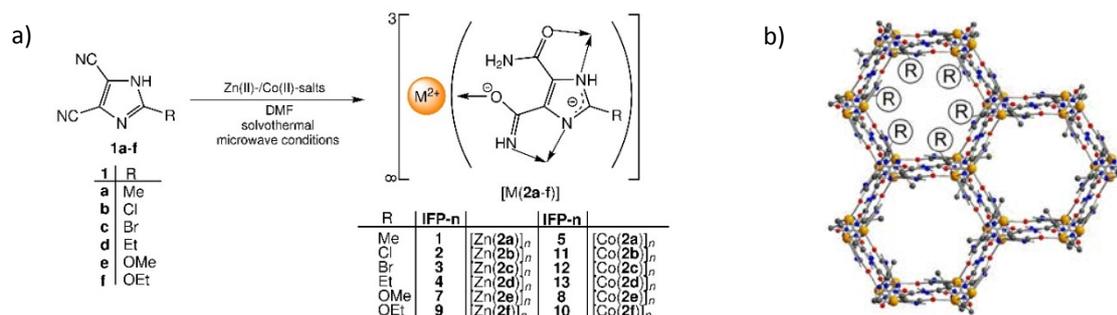


Figure 1. a) Syntheses of isostructural Zn(II)- and Co(II)-IFPs; b) sketch of the 1D hexagonal channels.

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INVESTIGATION OF NANODIAMONDS BY POSITRON ANNIHILATION SPECTROSCOPY

GULIDOVA Lyudmila¹, LAPTEV Roman¹, MIKHAYLOV Andrey¹, BORDULEV Iurii¹

I_gulidova@bk.ru

¹Tomsk Polytechnic University, Institute of Physics and Technology, General Physics Department, Tomsk, Russia

Carbon nanostructure materials have been extensively studied and found application in a wide range of science and engineering since the moment of their discovering. Carbon nanostructures such as nanodiamonds have unique structure. Nanodiamonds are chemically well-defined, and of high purity. Nanodiamonds are likely to share some of the unique properties of macroscopic diamond that are very attractive for a number of applications. The positron annihilation spectroscopy (PAS) is unique method for characterization of defects and pores of carbon nanostructure materials [1, 2].

The nanodiamond consists of a crystalline diamond core and amorphous or graphite shell with functional groups. The non-equilibrium conditions of the nanodiamonds synthesis influence on high density of defects and developed surface.

The samples were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and positron annihilation spectroscopy. The crystallinity and purity of the samples were obtained by XRD. The carbon material consists of nanodiamonds with an average size of 8 nm.

The functional groups on the nanodiamonds surfaces allow create carbon materials with desired properties. The cover around the core prevents the penetration of hydrogen into the nanodiamond as evidenced not high sorption capacity of these materials.

The compacted carbon powders were used for hydrogen saturation and positron annihilation measurements. Compaction process was carried out on hydraulic press at room temperature in the pressure range 100-700 MPa without using a binder.

Hydrogen concentration measurements were carried out by Gas Reaction Controller complex at room temperature and pressure of 8 atm. Samples were placed in a chamber, which was evacuated to the pressure of 10^{-6} atm.

As a source of the positron isotope ^{44}Ti with the activity of 24.5 μCi was chosen. The ^{44}Ti was placed between two copper capsules filled the compacted carbon powder. The method based on the interaction of positrons with electrons of sample. The time resolution of the system was 260 ps. The full information about spectrometry complex was presented at the article [3]. As the results of experiment the data about positron lifetime in compacted carbon powder and annihilation line Doppler broadening were taken.

The positron lifetime in the material after exposure, for example heat treatment, introduction of impurities, such as hydrogen, significantly differs from the positron lifetime in the initial material. The positron lifetime increases because of electron density change. Hydrogen saturation of nanodiamonds increases the positron lifetime. As the internal crystalline structure of the nanodiamond presumably does not available for hydrogen, therefore surface can change the positron lifetime.

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Study of porosity in a SiOCH low-k material by slow positron beam with secondary electron tagging for positron annihilation lifetime spectroscopy.

N. Djourelov¹, M. Lépinay², H. Marinov³

¹ Extreme Light Infrastructure - Nuclear Physics, Horia Hulubei National Institute for Physics and Nuclear Engineering, 30 Reactorului Street, P.O. Box MG-6, 077125 Magurele, Ilfov county, ROMANIA, e-mail: nikolay.djourelov@eli-np.ro

² STMicroelectronics, 850, rue Jean Monnet, Crolles Cedex, France

³ INRNE-BAS, 72 Tzarigradsko chaussee Blvd, 1784 Sofia, Bulgaria

Design and performance of a positron annihilation lifetime spectrometer (PALS) using a magnetically guided continuous positron beam and the signal from secondary electrons emitted from the sample is presented. The impact of plasma etching and chemical wet cleaning on solvent diffusion in porous network of a Si-OCH low-k dielectric material is studied. The porosity and pore size distribution by means of ellipso-porosimetry and of PALS are compared. The results of solvent diffusion kinetics, measured using probe molecules of different polarity, surface energies and molecular sizes are also discussed. Infrared spectroscopy, Doppler broadening of annihilation radiation and time-of-flight secondary ion mass spectrometry measurements are also performed to investigate material modifications causing variations of diffusion kinetics.

Preparation of carbon monoliths with adjustable porosities and structural characterization by an advanced evaluation method of wide angle X-ray scattering data

M. Loeh¹, F. Badaczewski¹, S. Hintner², J. Metz², B. M. Smarsly¹

¹Department of Chemistry, Justus Liebig University, Giessen, 35390, Germany, ²Schunk Kohlenstofftechnik GmbH, 35452 Germany.

*Bernd.Smarsly@phys.Chemie.uni-giessen.de

Macroporous carbon materials are typically used as catalyst supports or for energy storage or separation-adsorption applications as they display excellent flow-through properties as well as high surface areas depending on their distinct porosity. Here, macroporous carbon monoliths as well as monoliths exhibiting hierarchical porosity consisting of a continuous macro- and mesopores network were prepared by a nanocasting approach, using monolithic silica as the template and a coal tar pitch, liquid at room temperature, as the carbon precursor.

Although the macroscopic shape and the porosity are determined by the template, physical and chemical properties like, hardness, thermal and electric conductivity, chemical stability and corrosion resistance are determined by the carbon microstructure, i.e., the size and stacking of the graphene layers as well as the arrangement of the stacks and disorder effects. Hence a precise knowledge of the microstructure is desired to tune the properties for particular applications accordingly.

Besides Raman spectroscopy and HRTEM is Wide-Angle X-ray Scattering (WAXS) one of the suitable techniques for the structural characterization of carbon materials. However, the diffraction patterns for non-graphitic carbons show only diffuse maxima in the vicinity of the $(00l)$ and $(hk0)$ reflections of graphite. They display no general (hkl) reflections due to the rotational and translational disorder (turbostratic disorder) of the graphene layers. This disorder leads to an asymmetric shape of the $(hk0)$ reflections that often considerably overlap with the $(00l)$ reflections, so that an evaluation using standard line width analysis is ambiguous.^[2] Here, a novel approach for the evaluation of WAXS data is applied which provides quantitative structural information of the microstructure of such non-graphitic carbons on the nanometer scale.

The evaluation is based on a theoretical model developed by Ruland and Smarsly^[1] where the entire WAXS curve is fitted by a theoretical scattering function comprising several structural parameters. For instance, the average graphene layer size L_a , the height L_c of the graphene stacks, the average interlayer spacing a_3 , the average number N of graphene layers per stack as well as information on the degree of disorder within the graphene layers and in the stacking can be derived from the model.

This approach was used to quantitatively investigate the influence of the nanocasting process on the development of the carbon microstructure of the prepared porous carbons compared to the bulk coal tar pitch precursor. The overall nanocasting process was characterized utilizing scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and physisorption.

In contrast to the bulk pitch, the diffraction patterns of the milled carbon monoliths processed at 3000 °C displayed no (hkl) reflections as well as a significantly broader (002) reflection and a lower intensity of the (004) reflection, indicating a distinctly reduced stacking tendency in the carbon monoliths. Thus, the confined space within the mesopores of the silica template noticeably inhibit the evolution of the carbon microstructure, i.e. the transformation of the carbon precursor into a graphitic lattice.

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High Impact Polypropylene: Morphology generation during homo-stage

*Miguel Plata, Michael Bartke, Martin Luther University, Germany
Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands.*

Heterophasic propylene copolymers (Hecos's) are versatile polymeric materials used in various applications such as automotive, packaging, construction industry among others. Heterophasic propylene copolymers consist of two main components: a polymer matrix of isotactic polypropylene and a dispersed rubbery ethylene-propylene copolymer, which is not miscible into the matrix phase. While the matrix improves stiffness, the elastomeric phase enhances the impact strength and the mechanical behavior at low temperature.

Hecos's are produced by coordinative polymerization in at least two-stage processes. While the matrix material is either produced in gas-phase or bulk polymerization, the elastomeric phase is produced in all commercial processes by gas-phase polymerization.

Product properties of heterophasic propylene copolymers are influenced by the molecular structure of both matrix material and elastomeric material and the rubber content. Process kinetics and operability are also influenced by rubber distribution in the polymer particles and particle morphology in general.

The current contribution deals with the impact of homopolymerization conditions on particle morphology as a first step to influence rubber distribution in during the heco-stage.

Both prepolymerization and homopolymerization conditions are systematically varied and the resulting homopolymers are characterized in terms of morphology and process kinetics.

This research forms part of the research programme of the Dutch Polymer Institute (DPI), project 785.

Challenges of determining the porosity in different classes of materials - micro-/meso-/macroporosity in organosilicas and carbons

Malina Bilo, Mateusz Rogaczewski, Tamás Simon, Felix J. Brieler and Michael Fröba*
*Institute of Inorganic and Applied Chemistry, University Hamburg,
Martin-Luther-King-Platz 6, 20146 Hamburg, Germany
froeba@chemie.uni-hamburg.de, 0049 (0)40 42838 3100

In many fields of application such as optics^[1] or separation processes^[2,3] tailored porous materials are of high impact. In our research group we focus on porosity in different material classes ranging from carbons over silica to organosilicas and respective composite materials. Main aspects of our work are the design and synthesis of appropriate materials of different morphologies with adjusted pore characteristics. Investigations of some exemplary materials are described in here.

For the preparation of macroporous carbons like the one in figure 1 we use an exotemplate approach with spherical monodisperse PMMA particles as hard template, which define the size for the macropores. These macropores are connected via windows. One approach to generate smaller pores in carbon structures is the activation with KOH. Variation of the amount of KOH leads to different products with changes in their porous properties. Different results of the mercury porosimetry for KOH activated and unactivated carbons are noticeable. There is no extrusion of intruded mercury for the unactivated macroporous carbons but it occurs for activated ones with high amounts of KOH even though the window size of the carbons does not change. The changes of the micro- and mesoporous properties after activation with KOH are also significant and were studied with nitrogen physisorption experiments.

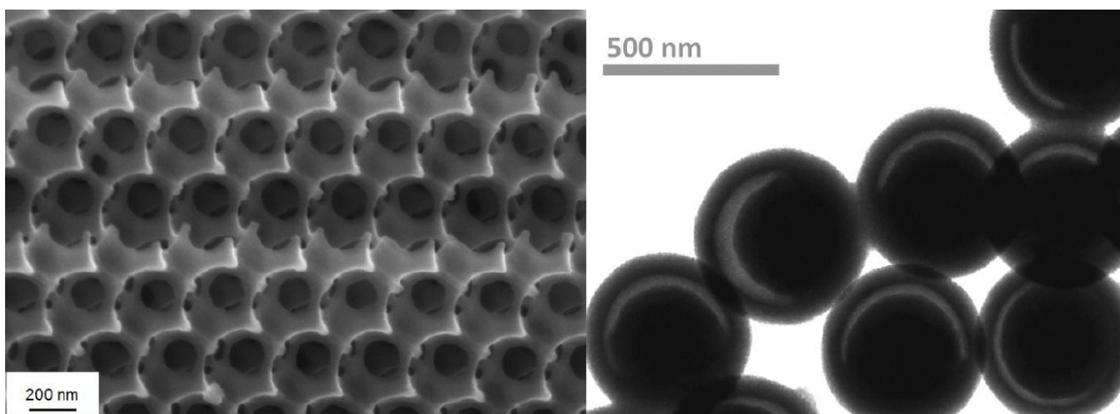


Figure 1: Left: SEM image of the highly ordered inverse opale structure of the macroporous carbon. Right: TEM-image of core-shell particles after the two-step synthesis approach.

Understanding Transport in Pore Spaces with Complex Pore Geometries

Daniel Schneider, Rustem Valiullin, Jörg Kärger
Faculty of Physics and Earth Sciences, University of Leipzig, Leipzig, Germany

This work deals with adsorption and desorption dynamics in materials with complex pore structures. The main question addressed is under which conditions the uptake dynamics, which is of importance in a variety of technological applications, can be described using a concept of effective diffusivity and, in contrast, when they are controlled by coupled local adsorption-diffusion processes. This problem is directly related to finding the conditions leading to the dynamics predictable on the basis of known transport properties of individual units composing the complex pore systems. In one part of the work, we consider sorption dynamics in closed-end channels and a collection of ink-bottle systems in the regime of capillary-condensation. In this case, due to the fact that the adsorption properties are unevenly distributed over space, we show that the uptake mechanism is determined by the position-dependent patterns of the adsorption process. The second part of the contribution deals with situations, in which adsorption occurs homogeneously over the pore space. By considering the general case of bi-porous materials, modeling a distribution of domains with different sorption capacities and transport properties, we show that uptake is reasonably described using the diffusion equation with an effective diffusivity.

Mono-energetic Positron Source (MePS) – a large-scale facility for Porosimetry at ELBE

T. T. Trinh^{1,2}, M. O. Liedke¹, W. Anwand¹, A. Wagner¹, R. Krause-Rehberg³, M. Jungmann³, M. Butterling¹, T. E. Cowan^{1,2}

¹ *Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, 01328 Dresden, Germany*

² *Technische Universität Dresden, Zellescher Weg 12, 01069 Dresden, Germany*

³ *Martin-Luther Universität Halle-Wittenberg, Von-Danckelmann-Platz 3, 06120 Halle, Germany*

Positron annihilation lifetime spectroscopy serves as a perfect tool for studies of open-volume defects in solid materials such as vacancies, vacancy agglomerates, and dislocations. The use of intense mono-energetic positrons (MEPs) for life-time experiments and conventional Doppler broadening, employed at the ELBE accelerator center, offers a non-destructive investigation of structures in porous media as well as depth dependent defect studies on thin films.

Positron-based spectroscopy methods at ELI-NP

Victor Leca*, Andreea Oprisa, and Nikolay Djourellov

Extreme Light Infrastructure-Nuclear Physics, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Street, Bucharest-Magurele, Romania

*Corresponding author: victor.leca@eli-np.ro

The positron (e^+), having the same mass and spin as the electron, but a positive charge, has the ability to detect open volume defects in materials and, therefore, can be used for materials studies [1]. A short description of the analytical methods based on moderated positrons to be implemented at ELI-NP, a new European user-facility currently under construction in Magurele-Bucharest (Romania), will be presented. The beam of short-pulse positrons with a narrow energy spread will be produced by inverse Compton scattering of a PW laser beam on a high-energy electron beam, followed by electron-pair creation on thin tungsten plates. The foreseen methods to be implemented at ELI-NP that make use of the high defect sensitivity of the positrons and of the properties of the annihilation radiation, are: Coincidence Doppler Broadening Spectroscopy (CDBS), Gamma-Induced Positron Annihilation Lifetime Spectroscopy (GiPALS), Positron Annihilation Lifetime Spectroscopy (PALS), and Time-of-flight Positron Annihilation initiated Auger Electron Spectroscopy (TOF-PAES) [2-4]. The TOF-PAES technique will be discussed in more details, as well as its potential application for spectroscopy studies of defects in oxide thin films and interfaces.

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Pulse stretching of a linac-based slow-positron beam for pore size analysis

K. Wada^{1*}, M. Maekawa², I. Mochizuki¹, and T. Hyodo¹

¹Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0003, Japan

²Quantum Beam Science Center, Sector of Nuclear Science Research, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

A pulsed intense positron beam at the Slow Positron Facility, KEK has been successfully used for the investigations of the positronium negative ions, positronium time-of-flight, and positron diffractions. However, it cannot be applicable to more conventional positron annihilation studies of materials and material defects and pores. This is because the pulse width, 1 μ s or 1-10ns (variable), is too long for a positron lifetime measurement and too short (or too many positrons are stuffed in a pulse) for the energy spectroscopy and angular correlation measurements of the annihilation γ -rays.

In order to make the high-intensity, energy-tunable slow positron beam useful for such ordinary positron annihilation measurements, including pore size analysis, a pulse stretching system (pulse width up to 20 ms and beam energy up to 5 keV) has been introduced and tested.

A cylindrical entrance electrode, a 6-m long trapping electrode, and an exit electrode were implemented in the system. The entrance electrode voltage, normally set at 5.1 kV, is temporarily lowered to 4.6 kV to let a 1- μ s width positron pulse with an energy of 4.8 ± 0.05 keV into the trapping electrode. Positrons then travel along a solenoid magnetic field down to and are reflected back from the exit electrode kept at 5.0 kV. The voltage of the entrance electrode is raised back to 5.1 kV before the positrons come back, and positrons are trapped. The trapping electrode voltage is then increased gradually, letting the positrons spill over the exit electrode. By adjusting the sweeping speed of the voltage of the trapping electrode, we obtain a pulse stretched up to 20-ms with a fixed energy of 5.0 keV. It is operated at 50Hz synchronized with the linac operation.

We have conducted a performance test of this system with a 2.5-keV incident beam. A gate valve downstream of the pulse stretch section was closed to let the positrons annihilate on the valve. The annihilation γ -rays were detected with a plastic scintillator mounted on a photomultiplier tube whose anode signals were observed by a digital oscilloscope. By observing the individual annihilation γ -rays while adjusting the width and the time dependent shape of the voltage of the trapping electrode, it was confirmed that the 50Hz positron pulse was certainly stretched up to 20 ms at the same frequency. The temporal distribution of the positrons in the stretched pulse is also adjustable by changing the temporal variation of the voltage of the trapping electrode.

This pulse stretch section can be used for a positron lifetime annihilation spectroscopy by repulsing to be around 100-ps pulse width at around 1MHz by further introducing a chopper and bunchers. The concept of the present system is also applicable for the elevation of the energy of a slow-positron beam after transporting with a lower energy.

* Corresponding author, email address: ken.wada@kek.jp

A simple function for pore-size estimation with PALS analysis

K. Wada* and T. Hyodo

Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0003, Japan

The lifetime of the spin-triplet Positronium, o -Ps, in materials is shorter than the vacuum value owing to pickoff quenching. The o -Ps lifetime has been related to the size of the pore where the o -Ps is trapped [1]. A recent work shows that the probability of the thermalized o -Ps pickoff quenching per collision is almost constant with all the molecules observed so far at room temperature [2]. It supports a prevailing assumption that the pickoff quenching probability is practically independent of the material comprising the pore wall unless paramagnetic centers exist there. Figure 1 shows experimental values of pickoff quenching cross-sections, σ_{pickoff} , for all the molecules previously reported against geometric collisional cross-section, σ_{geom} , estimated from viscosity. The values of σ_{pickoff} are roughly proportional to σ_{geom} , indicating that the pickoff quenching probability per collision, $\sigma_{\text{pickoff}}/\sigma_{\text{geom}}$, does not vary much among those molecules.

This presentation introduces a simple function relating o -Ps lifetime to pore size in a wide range [1], which combines a well-established Tao-Eldrup model for small pores and a model in classical picture for large pores with a parameter adjusted so that its Ps-lifetime to pore-size relation touches smoothly with that of the Tao-Eldrup model. This simple function has also been extended to an arbitrary temperature. A simple temperature dependence of the adjustable parameter makes the model agrees surprisingly well at any temperature with the quantum-mechanics-based extended Tao-Eldrup (ETE) model, which deals with o -Ps trapped in and in thermal equilibrium with a rectangular pore [3]. The present function is pore-shape free and much simpler to use.

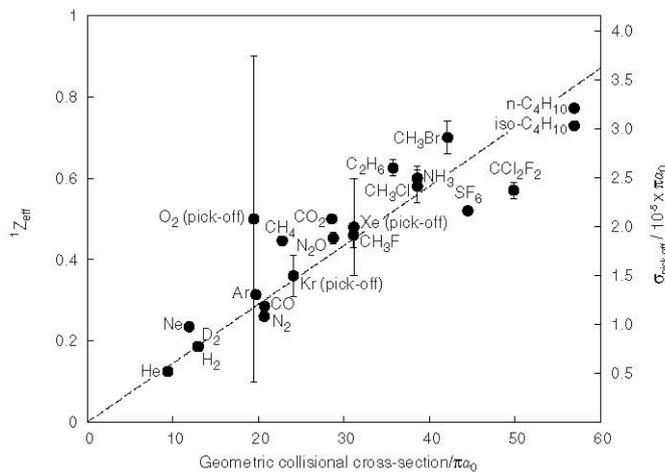


Figure 1: Experimental values of pickoff quenching cross-section against the geometric collisional cross-section (right vertical axis) estimated from viscosity. [2]

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* Corresponding author, email address: ken.wada@kek.jp

Soft-Templated Mesoporous CsTaWO₆ for Photocatalytic Hydrogen Production

Tobias Weller, Roland Marschall*

Institute of Physical Chemistry, Justus-Liebig-University Giessen, 35392 Giessen, Germany

** Roland.Marschall@phys.Chemie.uni-giessen.de, phone: +49-641-9934585*

One alternative to the limited resources of fossil fuels could be a hydrogen-based economy. A promising method to produce hydrogen is the photocatalytic splitting of water on the surface of a semiconductor.^[1] Considering the potential for the water splitting reaction, one can find a minimum band gap (E_g) of 1.23 eV. Kinetic hindering causes an overpotential for both parts of the redox reaction, resulting in a minimum E_g of approx. 2 eV ($\lambda \approx 620$ nm).^[2] Therefore, with photocatalytic water splitting most of the solar light could be converted into chemical energy. High crystallinity and a high surface area are required to increase the catalytic activity of a photocatalyst.^[1] There are different examples of mesoporous semiconducting oxides with photocatalytic activity in literature, such as Ta₂O₅^[3] and Mg–Ta oxide.^[4] However, there is no example for a mesoporous quaternary oxide. Here we present a soft-templating synthesis strategy for mesoporous CsTaWO₆ and its photocatalytic performance. CsTaWO₆ is a semiconductor with a band gap of 3.6 eV^[5] which can be decreased via nitrogen doping to approx. 2.3 eV.^[6] In a typical synthesis, Cs₂CO₃, TaCl₅ and WCl₆ in a molar ratio of 1:2:2 were dissolved in a solution of EtOH, THF, Pluronic P-123 and different additives and poured into Petri dishes. The solution was dried under controlled conditions and calcined at 550 °C. The as-synthesized mesoporous CsTaWO₆ shows a high crystallinity at moderate calcination temperatures with an average crystallite size of approx. 20 nm. The BET surface areas measured by N₂ physisorption are up to 78 m² g⁻¹ and the pore sizes range from 5 to 10 nm, depending on the additives. Figure 1 shows TEM images of mesoporous CsTaWO₆. First photocatalytic measurements demonstrate an increased activity in H₂ generation up to a factor of two, compared to non-porous CsTaWO₆ synthesized via sol-gel citrate route.^[5]

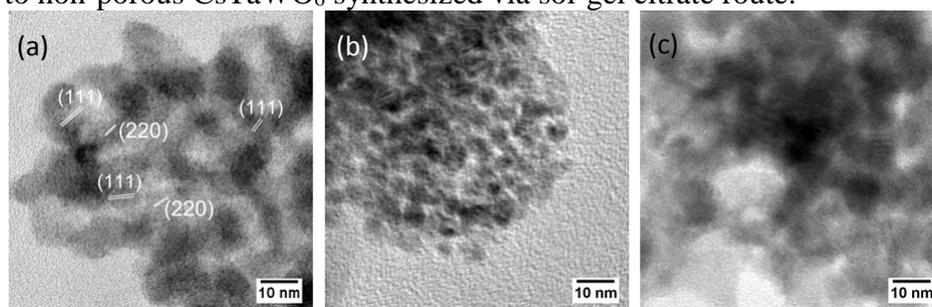


Fig. 1: TEM images of mesoporous CsTaWO₆ prepared with (a) no additives (b) citric acid and (c) sulfuric acid.

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Porosimetry with Positrons

S. Zieger, C. Bluhm, E. Hirschmann, R. Krause-Rehberg

Institut für Physik, MLU Halle-Wittenberg, Halle (Saale) 06099, Germany
reinhard.krause-rehberg@physik.uni-halle.de

Positron-Annihilation-Lifetime-Spectroscopy (PALS) is recognized as an alternative method to characterize porous materials concerning pore sizes and pore size distribution. This poster will give an overview over this technique. One advantage of PALS compared to nitrogen absorption or mercury intrusion: closed pore systems can be detected.

We can measure pores from 0.3 nm up to 50nm or even 70nm with a good resolution. Also temperature-dependent measuring is possible. Questions about the sensitivity of this method and requirements to the sample will be answered and some examples will be shown.

| Nr. | Surname | Given name | Affiliation | Email |
|-----|----------------|----------------|--|--|
| 1 | Krause-Rehberg | Reinhard | Univ. Halle | reinhard.krause-rehberg@physik.uni-halle.de |
| 2 | Attalah | Ahmed Gamal | Univ. Halle | agamal86_physics@yahoo.com |
| 3 | Zieger | Steve | Univ. Halle | steve.zieger@student.uni-halle.de |
| 4 | Bluhm | Chris | Univ. Halle | Chris92mx@web.de |
| 5 | Hirschmann | Eric | Univ. Halle | hirschmann.eric@web.de |
| 6 | Wagner | Andreas | HZDR | a.wagner@hzdr.de |
| 7 | Anwand | Wolfgang | HZDR | w.anwand@hzdr.de |
| 8 | Liedke | Maciej Oskar | HZDR | M.Liedke@fzd.de |
| 9 | Trinh | Trang | HZDR | t.trinh@hzdr.de |
| 10 | Enke | Dirk | Univ. Leipzig | dirk.enke@uni-leipzig.de |
| 11 | Kraatz | Matthias | IKTS Fraunhofer Dresden | matthias.kraatz@ikts.fraunhofer.de |
| 12 | Gulidova | Luydmila | Tomsk Polytechnic University | l_gulidova@bk.ru |
| 13 | Bordulev | Iurii | Tomsk Polytechnic University | bordulev@gmail.com |
| 14 | Hyodo | Toshio | KEK Tsukuba | hyodo96@gmail.com |
| 15 | Uhlig | Hans | Uni Leipzig | uhlig@inc.uni-leipzig.de |
| 16 | Patil | Pushkar Naresh | University of Trento and IPCB-CNR | pushkhem6@gmail.com |
| 17 | Wada | Ken | KEK Tsukuba | wada1275@gmail.com |
| 18 | Pecko | Stanislav | Slovak Univ. of Technology, Bratislava | xpekos@stuba.sk |
| 19 | Köhler | Nicole | ENAS Fraunhofer Chemnitz | Nicole.Koehler@enas.fraunhofer.de |
| 20 | Prochazka | Ivan | Charles University Prague | ivanp@mbox.troja.mff.cuni.cz |
| 21 | Glorius | Maja | Technical University Dresden | maja.glorius@tu-dresden.de |
| 22 | Reichenauer | Gudrun | ZAE Bayern | gudrun.reichenauer@zae-bayern.de |
| 23 | Rückriem | Michael | Porotec GmbH | michael.rueckriem@porotec.de |
| 24 | Tallarek | Ulrich | Philipps-Universität Marburg | tallarek@staff.uni-marburg.de |
| 25 | Reichenbach | Christian | Quantachrome GmbH | christian.reichenbach@quantachrome.de |
| 26 | Mascotto | Simone | Univ. Hamburg | Simone.Mascotto@chemie.uni-hamburg.de |
| 27 | Valiullin | Rustem | Univ. Leipzig | valiullin@uni-leipzig.de |
| 28 | Kuester | Christian | Univ. Leipzig | Christian Kuester <christian.kuester@uni-leipzig.de> |
| 29 | Schneider | Daniel | Univ. Leipzig | daniel.schneider@uni-leipzig.de |
| 30 | Matysik | Jörg | Univ. Leipzig | joerg.matysik@uni-leipzig.de |
| 31 | Zaleski | Radoslaw | Maria Curie-Skłodowska University Lublin | radek@zaleski.umcs.pl |
| 32 | Behrens | Karsten | Univ. Potsdam | kbehrens@uni-potsdam.de |
| 33 | Mayer | Erwin-Peter | Wacker Chemie Burghausen | erwin-peter.mayer@wacker.com |
| 34 | Schwokowski | Birgit | Wacker Chemie Burghausen | Birgit.Schwokowski@wacker.com |
| 35 | Hugenschmidt | Christoph | Technische Universität München | Christoph.Hugenschmidt@frm2.tum.de |
| 36 | Weller | Tobias | Univ. Giessen | tobias.weller@phys.chemie.uni-giessen.de |
| 37 | Loeh | Marc | Univ. Giessen | marc.loeh@phys.chemie.uni-giessen.de |
| 38 | Ellinghaus | Rüdiger | Univ. Giessen | ruediger.ellinghaus@phys.chemie.uni-giessen.de |
| 39 | Beck | Giuliana | Univ. Giessen | giuliana.beck@phys.chemie.uni-giessen.de |
| 40 | Rogaczewski | Mateusz | Univ. Hamburg | matthias.rogaczewski@chemie.uni-hamburg.de |
| 41 | Kuebel | Christian | Karlsruhe Institute of Technology | christian.kuebel@kit.edu |
| 42 | Bilo | Malina | Univ. Hamburg | malina.bilo@chemie.uni-hamburg.de |
| 43 | Simon | Tamás | Univ. Hamburg | tamas.simon@chemie.uni-hamburg.de |
| 44 | Liszka | Laszlo | CEA Saclay | Laszlo.LISZKAY@cea.fr |
| 45 | Djourelou | Nikolay | ELI-NP Project Bucharest | nikolay.djourelou@eli-np.ro |
| 46 | Leca | Victor | ELI-NP Project Bucharest | victor.leca@eli-np.ro |
| 47 | Staab | Torsten | Univ. Würzburg | torsten.staab@matsyn.uni-wuerzburg.de |
| 48 | Petschke | Danny | Univ. Würzburg | Danny.Petschke@matsyn.uni-wuerzburg.de |
| 49 | Antalyali | Günes | Univ. Würzburg | Guenes.Antalyali@matsyn.uni-wuerzburg.de |
| 50 | Greulich | Katharina | Philipps-Universität Marburg | Greulich@students.uni-marburg.de |
| 51 | Plata | Miguel | Univ. Halle, Dept. of Chemistry | miguel.plata@chemie.uni-halle.de |
| 52 | Meyer | Ralf | Univ. Leipzig | ralf.machern@gmail.com |
| 53 | Dornberg | Gregor | Univ. Leipzig | gregor.dornberg@uni-leipzig.de |
| 54 | Consolati | Giovanni | Polytechnic Univ. Milano | giovanni.consolati@polimi.it |