

MLZ Conference: Neutrons for Energy

Monday, 18 July 2016 - Friday, 22 July 2016

Hotel Wyndham Grand Axelmannstein, Bad Reichenhall, Germany



Book of Abstracts

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Welcome by MLZ directors

Session I: Fuel Cells 1 (Chair: Olaf Holderer) / 75

Neutron imaging of polymer electrolyte fuel cells (PEFCs)

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Polymer electrolyte fuel cells (PEFCs) are efficient energy converters mainly foreseen as a replacement for internal combustion engines in mobility application (e.g. automobiles, buses). They use hydrogen as a fuel and allow the vehicles to be free of local CO₂ and pollutant emissions, and the whole supply chain to be nearly CO₂ neutral if the hydrogen is produced from renewable sources. Currently, first models are being put on the market, but the effective contribution to CO₂ reduction will depend on the market penetration of this technology. In this context, an optimization of the PEFC technology in terms of costs is still highly desired. Besides the reduction of the material costs (e.g. membrane and platinum catalyst) per unit area, an increase of power density allows a reduction of the cell area for a specified power output, and thus contributes to the cost reduction. One of the important limiting factors for the power density is the accumulation of product water in undesired locations, which may have the further detrimental effect of reducing the cell lifetime.

In this context, in situ visualization of liquid water in operating fuel cells has attracted the attention of several researchers in the past 10-15 years. Among the different methods proposed (magnetic resonance imaging, x-ray radiography or tomography, optical imaging), neutron radiography bears the decisive advantage of allowing the imaging of relatively small thicknesses of water in fuel cells with no or minimal modifications, the fuel cell structural materials (e.g. aluminum or steel) being readily transparent for fuel cells.

In this talk, the use of neutron imaging in the past years will be presented through a series of examples including:

- 1) Conventional “through plane” imaging of large fuel cells
- 2) High resolution “in plane” imaging of downscaled cells
- 3) High throughput imaging of several cells at the same time

An outlook will also be given, in particular to discuss the boundaries between the application of neutron imaging and other techniques (e.g. x-ray imaging) in future applications. In this context, the combination of in situ imaging with advanced cell instrumentation will be presented.

Session I: Fuel Cells 1 (Chair: Olaf Holderer) / 45

Water distribution at different length scales in operando fuel cells

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Proton Exchange Membrane Fuel Cells (PEMFC) are one of the most promising technologies for powering automobiles and small portable electronics. The functional part of the PEMFC is composed of a membrane which is stacked between two electrodes: the Membrane Electrode Assembly (MEA). This MEA is held by a metallic framework composed of channels that collect the current produced and allow gasses to flow through the cell. Despite intensive research in the field, actual performance and durability of PEMFCs are important drawbacks that prevent large scale commercialization. These two aspects are linked to the way water is structured in the fuel cell at a microscopic and macroscopic scale. Our work focuses on investigating water distribution on these two length scales combining Small Angle Neutron Scattering (SANS) and neutron radiography. Indeed, the membrane present in the MEA is a nanostructured polymer with ionic domains which have a length scale that can be probed by SANS. We can thus monitor the microstructure of water inside the membrane by following the position of a so-called ionomer peak, but can also quantify the total amount of water with the incoherent background [1]. Neutron radiography nicely completes SANS as it gives information on water distribution at a macroscopic length scale, but also because it can probe the out of plane distribution of water (in contrast to SANS that is limited to in plane measurements), offering a 3 dimensional view of the system. The big advantage of SANS and neutron radiography over other techniques, such as small angle X-ray scattering, is that the signal is not very sensitive to the electrodes present in the MEA, allowing us to perform measurements while the fuel cell is functioning.

By reducing the size of the beam during the SANS experiment we can scan different parts of the MEA to get an actual mapping of water distribution inside the fuel cell [2]. This allows us to get information on water structuration as a function of the position in the membrane and amount of current drained. By completing the SANS data with neutron radiography measurements, we get information on length scales spanning from a microscopic to a macroscopic scale. Results show that while the membrane is much more hydrated near the air inlet regardless of the current drained, the amount of water outside the membrane only follows this trend when no current is drained. These results shed a new light on the different mechanisms governing water management inside a functioning fuel cell [3].

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Session I: Fuel Cells 1 (Chair: Olaf Holderer) / 11

Evidence for hydrated channels and connected water clusters in proton conductive membranes based on sulfonated syndiotactic polystyrene

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Syndiotactic polystyrene (sPS) is able to form different kinds of co-crystalline phases with guest molecules of various size, shape and property. Several advanced materials have been already produced based on sPS co-crystalline films with fluorescent, photoreactive, chiral and paramagnetic guest molecules. In particular, sulfonated sPS (ssPS) can be used as proton-conductive membrane (PCM) for fuel cells, as it presents high proton conductivity (comparable with Nafion), it shows a high chemical and thermo-mechanical stability and it has a low cost. In spite of extensive studies the microstructure of PCMs is still subject of active debates and many structural models have emerged to describe the hydrated membranes. In the current study the morphology of different sPS co-crystalline films (clathrate with guest molecules or as empty crystalline form) and the structural features of ssPS upon hydration were thoroughly understood by combining WAXS, FT-IR and TEM with SANS. By exploiting, on one hand, the neutron contrast variation enabled by the selective hydrogenation and deuteration of different regions and constituents of the sPS and ssPS films and, on the other hand, the separation of scattering features from different constituents on specific directions and sectors of the detection plan, using uniaxially stretched films, an unambiguous structural and morphological characterization of such complex systems could be achieved by SANS. The systematic composition and structural investigation on PCMs based on sPS films, starting from their co-crystallization with guest molecules through the sulfonation and the guest exchange processes (for varying the SANS contrast) and followed by subsequent hydration (using H₂O or D₂O for the contrast variation) from liquid phase or vapor phase using a humidity cell, has evidenced in the amorphous regions hydrated channels that connect water clusters and are aligned along the stretching direction. The high conductivity shown by the membranes is supported by these channels, while the mechanical reinforcement is provided by the oriented lamellar staples in the co-crystalline regions.

Session II: H2 Storage (Chair: Anatoliy Senyshyn) / 73

Exploring hydrogen and ammonia as energy storage alternatives to fossil fuels: in-situ neutron powder diffraction studies

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Demand-driven energy use and the intermittency of the majority of renewable energy options together necessitate the development of parallel energy-storage technologies from grid-balancing through to transportation. This talk focuses on the opportunities afforded by hydrogen and ammonia as future energy vectors and the role of in-situ neutron powder diffraction studies in identifying key material systems.

Session II: H2 Storage (Chair: Anatoliy Senyshyn) / 5

Hydrogen dynamics in defective graphene

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Understanding the adsorption of hydrogen atoms on graphene is of paramount importance in a number of fields as diverse as nanoelectronics, energy and hydrogen storage and interstellar chemistry and it appears closely linked to the controversial issue of its mobility at the carbon surface. The recent development of chemical method for producing graphene in gram-scale has opened the doors towards technological applications and characterization techniques that are usually reserved to bulk systems.

In this presentation, I will discuss the dynamics of atomic hydrogen, bonded at the surface of chemically produced defective graphene, as probed by inelastic neutron scattering (INS). The behavior of hydrogen onto the graphene planes appears strongly dependent on the specificity of the sample, namely the presence of surface defects, synthesis, manipulation and hydrogenation conditions. I will show that the hydrogen local environment can be efficiently investigated thanks to its influence on the dynamics of hydrogen itself.

Finally, I will present a brief overview about the complementary use of Neutron and X-Ray scattering in the study of the dynamical properties and local structure of materials for energy applications based on Carbon and beyond.

Session II: H2 Storage (Chair: Anatoliy Senyshyn) / 10

Neutron scattering insight at hydrogen storage in sub-nanopores

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Safe and effective hydrogen storage is widely recognized as a key technology for hydrogen economy in the 21st century, with porous materials being one of the highly potential storage media. The hydrogen storage in such materials is often realized by means of weak Van der Waals interactions between the stored molecule and the pore surface. However, in addition to the surface, interactions between guest and matrix can be expected to be sensitively influenced by structure of the confining host and, in particular, the dimension of the confinement cages. We have explored the microscopic mechanism of hydrogen storage in pores of sub-nanometer size in a broad range of materials, namely ice-based clathrates, recently synthesized CAU-1 metallic organic framework and porous carbide derived carbon (CDC) with help of neutron scattering techniques. Our observations reveal the large quantitative and qualitative impact of details of the confinement structure on the functionally decisive dynamic behavior of the stored molecules.

Thus, in clathrate hydrates we have found that by varying the size of the pore the diffusive mobility of confined hydrogen can be modified in both directions, i.e. reduced or enhanced compared to those in the bulk solid at the same temperatures [1],[2]. In the small cages with a diameter of 0.8 nm the confinement reduces diffusive mobility by orders of magnitude. The observed localization of the hydrogen around the center of the cage provides for the improved functional properties such as gas degassing temperature and the gas loading pressure. In contrast, in large cages with a mean diameter of 0.9 nm hydrogen molecules displays diffusive jump motion between different equilibrium sites inside the cages, observed at temperatures where bulk solid H₂ exhibits no visible mobility. Strong slow-down of diffusion was also observed in CDC with the pore size of 0.8 nm. The experimentally determined self-diffusion coefficient in TiC-CDC with cylinder like pores [3] is about $2.35 \pm 0.7 \text{ \AA}^2/\text{ps}$ at 100 K [4], which is only the third of the diffusion coefficient measured at surface of nanohorns at 25K [5]. In CAU-1 metallic organic framework the sub-nanometer size of the pores promotes the formation of the hydrogen bonds between hydrogen and linkers and the onset of guest-guest correlations [6]. Consequent shrinking of the host framework structure changes in the electronic potential surface inside the pores, leading to the formation additional occupational positions and increased hydrogen intake.

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Session III: Batteries 1 (Chair: Michael Hofmann) / 71**Neutron Depth Profiling: A challenging new method to in situ monitor Lithium in solid-state Li-ion batteries****Author:** Peter H.L. Notten¹**Co-author:** Ruediger-A. Eichel²¹ *Eindhoven University of Technology*² *Forschungszentrum Juelich***Corresponding Author:** p.h.l.notten@tue.nl

Planar thin-film lithium ion batteries nowadays reveal excellent reversible electrochemical performance¹. To increase the energy density of these thin-film batteries, novel approaches have been proposed. One of the new concepts is based on the etching of deep 3D-structures into a silicon substrate, increasing the effective surface area significantly. In combination with advanced materials new opportunities are obtained to increase the energy density further^{1,2}.

Silicon and Germanium turned out to be excellent candidates for Li-storage electrode materials. About 4 Lithium atoms can be stored per Si/Ge atom. The volume expansion is, however, tremendous inducing material deterioration. In order to cope with this various approaches has been adopted. Nano-wires were found to be too mechanically sensitive to be applied in all-solid-state battery stacks. Honeycomb structure has recently also been proposed³. Striking reversible materials deformation has been reported upon (de)lithiation⁴.

An elegant new in situ method has been proposed, denoted as Neutron Depth Profiling (NDP)⁵, which is based on low-energy neutron irradiation of ⁶Li present at various locations inside solid-state Li-ion batteries, leading to the formation of α - and tritons particles. By measuring the energy loss of these particles that reach the NDP-detector, the depth at which these were formed can be deduced. In this presentation the basic principles of this new in situ technique will be highlighted together with some experimental results obtained with all-solid-state batteries.

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5. J.F.M. Oudenhoven, F. Labohm, M. Mulder, R.A.H. Niessen, F.M. Mulder and P.H.L. Notten, *Adv. Mater.*, 23 (2011) 4103.

Session III: Batteries 1 (Chair: Michael Hofmann) / 52**Lithium-Ion Batteries monitored by Neutrons****Author:** Martin Muehlbauer¹**Co-authors:** Anatoliy Senyshyn²; Helmut Ehrenberg³; Michael Hofmann²; Michael Knapp⁴; Oleksandr Dolotko⁵¹ *Helmholtz Institute Ulm (HIU)*² *Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München (TUM)*³ *KIT*⁴ *KIT, IAM-ESS*⁵ *Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München (TUM),***Corresponding Author:** martin.muehlbauer@frm2.tum.de

Powering innumerable portable devices lithium-ion batteries are part of our everyday life. An increasing number of applications related to electromobility and energy storage calls for further improvements of their life span, energy/power density and rate capability. But still some of the processes inside lithium-ion batteries are not understood completely. Therefore single cells or even integrated batteries have to be investigated under real operating conditions to unravel details occurring in the millimetre to micrometre domain and reaching down to a nanometre or even atomic length scale. Neutrons offer a capability to conduct in operando investigations on standard size Li-ion cells. Light elements like lithium and other cations may be traced during intercalation and deintercalation providing information about structural changes and phase transitions in electrode materials. Neutrons are sensitive for different cations, e.g. they allow to follow the substitution of Li by Ni atoms in the structure of cathode materials [1]. Neutron imaging and spatially resolved diffraction experiments pointed out possible inhomogeneities of the state of charge inside 18650-type Li-Ion cells. Such inhomogeneities of the lithium concentration inside the anode for fully charged cells were found and could be quantified by spatially resolved neutron diffraction on a macroscopic length scale [2, 3]. Here a correlation between the cell design and the lithiation state of the graphitic anode has been found. Applying wavelength dependent imaging techniques enables to optimize contrast and transmission of a given sample and to reduce beam hardening artefacts during a tomographic reconstruction, which are present for a polychromatic neutron beam. The wavelength dependent neutron transmission signal is sensitive for Bragg edges of the different crystallographic phases occurring inside Li-ion cells. Given the necessary wavelength resolution this imaging technique might provide information on the homogeneity of the state of charge inside an operating cell similar to the results gained by spatially resolved neutron diffraction.

Findings based on a combination of electrochemical cell characterization, neutron imaging and scattering techniques will be presented. Obtained results will be discussed in terms of their influence for the future design of Li-ion cells, for example with respect to the cell geometry (tab positions) and the cell balancing.

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Session III: Batteries 1 (Chair: Michael Hofmann) / 26

Ionic diffusion in battery cathods, e.g. Na_{0.7}CoO₂

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Diffusion is one of the key areas in neutron spectroscopy. The accessible time scale covers fortunately the ionic diffusion in battery cathodes. Evenly important that state-of-the art instrumentation provides sufficient intensity and signal-to-noise ratio for measuring ionic diffusion in a host material, although pushing the experimental possibilities to the limits.

This talk will focus on atomic scale Na diffusion in Na_xCoO₂, which is the Na analogue of the commercially used Li compound. It belongs to the layered transition-metal oxide family with promising properties for commercial applications. Temperature dependent neutron powder diffraction (HRPT, PSI) revealed two phase transitions (at about T_A=290K and T_B=400K), which are connected to successive opening of Na diffusion paths. Between T_A and T_B the lattice deforms in a way that Na sides gets closer to each other allowing for quasi-1D (zig-zag) diffusion. Above T_B Na diffusion occurs in

a plane via jumps on the hexagonal lattice.

Inelastic fixed window scans from MARS, PSI ($\delta E=13\mu\text{eV}$) and from IN16b, ILL ($\delta E=0.85\mu\text{eV}$) indicate sudden change in the dynamics at the phase transition temperatures. At both instruments quasielastic spectrum is present above T_B , whereas at the new IN16b the QENS intensity is continuously increasing from T_A . The later being especially important because of probing the diffusion in the temperature range relevant for application. Puzzling is however the comparison of the results with muon-spin relaxation ($\mu^+\text{SR}$) data, which will be discussed in detail. This technique has been successfully applied in the last years to measure ionic diffusion in this type of materials. Although these results are only the first steps, the relevance of neutron scattering in fundamental understanding of ionic diffusion at the atomic scale is unquestionable for the design of novel cathode materials.

Session III: Batteries 1 (Chair: Michael Hofmann) / 4

Looking non-destructively at the aging mechanisms in commercial LiFePO₄//C 18650 cells with neutron diffraction and electrochemistry

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Aging in identical commercial 18650 LFP//C Li-ion cells, differing only in the choice of the carbon anode, was studied in a non-destructive way with neutron diffraction and electrochemistry. In all cells, the irreversible capacity losses due to active lithium losses upon battery formation and cycling were quantified by neutron diffraction. These values were validated by electrochemical techniques. The LFP//MCMB cell, having mesocarbon microbeads as carbon anode material, shows an excellent performance with only a 8% of relative capacity loss at 1C after 4780 cycles. The capacity drop was found to be related to the loss of active lithium and can be detected by neutron diffraction. The LFP//NC cell, having needle coke as carbon anode, suffers a higher irreversible capacity loss, probably due to formation of a thicker SEI layer. It also shows a poorer cycling performance compared to LFP//MCMB, with 23% relative capacity loss at 1C. Only 8% of this loss is due to decrease of active lithium amount and can be detected by neutron diffraction. No appreciable structural degradation of electrode materials can be seen in any cell with neutron diffraction. Based on the neutron diffraction results we can rule out a capacity decrease due to partial loss of carbon or LiFePO₄ active material from electrode delamination or particle isolation. For the mesocarbon microbead powder, XRD measurements reveal a larger *c*-lattice parameter and a smaller crystalline size, as compared to the needle coke powder. The comparative poor cycling performance of the LFP//NC cell is probably due to the higher initial irreversible capacity loss due to SEI formation (which grows more rapidly on aging), different charging kinetics and structural differences in the carbon powders at the anode.

Session IV: Photovoltaics (Chair: Henrich Frielinghaus) / 78

Hybrid halide perovskite solar cells, disorder, and the dynamics of methyl ammonium ions

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Hybrid organic-inorganic solar cells based on hybrid organic-inorganic halide perovskite structures are promising candidates for cheap, solution processed, highly efficient (>20%) solar cells with a short energy payback time. The materials display many interesting behaviours such as high dielectric constants, ionic transport, photostriction, and hysteresis in the photovoltaic properties, some of which have been proposed to be related to the presence of the polar organic cation methylammonium. I will discuss quasielastic neutron scattering measurements showing that dipolar CH₃NH₃⁺ ions reorientate between the faces, corners or edges of the pseudo cubic lattice cages in CH₃NH₃PbI₃ crystals with a room temperature residence time of around 14 ps. Free rotation, π flips and ionic diffusion are ruled out within a 1 - 200 ps time window. I will discuss the implications of these measurements, as well as structural and dynamic disorder in the crystals, for the properties and behaviour of perovskite semiconductor devices.

Session IV: Photovoltaics (Chair: Henrich Frielinghaus) / 58

Crystal structure and point defect characteristics of quaternary compound semiconductors by neutron diffraction.

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Quaternary semiconductors Cu₂BII₂CIVX₄(BII–Zn,Cd,Hg;CIV–Si,Ge,Sn;X–S,Se,Te) are considered as interesting material for applications in optoelectrics and non-linear optics. Cu₂ZnSn(S_{1-x}Se_x)₄ mixed crystals (CZTSSe) are promising semiconductor materials for absorber layer in thin film solar cells due to a direct band gap in the range 1-1.5 eV and a high absorption coefficient (>10⁴cm⁻¹). A record efficiency of 12.6% was reported for a CZTSSe based thin film solar cell, here the polycrystalline absorber layer exhibit an off-stoichiometric composition. The non-stoichiometry can be attributed to the presence of various point defects (such as vacancies, interstitials, antisites, etc.). These defects influence the generation, separation, and recombination of electron-hole pairs and overall, the efficiency of the photovoltaic device.

All of the compounds from the CZTSSe solid solution contain the isoelectronic cations Cu⁺ and Zn²⁺, which makes the accurate structure determination using X-ray diffraction not possible, due to their similar scattering factors. Neutrons diffraction can solve this problem; the coherent scattering lengths are sufficiently different for these cations. Using neutron diffraction it was shown that both of the stoichiometric end members of this solid solution, crystallize in the kesterite type structure (space group $I\bar{4}$). Moreover we have demonstrated that kesterite type materials can self-adapt to Cu-poor and Cu-rich compositions without any structural change except the cation distribution. A detailed structural analysis of stoichiometric CZTSSe as well as off-stoichiometric CZTS and CZTSe powder samples, grown by solid state reaction, was performed by neutron diffraction, the data were collected at the Berlin Research Reactor BER II at the Helmholtz-Zentrum Berlin für Materialien und Energie using the fine resolution powder diffractometer FIREPOD (E9) ($\lambda = 1.7982 \text{ \AA}$;RT). Rietveld refinement of neutron diffraction data using the FullProf suite software lead to accurate values of lattice constants and site occupancy factors. Applying the average neutron scattering length analysis method, the cation distribution was evaluated. Taking into account the necessity to keep the charge balance, point defect types and their concentrations have been elaborated from the cation distribution. We have shown that the evaluated off-stoichiometry and the concentration of intrinsic point defects correlate with the variation in chemical composition in CZTS/Se from Cu-poor to Cu-rich related stoichiometry deviations. Thus we have revealed the possibility to deduce occurring point defects from the chemical composition of the kesterite phase.

The correlated information about changes in lattice parameters and cation site occupancies in dependence on the off-stoichiometry in CZTS and CZTSe and on the Se content in stoichiometric CZTSSe and details on the existing intrinsic point defects and their concentrations will be discussed.

Session IV: Photovoltaics (Chair: Henrich Frielinghaus) / 46

Inelastic Neutron Scattering on Colloidal Nanocrystal Solids: Understanding the Importance of Surfaces

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Colloidally synthesized nanocrystals (NCs) are being developed for a large number of energy-related devices, including solar cells, thermoelectrics, and batteries. To function in solid-state devices, these solution-processed NCs are assembled into 3D superlattice structures, known as NC-solids. While phonon density-of-states ($g(\omega)$) have been measured and calculated in bulk crystalline semiconductors, phonons remain poorly understood in nanomaterials, despite the critical importance of phonons in determining how energy is gained, lost, and transported in materials.

I will present the first experimental investigation of the $g(\omega)$ of NC-solids carried out via Inelastic Neutron Scattering (INS) [1]. We determined the $g(\omega)$ of lead sulphide (PbS) NC-solids, explained the origins of their differences with the $g(\omega)$ of bulk PbS, and used our findings to gain insight into charge carrier recombination in PbS NC solar cells.

Specifically, we measured the $g(\omega)$ as a function of PbS NC size, and found low and high frequency phonon modes with large thermal displacements in nanosized PbS that are not present in bulk PbS. The experimental results were complemented with ab initio molecular dynamics (AIMD) simulations of the NCs, which showed that these modes come from the NC surface. The partial $g(\omega)$ in the core of the NCs remains as in the bulk. Using thermal admittance spectroscopy (TAS) measurements on a large number of PbS NC-based diodes, we measured the energy and rate of the electronic transitions. With the theoretical framework of Multi-Excitation Entropy, we could explain the unusually high transition rates by coupling of the quantum-confined electronic states of the NCs to the large displacement phonon-modes at the NC-surface.

To reduce the electron-phonon coupling and decrease charge recombination dynamics, we look toward the surface molecules (known as ligands) that are primarily used to tune the electric conductivity of NC-solids. We demonstrate that, contrary to previous thinking that certain ligands electronically passivate the nanocrystal and remove mid-gap electronic traps states, these best performing ligands (1) mechanically strengthen the surface of the NCs, dampening out high displacement surface modes, and (2) confine the electronic wavefunctions, decreasing their spatial overlap with the surface phonon modes.

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Session V: Batteries 2 (Chair: Helmut Ehrenberg) / 57

Developing new varieties of electrochemical cells for operando neutron diffraction investigations of lithium ion battery materials

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While the interest and frequency of performing operando neutron diffraction experiments for lithium ion batteries has increased significantly over the past few years, it is still not nearly as popular as operando X-ray diffraction. A major contributor to this is the high difficulty of constructing an electrochemical cell which balances both electrochemical performance, quality of the obtained diffraction pattern and cost of construction. Up until now most work has been performed on, often complex, custom cells built to target a specific feature such as fast cycling at the cost of data quality or data quality with high material loading [1-3].

A significant amount of work has been performed within our group on developing multiple varieties of electrochemical cells for operando neutron diffraction. Given the nature of neutron diffraction it is extremely difficult to develop a single cell to suit all objectives and materials. To this end we have designed two vastly different operando cells; a large wound 18650-like cell and a smaller, cheaper coin cell design. The 18650-like wound cell can contain up to 4 g of active material, is able to be cycled at faster rates and provides a diffraction pattern which is of high enough quality to extract accurate structural parameters. It does, however, require expensive deuterated electrolyte and specialised equipment. Alternatively, the coin cell design is cheap, does not require deuterated electrolyte, can provide good quality diffraction and reasonable electrochemical cycling rates. It is anticipated that the coin cell design will make neutron diffraction accessible to more research groups and also presents a viable cell design for operando neutron diffraction studies of sodium ion cells. Using LiFePO₄, LiNi_{0.5}Mn_{1.5}O₄ and Li_{0.18}Sr_{0.66}Ti_{0.5}Nb_{0.5}O₃ as case study materials this contribution will focus on the operando neutron diffraction results obtained from both cells, thus exploring the core strengths and potential of each design.

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Session V: Batteries 2 (Chair: Helmut Ehrenberg) / 49

Study of Sn and Fe based electrode materials for Alkali-ion batteries by in situ Mössbauer spectroscopy

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Li-ion batteries are widely used for electrochemical energy storage, because of their high energy density and efficiency. The most significant challenges in the development of advanced Li-ion batteries concern the electrode materials. Indeed, the electrodes properties critically determine the capacity, performance, and durability of alkali-ion batteries.

In the past five decades, Mössbauer spectroscopy has been an important analytical technique for investigating the structural, magnetic and electronic properties of energy materials. Mössbauer spectroscopy allows simultaneous investigation of bulk and surface characteristics. It is a non-destructive technique that can follow the behavior of electrode materials during the reaction process in situ and operando [1]. Its high resolution enables the observation of all Mössbauer active phases and the measure of their relative quantities .

Iron and tin containing materials are of considerable interest as electrode material for Li-ion batteries [2, 3]. In this presentation, we report in situ and operando measurements of new electrode materials based on Fe and Sn during electrochemical cycling by combining Mössbauer spectroscopy with complementary techniques (X-ray diffraction, magnetic measurements, impedance spectroscopy, etc.) to study and investigate the electrochemical behavior of the electrode materials.

Acknowledgment

A. Mahmoud and F. Boschini would like to kindly thank the Walloon region (Beware Fellowships Academia 2015-1, RESIBAT n° 1510399) and the FNRS for financial support. [Work by AM and RPH carried out in part while at Forschungszentrum Jülich GmbH].

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Session V: Batteries 2 (Chair: Helmut Ehrenberg) / 61

Neutron depth profiling, present day applications in Lithium ion batteries

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First used to measure Boron impurities in silicon wafers, neutron depth profiling has recently gained renewed attention as a non-destructive method for studying of lithium concentration variations along the electrode depth in lithium ion batteries. The presenter will demonstrate application to the high power density and environmentally benign cathode material LiFePO₄. The results obtained, both in operando as well as ex-situ, provide important insight for electrode design and inspire the development of novel computational methods.

Session V: Batteries 2a (Chair: Helmut Ehrenberg) / 74

Ion containing polymers for battery technology

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Polymer electrolytes have potential for use in next generation lithium and sodium batteries. Replacing the liquid electrolyte currently used has several advantages: it allows use of high energy density solid lithium as the anode, removes toxic solvents, improves safety, and eliminates the need for heavy casings. Despite their advantages, the conductivity of solid polymer electrolytes is not sufficient for use in batteries. As a result, considerable effort towards improving conductivity and understanding mechanisms of lithium transport has taken place over the last 30 years. This talk considers the interplay of conductivity, crystallinity, local coordination and polymer dynamics in solid polymer electrolytes. Using a combination of experimental and computational technique, we propose the possibility of high charge mobility using ion aggregates and percolated nanofiller networks

Poster Session - Board: 13 / 35

Structural features and proton transport of polymer electrolyte membranes for high-temperature fuel cells

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Proton conducting polymer electrolyte membranes, in particular, commercially available polybenzimidazole (PBI) attract increasing interest for high-temperature polymer electrolyte fuel cells (HT-PEFC) operating at 160-180°C. HT-PEFC are promising energy converters for stationary (e.g. based on natural gas reforming and combined heat generation) and mobile applications, such as auxiliary power units due to their high tolerance for fuel impurities, i.e. CO and environmentally friendly operation (water as by-product of electrochemical reaction) [1]. Excellent thermal and chemical stability of PBI-based membranes in combination with sufficient conductivity after impregnation with phosphoric acid (PA), which has the highest known intrinsic proton conductivity, assures sufficient conductivity of the these membranes.

In order to get a better understanding of the crucial parameters of the HT-PEFC, e.g. its conductivity and overall performance, structural features of PBI-based membranes have been investigated on the length scales ranging from sub-nm up to several micrometers [2]. Different scattering and imaging techniques such as X-ray diffraction (XRD), neutron diffraction with polarization analysis, small angle neutron- and X-ray scattering (SANS and SAXS respectively), polarized light- and transmission electron microscopy (TEM) have been used. Impact of the temperature changes as well as aging effects will be discussed. Obtained results are linked to proton diffusion measured over a wide time scale by means of pulsed-field-gradient nuclear magnetic resonance PFG NMR and neutron spectroscopy [3] as well as macroscopic parameters of the fuel cell.

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Poster Session - Board: 15 / 42

Low-temperature performance of Li-ion batteries probed by high-resolution neutron diffraction and electrochemistry

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Due to high power/energy density, good cycle life and excellent storage characteristics lithium ion batteries are considered as the major energy storage technology in the field of portable electronics and electric vehicles. Despite the overall success of Li-ion energy storage technology a number of research targets toward even higher energy/power density, lighter weight, safer and lower cost rechargeable batteries has been defined. Besides these factors, having undoubtedly high scientific and technological relevance, the stability of the Li-ion cells in a broad range of environmental conditions has to be addressed, where operating temperature is the most important criteria. According to the recommended range of Li-ion battery operation (typically -20-60°C for discharge and 0-60°C for charge) their use in countries with moderate and frigid climate in winter time becomes quite bounded. This becomes even more critical in aerospace applications, where stable energy storage and conversion is demanded over a long period of time under even more challenging environmental conditions. Therefore broadening the temperature range where lithium ion battery technology shows stable performance and characteristics is an emergent research task. In this context the lower temperature boundary of operation has obviously higher priority compared to the high temperature one.

The poor performance of Li-ion cells is usually ascribed to effects like low electrolyte conductivity, slow kinetics of charge transfer, increase of the solid-electrolyte interphase resistance or slowing down of lithium diffusion through it, lithium plating or to a combination of these different factors. Active research devoted to boost electrolyte performance further below the freezing point and towards higher conductivity. In the current contribution a combined in situ neutron powder diffraction and electrochemical study on Li-ion cells of 18650-type, in a temperature range -43-37°C is reported. The main focus is put on the role of the graphite anode (as a most likely source of failure) with respect to the low temperature performance of the cell. Instead of a quasi-continuous behaviour observed at ambient temperatures, a thermodynamic anomaly occurs at the graphite anode upon a discharge at low temperature, which is primarily reflected in the character of the LiC₁₂-to-graphite phase transformation and the unusual temperature dependence of LiC₆. Freezing of the liquid electrolyte at temperatures below -23°C in a long range ordered structure was experimentally determined with no hints for lithium plating observed [1]. Obtained anomalous behavior is associated to a thermodynamical instability of lithiated graphite phases at temperatures below -23°C, which influences the performance of Li-ion batteries at low temperatures.

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Poster Session - Board: 30 / 29

Neutron spin-echo spectroscopy: a tool for energy research

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Present and upcoming research facilities allowing very high resolution neutron spectroscopy to analyze transport processes in energy materials are presented and their potential is discussed. Among the in particular the possible future use of the refurbished J-NSE and the instrument at SNS as well as aspects of upcoming wide-angle NSE are addresses. Applications range from ion (H) transport in electrolytes for fuel cells and batteries to diffusion in storage materials.

Poster Session - Board: 11 / 28

Battery and materials research at the diffractometer STRESS-SPEC at FRM II

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At the German neutron source Heinz Maier-Leibnitz (FRM II) the diffractometer STRESS-SPEC is the dedicated instrument to tackle problems in the field of engineering and applied materials science. Modern materials science spans a wide field of scientific areas including the analysis of residual stresses, characterisation of textures and in-situ phase analysis of high performance alloys. More recently the possibility to perform spatial and time resolved diffraction has increased the interest in battery research at STRESS-SPEC. However, the different science topics require flexibility of the instrument setup. Consequently in order to address all these applications the instrument was designed to offer always a good compromise between flux and resolution for the respective measurement problem [1].

Several examples of measurements performed at STRESS-SPEC are shown in the following as a selective overview to demonstrate the wide range of possible energy related materials science applications.

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Poster Session - Board: 16 / 43

Crystal Structures and Thermoelectric Properties of A₈Al₈Si₃₈ (A = K, Rb and Cs)

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Intermetallic clathrates with the host-guest type structures attract an interest as perspective materials for thermoelectric applications. Recently, they were also proposed as possible materials for solar energy conversion [1] and as anode materials for lithium ion batteries [2-3]. The intermetallic clathrates are mainly formed by the group IV elements as the host atoms and alkaline or alkaline earth metals as the guests with the latter being the majority [4]. Particularly, the host framework can be formed by the partial substitution of group 14 elements by group 13 elements or transition metals.

We have prepared $A_8Al_8Si_{38}$ clathrates (A=K, Rb and Cs) [5] by a combined flux method that allows to obtain pure samples as crystalline gray powders. The crystal structures of these compounds were studied using high-resolution neutron powder diffraction. The neutron scattering experiments were performed on the powder diffractometer SPODI at the research reactor FRM-II (Garching, Germany). The Rietveld refinements of the crystal structures were carried out using the FullProf package [6]. The distribution of Al atoms in the framework as obtained from neutron data was additionally confirmed by solid state ^{27}Al -MAS NMR. Thermoelectric properties were investigated on the cold pressed pellets prepared in a High Pressure Multi-Anvil apparatus. The resistivity, thermal conductivity and Seebeck coefficient were measured in the temperature range from 2 to 400 K.

Studied compounds $A_8Al_8Si_{38}$ possess type-I clathrate structure and crystallize in the cubic space group $Pm\bar{3}n$ and lattice parameter $a = 10.48914(6)$ Å, $10.53163(7)$ Å and $10.58734(7)$ Å for $K_8Al_8Si_{38}$, $Rb_8Al_8Si_{38}$ and $Cs_7.9Al_7.9Si_{38.1}$, respectively. All host positions in the framework show mixed occupancy by Al and Si, but their distribution slightly varies depending on the type of guest atoms. All $A_8Al_8Si_{38}$ clathrates are n-type semiconductors with a relatively low thermal conductivity and a high Seebeck coefficient.

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Poster Session - Board: 28 / 24

MARIA –The high-intensity polarized neutron reflectometer of JCNS

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The high-intensity reflectometer MARIA of JCNS is installed in the neutron guide hall of the FRM II reactor in Garching and is using a combination of a velocity selector and a Fermi-Chopper for the

monochromatization of the neutron beam (1%,3%,5% or 10%). The full cross section of the beam is polarized by a double-reflecting super mirror and in the vertical direction the elliptically focussing neutron guide increases the flux at the sample position and consequently reduces the required sample size or measuring time. A flexible Hexapod, as sample table, can be equipped with an electromagnet (up to 1.1T) or a cryomagnet (up to 5T), low temperature sample environment, a UHV-chamber (10^{-10} mbar range) for the measurement of Oxide MBE samples (transfer forth and back) and last but not least with various soft matter cells. Together with the $400 \times 400 \text{ mm}^2$ position sensitive detector and a time-stable ^3He polarization analyser based on Spin-Exchange Optical Pumping (SEOP), the instrument is well equipped to investigate specular reflectivity and off-specular scattering from magnetic layered structures down to the monolayer regime. Furthermore the GISANS option can be used to investigate lateral correlations in the nm range. All the options, like GISANS, polarization and ^3He polarization analyser can be moved in and out of the beam in seconds by remote controlled push button operation and do not require any realignment.

MARIA is a state of the art reflectometer at a constant flux reactor. It gives you the opportunity to investigate easily reflectivity curves in a dynamic range of up to 7-8 orders of magnitude including off-specular scattering and GISANS measurement. Furthermore the high intensity allows for kinetic measurements down to a few seconds over a dynamic range of 3-4 orders.

Poster Session - Board: 10 / 25

Dynamic and Structure of Polymer-Cellulose Composite Electrolyte for Li-ion Battery

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Polymer electrolytes are safer, cleaner, and more flexible than liquid electrolytes that are currently being used in Li batteries. However, polyethylene oxide (PEO) based electrolytes are not stiff enough to prevent dendrite formation, which limits the use of Li metal as an anode. They also do not have high enough conductivity to be practical. In amorphous polymer electrolytes, stiffness and conductivity are inversely related because Li motion is coupled to polymer motion, and any attempt to improve conductivity through faster polymer motion results in decreased stiffness. The crystalline PEO6LiX complex is a tunnel-like polymer/salt structure that promotes fast Li motion. The application is limited because high ion conductivity is only observed with short molecular weight PEO, as the molecular weight increases, growth of crystalline lamellae fold tunnels on themselves and restrict conduction.

We show that high aspect ratio nanofillers based on cellulose nanowhiskers promote the formation of tunnel structures. These fillers offer controllable surface chemistry, degree of functionalization and aspect ratio, thus forming an ideal model system. In this work, we fabricate high molecular weight PEO/cellulose nano whiskers nanocomposites. Compared with unfilled electrolytes, room temperature ion conductivity increases up to 1100%. With wide angle x-ray scattering (WAXS), we observe that the structure transitions from amorphous to crystalline as we add cellulose nano whiskers. This is because the interaction between the acidic cellulose surface and polymer chains enhances crystallization. Based on the temperature dependence of conductivity, acidic cellulose nano whiskers reduce the activation energy for Li⁺ hopping. Using quasi-elastic neutron scattering (QENS), we find that the rotation of PEO6 channels are stabilized when acidic surfaces are present. We believe this is the origin of the low activation energy and high conductivity.

Poster Session - Board: 26 / 21

–Photons for Energy - Complementary Analytics

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New high performance materials like CoRe alloys which can improve the efficiency of gas turbines and Lithium ion batteries as energy storage device in electric vehicles or even large scale electric storage device combined with photovoltaic energy sources are just two examples of new materials which could help to solve the energy problem and reduce the worldwide CO₂ pollution.

X-ray diffraction is a powerful technique to analyze such materials on the atomic level to obtain complementary informations which are not accessible with neutron scattering measurements.

In this poster we will present three examples which demonstrate the capability of this technique. We will show the correlation of the variation in the crystallographic structure of the elements of CoRe-TaC alloys exposed to high temperatures or in battery pouch cells directly with the amount of Lithium incorporated in the cathode or the anode.

The first example shows the development of a new sample stage to measure thin pouchbag batteries in transmission setup using Mo radiation. This allows to measure a LiNMC (LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂) //graphite battery in operando and shows that it is possible to follow the structural changes due to the de-intercalation of Lithium simultaneously on the anode (graphite) and cathode (LiNMC) during charging and discharging with high speed and sufficient resolution. (Project ExZellTUM)

In the second example, we compare fresh and aged pouch cells of LiFePO₄/C chemistry to understand cell degradation. With in-operando XRD during cell cycling, we demonstrate differences in the structural evolution of crystalline phases in these cells. In the cathode of the fully discharged aged cell, weight fraction of LiFePO₄ has reduced whereas the FePO₄ weight fraction has increased. In the anode of the fully charged aged cell, the weight fraction of the LiC₆ phase has reduced. These changes are directly related to the loss of electrochemically active Li due to cell aging. (Project EEBatt)

The third example focuses on the formation and stability of Tantalum Carbide precipitates in Co-Re base superalloys. These precipitates are considered to be the main strengthening phase of the material and have a strong impact on the mechanical and thermal properties of the material. The alloys are exposed to temperatures up to 1500°C which severely changes the alloy's structure. The martensitic transformation of Co-Re matrix in fcc and hcp phase influences the TaC stability and is investigated by XRD.

The Poster will be completed by an overview about the current lab equipment, the techniques which are provided by the lab and a statistic about the usage of the lab.

Poster Session - Board: 8 / 23

In-operando neutron reflectometry studies on Li incorporation and volume modification of silicon electrodes in Li-ion batteries

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The rapid development of renewable energies, portable electronics and electric vehicles has encouraged the development of energy storage devices, such as Li-ion batteries, toward longer lifespan, higher energy density and power density. This necessitates the exploration of new materials for use in current Li-ion battery technology [1]. The lithium-ion battery storage technology has also the potential to play an important role in the off-grid renewable energy sector [2].

Due to its high theoretical specific capacity of about 4200 mAh/g amorphous silicon has become a promising anode material for future Li-ion battery applications and is on the way to replace graphite as dominating anode material in commercial batteries [3].

The objective of our work is to study Li incorporation into the electrode as well as the accompanying tremendous volume changes occurring during cycling. These phenomena are important to improve battery performance and to reduce irreversibility effects. For our experiments, we applied the non-destructive analysis technique of neutron reflectometry. This method allows to study processes and interface phenomena on nanometer length scales during cell operation in-operando.

The experiments were done using a self-constructed three electrode electrochemical half-cell setup. The working electrode consists of a nanometer-sized amorphous silicon thin film deposited by magnetron sputtering on a quartz block covered by a current collector. Counter and reference electrode are made of pure lithium metal foil. As an electrolyte, propylene carbonate with 1 M LiClO₄ is used [4].

Our experiments reveal that it is possible to monitor volume changes and Li content during cyclic voltammetry and galvanostatic experiments in-operando. Recent results are presented and discussed in the framework of literature data.

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Poster Session - Board: 27 / 41

Neutron backscattering for high energy resolution spectroscopy on energy related materials

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Neutron backscattering spectroscopy is an advanced method for studying the microscopic dynamics of materials related to energy and covering many of the topics of this conference. Its strength lies in the possibility to access a wide momentum transfer range up to to high Q with sub- μ eV energy resolution. IN16B at ILL with its high flux and signal-to-noise ratio is probably the most advanced spectrometer of this type [1].

A special feature of neutron backscattering at reactors is elastic and inelastic 'fixed window scans' [2] which allow for fast parametric studies with a high monochromatic flux which can be used in a selected narrow energy channel during the full measuring time and can be triggered by or scanned as a function of a sample parameter like temperature, pressure, electric field, light or other

stimuli. This allows to detect with high sensitivity the onset of dynamic processes as function of a control parameter, and thus to guide efficient full spectroscopic measurements on BS and TOF instruments. Spectroscopy can then be carried out in a relatively narrow energy range with classical backscattering, in a more extended range in future with BATS [3,4] or if needed to be combined with another TOF spectrometer to complement the energy range.

Recent backscattering experiments on IN16B cover topics like Hydrogen storage, Proton, Sodium, Lithium and Oxygen conduction, ionic liquids, membranes for fuel cells and batteries, materials related to organic and hybrid solar cells and catalysis. The high flux of IN16B has also created new possibilities for in situ or in operando experiments like the first attempt to carry out backscattering spectroscopy on a fuel cell in operation shows.

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Poster Session - Board: 20 / 1

Neutron Diffraction Studies of Catalytic GaN/ZnO Nanoparticles

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The search for the clean and recyclable energy sources is an ongoing effort for variety of scientific communities. One of the approaches is the hydrogen generation using solar water-splitting photocatalysis. The most promising materials for such catalysis are GaN/ZnO nanoparticles with extremely narrow energy-band gap. Their performance is significantly improved as compared to the bulk counterparts due to more efficient electron-hole pair separation, short electro-hole diffusion lengths to the interface and large interfacial surface area. However, our understanding of these materials is still very limited and it is not yet clear how the energy gap could be further reduced. It is partially related to the fact that interpretation of the x-ray scattering data of GaN/ZnO nanoparticles is difficult due to low contrast between the atoms. On the other hand, the crystal structure of nanoparticles can have size induced deviations from the average crystal structure. In this work we show how neutron diffraction and pair-distribution function (PDF) analysis successfully overcome those limitations and provide local and average structure of GaN/ZnO nanoparticles in a single neutron diffraction experiment. We used four different types of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanoparticles, with size of 10-50 nm and $x=0.075-0.56$, which show the narrow energy-band gap (2.21-2.61 eV). The neutron diffraction experiments were carried out at the Nanoscale-Ordered Materials Diffractometer (NOMAD) at Spallation Neutron Source in Oak Ridge National Laboratory. The Rietveld analysis of the data provided the average crystal structure, while PDF analysis was used to probe the local structure of our samples. The Rietveld analysis revealed hexagonal wurtzite structure of nanoparticles, in agreement with previous reports on bulk materials with a similar composition. However, the local structure was found to be substantially disordered. The level of disorder is size-dependent. Based on our results we propose how the composition, size and nitridation temperature might be varied in order to obtain GaN/ZnO nanoparticles with energy-band gaps below 2.21 eV.

Poster Session / 16

Materials for nuclear fusion examined by neutrons: Neutron computed tomography on carbon fiber composites for plasma divertors

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In the Wendelstein 7-x fusion experiment, plasma divertors are employed to delimit the plasma, and to extract thermal energy. Carbon fiber composite (CFC) plates are bonded to water-cooled copper blocks by copper solder that hooks into laser-drilled holes in the CFC.

After extensive irradiation in a plasma test facility, a slight increase in surface temperature was detected which was caused by localized failures in the interface. Three-dimensional high-resolution neutron computed tomography was performed on small cut-out test samples of the interface, and a liquid contrast agent that had penetrated into hollow spaces revealed delamination between the CFC and copper structure, which was caused by large differences in the heat expansion coefficients of the two materials. The tomographic examination yields an important contribution for the detailed interpretation of spatially extended interface failures.

Poster Session - Board: 3 / 6

Determination of anodic transition metal deposition with PGAA

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The performance degradation of graphite/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC) lithium ion cells, charged and discharged up to 300 cycles at different operating conditions of temperature and upper cutoff potential (4.2V/25°C, 4.2V/60°C, 4.6V/25°C) was investigated. A combination of electrochemical methods with X-ray diffraction (XRD) both in situ and ex situ as well as neutron induced Prompt-Gamma-Activation-Analysis (PGAA) allowed us to elucidate the main failure mechanisms of the investigated lithium ion cells. PGAA was used to determine the amount of anodic transition metal deposition. In situ XRD was used to calibrate the structure-capacity relationship and revealed slow kinetics of the lithium re-insertion into the NMC-host lattice. Ex situ XRD was then used to extract the amount of remaining lithium from cathodes and compare it to electrochemically observed capacity losses. Additional electrochemical methods then round up the picture of the cell aging investigation. The focus of the presentation will be on the determination of the anodic transition metal deposition with the PGAA technique and its relation to the aging behavior of the cells under the investigated parameters.

Poster Session - Board: 21 / 8

SANS experiments on wood during pretreatment in ionic liquid/water mixtures

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Cellulose makes up for most of the material in the lignocellulosic's cell wall, and it could provide an abundant source for fuels, materials and chemicals. Mild and selective conversion processes would be desirable for decentralized value-generation from the synthesis power of nature. However, the utilization is still difficult due to the composition and the structure of the biomass'cell wall. Cellulose shows a dense, crystalline structure and the access to these macromolecules is further restricted by lignin and hemicellulose. An efficient conversion hence requires the application of a pretreatment to gain access to cellulosic macromolecules for subsequent conversion processes.

Mechanistic understanding of the pretreatment can likely be gained at the molecular level. However, the cellulose in the cell wall exists in fibrils made of several cellulose chains, which are hold together via intermolecular hydrogen bonds. This regular arrangement forms crystalline structures that are a major obstacle in enzymatic hydrolysis [1]. Hence, molecular analysis needs to be extended by structural analysis to monitor the mechanistic steps of pretreatment.

Ionic liquids proved to be good solvents for the cellulose and the hydrophobic lignin [2], and the high concentrations of ions at elevated temperatures around 100°C give rise to chemical reactions that constitute the desired pretreatment and improve the enzymatic hydrolysis [3]. Due to the abundance of water in such processes, we systematically studied the effect of water on this pretreatment. Using small angle neutron scattering (SANS), the tissue after the pretreatment was compared to the native wood and a first time-resolved setup was established for this pretreatment.

At higher water contents, the crystallinity is enhanced, and the cell structure is rather preserved but cellulose fibrils show coalescence similar to what has been observed after pretreatment with dilute mixtures. In concentrated EMIMAc, the crystallinity of the cellulose is decayed, and the cell structure of the wood is rather destroyed [4]. The results indicate extraction and reorganization on the scale of macrofibrils, which is supported by other analytical methods supporting the results. A latest kinetic SANS study completes the whole picture drawn here.

Poster Session - Board: 6 / 13

Lithium Permeation through Ultrathin Silicon Layers measured by Neutron Reflectometry

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Neutron reflectometry (NR) was applied to measure non-destructively and in-situ Li permeation through thin silicon layers [1,2]. Such experiments are interesting for research on nanostructured electrode materials in lithium based batteries, Li ion selective electrodes, and sensors [1,2]. Understanding Li transport through interface layers in rechargeable batteries by in situ methods is a hot topic of current academic and industrial research [2]. Interface limited Li transport was recently proven to account for irreversible capacity losses [3].

Using NR we identified the control mechanism (diffusion or interface controlled) of Li permeation through thin Si layers embedded in oxide based solid state Li reservoirs. Stacks with a repetition of five [Si / 7LiNbO₃ / Si / 6LiNbO₃] units were used for analysis. Si layer thicknesses between 2

and 22 nm were studied. Two types of Bragg peaks were detected in the NR pattern. One originates from LiNbO_3/Si chemical contrast, the other from $^6\text{Li}/^7\text{Li}$ isotope contrast. Diffusion annealing at 240°C reduced only the intensity of second type of Bragg peak, demonstrating that the decrease is a measure of the ^6Li and ^7Li isotope exchange through the Si and interface layers. The presence of a diffusion controlled process was proven by a significant dependence of the Li isotope exchange time on Si layer thickness. The experiments showed that the lithium silicate interface layer, which appears by the proximity of silicon to oxide based solid state electrolytes or cathodes, does not limit Li permeation.

The temperature dependence of Li transport through thin silicon layers was also measured by NR between 85°C and 420°C. The obtained activation enthalpy of the Li permeability (diffusivity X solubility) of 1 eV is nearly identical for all Si layer thicknesses. Hence, the intrinsic process of Li transport is independent of the Si layer thickness. A strong increase of the pre-exponential factor (entropy factor) with decreasing Si layer thickness is also observed. This enhances the Li permeability by three orders of magnitude when the Si layer thickness is decreased from 22 to 2 nm at each temperature studied.

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Poster Session - Board: 14 / 38

Neutron diffraction study of Li diffusion in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ solid state lithium conductors

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Study of lithium diffusion in solid ionic conductors is a relevant part of characterization for both electrode materials and solid electrolytes for Li ion batteries. Understanding of processes supplementing lithium migration has an obvious significance for the further materials development and it was actively explored by a variety of experimental methods and techniques. While neutrons can localize light atoms in the presence of heavier ones, neutron powder diffraction is powerful tool for Li localization in the crystal structure of different compounds, which is highly relevant for understanding lithium diffusion in the materials.

All solid ceramic Li ion batteries have attracted attention as a safe, more stable alternative to conventional batteries based on liquid electrolytes, capable to operate at higher potentials. Among different materials the lithium titanium phosphate $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) is a promising solid-state Li^+ conductor. Although LTP possesses a remarkable chemical stability against ambient atmosphere, its ionic conductivity is rather low, but it can be enhanced by partial substitution of tetravalent cations (Ti^{4+})

by trivalent ones (Al³⁺, Fe³⁺, Y³⁺ etc.). The best result of the doping was obtained with aluminum, where the nominal composition Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) was reported to have the optimum Li ionic conductivity (~10⁻³ S/cm) [1], thus making it promising for applications. The crystal structure is the property defining ionic conductivity and, therefore, structural properties of LATP and related materials were actively studied. Different opinions on lithium positions in LATP have been reported in the literature [2, 3]. In order to resolve these controversies a systematic neutron powder diffraction study of crystal structure of LATP-based materials was performed on the number of samples with nominally similar compositions. Careful analysis aiming to determine nuclear density maps and to define the lithium diffusion pathways was carried out on the structural data. The diffusion pathways obtained using simulations (difference bond valence) and experiment (reconstruction of nuclear density maps using maximum entropy method, MEM) have been found very similar and indicate the three dimensional Li migration in LATP which likely occurs between 6b (Li1) and 36f (Li3) sites [4].

This work was supported by Deutsche Forschungsgemeinschaft (Projects EH 183/15-1, SE 2376/1-1 and HO 1165/18-1) and a Hans-L.-Merkle scholarship.

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Poster Session - Board: 5 / 12

Study of magnetocaloric materials in the system Mn_{2-x}M_xSb (M=Fe, Co)

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Magnetocaloric refrigeration is an emerging technology in today's cooling devices and it has a potential to save about 20-30 % of energy compared to conventional vapor compression technology. Nowadays, the most important issue is to find cheap and abundant materials exhibiting a sizable magnetocaloric effect. We report on preparation and characterization of compounds of general composition Mn_{2-x}M_xSb system with M = (Fe, Co). The substitution on the Mn site has an effect on magnetic properties and magnetic transitions. We synthesized samples of different stoichiometry by inductive melting of the elements in a cold crucible and performed studies using x-ray powder diffraction method and macroscopic magnetization measurements. Based on these data we could then calculate the entropy change. In the Fe-containing samples, in particular in Mn_{1.8}Fe_{0.2}Sb, we observe a small MCE associated to a paramagnetic-ferrimagnetic phase transition. The Co-doped samples reveal a more sizable MCE accompanying a ferri-to-antiferromagnetic phase transition. Currently we study the response of the lattice parameter to the magnetic transitions with low temperature powder diffraction (300-15 K).

Poster Session - Board: 24 / 59

In-beam activation analysis facility at MLZ

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Whenever neutrons are absorbed in atomic nuclei, mostly gamma photons, sometimes charged particles are emitted. Detecting them offers a set of nuclear analytical methods which are utilized in characterizing high-purity, or thin-layered materials also used in energy technology. Prompt Gamma Activation Analysis (PGAA), i.e. the technique based on the emission of gamma photon emitted during the irradiation, is mainly used for the determination of the light elements, typically for analyzing the major components of the sample. It offers a unique method for the analysis of hydrogen (or humidity/water content) down to ppm levels, and that of boron down to ppb levels. Neutron Activation Analysis (NAA), i.e. when the delayed gamma radiation is acquired, is mainly used for the determination of trace elements in various matrices, e.g. the impurities in silicon. When combining the two, both the matrix composition and the trace-element content can be determined accurately.

At MLZ, the PGAA facility has been reconstructed to enable both activation analyses at the cold neutron beam: in-beam activation analyses which combines the advantages of both nuclear analytical methods. Because of the highly different samples typically measured at MLZ, the irradiation and counting facilities need to be changed rapidly and flexibly, so that the detector efficiencies match the actual activation conditions. The reconstructed facility is presented.

It will also make possible to accommodate another nuclear analytical tool, neutron depth profiling (NDP), which has not yet been available at MLZ. Charged particles (alpha, triton, proton at various energies) are emitted from a set of light nuclei (Li, B, N etc.), whose distribution can be investigated with NDP in thin layers up to a few micrometers in thickness. Processes like charge-discharge of prepared Li-ion batteries can also be monitored in situ.

A few applications will also be presented like the analysis and the determination of the distribution of H and B in silicon ingots used in solar-cell production.

Poster Session - Board: 7 / 19

Pressure and temperature dependence of nuclear structure and magnetic properties in Mn₄FeSi₃

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Magnetic refrigeration based on the magnetocaloric effect holds a potential to replace conventional vapor compression cooling [1]. Compared to other magnetocaloric materials, the compounds in the system $\text{Mn}_{5-x}\text{Fe}_x\text{Si}_3$ have the advantage that they do not contain expensive rare earth elements like Gd, nor toxic elements like As. After characterizing the compound MnFe_4Si_3 regarding structure and magnetism [2] another compound -namely Mn_4FeSi_3 - of the system is now in the focus of our attention. Around the transition temperature of a magnetic phase transition it is supposed to undergo a structural phase transition from a hexagonal structure to an orthorhombic structure [3]. Investigation of both compounds and comparison of them might help understanding the underlying mechanism of the MCE in multiple site driven magnetocaloric materials, as the magnetic elements Manganese and Iron are distributed on at least two sites.

We performed neutron and x-ray powder diffraction experiments as a function of temperature on Mn_4FeSi_3 and could confirm that the magnetic transition at approx. 65 K is accompanied by a change in the symmetry presumably from $P6_3/mcm$ to $Cmcm$ indicating a close connection between lattice and spin degrees of freedom.

Synchrotron powder experiments varying pressure and temperature simultaneously were performed to follow the magnetic and associated structural transition. Volume changes and c/a ratio from both temperature and pressure dependant experiments clearly show that the influence of temperature is significantly stronger than the influence of hydrostatic pressure in this caloric material.

We were able to grow a large single crystal of the compound using the Czochralski Mehtod. Pressure dependent laboratory single crystal diffraction shows anomalies in the pressure dependence of the interatomic distances.

Macroscopic magnetization measurements performed on oriented single crystals of Mn_4FeSi_3 are currently being performed and will allow characterization of the anisotropy of the magnetic response of the material.

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Poster Session - Board: 18 / 54

Structural complexity and O₂- ordering in $\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ studied by single crystal neutron and x-ray diffraction

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Ruddlesden-popper phases and especially those with K_2NiF_4 -type structure, are of particular interest, as they exhibit high ionic and electronic conductivity already at moderate temperatures. They show a rather wide range of oxygen non-stoichiometric and are able to accommodate extra oxygen on interstitial lattice sites. Hole doping in Pr_2NiO_4 , either by substituting Pr with Sr cations or by O₂- ion intercalation on interstitial lattice sites modifies the structural (ordering of O₂- ions) and electronic ordering in $\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$. Contrary to Sr-doping a high oxygen doping level induces a

special lattice dynamics, allowing the apical oxygen atoms to easily move to vacant interstitial sites on a shallow energy diffusion pathway. We evidenced by high resolution neutron single crystal diffraction, large displacements of the apical oxygen atoms, resulting in a phonon assisted diffusion mechanism, activated at already moderate temperatures [1,2]. The orthorhombic/tetragonal phase transition at 360°C induces an anharmonic Debye Waller behavior of the Pr₂O₂ rock salt layer separated by NiO-layers showing a normal displacement behavior with T.

Hole doping of Pr₂NiO₄ by oxygen insertion and/or Pr/Sr substitution, results in the formation of complex superstructures, related to charge and/or oxygen ordering. We report here on the influence of x, δ and T for Pr_{2-x}Sr_xNiO_{4+ δ} , analyzed with X-ray and neutron diffraction studies.

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Poster Session - Board: 23 / 31

In-situ tensile deformation behaviour of a high ductile Mg-RE alloy via neutron diffraction

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The applications of magnesium alloys have been increasing now days, because they are not only developed as structural materials for transportation or other industrial applications, but also as biodegradable medical implant materials. A new Mg-RE alloy was developed by micro-alloying method (RE < 0.4 wt.%), which achieves high ductility and good corrosion resistance at MagIC, HZG. Both of the average tensile elongation and compression ratio at room temperature are over 30%. Meanwhile, the yield strength of tension is nearly the same as that of compression. In-situ tensile test were investigated by neutron to investigate first the deformation behavior; and second the texture evolution which can be related to the deformation mechanism, and finally to understand why the as-cast Mg-RE alloys show such a high tensile ductility.

Results showed that a dominated basal fiber texture was gradually developed with the increase of tensile strain. However, before the samples failed a (10.0) fibre texture showed a similar intensity to that in (00.2), which means more activations of the non-basal slip planes during tensile deformation. This could greatly contribute to a relatively high elongation of this new Mg-RE alloy at room temperature.

Poster Session - Board: 25 / 36

Strain Induced Martensitic Transformation in Austempered Ductile Iron (ADI)

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Austempered ductile iron (ADI) is a cast iron that has undergone a special heat treatment to greatly enhance mechanical properties. The heat treatment process of ADI consists of austenitization, quenching to a temperature between 250°C and 450°C and isothermal austempering [1, 2]. After such a heat treatment, the microstructure consists of acicular ferrite and high carbon enriched retained austenite.

The high carbon enriched retained austenite can transform to martensite during plastic deformation. The treatment parameters (austenitization temperature, austempering temperature, austempering time and alloying composition) can influence the retained austenite fraction, grain size and its stabilisation [2], which in turn will influence the deformation induced martensitic transformation.

The influence of different treatment and composition parameters on the martensitic transformation and texture formation during plastic deformation has been investigated using neutron diffraction. The combination of texture analysis and in-situ deformation tests allowed quantitative phase analysis and extraction of martensite phase fractions as a function of strain level.

The experiments allowed us to determine the influence of austempering temperature, Nickel content and plastic strain on the martensitic transformation kinetics in ADI.

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Poster Session - Board: 12 / 33

Proton dynamics in high temperature polymer electrolyte fuel cell membranes

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Polybenzimidazole (PBI, poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) membranes with phosphoric acid impregnation are a new promising material for high-temperature polymer electrolyte membrane fuel cells (HT-PEFC). PBI as membranes for fuel cells was introduced in the middle of the nineties as replacement for the well-investigated Nafion membranes, whose use is limited by the boiling temperature of water and thus, water-thermal management. After being impregnated with phosphoric acid (PA) PBI membranes show very good proton conductivity. Besides, the operating temperature of about 160°C of HT-PEFC results in a high CO tolerance of 1-2%. However, although PBI-based PEMFCs are well studied on macroscopic level (conductivity, rheology etc. [1, 2]), the

microscopic dynamics associated with the conductivity has not been investigated in detail except from molecular dynamics simulations [3, 4]. A method predestined for this purpose is quasielastic neutron scattering because of the high incoherent scattering cross section of protons and the spatial resolution of the technique.

In order to investigate the microscopic proton dynamics in these PA impregnated membranes over a wide dynamic range, data from three neutron scattering instruments were combined in time range after Fourier transform: the time-of-flight spectrometer CNCS at SNS, Oak Ridge (0.2–30 ps), the TOF-backscattering spectrometer BASIS at SNS, Oak Ridge (20–800 ps), and the backscattering spectrometer SPHERES at MLZ, Garching (70 ps–5 ns). To suppress the scattering from the polymer matrix, the difference between samples with PA and deuterio-PA was used as the basis of the evaluation.

A first description of the data using a model based on a distribution of relaxation times gave satisfactory results but left the microscopic picture open. Analysing the Q dependence of the characteristic times we could identify a region with an anomalous power law behaviour indicating diffusion on a fractal structure. A scattering function derived from a fractal-based model enabled us to describe the scattering on certain length scales.

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Poster Session - Board: 19 / 55

T-dependent structural studies of the oxygen ion conductor Pr_{1.5}Sr_{0.5}NiO_{4+d} investigated by single crystal neutron diffraction

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Mixed-ionic electronic conductors (MIEC) offer significant advantages over conventional cathodes especially in the intermediate temperature range for solid oxide fuel cell applications as well as for oxygen sensors. Ruddlesden-Popper type layered oxides which belong to K₂NiF₄ family are of great scientific interest in this field due to the interplay of the variable structure to tune functional properties. Among them, Pr₂NiO_{4+d} is a promising candidate as the compound shows the searched high oxygen mobility already at ambient temperature and the oxygen diffusion can be lowered by Sr doping.

Apical oxygen disorder is regarded as the fundamental prerequisite behind the high oxygen diffusion at moderate temperatures which is described by the phonon assisted diffusion mechanism. In this work, we have explored the effect of Sr doping and temperature on apical oxygen dynamics in Pr_{1.5}Sr_{0.5}NiO_{4+d} by single crystal neutron diffraction. Our diffraction measurements at RT revealed a tetragonal crystal structure for Pr_{1.5}Sr_{0.5}NiO_{4+d} when no structural transitions were evidenced up to 800 C [1]. High structural displacement factors were found for equatorial oxygens along the

c-axis and for apical oxygens in the ab-plane with respect to the tetragonal unit cell. Anisotropic displacement parameters are almost linearly increasing with temperature. Comparisons of our results with undoped samples [2] show that Sr doping highly reduces the anisotropic movement both for the apical and equatorial oxygen atoms. To describe the oxygen disorder in the anharmonic approximation at different temperatures, the observed neutron scattering density of the averaged structure was also explored using the Maximum Entropy Method (MEM). These results confirm the anharmonic flat square behavior for apical oxygens with the normal parallel to the c-axis at RT. The outer diameter of the flat square almost reaches up to 0.5 Å which is much less than 2 Å observed for Pr₂NiO_{4.25} at already RT.

We conclude from the comparison of our observation in Pr_{1.5}Sr_{0.5}NiO_{4+d} with published results from undoped compounds, that the presence of interstitial oxygen atoms at RT is enhancing the diffusion process by providing a shallow diffusion potential for apical oxygens.

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Poster Session - Board: 2 / 37

The GEMS-N Instrumental Suite and its Potential for the Characterization of Energy Related Material

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The MLZ outstation of the German Engineering Materials Science Center (GEMS) provides an instrumental suite that allows researchers in the field of energy related materials to characterize their systems over several orders of length-scales.

The diffractometer STRESS-SPEC (operated in cooperation with TUM) is a highly configurable instrument which enables spatial and time resolved characterization of the crystalline structures present in bulk samples. [1,2].

The small angle beamline SANS-1 (operated in cooperation with TUM) is a state of the art instrument for the characterization of large scale structures (on the order of 1 - 300 nm) in bulk systems [3,4].

The time of flight reflectometer REFSANS is dedicated to the characterization of surfaces and interfaces. Thanks to a versatile optics and chopper system structures can be detected and measured both in the in and out of plane directions of thin films. These complementary measurements are particularly relevant to the field of electrodes for instance in the case of hybrid solar cells where understanding the detailed structure of the interfaces can help developing new materials and processes leading to improved performance.[5]

Thanks to the high penetration of neutron in most materials the above mentioned complementary methods give access to in-situ and/or in-operando measurements in a non destructive way. In addition to these instruments which are typical of a large scale facility such as MLZ, GEMS also operates on-site the Materials Science Lab which provides access to a wide range of techniques such as optical microscopies, calorimetry, micro hardness tester, and to an excellent x-ray diffractometer equipped with a setup for in-situ battery characterization.

In this contribution we will present how the GEMS portfolio can contribute to a global understanding of structural problems in the field of energy related materials.

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J. Appl. Cryst. 48, 444-454 (2015)

Poster Session - Board: 9 / 18

Oxygen deficiency in High-Tc YBCO thin films identified by positron annihilation spectroscopy

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The availability of high-quality superconducting materials with high critical temperature T_c is of major interest in all kinds of applications for resistivity-less electron transport. In high-Tc $YBa_2Cu_3O_{7-\delta}$ (YBCO) oxygen deficiency, i.e. an increase of δ , leads to a higher T_c or even to a loss of superconductivity. Both the deeper understanding of the $T_c(\delta)$ dependence and the precise adjustment of T_c require information about the oxygen vacancies on a microscopic level.

In our study we investigated single crystalline YBCO thin films in order to probe the oxygen deficiency δ using the mono-energetic positron beam at the high-intensity positron source NEPOMUC at FRM II [1]. The samples were produced by pulsed laser deposition which enables epitaxial growth of YBCO in single crystalline quality with well-defined stoichiometry on SrTiO₃ substrates. By combining transport measurements, X-ray diffraction and (coincident) Doppler broadening spectroscopy ((C)DBS) of the positron-electron annihilation line we succeeded in correlating the relevant parameters T_c , expansion of the c-axis, δ , and S-parameter of the DBS-measurements. Hence the variation of δ could be measured in a non-destructive by DBS for a set of differently produced YBCO thin film samples. Moreover, scanning with the positron beam allowed us to analyze the spatial variation of δ and hence the critical temperature T_c between 25 and 90 K.

Within this contribution the basic properties of positron annihilation studies will be briefly explained. The benefit of positron beam experiments for the development and improvement of functional materials for energy applications will be elucidated by selected studies.

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Poster Session - Board: 29 / 17

Low dimensional lead bromide perovskite in light emitting application – investigation on structure evolution via neutron scattering

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Two dimensional functional materials have created intensive research interest for high efficiency solar cells. Recently low dimensional perovskite nanocrystals, such as 2D perovskite nanoplates have been reported to possess reduced fluorescence decay times, an increased exciton binding energy and low conductivity in certain crystallographic directions. Consequently, these lower dimensional perovskites can be utilized for light emitting applications. In the present work, 2D nanosheet perovskites are formed by using octylammonium bromide as capping ligands. GISANS combined with neutron reflectivity (NR) are applied to investigate the structure buried inside the thin films. GISANS had proven to be a powerful technique for thin film morphology investigations. NR guarantees that information about nanometer sized layers can be accessed. We present the determined results in terms of morphology formation evolution, stacked layered characteristic and optical properties.

Poster Session - Board: 1 / 2

Neutron scattering characterization of confined fluids for energy storage and environmental science

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Much to our regret, Yuri Melnichenko passed away on the 18th of March 2016. He submitted this abstract to our conference shortly before his death. We are deeply sorry that he could not join us for the meeting.



Figure 1: Yuri Melnichenko

Fluid-solid interactions in natural and engineered porous solids underlie variety of technological processes, including hydrogen storage, capture and sequestration of anthropogenic greenhouse gases, super capacitors, membrane separation, and catalysis. The size, distribution and interconnectivity of pores, the chemical and physical properties of the solid and fluid phases collectively dictate how fluid molecules migrate into and through the micro- and mesoporous media, adsorb and ultimately react with the solid surfaces. Due to the high penetration power and relatively short wavelength of neutrons, small-angle neutron scattering (SANS) as well as quasi elastic neutron scattering (QENS) techniques are ideally suited for in situ studies of the structure and dynamics of confined fluids under pressure as well as for evaluating structure of pores in engineered and natural porous systems. It has been demonstrated recently that SANS can also be used for determination of the volume of closed pores as a function of pore sizes in the range from micrometer to sub-nanometer pores. In this talk I will overview some recent developments in the SANS and QENS methodology and give several examples of how it can be used for in-situ studies of the abnormal densification of hydrogen in activated carbons at ambient temperatures, adsorption and dynamics of greenhouse gases in natural and engineered porous materials as well as in situ monitoring the ion adsorption in electrodes of batteries and super capacitors [1].

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Session VIII: Batteries & Fuel Cells (Chair: Werner Lehnert) / 77

Operando Diffraction During Li Battery Operation using Neutron and Synchrotron X-Ray Radiations

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Session VIII: Batteries & Fuel Cells (Chair: Werner Lehnert) / 15

Enhancing electrolysis performance of perovskite-type electrodes by polarization-driven exsolution of metallic catalyst particles: A synchrotron-based in-situ XRD and XPS study of near-surface chemistry

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Mixed ionically and electronically conducting perovskites are nowadays employed in electrochemical devices such as solid oxide fuel cells, gas separation membranes and membrane reactors. Their future application in solid oxide electrolysis cells (SOECs) is therefore almost obvious. For a successful introduction into SOECs, however, we need an in-depth understanding of their surface chemistry.

In this study, geometrically well-defined model-composite electrodes were investigated containing perovskite thin films such as La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF) and La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_{3-δ} (LSCrNi). On

LSF, electrolysis of water was performed at 620 °C and the electrochemical activity as well as the surface chemistry were simultaneously studied by impedance spectroscopy and near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), respectively. Upon cathodic polarization the evolution of metallic iron species was observed, which was accompanied by a strong increase of the electrode's water splitting activity. By means of in-situ surface XRD experiments the exsolved particles were identified to be α -Fe. After retracting the applied voltage the metallic iron was immediately re-oxidized and the high water splitting activity disappeared.

On LSCrNi electrodes it is shown that this boosting effect of exsolved transition metal particles can also be transferred to CO₂ electrolysis. Again simultaneous impedance and NAP-XPS measurements were performed to correlate electrochemical activity with surface chemistry and presence of metallic Ni was confirmed during electrolysis of CO₂ at 700 °C. In reference measurements on Ni free electrodes much lower electrochemical reaction rates were found, therefore confirming the beneficial effect of the exsolved Ni particles. Depending on the applied voltage the products of CO₂ splitting were either CO or graphitic carbon. Graphitic depositions, which were formed under too high cathodic polarization, led to a strong deterioration of the electrode performance. But retracting the voltage completely removed the carbon and the electrode was completely reactivated.

These results clearly identify perovskite electrodes decorated with exsolved metallic particles as catalytically superior in high temperature electrolysis of H₂O and CO₂. Hence, this novel type of electrolysis electrodes may open new pathways in the quest for optimized energy storage via SOECs.

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Operando Neutron Radiography Analysis of High-Temperature Proton Exchange Membrane Fuel Cell Based on Phosphoric Acid Doped PBI membrane by Using Hydrogen-Deuterium Contrast Method

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The energy shortage and environment pollution are two of the most important challenges for human race. With the advantage of zero-emission and high energy conversion efficiency, proton exchange membrane fuel cell (PEMFC) is recognized as an alternative solution for future energy conversion technology, and has been gained great development in recent years. The classical PEMFC which is based on PFSA-type membranes (e.g. the well-known Nafion) and operated between 60-90°C, still has some issues such as low carbon monoxide tolerance of the catalyst and complex water management. To overcome the disadvantages, high-temperature PEMFCs which are based on phosphoric acid doped PBI membranes, operated between 140-180°C, are in the focus of the current research.

In order to characterize high-temperature PEMFCs in-operando, the neutron radiography method can be used. This neutron imaging in combination with the deuterium contrast method was used to analyze the hydrogen distribution and exchange processes in a high-temperature PEMFC in-operando. The cell was operated at different steady state conditions (different current densities and stoichiometries). At each condition neutron images of the active area of the cell were taken and the data were used to analyze the changeovers of the fuel switched between hydrogen (H₂) and deuterium (D₂). We will demonstrate that local exchange between H and D (and vice versa) is influenced by the overall exchange dynamics and the current distribution within the cell. A change from H-to-D is different from a change from D-to-H. We found a faster proton-to-deuteron exchange when switching from H₂ to D₂ gas supply than for a change from D₂ to H₂ gas.

Session VIII: Batteries & Fuel Cells (Chair: Werner Lehnert) / 40**Neutron and X-ray Diffraction Studies of BaCe_{0.85}Y_{0.15}O_{2.925} for Application in Innovative Design of Fuel Cell****Author:** Kiril Krezhov¹**Co-authors:** Alain Thorel²; Anthony Chasnaud²; Gergana Raikova³; Ivaylo Genov³¹ *INRNE-BAS*² *ARMINES*³ *IEES***Corresponding Author:** kiril.krezhov@gmail.com

The aim of this study is a deeper insight into the conductivity mechanisms and water behavior in BaCe_{0.85}Y_{0.15}O_{3- δ} (BCY15) which is applied in an innovative design of solid oxide fuel cell, named dual membrane fuel cell (dmFC). The new design overcomes the disadvantages connected with the production of water at the electrodes. The innovative idea is the introduction of a separate compartment (central membrane CM) for the water formation and evacuation. It has mixed ionic (proton and oxide ion) conductivity and porous structure.

Specialized impedance measurements discovered good mixed ion (proton and oxide ion) conductivity in BCY15 at operating temperatures. Thus a “monolithic design”, which strongly simplifies the technology, has been proposed, since in O₂ flow BCY15 is oxide ion conductor, in H₂ flow it is proton conducting and in the central membrane it is mixed ion conducting. Applying several experimental approaches (complex permittivity, water vapour permeability and impedance measurements), new phenomena connected with the presence of water in the porous BCY structure were discovered - formation of an electrochemically active volumetric layer in the CM which facilitates the water formation and thus improves the operation of the dmFC design by decreasing its resistance. This phenomenon can facilitate also the splitting of water, which is of importance for operation in electrolyzer mode.

For deeper insight of the conductivity properties/mechanisms and water behaviour, fundamental studies on atomic level are in progress. The structural details of powder, dense and porous samples were investigated from full profile analysis of neutron and x-ray diffraction patterns. The basic constituent is BCY15 powder prepared by auto-combustion and calcination at high temperature, which crystallizes in the orthorhombic Pnma space group similarly to the parent BaCeO₃ stoichiometric perovskite and BaCe_{0.9}Y_{0.1}O_{2.95}. New studies are under development.

The research leading to these results has received funding from Bulgarian NSF under Grant No E02/3/2014

Session VII: Catalysis (Chair Mikhail Feygenson) / 3**Industrial applications of neutron scattering in catalysis****Author:** Peter Albers¹¹ *Evonik Technology & Infrastructure GmbH***Corresponding Author:** peter.albers@evonik.com

For an adequate characterization of industrial process catalysts, fuel cell catalysts and various other highly dispersed technical materials which show a high degree of structural complexity at several orders of magnitude the combination of quite different methods is essential. This includes standard routines of instrumental analysis, electron microscopy and surface spectroscopies as well as the development and adaptation of dedicated methods of materials research for the individual case, including neutron scattering.

Some experimental results from utilizing neutrons in tackling tough analytical problems in applied catalysis will be presented. These problems could not be resolved by means of up-to-date laboratory equipment and various established analytical techniques but with basic science.

A major focus is the hydrogen-related chemistry:

1. Catalyst coking (high temperature/low temperature cokes)
2. Catalyst poisoning and dew point corrosion (HCl)
3. Catalyst deactivation in large scale production plants over time of operation: snapshots from “cradle to grave”
4. Proton dynamics and morphology of carbonaceous catalyst supports
5. The Heck reaction: preferential adsorption of one isomer on a Pd/C catalyst
6. Hydrogen/catalyst interactions: dissociative chemisorbed hydrogen on Pt/C and Pt,Ru/C fuel cell catalysts
7. The Lindlar catalyst (Pd,Pb/CaCO₃): influence of controlled moderation on hydrogenation activity of supported palladium: hydrides formation and enantio-selectivity
8. Revealing the fine structure of Pearlman’s catalyst
9. “Working horse catalysts”: the selective hydrogenation of nitrobenzene - impact of alloying on precious metal morphology, particle size, catalytic activity, hydrogen storage properties and selectivity
10. “Hydrogen in and on metals”-in the case of supported nano-particles

Neutron spectroscopy picks up where other analytical methods leave off.

Session VII: Catalysis (Chair Mikhail Feygenson) / 32

Investigating guest selectivity and dynamics in porous framework materials using in situ neutron scattering and computational approaches

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Microporous solids capable of reversibly hosting specific guest molecules are being actively sought for a wide variety of applications in the energy sector, including CO₂ sequestration and conversion, gas separations, fuel storage, and catalysis. Classes of porous framework materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are considered especially promising for such applications due to their unrivalled structural and chemical tunability with respect to traditional solid sorbents such as zeolites [1].

Rational tuning of a framework material for improved performance requires that the nature of the interactions between the host framework and guest molecules be well-understood at the atomic level. Our research targets this detailed understanding of framework-guest systems using in situ neutron scattering experiments in which the framework structure and dynamics are probed as a function of guest loading and temperature. Rapid measurements performed using the high-intensity neutron diffractometer WOMBAT at OPAL (Australia) can capture structural changes in the framework before equilibration with the adsorbate, allowing us to approach more closely the real-world behaviour of a sorbent operating under continuous flow conditions. Our experimental results are supported

by comprehensive atomistic density functional theory-based (DFT) calculations from which various physical and dynamical properties are extracted.

We are currently investigating several MOFs which display unexpected sorption properties such as “reverse sieving”—that is, selectively absorbing larger gas molecules while rejecting smaller ones. Using in situ neutron diffraction to locate the preferred binding sites of guest molecules in the framework, inelastic neutron scattering methods to probe guest-dependent lattice dynamics and guest diffusion characteristics, and DFT molecular dynamics simulations to validate and interpret our experimental results, we are able to gain detailed information about the mechanisms of gas uptake and selectivity in these exciting new MOF materials.

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Session VII: Catalysis (Chair Mikhail Feyngenson) / 9

Proton dynamics of phosphoric acid in the catalytic layer of gas diffusion electrodes for HT-PEFC

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High-temperature polymer electrolyte fuel cells (HT-PEFC) are promising electrochemical energy converters. Because of the high operation temperature of 160°C - 180°C the HT-PEFCs have a high CO tolerance. [1]

Recent works on the development of HT-PEFC are focused mostly on the performance and technical optimization. However, the fundamental investigation of the proton conductivity will help to optimize performance and increase sufficiency of the fuel cells. For example, the understanding of proton diffusion mechanism in membrane electrode assembly (MEA) plays a key role in proton conductivity of fuel cells.

The present study focuses on dynamical properties of phosphoric acid (PA) in the catalytic layer for HT-PEFC. The catalytic layer is a composite material containing nanoporous carbon, poly(tetrafluoroethylene) (PTFE) and platinum (Pt) nanoparticles. Since the catalyst layer is in direct contact with the PBI membrane doped with PA it also contains some amount of acid, which is needed to provide good proton conductivity in the electrode. The contact between electrodes and the membrane is one of the important parameters, which influence the cell performance [1,2]. Knowledge about local PA dynamics and understanding the distribution of PA between structural elements of the catalyst could help to design more efficient electrodes for fuel cells.

Due to adsorption of the PA on the Pt particles the diffusion of protons in the catalytic layer can be different with respect to the membrane and bulk acid and thus, should be taken into account. Using quasielastic neutron scattering (QENS), proton dynamics can be studied on local length scales from few Angstrom and up to 10 nm. Backscattering spectroscopy was used to directly probe the dynamics of protons in nanoseconds range. The three approaches are considered for description of proton dynamics: the random jump diffusion model, distribution of jump lengths and, finally, the trap model. Extracted parameters such as diffusion coefficient, activation energies and time constants gives insight about dynamical behavior of the PA and its distribution in the catalytic layer.

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Session IX: Thermoelectrics & Magnetocalorics (Chair: Karin Schmalzl) / 47

Heat conduction in thermoelectric materials

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Energy efficiency of existing sources can be improved by reducing heat losses, thermoelectric materials has the capability of interconverting between electricity and a temperature gradient. The wanted properties of thermoelectrics can be summarized, as the a “Phonon-Glass, Electron-Crystal”(PGEC) [1]. In host-guest systems, the host structure is considered to be the electron crystal, while low frequency guest atom modes reduces the acoustic phonons realize the phonon-glass part. The type-I clathrates are state-of-the-art host-guest material with respectable thermoelectric properties [2]. The structure consists of a Ga/Ge framework forming two dodecahedral and six larger tetrakaidecahedral cages, which are occupied by the guest guest atoms. The thermal conductivity of the clathrates are about 1 W/mK, which is the same order of magnitude as amorphous glass.

Neutrons scattering has been used to elucidate structural and dynamic details in the clathrate system. Single crystal diffraction has been used to investigate the guest atom position in the large dodecahedral cage of Sr₈Ga₁₆Ge₃₀ synthesized using three different methods. Triple axis spectroscopy has been used to investigate the phonon dispersion relation for Ba₈Ga₁₆Ge₃₀. The dispersion relation measured along (330)+[hh0] revealed avoided crossing between the acoustic phonons and the guest atom mode. To further investigate the phonon lifetimes Spin-echo triple axis spectroscopy measurements were carried out at TRISP at FRM-II.

The neutron scattering experiments have delivered valuable insight into the atomic structure and motion of the host-guest clathrates. The neutron scattering experiments show that the low thermal conductivity can attributed to low phonon group velocities, caused by the band flattening due to interactions between the host structure and the guest atom.[3] Through the results we have been able to explain the low thermal conductivity and the results offer guidance in the search for new materials with improved thermoelectric properties.

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Neutron scattering studies on (Mn,Fe)₂(P,Si)-type magnetocaloric materials

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Magnetic refrigeration has been considered to be the most promising technology to replace vapor-compression for near room-temperature refrigeration applications. Magnetic refrigeration is based on the magnetocaloric effect (MCE). The MCE is a phenomenon, in which a temperature change is caused by exposure of a magnetic material to a changing magnetic field. The cooling efficiency of magnetic refrigeration systems can reach up to 60% of the theoretical limit, compared to about 45% in the best gas-compression refrigerators [1-2]. Magnetic cooling systems operate with less noises and use water-based coolants instead of ozone depleting or greenhouse gases, which makes it an environmentally friendly technology.

(Mn,Fe)₂(P,Si)-type compounds are, to date, the most promising materials for such applications due to the combination of outstanding magnetocaloric properties and low material cost. The giant MCE in (Mn,Fe)₂(P,Si) compounds originates from a magneto-elastic transition, i.e., the ferromagnetic-paramagnetic (FM-PM) magnetic transition is strongly coupled to a structure change without a symmetry change [3-4].

Due to the strong magnetoelastic coupling in the (Mn,Fe)₂(P,Si) compounds, the phase transition can be tuned by changing the Mn/Fe ratio and P/Si ratio, as well as by doping with light atoms [3-5]. Neutron diffraction is a well-suited tool to reveal the structural origin for the tunability of the phase transition, since it has the capability of distinguishing Mn from Fe and P from Si atoms, as well as detecting light atoms.

Our recent neutron diffraction experiments found that in contrast to the common PM-FM phase transition, an intermediate spin-density-wave (SDW) phase is observed for some compositions. The SDW-FM transition is accompanied by a significant increase in the Fe moment and a slight change in the Mn moment. This experimental finding fosters the strong magnetoelastic coupling and Fe moment instability in the (Mn,Fe)₂(P,Si) system.

Additionally, we performed xyz neutron polarization analysis in the PM regime of the (Mn,Fe)₂(P,Si) compound. The unambiguous separation of the magnetic scattering cross section from the nuclear and spin-incoherent contributions allows us to characterize the spatial correlations of magnetic spins in the PM state. The combination of neutron polarization analysis and muon-spin relaxation experiments provides us a better understanding of the magnetic correlations in the PM state of (Mn,Fe)₂(P,Si) compounds, on both the length- and time-scales.

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Inelastic neutron scattering on magnetocaloric compound MnFe₄Si₃

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The magnetocaloric cooling process is based on the magnetocaloric effect (MCE) where entropy changes of a magnetic material in an applied magnetic field are tied to adiabatic changes in temperature. An entropy transfer between crystal lattice and the magnetic spin system has to take place. A large MCE at room temperature and low magnetic field for a material with abundant and environmentally friendly elements opens the way for magnetic cooling devices.

The ferromagnetic compound MnFe_4Si_3 belongs to the series $\text{Mn}_{5-x}\text{Fe}_x\text{Si}_3$ and is a promising candidate material for such devices. It has a magnetic phase transition T_C at about 300K and shows a moderate MCE of 2.9J/(kg K) at a reasonable magnetic field change from 0 to 2T [1,2,3].

Up to now experimental studies focussed mainly on the atomic and magnetic structure of this compound and revealed an unusual temperature dependence of the lattice parameters and possibly marked different magnitudes of ordered magnetic moments on different magnetic sites [1,3]. To add to the understanding of the fundamental driving forces of the MCE inelastic neutron and inelastic X-ray scattering experiments have been undertaken on the selected compound MnFe_4Si_3 to study the spin and lattice dynamics and their interactions.

Magnon and acoustic phonon dispersion curves were obtained in the low energy regime ($E < 20\text{meV}$) combining inelastic X-ray and inelastic polarized neutron measurements. Experiments reveal a strong anisotropy between in and out-of-plane magnetic interactions. Comparing the experimentally determined phonon dispersion with on-going DFT calculations will help us to understand the electronic ground state of the system. Presently, spin wave calculations are being performed in order to extract relevant exchange couplings.

Investigations of the paramagnetic scattering above T_C in complement to the spin wave studies reveal sizable magnetic fluctuations in a large temperature range which are found to be isotropic. Characteristic length and energy scales will allow to address the question of the nature of its magnetism, e.g., itinerant versus localized. The study of the inelastic properties under the influence of different external parameters like magnetic field or temperature might be an essential step towards the understanding of the mechanism of MCE in this substance.

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Phonons in the filled skutterudites under high pressure studied by nuclear inelastic scattering

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The world's demand of the sustainable energy and efficient heat-to-energy conversion brings high interest to the thermoelectric materials. Between all new materials one of the promising classes is the structures containing empty voids filled by loosely bound "rattling" atoms, like skutterudites and clathrates which strongly scatter the propagating acoustic phonons thus decreasing the thermal conductivity. Even after 20 years of the intensive study the microscopic mechanism of the suppression of the thermal conductivity is unclear and highly debated. The original idea of the non-correlated, independent of the host structure, vibrations of the "rattling" atoms [1] has been contested by the inelastic neutron and nuclear inelastic measurements [2,3]. At the same time, purely harmonic Einstein oscillation of the "rattling" atoms cannot explain the reduced thermal conductivity. Thus, the strongly anharmonic interatomic potential of the "rattling" atoms and the hybridization of the "rattling" optic mode and acoustic propagation mode were suggested as a possible origin of the thermal conductivity suppression [4].

Here, we report [5] on study of the lattice dynamics in the filled skutterudite $\text{EuFe}_4\text{Sb}_{12}$ by nuclear

inelastic scattering, a technique which through its element selectivity provides partial densities of phonon states individually for all three elements presented in the compound. This allows us to compare vibrations of the guest atoms and of the host structure. In order to study the anharmonicity of the vibrations the system was investigated under high pressure in combination with the powder X-ray diffraction. As result the element specific Grüneisen parameters were obtained for a set of individual phonon modes. A large Grüneisen parameter was found for the “rattling” mode which is hybridized with the acoustical phonons at ambient and moderate pressure. However, at critical pressure of 12 GPa the Grüneisen parameter for the “rattling” mode is reduced and phonon modes decouple. The results of this study are important for understanding of the microscopic mechanism of the lattice dynamics in the guest-host structures like filled skutterudites.

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Session X: Engineering (Chair: Ralph Gilles) / 44

Neutron scattering contribution to understanding and development of high-temperature materials

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High-temperature materials are essential for energy conversion in turbines, which also includes conversion to kinetic energy for transport. Their continued development is a prerequisite for more efficient use of the available fuel resources. Understanding the basic properties of promising new materials as well as optimization of the existing ones can ensure an environmentally friendly operation of turbines.

Neutron scattering helps significantly in development of such advanced materials. Its particular advantage is the possibility to investigate structural and microstructural evolution in situ under operational conditions of materials.

Examples of structure and microstructure characterization of several types of materials important for high-temperature applications by neutron scattering are shown. First example is a contribution of in-situ Small-Angle Neutron Scattering (SANS) to understanding the behavior of Ni-base superalloy. It was found that additional γ' -precipitates are formed in Inconel-type superalloys after reheating above 570°C. These small precipitates influence mechanical properties of the alloy. Temperature dependence of their size and volume fraction as well as the kinetics of precipitate growth at 700 and 800°C were determined.

Secondly, investigation of porosity in ceramic thermal barrier coatings by means of combined in-situ and ex-situ SANS is presented. Such coatings enable an increase of temperature in the combustion chamber of turbines employing Ni-base superalloys by more than 100 K. The pores strongly affect the thermal and mechanical properties. The in-situ measurement at high temperatures revealed that an unexpected population of nanometer-sized pores is created at about 800°C, which later sinters under simulated operational conditions at 1200°C.

Structure and microstructure evolution of newly developed Co–Re alloys at high temperatures studied by in-situ neutron diffraction and SANS is presented. Co–Re-base alloys strengthened by carbides are candidates as new high-temperature material for gas turbines (foreseen temperature during operation \approx 1200°C). TaC carbides were found to be a promising option for strengthening phase as they do not dissolve up to at least 1300°C. The stability of the matrix and of the TaC phase as well as the influence of boron content on the microstructure of Co–Re alloys at high temperatures were investigated.

Although a variety of material parameters can be presently obtained, further improvement of neutron scattering techniques capability for development of high-temperature materials is desirable. Particularly, sample environment for in-situ and in-operando experiments can still be improved. For example, thermo-mechanical tests at foreseen operation temperatures of Co–Re alloys in vacuum or inert atmosphere would be of advantage. Testing environment for BEER@ESS engineering diffractometer planned also with this outlook will be presented.

Session X: Engineering (Chair: Ralph Gilles) / 48

PAS studies of neutron and hydrogen treated reactor steels

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Nuclear materials degradation caused by radiation exposure can be experimentally simulated via ion implantation. In our case, German reactor pressure vessel (RPV) steels were studied by positron annihilation lifetime spectroscopy (PALS). This unique non-destructive method can be effectively applied for the evaluation of microstructural changes and for the analysis of degradation of reactor steels due to neutron irradiation and proton implantation. Studied specimens of German reactor pressure vessel steels are originally from CARINA/CARISMA program. Eight specimens were measured in as-received state and two specimens were irradiated by neutrons in German experimental reactor VAK (Versuchsatomkraftwerk Kahl) in the 1980s. One of the specimens which was in as-received and neutron irradiated condition was also used for simulation of neutron damage by hydrogen nuclei implantation. Defects with the size of about 1-2 vacancies with relatively small contribution (with intensity on the level of 20-40 %) were observed in “as-received” steels. A significant increase in the size of the induced defects due to neutron damage was observed in the irradiated specimens resulting in 2-3 vacancies. The size and intensity of defects reached a similar level as in the specimens irradiated in the nuclear reactor due to the implantation of hydrogen ions with energies of 100 keV (up to the depth <500 nm). Actual results from German reactor steels were compared to previous experiences with Russian and Japan reactor steels studied after different loads.

Acknowledgment

This article was created with the support of the Ministry of Education, Science, Research and Sport of the Slovak Republic within the Research and Development Operational Programme for the project “University Science Park of STU Bratislava”, ITMS 26240220084, co-funded by the European Regional Development Fund. This article was also granted by VEGA 1/0204/13.

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Dependence of Ta-C precipitate stability and growth on allotropic Co-Re matrix transformation

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There is a need to supplement Ni-base superalloys in future gas turbines with turbine entry temperatures > 1500 °C to improve their efficiency. Co-Re alloys are a promising candidate, since they have high melting point > 1700 °C, as well as the required strength. Measurements by means of small-angle neutron scattering (SANS) and neutron diffraction (ND) were an important part of their development in the past several years [1],[2]. The complex interplay between the different nanoscale and mesoscopic phases could be studied in-situ at high temperatures. Especially with SANS, it was possible to observe the size distribution of fine Tantalum mono-carbide precipitates and their evolution within the matrix of a Co-Re-Ta-C alloy. Similar to pure Co-alloys, the Co-Re matrix undergoes an allotropic transformation hcp ↔ fcc at temperatures > 1100 °C, where the exact temperature depends on composition. Alloys without Cr contain some remnant metastable fcc at room temperature. The amount and size distribution of the TaC phase strongly depends on the C/Ta ratio in the alloy [3]. Addition of Chromium is important to improve oxidation behavior of the alloy system. However, Cr also has an affinity to C and forms carbides. It is also a hcp stabilizer of the Co-Re matrix. Alloy with Ta content of 1.2 at% with varying C/Ta ratio from 0.5-1 was studied in order to investigate the TaC phase stability. Currently, the influence of different heat treatments on the TaC precipitates are under investigation. In-situ SANS and microscopic studies show that precipitates coarsen but remains small (< 80 nm) at temperatures up to 1300 °C.

In this contribution, the influence of the Co matrix transformation on the fine TaC precipitate morphology is presented. Moreover, the influence of Chromium addition to the alloy is discussed.

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Joint Session MLZ/MML: Methods (Chair: Sebastian Busch) / 70

Neutron imaging techniques for the study of energy related materials, structures and processes

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The demands for a transition from nuclear and fossil energy generation processes towards more environmental neutral ones have induced new research fields for innovative materials, energy conversion procedures and energy storage devices. For a perfect understanding and the determination of the performance modern research tools are utilized and common.

In this context, neutron imaging methods provided at a few places like MLZ (ANTARES, NECTAR at FRM-2) and PSI (NEUTRA, ICON at SINQ) can play an important role. Alternatively and complementarily to X-ray studies it becomes possible to investigate light and most relevant materials like hydrogen and lithium even within thick metallic structures (pressure vessels, heaters, coolers, ...). These investigations can be performed on versatile length scales of 40 cm down to 1 cm while obtaining a spatial resolution of 100 μm to 5 μm , accordingly. On the other hand, time series from transition processes can be monitored with a frame rate of about 25 Hz in continuous mode. If repetitive processes (e.g. running engines) have to be observed, repetition rates up to 8000 rpm are common.

Based on these advanced techniques which are available in 2D and 3D, we have selected in our contribution to the conference the following results, available as demo for further investigation by our customers and researchers:

- Time- and space-resolved water distribution in sorption enhanced methanation reactors

We measured the spatial water distribution in a model sorption enhanced methanation reactor using time resolved neutron imaging. Due to the high neutron attenuation coefficient of hydrogen, the absorbed water in the sorption catalyst gives a high contrast allowing us to follow its formation and map its distribution. At the same time, the product gas was analysed by FTIR-gas analysis. The measurements provided important insights into functioning of sorption reactors and are essential for the future design and upscaling.

Further investigations mentioned and illustrated in the talk are:

- Hydrogen storage processes visualized and quantitatively observed
- Li-ion migration in batteries during charging and discharging processes
- Fuel cell performance determination in-situ and under variable operation conditions
- Diesel fuel injection processes and the cavitation problems in injection nozzles
- The accumulation process of soot in Diesel particulate filters

Most of the topics are still under investigation with partners from industry and research labs. Unfortunately, some industry projects are still confidential and cannot be communicated freely.

Next to the "standard" neutron imaging techniques, we are already on the way to implement advanced methods like neutron grating interferometry or energy-selective studies into the daily practice for our customers.

Joint Session MLZ/MML: Methods (Chair: Sebastian Busch) / 34

Neutron imaging applications for energy research

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Neutron imaging is a valuable tool for non-destructive testing of a huge variety of samples. The high sensitivity of cold neutrons for light elements such as H and Li combined with a good penetration of many metals may provide complimentary information to standard x-ray or synchrotron CT. Particularly in energy production and -storage the materials mentioned above are frequently employed. This renders imaging with cold neutrons an ideal technique for the study of static and dynamic processes in batteries, fuel cells and hydrogen storage materials. Examples include the transport of electrolyte in batteries, water management in fuel cells and hydrogen uptake in hydrogen storage tanks.

Furthermore, MLZ operates a unique imaging facility employing fission neutrons which show much higher penetration for heavy elements while still being sensitive for light elements as hydrogen. This is particularly beneficial for the investigation of massive hydrogen storage tanks which are needed to sustain high pressures at high temperatures.

In our presentation we will give an overview of the two neutron imaging instruments ANTARES (cold neutrons) and NECTAR (fast neutrons) operated at MLZ and show typical applications of neutron radiography and tomography for energy related research.

Joint Session MLZ/MML: Methods (Chair: Sebastian Busch) / 27

Neutron depth profiling at the focused neutron beam of MARIA: towards studies of Li kinetics in all solid state batteries.

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Neutron depth profiling (NDP) allows for the determination of the in depth distribution of an appropriate light elements in a few micrometers of solids. It is based on the energy analysis of charged particles produced upon the capture of thermal (cold) neutrons by isotopes with a large neutron cross-section. This technique is the method of choice for studies of Li migration in all solid state batteries. However, the required high depth resolution and high counting rates can only be achieved at the high flux facilities. We have recently built a new multi detector NDP facility designed for the focused neutron beam of reflectometer MARIA (MLZ) that will allow us to do fast NDP measurements on a minute rate. This paves the way to in situ/ in operando studies of Li migration and makes exploring the fast battery charging and the battery degradation in time possible.

Joint Session MLZ/MML: Methods (Chair: Sebastian Busch) / 39

Neutron Imaging of Complex Metal Hydrides

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Hydrogen is a promising energy carrier for the future, especially for mobile applications. It can be stored safely and reversibly at high volumetric densities in hydrogen storage tanks filled with light metal hydrides.

Due to the sensitivity of neutrons towards hydrogen, in situ Neutron Radiography (NR) is the ideal technique for time-resolved investigations of the hydrogenation process of metal hydride powder beds and pellets inside a hydrogen storage storage tank. Neutron Computerized Tomography (NCT) provides additional 3D information about the material structure and hydrogen distribution.

While low and medium temperature hydrides [1,2] have already been studied by NR and NCT, first-time in situ NR measurements of a hydrogen storage tank filled with the high-temperature complex hydride LiBH₄-MgH₂ at NECTAR and ANTARES beamlines at FRM II have been performed. Combining cold and fission neutron spectra of both instruments and using a new method for the quantitative investigation of neutron imaging data [3,4], a precise study of the hydrogen distribution in this high-temperature hydride is possible. Effects of temperature field and material packing density were investigated and the 3D structure was analyzed additionally by NCT. The results allow for tailoring of the material in terms of capacity, kinetics and safety.

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MML Session / 80

In-Situ investigations of the diffusion brazing process of gamma-TiAl with high energy X-ray diffraction

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Metal oxide surfaces: case study on Fe₃O₄

MML Session / 82

Electron and soft x-ray spectroscopy of materials and interfaces for energy conversion

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The GEMS-N Instrumental Suite and its Potential for the Characterization of Energy Related Material

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MML Session / 84

Pressure and temperature dependence of nuclear structure and magnetic properties in Mn₄FeSi₃

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MML Session / 85

SANS experiments on wood during pretreatment in ionic liquid/water mixtures

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Structural features and proton transport of polymer electrolyte membranes for high-temperature fuel cells

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Metal oxide surfaces: case study on Fe₃O₄**Author:** Heshmat Noei¹**Co-authors:** Andreas Stierle²; Björn Arndt²¹ DESY NanoLab, Deutsches Elektronen-Synchrotron, Notkestraße 85, D-22607 Hamburg, Germany² DESY NanoLab, Deutsches Elektronen-Synchrotron, Notkestraße 85, D-22607 Hamburg, Germany and Physics Department, University of Hamburg, D-20355 Hamburg, Germany**Corresponding Author:** heshmat.noei@desy.de

Magnetite (Fe₃O₄) is one of the most important transition metal oxides found with wide industrial applications due to its surface reactivity, as well as its exceptional electronic and magnetic properties. It is involved in the catalysis of the water–gas shift reaction, Fischer–Tropsch synthesis, and it also raised some interest due to its possible application for groundwater remediation and in spintronic devices. Since these applications depend on the surface structure of the material, a correct description is fundamental for a deeper understanding of the processes involved. In this contribution, we studied the atomic structure and the interaction of organic molecules with magnetite. The binding of simplest carboxylic acid, formic acid (HCOOH), to magnetite is studied as an important model system with regard to understanding the grafting of more complex molecules via carboxylate groups. Furthermore, the adsorption and interaction of large molecules with magnetite show the formation of nanocomposites. The self-assembly of nearly spherical iron oxide nanoparticles in supercrystals linked together by a thermally induced crosslinking reaction of oleic acid molecules leads to a nanocomposite with exceptional bending modulus, hardness and strength.

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Operando Diffraction During Li Battery Operation using Neutron and Synchrotron X-Ray Radiations**Author:** Jean-Noël Chotard¹**Co-authors:** Christian MASQUELIER¹; Emmanuelle SUARD²; François FAUTH³; Laurence CROGUENNEC⁴; Matteo BIANCHINI⁵¹ Laboratoire de Réactivité et Chimie des Solides² ILL, Grenoble, France³ CELLS - ALBA Synchrotron, Cerdanyola del Vallès, Barcelona, Spain⁴ ICMCB-CNRS, Pessac, France⁵ LRCS/ICMCB-CNRS/ILL**Corresponding Author:** jean-noel.chotard@u-picardie.fr

Performing in situ and operando measurements on electrode materials for Li-ion and Na-ion batteries is of importance for their understanding and improvement. Electrode materials need to be studied in their environment (in situ) and in real time while they function (operando), since they normally

operate in non-equilibrium conditions. Real-time experiments upon charge/discharge of the electrodes (i.e. upon lithium or sodium extraction/insertion from/into the electrodes) unveil dynamics that are not accessible by other means and allow a more complete understanding of the electrodes' functioning. The use of different probes is an important requirement for the study of such reactions. The combined use of X-Ray Powder Diffraction (XRPD), Synchrotron radiation XRPD and Neutrons Powder Diffraction (NPD) allows observing any atomic element in any crystalline electrode. However, custom setups are required to carry out operando diffraction experiments on batteries. We recently designed an electrochemical cell manufactured with a completely neutron-transparent (Ti,Zr) alloy [1]. Used with deuterated electrolytes, the cell is able to combine good electrochemical properties and the ability to collect ND patterns operando, with good statistics and no other Bragg peaks than those of the electrode material of interest. Importantly, this allows detailed structural determinations by Rietveld refinement during operation. The cell was validated using well-known battery materials such as LiFePO_4 and $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ demonstrating real operando experiments conducted on the D20 high flux neutron powder diffractometer at ILL Grenoble, France. Importantly, we showed the possibility to succeed in reliable structural refinements (by the Rietveld method) and thus to observe structural modifications in details, from unit cell parameters to atomic coordinates and even site occupancy factors. We will discuss a few studies done with this setup, namely the observation of lithium extraction from different samples in the family of spinels $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$. We performed NPD in real time on three samples (LiMn_2O_4 , $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{Li}_{1.10}\text{Mn}_{1.90}\text{O}_4$) and showed how the Li/Mn ratio influences the phase diagram of the material [2]. New insights obtained from high resolution –high flux Synchrotron X-Ray diffraction data will be presented, in particular the existence of a Li^+ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ordering within the spinel-delithiated composition $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ [3].