

MLZ Conference: Neutrons for Energy

Monday 18 July 2016 - Friday 22 July 2016

Hotel Wyndham Grand Axelmannstein, Bad Reichenhall, Germany

Programme

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Monday 18 July 2016

Registration (11:00-12:30)

Lunch (12:30-13:50)

Welcome by MLZ directors (13:50-14:00)

Session I: Fuel Cells 1 (14:00-15:30)

time [id] title

14:00 [75] **Neutron imaging of polymer electrolyte fuel cells (PEFCs)**

Presenter: Dr. BOILLAT, Pierre (Paul Scherrer Institut (PSI))

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.

14:50 [45] Water distribution at different length scales in operando fuel cells

Presenter: Dr. MARTINEZ, Nicolas (SPrAM, INAC, CEA Grenoble)

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 allows 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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[3] Morin A, Gebel G, Porcar A, Peng Z, Martinez N, Guillermo A, Lyonnard S. under review

15:10 [11] Evidence for hydrated channels and connected water clusters in proton conductive membranes based on sulfonated syndiotactic polystyrene

Presenter: Dr. SCHIAVONE, Maria Maddalena (Jülich Centre for Neutron Science - Outstation at MLZ, Forschungszentrum Jülich GmbH, Germany)

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.

Coffee Break (15:30-16:00)**Session II: H₂ Storage (16:00-17:50)**

time [id] title

16:00 [73] Exploring hydrogen and ammonia as energy storage alternatives to fossil fuels: in-situ neutron powder diffraction studies

Presenter: Prof. DAVID, William (STFC)

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.

16:50 [5] Hydrogen dynamics in defective graphene

Presenter: Dr. CAVALLARI, Chiara (ESRF - European Synchrotron Radiation Facility, Grenoble, France)

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.

17:10 [10] Neutron scattering insight at hydrogen storage in sub-nanopores

Presenter: Dr. RUSSINA, Margarita (Helmholtz Zentrum Berlin für Materialien und Energie)

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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Dinner (18:00-19:30)

Tuesday 19 July 2016

Session III: Batteries 1 (08:40-10:30)

time [id] title

08:40 [71] Neutron Depth Profiling: A challenging new method to in situ monitor Lithium in solid-state Li-ion batteries

Presenter: Prof. NOTTEN, Peter H.L. (Eindhoven University of Technology)

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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09:30 [52] Lithium-Ion Batteries monitored by Neutrons

Presenter: MUEHLBAUER, Martin (Helmholtz Institute Ulm (HIU))

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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09:50 [26] Ionic diffusion in battery cathods, e.g. Na_{0.7}CoO₂

Presenter: Dr. JURANYI, Fanni (Paul Scherrer Institute)

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 sites 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 (μ^+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.

10:10 [4] Looking non-destructively at the aging mechanisms in commercial LiFePO₄/C 18650 cells with neutron diffraction and electrochemistry

Presenter: PAUL, Neelima

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.

Coffee Break (10:30-11:00)**Session IV: Photovoltaics (11:00-12:30)**

time [id] title

11:00 [66] tba

*Presenter: BARNES, Piers*11:50 [58] **Crystal structure and point defect characteristics of quaternary compound semiconductors by neutron diffraction.***Presenter: Dr. GURIEVA, Galina (Helmholtz-Zentrum Berlin)*

Quaternary semiconductors $\text{Cu}_2\text{BIIICIVX}_4(\text{BII}-\text{Zn,Cd,Hg,CIV}-\text{Si,Ge,Sn;X}-\text{S,Se,Te})$ are considered as interesting material for applications in optoelectrics and non-linear optics. $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ 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 ($>10^4\text{cm}^{-1}$). 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 Zn^{2+} , 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 $\bar{4}2m$). 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.

12:10 [46] Inelastic Neutron Scattering on Colloidal Nanocrystal Solids: Understanding the Importance of Surfaces

Presenter: Prof. WOOD, Vanessa (ETH Zurich)

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 trap 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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Lunch (12:30-14:00)**Session V: Batteries 2 (14:00-15:30)**

time [id] title

14:00 [57] Developing new varieties of electrochemical cells for operando neutron diffraction investigations of lithium ion battery materials

Presenter: Prof. EDSTRÖM, Kristina (Uppsala University)

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 LiFePO_4 , $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ and $\text{Li}_0.18\text{Sr}_0.66\text{Ti}_0.5\text{Nb}_0.5\text{O}_3$ 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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14:50 [49] Study of Sn and Fe based electrode materials for Alkali-ion batteries by in situ Mössbauer spectroscopy

Presenter: Dr. MAHMOUD, Abdelfattah (LCIS/ GREENMAT, Institute of Chemistry B6, University of Liège, Allée de la Chimie 3, B-4000 Liège, Belgium)

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

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15:10 [61] Neutron depth profiling, present day applications in Lithium ion batteries

Presenter: Mr. VERHALLEN, Tomas (Tudelft)

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.

Coffee Break (15:30-16:00)

Session V: Batteries 2a (16:00-16:50)

time [id] title

| | |
|-------|--|
| 16:00 | <p>[74] Ion containing polymers for battery technology <i>Presenter: Prof. MARANAS, Janna (Penn State University)</i></p> <p>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</p> |
|-------|--|

Poster Session: Session I & Dinner Buffet (16:50-19:30)

The posters will be available during both poster sessions.

The poster format shall be A0, portrait orientation.

| [id] title | presenter | board |
|---|-----------------------|-------|
| [25] Dynamic and Structure of Polymer-Cellulose Composite Electrolyte for Li-ion Battery | Mr. ZHAN, Pengfei | 10 |
| [13] Lithium Permeation through Ultrathin Silicon Layers measured by Neutron Reflectometry | Dr. HÜGER, Erwin | 6 |
| [12] Study of magnetocaloric materials in the system $Mn_{2-x}M_xSb$ (M=Fe, Co) | Mr. CHIKOVANI, Mamuka | 5 |
| [23] In-operando neutron reflectometry studies on Li incorporation and volume modification of silicon electrodes in Li-ion batteries | Mr. JERLIU, Bujar | 8 |
| [19] Pressure and temperature dependence of nuclear structure and magnetic properties in Mn_4FeSi_3 | HERING, Paul | 7 |

| | | |
|---|---|----|
| [28] Battery and materials research at the diffractometer STRESS-SPEC at FRM II | Dr. HOFMANN, Michael Dr. GAN, Weimin | 11 |
| [42] Low-temperature performance of Li-ion batteries probed by high-resolution neutron diffraction and electrochemistry | SENYSHYN, Anatoliy | 15 |
| [35] Structural features and proton transport of polymer electrolyte membranes for high-temperature fuel cells | Dr. IVANOVA, Oxana | 13 |
| [43] Crystal Structures and Thermoelectric Properties of $A8Al8Si38$ (A = K, Rb and Cs) | Dr. BARAN, Volodymyr | 16 |
| [33] Proton dynamics in high temperature polymer electrolyte fuel cell membranes | Dr. ZORN, Reiner | 12 |
| [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 | Mr. MAITY, Sumit | 19 |
| [2] Neutron scattering characterization of confined fluids for energy storage and environmental science | Dr. MELNICHENKO, Yuri | 1 |
| [6] Determination of anodic transition metal deposition with PGAA | SEIDLMEYER, Stefan | 3 |
| [38] Neutron diffraction study of Li diffusion in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ solid state lithium conductors | MONCHAK, Mykhailo | 14 |
| [54] Structural complexity and O ²⁻ ordering in $Pr_{2-x}Sr_xNiO_{4+\delta}$ studied by single crystal neutron and x-ray diffraction | Mr. DUTTA, Rajesh | 18 |
| [1] Neutron Diffraction Studies of Catalytic GaN/ZnO Nanoparticles | Dr. FEYGENSON, Mikhail | 20 |
| [8] SANS experiments on wood during pretreatment in ionic liquid/water mixtures | Dr. FRIELINGHAUS, Henrich | 21 |
| [59] In-beam activation analysis facility at MLZ | REVAY, Zsolt | 24 |
| [31] In-situ tensile deformation behaviour of a high ductile Mg-RE alloy via neutron diffraction | Dr. HUANG, Yuanding Dr. GAN, Weimin | 23 |
| [29] Neutron spin-echo spectroscopy: a tool for energy research | Dr. MONKENBUSCH, Michael | 30 |

| | | |
|---|-----------------------------|----|
| [36] Strain Induced Martensitic Transformation in Austempered Ductile Iron (ADI) | Dr. HOFMANN, Michael | 25 |
| [24] MARIA – The high-intensity polarized neutron reflectometer of JCNS | MATTAUCH, Stefan | 28 |
| [21] – Photons for Energy - Complementary Analytics | KRIELE, Armin | 26 |
| [41] Neutron backscattering for high energy resolution spectroscopy on energy related materials | Mr. FRICK, Bernhard | 27 |
| [17] Low dimensional lead bromide perovskite in light emitting application – investigation on structure evolution via neutron scattering | Mr. WANG, Rui | 29 |
| [37] The GEMS-N Instrumental Suite and its Potential for the Characterization of Energy Related Material | Dr. MOULIN, Jean-Francois | 2 |
| [18] Oxygen deficiency in High-Tc YBCO thin films identified by positron annihilation spectroscopy | Dr. HUGENSCHMIDT, Christoph | 9 |
| [16] Materials for nuclear fusion examined by neutrons: Neutron computed tomography on carbon fiber composites for plasma divertors | SCHULZ, Michael | |

Wednesday 20 July 2016

Session VIII: Batteries & Fuel Cells (08:40-10:30)

time [id] title

08:40 [77] **Operando Diffraction During Li Battery Operation using Neutron and Synchrotron X-Ray Radiations**

Presenter: Dr. CHOTARD, Jean-Noël (Laboratoire de Réactivité et Chimie des Solides)

09:30 [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**

Presenter: OPITZ, Alexander (TU Wien)

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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (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 CO_2 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 CO_2 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 CO_2 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 H_2O and CO_2 . Hence, this novel type of electrolysis electrodes may open new pathways in the quest for optimized energy storage via SOECs.

09:50 [53] 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

Presenter: Mr. LIN, Yu (Forschungszentrum Jülich GmbH)

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.

10:10 [40] Neutron and X-ray Diffraction Studies of BaCe_{0.85}Y_{0.15}O_{3-δ} for Application in Innovative Design of Fuel Cell*Presenter: Dr. KREZHOV, Kiril (INRNE-BAS)*

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

Coffee Break (10:30-11:00)**Session VII: Catalysis (11:00-12:30)**

time [id] title

11:00 [3] Industrial applications of neutron scattering in catalysis

Presenter: Dr. ALBERS, Peter (Evonik Technology Infrastructure GmbH)

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.

11:50 [32] Investigating guest selectivity and dynamics in porous framework materials using in situ neutron scattering and computational approaches

Presenter: AUCKETT, Josie (The Bragg Institute, Australian Nuclear Science and Technology Organisation)

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.

[1] Li JR, Kuppler RJ and Zhou HC (2009) “Selective gas adsorption and separation in metal-organic frameworks”, *Chemical Society Reviews*, 38:1477-1504.

12:10 [9] Proton dynamics of phosphoric acid in the catalytic layer of gas diffusion electrodes for HT-PEFC

Presenter: Dr. KHANEFT, Marina (Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH)

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.

****References:****

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Lunch (12:30-14:00)**Conference Excursion and Conference Dinner: Departure of Bus at****14:45 (14:45-22:00)**

time [id] title

| | |
|-------|------------------|
| 14:45 | Departure of bus |
|-------|------------------|

Thursday 21 July 2016

Session IX: Thermoelectrics & Magnetocalorics (08:40-10:30)

time [jd] title

08:40 [47] Heat conduction in thermoelectric materials

Presenter: Prof. CHRISTENSEN, Mogens (Aarhus University)

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.

[1] G. A. Slack, CRC Handbook of Thermoelectrics, 407 (1995).

[2] A. Saramat, G. Svensson, A. E. C. Palmqvist, C. Stiewe, E. Mueller, D. Platzek, S. G. K. Williams, D. M. Rowe, J. D. Bryan, and G. D. Stucky, J. Appl. Phys. 99, 023708 (2006).

[3] M. Christensen, A. B. Abrahamsen, N. B. Christensen, F. Juranyi, N. H. Andersen, K. Lefmann, J. Andreasson, C. R. H. Bahl, and B. B. Iversen, Nature Materials 7, 811 (2008).

09:30 [60] Neutron scattering studies on (Mn,Fe)₂(P,Si)-type magnetocaloric materials

Presenter: Mr. MIAO, Xuefei (Delft University of Technology)

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-parameter (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.

[1] E. Brück, Journal of Physics D: Applied Physics 38, R381 (2005).

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[3] N. H. Dung, Z. Q. Ou, L. Caron, et al, Advanced Energy Materials 1, 1215 (2011).

[4] X. F. Miao, L. Caron, P. Roy, et al, Physical Review B 89, 174429 (2014).

[5] X. F. Miao, L. Caron, Z. Gercsi, et al, Applied Physics Letters 107, 042403 (2015).

09:50 [14] Inelastic neutron scattering on magnetocaloric compound MnFe₄Si₃

Presenter: Mr. BINISKOS, Nikolaos (Jülich Centre for Neutron Science, Forschungszentrum Juelich GmbH, Outstation at ILL, Grenoble, France/CEA-Grenoble, INAC MEM, 38054 Grenoble, France)

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 MnFe₄Si₃ belongs to the series Mn_{5-x}Fe_xSi₃ and is a promising candidate material for such devices. It has a magnetic phase transition TC 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 MnFe₄Si₃ to study the spin and lattice dynamics and their interactions.

Magnon and acoustic phonon dispersion curves were obtained in the low energy regime (E<20meV) 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 TC 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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10:10 [56] Phonons in the filled skutterudites under high pressure studied by nuclear inelastic scattering*Presenter: SERGEEV, Ilya (DESY)*

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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- [4] N. Bernstein, J. L. Feldman, and D. J. Singh, Phys. Rev. B 81, 134301 (2010).
- [5] I. Sergueev, K. Glazyrin, I. Kantor, et al., Phys. Rev. B 91, 224304 (2015)

Coffee Break (10:30-11:00)**Session X: Engineering (11:00-12:30)**

time [id] title

11:00 [44] Neutron scattering contribution to understanding and development of high-temperature materials

Presenter: Dr. STRUNZ, Pavel (Nuclear Physics Institute)

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 $\approx 1200^\circ\text{C}$). 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.

11:50 [48] PAS studies of neutron and hydrogen treated reactor steels

Presenter: Prof. SLUGEN, Vladimir (FEI STU Bratislava)

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 (Versuchatomkraftwerk 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

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12:10 [30] Dependence of Ta-C precipitate stability and growth on allotropic Co-Re matrix transformation*Presenter: KARGE, Lukas*

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 $hcp \leftrightarrow fcc$ 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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Lunch (12:30-14:00)**Joint Session MLZ/MML: Methods (14:00-15:50)**

time [id] title

14:00 [70] Neutron imaging techniques for the study of energy related materials, structures and processes

Presenter: Dr. LEHMANN, Eberhard (PSI)

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.

14:50 [34] Neutron imaging applications for energy research

Presenter: SCHULZ, Michael

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, fuels 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.

15:10 [27] Neutron depth profiling at the focused neutron beam of MARIA: towards studies of Li kinetics in all solid state batteries.

Presenter: Dr. VEZHLEV, Egor (Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH)

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.

15:30 [39] Neutron Imaging of Complex Metal Hydrides

Presenter: Dr. PRANZAS, P. Klaus (HZG)

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 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 $\text{LiBH}_4\text{-MgH}_2$ 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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Coffee Break (15:50-16:10)**Poster Session: Joint Poster Session MLZ/MML (16:10-17:30)**

The posters will be available during both poster sessions.

The poster format shall be A0, portrait orientation.

Dinner (18:00-19:30)

Friday 22 July 2016

MML Session I (08:30-10:30)

Coffee Break (10:30-11:00)

MML Session II (11:00-12:30)

Lunch (12:30-14:00)