Neutron and X-ray Methods for the Characterization of Solid Oxide Fuel Cell Materials, Cells, and Stacks

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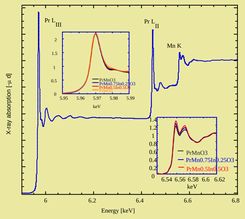
The solid oxide fuel cell (SOFC) is an emerging energy technology, and there is need for improvement of materials and design. Also, many materials, processing and operation details are not yet understood. Related devices such as batteries, capacitors and PEM fuel cells have benefited from materials analysis and characterization techniques that require synchrotron radiation or neutrons. On the other hand, SOFC systems can provide a nice playground for Physicists, Chemists who are interested in basic research. The materials involved in SOFC may represent strongly correlated fermion systems, for instance. The topology of the pore space in electrodes and electrolyte has influence on the fluid dynamics. We give here a brief, rudimentary, preliminary overview of a set of new and ongoing experiments that aim at understanding and improve materials and systems relevant to SOFCs.

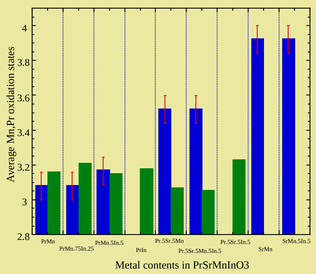
X-ray absorption near-edge structure spectroscopy (XANES)

XANES is a relatively easy and convenient tool for the analysis of the oxidation states of prominent elements in a material. We have applied XANES to cathodes, anodes, and electrolytes.

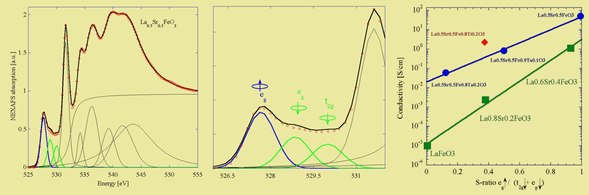


Left: X-ray absorption spectrum for Pr L3 and L2 and the Mn K-shell in a potential cathode material. Mn^{3+} and Mn^{4+} could be identified by the chemical shift as well as by the for Mn4+ typical quadrupol transition peak at the pre-edge region. Valence of Pr in our materials is generally Pr^{3+} due to the pronounced single white line. Small contaminations with Pr^{4+} are visible (see below). Experiments were carried out ex-situ. For better understand-ing of SOFC material under realistic operation conditions, it is necessary to measure at elevated temperatures, up to 800°C-900°C, and under oxidizing conditions.

Right: X-ray absorption near-edge spectroscopy allows us to determine the valence of the **Pr** (**green**) and the **Mn** (**blue**). To test a current approach for cathode materials tailoring, it is necessary to know the precise valence of the cations. Also, defect chemistry modelling typically requires accurate information on the oxidation state of the constituents in the reaction balancing. Here we see that Mn is the chemically active species, whereas Pr plays chemically no dominant role.

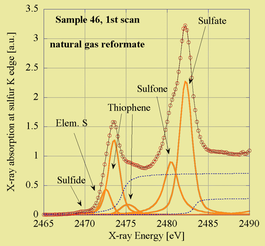


Metal contents in PrSrMnInO3



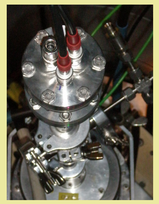
Top: Understanding the enhanced conductivity of LaSrFe-based SOFC cathode materials in terms of electron hole doping by oxygen XANES. We find quantitative systematic correlation between XANES and conductivity.

Right: Sulfur poisoning of SOFC anodes is for the first time addressed with S(1s) XANES. We are able to perform a full molecular speciation of SOFC anodes after operated with sulfur containing fuel. A novel discovery is that organic heterocyclic sulfur species such as thiophene obviously survive the quite high temperatures during SOFC operation, such as 800°C. Sulfate is another very prominent species suspected, and now for the first time detected.

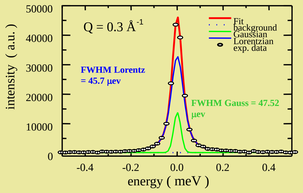


Quasi-elastic neutron scattering (QENS) probes proton diffusion in electrolytes

We probe protons in ceramic proton conductors with quasi elastic neutron scattering on the molecular level in order to understand the fundamental processes that govern proton or hydrogen „logististics“ in condensed matter.

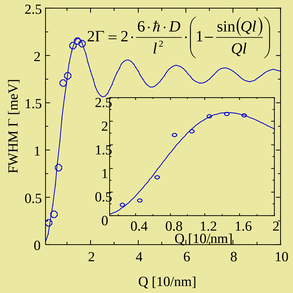


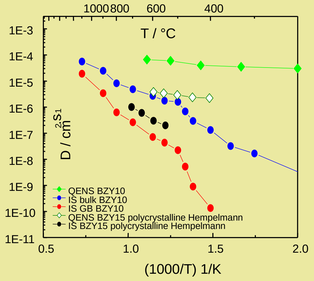
Left: Neutron time-of-flight beamline FOCUS at PSI/SINQ. **Middle:** Empa researcher setting up a computer macro for electrochemical/neutron in-situ experiments. **Right:** In-situ cell.



Left: Elastic neutron peak from QENS, deconvoluted in one Gaussian and one Lorentzian contribution. Instrument broadening causes Gaussian contribution. The Lorentz contribution results from the motion of atoms.

Right: For large Q, line width Γ oscillates with Q. Data contain information on the diffusion mechanism. The Q-dependence of the quasielastic line width shows characteristic traits of jump-diffusion. For incoherent scattering of the nuclei in the lattice, the quasi elastic spectrum can be calculated in the frame work of the Chudley-Elliott model and the probability of finding the particle at time t. We fitted the model (see equation for 2Γ(Q)) to our data and obtain l≈3 Å for the effective jump length, which is about the distance between two oxygen atoms in the lattice.





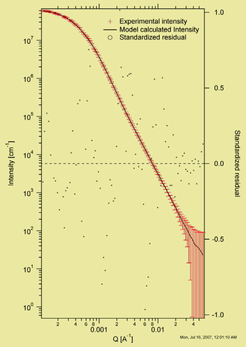
Exposing BZY ceramic bars to water vapour makes them absorbing and dissociating the H_2O into OH^- and H^+; H^+ will then be available in the lattice as thermally activated, free moving protons. Such proton charged bars were measured with QENS in-situ between ambient temperature and 500°C.

Left: Diffusion constants as obtained from impedance spectroscopy for the bulk and grain boundaries, and from QENS. Data from Hempelmann et al. have different stoichiometry ($BaZr_{0.85}Y_{0.15}O_{3-\delta}$ Gross, Hempelmann et al., Solid State Ionics 145, 2001, 325-331).

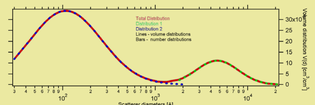
Impedance spectroscopy (IS) and QENS may show a large difference in obtained diffusion constants. IS evaluates an effective conductivity diffusion coefficient D, whereas QENS detects a chemical diffusion constant.

Porosity gradient in SOFC cells probed with ultra-small angle X-ray scattering

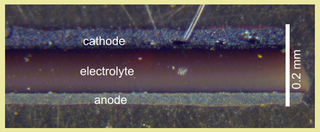
Almost all electrochemical energy conversion and storage devices are made from electrodes and electrolytes which by principle have to differ in porosity. For SOFCs, the electrolytes have to be gas tight, which means they should not possess an open porosity. The anode, this is the fuel electrode, should possess a high porosity. The same hold for the cathode. We present here an approach where we subject a 40 micrometer thin slice cross section a SOFC cell (cathode, electrolyte, anode total 200 micron thickness) to ultra small angle X-ray scattering (USAXS) with 10 micron spatial resolution. The USAXS method allows to determine internal surface areas, porosities, particle size and void size, and fractal dimensions ranging from 1 nm to 1 micrometer. Sulphur poisoning is a current problem in SOFC technology. One goal is to detect the coarsening of Ni-clusters in the anode during exposure to sulphur-rich fuel.



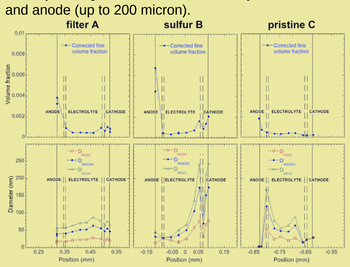
Left: Original USAXS scattering curves recorded across the cell assembly at 10,000 eV. Differences on the small Q tail can be assigned to different micro-and nanostructure of the anode vs. cathode or electrolyte. The transmitted intensity depends on the X-ray optical density of the material and its porosity. **Below:** Corresponding pore size distribution as obtained from least square fitting of model to the USAXS data.



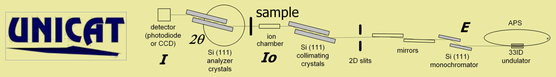
The synchrotron beam position is kept fixed, while the sample is positioned so that an USAXS curve is acquired through the 40 micron thin sample at the topmost cathode position in transmission (position 0 micron). Then the sample is moved by 10 micron and another curve is recorded at a by 10 micron deeper region in the cathode, and so on. In this way, several dozen scattering curves provide information on structural parameters for virtually all regions in cathode, electrolyte, and anode (up to 200 micron).



Top: SOFC assembly with 200 micrometer nominal thickness, made of 2 anode layers, 2 cathode layers, and 1 electrolyte layer in the center.



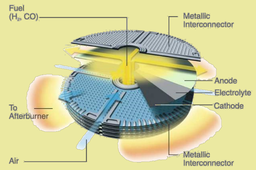
Left: Void and pore size distribution at one particular depth position in the virgin-like anode. Three major size modes are evident: micropores with 8 nm diameter, mesopores with 40 nm, and a very broad distribution of macropores around 1 micron. For the operated anode (not shown here), we find that near the anode/electrolyte interface the micropores distribution vanishes, possible due to anode-electrolyte reactions.



Imaging of SOFC stacks with neutron tomography

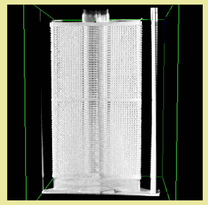
With neutrons we can directly see through an SOFC stack, although such stacks are rigid bodies that contain steel and ceramics. The stack shown here has a height of approximately 40 cm and a diameter of ca. 20 cm. To support thermomechanic studies carried out at EMPA, we have – to our knowledge - acquired the very first such neutron radiography images of a SOFC stack.

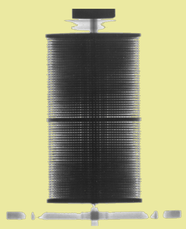
Top: Neutron tomography beamline at SINQ/PSI in Villigen. This beamline has been very successful with research on polymer electrolyte membrane fuel cells.



Left: The stack is built from alternating assemblies of thin ceramic cells (cathode, electrolyte, anode) and metallic interconnectors, micro-patterned to provide for air, fuel, and exhaust flows. They are put under vertical pressure to allow for good electric contact, but uneven pressure distribution may cause fracture.

The neutron radiography images **below** show i) a digital section of a stack showing the median plane, ii) a frontal image that permits to look through air channels and other micropatterns, and iii) a close-up image revealing the supposedly even spacing of interconnectors and cell assemblies.
Image quality will be better with longer data acquisition time and will then allow for detailed analysis of specific regions prone to failure (resolution better than 1 mm).





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