

LOOKING INSIDE FUTURE GENERATIONS OF BATTERIES

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We all know the great frustrations of cell phones that need to be charged every day, laptops running out of battery power too fast and the high cost of a new rechargeable battery to replace an old one. These everyday frustrations highlight some of the major problems related to present-day Li-ion battery technology, which is the preferred form of energy storage for today's consumer electronics. It also illustrates some of the major obstacles in the development of batteries for large scale energy storage, e.g. electrical vehicles, storage of renewable energy and grid stabilization. Thus development of novel materials for Li-ion storage with improved electrochemical properties or realization of rechargeable ion batteries based on cheaper and more abundant metals is required to move towards future generation batteries.

Operando battery studies

Every time a rechargeable metal-ion battery is charged or discharged the electrodes undergo phase transitions, e.g. between the Li-rich and Li-poor phase. However, the fundamental mechanisms accompanying delithiation and relithiation and how they rely on materials characteristics such as particle size and composition are still not fully understood. Detailed insight into these mechanisms is of vital importance for practical applications as the reversibility and stability of the structural transformations determine the energy, power, and lifetime of the system. Studying the electrochemically driven phase transition *operando*, i.e. while they occur and being able to relate the structural transformations directly to the electrochemical observations is of vital importance as the dynamic conditions under battery operation inherently are far from equilibrium. Structural diffraction studies of energy storage materials carried out *in situ*, i.e. as energy release and uptake occurs, are in general a very powerful tool to understand the underlying mechanisms.¹⁻³ Recently, a novel *operando* battery test cell for synchrotron diffraction studies was employed to investigate a novel high power nanoscale cathode material, $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$. Surprisingly this material exhibits a completely different phase transformation pathway than the extremely well studied case of olivine LiFePO_4 dominated by solid solution formation and a high degree of metastability.^{4,5}

Going beyond lithium

Moving the ion battery technology from lithium to other metals sets new requirements on the electrode materials, e.g. for Na-ion batteries lack of well-functioning sodium-bearing anodes has limited the number of usable cathode materials. We have overcome this by for the first time demonstrating $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ to be a suitable sodium-bearing anode material for aqueous sodium-ion batteries.⁶ Furthermore, cathode materials traditionally employed for Li-ion storage is found to function well in aqueous Na-ion batteries, even though the phase transition mechanism is significantly affected by incorporation of the larger Na-ion. The next step in this development is to prepare and investigate novel electrode materials for Mg- and Al-ion storage by the newly available *operando* technique. Perspectives of this future line of research will be discussed in this talk.

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Dorthe B. Ravnsbæk received her Ph.D. degree in nanotechnology at iNANO, Department of Chemistry in 2011 for her work on novel materials for hydrogen storage. Early 2012 Dorthe joined the Department of Material Science and Engineering at MIT as a post doc funded by the Carlsberg Foundation. At MIT she has been working on developing and investigating novel cathode materials for Li- and Na-ion batteries. This winter Dorthe was awarded a VKR Young Investigator Project and is now starting her individual research career on novel types of batteries at iNANO and Department of Chemistry as Assistant Professor. Dorthe's research interest focuses on energy storage, inorganic material synthesis and material characterization by *in situ* synchrotron X-ray diffraction and electrochemical methods. Dorthe's scientific work has to date lead to 34 papers published in peer reviewed journals (H-index of 13), 18 talks at international conferences (hereof 8 invited) and several awards, e.g. EuroScience: European Young Researcher Award 2011, Danish Academy of Science PhD award 2012 and The Danish Council for Strategic Research's Award for Excellent International Research Collaboration in 2014.

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TOWARDS HYBRID ORGANIC-INORGANIC MATERIALS

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Organic-inorganic hybrids are sophisticated materials composed of a combination of organic and inorganic structural motifs, and they adopt properties from both components. Hybrids count several classes of compounds, two examples are (1) metal-organic frameworks (MOFs) in which metal centers are connected *via* organic linkers and (2) two-dimensional inorganic layers with metal-organic complexes sandwiched in-between. Independent design of the organic and inorganic parts allows tailoring of the material porosity and properties. Hybrid chemistry opens a completely new avenue for functionalizing materials and it has manifested itself as especially promising for heterogeneous- and photocatalysis.

To develop new functional hybrids a strong background in both molecular synthesis and materials chemistry is necessary. This combination is relative rare as research tend to focus at either molecular or materials aspects of chemistry. I have a strong background in materials chemistry and my recent postdoctoral stay in Göttingen has taught me molecular synthesis. My combined skills allow me to master molecular as well as solid state synthesis and characterization. In this talk I will give an overview over the metal-organic chemistry undertaken during my stay in Göttingen, and I will give an introduction to my future plans for hybrid materials.

Molecular chemistry

Selenium-nitrogen chemistry: Chalcogenide chemistry is rich and diverse due to various stable oxidation states and coordination geometries [1]. Selenium-nitrogen chemistry is comparatively less developed than sulfur-nitrogen chemistry due to the rich redox chemistry of selenium and its ability to polymerize, two properties which are difficult to control. I will present a study on the synthesis, characterization and complex formation of the air, moisture and temperature sensitive molecule $\text{Se}(\text{N}t\text{Bu})_2$ ($t\text{Bu}$ = tert-butyl), the diimido selenium equivalent to SO_2 [2].

Tripodal iminophosphoranes: Tripodal ligands where three ligand arms coordinate to a central metal atom are versatile to stabilize metals in a well-defined ligand sphere. The P-N bond in iminophosphoranes is strongly polarized (P^+-N^-) giving them a high donor-capacity. The potential of iminophosphoranes in coordination chemistry has been demonstrated, and they are promising for homogeneous catalysis. I will give a short overview over synthesis of tripodal iminophosphorane complexes [3].



Nina received her Ph.D. in chemistry from Aarhus University in 2009, where she stayed as a postdoctoral fellow in the research group of Bo B. Iversen for two years before moving on to Germany. She just finished a two-year postdoctoral stay funded by the Villum Foundation at Georg-August-Universität Göttingen in the group of Dietmar Stalke. She was in 2014 awarded a stipend from the Villum Foundation Young Investigator Programme to build up at independent research profile in organic-inorganic hybrid materials at the Interdisciplinary Nanoscience Center at Aarhus University. Her research interests include advanced synthesis and characterization of inorganic and metal-organic porous and molecular compounds for e.g. catalytic applications.

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Hybrid materials

My future research plan at iNANO is to develop and investigate advanced functional organic-inorganic hybrid materials through functionalization of the inorganic matrix as well as of the organic guest. Materials of interest are two- and three-dimensional porous compounds for heterogeneous catalysis [4] and semiconductors for photocatalysis and tuning of their optical properties [5].

The inorganic matrices will be synthesized solvothermally, and the designed cationic (metal-)organic guest will be prepared by applying wet-chemistry approaches. The hybrid is formed by combining the two parts using: (1) *in situ* implementation of the cation as the anionic structure is formed, or (2) by post-synthetic modification of the initially formed matrices. The methods allow development of multifunctional materials. Detailed structural and physical characterization will be performed to understand the relationship between structure and property.

Fundamental for hybrid materials is fine-tuned molecular chemistry. Its approach to e.g. catalysis therefore differs substantially from conventional catalysis where physical parameters such as catalyst size and texture determine their performance. Hybrid chemistry is still in its infancy, but has an enormous potential for the development of new functional materials!

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FROM METAL TO COMPLEX HYDRIDES AND BEYOND

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The reserves of fossil fuels worldwide are limited and the combustion of the carbon fuels leads to a severe increase of the CO₂ concentration in the atmosphere. The latter is responsible for the climate change. Industrialization was based on an open cycle, i.e. mining of materials and fossil fuels, manufacturing the products and disposal of the used materials as well as release of the CO₂ in the atmosphere. The sustainability of the post industrialization era is determined by the ability to close the materials cycles i.e. to change from fossil fuels as energy carriers to renewable energy. Since renewable energy (solar, geothermal and planet movement) occurs in energy fluxes, an appropriate energy carrier has to be synthesized. Furthermore, all products used have to be recycled and the materials reused, otherwise the industrialization of the world largest countries India and China will not be possible.

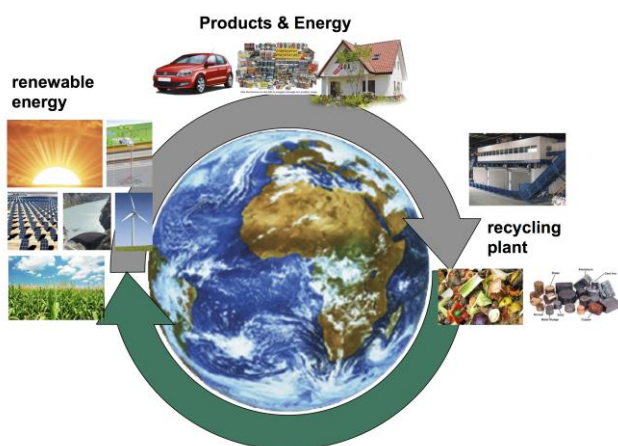


Fig. 1 Closing the materials cycle

The hydrogen cycle can be realized by only technical means, i.e. no living matter is required and only water is used as a material resource. The storage of hydrogen in metals and complex hydrides as stable compounds offers a great volumetric storage density, however the gravimetric storage density is limited to less than 25mass% in the materials. In order to replace fossil fuels without scarification on energy density, synthetic fuels based on hydrogen e.g. NH₃ or C₈H₁₈, have to be developed. The latter also represents an effective CO₂ sink for the atmosphere if it is produced in excess to the consumption

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Short CV of Andreas Züttel (andreas.zuettel@empa.ch)



Born 22. 8. **1963** in Bern, Switzerland. **1985** Engineering Degree in Chemistry, Burgdorf, Switzerland. Exchange student research work "Polyurethan network formation" with Dow Chemical in Terneuzen, Netherlands. **1990** Diploma in Physics from the University of Fribourg (UniFR), Switzerland. **1993** Dr. rer. nat. from the science faculty UniFR. **1994** Post doc "Amorphous hydrides and optical films" with AT&T Bell Labs in Murray Hill, New Jersey, USA. **1996** Head of the Metalhydride and Energy Storage Group in the Physics Department UniFR. **1997** Lecturer at the Physics Department UniFR. **2001** Vice president of the Swiss hydrogen association "Hydropole". Member of the Scientific Advisory Board of IMRA EUROPE. Member of the Advisory Committee of HERA. **2003** External professor at the Vrije Universiteit Amsterdam, Netherlands. **2004** Habilitation in experimental physics at the science faculty UniFR. Vice-President of the Swiss Physical Society (SPS), President of the Swiss Hydrogen Association „HYDROPOLE“. **2006** Head of the section "Hydrogen & Energy" at EMPA the Swiss National Institution for Materials Sciences and Technology. Prof. tit. in the Physics department UniFR. **2007** Organizer of the Int. Symposium "Hydrogen & Energy". **2008** Editor of the book „Hydrogen as a Future Energy Carrier“, Member of the scientific advisory board of HyCentA, Graz and UK-SHEC. Member of the Steering Committee (ISC) for the International Symposia on MH Systems. **2009-2010** Head of the Research Program „Material Sciences & Technology for Energy“ at EMPA. **2009** Guest Professor at IMR, Tohoku University in Sendai, Japan. 2012 Visiting Professor at Delft Technical University, The Netherlands

MATERIALS SCIENCE AT HIGH PRESSURES

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Application of high pressure offers great opportunities in both solvothermal and solid state chemistry. Understanding of reaction kinetics and structure-property relations as a function of applied conditions is a key requirement for the development of novel energy- and nanomaterials. Processes at high pressure *and* high temperature are however inherently difficult to study and challenge experimentalist to develop tools to study them as they occur.

Solvothermal synthesis

Water near its critical point ($T_C = 374$ °C, $P_C = 221$ bar) has great potential for green, versatile and large scale production of nanoparticles of energy materials. The advantages of supercritical water have been used extensively in solvothermal continuous flow reactors, which offer rapid investigation of synthesis parameter space and relatively easy scaling of the systems compared to static batch reactors. In Aarhus we have focused on the synthesis of a wide range of metal and metal oxide nanoparticles. Due to the high pressure and temperature involved, supercritical synthesis remained a "black box" for many years. Since 2005, we have developed various pressure cells to study solvothermal synthesis of nanoparticle formation *in-situ* at conditions near and beyond the critical point water. The cells have been used in numerous studies using powder X-ray diffraction [1], combined with small angle X-ray scattering [2], and more recently expanded to total scattering analysis (PDF) [3]. Furthermore, more advanced setups have been tested to mimic the synthesis conditions in flow reactor more directly. Intrinsic properties of the reaction conditions put severe restrictions on these experiments and the studies resulted in the design of a novel type of reactor operating with a pulsed-flow, which allows both *in situ* studies and synthesis in the laboratory [4]. The talk will be a short overview of the developed tools, selected examples of studies and some future perspectives.

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High pressure chemistry of solids

For chemistry in the solid state the pressures required to effectively influence reaction pathways are 2-3 orders of magnitude higher than typical pressures used in solvothermal chemistry. This much more extreme pressure range offers a new set of experimental challenges. These challenges are overcome by the use of large volume multi-anvil presses and diamond anvil cells. Since 2012 we have established the first high pressure laboratory in Denmark performing both high pressure solid state synthesis and high pressure x-ray crystallography. The instrument will be used for synthesis of new materials such as topological insulators, thermoelectric materials, and superconductors. The talk will give a status report of the development of the high pressure facilities in Aarhus and examples of recent and ongoing studies of perovskite and pyrochlore compounds [5,6].



Martin received his Ph.D. degree in materials chemistry in 2009 from Aarhus University and then spent three years as a postdoctoral researcher at Princeton University. In 2012 he became Assistant Professor at iNANO and Dept. of Chemistry, Aarhus University. He was awarded a *Young Investigator Grant* by the Villum Foundation (2012) and received an instrument grant from the Carlsberg Foundation (2013). His research interests are focused on synthesis and structure-property relations of inorganic materials and the utilisation of synchrotron X-ray radiation for materials characterization with special interest in crystallography, *in-situ* studies and high pressure.

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Album Future Generations. Stars Lyrics. [Verse 1] All this time I've, been looking at the stars (stars) I never wondered What they really are, (are) It doesn't matter to me Baby I just wanna live right You know that I can be The shining light of your life. [Chorus] If you come to me close We cut the cable to outside It's taken years to open But lately I've been close, the time (time) I close the time. [Verse 2] Mind is aching As I look into the dark, (dark) My hands are shaking Will they make their mark, (mark) Oh come on come on come on You gotta be something else It' What will the future look like, since people are offended by small things and our lives are constantly shaped by what others don't like? Who is the pettier person, the one offended by a small thing, or the one offended by someone else's offense at a small thing? My life is never shaped by what others don't like. I suspect in the future, people will acquire a bit more self-possession and respect for other's right to like or dislike, love, want and need as they please: their own self to give, their own unimpeachable call what to give and who to. Sharing freely and easily what they find good