



Swiss Science Concentrates

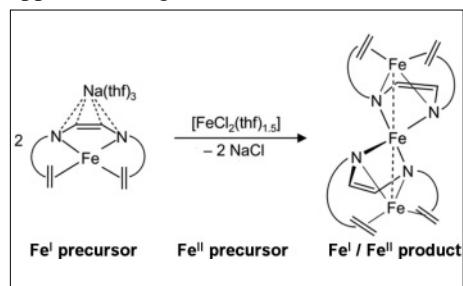
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Low-Valent Iron: An Fe(I) Ate Compound as a Building Block for a Linear Trinuclear Fe Cluster

C. Lichtenberg*, L. Viciu, M. Vogt, R. E. Rodríguez-Lugo, M. Adelhardt, J. Sutter, M. M. Khusniyarov, K. Meyer, B. de Bruin, E. Bill, and H. Grützmacher*, *Chem. Commun.* **2015**, *51*, 13890. ETH Zürich

The cluster structure of polynuclear iron compounds can determine the characteristics of (multi-)redox processes, enable cooperative reactivity, and allow the precise adjustability of magnetic properties. Lichtenberg, Grützmacher and co-workers present a low-valent trinuclear iron complex with an unusual linear Fe(I)–Fe(II)–Fe(I) unit. The metal complex is prepared by a rational approach using a salt metathesis reaction between a new anionic

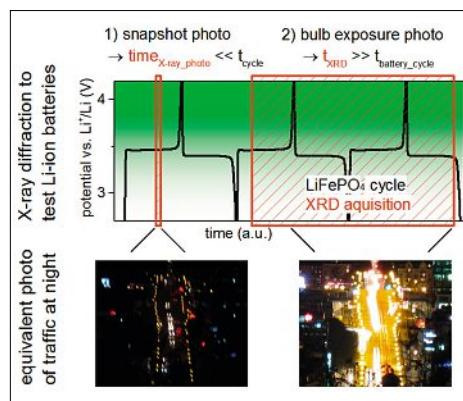


Fe(I) containing heterocycle and FeCl_2 . Its electronic structure was studied by single crystal XRD analysis, EPR and Mössbauer spectroscopy, and magnetic susceptibility measurements.

Combined Operando X-ray Diffraction–Electrochemical Impedance Spectroscopy Detecting Solid Solution Reactions of LiFePO_4 in Batteries

M. Hess*, T. Sasaki*, C. Villevieille, and P. Novák, *Nat. Commun.* **2015**, *6*, 8169. PSI Villigen

Lithium-ion batteries are widely used for portable applications today. Unfortunately, they often suffer from limited recharge rates. Hess, Sasaki and collaborators report a combination of high-resolution operando synchrotron X-ray diffraction and electrochemical impedance spectroscopy to directly track non-equilibrium intermediate phases in lithium-ion battery materials. This technique uses a bulb exposure of X-rays on battery materials similar to the bulb exposure on standard photo cameras. LiFePO_4 , for example, is known to undergo phase separation when cycled under low-current-density conditions. Operando X-ray diffraction under ultra-high-rate alternating current and direct current excitation reveals a continuous but current-dependent, solid solution reaction between LiFePO_4 and FePO_4 .



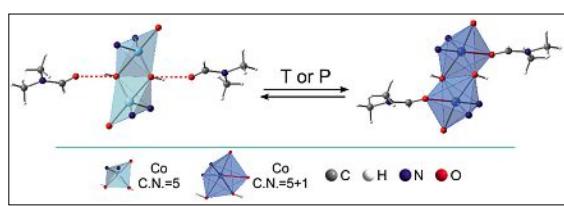
This study changes the understanding of the intercalation dynamics in LiFePO_4 .

Prepared by Caroline D. Bösch, Markus Probst, Yuliia Vyborna, Mykhailo Vybornyi, Simon M. Langenegger and Robert Häner*. Do you want your article to appear in the SWISS SCIENCE CONCENTRATES highlight? Please contact robert.haener@dcb.unibe.ch

Solid-State Reversible Nucleophilic Addition in a Highly Flexible MOF

A. Lanza*, L. S. Germann, M. Fisch, N. Casati, and P. Macchi*, *J. Am. Chem. Soc.* **2015**, *137*, 13072. University of Bern and PSI Villigen

In this paper, Lanza, Macchi and co-workers describe



a flexible and porous MOF based on Co^{II} connectors and benzotriazolide-5-carboxylato linkers. The MOF reacts selectively with guest molecules trapped in the channels during the sample preparation or after an exchange process. Upon mild compression or cooling, the Co atoms are able to extend their coordination, binding the nucleophilic guest molecules. The transformation involves all Co atoms with methanol as guest, whereas only part of them with the larger dimethylformamide. The addition is reversible and upon decompression or heating, the initial phase is reobtained. This peculiar example of chemisorption may have enormous implications for gas storage, selective sieving and potentially for catalysis. Further study is ongoing in the same research group.

Enantioselection on Heterogeneous Noble Metal Catalyst: Proline-Induced Asymmetry in the Hydrogenation of Isophorone on Pd Catalyst

L. Rodríguez-García, K. Hungerbühler, A. Baiker, and F. Meemken*, *J. Am. Chem. Soc.* **2015**, *137*, 12121. ETH Zürich

In the (S)-proline-mediated asymmetric hydrogenation of isophorone (IP) on supported Pd catalyst, excellent enantioselectivity is achieved, with an enantiomeric excess of up to 99%. The role of the heterogeneous catalyst has been the subject of a controversial debate. Meemken and collaborators investigated the enantioselectivity-controlling steps on the metal surface using attenuated total reflection infrared spectroscopy. The results demonstrate the existence of two competing enantioselective processes leading to opposing enantioselection. Depending on surface coverage of the Pd catalyst, the reaction is controlled either by kinetic resolution ((S)-pathway) or by chiral catalysis ((R)-pathway). The unravelled (R)-reaction pathway emphasizes an intriguing strategy for inducing chirality in heterogeneous asymmetric catalysis.

