

energy density limit. Further, for application in electric vehicles there is increasing focus on producing a low cost, highly stable battery with high capacity. In line with this has been the re-emergence of aqueous electrolyte based cells [1]. Defect perovskite structures such as  $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$  and  $\text{Li}_{3x}\text{La}_{0.33-x}\text{NbO}_3$  present a possible choice of cathode for these cells due to their ideal voltage range, high ionic conductivity, structural flexibility and high intercalation limits [2-3]. However, in order to further develop the properties of defect perovskites a thorough understanding of the structural changes which occur during lithium intercalation and how these affect the electrochemical properties is essential.

We have previously synthesised the defect perovskite compounds  $\text{Sr}_{0.8}\text{Ti}_{0.6}\text{Nb}_{0.4}\text{O}_3$  (STN) and  $\text{Li}_{0.18}\text{Sr}_{0.66}\text{Ti}_{0.5}\text{Nb}_{0.5}\text{O}_3$  (LSTN). While STN intercalated only a small amount of lithium via chemical means, LSTN readily intercalated lithium. A combination of neutron diffraction studies and bond valence calculations has provided significant insight into the early stages of structural changes during intercalation as well the diffusion properties of the material.

Both STN and LSTN have been able to intercalate lithium electrochemically exhibiting a sloping discharge profile between 1 – 2 V (Fig. 1). This type of voltage profile would normally be associated with solid solution type intercalation behaviour. However, both in-situ neutron and ex-situ synchrotron diffraction experiments have revealed multiphase intercalation behaviour.

This contribution will address the structural changes which occur in STN and LSTN during chemical and electrochemical intercalation and the connection of these structural changes to the observed properties.

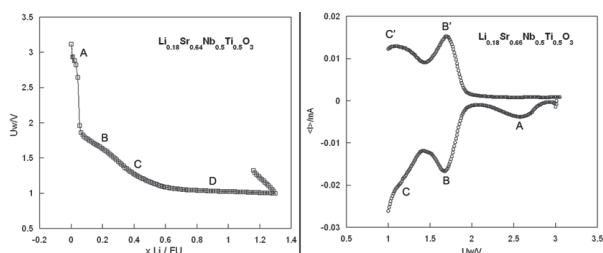


Figure 1: Cyclic voltammogram showing the voltage output during intercalation into LSTN and the location of several electrochemical processes.

[1] I. J.-Y. Luo, W.-J. Cui, P. He, Y.-Y. Xia, *Nat. Chem.* 2, (9), 760-765. [2] Y. Inaguma, C. Liqun, M. Itoh, T. Nakamura, *Solid State Commun.* **1993**, 86 (10), 689-693. [3] A. Nadiri, G. Le Flem, C. Delmas, *J. Solid State Chem.* **1988**, 73, 338-347.

**Keywords:** battery, perovskite, diffusion

## MS39.P09

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### Structure and dehydrogenation properties on ammine borohydride system as hydrogen storage materials

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Complex metal hydride materials have received a great deal of attention owing to their high gravimetric hydrogen contents [1, 2]. Recently several novel ammine borohydride complex materials, which contain high wt % hydrogen, have been synthesized. The use of ammonia complex of metal borohydrides  $\text{Me}(\text{BH}_4)_x \cdot n\text{NH}_3$  (Me = Li, Mg, Al, Zn, Ca) has shown to be a considerable strategy for achieving improved

dehydrogenation mechanism by the interaction between  $\text{NH}_3$  and  $\text{BH}_4$  molecules. Several compounds release most of hydrogen at a relatively low temperature with no undesirable gas emission. The structures have subsequently been solved by synchrotron powder diffraction method. First principles calculations were performed using density functional theory (DFT), with the projected augmented wave method, to evaluate the electronic properties. The ground state structures are subjected to full structural optimization. The chemical bonding of the material has been analyzed by means of electron localization function (ELF). The development of materials which allow the low temperature release of a large volume of hydrogen is significant, thereby demonstrating the potential of to be used as solid hydrogen storage.

[1] M. Takimoto, Z. Hou, *Nature* **2006**, 443, 400. [2] D. Ravnsbaek, Y. Filinchuk, Y. Cerenius, *et. al. Angew. Chem. Int. Ed.* **2009**, 48, 6659.

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## MS39.P10

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### Altering the properties of metal borohydrides by substitution

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Effective hydrogen storage is one of the bottlenecks for widespread use of hydrogen as a clean energy carrier. Hydrogen storage in solids, most notably metal hydrides, is the only option which can potentially meet the requirements for volumetric hydrogen density. To achieve high gravimetric hydrogen densities, the research focuses on light element such as aluminum and boron. However, no complex hydride with suitable stability and high hydrogen content has yet been found.

The heavy intermetallic hydrides have highly tunable properties by metal substitution over wide compositional ranges, but this possibility is lacking for complex metal hydrides which take stoichiometric metal compositions. However, the use of anion substitution has turned out to be a viable method to change the stability of metal hydrides, e.g. by partly substituting  $\text{H}^-$  by  $\text{F}^-$  in  $\text{Na}_3\text{AlH}_6$  [1].

The system  $\text{NaBH}_4 - \text{NaCl}$  has been investigated by powder (lab and synchrotron) X-ray diffraction (PXD), powder neutron diffraction (PND) and various thermal methods. A continuous range of chlorine substitution in  $\text{NaBH}_4$ ,  $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$  ( $0 < x < 1$ ) has been obtained by ball-milling mixtures of  $\text{NaBH}_4$  and  $\text{NaCl}$  up to 24 hours. The  $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$  phases take NaCl-type structures and show almost ideal Vegard's law behavior. In-situ SR-PXD shows a gradual depletion in  $\text{BH}_4^-$  upon thermal decomposition and hydrogen release and  $\text{NaCl}$  is the only crystalline final decomposition product. The changes in thermal stability upon chlorine substitution are small, with only a slight stabilization with increasing chlorine content. On the other hand, a drastic change in the order-disorder temperature is observed. Hydrogen ordering in  $\text{NaBH}_4$  induces a phase transition from cubic to tetragonal symmetry around 190 K, however, no phase transformation was observed in  $\text{Na}(\text{BH}_4)_{0.75}\text{Cl}_{0.25}$  down to 9 K by PND. Phase transformations in more dilute systems are under investigation.

Halide substitution in  $\text{Ca}(\text{BH}_4)_2$  mixed with calcium halides has been investigated by in-situ SR-PXD. No substitution of  $\text{BH}_4^-$  by  $\text{Cl}^-$  is observed in the low-temperature modification  $\alpha\text{-Ca}(\text{BH}_4)_2$ , but an appreciable chlorine substitution is observed into the high-temperature phase  $\beta\text{-Ca}(\text{BH}_4)_2$ . No substitution with bromide or iodide was achieved.

## Poster Sessions

The first borohydrides with both mixed cations and anions,  $\text{LiCe}(\text{BH}_4)_3\text{Cl}$  has recently been synthesized from  $\text{LiBH}_4$  and  $\text{CeCl}_3$ . The product, which has earlier been mistaken for  $\text{Ce}(\text{BH}_4)_3$  [2,3], is structurally characterized by combined PXD and PND. Li is found in two very different chemical environments; one which resembles  $\text{LiCl}$  and one similar to  $\text{LiBH}_4$ . The compound gives off 6 wt% of almost pure hydrogen gas around 250°C. Preliminary results show limited reversibility due to formation of  $\text{CeH}_x$ .

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[1] H.W. Brinks, A. Fossdal, B.C. Hauback, *Journal of Physical Chemistry C* **2008**, *112*, 5658-5661. [2] F.C. Gennari, M.R. Esquivel, *J. Alloys Comp.* **2009**, *485*, L47-L51. [3] B.J. Zhang, B.H. Liu, Z.P. Li, *J. Alloys Comp.* **2011**, *509*, 751-757.

**Keywords:** hydrogen storage, powder X-ray diffraction, powder neutron diffraction

### MS39.P11

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**Single crystal neutron diffraction study on  $\text{Rb}_{0.51}\text{Tl}_{0.49}\text{H}_2\text{PO}_4$**   
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In this work, we present a crystal structure investigation on  $\text{Rb}_{0.51}\text{Tl}_{0.49}\text{H}_2\text{PO}_4$  by single crystal neutron diffraction. The title compound, which is isostructural to  $\text{TlH}_2\text{PO}_4$  (TDP), crystallizes in the monoclinic space group  $\text{P12}_1/\text{a1}$  with  $a = 14.428(1)$  Å,  $b = 4.543(5)$  Å,  $c = 6.400(9)$  Å and  $\beta = 91.77(9)^\circ$ . TDP is characterized by a two-dimensional network of hydrogen bonds. Although the ionic radii of  $\text{Tl}^+$  and  $\text{Rb}^+$  are almost same (1.47 Å), the crystal structures of  $\text{RbH}_2\text{PO}_4$  (RDP) and TDP are different from each other. The disordered H-distributions have been investigated in detail [1,2]. Highly perfect mixed crystals were grown from aqueous solution. Diffraction data at room temperature were measured up to  $(\sin\theta/\lambda) = 0.827\text{Å}^{-1}$  with the single crystal neutron diffractometer HEiDi at the FRM-II, Germany. Compared to previous work [3], adding more  $\text{Rb}^+$  ions into the crystal structure causes a slight change in the geometry of the oxygen coordination of the  $\text{Rb}^+/\text{Tl}^+$  site, which is distorted according to the stereochemical activity of the lone-pair electrons of the  $\text{Tl}^+$  ions. The fact that the crystal structures of  $\text{Rb}_{0.51}\text{Tl}_{0.49}\text{H}_2\text{PO}_4$ ,  $\text{Rb}_{0.46}\text{Tl}_{0.54}\text{H}_2\text{PO}_4$  and TDP are rather similar in the room temperature phase is consistent with the previous NQR investigation results [4] which showed that the mixed crystals  $\text{Rb}_x\text{Tl}_{1-x}\text{H}_2\text{PO}_4$  for the composition range  $0.2 \leq x \leq 0.8$  are isotopic to TDP. Contrary to TDP, no phase transition was found by NQR for the mixed crystals at low temperature [4]. However, until now, there exists no further investigation concerning a possible phase transition in the  $\text{Tl}^+$ -dominated mixed system. Therefore, it could be very interesting to investigate the mixed crystals more systematically and as a function of temperature in order to better understand the role of the lone-pair electrons of the  $\text{Tl}^+$  ions for the phase stability and to follow the disorder behavior of the hydrogen atoms.

[1] S. Mattauch, G. Heger, K.H. Michel, *Cryst. Res. Technol.* **2004**, *39*, 1027-1054. [2] I.H. Oh, S. Mattauch, M. Merz, G. Heger, *Acta Cryst. B* **2006**, *62*, 719-728. [3] I.H. Oh, S. Mattauch, G. Heger, C.E. Lee, *Journal of the Physical*

*Society of Japan* **2008**, *77*, 094602. [4] J. Seliger and V. Zagar, *Physical Review B* **1995**, *52*, 1070-1077.

**Keywords:** hydrogen bonding, neutron diffraction, structure analysis

### MS39.P12

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**Li insertion in ball milled graphitic carbons by total XRD**  
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Currently a significant research effort is under way worldwide to find advanced negative electrode materials for Li-ion batteries. Graphitic carbon is currently the material of choice because it can accommodate Li atoms fast, reversibly and without generating much mechanical stress. In normal conditions pristine graphitic carbon can accommodate up to one Li atom per six carbon atoms. Real life applications, however, demand higher Li storage capacities and scientists have been looking into ways to go beyond what bulk  $\text{LiC}_6$  can offer. It has been found that ball milled graphitic carbons show increased Li storage capacity. The increase has been explained in terms of the "stacks of fallen cards" model which features breaking, upon the impact of ball milling, of the extended graphitic layers into smaller pieces that are randomly oriented with respect to each other thus posing a diminished steric hindrance for Li to intercalate. The increased Li storage capacity, however, has been found to fluctuate with the milling time puzzling scientists for more than a decade. We will present results from total x-ray diffraction [1] and reverse Monte Carlo modeling [2] studies on ball-milled graphitic carbons, both as made and electrochemically lithiated. Experimental and modeling results show that ball milling for short times breaks the graphitic layers into smaller pieces as well as generates extended atomic vacancies. Those increase the overall ability of the material to accommodate lithium. Ball milling for longer times keeps generating even more atomic vacancies in the graphitic layers. Carbon atoms displaced from the layers, however, move in between the layers turning heavily ball milled graphitic carbons into an assembly of almost fused together layers that have an impaired ability to accommodate Li atoms. This helps explain well the initial substantial increase and then decrease in the Li storage capacity of ball-milled graphitic carbons [2]. The study [3] demonstrates the great ability of total x-ray diffraction to provide precise structural information for complex materials that are being increasingly explored for energy applications.

[1] V. Petkov, *Materials Today* **2008**, *11*, 28-38. [2] F. Disma, L. Aymard, L. Dupont, J.M. Tarascon, *J. Electrochem. Soc.* **1996**, *143*, 3959-3972. [3] V. Petkov, A. Timmons, J. Camardese, Y. Ren, *Mat.Chem.* **2011**, in press.

**Keywords:** nano, WAXS, structure

### MS39.P13

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**X-ray and neutron studies of defect formation in  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$**   
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Lithium iron phosphate is a very promising material for applications in Li-ion batteries for electric and hybrid cars [1]. The