

## 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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**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.

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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.

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### 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