

# EXPLORATION OF NEW BORATE BASED CATHODE MATERIALS FOR LITHIUM- AND SODIUM ION BATTERIES

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In the search for new polyanionic cathode materials for Li- and Na-ion batteries, borate based materials could lead to increased capacities since the borate anion  $\text{BO}_3^{3-}$  presents the lightest group among all polyanions. However, so far only materials consisting of an *ortho* borate  $\text{BO}_3^{3-}$  polyanionic framework have been considered as potential positive electrode materials.<sup>1,2</sup> Because the borate  $\text{BO}_3^{3-}$  group has a weak inductive effect on the transition metal, the redox voltage is rather low compared to other common polyanionic cathode materials like  $\text{LiFePO}_4$  or  $\text{LiFeSO}_4\text{F}$ .<sup>2</sup>

One strategy to increase the redox potential versus lithium or even sodium for a polyanionic material, containing the same transition metal, has been shown for  $\text{LiFePO}_4$  and its counterpart  $\text{Li}_2\text{FeP}_2\text{O}_7$ . Replacing the *ortho*-phosphate  $\text{PO}_4^{3-}$  by a *di*- or *pyro*- phosphate group  $\text{P}_2\text{O}_7^{4-}$  which is more electron withdrawing, leading to an elevated redox potential.<sup>3</sup>

So to combine the advantage of the light weight of borate groups and simultaneously increase the redox potential of the transition metal, our approach is to apply this strategy of using condensed polyanionic groups, for instance moving from borate  $\text{BO}_3^{3-}$  to pyroborate  $\text{B}_2\text{O}_5^{4-}$  or pentaborate  $\text{B}_5\text{O}_{10}^{5-}$ .

In this context we prepared a lithium copper pyroborate  $\text{Li}_6\text{CuB}_4\text{O}_{10}$  using ceramic synthesis and investigated its electrochemical and structural properties by a variety of in situ and ex situ XRD as well as galvanostatic electrochemical methods combined with TEM and EPR spectroscopy. This material shows a 4.0 V redox potential versus lithium and a n.a.c. conductivity around  $10^{-2.5}$  S/cm at temperatures higher than 300°C, determined by temperature controlled impedance measurements.

To further probe the electrochemical activity of new polyborate based materials, we successfully prepared a new group of sodium transition metal pentaborates  $\text{Na}_3\text{MB}_5\text{O}_{10}$  (M = Mn, Fe, Co) by a ceramic process. We solved their crystal structure using synchrotron diffraction and characterized these materials in terms of magnetism, optical and electronic properties since their electrochemical activity versus sodium was rather small.

Finally we studied the reversible conversion reaction, of a bismuth oxyborate  $\text{Bi}_4\text{B}_2\text{O}_9$  versus Li/ Na potential application as a high energy density cathode material. This material shows a moderate capacity even at elevated C-rates and a good capacity retention rates (150 mAh/g at 1C over 20 cycles) with a small polarization (0.4 V). We studied the conversion mechanism and influence of different parameters like electrolyte, carbon content and milling time on the electrochemical behavior.

- [1] V. Legagneur, Y. An, A. Mosbah, R. Portal, A. Le Gal La Salle, A. Verbaere, D. Guyomard, Y. Piffard, Solid State Ionics 139 (2001) 37-46.
- [2] A. Yamada, N. Iwane, Y. Harada, S. Nishimura, Y. Koyama, I. Tanaka, Adv. Mater. 22 (2010) 3583-3587.
- [3] S. Nishimura, M. Nakamura, R. Natsui, A. Yamada, J. Am. Chem. Soc. 132 (2010) 13596-13597.