Abstract

The increased need of energy storage, via the development of Li- and Na-ion batteries, requires a continuous search for new positive electrode materials having higher energy density while being safe and sustainable. For this purpose we explored borate base compounds capable of reacting with Li/ Na-ions in a reversible way either through intercalation/deintercalation or conversion reactions. During this survey we focused on identifying candidates possessing a polyborate anion (B_xO_y with x > 1), that are expected to show elevated redox potentials compared to BO_3 based materials. Using $Li_6CuB_4O_{10}$ as a model compound we showed the possibility to achieve redox potentials of 4.2 and 3.9 V vs. Li^+/Li^0 for the α- and β-polymorphs, respectively.This redox activity was rationalized through complementary EPR spectroscopy and DFT calculations. We further reveal the structural and synthetic relation between the two polymorphs and show a surprisingly high ionic conductivity of 1.4 $mS \cdot cm^{-1}$ at 500°C for α-$Li_6CuB_4O_{10}$, related to a structural transition. Moreover we were able to prepare two new sodium transition metal pentaborates $Na_3MB_5O_{10}$ (M = Fe, Co) possessing an open structure feasible for Na^+ migration. For M = Fe we observed a reversible Na intercalation at an average potential of 2.5 V vs. Na^+/Na^0, opposed to $Na_3CoB_5O_{10}$ which turned out to be electrochemical inactive. Finally deviating from classical insertion/ deinsertion compounds, we studied the electrochemical driven reaction mechanism of a bismuth oxyborate $Bi_4B_2O_9$ versus Li through electrochemical measurements combined with XRD and TEM investigations. Remarkably, we found that it is possible to reversible cycle this material between 1.7 and 3.5 V with an average redox potential of 2.3 V vs. Li^+/Li^0 with only 5wt% carbon additive and a small polarization ~300 mV. Owing to the complexity of 3d-metal borate chemistry encountered through this PhD, the chances of having a borate positive electrode for next generation of Li-ion batteries are rather slim.