

STRATEGIES FOR IMPROVING THE HYDRIDOBORATE SOLID-STATE ELECTROLYTES AT ROOM TEMPERATURE

Radovan Černý

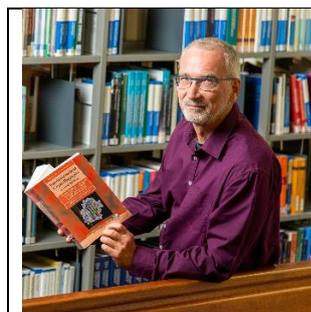
Laboratory of Crystallography, DQMP, University of Geneva, Switzerland

e-mail: Radovan.Cerny@unige.ch

Sodium salts of large-cage hydridoborates $[B_xH_x]^{2-}$ ($x = 10,12$), and their C-derivatives $[CB_{x-1}H_x]^-$ have proven to be promising Na-based solid-state electrolytes. Indeed, they show an excellent electrochemical stability, arising from the strong electron delocalization on the anion cluster, as well as low area resistance, low density and soft mechanical properties [1]. Fast cationic motion generally occurs after a polymorphic transition towards higher-symmetry phases. This order-disorder phase transition provides structures with more free sites for the cations, improved conduction pathways as well as an increased rotational energy of the anion cages, which enhances the cation motion. However, such phase change occurs usually above room temperature (*rt*), thus hampering practical applications. Lowering (or suppressing) the phase transition has been made possible by chemical tuning (anion substitution) or physical treatments implying either the formation of composites, nanoconfined materials or by mixing anionic (or neutral) hydridoborate clusters [2-4]. Following this approach, we discovered $Na_4(CB_{11}H_{12})_2(B_{12}H_{12})$ featuring a superior ionic conductivity of 2 mS cm^{-1} at *rt*, with a low activation energy of 314 meV [3]. Electrochemical stability of 4.1 V vs. Na^+/Na is compatible with high-voltage operating positive electrodes.

Recently, we have shown an effect of mechanical milling in stabilizing at *rt* the superionic conductive phase of a single-anion material, $NaCB_{11}H_{12}$ [5]. The high-energy ball milling quenches the metastable, body-centred cubic (*bcc*) polymorph, which exhibits a large number of available Na^+ sites. Macroscopically, this results in a conductivity of 4 mS cm^{-1} at 20°C , without altering the electrochemical stability. Preliminary electrochemical tests show that *bcc*- $NaCB_{11}H_{12}$ withstand a critical current density of 0.12 mA cm^{-2} .

- [1] R. Černý, M. Brighi, F. Murgia, *Chemistry* (Easton). **2020**, 2, 805
- [2] M. Brighi, F. Murgia, R. Černý, *Cell Press Phys Sci*. **2020**, 1, 100217
- [3] M. Brighi, F. Murgia, Z. Łodziana, P. Schouwink, A. Wołczyk, R. Černý, *J. Power Sources*. **2018**, 404, 7
- [4] L. Duchêne, R.-S. Kühnel, D. Rentsch, A. Remhof, H. Hagemann, C. Battaglia, *Chem. Commun.* **2017**, 53, 4195.
- [5] F. Murgia, M. Brighi, L. Piveteau, C. E. Avalos, V. Gulino, M.C. Nierstenhöfer, P. Ngene, P. de Jongh, R. Černý, *Appl. Materials Interfaces*. **2021**, 13, 61346



Radovan Černý received his PhD from the Charles University, Prague, in the field of solid-state physics. After one-year stay at the Inst. of mineralogy and crystallography, University of Göttingen, he has been working at the University of Geneva first as post-doc and later on as "Maître d'enseignement et de recherche" and since 2012 as associated professor. His scientific interest is crystallography in general, and more specifically the methodology of powder-diffraction. His work on metal hydrides has started in Geneva, first as solid stores for hydrogen and later on as solid-state electrolytes.