TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG

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CryPhysConcept

Mit Kristallphysik zum Zukunftskonzept elektrochemischer Energiespeicher

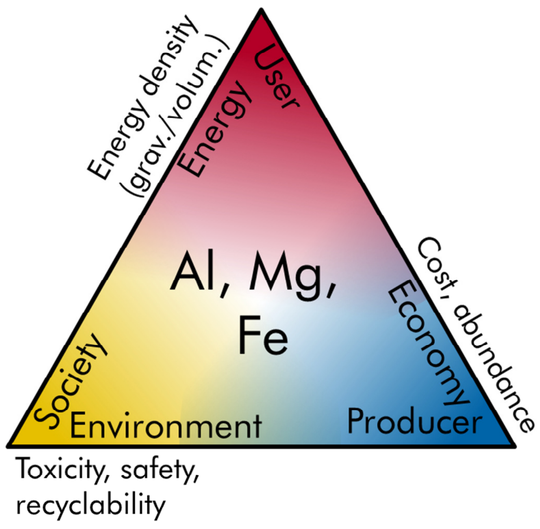
Application of crystallography in electrochemistry – *En route* to new concepts for energy storage

F. Meutzner[1,], T. Nestler[1], J. Hanzig[1], R. Schmid[1], C. Cherkouk[1], T. Leisegang[2], D. C. Meyer[1]*

[1] TU Bergakademie Freiberg | Institut für Experimentelle Physik | Leipziger Straße 23 | 09596 Freiberg | Germany

[2] Fraunhofer-Technologiezentrum Halbleitermaterialien | Am St.-Niclas-Schacht 13 | 09599 Freiberg | Germany

Motivation

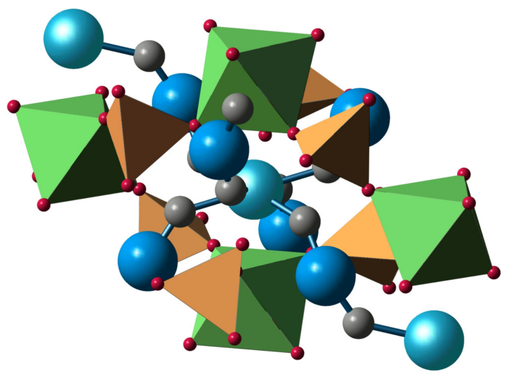


- Electrochemical energy storage: most promising candidate for renewable ressource technologies, mobile devices and electromobility,
- Lithium (Li) most prominently used: limited abundance, pessimistic predictions show problems in the next 50 – 100 years,
- Materials of higher abundance and more efficient recyclability should be investigated,
- CryPhysConcept (BMBF-financed joint research project): Combine crystallography, electrochemistry and resource aspects to find new concepts for electrochemical energy storage,
- Crystallography especially important for ionic diffusion and intercalation

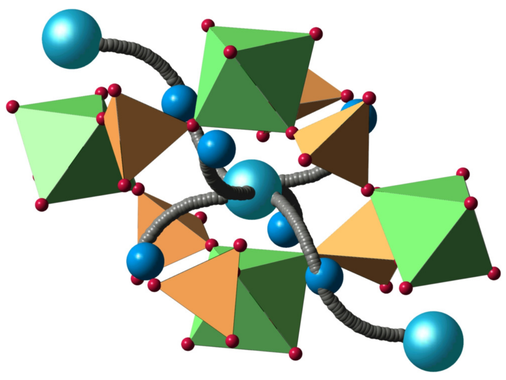
The "Crystal electrochemistry" approach

NaSICon – an example

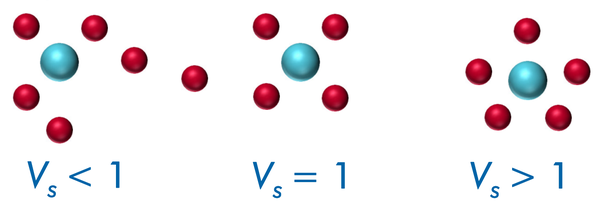
- NaSICon – Na^+-Super Ionic Conductor – solid electrolyte of high ionic conductivity mainly used in Na-S batteries,
- $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0<x<3$,
- 3D-ionic conductivity mediated by two Na-sites and a proposed intermediate site between Na1 and Na2 [1, 2]



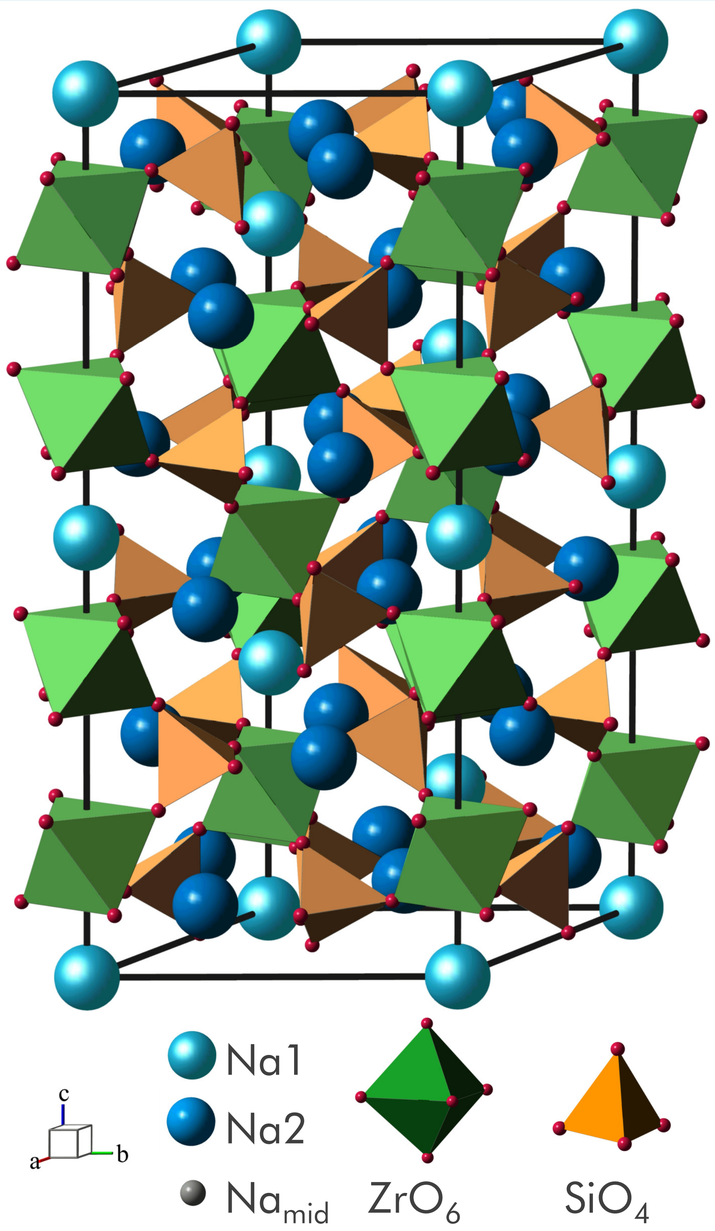
Bond Valence Sum



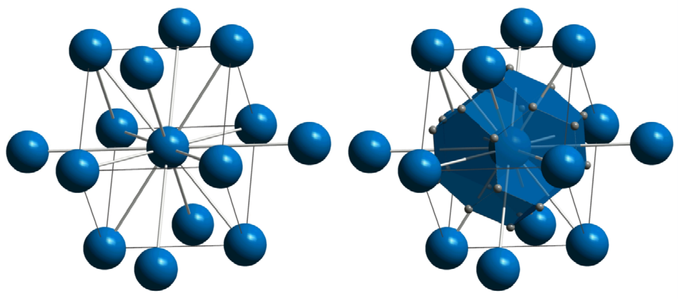
- Measure of bond strength and valence, depends on bond length, coordination number and chemistry [3],
- BVS ($V_s(x, y, z)$) of arbitrary site [4]:
  - $V_s < 1$: ion can migrate,
  - $V_s = 1$: energetically right site,
  - $V_s > 1$: ion cannot enter,
- Map whole structure



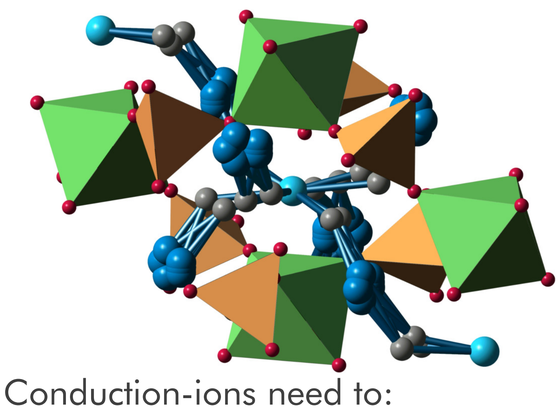
Crystal Structure ($R\bar{3}c$)



Voronoi-Dirichlet Approach



- Developed by V. A. Blatov [5],
- *Voronoi-Dirichlet Polyhedra* of structure, except conduction-ions,
- Vertices of *VDP* correspond to voids in the structure (ions possible to enter),
- VDP-edges are channels between voids



- Conduction-ions need to:
  - Fit in void,
  - Travel through channel,
- Program TOPOS: *VDP*-algorithm and data base handling [6]

Outlook

- Build database for ternary Al and Fe-oxides from the ICSD,
- Use TOPOS for datamining (intercalation and ionic conduction),
- Apply Voronoi-Dirichlet and Bond Valence Sum approach to identify possible intercalation compounds and ionic conductors for multivalent ions,
- Experimental evidence of intercalation/ionic diffusion,
- Influence of crystal structure on electrochemical properties

[1] Kohler *et al.*: *Mat. Res. Bull.* **18**, 589–592 (1983).
[2] Boilot *et al.*: *Mat. Res. Bull.* **22**, 669–676 (1987).
[3] Brown: *Chem. Rev.* **109**, 6858 (2009).
[4] Mazza: *J. Solid State Chem.* **156**, 154–160 (2001).
[5] Blatov *et al.*: *Acta Crystallogr. B* **62**, 1010–1018 (2006).
[6] Blatov *et al.*: *Cryst. Growth Des.* **14**, 3576–3586 (2014).

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* contact: falk.meutzner@physik.tu-freiberg.de,
http://www.exphys.tu-freiberg.de

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