Review of physical properties of NASICON materials for use in sodium batteries

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The structure, compositional diversity and ionic conductivity of Na^+ ion-conducting NASICON materials are reviewed in order to correlate the lattice parameters and specific crystal structure data with the sodium mobility and the activation energy.

Correlation structure / ionic conductivity:

General formula of a sodium NASICON material:

$$Na_{1+2x+y}M^{II}{}_xM^{III}{}_yM^{IV}{}_{2-x-y}(SiO_4)_z(PO_4)_{3-z}$$

Extensive study for approximately 150 compositions:

- Introduction of a geometrical parameter: the effective ionic radius r_{eff}

$$r_{eff} = \frac{x \times r_{M^{II}} + y \times r_{M^{III}} + (2-x-y) \times r_{M^{IV}}}{2}$$

- Illustration of an optimal size for M^{II}, M^{III} and M^{IV}, $r_{eff} \approx r_{Zr^{IV}} = 0{,}72$ Å
- Impact of the amount of Na per formula on the conductivity.
- Importance of the substitution of P with Si

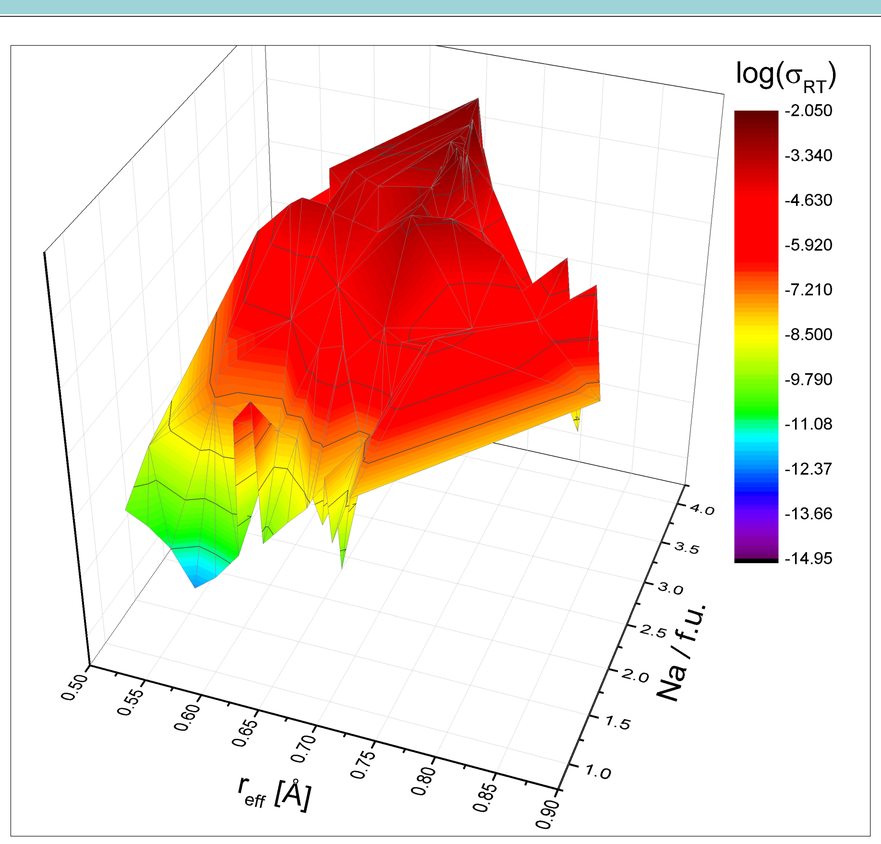

Figure 1: $\log(\sigma_{RT})$ as a function of the Na content per formula and the effective ionic radius of the cations in $Na_{1+2x+y}M^{II}{}_xM^{III}{}_yM^{IV}{}_{2-x-y}(SiO_4)_z(PO_4)_{3-z}$.

Bottleneck for Na^+ conduction, correlation with the activation energy:

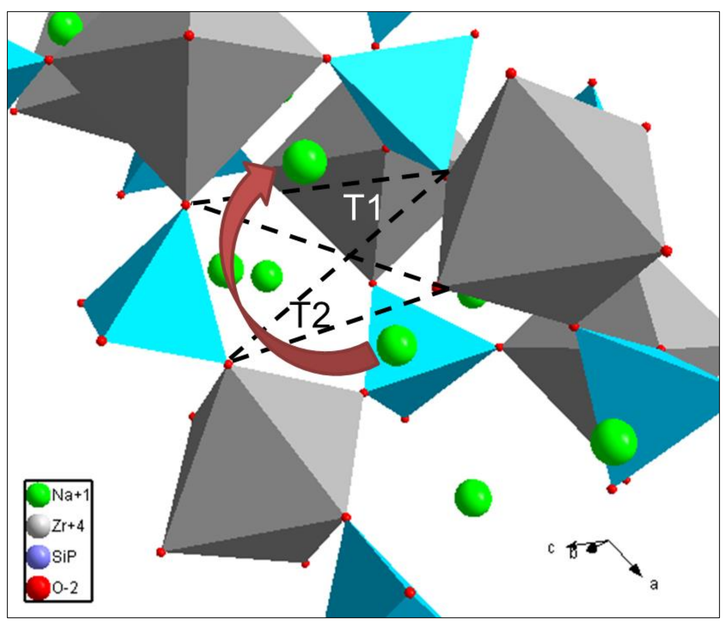

Figure 2: representation of the geometric bottleneck for the Na^+ conduction and the path of Na^+ ion hoping in $Na_3Zr_2(SiO_4)_2(PO_4)$

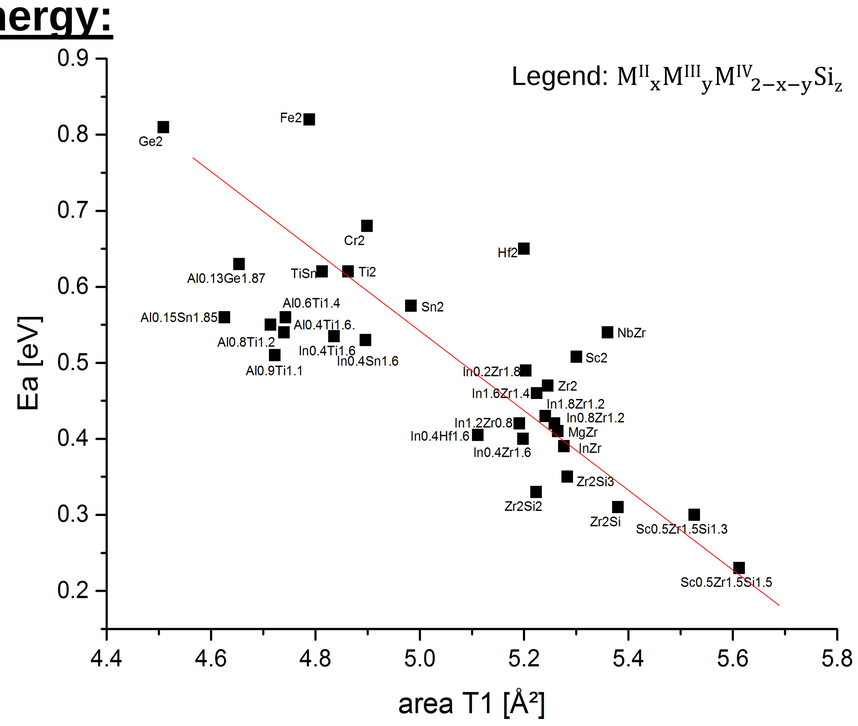

Figure 3: Influence of the area T1 on the activation energy for different NASICON materials

Factors influencing the bottleneck for the Na^+ conduction:

- Size of the cations M^{II}, M^{III}, M^{IV} (r_{eff})

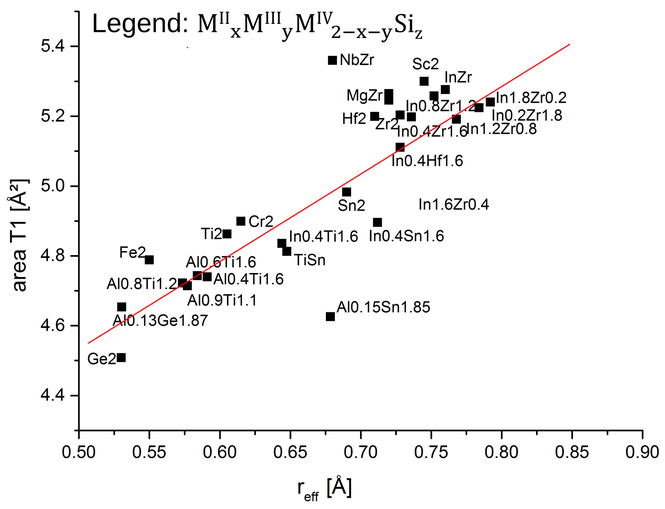

Figure 4: Influence of r_{eff} on the area T1

- Presence of Si in the formula

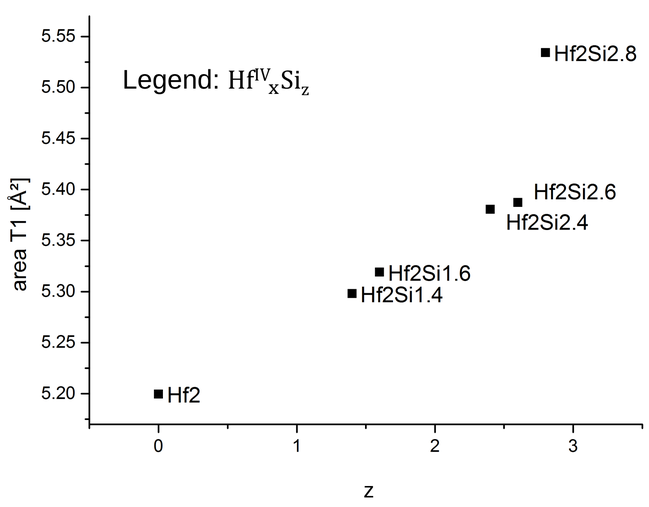

Figure 5: Influence of the amount of Si per formula on the area T1 (example of Hf-based NASICON. Vogel, E.M. et al. Solid State Ionics, 1984. **14**: p. 1-6.)

The activation energy is correlated to the geometric bottleneck for the Na^+ conductivity, the area T1, which increases with the size of the cations M^{II}, M^{III} and M^{IV} and the presence of Si in the formula. The existence of an optimal size for M^{II}, M^{III} and M^{IV}, $r_{eff} \approx r_{Zr^{IV}} = 0{,}72$ Å can not be explained only by a geometrical parameter.