Thermodynamic Modelling and Experimental Study of NASICON Sub-systems for Application as Solid State Electrolyte

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Solid state electrolytes are crucial for enhancement of the safety and practicability of batteries. NASICON (***Na S*uper *I*onic *Con*ductor**) is proposed as replacement for β″-Al_2O_3 [1], because of its excellent structural strength and conductivity which is attributed to its structure wherein Na migrates in 3D voids providing ionic conductivity of 0.2 $S \cdot cm^{-1}$ (300 °C). Furthermore, the processing temperature is relatively low (~700 °C), and high Na abundance makes it cheaper than Li-ion batteries.

The NASICON phase with formula $\mathbf{Na_{1+x}Zr_2Si_xP_{3-x}O_{12}}$ **[0≤x≤3]** is found to be conductive and is a part of the complex Na_2O-SiO_2-P_2O_5-ZrO_2 system. For a successful material design, thermodynamic properties (phase equilibria, heat capacity, stability, etc.) for all subsystems must be known, and for prediction of the properties, a reliable and consistent database is imperative. To accomplish these milestones, a thermodynamic database of the quaternary oxide system including the NASICON phase is being developed using *Cal*culation of *Pha*se *D*iagrams **(CALPHAD)** method.

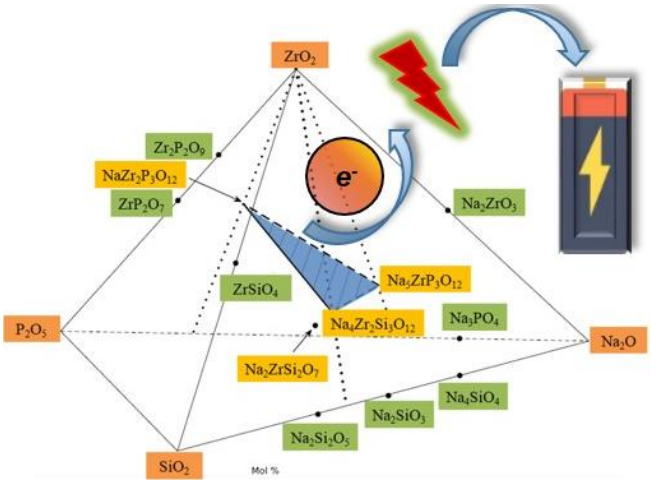

Figure 1 Schematic representation of NASICON system

As part of this development, underlying binary systems such as ZrO_2-P_2O_5, ZrO_2-SiO_2, Na_2O-ZrO_2, and ternary systems such as ZrO_2-SiO_2-P_2O_5 are studied. After preliminary results, the phase diagram construction is in progress with DTA/TG, XRD, and the experimental data along with literature values after critical analysis will be utilized for generation of Gibbs energies for all phases in the system. Using the thermodynamic dataset obtained, phase equilibria are predicted in agreement with the experimental data. The current state of work will be presented.

References:

1. J. B. Goodenough: "Fast Na^+-ion transport in skeleton structures", Mater. Res. Bull. **11**(2) (1976) 203-220.
2. U. Warhus: "Thermodynamics of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$)", J. Solid State Chem. **72**(1) (1988) 113-125.