Heat Capacity and Thermal Transport Properties of Glass-Ceramic Solid Electrolytes

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Within the current state of development, liquid electrolytes are utilized in Li-ion batteries for energy storage with high capacity and power density. These organic liquids serving as the solvents for Li salts are not thermally stable and tend to degrade at higher temperatures. Most of these liquids are flammable which can be an important security issue in high power battery systems. With regard to security and stability, ceramic solid electrolytes offer a number of advantageous properties. Even at higher temperatures they are very stable and do not degrade, and therefore reduce the efforts of a sophisticated thermal management in All-Solid-State battery systems.

Although there are numerous studies on the ionic transport in Li-conducting solid electrolytes, the thermo-physical properties have been studied only in a small number of publications. Particularly, the thermal transport behavior and the specific heat of glass-ceramic Li- or Na-based titanium or germanium phosphates have not been investigated up to now. However, these properties might give additional insights in the physics of superionic conductors.

Within this work we have studied three NASICON (**Na** **S**uper**i**onic **Con**ductor) structured ceramic systems, which are candidate materials for solid state electrolytes for Li-ion cells but also for systems beyond Lithium ion technology. Namely, LAGP ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, x≈0.5), LATP ($Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, x≈0.5) and NAGP ($Na_{1+x}Al_xGe_{2-x}(PO_4)_3$, x≈0.5) substrates were prepared using a melt quenching route and by applying different compaction methods. In order to develop a better understanding of the relationship between the specific microstructure and the ionic conductivity as well as the thermodynamic properties the samples were characterized by applying thermos-physical measurement techniques. The ionic conductivity was measured using impedance spectroscopy while the thermal diffusivity and the specific heat were determined by Laser Flash technique and differential scanning calorimetry, respectively. Additionally, thermal analysis was performed to evaluate the glass transition as well as the crystallization temperatures in order to characterize the thermal stability at higher temperatures and to identify the optimum temperature range for the thermal post-processing. The glass-ceramic systems were compared regarding their ionic conductivity and thermodynamic behaviour.