**Mircrocontanct impedance spectroscopy on Li- and Na-ion conducting solid electrolytes**

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NASICON-type structured materials (**Na S**uper-**I**onic **Con**ductor, with space group ) are promising solid electrolytes with total ion conductivity of about 10-4 to ~10-2 Scm–1. [1]

Due to the very high bulk Li+/Na+ conductivity in this class of materials the corresponding arc in the complex impedance plane response in the high MHz range and can be only resolved at very low temperatures. [2,3] Determination of the ionic bulk conductivity is strongly simplified when large sized single crystals are available; as for polycrystalline pellets macroscopic electrodes may be used in electrical measurements and electrical properties can be determined without being restricted by the need for a proper separation of partly large grain boundary resistances. Here, a modification of conventional impedance spectroscopy comes into play: microelectrodes deposited on large single crystals or grains of a polycrystalline sample still allow impedance measurements which are unaffected by the resistivity of grain boundaries. [4-6] This is caused by the spatially very constricted current distribution between neighboring microelectrodes. However, so far this technique of local impedance measurements was rarely applied to determine bulk Li+/Na+ conductivities.

In this contribution microcontact impedance spectroscopy and single crystal X-ray diffraction was applied to small Li1+*x*Al*x*Ti2-*x*(PO4)3, and Na3Sc(PO4)3 single crystals to exactly determine the ionic bulk conductivity at room temperature. [7,8] This enables a precise analysis on transport properties and a better understanding of the structure–property relationship of Li+/Na+-based NASICON-structured materials.

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