Microelectrodes in Solid State Ionics

Jürgen Fleig
Max Planck Institute for Solid State Research
Heisenbergstr. 1, 70569 Stuttgart, Germany

In solid state ionics, microelectrodes are far less commonly used than in liquid electrochemistry and semiconductor technology. In particular, quantitative investigations of electrical and electrochemical properties are comparably rare which can be attributed to several experimental as well as theoretical difficulties associated with such measurements. However, electrical measurements using microelectrodes may yield very valuable information that cannot be obtained from conventional electrical measurements using macroscopic electrodes.

In this talk, the large potential of microelectrode measurements in solid state ionics will be demonstrated by means of several examples.

i) Ionic solids frequently exhibit an inhomogeneous chemical composition. Microelectrodes are perfectly suited to investigate such inhomogeneities with spatial resolution. This is demonstrated for SrTiO$_3$ single and polycrystals with non-stoichiometry profiles.

ii) Structural and chemical properties of grain boundaries in polycrystalline materials can vary from boundary to boundary. Microelectrode experiments are helpful in determining the distribution of grain boundary properties in ceramics with highly resistive grain boundaries. This is shown for SrTiO$_3$ and Mn-Zn ferrite polycrystals.

iii) In conventional impedance spectroscopy, highly conductive grain boundaries are easily ignored. A comparison of experimental data obtained with microelectrodes on a grain and on a grain boundary allows the detection and quantification of highly conductive grain boundaries; this is exemplified for AgCl.

iv) Microelectrodes can serve as model electrodes with well-defined three phase boundaries and interfaces. Measurements at Sr-doped LaMnO$_3$ microelectrodes on yttria-stabilized zirconia, for example, yielded an improved understanding of electrochemical processes at SOFC electrodes.

v) Microelectrodes are very sensitive to highly conductive surface layers and therefore suited to investigate ionic materials with high surface conductivity, e.g. due to gas-solid interactions.