## $\label{eq:charge} \begin{array}{l} {\rm Charge\ Attachment\ Induced\ Ion\ Transport\ -\ A\ New\ Approach\ to}\\ {\rm Electro-Diffusion,\ Chemical\ Diffusion\ and\ Grain\ Boundary\ Diffusion} \end{array}$

Karl-Michael Weitzel

Fachbereich Chemie, Physikalische Chemie, Philipps Universität Marburg, Hans Meerweinstraße, 35032 Marburg, Germany

 $E ext{-Mail: weitzel@chemie.uni-marburg.de}$ 

The charge attachment induced transport (CAIT) is a recently developed technique for investigating ion transport in the solid state. It is based on attaching ions to the surface of a solid sample in contact with a single metal electrode. This causes gradients of the electrical potential and/or the particle density across the sample and consequently transport of particles towards the backside electrode. If ions of different chemical identity are involved concentrations profiles will evolve. These concentration profiles can be measured quantitatively by means of ToF-SIMS and modelled quantitatively by means of Nernst-Planck-Poisson theory providing unique access to position and concentration dependent transport coefficients.

Three major examples will be discussed.

- The competition between Na<sup>+</sup> and K<sup>+</sup> in a mixed Na-K-borosilicate glass has been investigated by charging the sample surface with Cs<sup>+</sup> ions. Analysis of the Cs, K and Na profiles arising allows the derivation of concentration dependent diffusion coefficients in particular for the native Na<sup>+</sup> and K<sup>+</sup> in the glass [1].
- The mobility of Na<sup>+</sup> and Ca<sup>2+</sup> in Na-Ca-phosphate glass has been investigated by charging the sample with K<sup>+</sup> ions. The concentration profiles arising demonstrate the depletion of Na and Ca by means of electrodiffusion. On a much longer time scale these concentration profiles are demonstrated to evolve further by chemical diffusion leading to a partial refilling of the former depletion zone. Theoretical analysis demonstrates that for chemical back diffusion D(Ca) > D(Na) [2].
- In a thin film sample of  $PrMnO_3$  the electrical conductivity is so high that the surface is not charged but alkali metal is deposited at the front of the sample. In this case concentration driven diffusion of the alkali metal into the perovskite is observed. Theoretical analysis clearly reveals a completion between bulk and grain boundary diffusion, which is also supported by high resolution FIB-TEM [3].

Acknowledgements. Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG We 1330/17-1) is gratefully acknowledged.

- Transport of Ions in a Mixed Na<sup>+</sup>/K<sup>+</sup> Ion Conducting Glass-Electrodiffusion Profiles and Electrochemical Interphase Formation, J. Martin, S. Mehrwald, M. Schäfer, T. Kramer, C. Jooss, K.-M. Weitzel, Electrochim. Acta 191 (2016) 616.
- [2] Electrodiffusion versus Chemical Diffusion in Alkali Calcium Phosphate Glasses: Implication of Structural Changes, A. Hein, J. Martin, M. Schäfer, K.-M. Weitzel, J. Phys. Chem. C 121 (2017) 3203.
- [3] Charge Attachment Induced Transport Bulk and Grain Boundary Diffusion of Potassium in PrMnO<sub>3</sub>, J. Martin, M. Gräf, T. Kramer, C. Jooss, M.-J. Choe, K. Thornton, K.-M. Weitzel, Phys. Chem. Chem. Phys., in press, 2017 (DOI: 10.1039/c7cp00198c).

