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This Week's Citation Classic

Steele B C H & Alcock C B. Factors influencing the performance of solid oxide electrolytes in high-temperature thermodynamic measurements. *Trans. AIME* **233**:1359-67, 1965.

Ionic conductivity (σion) values of zirconia and thoria based solid electrolytes exhibited a maximum value which was associated with an optimum concentration of charge carriers fixed by the electrolyte composition. In contrast the partial electronic conductivity (σe) was strongly influenced by the imposed oxygen partial pressure. The ratio of σion/σe established the ionic regime available for thermodynamic measurements. [The *SCI*® indicates that this paper has been cited over 100 times since 1961.]

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"The behaviour of solid electrolytes now elicits worldwide interest as these materials find widespread application in a variety of novel energy conversion systems and chemical information transducers. However, 21 years ago when I first became interested in these 'superionic conductors' there was little relevant theoretical and experimental information available which I could use in planning my research investigation. Stimulated by the papers of the late Carl Wagner I had decided to leave the technical ceramics industry in which I was then working in order to carry out a Ph.D. investigation at Imperial College on these fascinating materials[1] In the department of metallurgy I was fortunate in meeting Ben Alcock who was also interested in these materials and he encouraged me to initiate an appropriate research programme. My initial appointment in 1958 at Imperial College as Nuffield Investigator did not allow much time to be spent on my own research project. I was also aware that Carl Wagner's group at Gottingen in Germany was working on similar problems, and I recall many moments of frustration at the slow progress of my Ph.D. investigation which eventually took six years! My programme was concerned with the application of solid oxide electrolytes to investigate the thermodynamic and structural characteristics of the Nb-O system, and part of the results are incorporated in the above paper.

"The paper itself combined original data on the ionic and electronic conductivities of zirconia and thoria based electrolytes as well as reviewing current theoretical models for the electrical transport behaviour of these materials. The contents confirmed that the onset of p-type or n-type conductivity delineated the boundaries between which oxygen ion conduction was predominant as required for emf and thermodynamic measurements. The paper also clearly demonstrated for the first time in superionic conductors that there is an optimum concentration of charge carriers resulting in a conductivity maximum. The factors influencing the concentration and distribution of ionic charge carriers are now an important feature of many current investigations on superionic conductors. The review content of the paper probably also provided a useful introduction to the topic of solid state ionics as technological applications of solid oxide electrolytes begin to be realised with their incorporation in high temperature oxygen monitors, fuel cells, and electrolysers. In spite of these applications I am conscious of the fact that many of the fundamental queries I posed in the paper 15 years ago about the mechanism of p-type conduction, and about the factors influencing the relevant electrode kinetics still remain unanswered and provide useful investigations for current Ph.D. students in the Solid State Ionics group at Imperial College."

1. **Kiukkola K & Wagner** C. Measurements on galvanic cells involving solid electrolytes. *J. Electrochem. Soc.* **104**:379-87, 1957.