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FLUORINE SOLID ELECTROLYTES: FUNDAMENTALS AND APPLICATIONS

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Fast ion transport in solids is a very active area of study in solid state chemistry and physics. To date a variety of solids with high values of ionic conductivity are known. The transport-structure relations of solid electrolytes have been studied in great detail, and the acquired fundamental knowledge has guided solid state chemists searching for new high-conductivity solid electrolytes. Besides developing new materials, the solid electrolyte properties of existing solids have been improved by modifying the compositions and structures by doping. Prime examples are anion-excess fluorite (CaF_2) structure metal fluorides and anion-deficient tysonite (LaF_3) structure metal fluorides. Upon doping a room temperature conductivity enhancement of 10^9 has been achieved in several of these solid solutions (1,2). In the anion-deficient solid solutions conductivity occurs by a vacancy mechanism, while interstitial fluoride ions represent the conducting species in the anion-excess solid solutions. The concentrated anion-excess solid solutions show a remarkable increase in the fluoride interstitial conductivity, while the anion vacancy conductivity of the tysonite structure solid solutions usually reveals a maximum with increasing solute contents (3). Especially in the concentrated solid solutions the ionic conductivity is strongly influenced by defect association and clustering phenomena, short range ordering and ion size effects. The bound defects give rise to dielectric relaxation phenomena.

While the measurement of electrical conductivity represents a very sensitive technique to investigate ionic transport, other dynamic techniques such as nuclear magnetic resonance (NMR) relaxation, thermal depolarization - ionic thermal current (ITC), and thermally stimulated (de)polarization current (TSPC, TSDC) - and a.c. dielectric relaxation are currently employed to study diffusive and localized motions of point defects in the present solid solutions. In addition, these techniques provide information that contributes to unraveling the defect structure. In fact, the defect structures and the dynamical behaviour of bound ionic defects have been investigated down to 10 K by TSDC and neutron scattering experiments. In $Ba_{1-x}La_xF_{2+x}$ and $Ba_{1-x}U_xF_{2+2x}$ fluorite structure solid solutions (222) and (212) clusters occur, respectively. The freedom of orientation of (212) clusters differs from that of (222) clusters, and this difference is reflected in low-temperature dielectric spectra. Besides, in all dielectric spectra the relaxation of macroscopic space charge, i.e. ionic conductivity, is observed. The contribution of ionic conductivity to the dielectric spectra is found to be in line with the high-temperature ionic conductivity as obtained from impedance spectroscopy (4).

Tysonite structure solid solutions like $La_{1-x}Ba_xF_{3-x}$ have electrical properties which are in a number of ways more complex than those with the fluorite structure. In comparison with the fluorite structure the tysonite structure is more complex in that three different fluoride sublattices can be

discerned. This anion array leads to dielectric relaxation phenomena resembling dipolar relaxations of associated defects. However, the vacancy mobilities differ in the different sublattices, and instead of associated defects exchange between the different anion sites seems to play a dominant role in the ion dynamics (3).

It is the aim of the present survey to high-light the recent progress made in the study of the relations between chemical compositions, defect structures, and ionic conductivity of these fluorine solid electrolytes. In addition to diffusive motions the localized motions of fluoride ion interstitials and vacancies as studied with thermal depolarization techniques will be discussed. Finally some applications of fluorine solid electrolytes in electrochemical systems will be surveyed.

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