

Electrochemical studies with fluoride electrolytes

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ABSTRACT - Although zirconia and thoria-based electrolytes have proved very valuable in the measurement of the thermodynamic properties of many oxide and alloy systems, there are systems for which the use of fluoride electrolytes are preferred. Refractory compounds involving the alkaline earth and rare earth elements can be studied with these electrolytes, but the use of fluoride solid solutions such as $\text{SrF}_2 - \text{LaF}_3$ is more convenient experimentally than the pure fluorides. This is because a steady EMF is normally achieved much more rapidly with the solid solutions. Examples are given of the incorporation of oxide, hydride and carbide dispersed phase in the fluoride electrolyte to enable the measurement of the thermodynamic properties of oxides, carbides, hydrides not accessible by the use of oxide electrolytes.

INTRODUCTION

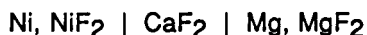
The use of stabilized zirconia as the electrolyte in galvanic cells for the determination of the thermodynamic properties of oxide systems has been widely exploited since the original paper of Wagner and Kiukkola [1]. In a recent review paper, Pratt [2] lists about one hundred oxide systems which have been studied using this electrolyte, and this constitutes the most important experimental contribution to our present knowledge of oxide thermodynamics. The reasonably well-defined limitations in ranges of temperature and oxygen potential over which the technique can be applied using zirconia-based electrolytes [3] have been augmented to a limited extent by the use of thoria-based electrolytes [4].

In a typical cell such as

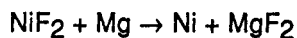


the use of the solid state electrochemical technique has supplied the most accurate data available at the present time. It may be applied to systems in the temperature range 300 - 1600°C and under oxygen partial pressures from 1 atmosphere to 10^{-35} atmos. This extremely versatile technique cannot however be applied to a number of solid state thermodynamic studies especially those involving stable oxides such as the alkaline earth and rare earth oxides, and alternative procedures are required.

The use of alkaline earth fluorides as solid electrolytes followed the demonstration by Ure [5] that the fluoride ion has unit transport number in CaF_2 and SrF_2 . The electrolytes were used soon thereafter to determine the relative thermo- dynamic properties of metal fluorides [6] in cells such as



in which the cell reaction is

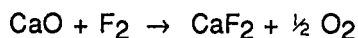


SIMPLE FLUORIDE ELECTROLYTES FOR OXIDE ELECTRODES

The use of fluoride electrolytes as alternatives to zirconia for the establishment of the thermodynamic properties of oxides was first indicated in a paper by Benz and Wagner [7] who studied the Gibbs energy of formation of calcium silicates. Essentially, a cell composed of electrodes and electrolytes such as



is a fluoride electrolyte-galvanic cell in which the fluorine potentials at the electrodes are determined by the calcium activities exerted by the calcium oxide-containing electrodes when immersed in a fixed oxygen pressure. In the left hand electrode, since calcium oxide is present at unit thermodynamic activity, the fluorine pressure exerted at the $\text{CaO} \mid \text{CaF}_2$ interface under one atmosphere oxygen pressure will be lower than that at the right hand electrode where the CaO activity is less than unity. Here the coexistence of calcium orthosilicate with pure silica reduces the calcium oxide activity. The two fluorine pressures may be calculated from the equation

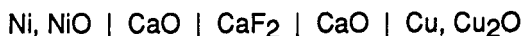


$$K = \frac{a_{\text{CaF}_2}}{a_{\text{CaO}}} \cdot \frac{p_{\text{O}_2}^{1/2}}{p_{\text{F}_2}}$$

In the cell, the activity of calcium fluoride, $a_{\text{CaF}_2} = 1$ and p_{O_2} is common to both electrodes, hence the fluorine pressure exerted at each electrode is inversely related to the CaO activity. Clearly the oxygen pressure which must be imposed need only be high enough to ensure the correct valence states of the cations in the electrodes, and need not be the same on both electrodes. When one electrode contains a non-stoichiometric oxide then the exact value of the oxygen partial pressure must be controlled in order to define the stoichiometry. A number of studies were subsequently made in Moscow by Rezukhina and Levitskii and their coworkers which established the use of fluoride electrolytes for the determination of Gibbs energies of formation of a number of technologically important alkaline earth refractory compounds in cells such as that used by Levitskii et al. in the Sr-Al-O system [8]. The situation is very much simpler, therefore, in the study of alkaline earth compounds containing ions such as silicon, or aluminum which appear in one valency only, than when the accompanying ion can have a number of valencies over a comparatively wide range of oxygen potentials such as tungsten, for example. The application of fluoride electrolytes to the direct study of oxide systems would thus appear to be limited, unless the oxygen partial pressure in each electrode is independently controlled.

A considerable expansion of the application of fluoride electrolytes to the study of oxide systems is achieved when a stable oxide layer is interposed between the fluoride electrolyte and each electrode. Ramanarayan, Narula and Worrell [9] first demonstrated that if a single crystal CaF_2 electrolyte was heated in moist air, superficial oxidation occurred and the electrolyte could then

be used in the cell which can be written as



It has been demonstrated in our laboratory that if strontium oxide is dispersed in a polycrystalline SrF_2 electrolyte to the extent of about 5 volume percent, the composite could also be used as the electrolyte in a similar cell



SOLID SOLUTION FLUORIDE ELECTROLYTES

The chief drawback to these systems in which the simple fluorides CaF_2 or SrF_2 are used as electrolytes, when compared with zirconia, is that the rate of achievement of a steady EMF is very much slower. Thus at temperatures around 1000 K most cells using zirconia electrolytes reach a steady potential in less than one hour, at constant temperature, but cells employing these simple fluoride electrolytes usually require several hours and even days to reach a steady voltage.

The rate of equilibration can be considerably increased if fluoride solid solutions are used instead of the simple fluoride as the electrolyte. The electrical conductivity by fluoride ion migration of strontium fluoride can be enhanced by two orders of magnitude when lanthanum fluoride is added to form a solid solution. Lanthanum fluoride, which also has a very high fluoride ion conductivity yields enhanced electrical conductivity when strontium or barium fluoride are dissolved in solid solution. Clearly in the SrF_2 -based solution, the addition of LaF_3 increases the interstitial fluoride ion concentration, and in the LaF_3 -based solution, the addition of SrF_2 increases the fluoride ion vacancy concentration. [Fig. 1]. Conductivity measurements carried out in our laboratory show that the lanthanum fluoride solution in strontium fluoride has a maximum conductivity at about 30 mole percent LaF_3 . This composition was adopted in subsequent studies. The lanthanum fluoride electrolyte will only dissolve a few mole percent of SrF_2 or BaF_2 and 5 mole percent has been used in the present studies.

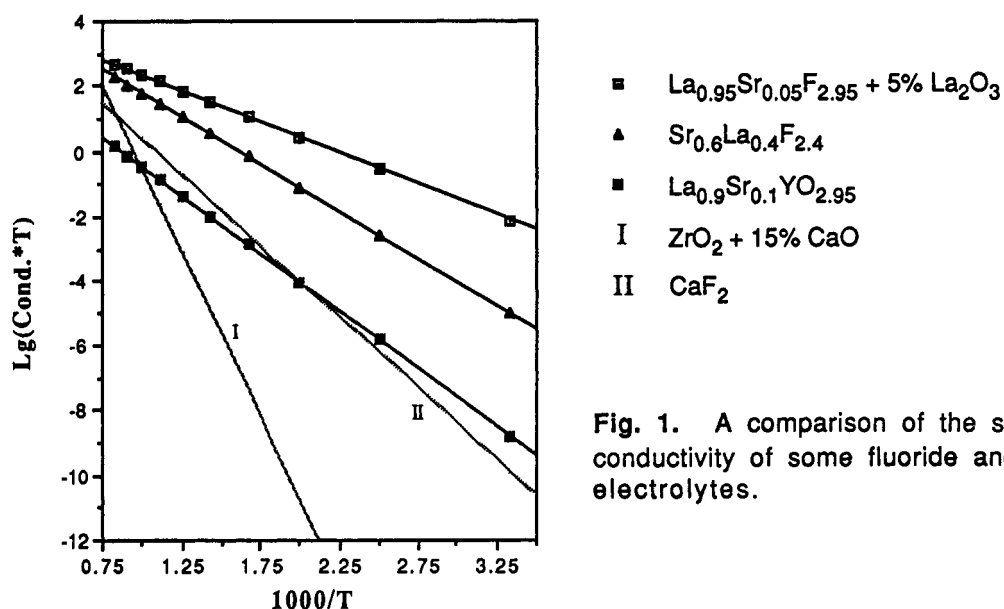


Fig. 1. A comparison of the specific conductivity of some fluoride and oxide electrolytes.

ADVANTAGES OF FLUORIDE ELECTROLYTES FOR OXIDE SYSTEMS

Because these fluoride electrolyte cells are made from very stable fluorides, the presence of metals which form stable oxides at the electrode/electrolyte interface does not lead to any chemical change in the electrolyte. Thus the presence of niobium metal at the electrode/electrolyte interface in a cell employing a zirconia-based electrolyte, would lead to reduction of the electrolyte with introduction of a significant electronic contribution to the electrolyte conductivity. However when the fluoride electrolytes containing a dispersed SrO or La₂O₃ phase are placed in contact with niobium, no condensed-phase chemical change occurs in the electrolyte. These electrolytes may thus be used in the elucidation of the thermodynamics of oxides having considerably greater stability than those which can be studied with zirconia-based electrolytes. For example a stable EMF, close to that calculated from the best thermodynamic data, was obtained for the cell

Cr, Cr₂O₃ | SrF₂ - LaF₃ - 5% SrO | Nb, NbO

at 1000 K.

The rate of achievement of a steady potential in cells employing these high-conductivity fluoride electrolytes has been found to be quite rapid, and in most cases the achievement of a steady EMF is rate-determined more by electrode kinetics than at the electrode/electrolyte interface. In a series of studies with metal/metal oxide electrodes, it was found that a steady EMF could be attained as soon as the cell assembly reached a constant temperature throughout, providing the metal at each electrode was liquid. At the temperature where one electrode had solid metal only, the achievement of a steady potential occurred considerably more slowly. At low temperatures, below 600 K, some cells did not achieve the calculated EMF, but these were always smaller than calculated.

The essential contribution of a liquid phase in each electrode was clearly demonstrated by the fact that the cell

O₂, H₂O (liquid) | LaF₃ - BaF₂ | Ar, O₂, H₂O (liquid)

could be operated with a rapid response time down to 30°C. The EMF followed variation of the the Ar/O₂ ratio in the right hand electrode within 20 minutes of variation in the gas composition and some of this time was used up in establishing a new oxygen content of the liquid water phase with which the gas mixture was in contact.

NON-OXIDE ELECTRODES

The fact that a fluoride electrolyte could be used with metal/metal oxide electrodes in a galvanic cell after dispersal of an appropriate oxide phase within the electrolyte, suggested that other possibilities using other dispersed phases, such as hydrides, sulfides and carbides should be attempted.

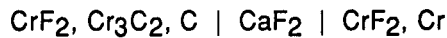
Accordingly, a cell was constructed in which the electrolyte was SrF₂ - LaF₃ containing 5 mole percent of SrH₂ as a dispersed phase. The electrodes were gaseous electrodes of argon/hydrogen mixtures and contacts to the electrolyte were made with iron foil and stainless steel wires. The electrochemical

performance of the cell was studied at temperatures between 600 and 700°C and the EMFs were obtained when one electrode was a standard gas mixture Ar, H₂ and the other was a systematically varied argon/hydrogen mixture. The resultant EMFs obeyed the Nernst Equation

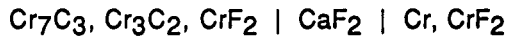
$$E = \frac{RT}{2F} \ln \frac{p_{H_2} \text{ (standard)}}{p_{H_2} \text{ (Ar, H}_2 \text{ mixture)}}$$

with zero EMF when the two hydrogen partial pressures were equal.

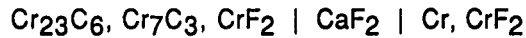
Fluoride electrolytes have been used in galvanic cells for the determination of the thermodynamic properties of carbides [10]. The cells are usually arranged so that carbon is present in one electrode at a well-defined activity, and that, in fact, the cell measures the chemical potential of the metal which is combined in the carbide. Thus, for the determination of the standard Gibbs energy of formation of the chromium carbide Cr₃C₂, Du Sichen et al, [11] determined the chromium activity of this phase when saturated with carbon in the cell



The mixture of phases in the left hand electrode fixes the fluorine pressure exerted by chromium difluoride in which the chromium activity is equal to that of the Cr₃C₂, C mixture. Once the properties of this phase are known, the Gibbs energy of formation of the other chromium carbides Cr₂₃C₆ and Cr₇C₃ can be obtained using data from the cells

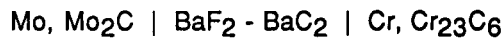


and



both of which are fluoride cells which determine the chromium activities in the left hand electrodes.

It would be desirable to determine the carbon activities in carbide phases using a system which responds directly to the carbon activity rather than indirectly, through a metal activity as shown in the previous example. Coulters and Belton [12] made a cell employing an electrolyte of BaF₂ containing 1% BaC₂, possibly in solid solution. Using this electrolyte they measured the Gibbs energy of formation of a number of carbide phases in cells such as

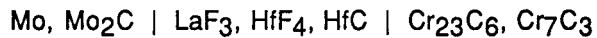


obtaining results in good agreement with literature data.

The selection of alkaline earth and rare earth fluorides as materials for electrolytes is based upon the need to find chemically stable electrolytes which will not undergo reaction with the electrode materials. Unfortunately these elements form carbides of only moderate stability, and hence the use of a carbide solution or dispersed phase in these fluorides has only limited value in the measurement of carbide thermodynamics. More stable carbides, together with highly stable fluorides, are to be found in Groups IV and V of the Periodic Table.

The pure tetrafluorides and pentafluorides of these elements have a tendency to vaporize at low temperatures in the molecular form, and these fluorides could therefore only be used as components of high temperature electrolytes in solid solution.

Following the work of Coultters and Belton, it seemed probable that an electrolyte basically of lanthanum fluoride, LaF_3 , containing hafnium tetrafluoride, HfF_4 , and hafnium carbide HfC , either in solution or as a dispersed phase would function as a satisfactory electrolyte for the determination of carbide thermodynamics. Preliminary results on the cells



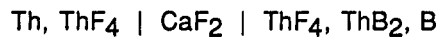
confirm this expectation.

It should be admitted at this point that some success has been achieved in the measurement of carbide thermodynamics using stabilized zirconia as the electrolyte. For example, the results calculated from the cell



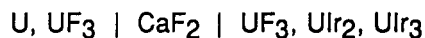
used by Mabuchi et al. [13] agree quite well with the results of Du Sichen et al. who used the CaF_2 electrolyte. However, the presence of a separate oxide phase in the electrodes could lead to a significant dissolution of oxygen in the carbide phase in many other carbide systems, and should therefore be avoided.

Other systems which have been studied using fluoride electrolytes include an early study of borides with, for example, the cell



used by Aronson and Auskern, which essentially measures thorium activity in the boron-saturated ThB_2 [14].

Kleykamp has made a number of determinations of the Gibbs energies of formation of uranium intermetallic compounds, reported and analyzed by Chiotti et al. [15] with cells such as



Clearly in these systems the use of a zirconia-based electrolyte would be impossible because reduction of the electrolyte would occur at high uranium activities.

Finally the dispersed phase system has been used for the determination of the relative thermodynamic properties of sulfides in, for example the cell [16]



and in the more conventional and more slowly responding cell [17]



These systems need more development especially with regard to the complications which ensue under industrial conditions when the sulfur potential must be measured in the presence of a significant oxygen potential.

CONCLUSION

Fluoride electrolytes, especially those solid solutions having a high ionic conductivity serve as a useful adjunct to the zirconia and thoria electrolytes for electrochemical studies of high temperature systems. It is to be expected that many new studies will be undertaken in systems where the oxygen potential is too low for the oxide electrolytes, and that the temperature range will be substantial, beginning at lower temperatures than are possible with the oxide electrolytes, but probably being limited to an upper temperature limit around 1100°C. This upper limit will be determined by the effects of fluoride vaporization which is significant at temperatures considerably below the melting point.

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