Example 6.1

An electrode selective to ions (type I) and reference electrode is immersed in a solution containing type I ions of activity 1.5 × 10^{-3} M when the potential of the selective electrode is 0.21 V. If the same electrode is dipped in a solution that has activity of type I ion 1.6 × 10^{-3} M, and its selectivity coefficient with respect to another type, type II (with activity 1.1 × 10^{-3} M) in the solution is 2.5 × 10^{-1}, what would be the electrode potential? Assume solution temperature as 25°C and unit ion charges for both types.

Solution

Using Eq. (6.23),

$$-0.21 = E_{\mathrm{I}} = E^0 \frac{0.0591}{1} \log(1.5 \times 10^{-3})$$

so that

$$E^0 = -0.2693 \text{ V};$$

Now, using Eq. (6.32), with $(K_{s2}\ \mu_{s2})/\mu_m = 0.25$, $\alpha_{s2} = 1.1 \times 10^{-3}$, and $\alpha_m = 1.6 \times 10^{-3}$,

$$E = E^0 + \left(\frac{0.0591}{1}\right) \log\left\{1.6 \times 10^{-3} + (0.25 \times 1.1 \times 10^{-3})\right\}$$

$$= -0.2693 + 0.05935$$

$$= -0.20995\text{V}$$

Example 6.2

Calculate the half-cell potential of an Ag electrode dipped in a solution that has 1.5 × 10^{-2} M Ag^- concentration.

Solution

$$\mathrm{Ag}^+ + \mathrm{e} \rightleftharpoons \mathrm{Ag(s)},$$

$$E^0 \text{ (from table)} = +\ 0.799 \text{ V}$$

Hence,

$$E = 0.799 + \frac{0.0591}{1} \log(1.5 \times 10^{-2})$$

$$= 0.8583 \text{ V}$$

6.9 ELECTROCERAMICS IN GAS MEDIA

A number of ceramic oxides have been developed over the past two decades and some are still being developed which function to show some electrical properties such as develop an emf, change conductivity or surface ionic conductivity and so on, when placed in a gas media. A list of these properties with respect to the materials is given in Table 6.2 which is not comprehensive by any means.

Table 6.2 Functional properties and applications of electroceramics

S.No.	*Functional properties and their representation*	*Material*	*Applications*
1.	Ionic conductivity; uses Nernst Eq.	ZrO_2	Solid analyte, mainly as O_2 sensors
	$Emf = \frac{RT}{4F} \ln\left\{\frac{P(O_2)_g}{P(O_2)_r}\right\}$	Nasicon	Solid electrolyte, mainly as gas sensors
	(P = partial pressure)	β, β''-alumina	Solid electrolyte in potential generation
2.	Semiconductivity, conductivity depends on temperature and partial pressure of O_2,	SnO_2, ZnO	Gas sensors, mainly hydrocarbon gases
	$\sigma = \sigma_0 e^{-E/kT} \cdot \frac{1}{(P(O_2))^{1/m}}$	TiO_2	O_2 sensors
	(E = activation energy, m = constant $4 < m < 6$, k = Boltzmann constant)	Oxides such as $SrTiO_3$, $BaTiO_3$, $SrSnO_3$ (called pervoskites)	O_2 sensors
3.	Surface property		
	(a) Varistor	$BaTiO_3$	Electronic sensors
	$\frac{J_1}{J_2} = \left\{\frac{(\text{Electric field})_1}{(\text{Electric field})_2}\right\}^{\alpha}$		
	α = varistor constant, $1 < \alpha < \infty$; typically 25–50		
	(b) Surface ionic conductivity	SiO_2, $ZnCr_2O_4$	Humidity sensors

The transfer characteristic of a metal oxide sensor is approximated by the relation

$$\frac{R_j}{R_0} = \left\{a_j(\chi_j) + 1\right\}^{n_j} \tag{6.43}$$

where R_j is its resistance with gas j,

χ_j is the concentration,

R_0 is the resistance with air as the gas,

a_j is a coefficient for the gas, and

n_j is an index.

6.9.1 Ionic Conductors

Zirconia

ZrO_2 exists in the crystalline modifications in different temperature ranges.

In the range 2680°C (melting point) to 2372°C, zirconia crystallizes in face-centred cubic structure; between 2372°C and 1200°C, it appears as tetragonal; and from 1200°C to about room temperature, it has the monoclinic form (all these are at atmospheric pressure). At a high pressure, a stable orthorhombic structure is also known.

When phase transformation occurs from tetragonal to monoclinic structure, there is a volume expansion to the extent of 3–5% which leads to cracking in the material. Hence, zirconia is made only in small pieces by taking care of volume stability. Addition of oxides of yttrium, calcium, or magnesium by certain amounts leads to cooling of the cubic structure without transformation. Depending on the mole percentage of Y_2O_3 the structure at room temperature is determined. Thus with 1.8%, a monoclinic phase exists; upto about 2.5%, tetragonal phase with a little cubic phase exists; and beyond about 16%, only cubic phase can be available in stable form. With CaO and MgO, similar phase diagrams (Fig. 6.18) are known but these are not very well established. For application, the phase structure is required to be known, however, and the type and amount of coexisting phases, their distribution, transformation kinetics, added cation and so on, do determine the properties of zirconia.

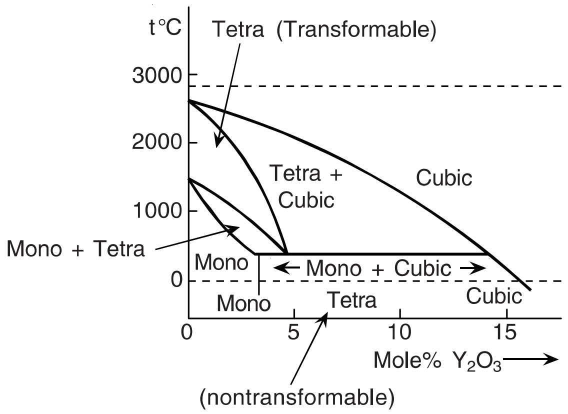

Fig. 6.18 Phase diagram of ionic conductors.

As zirconia based oxygen sensors are widely used in industries for combustion control, engine control and so forth, the ionic properties of zirconia with different cations varying with temperature are shown in Fig. 6.19.

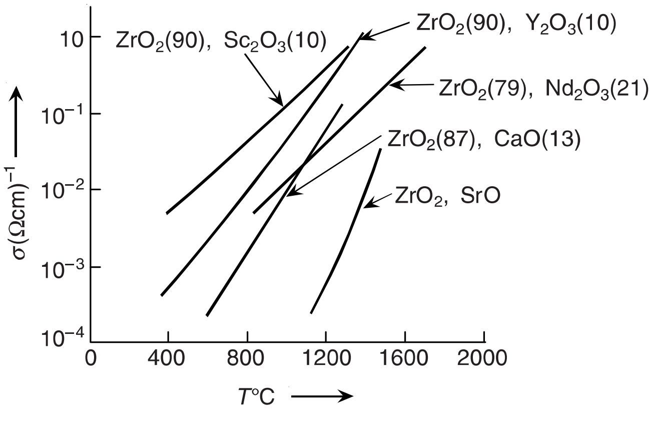

Fig. 6.19 Conductivity–temperature plots of some ionic conductors.

Conduction phenomenon in zirconia has only been recently realized. When Zr^{4+} cations are replaced by lower charge cations such as Y^{3+}, Ca^{2+} and so on, vacant spaces are formed in anionic oxygen lattice, but the distribution of these vacant sites and the occurrence of low charge cations are only statistical in nature. As these vacancies can move through the lattice, the charge transport thus occuring, produces conductivity. However, the size of cation that replaces Zr^{4+} determines the energy required for such charge transportation. Now as Ca^{2+} has a higher radius of 0.99 μm and Y^{3+} has a radius 0.92 μm whereas Zr^{4+} has that of 0.79 μm, replacement with Y^{3+} gives higher conductivity than with Ca^{2+}. The higher energy requirement is said to be due to the fact that oxygen moves only through a tetrahedral face formed by three cations. Further, the maximum ionic conductivity occurs for different mole per cent of either Y_2O_3 or CaO. In the former case, it is about 8–9% while for the latter it is about 12–13%. Even these maximum σ-values are also not same.

NASICON

It is a sodium solid electrolyte series with the chemical composition $Na_{1+x} Zr_2 Si_x P_{3-x} O_{12}$ with x varying from 0–3, the maximum being obtained at $x = 1.9–2.2$. Because of presence of sodium, its conduction property is very good. With $x = 2$, the structure of NASICON is rhombohedral. It consists of octahedral ZrO_6 groups separated by tetrahedral PO_4 or SiO_4 and a three-dimensional framework is made that appear as infinite ribbons which are quite loose and provide conduction channels for Na^+.

β-alumina

It belongs to the set of sodia-alumina ($Na_2O–Al_2O$) compounds that have been obtained from sodium aluminate ($NaAl_{11}O_{17}$). They are solid electrolytes and used at high temperature. They permit fast diffusion of Na^+, and hence, have high ionic conductivity but low electronic conductivity. They are quite inert chemically and possess good thermal and mechanical strength. A variation in the form is $Na_2O–5Al_2O_3$ which is called β''-alumina. These are the two most common types though there are others as well. In fact, β''-alumina is thermodynamically unstable and is made stable by 'ternary processing' by addition of cations such as Mg^{2+} and Li^+.

β-alumina is hexagonal and layered while Li^+-stabilized β''-alumina is rhombohedral. The latter has higher ionic conductivity than the β-alumina.

Figure 6.20 shows the comparative study of the variation of ionic conductivities of the different ceramics as discussed in the preceding paragraphs.

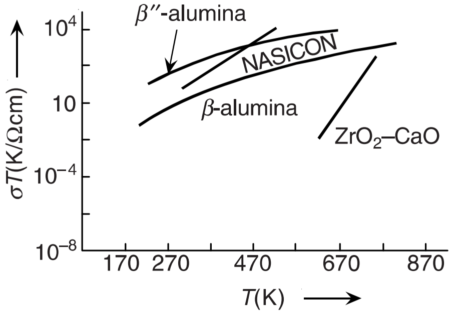

Fig. 6.20 Ionic conductivities of some ceramics.

Tin oxide

It is an oxygen deficient n-type semiconductor and crystallizes in a rutile structure. It is commercially used as gas sensors—particularly for reducing gases in industrial and domestic conditions, for alarm generation and known as *Tagushi Gas Sensors* (TGS). Various dopants and