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# TRANSPORT PROPERTIES IN CERAMIC IONIC CONDUCTORS

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## 1. INTRODUCTION

The electrical conductivity, under the influence of an electric field, can occur with or without mass transport: the conduction is due to the migration of ions (ionic conductor) in the former case and to the migration of electrons (electronic conductor) in the latter one. Metals, alloys, intermetallic compounds, semiconductors and in general all the materials having free or weakly bonded electrons are electronic conductors. Electrolytic solutions, fused salts, some ionic solids and in general all systems having free ions are ionic conductors. In electrolitic solutions as well as in fused salts different ions can be involved in the transport phenomena while in solid electrolytes, generally, only one type of ions migrates, all the other ones are fixed in their lattice positions. Mixed ionic and electronic conductivity is also possible in many cases.

## 2. CORRELATIONS BETWEEN STRUCTURE AND IONIC MIGRATION

In an ideal crystal, in which the regular and infinite arrangement of the atoms in all their lattice positions exists, the migration of ions is impossible or very difficult. Fortunately, in nature there are no ideal crystals but real ones having defects. It is the presence of defects that induces electrical ionic conductivity in solids. The crystals are imperfect because the presence of defects decreases the Gibbs free energy. To create a defect in a crystal a certain amount of energy $\Delta H$ is necessary; the presence of this defect produces an increase in entropy $\Delta S$. Such an increase in entropy is due to the large number of positions which this defect is able to occupy (configurational entropy) any temperature, a minimum in free energy occurs at a certain well defined number of defects (for any compound); increasing this number of defects, the amount of entropy which arises on creating further defects is not enough to compensate for the energy necessary to make these extra defects and the Gibbs free energy increases (see fig.1).

Defects can be classified as:

a) Extended defects
b) Point defects

If one depicts the crystalline structure of a solid as a lattice in which the ions are stiff spheres having a ready radius, the feature of the solids with extended defects is the presence of a perfectly ordered sublattice and of a sublattice in a total disorder. The disordered sublattice includes many empty lattice positions (having the same potential energy of the full ones) available for the motion of the ions. As an exampleis reported the case of $\beta$-Na alumina ($Na_2O.11Al_2O_3$) which is crystal structure builts of closed packed layers of oxide ions, staked in three dimensions, but every fifth layer has three-quarters of its oxygens missing(see fig.2). The $Na^+$ ions are in the oxygen deficient layers and can migrate because there is a greater number of sites available than $Na^+$ ions. The point defects involves the presence of two closed defects which may be vacancies or interstitial positions. The Schotty defect is a stoichiometric defect constituted of a same number of vacancies in the anionic and cationic sublattice (fig.3). The formation of this lattice disorder is represented by the following reaction:

$$\text{nill} \rightleftharpoons V_A + V_C$$

$V_A$ and $V_C$ are the anionic and cationic vacancies. The Frenkel is also a stoichiometric defect and implies the presence of a same number of vacant and interstitial positions (fig.4).

The reaction producing this type of defect, in the case the cationic sublattice is involved, is:

$$C_A \rightleftharpoons C_i + V_C + A_A$$

and in the case the anionic sublattice is involved:

$$C_A \rightleftharpoons C_C + V_A + A_i$$

$C_i$ and $A_i$ are the cations and the anions in the interstitial positions, $V_C$ and $V_A$ the cationic and the anionic vacancies, $C_C$ and $A_A$ the cations and the anions in their lattice positions. As an example is reported the case of $ZrO_2$. This compound shows an oxygen ionic conductivity according to the Frenkel desorder:

$$O_O \rightleftharpoons V_O + O_i$$

In equilibrium conditions, only when the concentration of defects is significant the ionic conduction takes place; for this compound the concentrations of the defects is significant only at higher temperatures. Nevertheless it is possible to decrease the operating temperature of this solid electrolyte doping $ZrO_2$ with $Y_2O_3$. The presence of $Y_2O_3$, neglecting the effect of the stabilization at low temperature of the flouritic structure, in the $ZrO_2$ increases the number ofthe oxygen vacancies according to:

$$Y_2O_3 \rightleftharpoons 2Y' + V_O^{\bullet\bullet} + 3O_x$$

increasing the total ionic conductivity of the zirconium dioxide, also at low temperatures .

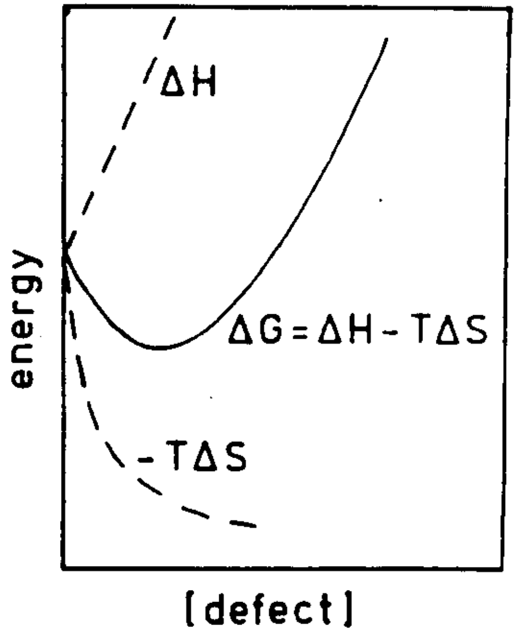


fig. 1

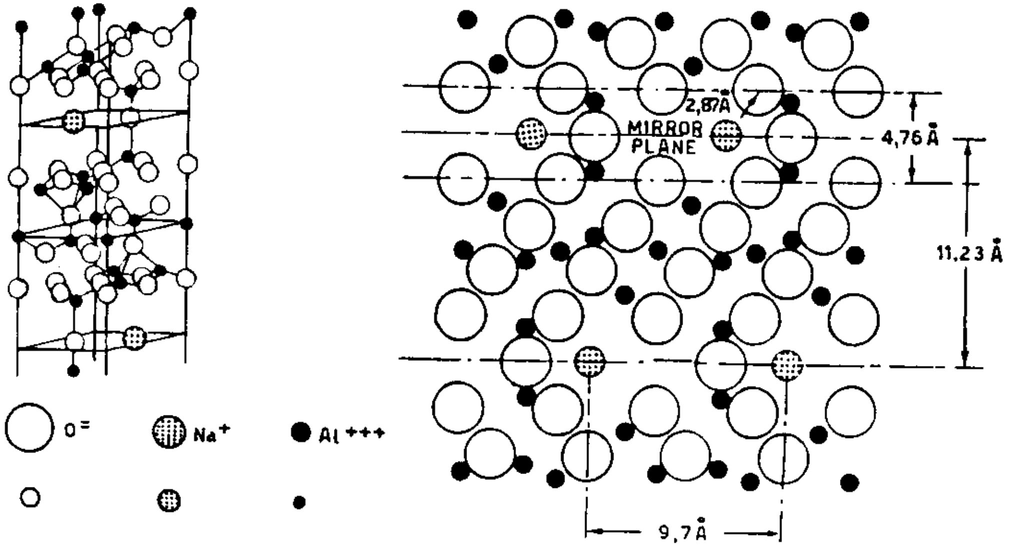


Fig. 2

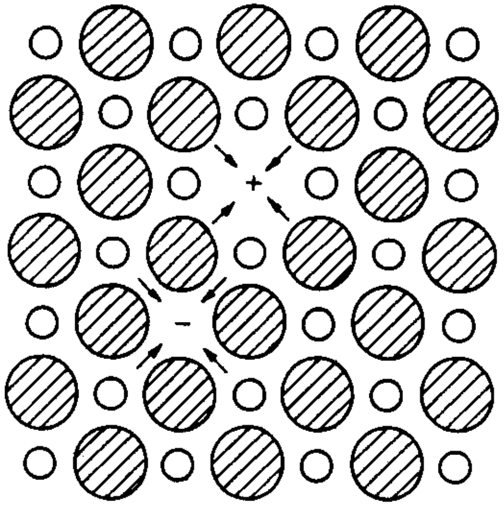


fig. 3

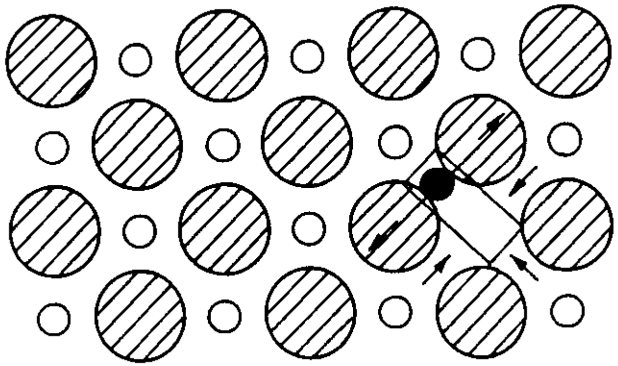


fig. 4

# DIFFUSION AND IONIC MIGRATION IN SOLIDS

## 1. INTRODUCTION

The presence of lattice defects in a solid can explain the transport ionic processes (charge and mass), under chemical gradient -diffusion- or electric field -migration- as the jump of an ion from a lattice position to an empty closed one.

## 2. DIFFUSION COEFFICIENT RELATED TO THE MICROSCOPIC BEHAVIOUR OF INDIVIDUAL PARTICLES

If one considers the transport process only due to the gradient of chemical potential, whenever a concentration gradient is established in a given system a flow of particles (J) takes place from the higher to the lower concentration; J is proportional to gradient concentration according to theFick's first law:

$$J = -D \operatorname{grad} C \tag{1}$$

D is the diffusion coefficient and C the concentration of the diffusive chemical species. The concentration gradient, in absence of external forces, tends to zero in the time. It is now possible to imagine:

i) a lattice in which some atoms have been substituted with isotopes and exchange their sites with "normal" atoms;
ii) a variation of the isotopes concentration along only a coordinate (x).

The concentration of the isotopes is then a function of time and of the distance x. The diffusion flow can be calculated counting the number of marked atoms which cross, in the t time, a hypotetical surface (of unit area)in the plane $X_0$ and perpendicular to the x axis. As it has been assumed the absence of external forces, the displacement probability can be considered the same along both positive and negative x direction of the axis. A marked atom makes a large number of jumps but a short mean displacement, theprojection of which along x axis is X. As the distribution function, defined as the probability that at a time t a particle has made a displacement with a projection between X and X + dX, is f(X,t)dX, it follows that:

$$\int_{-\infty}^{+\infty} f(X,t)\, dX = 1 \qquad (2)$$

Considering a large number of particles, the mean displacement $<X>$ is:

$$<X> = \int_{-\infty}^{+\infty} X \; f(X,t)\, dX \qquad (3)$$

and the mean square displacement $<X^2>$ is:

$$<X^2> = \int_{-\infty}^{+\infty} X^2 \; f(X,t)\, dX \qquad (4)$$

As the net diffusion flow of particles:

$$J = J_l - J_r \qquad (5)$$

is the difference between the number of marked ions which cross the plane x0 from the left and the number of particles which cross the same plane $x_0$ fromthe right, during the same time t; defining C(x) the number of marked ions(per unit volume) in the plane of abscissa x, the flow ($J_l$) of all the particles initially situated at the left side of the plane $x_0$ is:

$$J_l = 1/t \int_{-\infty}^{x0} C(x) \left[ \int_{x0-x}^{\infty} f(X,t)\, dX \right] dX \qquad (6)$$

and the flow ($J_r$) of all the particles at the right of the same plane is:

$$J_r = 1/t \int_{x0}^{\infty} C(x) \left[ \int_{x0-x}^{\infty} f(X,t)\, dX \right] dX \qquad (7)$$

Expanding C(x) around the plane $x_0$, integrating and rearranging oneobtains:

$$J = -\left(<X^2>/2t\right) \delta C/\delta X \qquad (8)$$

Comparing the right hand side of eq.(1) and eq.(8) one obtains:

$$D_X = <X^2>/2t \qquad (9)$$

In a cristall, more generally, the mean square displacement is:

$$<x^2>\ (t) = b \cdot D \cdot t \qquad (10)$$

b is a geometrical coefficient which assumes a value equal to the total number of possible final jump positions. It is possible, using the random walk theory, to calculate the mean squaredisplacement considering a particle which makes N random jumps, havingthe same length r, per unit time:

$$<X^2>(t) = N \cdot t \cdot r^2 \qquad (11)$$

from eq.(9) and eq.(10) one obtains D (macroscopic magnitude) from themicroscopic behaviour of individual particles:

$$D = a \cdot N \cdot r^2 \qquad (12)$$

with a = 1/b. In an ideal random walk the jump direction is indipendent from the previous one; because in the case of any diffusion mechanism the jump direction is dependent from the earlier situation a correction factor (f) is introduced:

$$D = a \cdot N \cdot r^2 \cdot f \qquad (13)$$

## 3. DIFFUSION COEFFICIENT AS A FUNCTION OF THE DEFECTS ENERGY FORMATION

In an isotropic solid having ionic conduction, the motion of the ions in the lattice may be pictured as the jump of an ion to the nearest neighbour available site having a distance r. The presence of defects in a cristallinduces conduction mechanisms. A particle is able to occupy a defect when two conditions are simultaneously fullfilled:

i) the particle has a defect available on a nearest neighbour site
ii) the particle has sufficient energy to exceed the potential barrier between two positions.

Supposing the ions jump due to a thermal activated mechanism, the ionic migration may be treated with the method of critical vibration amplitude. It is possible to demonstrate, in the case of random jumps, the probability (P) of a jump depends exponentially on the barrier energy between the initial and final position according to:

$$P = F \exp(-E/KT) \tag{14}$$

F is the normal vibration frequency, E the value of the energy barrier. The number of jump (N) may be calculated as:

$$N = n*P \tag{15}$$

n is the number of particles. The number of the migrating particles, as a function of the temperature, is:

$$n = n_0 \exp(-W/KT) \tag{16}$$

W is the defects energy formation and KT the lattice thermal energy. Then the eq.(13) becomes:

$$D = f*a*P*n*r^2 = f*a*r^2*n_0 \exp(-W/KT)*F \exp(-E/KT) \tag{17}$$

relationship between the diffusion coefficient and the energy formation of the lattice defects.

## 4. RELATIONSHIP BETWEEN DIFFUSION COEFFICIENT AND IONIC ELECTRICAL CONDUCTIVITY

The flow ($J_c$) due to the migration of the number n of particles, having(ze) charge, under a gradient of external electric potential (V) may be written as:

$$J_c = n*r^2*(ze)^2*P*V/KT \tag{18}$$

Remembering the definition of electrical conductivity ($\sigma$):

$$\sigma = J_c/V \tag{19}$$

and substituing Jc with eq.(18), P with eq.(14) and n with eq.(16) one obtains:

$$\sigma = [n_0*(ze)^2*r^2*F/KT] \exp-\{(W+E)/KT\} \tag{20}$$

or more generally:

$$\sigma = (\sigma_0/T) \exp(-E^*/KT) \tag{21}$$

In an electric field, in which an ensemble of charged particles is in equilibrium conditions, the sum of the diffusion current:

$$J = -D \text{ grad } C \tag{22}$$

and of the electrical current is zero:

$$-(ze)*D_\sigma \text{ grad } C + \sigma V = 0 \tag{23}$$

In an electrical field, according to the Maxell-Boltzman statistical distribution, the allocation of the particles is:

$$\text{grad } C = C*(ze)*V/KT \tag{24}$$

combining eq.(23) and eq.(24) one obtains the well known Nernst-Einstein equation

$$D_\sigma = KT\sigma/C*(ze)^2 \tag{25}$$

Because the electrical conductivity can be written as follows:

$$\sigma = \Sigma_i \; n_i*u_i*(ze) + n_e*u_e*e \tag{26}$$

and considering, in the case of a pure ionic conducting solid, the conductivity due only to a single ionic species:

$$\sigma = \sigma_i = n_i*u_i*(ze) \tag{27}$$

The relashionship between the ionic diffusion coefficient of a chemical species i and its mobility is obtained substituing eq.(27) in eq.(25):

$$D_X = u*KT/(ze) \tag{28}$$

# APPLICATIONS OF CERAMIC IONIC CONDUCTORS

## 1. INTRODUCTION

Electrolitic solutions as well as fused salts are used as electrolytes in galvanic cells; solid ionic conductors can be used for solid state galvanic cells which consist of at least two electrodes (electronic conductor) separated by a solid electrolyte (ionic conductor). In such asystem a reduction (cathodic) and an oxidation (anodic) reaction takes place to the electrode which accepts and releases electrons respectively. The general chemical reaction to describe an electrochemical reaction is:

$$\mathrm{Ox} + \mathrm{ne} \rightleftharpoons \mathrm{Red}$$

the electron is considered a chemical species and "e" corresponds to a mole of electrons ($6.02252\ 10^{23}$ electrons). The amount of charge of an electron mole is 96487 coulombs (Faraday) and it is the amount necessary to reduce or to oxidize an equivalent gram of chemicals.

## 2. RELATIONSHIP BETWEEN GIBBS ENERGY AND ELECTROMOTIVE FORCE

According to the first law of thermodinamics the internal energy (U) of asystem is correlated to heat (Q) and work (W) by:

$$dU = \delta Q + \delta W \qquad (1)$$

If one considers the work as the sum of the mechanical and electrical one,in a reversible process:

$$\delta W = -pdV + \delta W_e \qquad (2)$$

Regarding only reversible processes, the heat exchanged between the system and the surrounding can be correlated to the corresponding entropy change(second law of thermodinamics):

$$\delta Q = \delta Q_{rev} = TdS \qquad (3)$$

Combining eqs.(1-3) and solving for We ,one obtains:

$$\delta W_e = dU - TdS + pdV \qquad (4)$$

The total differential of the Gibbs energy, at pressure and temperature constant, is:

$$dG = dU - TdS + pdV \qquad (5)$$

Comparing eq.(4) and eq.(5):

$$\delta W_e = dG \qquad (6)$$

The maximum (reversible) electrical work done on or by the system is equal to the change in the Gibbs free energy of the system; because the electrical work, at pressure and temperature constant, is:

$$\delta W_e = -nFdE \qquad (7)$$

E is the open circuit voltage (f.e.m.), n the number of electrons involved in the electrochemical process and F the Faraday constant.
Integrating and comparing the equations one obtains:

$$\Delta G = -nFE \qquad (8)$$

E is taken as positive if the right hand electrode of the galvanic cell is positive (Stokolm convention); the flow of charge across the cell is called positive if a positive current flows from the left to the right hand side of the galvanic cell.

## 3. APPLICATIONS

Because the e.m.f. of a galvanic cell is related to the Gibbs free energy of the reaction cell, it is possible experimentally to determine:

a) Gibbs reaction (or formation) energy
b) Reaction enthalpy and entropy
c) Activity of a chemical species

and it is possible to obtain energy by fuell cell.

### 3.1 Gibbs Formation Energy

The thermodinamics of oxides was widely studied using solid state electrochemical cells provided electrolyte having oxygen ions conduction. It is considered the following cell:

$$\begin{array}{c} \mathrm{Pt} \mid \mathrm{Ni,NiO} \mid \mathrm{ZrO_2(Y_2O_3)} \mid \mathrm{Cu_2O,Cu} \mid \mathrm{Pt} \\ (-) \qquad 1 \qquad \underset{\longleftarrow}{O^{=}} \qquad 2 \qquad (+) \end{array} \qquad \text{(I)}$$

The anodic reacion is

$$\mathrm{Ni} + \mathrm{O}^{=} \rightleftharpoons \mathrm{NiO} + 2e \qquad (9)$$

and the cathodic one:

$$\mathrm{Cu_2O} + 2e \rightleftharpoons 2\mathrm{Cu} + \mathrm{O}^{=} \qquad (10)$$

The cell reacion is:

$$\mathrm{Ni} + \mathrm{Cu_2O} \rightleftharpoons \mathrm{NiO} + 2\mathrm{Cu} \qquad (11)$$

and the change in free energy is:

$$\Delta G^{\circ} = \mu^{\circ}_{NiO} + 2\mu^{\circ}_{Cu} - \mu^{\circ}_{Ni} - \mu^{\circ}_{Cu_2O} \qquad (12)$$

Because the $\Delta G^{\circ}$ of the cell (I) reaction may be written as:

$$\Delta G^{\circ} = \Delta G^{\circ}_{NiO} - \Delta G^{\circ}_{Cu_2O} \qquad (13)$$

according to eq.(8):

$$\Delta G^{\circ}_{NiO} = -2 \cdot F \cdot E + \Delta G^{\circ}_{Cu_2O} \qquad (14)$$

At pressure and temperature constant, knowing the value of the cell e.m.f.and the value of ΔG of $Cu_2O$ in the same operating conditions it is possibleto calculate the NiO Gibbs formation energy.

### 3.2 Reaction Entropy and Enthalpy

In order to evaluate the entropy reaction it is necessary to analyze the variation of the e.m.f. as a function of the temperature. Applying the Gibbs-Heltmhotz equartion:

$$(\delta \Delta G/\delta T)_p = -\Delta S \qquad (15)$$

and remembering eq.(8) one obtains:

$$\Delta S = nF(\delta E/\delta T)_p \qquad (16)$$

the expression for the entropy of the cell reaction. The enthalpy of the cell reaction is related to the corresponding Gibbs energy according to :

$$\Delta H = \Delta G + T\Delta S \qquad (17)$$

Replacing ΔG and ΔS with eqs.(8) and (16) respectively one obtains:

$$\Delta H = -nF[E - T(\delta E/\delta T)_p] \qquad (18)$$

the expression for the enthalpy of the cell reaction.

### 3.3 Activity of a Chemical Species

The electromotive force of a galvanic chain, as above mentioned, is proportional to the ΔG of the reaction and consequently to the algebric sum of the chemical potential of the species present in the overall reaction cell. According to this statement it is possible to measure the activity ofa chemical species by e.m.f. cell measurements.

#### 3.3.1 Determination of the gaseous chemical species activity

The determination of oxygen partial pressure, in situ and on-line, by solid state galvanic cell is widely used also in industrial applications. The galvanic cell is the following:

$$Pt \mid O_2(p1) \mid ZrO_2(Y_2O_3) \mid O_2(p2) \mid Pt \qquad (II)$$

p2 is bigger than p1. At the interface 1 the following equilibrium reaction takes place:

$$2O^{=} \rightleftharpoons O_2(p1) + 4e \qquad (19)$$

and at the interface 2:

$$O_2(p2) + 4\,e \rightleftharpoons 2O^{=} \qquad (20)$$

The overall reaction cell is:

$$O_2(p2) \rightleftharpoons O_2(p1) \qquad (21)$$

remembering eq.(8) and replacing the DG with the algebric sum of the chemical potential, one obtains:

$$4FE = \mu^o + RTln(p2) - \mu^o - RTln(p1) \qquad (22)$$

assuming the activity of oxygen uqual to its partial pressure. $\mu^o$ is the standard oxygen chemical potential. From eq.(22) it follows:

$$E = (RT/4F)\ ln(p2/p1) \qquad (23)$$

Knowing the operating temperature of the electrochemical cell as well as one of the oxygen partial pressure, it is possible to determine the other one.

3.3.2 Determination of the solid chemical species activity .

The activity of the A chemical species in a solid phase AB can bedetermined by the following galvanic cell:

$$Pt \mid A,AO \mid ZrO2(Y2O3) \mid AB,AO \mid Pt \qquad (III)$$

At the interface 1 takes place the reaction:

$$A(1) + O \rightleftharpoons AO(1) + 2e \qquad (24)$$

and at the interface 2:

$$AO(2) + 2e \rightleftharpoons A(2) + O^{=} \qquad (25)$$

The overall reaction may be considered as the migration of A from 1 to 2 interface:

$$A(1) \rightleftharpoons A(2) \qquad (26)$$

Remembering eq.(8) and replacing DG with the algebric sum of the chemical potentials, one obtains:

$$2FE = \mu^o + RTlna_{A1} - \mu^o - RTlna_{A2} \qquad (27)$$

Since the standard chemical potential are the same for the same chemical compound as well as the activity of A in the left hand side of the cell is egual to 1, it follows:

$$E = -(RT/2F)\ lna_{A2} \qquad (28)$$

Relationship between e.m.f. of the cell and activity of A in the solid phaseAB.

### 3.4 Solid Oxide Fuel Cells

A solid oxide fuel cell is an electrochemical device which exploits the water formation reaction to generate electrical power (fig.1).

In a solid oxide fuel cell fed with hidrogen and oxygen, the following reactions take place:

$$H_2 + O^{=} \rightleftharpoons H_2O + 2e \qquad (29)$$

and

$$1/2O_2 + 2e \rightleftharpoons O^{=} \qquad (30)$$

The overal cell reaction is:

$$H_2 + 1/2\,O_2 \rightleftharpoons H_2O \qquad (31)$$

The e.m.f. of the cell is:

$$E = -\Delta G/2F \qquad (32)$$

$\Delta G$ is the Gibbs free energy of the reaction (31). The ideal efficiency of a simple fuel cell is the change in free energy, which is the maximum useful work obtained from any system, devided by the heat of reaction:

$$\eta = \Delta G/\Delta H = 1 - (T\Delta S/\Delta H) \qquad (33)$$

which is less than unity, even in a cell operating reversibly, so long as heat ($T\Delta S$) is being rejected. Westinghouse Co. has realized such devices with tubular geometry (figs.2, 3 and 4) and at the present are available on the market 3kW generators.

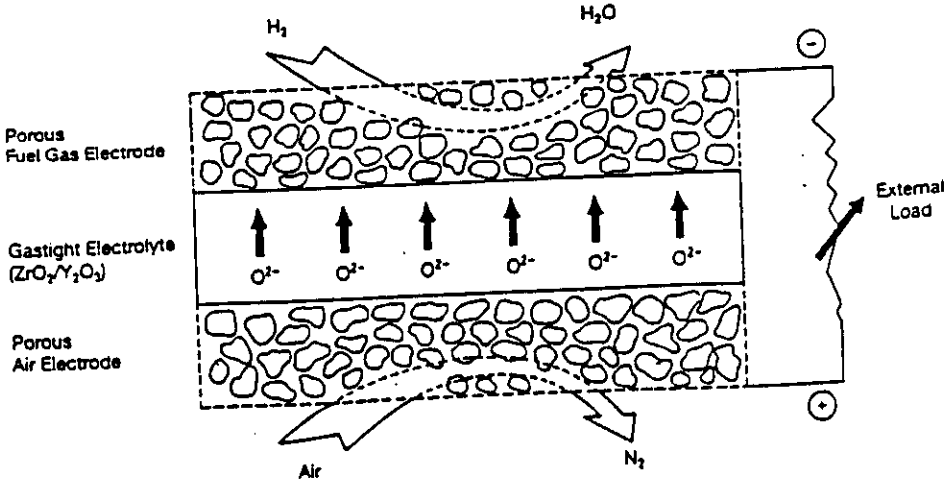
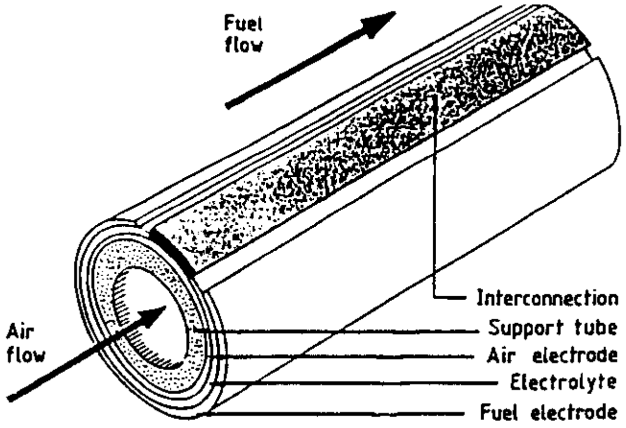
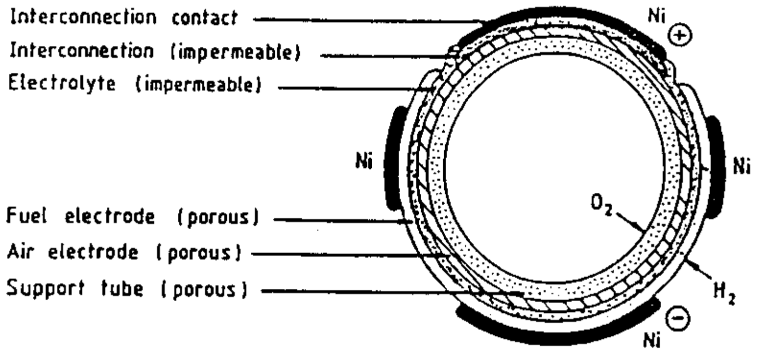


fig. 1



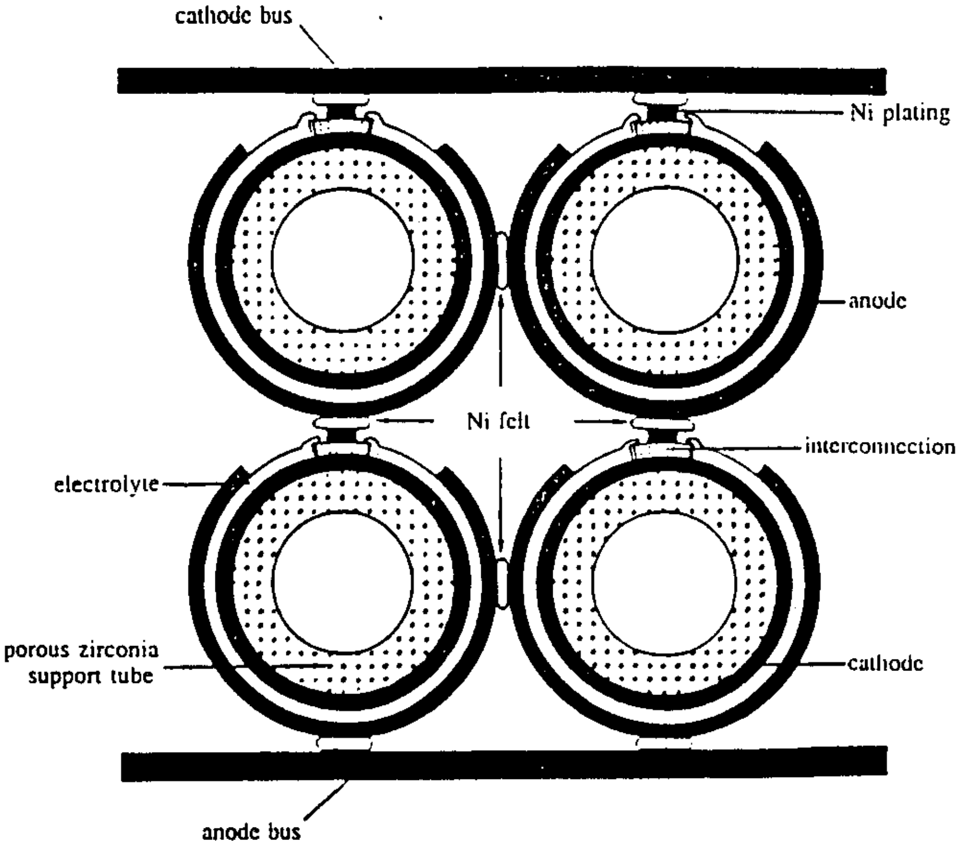
Arrangement of single solid oxide fuel cell.

fig. 2



Cross section of SOFC tube.

fig. 3



Cell-to-cell connections between SOFCs.

fig. 4

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