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# Production of Carbon Monoxide by Direct Thermal Splitting of Carbon Dioxide at High Temperature

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The direct thermal decomposition of carbon dioxide $CO_2$ to produce carbon monoxide CO have been studied as a mean of conversion and storage of a thermal energy, such as the solar heat, into a gaseous fuel. The process under investigation consists to displace the dissociation equilibrium of carbon dioxide by a selective pumping of oxygen at high temperature through a semipermeable membrane. Large amounts of carbon monoxide have been produced after the extraction of the oxygen arising from the $CO_2$ dissociation with the aid of a membrane made of calcia-stabilized zirconia. The variations of the flow of CO evolved from the reactor vs. temperature and oxygen partial pressure are in good agreement with the theoretical variations that may be deduced from the general equations of electrochemical transport in stabilized zirconia. Thereby, the efficiency of this process appears to be directly limited by the low oxygen permeation rate through the material used as oxygen selective membrane.

In the last past years, many investigations have been devoted to the conversion and storage of primary energies, such as the solar heat.[1] Indeed, although inexhaustible, the solar energy is subject to considerable variations with the lattitude and also to diurnal or seasonal variations. Accordingly, the utilization of solar energy on a large scale needs its conversion into a convenient form for a subsequent use. Various ways have been investigated, in which the solar radiation could be used either through quantum effects, this is the case of the solar cells for a direct conversion to electricity[2] and the hydrogen production via a water photoelectrolysis process,[3] or as a source of thermal energy for a thermochemical conversion and storage.[4] Recently another approach has been considered, in which the solar heat could be used to perform a direct thermal splitting of water at high temperature and to produce hydrogen.[5,6] This process implies to separate the hydrogen and the oxygen arising from the steam dissociation, in order to avoid the recombination reactions at lower temperatures. This may be achieved at high temperature with the use of a membrane semipermeable to oxygen while impervious to other gaseous components.[7] Such a membrane must be characterized by a mixed, ionic and electronic, electrical conductivity and located in a gradient of oxygen chemical potential,[6] as shown in Fig. 1. The ionic component $\sigma_i$ of the conductivity allows the oxygen to diffuse through the membrane as $O^{2-}$ ions, while the electronic component $\sigma_e$ ensures an internal partial short-circuit which is required for the reactions of oxygen exchange at the two electrolyte-gaseous phase interfaces (Fig. 1).

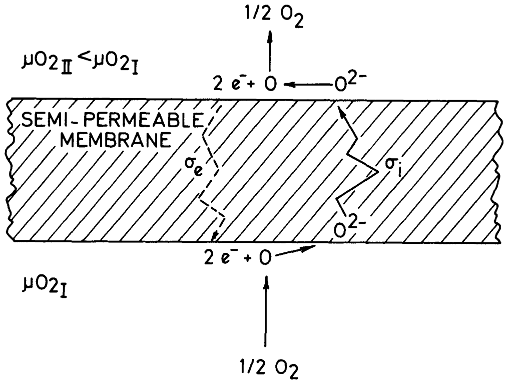

Fig. 1. Schematics of a membrane semipermeable to oxygen located between two different oxygen chemical potentials $\mu O_2(I)$ and $\mu O_2(II)$.

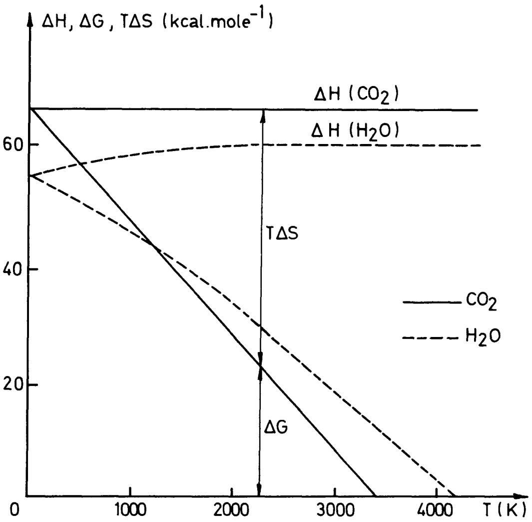

Fig. 2. Temperature dependences of the quantities of energy required for the dissociation of one mole of $CO_2$ or one mole of $H_2O$, after Ref. 8.

On using calcia-stabilized zirconia as oxygen semipermeable membrane, noticeable amounts of hydrogen have been produced by this technique.[6] However, the efficiency of such a process is unavoidably limited by the low dissociation rate of water vapor, which reaches only 4% about at 2300 K under normal pressure conditions. Thus, the use of a gaseous component characterized by a higher dissociation rate would be more convenient. Carbon dioxide $CO_2$ seems

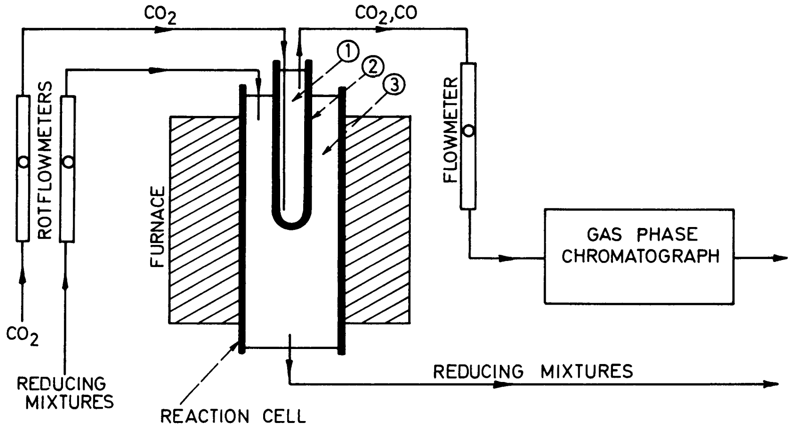

Fig. 3.Schematic illustration of the experimental set-up. ①: compartment I, ②: oxygen semipermeable membrane, ③: compartment II.

to be a good candidate owing to the potential applications of the gaseous fuel CO[2] which may be obtained by direct thermal splitting of $CO_2$. Moreover, the energy balance of the decomposition reaction is more propitious in the case of carbon dioxide than for water vapor.

The total quantity of energy $\Delta H$ required for the decomposition of one mole of $CO_2$ (or one mole of $H_2O$) may be supplied by means of a thermal energy $T\Delta S$ and/or an additional energy, such as a mechanical or an electrical energy, corresponding to the free enthalpy term $\Delta G$[8] so that:

$$\Delta H = \Delta G + T\Delta S.$$

The temperature dependence of the various energies $\Delta H$, $\Delta G$, and $T\Delta S$ involved for the dissociation of one mole of $CO_2$ or one mole of $H_2O$ may be deduced from the classical thermodynamic relationships and are depicted in Fig. 2. It clearly appears that, at high temperature, a major part of the total energy $\Delta H$ may be supplied by means of a thermal energy corresponding to $T\Delta S$. Furthermore, $T\Delta S$ is equal to 66% of the total energy required for the decomposition of one mole of $CO_2$ at 2250 K and only 50% in the case of one mole of $H_2O$ at the same temperature.[8]

The purpose of the present work was to investigate the possibility of production of CO by direct thermal splitting of carbon dioxide on using a calcia-stabilized zirconia wall as oxygen semipermeable membrane.

## Experimental

The experimental set-up mainly consists of a reaction cell, a laboratory built high temperature furnace working under oxidizing conditions,[9] a gas phase chromatograph and gas flowmeters (Fig. 3).[10]

The reaction cell is chiefly made up of a closed-end tube of calcia-stabilized zirconia, 2 mm thick and 10 mm in inner diameter, which acts as oxygen semipermeable membrane. Its chemical composition corresponds to 0.9 $ZrO_2$–0.1 CaO and the concentrations of the main impurities are ; 0.18 wt% $Fe_2O_3$, 0.81wt% $SiO_2$, 0.33wt% MgO, and 0.3 wt% $Al_2O_3$. The cell is located inside the high temperature furnace, the heating elements of wich are made of partially stabilized zirconia which allows the zirconia tube to be heated at temperatures up to 2500 K. However, owing to the difficulty of temperature measurements in the center of the reaction cell and to the thermomechanical characteristics of the cell itself, the usefull temperature range has been reduced to approximately 1700—2100 K.

The inner part of the zirconia tube, compartment I, is fed with pure carbon dioxide, with a flow-rate of 1000 $cm^3 h^{-1}$, under isobaric conditions ($10^{-1}$ MPa). In the hot zone of the cell, carbon dioxide partially dissociates and the oxygen arising from the dissociation reaction diffuses through the zirconia wall into compartment II. The oxygen partial pressure in compartment II, $pO_2(II)$, must be much lower than the oxygen partial pressure in compartment I, $pO_2(I)$, that is fixed in dynamical conditions by the dissociation equilibrium of carbon dioxide. This has been conveniently achieved, in the present study, by the use of CO–$CO_2$ mixtures which allow to vary the oxygen partial pressure $pO_2(II)$ in a large range, independently of the oxygen flux through the membrane. The flow-rate of CO–$CO_2$ mixtures in compartment II is equal to $18.5\times10^3$ $cm^3 h^{-1}$.

After migration of oxygen, the composition of the dissociated gas phase is checked out by chromatography at the gas outlet of compartment I.

Under stationary conditions, the mass flow balance implies that the flow of carbon monoxide $D_{CO}$ evolved from the compartment I is twice the flow of oxygen $D_{O_2}$, through the effective permeation area S of the zirconia membrane, which is given by :

$$D_{co} = 2D_{O_2} = 2J_{O_2}\cdot S \qquad (1)$$

where $J_{O_2}$ is the flow of oxygen per unit area of the semipermeable membrane.

From the measurement of temperature gradients along the zirconia tube,[10] the effective permeation area has been estimated to about 4 $cm^2$.

## Theoretical Considerations

The partial current density $\vec{J_k}$ arising from the flow of charged species $k$ in a solid electrolyte located in a chemical potential gradient is derived from the general equations of electrochemical transport and is given by:[11]

$$\vec{J_k} = -\frac{\sigma_k}{z_k q}\overrightarrow{\nabla\eta_k}, \qquad (2)$$

where $\sigma_k$ is the partial electrical conductivity of the electrolyte, $z_k$ the valence of particles $k$ and $q$ the electronic charge. $\overrightarrow{\nabla\eta_k}$ denotes a gradient of electrochemical potential which results from gradients of chemical potential $\overrightarrow{\nabla\mu_k}$ and electrical potential $\overrightarrow{\nabla V}$:[12]

$$\overrightarrow{\nabla\eta_k} = \overrightarrow{\nabla\mu_k} + z_k q\overrightarrow{\nabla V}.$$

In the case of stabilized zirconia, the electrochemical transport at high temperature arises from the motion of both $O^{2-}$ ions and electrons.[13] The total current density $\vec{J_t}$ is then the sum of the contributions due to ionic species $\vec{J}_{O^{2-}}$ and electrons $\vec{J_e}$. It is deduced from Eq. 2 and writes:

$$\vec{J_t} = \frac{\sigma_e}{q}\overrightarrow{\nabla\eta_e} + \frac{\sigma_i}{2q}\overrightarrow{\nabla\eta_{O}^{2-}}, \qquad (3)$$

where $\sigma_i$ and $\sigma_e$ denote the partial ionic and electronic conductivities of stabilized zirconia.

Moreover, on assuming that the thermodynamic equilibrium between ionic and electronic species:

$$O^{2-} \rightleftharpoons 1/2\,O_2 + 2e^-$$

remains locally undisturbed by the partial current flows, it is possible to relate the total current density $\vec{J_t}$ to the chemical potential gradient of oxygen $\overrightarrow{\nabla\mu_{O_2}}$ by the following relationship:[11]

$$\vec{J_t} = \frac{\sigma_t}{q}\overrightarrow{\nabla\eta_e} + \frac{\sigma_i}{4q}\overrightarrow{\nabla\mu_{O_2}}, \qquad (4)$$

where $\sigma_t$ is the total conductivity of the material ($\sigma_t = \sigma_i + \sigma_e$).

Under stationary conditions, if no electrical current flows through an external circuit, the total current density in the material would be equal to zero and it follows from Eqs. 2 and 4:[11]

$$\vec{J}_{O^{2-}} = -\vec{J_e} = \frac{\sigma_e}{4q}t_i\overrightarrow{\nabla\mu_{O_2}}, \qquad (5)$$

where $t_i$ denotes the ionic transference number of stabilized zirconia ($t_i = \sigma_i/\sigma_t$).

Owing to the very wide electrolytic domain of stabilized zirconia,[14] the ionic transference number $t_i$ is close to unity in large ranges of temperature and oxygen partial pressure. In the same domain, the electronic conductivity writes:[15]

$$\sigma_e = \sigma_e^\circ \exp\left(-\Delta E/k_B T\right)\,pO_2^{-1/4}, \qquad (6)$$

where $\sigma_e^\circ$ is a constant, $\Delta E$ the activation energy, $k_B$ the Boltzmann constant and $pO_2$ the oxygen partial pressure of the surrounding atmosphere. From the different values reported in the litterature, Heyne and Beekmans[15] have proposed a mean value of 3.7 eV for the activation energy of the n-type electronic conductivity of stabilized zirconia.

Combining Eqs. 5 and 6 with the condition $t_i \simeq 1$, the ionic current $J_{O^{2-}}$ through a stabilized zirconia membrane is obtained after integration over the thickness L of the membrane and is given by:

$$J_{O^{2-}} = \frac{k_B T}{qL}\sigma_e^\circ \exp\left(-\Delta E/k_B T\right)\left[pO_2(\mathrm{II})^{-1/4} - pO_2(\mathrm{I})^{-1/4}\right], \qquad (7)$$

where $pO_2(\mathrm{I})$ and $pO_2(\mathrm{II})$ are the oxygen partial pressures at the two electrolyte-gaseous phase interfaces.

The oxygen flow $J_{O_2}$ through the membrane is then derived from Eq. 7:

$$J_{O_2} = \frac{k_B T}{4qFL}\sigma_e^\circ \exp\left(-\Delta E/k_B T\right)\left[pO_2(\mathrm{II})^{-1/4} - pO_2(\mathrm{I})^{-1/4}\right], \qquad (8)$$

where $F$ is the Faraday constant.

The flow of carbon monoxide $D_{CO}$ evolved from the reactor is directly related to $J_{O_2}$ [Eq. 1] and would then obey the same dependences against temperature and oxygen partial pressures.

## Results and Discussion

The composition of the gas phase evolved from compartment I is plotted in Fig. 4 vs. the cell temperature, for different values of the ratio $CO_2/CO$ of the reducing mixtures flowing in compartment II. For $CO_2/CO$ ratio lower than 10, the amount of produced carbon monoxide increases rapidly with the cell temperature. At 1954K, in the most reducing conditions ($CO_2/CO = 0.01$), which corresponds to an oxygen partial pressure $pO_2(\mathrm{II})$ of about $10^{-11}$ MPa, 21.5 mol% of carbon dioxide have been converted to CO.

Such a value is much higer than the dissociation rate of $CO_2$ which is expected to reach 1.2% at the same temperature without any transfer of oxygen through a semipermeable membrane. Thus, under the influence of the selective pumping of oxygen through the zirconia wall, the thermodynamical equilibrium

$$CO_2 \rightleftharpoons CO + 1/2\,O_2 \qquad (9)$$

is strongly displaced to the right hand side.

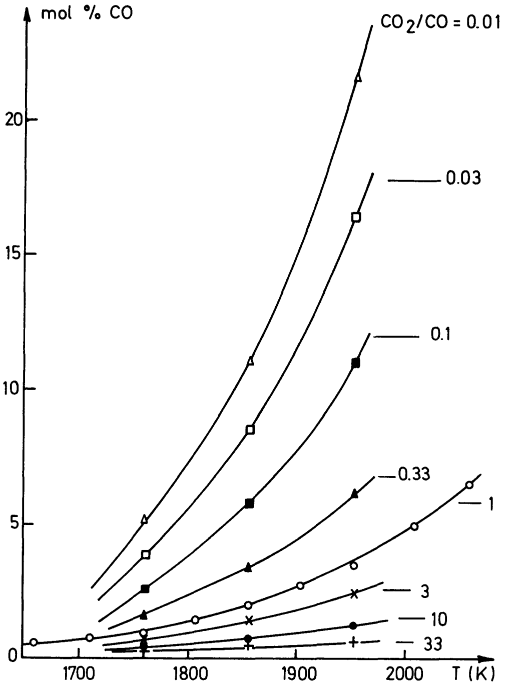

Fig. 4. Variations of the concentration of CO in the gas phase evolved from compartment I against temperature, for different composition of the CO–CO₂ mixtures flowing in compartment II.

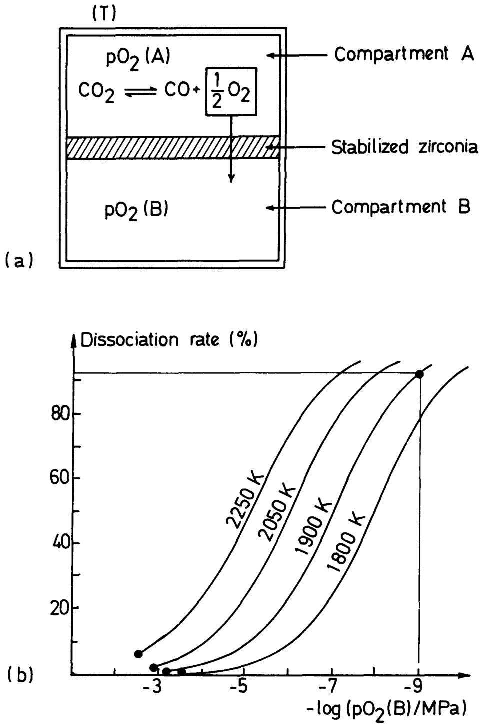

Fig. 5. Schematic of a reaction cell working under static conditions (a) and variations of the dissociation rate of $CO_2$ obtained with such a cell versus $pO_2$(B) (b), after Ref. 8.

Nevertheless, due to the dynamical conditions used in the present technique, only a fraction of the introduced carbon dioxide is converted to CO. Indeed, let us consider a reaction cell working under static conditions and made up of a stabilized zirconia wall which separates two compartments A and B having the same volume (Fig. 5a). The calculated values of the dissociation rate of $CO_2$ that may be reached under these conditions are plotted in Fig. 5b as a function of the oxygen partial pressure $pO_2$(B) fixed in compartment B before the experiment.[8] At a given temperature, the oxygen arising from the dissociation reaction would flow through the zirconia membrane until the oxygen partial pressures $pO_2$(A) and $pO_2$(B) are equal. Thus, at 1900 K, for an oxygen partial pressure $pO_2$(B) initially fixed at $10^{-9}$ MPa, 93% about of the introduced carbon dioxide would be converted to CO before the system reaches the thermodynamical equilibrium.[8]

In the present case, the oxygen partial pressure $pO_2$(I) in compartment I is smaller than the value predicted by the dissociation equilibrium of $CO_2$, owing to the oxygen transfer through the membrane. It has been however derived from the equilibrium constant K relative to equilibrium (9).

$$K = \frac{pCO\ pO_2(I)^{1/2}}{pCO_2} \qquad (10)$$

where the partial pressure of carbon monoxide, pCO, has been deduced from the CO content measured by chromatography in the gas phase evolved from compartment I.

The oxygen partial pressure $pO_2$(II) is fixed by the CO–$CO_2$ mixtures. Due to the high buffer capacity of these mixtures, for $CO_2$/CO ratio higher than 0.03, the oxygen partial pressure $pO_2$(II) is not affected by the oxygen transfer through the membrane. For $CO_2$/CO ratio smaller than 0.03, the quantity of oxygen flowing through the zirconia wall is high enough to slightly modify the composition of the CO–$CO_2$ mixtures and small corrections may be applied in the calculation of $pO_2$(II).[10]

The flow of carbon monoxide $D_{CO}$ evolved from compartment I has been plotted in Fig. 6 against the difference of oxygen partial pressures $\Delta pO_2^{-1/4} = [pO_2(II)^{-1/4} - pO_2(I)^{-1/4}]$, for three temperatures. The flow of CO appears to be directly proportional to $\Delta pO_2^{-1/4}$, since the log $D_{CO}$ vs. log $\Delta pO_2^{-1/4}$ plots are characterized by straight lines, the slopes of which are not far from to unity. Owing to the proportionality relationship between $D_{CO}$ and $J_{O_2}$ [Eq. 1], this is in good agreement with the theoretical dependence of the oxygen flux $J_{O_2}$ against $\Delta pO_2^{-1/4}$, predicted by Eq. 8.

Furthermore, according to Eq. 8, the semi-permeability coefficient, which is defined as the ratio of the oxygen flux to the difference $\Delta pO_2^{-1/4}$, varies with the temperature according to an Arrhenius law (Fig. 7), the activation energy of which amounts to about 3.55 eV. Such a value agrees with the mean activation energy for the n-type electronic conductivity of stabilized zirconia proposed by Heyne and Beekmans

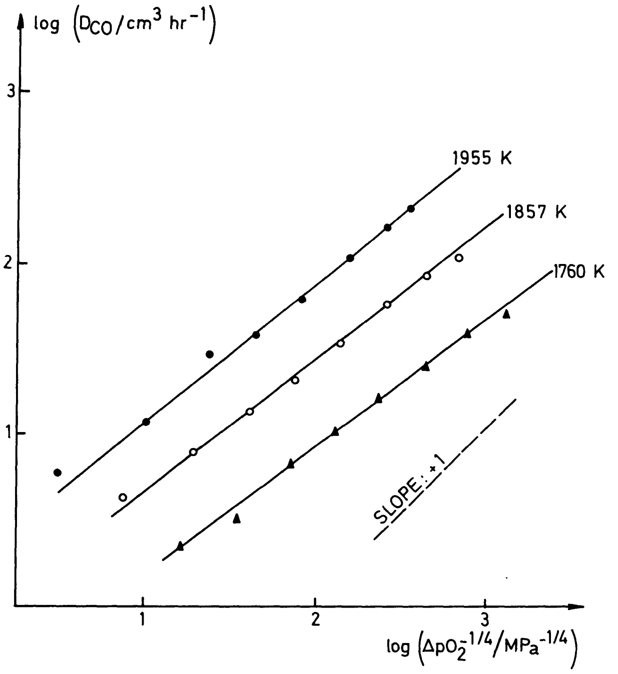

Fig. 6. Dependence of the flow of CO evolved from the reactor on the difference $\Delta pO_2^{-1/4}$.

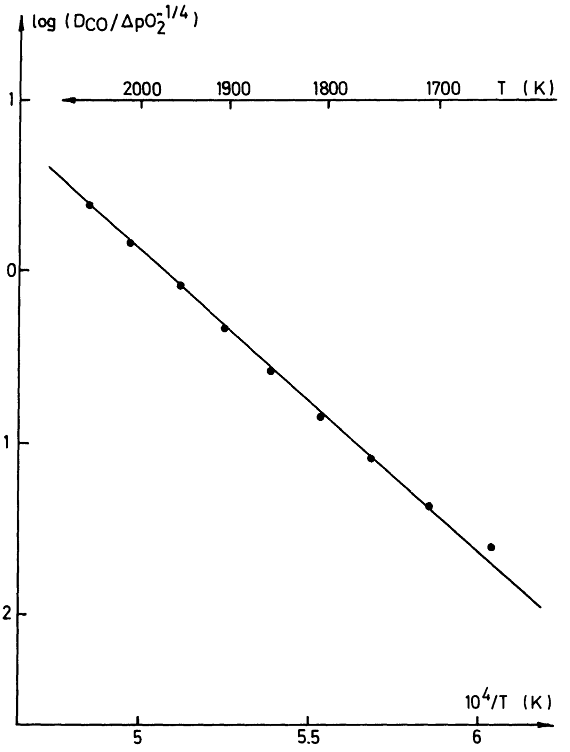

Fig. 7. Variation of the ratio $D_{CO}/\Delta pO_2^{-1/4}$ vs. temperature.

(3.7 eV).[15)]

These two results clearly show that the oxygen flow $J_{O_2}$ and the flow $D_{CO}$ evolved from the compartment I correspond to the maximum flows that it is presently possible to obtain, since they directly depend on the specific characteristics of the oxygen semipermeable membrane. Thus, the efficiency of the process under investigation appears to be primarily limited by the low value of the electronic conductivity of the stabilized zirconia wall.

Indeed, the general expression of the current density $\vec{J}_{O^{2-}}$ due to the motion of $O^{2-}$ ions in an oxide solid electrolyte [Eq. 5] may also be written:[16)]

$$\vec{J}_{O^{2-}} = \frac{\sigma_t}{4q}\, t_i\, t_e\, \overrightarrow{\nabla\mu_{O_2}} \tag{11}$$

where $t_e$ is the electronic transference number of the material ($t_e=\sigma_e/\sigma_t=1-t_i$).

Thereby, the oxygen flux $J_{O_2}$, and consequently the amount of produced carbon monoxide, would be maximum for equal ionic and electronic transference numbers ($t_i=t_e=0.5$). The material used as oxygen semipermeable membrane would present equal ionic and electronic conductivities in the range of oxygen partial pressure [$pO_2$(I), $pO_2$(II)].

In the case of stabilized zirconia, such a behavior is observed for an oxygen partial pressure which is much smaller than $pO_2$(I) and $pO_2$(II) and rises from $10^{-21}$ MPa at 1673K to $10^{-13}$ MPa at 2073K.[17)]

## Conclusion

The present study has demonstrated the possibility of production of CO by direct thermal splitting of carbon dioxide at high temperature and extraction of oxygen by means of a semipermeable membrane.

On using calcia stabilized zirconia (10 mol% CaO) as oxygen semipermeable membrane, about 100 to 200 cm³ h⁻¹ of CO have been produced at 1960 K for a $CO_2$ consumption of 1000 cm³ h⁻¹. The variations of the flow of CO evolved from the reaction versus the cell temperature and the difference $\Delta pO_2^{-1/4}$ agreed with the theoretical variations deduced from the general equation of electrochemical transport in stabilized zirconia. Therefore, such a process appears to be very interesting with respect to energy conversion applications.

Various parameters could allow to appreciably increase the quantities of produced carbon monoxide. This would be the case on using a semipermeable membrane with a smaller thickness and/or a larger permeation area. Nevertheless, the efficiency of the process is primarily controlled by the electrical properties of the material used as oxygen selective membrane. Thus, in the present case, any improvement of this technique is submitted to an enhancement of the electronic conductivity of stabilized zirconia.

Fluorite type solid solutions may be observed between zirconia $ZrO_2$ and ceria $CeO_2$, which is known to exhibit an electronic conductivity, in large range of composition.[18)] The addition of a third oxide, the cation of which has a lower valency than zirconium Zr(IV) or cerium Ce(IV) ions, such as yttria $Y_2O_3$, could enhance the ionic conductivity of these compounds. The study of the electrical properties of the solid

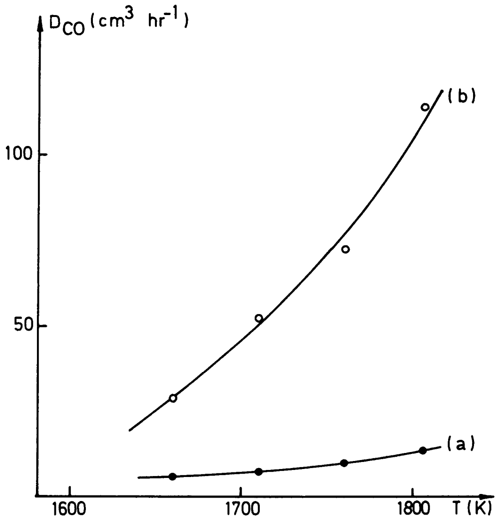

Fig. 8. Variations of the flow of CO evolved from the reactor against temperature in the case of a calcia stabilized zirconia membrane (a) or a ceria-doped stabilized zirconia memberane (b). The composition of the CO–$CO_2$ mixture in compartment II corresponds to $CO_2/CO=1$.

solutions of the ternary $ZrO_2$–$CeO_2$–$Y_2O_3$ system has shown that they would present, in the temperature and oxygen partial pressure ranges of interest for this process, a mixed electrical conductivity with equivalent ionic and electronic components.[19] Moreover, the solid solution containing about 20 mol% of cerium oxide $CeO_2$ appears to be the most suitable for this application.[16] This has been confirmed by preliminary results obtained on using such a solid solution as oxygen selective membrane. The flows of CO produced with the aid of either "pure" stabilized zirconia or ceria-doped stabilized zirconia as semipermeable membrane are compared in Fig. 8. They clearly indicate that the solid solution of the $ZrO_2$–$CeO_2$–$Y_2O_3$ system is characterized by a higher oxygen semipermeability. The use of this material in a process of thermal energy conversion and storage based on the direct thermal splitting of $CO_2$ is thus very promissing and presently under investigation.

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