

Development of Novel Materials for Reduction of Greenhouse Gases and Environmental Monitoring Through Interface Engineering

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Abstract The present work considers research strategies to address global warming. Specifically, this work considers the development of technologies of importance for the reduction of greenhouse gas emission and, especially, the materials that are critical to these technologies. It is argued that novel materials that are essential for the production of environmentally friendly energy may be developed through a special kind of engineering: *interface engineering*, rather than through classical bulk chemistry. Progress on the interface engineering requires to increase the present state of understanding on the local properties of materials interfaces and interface processes. This, consequently, requires coordinated international efforts in order to establish a strong background in the science of materials interfaces.

This paper considers the impact of interfaces, such as surfaces and grain boundaries, on the functional properties of materials. This work provides evidence that interfaces exhibit outstanding properties that are not displayed by the bulk phase. It is shown that the local interface chemistry and structure are entirely different than those of the bulk phase. In consequence the transport of both charge and matter along and across interfaces, that is so important for energy conversion, is different than that in the bulk. Despite that the thickness of interfaces is of an order of a nanometer, their impact on materials properties is substantial and, in many cases, controlling. This leads to the conclusion that the development of novel materials with desired properties for specific industrial applications will be possible through controlled interface chemistry. Specifically, this will concern materials of importance for energy conversion and environmental monitoring. Therefore, there is a need to increase the present state of understanding of the local properties of materials interfaces and the relationship between interfaces and the functional properties of materials. In order to accomplish this task coordinated international efforts of specialized research centres are required. These efforts are specifically urgent regarding the development of materials of importance for the reduction of greenhouse gases. Success of research in this area depends critically on financial support that can be provided for projects on materials of importance for a sustainable environment, and these must be considered priorities for all of the global economies.

The authors of the present work represent an international research group that has entered into a collaboration on the development of the materials that are critical for the reduction of greenhouse gas emissions.

1. Introduction

1.1. Urgent Need to Reduce Environmental Pollution

There is growing international concern regarding the increase in environmental pollution. Specifically, there is an urgent need to decrease the emission of greenhouse gases. If drastic measures to reduce this emission are not undertaken, there is a real danger of a global environmental disaster. Scientists predict

that an increased sea level will threaten the nations of the Pacific islands, the elevation of many of which is only several meters above sea level. A recent report of Australia's Commonwealth Science, Industry and Research Organization (CSIRO) predicts that the Great Barrier Reef may be irreversibly damaged within 50 years if the greenhouse effect continues to increase at the present pace. The list of problems related to global warming is long and alarming.

Due to the severe impact of global warming on

contemporary civilization, the United Nations Environment Programme and the World Meteorological Organization established the Intergovernmental Panel on Climate Change (IPCC) in 1988. The role of IPCC is to coordinate the activities required to reverse global warming in an international scale. A series of international conferences, discussing the measures that should be undertaken has been organized. The aim of these conferences is to discuss the most important issues related to global warming and its consequences. The importance of the problem is emphasized by the fact that these conferences usually are attended by senior level environment ministers of the country members of the United Nations. The conference held in 1997 in Kyoto (The Conference of the Parties to the United Nations Framework Convention on Climate Change held in Kyoto, December 1-10, 1997) resulted in several important conclusions concerning aiming at the reduction of greenhouse gas emission that should be undertaken by the international community.¹⁾

The purpose of the present paper is to consider the development of novel materials that are needed urgently in order to enable the development of novel technologies that allow reduction of environmental pollution. This paper provides a scientific evidence that the materials desired for specific applications can be processed through interface engineering rather than through bulk chemistry. Therefore, the development of the science and engineering of materials interfaces is critical to the development of novel functional materials, which are required for the production of environmentally friendly energy.

1.2. Need to Develop Novel Materials for Energy Conversion and Environmental Monitoring

The imperative to reduce greenhouse gas emission imposes a need for the development of a new generation of functional materials that are required for the novel technologies and devices. Specifically, there is a need for progress in the following areas:

- 1) Materials and devices for energy conversion in order to reduce greenhouse gas emission,
- 2) Materials and devices for chemical gas sensing in order to monitor and measure greenhouse gas emission.

This work considers the technologies that are critical for reduction of greenhouse gas emission through production of environmentally friendly energy. This work also considers the devices that are important for environmental monitoring in respect to the gases

causing the greenhouse effect. It is postulated that novel functional materials are required for the development of these technologies and devices. This work provides evidence that these materials may be developed through a special kind of engineering: *interfaces engineering*, rather than through classical bulk chemistry.

2. Why Materials Interfaces are Important

The chemical composition of solid interfaces, such as external surfaces and grain boundaries, differs from that of the bulk phase as a result of the excess of interface energy and related effects, such as segregation and adsorption. Fig. 1 illustrates surface segregation, involving transport of defects from the bulk phase (b) to the surface layer (s), that leads to decrease of energy from the level of G_b to G_s . Fig. 2 shows the effect of segregation on surface vs bulk composition of Ni-Cu alloy.²⁾ It appears that this difference has a substantial effect on properties of engineering materials. An awareness is growing that the functional properties of ceramic materials are strongly influenced, or even controlled, by interfaces, such as grain boundaries or gas/solid interfaces, rather than the bulk chemistry alone.³⁻⁷⁾ Consequently, the development of new materials technologies requires an increase in the present state of understanding on:

- 1) Local properties of interfaces,
- 2) Impact of interfaces on functional properties of materials. and

Progress in this area, forming bases of a new scientific discipline: *Science and Engineering of Materials Interfaces*, is the condition of developing the process-

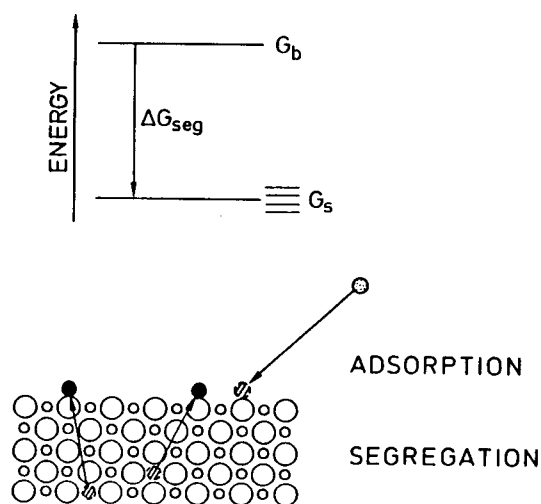


Fig. 1. Schematic illustration of segregation and adsorption as well as related change of energy.

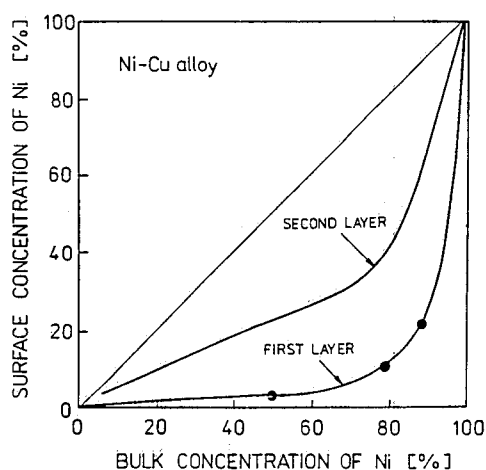


Fig. 2. Surface vs bulk Ni concentration in Ni-Cu alloy.²⁾

ing of new materials with specific properties that are desired for modern day technology and, specifically, the materials-related technologies of importance for sustainable environment. In order words the knowledge on (1) and (2) is essential to process novel materials of desired properties through imposition of specific interface chemistry and microstructure.

Progress in this area could only be achieved through integrated international efforts of specialized research centers that can *provide a critical mass* of expertise and research potential.

The purpose of this paper is to consider the impact of interfaces on functional properties of materials. It also considers an importance of the science and engineering of materials interfaces on the development of novel materials-dependent technologies and, specifically, the technologies of importance for the reduction of greenhouse gases and environmental monitoring.

3. Properties of Materials Interfaces

3.1. General

The present knowledge on interfaces of materials is limited to a number of isolated experimental data that indicate the following:

- 1) Interface properties are quite different from those of the bulk phase, and
- 2) Interfaces have a controlling effect on the properties of materials, specifically, functional materials. So far, however, there is no consistent theory that describes the interface properties of materials and the impact of interfaces on functional properties of materials.

The purpose of this section is to provide several

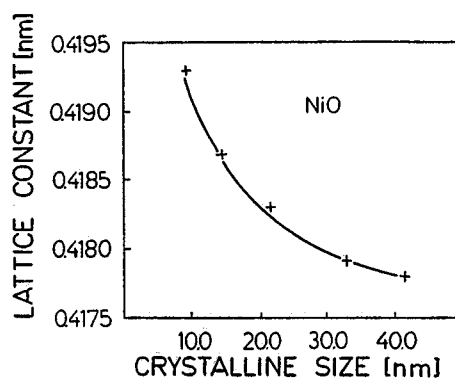


Fig. 3. Lattice constant of NiO vs grain size.⁸⁾

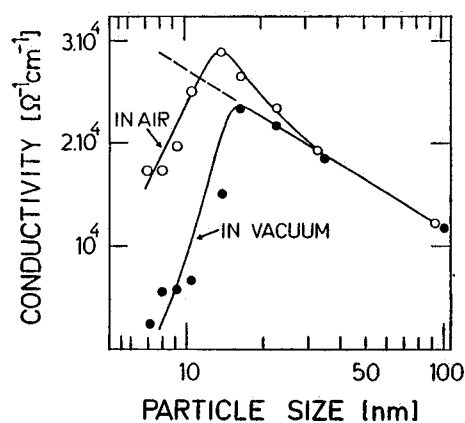


Fig. 4. Electrical conductivity of NiO vs particle size.⁵⁾

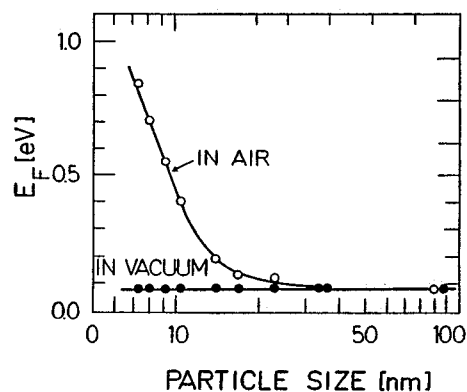


Fig. 5. Fermi energy (determined by thermopower) of NiO vs particle size.⁵⁾

examples illustrating the unusual properties of solid interfaces which are entirely different from those of the bulk phase.

3.2. Structure

There is increasing evidence that the coordination of surface ions, that is lower than that in periodic structure of the bulk phase, and the related interface energy result in the formation of low-dimensional interface structures that exhibit outstanding properties not displayed in the bulk phase.⁴⁾ It has been shown

that the effective lattice constant of fine grained NiO sharply increases below a grain size of 40 nm (Fig. 3) as a result of structural deformations within the interface layer.⁷⁾ It also has been documented that the electrical properties of the interface layer up to 40 nm are entirely different from those of the bulk phase (Figs. 4 and 5).⁸⁾ This effect is a key in correct understanding the available phase diagrams of materials that, consequently, should be considered as a function grain size. It has been documented that phase diagrams developed for the bulk phase cannot be used as a base to consider structure of the interface layer.⁹⁾ For example, the surface layer of CoO consists of a thin layer of Co_3O_4 , even though only CoO should exist under the conditions imposed on the bulk phase.⁹⁾ Similar surface structures have been observed for BaTiO_3 . It was shown that the bulk phase of BaTiO_3 exhibits the tetragonal structure, which is in agreement with the phase diagram established, while the surface layer exhibits the cubic structure. The space between the two structures is characterized by a tetragonality gradient within the grain (Figs. 6 and 7).¹⁰⁻¹²⁾ This effect indicates that:

- 1) Existing theories on phase transitions require verification in respect to fine grained materials, and
- 2) Interface layer can be considered to be a low-dimensional structure with specific properties.

Characterization of this structure is one of the keys to processing novel materials with desired properties for specific applications. Further studies are needed to characterize the local interface structure and its impact on materials properties.

3.3. Non-stoichiometry

It has been shown that non-stoichiometry of the bulk phase and the related concentration of defects are different from those of the surface layer.^{4-6,13,14)} Segregation results in enrichment of the surface of

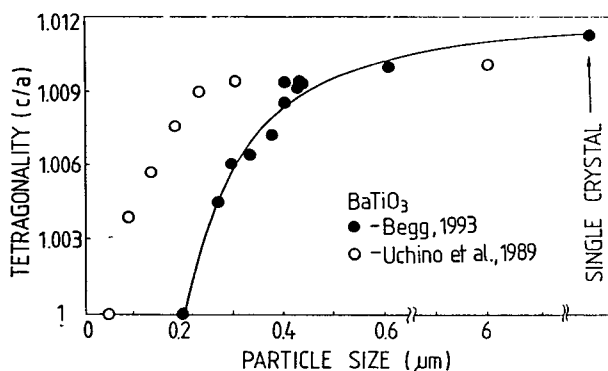


Fig. 6. Tetragonality for BaTiO_3 of different particle size as well as for a single crystal.^{10,11)}

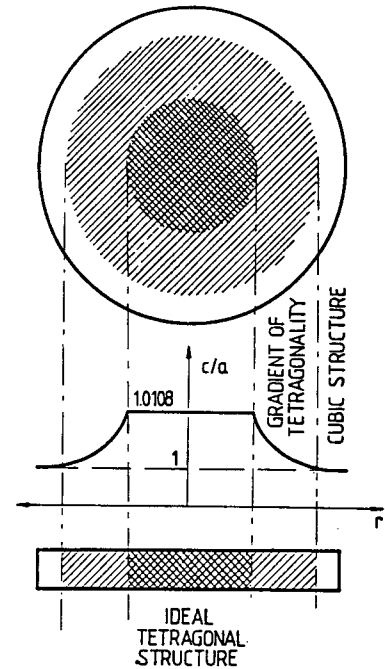


Fig. 7. Surface layer model of BaTiO_3 proposed by Niepce.¹²⁾

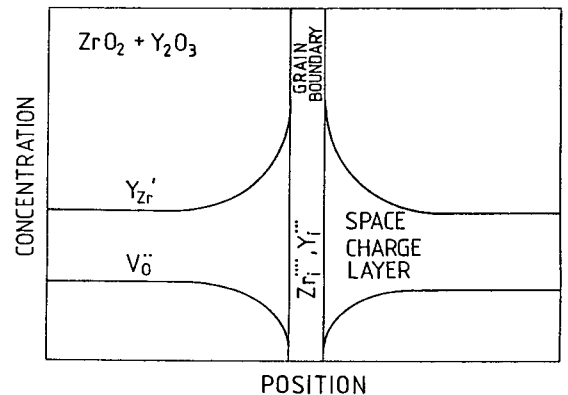


Fig. 8. Effect of segregation on defect disorder for the bulk phase and the grain boundary layer of yttria-stabilised zirconia.¹⁵⁾

binary metal oxides, such as NiO, by metal vacancies by a factor of 40.¹³⁾ The effect of the formation of a non-stoichiometry gradient has been also confirmed for other materials, including zirconia and its solid solutions (Fig. 8).¹⁵⁾

The experimental material that has been accumulated so far indicates that, while bulk non-stoichiometry in equilibrium is determined by the conditions corresponding to the equilibrium, such as temperature and gas phase composition, the non-stoichiometry of the interface layer is also a function of position, such as distance from the interface.

There is a need to develop a theory that could describe correlation between defect disorder of the in-

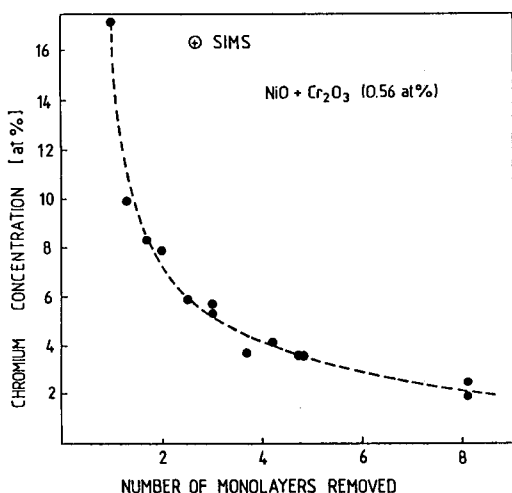


Fig. 9. Surface Cr concentration in Cr-doped NiO single crystal vs number of monolayers removed according to secondary ion mass spectroscopy.¹⁶⁾

interface layer and the defect-dependent properties that are essential for applications. This will be possible after a substantial empirical material on the non-stoichiometry of the interface layer of compounds and the local defect chemistry is accumulated.

3.4. Composition

There is a considerable amount of experimental data indicating that segregation results in enrichment of the interface layer of ceramics with defects, impurities and solutes.^{4~6,16~21)} Fig. 9 shows the extent of Cr segregation in NiO single crystal.¹⁶⁾ A similar effect has been reported for Cr-doped CoO (Fig. 10).¹⁷⁾ According to X-ray photoelectron spectroscopy data, the segregation of Cr results in an enrichment of the interface layer in Cr by a factor of 100 (Fig. 9). Extensive studies of segregation also have been reported for alumina.^{18~20)} Fig. 11 shows the dynamics of competitive segregation of Ca and Y in Al₂O₃.¹⁸⁾

In order to understand the effect of the segregation-induced enrichment on properties, further studies are needed to determine segregation equilibria and, specifically, multi-segregation equilibria, for well defined materials. These data can be used to determine the desired interface composition and, consequently, to establish the processing conditions required to achieve desired properties through controlled interface chemistry.

3.5. Semiconducting Properties

The mechanism of incorporation of foreign elements into the bulk phase of metal oxides differs from that for the interface layer. This results in the formation of a potential barrier across the interface

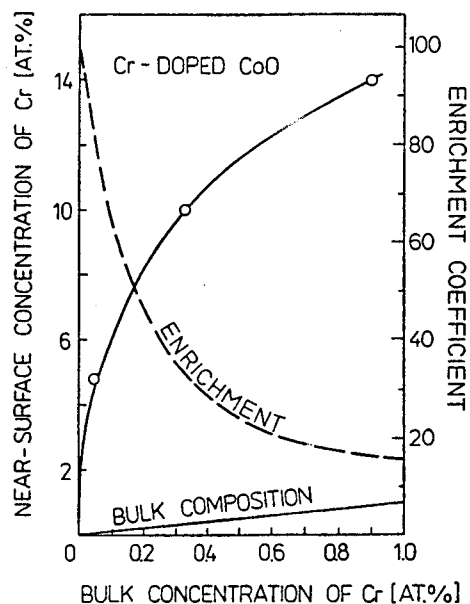


Fig. 10. Surface vs bulk Cr concentration in Cr-doped CoO.¹⁷⁾

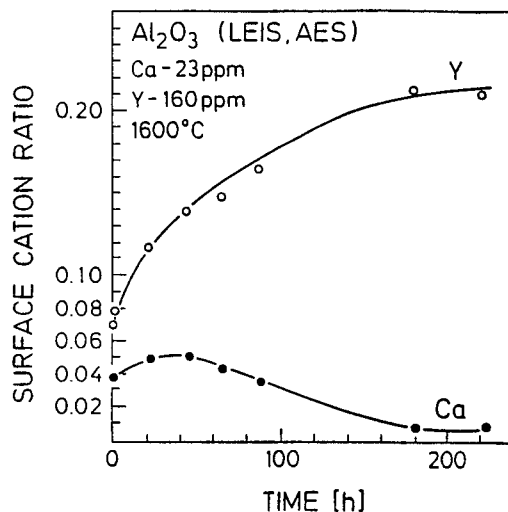


Fig. 11. Changes of surface concentration of Ca and Y as a function of annealing time of alumina at 1600°C.¹⁸⁾

layer.

It has been shown that Cr acts as a donor in the bulk of NiO, resulting in an increase in the Fermi level, while at the surface, Cr results in the formation of acceptors (Fig. 12).²¹⁾ In consequence, this leads to the formation of a Schottky-type barrier. This effect may have an impact on the preparation of the materials for electronics. A similar effect has been observed for CoO.⁹⁾

3.6. Diffusion

Grain boundary diffusion in solids is, in the vast majority of cases, substantially faster than bulk diffusion.^{22~28)} The enhancement of the grain boundary transport is enormous, with the enhancement factor

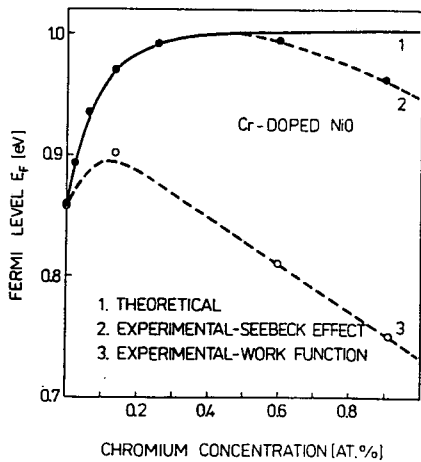


Fig. 12. Effect of composition on Fermi energy level, E_f , in the bulk phase (according to thermopower - curve 2) and at the surface (according to work function - curve 3) for Cr-doped NiO.²¹⁾

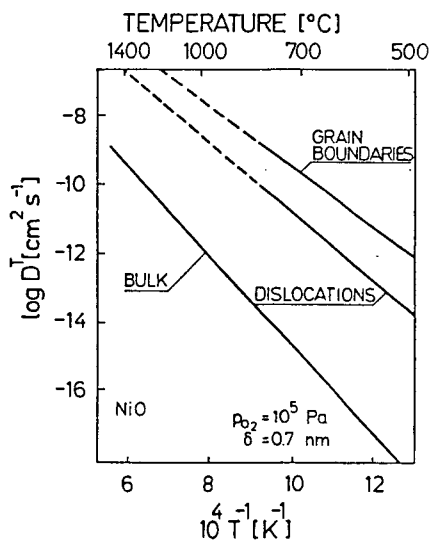


Fig. 13. Grain boundary, dislocation and bulk diffusion of Ni in NiO.²³⁾

as large as 10^4 – 10^5 (Fig. 13).²³⁾

Most of the experimental data on grain boundary diffusion are for metals.²²⁾ In contrast to metals, the reported experimental data for materials based on non-stoichiometric compounds are scarce and limited mainly to several binary metal oxides.^{23~27)} There is an urgent need to accumulate more data on grain boundary diffusion for compounds that would allow the establishment of a relationship between the local grain boundary composition and the enhancement effect as well as verification of the present theories

that have been developed for compounds.

So far, little is known about the reasons for the substantial grain boundary transport enhancement in comparison to that in the bulk phase. It would be expected that this enhancement is determined by the local grain boundary microstructure and composition. Accordingly, it would be expected that modification of this microstructure and composition will affect diffusion along the grain boundaries.

Further studies are needed on the effect of grain boundary processing of materials on the local grain boundary microstructure and composition and, consequently, on the transport kinetics along and across grain boundaries. It is especially important to understand the effect of grain boundary chemistry on the local transport kinetics of oxygen in oxygen ion conductors, such as zirconia and ceria. This understanding is essential for processing solid electrolytes with enhanced properties through interface engineering. Such electrolyte will allow construction of a new generation of high performance solid oxide fuel cells operating at substantially lower temperatures than it is possible now. Moreover, the development of fast ion conducting materials is critical to construct electrochemical gas sensors for environmental gases that can operate at room temperature (at present these sensors require about 700°C).

3.7. Summary

The experimental material presented above indicates that non-stoichiometry of compounds, and related defect chemistry, are well defined for the bulk phase. On the other hand, segregation results in the formation of strong non-stoichiometry gradients in the boundary layer leading, in consequence, to the formation of chemical potential gradients and related electric fields in this layer (Fig. 14). These gradients have a substantial impact on materials properties. Therefore, there is an urgent need to understand the local interface properties imposed by these gradients.

In summary the empirical material accumulated so far indicates that:

- 1) Interface properties of materials are entirely different from those of the bulk phase; however, rules governing this phenomenon are not well understood.
- 2) Interfaces have a substantial, or even controlling, effect on materials functions.
- 3) Development of novel ceramic materials will be determined by progress in interface engineering: the science of processing of interfaces in order to obtain desired materials functions.

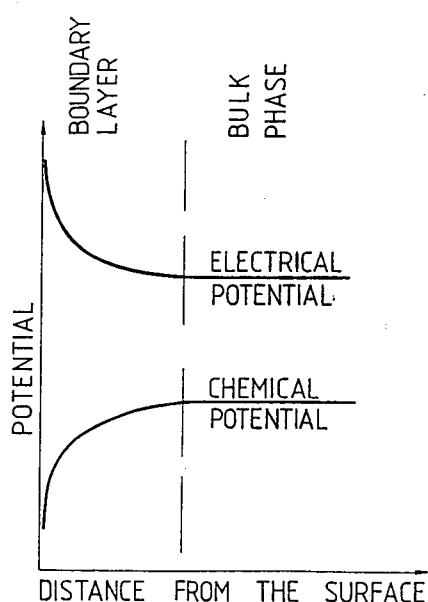


Fig. 14. Schematic illustration of segregation-induced chemical potential barrier and related electrical potential barrier in the boundary layer.

4. Basic Questions in Respect to Interface Engineering

In respect to research in the area of the science and engineering of materials interfaces, the following questions may be asked:

1. Which are the local properties of the interface layer in respect to chemical composition, structure, diffusion, defect disorder, and semiconducting properties? How do these properties differ from those of the bulk phase? What is the effect of segregation on interface properties?

2. What is the relationship between the interface properties and materials functions of technological importance? What is the effect of interface properties on the reactivity at the solid/solid and gas/solid interfaces with respect to heterogeneous reactions occurring during the processing of materials?

3. How may the local interface properties be modified in respect to structure, composition and transport in a controlled and reproducible manner? How can the effect of segregation be used to impose a desired interface composition?

4. How can novel materials be developed using interface processing?

Answering these questions is critical for progress in materials science and engineering in respect to the impact of interfaces on materials properties. This requires the development of general theoretical models

that describe the local interface properties and the impact of interfaces on materials functions. This can be achieved after a substantial amount of empirical material has been accumulated. It is especially important to characterize the segregation-induced low-dimensional interface structures. Finally, there is a need to develop procedures that allow modification of interface properties in a reproducible and controlled manner, to impose low-dimensional interface structures of desired properties (so far, most of electronic materials have been fabricated on an empirical manner rather than based on knowledge²⁹). Ultimately, answering of the above questions is essential for the formation of a strong scientific background that is required for construction engineering projects with respect to the materials of relevance to environmental protection, such as the materials for energy conversion and environmental monitoring.

5. Materials, Devices and Technologies for Energy Conversion and Environmental Monitoring—Selected Issues

This section considers the technologies that are of paramount importance for reduction of greenhouse gas emission and environmental monitoring and which are critically dependent on progress of interface engineering.

5.1. Fuel Cells

Fuel cells allow conversion of chemical energy from gaseous fuels into electricity with efficiency twice of devices using traditional combustion. Consequently, the use of fuel cells will allow a substantial reduction in the emission level of greenhouse gases. A schematic illustration of a solid oxide fuel cell is shown in Fig. 15.

The main research effort in the development of fuel cells, involving both solid oxide fuel cells (SOFCs) and polymer fuel cells, is focused on the development specific materials, such as electrodes and electrolytes.^{30, 31} Further research on the development of solid electrolytes with enhanced properties for construction of high-performance fuel cells is needed. Possible candidates for the electrolyte in high-performance SOFCs include a mullite/zirconia composite,³² zirconia³⁰ and ceria.³⁰ Studies on the effect of interface chemistry on interface transport kinetics of oxygen in these materials are required.

It has been documented that the performance of electrochemical devices is influenced strongly, or even determined, by the transfer of charge at the three-

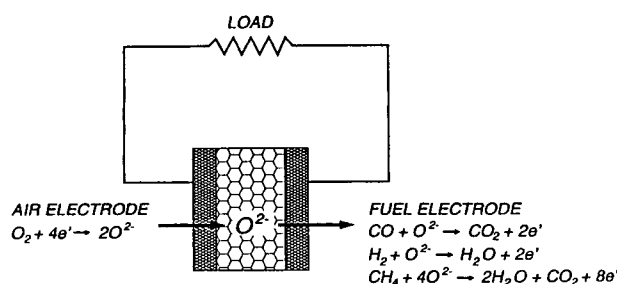


Fig. 15. Schematic illustration of solid oxide fuel cell involving CO, H₂ and CH₄ as fuels.

phase boundary (TPB).^{33,34)} In the case of metal electrodes, such as Pt, the TPB is limited to the perimeter of the electrode. Such an electrode is satisfactory for the determination of the Nernst signal of solid-state galvanic cells when the transport of matter through the cell is very low, as is the case for electrochemical gas sensors. However, for SOFCs, when a high current is to be passed through the cell, its performance is determined by the TPB.

In the case of electrodes made of perovskite-type oxide materials, such as (La,Sr)MnO₃ (LSM), the TPB area is still very critical owing to the low ionic conduction.^{35,36)} The TPB of the LSM electrodes may be increased through controlled microstructure and, specifically, increased porosity.^{30,31)} Thus, oxygen can be transported through the pores to the TPB located at the electrode/electrolyte interface.

By replacement of Mn in LSM by Co, (La,Sr)CoO₃ (LSC) is obtained. LSC exhibits substantially higher ionic conductivity than LSM by 4–6 orders of magnitude.³⁰⁾ Accordingly, oxygen reduction and related charge transfer for the LSC electrodes occur over the entire area of the electrode/gas interface with lower polarization losses.

The use of oxide electrodes, such as LSM and LSC, requires good adhesion between the electrode material and the solid electrolyte in order to enable efficient transfer of charge and matter through the contact between the two. Another problem related with the use of perovskite-type electrodes concerns their stability. Both LSM and LSC may react with the electrolyte material thus resulting in deterioration of the properties of both electrode and electrolyte.

Another approach, aiming at elimination of metal electrodes, consists of functionalizing the boundary layer of the solid electrolyte, such as zirconia, in order to combine the functions of both oxygen conductor and metallic conductor.^{35,37–41)} The electrode serves as a catalyst, which provides (or removes)

electrons to (or from) the reaction site whenever such a supply is required. It is well known that zirconia exhibits mixed conductivity at very low $p(O_2)$, corresponding to $\sim 10^{-23}$ Pa at 1273 K and 10^{-32} Pa at 1073 K.^{31,42–45)} Thus, metallic electrodes are not required. However, the intention of many researchers is to process zirconia with increased electronic conductivity within the boundary layer under conditions of $p(O_2)$ and temperature that are comparable to the operational conditions of SOFC's, i.e., at 10^5 Pa and 10^{-15} Pa for the air and the fuel electrode, respectively. The search for zirconia of enhanced electronic conduction involves the introduction of different dopants that result in an increase in the concentration of electronic charge carriers at the oxygen/zirconia interface. A clear advantage of this approach, over those that require application of the electrode as an separate phase, is that an electrolyte within a single phase combines two functions:

- 1) an ionic conductor (electrolyte) and
- 2) an electronic conductor (electrode).

Such functionalization may be achieved through interface engineering using segregation-induced effects^{46–57)} to impose the required interface composition,⁵⁸⁾ rather than through bulk chemistry. Specifically, knowledge of the phenomenon of segregation, with respect to the kinetics and their impact on the formation of local electric fields in the interface layer, is required to functionalize the electrolyte interface in a desired way. In general segregation may be used as a technology to modify interface properties in a controlled manner.

In conclusion, progress on high performance fuel cells will be determined by the development of more efficient ionic conductors and electrode materials. Also, a better understanding of interface phenomena in fuel cells, such as the gas/solid and solid/solid kinetics, is crucial for overcoming the problems that are related to interfaces in fuel cells and, consequently, for construction of devices with enhanced performance.

5.2. Hydrogen Generation through Electrochemical Water Decomposition using Solar Energy

Burning hydrogen in any device does not lead to the formation of greenhouse gases at all. Therefore, hydrogen is 100% environmentally safe and, as such, should be considered as the fuel of the future. Hydrogen as a fuel may have a great variety of applications, such as car propulsion, heating and the production of electricity. Concordantly, there is an ur-

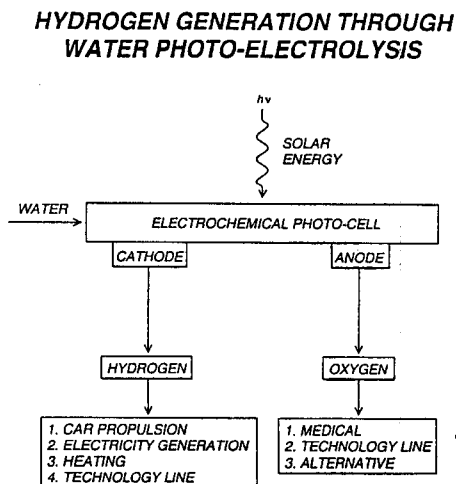


Fig. 16. Schematic illustration of the hydrogen generation technology, based on electrochemical water decomposition using solar energy, and related applied aspects.

gent need to accelerate the research on materials that are important for the production of hydrogen from water. These materials include:

- 1) Photo-electrodes for electrochemical water decomposition and
- 2) Photo-catalysts for water decomposition.

A potential mean of hydrogen generation through photo-electrochemical water decomposition and related applied aspects is illustrated in Fig. 16.⁵⁹⁾

At present more than 90% of world energy production is provided by non-renewable energy sources, such as coal and mineral oil.¹⁾ These processes have a negative impact on the environment. Therefore, there is an increasing need to develop alternative energy sources. This will result in the development of technologies that allow the production of environmentally friendly energy, such as fuel cell technology and solar electricity. If only 0.1% of the earth's surface is covered with collectors converting solar energy at an efficiency of 10%, this amount of energy would be sufficient to satisfy the world's total energy demand. Unfortunately, so far, the use of renewable energy sources, such as solar energy, is very limited due to lack of integrated technologies.

Hydrogen generation from water using solar energy is especially attractive. It is expected that worldwide efforts in the development hydrogen technologies will intensify. In this respect two technologies have been the subject of research:

- 1) High-efficiency photo-electrochemical process.
- 2) Photo-catalytic process.

An advantage of the electrochemical process is

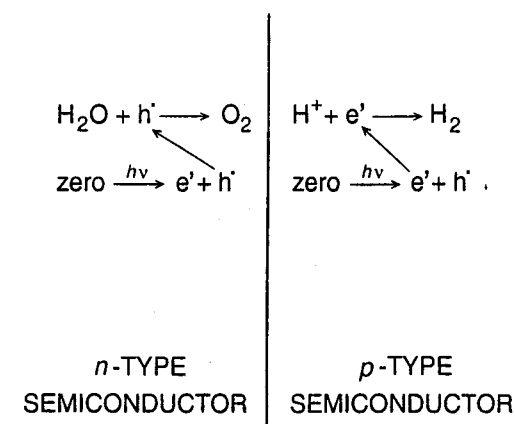


Fig. 17. Electronic mechanism of water decomposition taking place at a semiconducting oxide surface.⁵⁹⁾

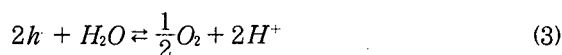
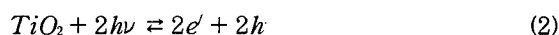
that hydrogen and oxygen, formed in the technological process, are being separated while a mixture of both gases is formed in the catalytic process. One of the candidates for a photo-electrode is TiO_2 and its solid solutions.

It is expected that research on hydrogen production and its utilization will have priority status. The research should include the construction of hydrogen photo-reactors to be installed on the roofs of individual houses. Potential domestic applications include heating, car propulsion and electricity generation.

A photo-decomposition of water may be represented by the following general reaction:



where $h\nu$ represents the energy of light. The electrochemical process⁵⁹⁾ may be represented by the following reactions, which take place at the anode (Fig. 17):



and at the cathode:



The quantum efficiency of the anode depends on the band gap width, the Fermi energy level, and the concentration of electronic defects available for the reaction. At present binary metal oxides, such as TiO_2 and its solid solutions, exhibit the best quantum effi-

ciency when they act as the anode. Doping of the anode material with acceptors, such as Cr and Al, is expected to improve its properties. The effectiveness of charge separation is essential for quantum efficiency. So far, however, there are no reports on an anode preparation procedure that have an impact on charge separation. It should be expected that the desired properties of the electrode material can be achieved through surface processing that allows to impose surface electrical barrier required for charge separation.

Alternative method of hydrogen generation from water using solar energy are based on photo-catalysis⁶⁰⁾ and mechano-catalysis.⁶¹⁾ A disadvantage of these processes, compared to that based on the photo-electrochemical process, is that mixture of both hydrogen and oxygen is formed. Thus, an additional technology is required to separate the two gases.

In conclusion, the development of electrode materials, such as photo-cathodes, is critical to the construction of electrochemical reactors that enable the production of hydrogen from water decomposition using solar energy. Specifically, it is important to develop procedures that allow the production of the cathode materials of specific band gap and that exhibit surface *vs* bulk properties that allow effective charge separation and, consequently, effective decomposition of water.

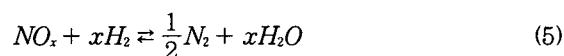
5.3. Catalytic and Electro-Catalytic Conversion of Greenhouse Gases

The development of catalysts and electro-catalysts for the conversion of pollution-generating gases into gases that are environmentally friendly requires an increase in the present state of understanding of the mechanisms of catalytic processes and, specifically, their electronic mechanisms.⁶²⁾ This understanding will allow the processing of catalysts with enhanced properties through interface engineering.

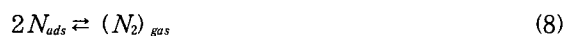
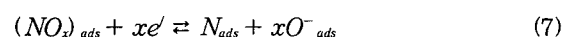
The basic properties of catalysts, such as activity and selectivity, are determined entirely by the gas/solid interface and, specifically, by the outermost surface layer, where interaction with the gas phase results in the formation of catalytically active centers. Therefore, progress in catalysis is determined by understanding of the mechanism of the gas/solid processes. This can be achieved through *in situ* monitoring of the catalyst surface during the catalytic process.

Catalytic or electro-catalytic conversion of NO_x serves as an example of the importance of interfaces

in the development of catalysts with required/enhanced properties. The most important step in the conversion involves the reduction of NO_x to N₂ and water, which can be represented by the following equilibrium:



Alternatively, when hydrogen is not available, the reaction may lead to the formation of nitrogen while oxygen is incorporated into the catalyst lattice, provided oxygen vacancies are available at the concentration that is required to reduce NO_x. This process may be represented by the following quasi-equilibria:



Accordingly, an increase of the concentration of oxygen vacancies within the surface layer of the catalyst above a certain critical level may lead to a shift of the equilibrium (Eq. 9) to the right. This may be achieved electrochemically by imposing an electric field over this layer.

In deriving the equilibria of Eqs. (5)–(9) it has been assumed that nitrogen is adsorbed in a neutral form. Verification of this assumption and the related equilibria of Eqs. (6)–(8), will be required.

In the case of both mechanisms, the conversion of NO_x results in the formation of gases that are 100% environmentally friendly, these being nitrogen and water.

Processing of the catalyst surface in order to assume a desired activity and selectivity is the most critical part of the research. This can be achieved by *in situ* monitoring of the charge transfer accompanying these processes and, consequently, understanding the mechanism of the catalytic process.⁶³⁾ Thus, surface processing of the catalyst should satisfy the required charge neutrality conditions. Further studies are needed in order to produce data revealing the effect of surface processing on the effectiveness of the catalytic process.

The reports on conversion of NO_x that have been reported so far concern catalytic processes that oper-

ate at 350°C or well below this temperature.⁶⁴⁾ Consequently, the implementation of these technologies requires cooling the exhaust gases from the temperature at the exit of combustion chamber, which is about 600°C, to the level at which the catalytic process takes place, which is 350°C or below. This requirement imposes certain complications, such as the installation of a cooling system. Another essential requirement of existing technologies is that the availability of hydrogen in the reaction mixture is required in order to lower the oxygen activity to a sufficiently low level for the reduction of NO_x. Consequently, there is a need to develop procedures that allow effective catalytic conversion up to 600°C, i.e., at the temperature level of exhaust gases as they leave the combustion chamber. Consequently, catalytic conversion at elevated temperatures does not impose the requirement of a costly cooling system. Recently initiated research at Nagoya University aims at the development of such a catalyst, which contains a Ba-Mn-Al oxide layer.^{65, 66)}

There is also a need to develop procedures that allow catalytic conversion without the presence of hydrogen in the reaction mixture and, moreover, with the presence of air in the exhaust gas. In this case, lowering the oxygen activity within the adsorbed layer, where the catalytic process takes place, could be achieved by lowering the oxygen chemical potential electrochemically. In consequence, oxygen activity within the adsorbed layer could assume a very low value that is sufficient for the conversion to take place while oxygen activity in the gas phase may still be very high.

In situ determination of the charge transfer accompanying various steps of the catalytic process is required in order to understand its mechanism and, consequently, to optimize the catalysts' performance.

5.4. Power Generation Using Solar Energy

There has been intensive research in the development of electricity generation using solar energy.⁶⁷⁾ The most advanced technology is based on solar cells based on silicon technology. The principle of this technology involves the generation of a voltage across a cell that is composed of n-type and p-type silicon, forming a Schottky barrier over their junction. This barrier serves to separate charge that is generated as a result of Si ionizations due to the solar beam. The idea of a solar power generator is shown schematically in Fig. 18.

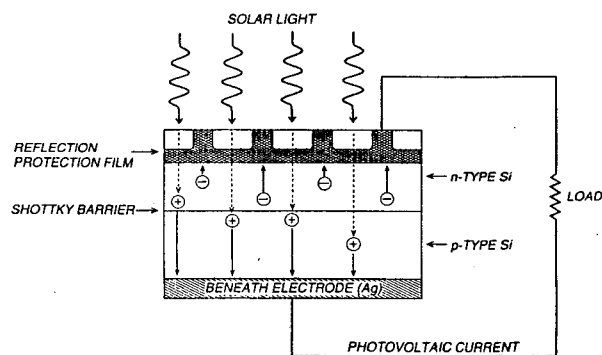


Fig. 18. Schematic illustration of a Si-based solar cell.

A device for electricity generation using dye-sensitized TiO₂ photovoltaic cells has been developed by Gratzel et al.^{68, 69)}

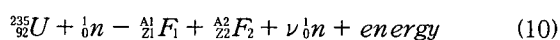
Progress in high-light-efficiency power generation is determined by the development of materials that allow high degree of absorption of solar energy and to efficient charge separation.

5.5. Nuclear Energy

There has been observed an increase in use of nuclear energy in the most industrial countries, such as USA, Japan, Germany and France. Despite its clear advantages the nuclear energy is very unpopular in some countries, such as Australia and Poland. This is due to concern of possible impact of nuclear wastes on environment. Due to this concern both Australia and Poland still do not have power nuclear reactors. However, burning fossils may be much more dangerous for environment than handling and storing of nuclear wastes. It should be expected that future of nuclear energy will be much brighter after radioactivity of nuclear wastes has been efficiently tackled through appropriate processing. And this seems to be the matter of a near future.

5.5.1. Fission Energy

Nuclear energy generation by the fission of uranium (U-235) due to neutron absorption may be represented by the following reaction:



where F₁ and F₂ denote two fission fragments, such as ⁹⁰Kr and ¹⁴⁴Ba, n is neutron, ν is the number of neutrons emitted (that can vary between 2 and 3), and Z and A denote the atomic number and atomic weight, respectively. The amount of energy produced by the fission of U-235 is about 190 MeV which corresponds to 8 × 10¹⁰ kJ per kg of U-235. Taking into

account this enormous amount of energy, nuclear fission may be considered an important alternative in the production of energy that does not produce greenhouse gas emission, assuming that effective technologies for nuclear waste immobilization can be developed. In this respect, the geological disposal of high-level radioactive waste is under consideration.⁷⁰⁾

An important problem concerns fission gas release, which must be prevented. It is essential that this gas remains within the fuel pellets. An understanding of the interface properties of the fuel material and, specifically, grain boundary diffusion, is essential to tackle this problem. The gas release may be blocked effectively by:

- 1) Reduction of the amount of grain boundaries and pores available for transport, and
- 2) Blocking grain boundaries through engineering the grain boundaries so that they exhibit slow transport.

Research on waste immobilization aims at the development of:

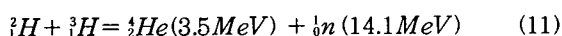
- 1) Materials that effectively isolate the nuclear waste from the geological environment and
- 2) Novel nuclear processes that reduce radioactivity through nuclear transmutation and annihilation.

According to the present state of research in this area, the level of nuclear waste, in respect to both the life length of the isotopes emerging from the nuclear technology cycle and their amounts, will be reduced to almost nil by the year 2060.⁷⁰⁾ If this is true, then we may have to modify our perspective concerning nuclear energy, which may be not only one of the most efficient sources of energy but also the energy that is environmentally friendly.

5.5.2. Fusion Energy

Although research in fusion technology is advanced, construction of the first experimental reactor (International Thermonuclear Experimental Reactor) is expected to be only in 2020.⁷⁰⁾ This research aims principally at overcoming materials-related problems.

The most feasible D-T (deuterium-tritium) reaction yields a helium ion and a neutron:



The ignition energy for the D-T process is 4.4 keV, compared with the 48 keV required for D-D reaction. Eqn. (11) requires tritium that can be generat-

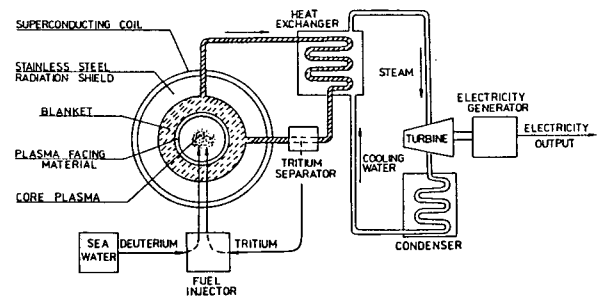
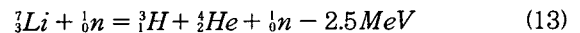
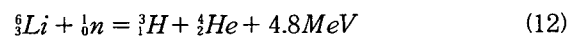


Fig. 19. Schematic diagram of a nuclear fusion reactor.

ed according to the following processes⁷⁰⁾:



By using the neutrons from the fusion reaction for breeding tritium, the amount of thus generated energy is about 10^{14} J per kilogram of tritium. A schematic drawing of a nuclear fusion reactor is shown in Fig. 19.

An advantage of nuclear fusion over nuclear fission is that there is a substantially larger amount of energy produced in comparison to the amount of nuclear waste that is generated. Specifically, the radioactive waste formed in nuclear fusion includes only:

- 1) Tritium, which is a short-life isotope (13.5 years of half-life) and
- 2) Radioactive materials formed due to *activation* of the reactor materials during the nuclear process.

It should be emphasized that radioactive nuclear wastes from fusion exhibit substantially lower activities than those from fission.⁷⁰⁾

Progress in this area is determined by the development of novel materials for the construction of the fusion reactor and, specifically, the plasma facing material and blanket breeder. An understanding of interface properties of these materials is crucial to the development of this technology.

5.6. Thermoelectric Energy Conversion

The thermoelectric effect allows conversion of heat energy into electrical energy and *vice versa*. Thus, thermoelectric energy conversion devices may be used for cooling devices without the use or production of greenhouse gases in their technology as well as for power generation using renewable heat energy, such as solar energy.

Principle of the thermoelectric effect is based on the Seebeck effect, that consists in the formation of

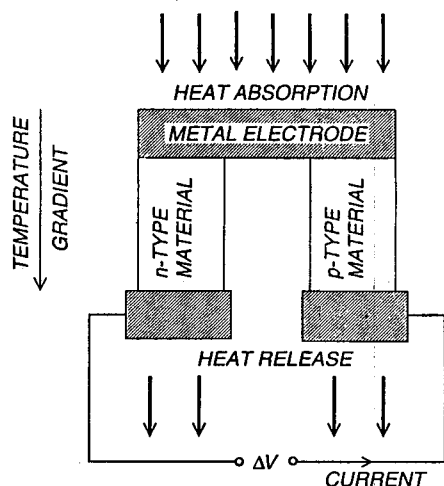


Fig. 20. Schematic illustration of a thermoelectric double cell.

a seebeck voltage across an imposed temperature gradient over a semiconducting material (Fig. 20). Alternatively, a temperature gradient may be generated across this material along an imposed potential difference (peltier effect). Polarity of these effects depends on the type of semiconducting material.⁷¹⁾

Thermoelectric efficiency is described by Eq. (14), which gives the relationship between the thermoelectric coefficient Z (termed also as figure of merit), Seebeck coefficient, α , thermal conductivity, κ , and electrical resistivity, ρ ⁷¹⁾:

$$Z = \frac{\alpha^2}{\kappa \rho} \quad (14)$$

Figure 20 shows the principle of operation of thermoelectric devices. In this case, both n-type and p-type materials are connected in series, forming a panel. Imposition of a temperature gradient on the panel leads to the formation of a voltage across both materials of different polarity. Thus, the voltage produced across this panel is the sum of the individual voltage components. The application of constant heat on one side results in the generation of electricity on the other (cool) side. Alternatively, application of a voltage across the panel will result in heating of one side and cooling of the other. Thermoelectric materials include Bi_2Te_3 , SiGe , FeSi_2 , CoSb and IrSb_3 .⁷¹⁾ The most promising materials for novel thermoelectric devices are TiO_2 and Cu_2O .

Current research aims at the development of materials that exhibit high values of thermoelectric coefficient Z . Progress in this area is determined by an understanding of the effect of grain boundaries on the

coefficient Z . So far, it is known that this effect is substantial. Specifically, it is known that there is a substantial contribution of the grain boundaries to the overall resistivity. This resistivity can be reduced either by reduction of the amount of grain boundaries or by the formation of grain boundaries that do not have a negative effect on thermoelectricity.

5.7. Devices Based on High-Temperature Oxide Superconductors

The impact of high-temperature oxide superconductors on the development of novel technologies is clear. The most spectacular one is that superconductors allow electricity transmission without energy loss. This energy savings may be substantial. There is a long list of applications of these materials that includes new electronic and magnetic devices.

It has been documented that both the critical current and critical temperature of high-temperature superconductors are determined by interfaces.⁷²⁾ Therefore, processing of materials with enhanced properties is determined by appropriate interface engineering.

5.8. Chemical Gas Sensors

In the case of chemical gas sensors, the sensing signal is generated at interfaces. Therefore, the sensitivity, selectivity and response time of sensors are controlled by the local properties of the interface layer, which can be engineered according to the requirements of the environment or workplace.

There is an urgent need to develop chemical gas sensors that allow monitoring of the gases responsible for air pollution and, specifically, for the greenhouse effect. So far, sophisticated and expensive equipment, such as gas analyzers based on infra-red and ultra-violet absorption spectrophotometry, pulse fluorescence, and flame photometry, have been used to determine air quality. Although this equipment allows very precise gas phase analysis, it has two substantial disadvantages:

- 1) High costs, and
- 2) Large dimensions.

A large group of sensors, which have been used for environmental monitoring, is based on liquid or wet electrochemistry. These sensors, that are commercially available, have severe disadvantages:

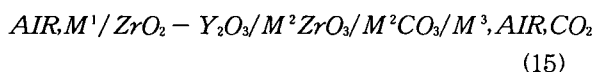
- 1) Large dimensions,
- 2) Long response time,
- 3) High costs, and
- 4) Limitation to the environments where the temperature is at room temperature.

During the last decade there have been efforts to develop chemical gas sensors that are based on solid-state technology.^{73,74)} The advantages of these sensors, over wet technology sensors, involves mainly:

- 1) Possibility of miniaturization,
- 2) Easy performance and calibration,
- 3) Low cost,
- 4) Short response time, and
- 5) High selectivity.

Their main disadvantage is that the operation temperature must be elevated (in the case of zirconia-based sensors the operation temperature range is 500–700°C). In certain cases, such as car exhaust systems, the temperature of the natural environment (exhaust port) is elevated and so zirconia-based sensors are ideal. At present the technology of chemical gas sensors based on solid-state technology is in an incubation stage, so the market is predominated by sensors based on wet technology.

The principle of operation of electrochemical gas sensors is based on generation of electromotive force (EMF) of a galvanic cell. The sensor for CO₂ may be represented, as an example, by the following cell:



where M¹, M² and M³ denote metals. The relation between EMF of the cell and activity of selected gas phase components (a_i), such as CO₂, is given by the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \sum \nu_i \ln a_i \quad (16)$$

where E is EMF, E[°] is the EMF related to standard activities, n is the number of electrons involved in the reaction of the cell, F is the Faraday constant, and ν_i and a_i denote stoichiometry and activity coefficients, respectively. Cell calibration allows to determine the E[°] component. Solid state sensors include a great variety of sensors, such as semiconducting sensors, thin film sensors, structural sensors and catalytic sensors, however, the electrochemical sensors have the best selectivity. An oxygen concentration cell, that serves as an oxygen sensor, is schematically shown in Fig. 21.

There is a need to develop solid-state sensors for air quality and occupational monitoring of the concentration of pollution-generating greenhouse gases. These sensors are required for establishment of an

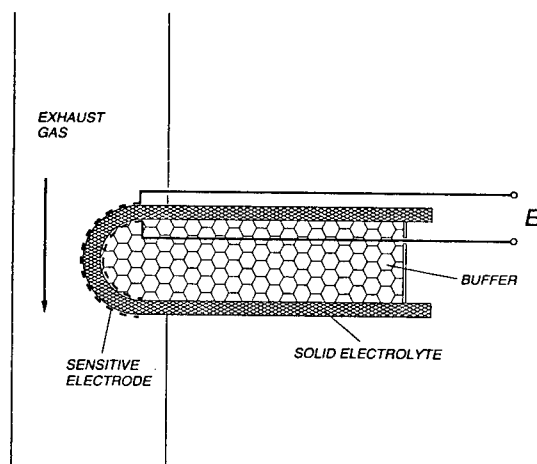


Fig. 21. Schematic illustration of an electrochemical oxygen sensor. The buffer, composed of a metal-metal oxide mixture, serves to impose of constant (reference) oxygen activity.

efficient air monitoring system for environmental gases, such as CO₂ and NO_x.

There is a great variety of chemical gas sensors that are based on the determination of different properties.^{73,74)}

5.9. Alternative Technologies

Emission of CO₂ and other pollution-generating gases, produced by burning fossils, is increasing with an alarming pace (Fig. 22).⁷⁵⁾ A global warming potential of other pollution gases may be substantially higher than that of CO₂ (i.e. for NO_x and CCl₄ it is 40 and 1300⁷⁵⁾). Therefore, there is a list of the technologies that have been considered for reduction of their emission.

In general the technologies based on renewable sources are the most important, such as solar, wind and hydroenergy. Active solar heating for domestic purposes may substantially reduce electricity consumption. An increase of the application of hydro-power and wind energy has been observed.

Emission of CO₂, and other pollution-generating gases, from power stations using fossils can be removed using the following separation procedures⁷⁵⁾:

- 1) Separation by absorption. This technology is based on reactive or physical solubility of selected gas phase components in liquids.
- 2) Separation by adsorption. In this technology the pollution-generating gas is adsorbed on the surface of active solids, such as molecular sieves and silicates.
- 3) Separation using membranes. This technology is based on selective permeation of certain gases

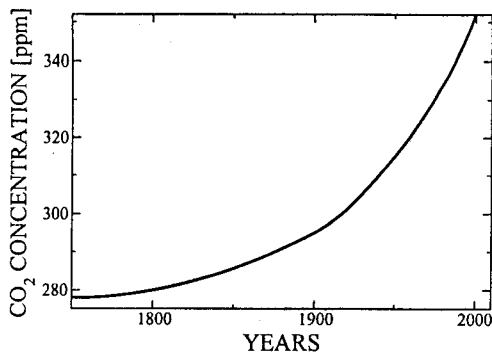


Fig. 22. Increase of the atmospheric CO₂ during the past 250 years.⁷⁵⁾

through membranes after a partial pressure gradient.

4) Refrigeration. This procedure allows separation of a pollution gas phase component by cooling the gas mixture and freezing out the desired pollution-generation component.

5). Electrochemical transport. In this procedure the desired gas phase component can be transported through an ionic solid, in the form of an ion, under electric field.

A great disadvantage of the above technologies is that thus recovered pollution gases should be stored in a way that does not allow their emission to atmosphere. The following disposal technologies have been considered for CO₂⁷⁵⁾:

1) Disposal in the deep see. In this technology CO₂ is injected into low oceans levels (below 3000 m).

2) Disposal in a liquid phase. This technology is based on the fact that density of liquid CO₂ is larger than that of water. Therefore, this liquid may sink to lower sea levels. This, consequently, results in an increased residence time.

3) Conversion into solid materials.

6. Studies Required

6.1. Well Defined Specimen

Comparison of experimental data for specimens of different impurity level and different microstructures can lead to confusing conclusions that do not allow the derivation of a clear picture of materials properties.⁷⁵⁾ Therefore, there is a need for experimental data using well defined specimens of either high purity or well known impurity level. Since it is almost impossible to prepare pure specimens, there is a need to determine their impurity levels with high accuracy, possibly at the ppb (part per billion) level. Since the effect of impurities on properties may be substantial, only results for specimens of the same impurity lev-

els are suitable for comparison. Furthermore, the grain size and microstructure may have a substantial impact on the properties of ceramic materials. Therefore, only data for the specimens of controlled grain size and microstructure can be compared. In order to understand the effect of microstructure, both specimens of high density and single crystals should be studied. It should be realized that specimens prepared by different chemical routes, such as the oxalate route or the sol-gel process, may exhibit different microstructure.

The formation of solid solutions with (i) aliovalent ions in order to impose a desired charge neutrality condition, and (ii) other ions required to stabilize desired structures, is an important way to modify properties of non-stoichiometric compounds in a controlled manner. In this respect, it is important to verify whether these solid solutions exhibit homogeneous compositions.

An important aspect of materials processing concerns the composition of the gas phase during processing. Consequently, the processing of materials with well defined properties should be prepared under a gas phase of well defined composition. Specifically, in respect to oxide materials, it is important that processing takes place under a gas phase of well defined oxygen activity.

6.2. New Techniques

Experimental data on the surface properties of solids produced by classical surface sensitive tools, such as the techniques based on electron and ion spectroscopy, usually correspond to room temperature and ultra-high vacuum (UHV), i.e., the conditions at which these tools operate. Under these conditions, the surfaces of metallic solids it is relatively easy to remove adsorbed impurities and, therefore, to be well defined. In contrast to metals, it is very difficult to have a well defined surface of non-stoichiometric compounds. Thus, the experimental data frequently are dictated by the cleaning procedures rather than by specific materials properties. An awareness is growing that surface properties of compounds are strongly influenced by the rate of cooling or quenching from the temperature of their processing - that usually takes place at elevated temperatures - to room temperature, at which temperature experimental data are taken.⁷⁶⁾ It already has been documented that cooling results in the formation of non-equilibrium concentration gradients of defects within the surface layer. The extent and direction of these gradi-

ents depend on the rate of cooling and the gas phase environment during cooling.

A non-stoichiometric compound can be defined when in equilibrium with gas phase environment corresponding to its stability range. This is possible at elevated temperatures, at which equilibrium can be reached relatively quickly. In this case, the properties of compounds, including the properties of the surface layer, are entirely independent of the experimental procedures applied before the experimental data are collected, such as rate of heating and cooling. Thus, both bulk and surface properties are determined only by the temperature and the gas phase composition corresponding to the equilibrium state. Concordantly, it is important to remember that the experimental data of compounds obtained at room temperature must be considered in respect to the cooling and cleaning procedures applied.

The surface properties of metal oxides, such as non-stoichiometry, electrical conduction and other defect-related properties, are determined by temperature and oxygen partial pressure, when the gas/solid equilibrium is reached. Then, the surface layer also is in equilibrium with the bulk phase (but this does not mean that the related properties are the same). Therefore, there is a need to characterize the surface properties of compounds at elevated temperatures and under controlled gas phase environment when the surface is well defined and so when surface data can be considered to be materials data. Therefore, it is essential to develop surface-sensitive tools able to characterize surface of compounds in thermodynamic equilibrium.

So far, the best methods for providing information about the properties of compounds at elevated temperatures and under controlled gas phase composition are these based on the determination of electrical properties. Both electrical conductivity and Seebeck effect provide information about bulk properties while the work function is a surface-sensitive property. Although these methods provide only indirect information about fundamental materials properties, such as chemical composition, structure and non-stoichiometry, the electrical methods are extremely sensitive and can be applied in aggressive environment.

There is a need to develop new techniques adequate to characterize complex nature of ceramic interfaces and to use the existing surface sensitive techniques for ceramic systems more widely. Specifically, there is an urgent need to develop techniques

that can determine the properties of the interface layer *in situ* at elevated temperatures and under controlled gas phase composition, i.e., in environments comparable or identical to those of ceramic processing. A high-temperature Kelvin probe, which allows determination of work function of materials up to 1000°C under controlled gas phase composition, is a unique surface sensitive tool that enable *in situ* studies of surface properties.

The use of synchrotron-based techniques⁷⁷⁾ and impedance spectroscopy⁷⁸⁾ can probe the interface region and can give both geometrical structure and electronic information.

6.3. Interface Processing

Surface and grain boundary segregation has a strong impact on the processing of ceramic materials and plays an important role in their final physical, chemical, mechanical and optical properties. Therefore, the preparation of advanced functional ceramics of desired properties is likely to be achieved through a better understanding of grain boundary properties. This will allow the processing of novel materials with enhanced properties through controlled interface chemistry. A broader knowledge of segregation in non-stoichiometric compounds and its impact on the defect chemistry of the grain boundary region is required to reach this goal.

To understand the role of interfaces on processes, characterization of the interface region should be performed *in situ* at elevated temperatures and under controlled gas atmospheres corresponding to technological processes. So far, the majority of research on surface science has been limited to ultra high-vacuum and low-temperature conditions. Accordingly, the existing gap between surface science and high-temperature chemistry should be bridged. This can be tackled by a new scientific discipline of high-temperature surface chemistry.

6.4. Thin Films

Thin films exhibit properties that are different from those of the bulk phase. This is due to the large surface-to-volume ratio and specific microstructure. Studies of thin films are appropriate to characterize the low-dimensional surface structures, if these structures and thin films exhibit comparable thickness.

6.5. Theoretical Methods

Modern theoretical methods are able to tackle difficult problems relevant to the bulk phase, such as the determination of defect structure.⁷⁹⁾ So far, however, these methods are incapable to determine structure-

**STRATEGY OF RESEARCH
ON THE DEVELOPMENT OF NEW MATERIALS
FOR SUSTAINABLE ENVIRONMENT**

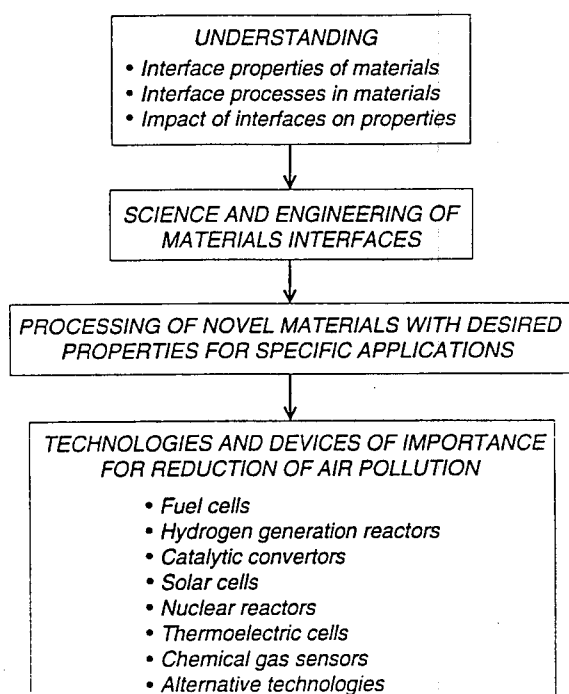


Fig. 23. Research strategy to reduce emission of greenhouse gases.

related properties of the interface layer. The development of such methods, which would be able to determine the local properties of the interface layer in non-stoichiometric compounds, is needed. These methods would allow the prediction of the processing procedures required to achieve the properties critical for high-performance applications.

7. Conclusions

The need to develop novel functional materials that are required for high-performance devices for energy conversion and environmental monitoring is clear. The present work provides evidence that this can be achieved through novel materials processing: interface processing, rather than through bulk chemistry alone. Therefore, there is a need to increase the present state of understanding of materials interfaces and their impact on the properties of relevance to the development of new energy sources that are environmentally friendly. Consequently, progress in the science and engineering of materials interfaces is required. This can be achieved only through coordinated efforts of specialized research centers that are focused on the development of the materials that

allow the production of environmentally friendly energy. Establishment of an international research program on the science and engineering of materials interfaces would be essential to stimulate these efforts.

A research strategy for the development of the materials required for novel technologies critical for reduction of environmental pollution is shown in Fig. 22.

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