ADVANCED MATERIALS

Intelligent Materials— A New Frontier

Functional Ceramics
Ceramic Sensors
Sensor Tuning

By Hiroaki Yanagida*

1. The Need for Intelligent Materials

The incentive for materials R& D is to achieve improvements in either manufacture or performance, or to introduce novel functions. Until very recently only the first two of these have been recognized as important. Improved manufacturing methods have led to large scale production systems. Iron and plastics are examples of progress in this direction. Research on engineering ceramics has been aimed at improving performance, in particular to give improved durability under severe conditions. There is another direction for R& D in materials, namely the introduction of novel functions. Various specialized functions have been discovered. Nonlinear electrical and/or optical behavior, various types of transducers, chemically interesting properties, etc. give rise to many types of novel devices, using what are described as functional materials.

Materials with excellent performance *and* novel functions are ideal candidates for future technology. One such class of materials is that of functional ceramics. Various functional ceramics have already been developed or are still undergoing development. Some of these have the special properties mentioned above. It may be said that no electronic devices can be constructed without ceramic components. Various novel devices have been developed using functional ceramics. These might be described in a sense as keys to the development of an advanced technological society.[1]

The ultimate functions may be those with "intelligence". There are potential demands for so-called intelligent materials. Although computers with integrated circuits are normally used to control operations or to make judgements, neither these nor any other devices containing electrical connections can be introduced into hazardous environments. Some operations or judgements therefore need to be carried out within materials which satisfy the required safety conditions. Even under non-hazardous conditions, where computers are used for complicated functions the result is often a tangle of electrical leads, a situation which has been referred to by medical electronics scientists as the "spaghetti syndrome".[2] Here again it is an advantage if some of the intelligent judgements can be made within materials. Thus there is a need for intelligent materials.

Examples of what is meant by the term intelligent are concepts such as self-recovery, self-adjustment or control, self-diagnosis, stand-by capability for detecting nonlinear onset, ability to be externally tuned, etc. These concepts seem to be realized only in living organisms, which, however, cannot survive in hostile environments, and in some senses, therefore, intelligent materials must perform better than living organisms, by being able to withstand very hos-

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tile environments. Nevertheless, to achieve intelligence in materials one must learn from living organisms which are not necessarily ideally adapted, since in the modern technological age hostile conditions of previously unknown kinds are encountered. To carry out work in environments which human beings could not tolerate, robots with capabilities exceeding those of living organisms, and able to withstand such severe conditions, must be used. Living organisms lack some important sensing mechanisms, e.g. the ability to detect insufficient oxygen pressures or the presence of so toxic a gas as carbon monoxide. With the help of intelligent materials, living organisms can survive under severe conditions.

2. Functions Required from Intelligent Materials

Some of the functions that may be demanded of intelligent materials have already been mentioned above. The meanings of these functions will be explained in this section.

2.1. Self-recovery

Most materials inevitably degenerate continuously until they are no longer usable. Living organisms, on the other hand, frequently recover their original function and performance through a self-recovery mechanism. They may recover through resting, for example. A disadvantage arising from the lack of a self-recovery mechanism is seen in the case of the humidity sensor consisting of a porous ceramic semiconductor. The conductivity of the porous material usually increases with adsorption of water vapor under humid conditions, and decreases with removal of adsorbed water molecules under dry conditions. Removal is, however, very slow at room temperature. A large hysteresis loop is observed in the humidity-conductivity characteristic. A measured conductivity value will not necessarily indicate the humidity level existing at the time of the reading. In order that the water molecule adsorption sites should remain fully active one must frequently carry out a so-called cleaning operation to remove the adsorbed water molecules at high temperature. During such cleaning treatments the sensor cannot supply any information about humidity.

A few years ago we constructed a new type of ceramic humidity sensor.[3] This uses point contacts between a p-type semiconductor (copper oxide or nickel oxide) and an n-type semiconductor (zinc oxide). The voltage-current characteristic changes with humidity as shown in Figure 1. The mechanism of this device has been analyzed as follows.[3c] The amount of water adsorption in the vicinity of the hetero contacts changes with humidity, as is also found for porous humidity sensors of the usual type with homo phase contacts. Electron holes are injected from the p-type semiconductor electrode into the adsorbed water molecules, giving rise to protons in the adsorbed water phase. The positive charge is liberated at the surface of the n-type semiconductor electrode. As a consequence of this process the adsorbed water is electrolyzed. During measurements the cleaning process is always working, since the cleaning or self-recovery treatment is itself the working mechanism.

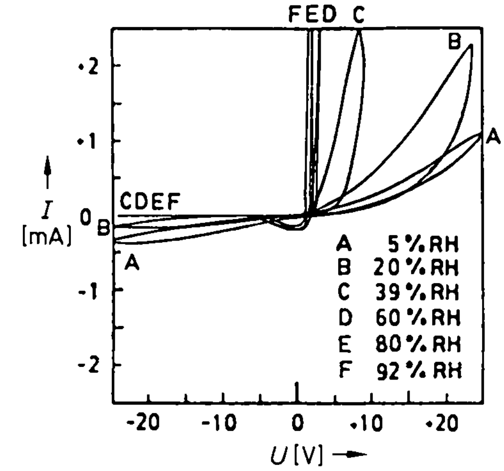

Fig. 1. Humidity dependent voltage-current characteristic changes of an intelligent humidity sensor made of hetero-contacts between copper oxide and zinc oxide [5]. RH = relative humidity.

The change from the usual porous ceramic humidity sensors to the p/n contact type discussed here is from single phase contacts to two different phase contacts. The morphology appears to be very similar in the two cases. However, the working mechanism is significantly different. Both are typical examples of two-dimensional structures,[4] as shown in Figure 2. However, the p/n contact type has greater potential than the former type, at least as far as intelligence is concerned. Table 1 gives a comparison between the usual porous type ceramic humidity sensor and the p/n contact type.

Fig. 2. Difference in structure and working mechanism between single phase contact type (left) and two phase contact type humidity sensors (right). Left is a porous zinc oxide humidity sensor and right a p/n hetero-contact type humidity sensor.

2.2. Self-adjustment or Control

The types of control systems that have been proposed are many and varied. Most of them use feedback logic with conventional electric circuits. There are, however, some self-control devices without feedback circuits, although they may still be primitive from an intelligence standpoint.

Table 1. Comparison of two types of ceramic humidity sensors.

	porous zinc oxide humidity sensor	CuO/ZnO contact humidity sensor
structure [4]	open interface between identical materials	open interface between different materials
measurement	conductivity change	*U/I* characteristic
mechanism	protonic conduction	electrolysis of adsorbed water
hysteresis	causes problems	none, no problems
cleaning	necessary	not needed (working mechanism itself gives cleaning)
self-recovery	ineffective (frequent cleaning treatments needed)	effective

The temperature of heating elements may be roughly controlled if the resistance increases with temperature, as occurs in silicon carbide heating elements above 1000°C. The most typical self-control mechanism is seen in perovskite type ceramic (PTC) heating elements; semiconductor PTCs are well known and used in practical applications. They have very low resistivity below the transition temperature, and can be used for heating elements in this range. Above the transition temperature the resistivity begins to increase dramatically. The change in resistivity can be used to measure the temperature. The resistivity reaches a very high value, so that only a very small current passes. This constitutes a switch which does not rely on a change in contact behavior. Through the intrinsic properties of the material, the element performs simultaneously the functions of heater, temperature monitor and switch. Here again the origin of the intelligent character lies in a type of two-dimensional structure:[4] a closed interface between identical materials, with the phenomenon occurring across the interface.

2.3. Self-diagnosis

The reason why we try to improve the performance of materials is that we hope to use the materials for as long as possible. We also try to establish methods whereby the life of the materials in a particular application can be predicted. However, in a significant proportion of samples the lifetime is shorter than that predicted. We therefore need to periodically check the condition of the materials during use. One method of monitoring which can be used is to observe acoustic emission from the materials. However, it is not practicable to install acoustic emission apparatus in every application. When living organisms go wrong, they signal to others that they are in difficulties, and help from others may then relieve their problems. Although they may not have the self-recovery mechanism within themselves, they can receive help by telling others of the difficulty occurring in them. If materials could be made with such a self-diagnostic mechanism, we could take action to avert disasters caused by failures of materials. We could also avoid unnecessarily sacrificing materials through replacing them prematurely lest they should fail.

2.4. Stand-by Capability

Machines are sometimes criticized because their response is slower than that of living organisms. For example, the motion of robots is slower than that of humans. Machines are also said to be incapable of releasing stored energy as rapidly as living organisms. A flea can jump very high very quickly. Rockets, on the other hand, take off very slowly. Most machines cannot release a very high concentration of energy within a very short time. The difference is in the stand-by mechanism. There are, nevertheless, some cases where devices have an effective stand-by mechanism. Consider the mechanism of amplification in transistors. Between source and sink a large bias is applied. Unless the barrier height is reduced no significant current flows from source to sink. The barrier (or gate) works as a trigger. The humidity sensor of the p/n contact type, which was discussed earlier from the standpoint of self-recovery, may also be analyzed in terms of its stand-by capability. Under dry conditions only a very small current flows through the contacts, although there is a bias across the p/n contact, whereas in humid conditions the current increases with the adsorption of water molecules. The sensor behaves like a hungry animal waiting for food.

If materials can be equipped with a stand-by mechanism in which they wait for nonlinear onset triggered by certain signals, they become interesting candidates for use as intelligent materials.

2.5. Ability to be Externally Tuned

Sometimes we need to change the behavior or characteristics of materials from outside. We may call this "tuning" the device. This avoids having to employ a large number of different components. The most convenient form of control signal is to change an applied voltage. Various ceramic capacitors exist whose capacitance varies with the applied voltage. The optical transmission of ferroelectric ceramic films made of PLZT (lead lanthanum zirconate and titanate) can be altered by changing the applied voltage, which is known as the Kerr or Pockels effect. The p/n contact humidity sensor also works as a very selective carbon monoxide gas sensor.[5] The selectivity towards carbon monoxide arises from selective adsorption of carbon monoxide at the copper oxide surface. The capacitance of the p/n contact increases when carbon monoxide is introduced into the ambient atmosphere (nitrogen and oxygen). The sensitivity changes with the bias applied across the p/n contact as shown in Figure 3. The maximum sensitivity is obtained when the CuO side is positively biased at about 0.5 V. This effect constitutes a tuming. The chemical

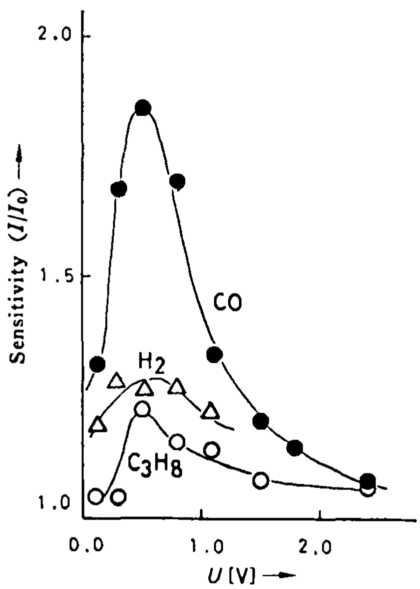

Fig. 3. Tuning of the sensitivity to carbon monoxide by bias in the CuO/ZnO contact type gas sensor [5]. ●: with CO, Δ: with H_2, O: with C_3H_8; gas concentrations: 8000 ppm; temperature: 260°C.

reaction between carbon monoxide adsorbed on the positively charged copper oxide surface and oxygen adsorbed on the negatively charged zinc oxide surface, giving rise to carbon dioxide, is enhanced when the bias is greater than 0.5 V. If this explanation is correct, we have here an electric field controlling a chemical reaction.

A difficulty in applying control voltages is the need to connect leads. If the tuning is achieved by optical or magnetic means, the materials can be regarded as being more intelligent.

3. Conclusion

Intelligent materials can be developed through learning about the mechanisms in living organisms. However, we require materials that can be used in environments not tolerated by living organisms. Intelligent materials perform better than living organisms from the durability standpoint. Key functions for intelligent materials are self-recovery, self-adjustment or control, self-diagnosis, stand-by capability, and ability to be externally tuned. Some examples of intelligent materials have been discussed here. One example in which we can see self-recovery and stand-by capabilities, and ability to externally tune the behavior, is the p/n (CuO/ZnO) contact structure. Research and development on intelligent materials has only just begun. It is one of the most challenging frontiers of materials science.

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From Electronic/Ionic Conductors to Superconductors: Control of Materials Properties

**High T_c Perovskites
Electron/Ion Transfer
Topotactic Reactions**

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1. Introduction

Modern materials science may be defined in analytical terms as the effort to understand the macroscopic properties of solids by considering their structure on the microscopic (atomic) level. The term "structure" comprises here the geometrical/crystallographic aspects, the total of electronic interactions between the atoms which constitute the material, and the lattice dynamics. In synthetic terms one major approach in materials science is the aim of "tailoring" materials with a given set of particular properties on the basis of analytical knowledge in order to meet optimally and economically the needs of specific applications. The thermal synthesis of solid compounds is usually related to a substantial structural reorganization at high temperatures. However, the properties of the products are not

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