

Solid-state potentiometric gas sensors—a supplement

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Abstract Potentiometric in situ gas probes with solid electrolytes were described for the first time 50 years ago. It is the intention of the present communication to give some additions on oxygen sensors in reducing gases which have been neglected in a recent review (*J Solid State Electrochem*, 13:3, 2009). Today, the most frequently used solid electrolyte gas sensors are the lambda probes. In their electrodes is a very quick change between gas phases with excess of oxygen and excess of components of reducing gases. Changes in the interpretation of the mechanism of the interaction between gas and solid electrolyte in the gas sensors are discussed. At low temperatures, mixed potentials appear which have to be expected at oxygen electrodes also with air and technical oxygen, if these gases are not cleaned particularly. Among the CO₂ sensors, the system with the reference electrode SiO₂, Na₂Si₂O₅ on β-alumina must be mentioned. This system has special advantages and in the commercially available device it reaches excellent long-term stability. A report about long-term measurements of SO₂ traces in air is worth mentioning. For measurements of SO₂ in industrial gases, Westinghouse has offered a complicated system in the 1980s.

Keywords Potentiometric gas sensors · Solid electrolytes

A recently published review on solid-state potentiometric gas sensors [1] was devoted to the current status and future trends. Although some older works were included, no representation of the historical development was intended. Because the older literature is only partially considered,

there are some relevant gaps which we like to fill here. Also, the current status of the newer literature is not completely recorded. Actually, the field of solid-state potentiometric gas sensors is very large so that a detailed review cannot take all publications into account. But there are some main issues which should not be missing. Therefore, some additional information is given here to amend the mentioned review. The historical beginnings have been treated in more detail on the occasion of the 50th anniversary of in situ solid electrolyte oxygen sensors, i.e., the principle of the lambda probes [2].

Retrospection on sensors with oxide-ion-conducting solid electrolytes

The idea to measure in situ partial pressures of gases with the help of galvanic solid electrolyte cells by potentiometry was first described in a 1958 patent specification [3, 4]. This idea originated during the work on solid oxide fuel cells at the University of Rostock, Germany [5, 6]. The task was to prove that thermodynamically precalculable electric potential differences (E_{cell}) of fuel cells with oxide-ion-conducting solid electrolytes are actually available experimentally. When the proof with cells using gases of predefined composition was successful [7], the idea seemed to be reasonable that—the opposite way around—gas partial pressures should be calculable from the electromotive force (emf) measured at cells with an unknown gas on the basis of the thermodynamic relations. The E_{cell} to be expected thermodynamically can serve as base for the examination of the question to what extent electronic conductivity, leaks, permeabilities, reaction inhibitions, or other effects affect the measurements.

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For the first time in November 1955, oxygen partial pressures were calculated with results of measurements using solid electrolyte cells with nitrogen-containing hydrogen. The priority with respect to activities of the Westinghouse Electric Corporation in Pittsburgh USA [8, 9] was attested in a lawsuit between Westinghouse and the Canadian Company Babcox & Wilson Industries Ltd. in the 1980s by an explanation with 18 chapters in German and English given to two Canadian lawyers [10]. But it did not come to any publication of the explanation because in 1989 the parties achieved outside the court an agreement on reason of convincing arguments.

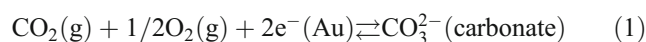
In the first calculations and in the research on fuel cells, the function of the oxygen-measuring cells in reducing gaseous phases was already needed. This function plays an important role among others in the cleaning of waste gases. To remove nitrous oxides, reducing conditions must be adjusted in the waste gas. Very quick changes between oxygen excess and oxygen deficiency for the cleaning of the waste gases of motor vehicles of CO and CH_x as well as NO_x are controlled with help of oxygen sensors. These environmentally very important sensors are the lambda probes; million times used today and not mentioned in the review on solid-state potentiometric gas sensors [1].

In the patent specification [3], the potentiometric method was called “electrochemical partial manometry” and besides the determination of the partial pressure of oxygen also that of fluorine, chlorine, and bromine was included. Further, it was mentioned that, based on single partial pressure measurements, also gas mixtures, e.g., CO, CO₂, and H₂, H₂O can be indirectly analyzed. The patent claim, however, is not aimed at the simple potentiometric method but:

Method of gas analysis at higher temperatures with help of galvanic solid electrolyte cells, said method using as solid electrolyte only a substance, which besides more or less, at the best completely missing electronic conductivity have a conductivity only for that ion, with which the gas for analysis can come in interaction.

After this, the method was intended for the analysis of gases with O₂, F₂, Cl₂, or Br₂ at solid electrolytes with unipolar conductivity for oxide, fluoride, chloride, or bromide ions. Other authors have pursued the basic idea also for sulfide [11] and for nitride ions [12, 13] (without success). Only in 1977 was the simple basic idea replaced when Gauthier et al. measured CO₂ and SO₂ with potassium-ion-conducting carbonates or sulfates, respectively [14]. Their results clearly showed that for the sensor function it is only important that the gas participate in an electrode equilibrium with an ionic component of the solid and a conductivity of the solid exists by any ion. For

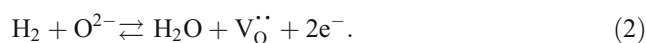
example, at a gold electrode in intimate contact with a carbonate and CO₂, the reaction



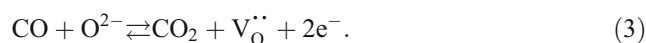
proceeds. At the surface of the carbonate, an excess of negative charges results. The potential is measurable if ions can be transported through the carbonate. It is insignificant which sort of ions closes the electrical circuit. It is not necessary that the gas to be analyzed must form also the mobile ion of the solid electrolyte.

It follows from the idea of the patent claim in 1958 that in H₂, H₂O and in CO, CO₂ gas mixtures with oxide-ion-conducting solid electrolytes the oxygen partial pressures are measured based on the chemical equilibrium of oxygen with these gases. However, calculations give oxygen partial pressures for such gas mixtures smaller than 10⁻²⁰ atm. At such low pressures, practically no oxygen molecule can exist together with H₂ in the anode chamber of solid electrolyte cells. It is only imaginable that O or O₂ appears during extremely small fractions of a second. But the explanation is more obvious [15].

In the electrode reaction, H₂ takes up oxide ions of the solid electrolyte in one direction, and H₂O gives oxygen in vacancies of the solid electrolyte in the other direction :



Hence, molecular oxygen is not involved in the electrode reaction. The same is true for the CO, CO₂ system:



H₂ and H₂O or CO and CO₂ react at sufficiently high temperature with the solid electrolyte in the ratio according to the equilibria governed by the law of mass action from which the very small oxygen partial pressures follow.

Between the potential equations of the electrodes with the reactions 2 and 3 and that for the electrode reaction with molecular oxygen



there are continuous transitions, which were calculated in 1964 [4, 16].

The insight that in reducing gases the reactions 2 and 3 proceed, but not reaction 4, has a practical meaning. It explains why there are different lower temperature ranges, up to which reliable gas analysis with oxide-ion-conducting solid electrolytes is possible. With CO, CO₂ concentration cells, the expected E_{cell} could be measured with Fe₃O₄ electrodes from high temperatures up to about 700°C [5, 7], with Ni electrodes (within the scope of trials for the electrochemical measurement of absolute temperatures [17, 18]) only up to about 900°C. Compared with this, the expected E_{cell} was measurable at H₂, H₂O concentration

cells with Pt electrodes down to about 300°C [19]. Reaction 3 apparently is kinetically inhibited much stronger than reaction 2.

Inexplicable behavior of oxygen electrodes was already observed in the first investigations at gas cells with oxide-ion-conducting solid electrolytes [4]. Figure 1 shows results of measurements at oxygen air cells with different electrolyte material. It is easily understandable that the measured electromotive forces are smaller than expected in the upper temperature range. This is caused by a p-type electronic conductivity in the anion sublattice of the oxidic phases with oxide ion vacancies (or by deviations, e.g., thermoelectric forces) and in the case of the Ce–La-mixed oxide by the increasing formation of Ce³⁺ ions with increasing temperature and the electronic conduction via Ce³⁺/Ce⁴⁺ in the cation sublattice. But, for a long time, the course of the curves in the lower temperature range was completely incomprehensible. With any oxidic solid electrolytes (and also with different electrode materials [5]), electromotive forces were obtained which apparently violate the thermodynamic laws.

The course of the electromotive force of oxygen air cells at low temperatures was for the first time elucidated after more than 20 years, and the combustible gas sensitivity of the oxygen electrodes at oxide-ion-conducting solid electrolytes was found as the cause [20, 21]. There was the rather unreflected idea that no interfering combustible molecules exist in air and pure oxygen at temperatures around 600°C. Actually, air and also pure oxygen can be clean of combustible pollutions only if these gases were led over a heated combustion catalyst (e.g., by using MnO₂ and CuO at 550°C [21]). Only then can the emf of oxygen air cells be measured down to 300°C (Fig. 2).

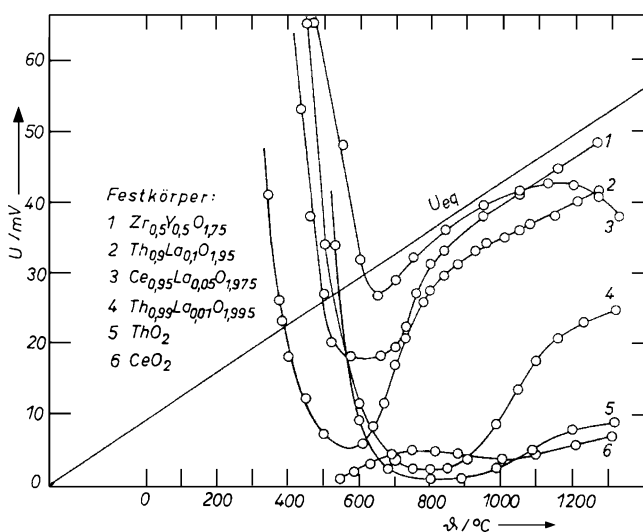


Fig. 1 Results of measurements of the emf of oxygen air cells with different solids as electrolytes [5]

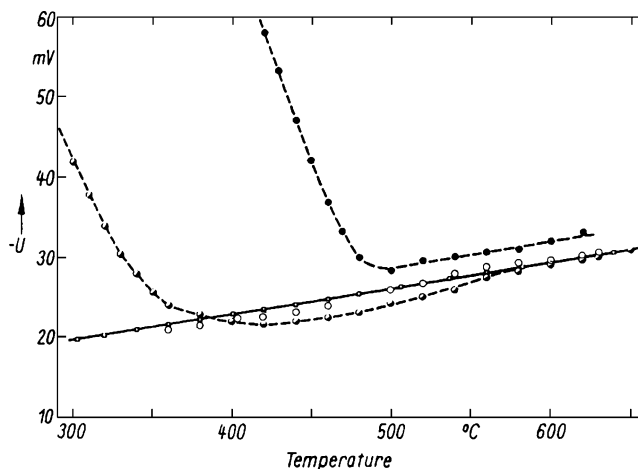


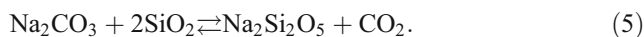
Fig. 2 Results of measurements of the emf of an oxygen air cell with differently well-cleaned gases [21]

This result means that at all investigations of cells with an oxygen or air electrode are expected to show a “non-Nernstian behavior” if the oxygen or the air is not especially cleaned.

In connection with the development of lambda probes, Fleming recognized in 1976 that the undesirable temperature-dependent shifting of the signals is caused by the competition of O₂ and CO for triple-point adsorption sites on the sensor anode [22]. Generally, beside O₂, oxidizable gas molecules (CO, H₂, hydrocarbons, and other organic compounds, also SO_x and NO_x) are more or less effectively adsorbed at interfaces of the electrodes depending on temperature and they may participate in electrode reactions competing with the electrode reaction of oxygen. This leads to nonequilibrium potentials, nonideal, and non-Nernstian behavior, and a combustible gas sensitivity of the electrodes results. Since more than 20 years ago, many attempts have been made to use this sensitivity in special mixed potential sensors.

Remarks on solid electrolyte sensors for CO₂ and SO₂

Since more than 10 years ago, there is a solid-state potentiometric CO₂ sensor commercially available, which, unfortunately, has not been mentioned in the review [1]. This is the sensor produced by the ZIROX GmbH Greifswald on the base of the cell reaction



In 2004, a comparison of a sensor based on this principle with the sensor produced by Figaro Engineering in Japan has been published and important advantages of the ZIROX-type sensor could be reported [23]. The ZIROX

sensors for 1 vol ppm to 20 vol% CO₂ reach long-term stabilities from 1 to 4 years depending on operating conditions.

This sensor in principle corresponds to the system used by Maier et al. successfully with TiO₂ and Na₂Ti₆O₁₃ [24]. In sensors of this type, the electrode chambers do not have to be separated from each other (the reference electrode is open) and they are stable provided that the pure substances involved are stable. The sensor with SiO₂ has the advantage that the thermodynamic data of all substances involved in the cell reaction are known and can be used for the precomputation of the cell voltage equation. This way, a reliable base exists for the assessment of the question as to what extent measurements are affected by side effects. This advantage was used for detailed examinations of sensors with SiO₂ also at measurements under reducing gases [23].

Thermodynamic data are also available for corresponding sensors with MoO₃, WO₃, and ZrO₂ [25]. At the given temperature ranges and standard pressure, the following equations for the CO₂ concentration φ are valid for the sensors

$$\text{with SiO}_2\{574 - 678^\circ\text{C}\} \\ E_{\text{cell}}/mV = 423.8 - (0.7120 - 0.04309 \ln[\varphi(\text{CO}_2)]) T/K, \quad (6)$$

$$\text{with MoO}_3\{450 - 593^\circ\text{C}\} \\ E_{\text{cell}}/mV = 131.4 - (0.857 - 0.04309 \ln[\varphi(\text{CO}_2)]) T/K, \quad (7)$$

$$\text{with WO}_3\{450 - 587^\circ\text{C}\} \\ E_{\text{cell}}/mV = 129.9 - (0.730 - 0.04309 \ln[\varphi(\text{CO}_2)]) T/K, \quad (8)$$

$$\text{with ZrO}_2\{527 - 627^\circ\text{C}\} \\ E_{\text{cell}}/mV = 807.7 - (0.695 - 0.04309 \ln[\varphi(\text{CO}_2)]) T/K. \quad (9)$$

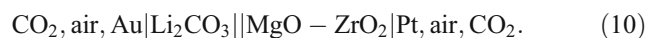
The sensors with MoO₃ and WO₃ showed a marked sensitivity for CO₂ but no stability. The cell voltage did not follow the thermodynamically expected results because, when the cells were heated up, the stoichiometry of these oxides obviously varied and with that their thermodynamic data [23, 26]. There is a completely different problem if one wants to produce sensors with ZrO₂. Na₂ZrO₃ decomposes already at relatively small and at all higher CO₂ concentrations, i.e., the reaction equation corresponding to Eq. 5 then runs backwards and the sensor with ZrO₂ is not stable.

In principle, every alkali ion conductor should be suitable for the production of CO₂ sensors with open reference electrode. However, it was found that electrolytes of the NASICON type slowly react with electrode substances and by that the cell voltage gradually differs from the results expected thermodynamically [26]. Also,

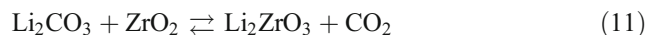
the thermodynamic expectations were not met when solid zirconia electrolyte powder was added to the two electrode mixtures [23]. By doing so, the oxygen needed for the electrode reaction should be available more easily. However, the formation of Na–Zr silicates apparently led to considerable interferences. The activity of Na₂O in the components of the cells is in the equilibrium of the cell reaction without importance; however, it can play a role in the conditioning period and for the response times [23].

Generally, long-term stability of CO₂ sensors can be obtained only if the electrodes are produced with stable pure substances which do not form any separate mixed phases with each other or with components of the cell arrangement. It is very easy to produce CO₂-sensitive electrodes but the choice of stable reference electrodes is very restricted. The system with SiO₂ is a particularly favorable case.

Perhaps with the successful CO₂ sensors the cell arrangement of Miura et al. can compete because it has an open reference electrode and is insensitive against O₂ also [1, 27]. Therein, the combination of a cation conductor with an anion conductor is used :



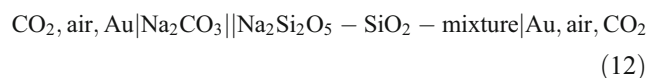
At the contact between carbonate and MgO-stabilized ZrO₂, Li₂ZrO₃ can be formed in a spontaneous chemical reaction (<0 at 600°C and $\varphi < 6$ vol% CO₂). The authors assume that the reaction for forming this ion bridge



delivers the emf for the determination of CO₂. They confirmed this assumption with results of measurements at 600°C.

However, for the long-term stability, it is questionable whether Li₂CO₃ (melting temperature 720°C) may fade away by creeping over oxidic surfaces or volatilizing. As soon as contacts result between particles of the gold electrode and the zirconia solid electrolyte, an oxygen cell will result. Then, the cell voltage is zero if there is the same oxygen partial pressure at the two electrodes of the cell. Hence, there are doubts that with the cell arrangements described by Miura et al. the long-term stability of 1 year necessary for commercially applicable sensors is attainable. The creeping of the carbonates over oxidic surfaces is generally a property which can considerably interfere in applications of sensors for potentiometric measurements of CO₂.

An ion bridge is also formed spontaneously if the sensor with SiO₂ is made without a special solid electrolyte [28]. In the cell



at the interface $\text{Na}_2\text{Si}_2\text{O}_5$ is formed as a sodium ion conductor. This formation reaction and the cell reaction 5 determining the emf are the same. But such sensors have no long-term stability because SiO_2 is gradually consumed.

For the measuring of SO_2 , the solid electrolyte with the specific composition $(\text{K}_2\text{SO}_4)_{0.99}(\text{BaSO}_4)_{0.1}$ was found to be resistant against changes of the temperature and being gastight at long term. This allowed a four-capillary alumina tube to be sealed gastight when the end of the tube was pressed onto the electrolyte pellet with the electrodes at 700°C [29]. With that electrolyte at platinum electrodes, traces of SO_2 in air (between 0.04 and 0.14 vol ppm) were measured continuously for about 4 weeks (reference gas 14 vol ppm SO_2) at 840°C . A general problem in SO_x measurements consists in the fact that SO_x in gas pipes made of glass or ceramic is adsorbed together with water vapor at the surfaces and is only slowly desorbed when a gas with low SO_x concentration is flowing through.

For the measurement of SO_2 in combustion exhausts, the Westinghouse Electric Corporation had developed an expensive system in the 1980s [30, 31]. Two electrically heated in situ probes (operating temperature 843°C) were used, one with zirconia solid electrolyte for O_2 measurements and one with potassium sulfate solid electrolyte. From the two signals, the SO_2 concentration was calculated. For the regular repetition of calibrations, the probes were automatically fed for some time with test gases from steel bottles. The successful development of the SO_2 cell has been the result of using a potassium-ion-conducting ceramic tube as a gastight membrane electrolyte [32] (a special mullit [33]). The system was applied in coal-fired plants downstream of the wet scrubber, in cement kilns, and in other plants. After the takeover by the Rosemount Analytical Inc. [34], the production of the system which was susceptible to interferences was terminated in the 1990s.

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