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## Galvanic solid electrolyte cells for the measurement of CO<sub>2</sub> concentrations

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**Abstract** The first commercially offered CO<sub>2</sub> sensors with galvanic solid electrolyte cells have very different properties. A review of the numerous carbonate cells described in the literature shows that it is easy to obtain CO<sub>2</sub>-sensitive systems with Au, Na<sub>2</sub>CO<sub>3</sub> measuring electrodes. The problems of obtaining reproducible CO<sub>2</sub> sensors with long-term stability mainly concern the reference electrode. Only electrodes composed of pure solid substances, stable under the operational conditions, promise the desired properties. Reference electrodes with the oxides of Mo, W, Sn, Ti, Si and Ge have been tested, with different degrees of success. With silica and sodium silicate on  $\beta$ -alumina, a CO<sub>2</sub> sensor results that can be used also in reducing gas phases and without calibration because the evaluation of the signals is possible by a thermodynamically precalculated equation. The volatility of Na<sub>2</sub>CO<sub>3</sub> is presumably caused by the vapor pressure of thin layers of the creeping substance and by the formation of gaseous Na<sub>2</sub>(OH)<sub>2</sub>. The properties of Na<sub>2</sub>CO<sub>3</sub> are particularly unfavorable for planar sensors. The sensor signals are independent of the partial pressure of O<sub>2</sub> and H<sub>2</sub>O, but the participation of O<sub>2</sub> in the electrode reactions causes cross sensitivities not only for carbon-containing gases but also, for example, for NH<sub>3</sub> and H<sub>2</sub>. The cross sensitivities against halogens and SO<sub>2</sub> are irreversible. At sudden changes of the CO<sub>2</sub> concentration the sensor signal follows within less than a few seconds, but questions remain concerning the observable differences in the response times of differently arranged sensors. The response times are highly important for a sensor arrangement that is aimed at simultaneous measurements of CO<sub>2</sub> and O<sub>2</sub> in real time for each breath.

**Keywords** Breath gas sensor · Carbon dioxide sensor · Silica–sodium silicate reference electrode · Sodium carbonate · Solid electrolyte sensors

### Introduction

CO<sub>2</sub> sensors which contain galvanic solid electrolyte cells have been offered commercially since about 1998 (Table 1) [1, 2, 3]. They are in competition with miniaturized and economically produced optical devices which measure infrared absorption. The devices with CO<sub>2</sub> sensors developed until now show considerable differences in their structure and properties. It is questionable whether the optimal variants have been found and whether existing problems can still be overcome. Statements concerning this matter require a critical comparative view on previous efforts in the development of CO<sub>2</sub> solid electrolyte sensors and discussion of the encountered difficulties.

In several papers on galvanic solid electrolyte cells for CO<sub>2</sub> measurement, earlier recommended systems have been discussed [4, 5, 6, 7, 8]. In the present review we have tried to facilitate a comparison with the help of tables in which the cells are represented by cell symbols, the investigation temperatures and the cell reactions, ordered according to the year of investigation.

In the cell symbols, vertical bars separate parts of the cell in series, and indicate interfaces which are passed by charge carriers in the electrical circuit. The substances essential for the cell reaction are placed, separated by comma, next to the electrically conducting substances. Substances which are put in the cell as a mixture without forming a homogeneous phase are separated by comma and set in square brackets. Gases at interfaces between different ion conductors are enclosed in braces. The sequence of the substances and characters in the cell symbols determine properties of the cells. The terminals of the cells are omitted in the symbols with the understanding that they must consist of identical material to avoid thermoelectric forces. Some cell symbols and cell

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**Table 1** Specifications of commercial CO<sub>2</sub> solid electrolyte sensors

	Figaro [1, 2]	Zirox [3]
Sensing element structure	Planar support with heater and sensor layers	Tube with stack of tablets in isolated furnace
Heater power consumption	Approx. 1.25 W	Approx. 6 W
Typical detection range	300–5000 vol ppm CO <sub>2</sub>	1–1000 vol ppm; other ranges up to 20 vol% CO <sub>2</sub> optional
Feeding of the gas	Sensor placed in the gas	Diffusion from the environment (standard) Passing through (ca. 3 L/h) (optional)
Response time	$t_{90}$ approx. 2 min	$t_{90}$ 1–2 min
Measurement accuracy	Approx. $\pm 20\%$ at 1000 ppm CO <sub>2</sub>	Rel. error $< 5\% \pm 5$ vol ppm
Conditioning period before test	7 days	20 min heating time; the declared accuracy is reached in 30 min (after switch off $> 1$ day the rel. error is ca. 10% for ca. 15 h)
Calibration	With fresh air (assumed 350 vol ppm CO <sub>2</sub> )	Without calibration; signal evaluation on the basis of the thermodynamically given equation

**Table 2** Investigated CO<sub>2</sub> sensor systems of older types (CSZ and YSZ: calcia- and yttria-stabilized zirconia)

No.	Year	Cell symbol (measuring electrode I solid electrolytes I reference electrode)	$\vartheta/^\circ\text{C}$	Overall cell reaction (presumed)	Ref.
1	1977	Pt, CO <sub>2</sub> , O <sub>2</sub> I [K <sub>2</sub> CO <sub>3</sub> , Ag <sub>2</sub> SO <sub>4</sub> ] I Ag	726	$\text{Ag}_2\text{CO}_3 \rightleftharpoons 2\text{Ag} + \text{CO}_2 + \frac{1}{2}\text{O}_2$	[9, 10, 11]
2	1984	Au, CO <sub>2</sub> (g), O <sub>2</sub> (g) I K <sub>1.6</sub> Sr <sub>0.2</sub> CO <sub>3</sub> I CO <sub>2</sub> (g'), O <sub>2</sub> (g'), Au	450–700	$\text{CO}_2(\text{g}') + \frac{1}{2}\text{O}_2(\text{g}') \rightleftharpoons \text{CO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	[12]
3	1984	Au, CO <sub>2</sub> (g), O <sub>2</sub> (g) I K <sub>2</sub> CO <sub>3</sub> {CO <sub>2</sub> (g'), O <sub>2</sub> (g')} CSZ I CO <sub>2</sub> (g'), O <sub>2</sub> (g'), Au	753	$\text{CO}_2(\text{g}') + \frac{1}{2}\text{O}_2(\text{g}') \rightleftharpoons \text{CO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	[28, 29, 30]
4	1987	Au, CO <sub>2</sub> , O <sub>2</sub> I Na <sub>2</sub> CO <sub>3</sub> I Nasicon I Na <sub>2</sub> CO <sub>3</sub> , CO(g'), CO <sub>2</sub> (g'), Au	730–887	$2\text{CO}_2(\text{g}') \rightleftharpoons \text{CO}(\text{g}') + \text{CO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	[15]
5	1987	Au, Ar, H <sub>2</sub> , H <sub>2</sub> O, CO, CO <sub>2</sub> I Na <sub>2</sub> CO <sub>3</sub> I Nasicon I Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> (g'), O <sub>2</sub> (g'), Au	780–820	$2\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{CO}_2(\text{g}') + \frac{1}{2}\text{O}_2(\text{g}')$	[16]
6	1987	Au, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub> I Nasicon or Na-β-Al <sub>2</sub> O <sub>3</sub> I O <sub>2</sub> , Au	330–560	$\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{O}(\text{dissolv. s.e.}) + \text{CO}_2$	[17]
7	1987	Au, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub> I Nasicon (joined by melting) I YSZ I O <sub>2</sub> , Au	530–730	$\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{O}(\text{dissolv. Nasicon}) + \text{CO}_2$	[17]
8	1990	Pt, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub> I Na-β-Al <sub>2</sub> O <sub>3</sub> thin film I CSZ thin film I O <sub>2</sub> , Pt	350–587	$\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{O}(\text{dissolv. s.e.}) + \text{CO}_2$	[18, 19]
9	1991	Pt, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub> I Na-β,β'-Al <sub>2</sub> O <sub>3</sub> I Na enclosed	350–550	$\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na} + \text{CO}_2 + \frac{1}{2}\text{O}_2$	[27]
10	1992	Au, CO <sub>2</sub> (g), O <sub>2</sub> (g) I (Na <sub>2</sub> CO <sub>3</sub> ) <sub>0.99</sub> (BaCO <sub>3</sub> ) <sub>0.01</sub> I CO <sub>2</sub> (g'), O <sub>2</sub> (g'), Au	450–650	$\text{CO}_2(\text{g}') + \frac{1}{2}\text{O}_2(\text{g}') \rightleftharpoons \text{CO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	[13]
11	1993	Au, CO <sub>2</sub> , O <sub>2</sub> I [Na <sub>2</sub> CO <sub>3</sub> , BaCO <sub>3</sub> ] I Nasicon I Na <sub>x</sub> CoO <sub>2-y</sub> , Pt, enclosed	470–550	$\text{Na}_2\text{CO}_3 + n\text{Na}_x\text{CoO}_{2-y} \rightleftharpoons n\text{Na}_{x+2/n}\text{CoO}_{2-y} + \text{CO}_2 + \frac{1}{2}\text{O}_2$	[20, 21]
12	1993	Au, CO <sub>2</sub> , O <sub>2</sub> (g) I [Na <sub>2</sub> CO <sub>3</sub> , BaCO <sub>3</sub> ] I Nasicon I O <sub>2</sub> (g'), Pt under glass	420–560	$\text{Na}_2\text{CO}_3 + \frac{1}{2}\text{O}_2(\text{g}') \rightleftharpoons \text{Na}_2\text{O}(\text{dissolv. s.e.}) + \text{CO}_2 + \frac{1}{2}\text{O}_2(\text{g})$	[22, 23, 24, 25]
13	1995	Pt I Au, CO <sub>2</sub> , O <sub>2</sub> I Li <sub>2</sub> CO <sub>3</sub> (joined by melting) I MgO-stab. ZrO <sub>2</sub> I O <sub>2</sub> , Pt	500–650	$\text{Li}_2\text{CO}_3 \rightleftharpoons \text{Li}_2\text{O}(\text{dissolv. Li}_2\text{CO}_3) + \text{CO}_2$	[32]
14	1997	Pt I [Me <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub> , Au I YSZ I CO <sub>2</sub> , O <sub>2</sub> , Pt	350–680	$0 \rightleftharpoons 0$	[33]
15	1997	Au, CO <sub>2</sub> , O <sub>2</sub> I [Li <sub>2</sub> CO <sub>3</sub> , Li <sub>3</sub> PO <sub>4</sub> , LiAlO <sub>2</sub> ] I [LiCoO <sub>2</sub> , 5 mol% Co <sub>3</sub> O <sub>4</sub> ] I Pt	350–400	$\text{Li}_2\text{CO}_3 + 2/x\text{Li}_{1-x}\text{CoO}_2 \rightleftharpoons 2/x\text{LiCoO}_3 + \text{CO}_2 + \frac{1}{2}\text{O}_2$	[34]
16	1999	Au, CO <sub>2</sub> , O <sub>2</sub> I [Li <sub>2</sub> CO <sub>3</sub> , 20 wt% MgO] I Li <sub>2</sub> Mn <sub>2</sub> O <sub>4</sub> I Au	300–400	$\text{Li}_2\text{CO}_3 + n\text{Li}_x\text{Mn}_2\text{O}_4 \rightleftharpoons n\text{Li}_{x+2/n}\text{Mn}_2\text{O}_4 + \text{CO}_2 + \frac{1}{2}\text{O}_2$	[26]
17	2000	Au, CO <sub>2</sub> , O <sub>2</sub> , Li <sub>2</sub> CO <sub>3</sub> I Nasicon I Au, O <sub>2</sub> (g') (enclosed by Al <sub>2</sub> O <sub>3</sub> and glass)	450	$\text{Li}_2\text{CO}_3 + 2\text{Na}^+(\text{dissolv. s.e.}) + \frac{1}{2}\text{O}_2(\text{g}') \rightleftharpoons 2\text{Li}^+(\text{dissolv. s.e.}) + \text{Na}_2\text{O}(\text{dissolv. s.e.}) + \text{CO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	[1]

reactions could not be taken from the original papers but are formulated by the author.

### Review of CO<sub>2</sub> sensor systems of the older types

In Table 2, variants of older cell types are listed. In 1977, Gauthier and Chamberland [9] showed the possibility to measure CO<sub>2</sub> concentrations with solid electrolyte cells, using the hygroscopic K<sup>+</sup> conductor K<sub>2</sub>CO<sub>3</sub> (cell no. 1).

However, detailed investigations did not lead to a stable reference system with silver [12]. The K<sup>+</sup> conductivity could be increased considerably by admixture of SrCO<sub>3</sub> (cell no. 2). With composites of Na and Ba carbonates, solid electrolytes were obtained which were gastight, not hygroscopic and suitable for long-term stable CO<sub>2</sub> concentration cells (cell no. 10 [13]; on a Na-Ba-carbonate electrode, see [14]). Equipment with such cells is, however, awkward and expensive, and the necessary gastight separation of the electrode chambers only lasts

if the cell is kept constantly at the operational temperature.

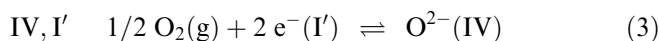
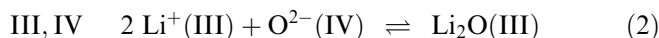
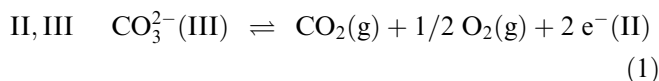
With the investigations of Maruyama et al. [15, 16, 17] the development of CO<sub>2</sub> sensors using Nasicon or β-alumina started in 1987 (cells no. 4–7). For CO<sub>2</sub> measurements in reducing gaseous phases, gas concentration cells were used, in which Nasicon served as a Na<sup>+</sup> membrane between electrodes with Na<sub>2</sub>CO<sub>3</sub> (in cells no. 4 and 5). An essential simplification was reached with an arrangement (cell no. 6) without dependence of the signals on the O<sub>2</sub> partial pressure, in which the alkali oxide activity in the Nasicon or β-alumina at the interface with the reference electrode should serve as a stable basis for measurement. Sensors of this type were prepared with thick and thin film techniques (cell no. 8). It was tried to reduce the drifting of the signals of these planar sensors by covering the reference electrode with glass (cells no. 11 and 12). However, the preparation, particularly with melting processes, led to quite different Na<sub>2</sub>O activities in the reference electrodes. In addition, the signals were dependent on the O<sub>2</sub> partial pressure again. Non-stoichiometric phases like Na<sub>x</sub>CoO<sub>2-y</sub> (cell no. 11) yield reference potentials dependent on *x* and *y* [20]. Also, for an arrangement with Li<sub>2</sub>CO<sub>3</sub> and LiMn<sub>2</sub>O<sub>4</sub> as a phase with a relatively stable Li<sub>2</sub>O activity (cell no. 16), no thermodynamic equation is known that could serve as a basis for the signal evaluation. The signals of such sensors also drift.

Long-term stable signals that follow an easily calculable thermodynamic relation were expected for a sensor with liquid sodium as the reference substance (cell no. 9). However, apart from the problems of handling liquid sodium and evaluating the resulting signal, which is very high compared to the changes caused by variation of the CO<sub>2</sub> concentration, a side reaction to give Na<sub>2</sub>O<sub>2</sub> interferes and the dependence on the O<sub>2</sub> partial pressure was unfavorable as well. Alloys of sodium were also checked [21]; however, CO<sub>2</sub> sensors using them are not known.

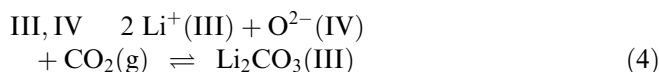
It was tried repeatedly to make sensors in which stabilized ZrO<sub>2</sub>, an oxide ion-conducting solid electrolyte, is sandwiched between the electrodes and carbonate (cells no. 3 and 13), Nasicon (cell no. 7) or β-alumina (cell no. 8). The quite different results of the different authors are based on the reactions at the interfaces between the anion and cation conductors that were used. These reactions depend on whether the cation conductor covers the anion conductor in a gastight manner or is porous and thus the interface is exposed to the gas which surrounds the sensor. A third case is present when the same gas surrounds the contact between the ion conductors and the electrode on the oxide ion conductor (cell no. 3). The gas sensitivity of the contacts between a potassium and an oxide ion conductor was already recommended for the measurement of SO<sub>x</sub> and CO<sub>2</sub> (in “contact gauges”) and discussed in papers from 1978 to 1985 [28, 29, 30, 31].

Cells no. 13 and no. 14 will be compared here. In the cell no. 13 the five electrically conducting phases, I, II, III, IV and I', are placed in series and the metallic gold phase touches only the Li<sub>2</sub>CO<sub>3</sub> that was deposited and

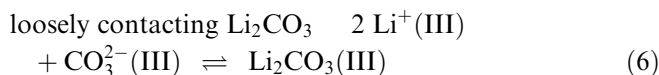
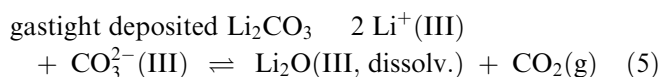
quenched from a melt, and not the oxide ion conductor. When the phases III and IV are in gastight contact, the following reactions take place between phases II and I':



If the Li<sub>2</sub>CO<sub>3</sub> covers the oxide ion conductor only loosely so that the interface is exposed to the CO<sub>2</sub>-containing gas, then the reaction at the III,IV interface changes:



The summation of all reactions in the electrical circuit, i.e. the reactions between the phases II to I' and the electron transition reactions between the phases I, II and I', leads to different overall reactions:



The cell voltage depends on the CO<sub>2</sub> partial pressure in the first case, but not in the second. In the investigations of cell no. 14, the oxide ion conductor was contacted metallically on both sides and a carbonate or, in addition, a silicate was deposited on one side. The carbonate is, as the cell symbol indicates, in a side place and is not in the electric circuit. Hence, it does not have an effect on the cell voltage. Cell no. 14 is an oxygen concentration cell with a zero cell voltage, if the chemical potential of the oxygen is the same on both sides.

All sensor systems of Table 2 (apart from cell no. 14) have a CO<sub>2</sub>-sensitive carbonate electrode. Problems are caused mainly by the reference electrodes. In most of the systems the cell voltage depends on composition variables of the constituents of these electrodes. Only in the case of the gas concentration cells (cells no. 2–5 and 10) can the cell voltage be used for a direct analytical evaluation, if the oxygen partial pressure in the measuring gas and the gas concentrations at the reference electrode are known. In the other cases, calibrations are necessary because a thermodynamic relation is not known. The sensor signals in these cases are frequently not only dependent on the activity of a substance in a solid phase, but, similar to the gas concentration cells, also on the O<sub>2</sub> partial pressure in the measuring gas. In potentiometric sensors the alkali oxide activities in solid phases often remain relatively constant over a long time; however, their values depend on the preparation conditions of the

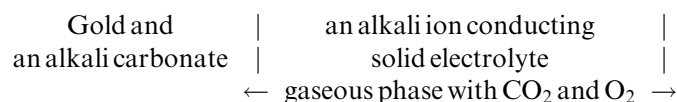
sensor. They vary particularly strongly under melting glasses and under the influence of water vapor. In Table 2, sensors are listed that exhibit a sufficient CO<sub>2</sub> sensitivity. However, because the reference electrodes with gas mixtures are awkward and the reference electrodes with solids have not a calculable or at least exactly reproducible potential and require repeated calibrations, all these sensor systems do not satisfy normal claims as modern devices.

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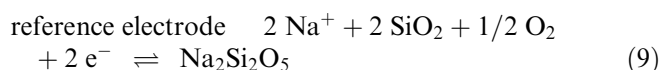
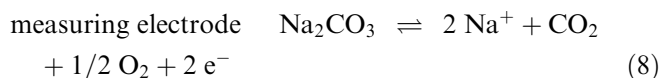
### Fundamentals of CO<sub>2</sub> sensors with reference electrodes composed of pure solid substances

The starting point for the development of basically improved CO<sub>2</sub> sensor systems was the thermodynamic investigation of the formation of sodium zirconate from ZrO<sub>2</sub> and sodium carbonate (cell no. 1 in Table 3). The three solid substances involved operate as pure phases so that the e.m.f. of the cell is determined by the thermodynamic standard quantities of these substances and the CO<sub>2</sub> concentration alone. The investigation of the cell was undertaken to determine the thermodynamic data. On the other hand, for corresponding cells with substances with known thermodynamic data, the cell voltage equation for CO<sub>2</sub> measurements is calculable. These fundamentals have been explained elsewhere (see e.g. [7, 8]).

The sensor type can be described generally with the cell symbol:



Galvanic solid electrolyte cells which correspond to this type are arranged in Table 3 with the cell symbol and cell reaction. The electrode reactions in cell no. 7 can be taken as an example:



If both electrodes are in the same gas, the effect of oxygen is compensated at equilibrium and O<sub>2</sub> does not appear in the overall reaction (see Table 3). For the electric potential difference between the electrodes of the galvanic cell for zero current, i.e. when all local charge transfer equilibria and chemical equilibria are established, in the following the term “equilibrium cell voltage” ( $U_{\text{eq}}$ ) is used. For  $U_{\text{eq}}$  of cell type (7) the general equation:

$$U_{\text{eq}} = U_{-\theta} + (RT/2F) \ln [\varphi(\text{CO}_2)p/p_{-\theta}] \quad (10)$$

is valid where  $U_{-\theta}$  is the standard cell voltage and  $p_{-\theta}$  is the standard pressure.

With the values of the MICROTHERM data bank [41] at standard pressure, the following equation holds within the temperature range 450–574 °C:

$$U_{\text{eq}}/\text{mV} = 437.9 - (0.7289 - 0.04309 \ln [\varphi(\text{CO}_2)])T/\text{K} \quad (11)$$

Figure 1 gives a summary of calculated standard cell voltages ( $U_{-\theta}$ ) of some interesting systems in dependence on the temperature. The standard cell voltages will be experimentally obtained only if all the solid substances involved in the cell reaction actually react at the temperature and pressure of the system in their pure states and in their stable modifications. No substance should decompose at the cell temperature and no solid solution should be involved in the cell reaction.

For comparison of measurements with variations of systems and concentrations, the subtraction of the concentration term of Eq. 10 from the measured voltages is useful. This means that the cell voltage is calculated assuming the validity of the ideal gas law for  $p_{-\theta}$  and  $\phi(\text{CO}_2)=1$ . In the following, presentations of results these voltages are marked by  $U_{-\theta}$  in the figures, although the requirement of the standard state of the solid phases may not be strictly fulfilled. The name for  $U_{-\theta}$  is set in parenthesis (“standard cell voltages”), if the standard states are not guaranteed.

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If all prerequisites for  $U_{-\theta}$  are given, the determination of the CO<sub>2</sub> concentration from the sensor signal measured in equilibrium is possible by using the general equation:

$$\varphi(\text{CO}_2) = \exp [2F(U_{\text{eq}} - U_{-\theta})/RT] \quad (12)$$

The standard cell voltage may have been determined from thermodynamic data or by electrochemical measurements.

Different, mainly practical, aspects of sensor type (7) are treated in the following.

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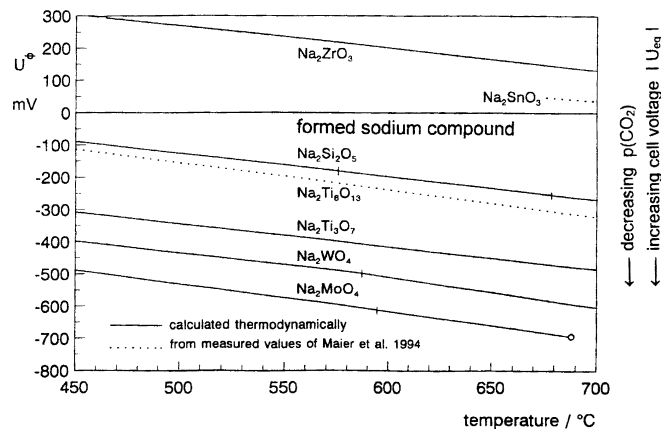
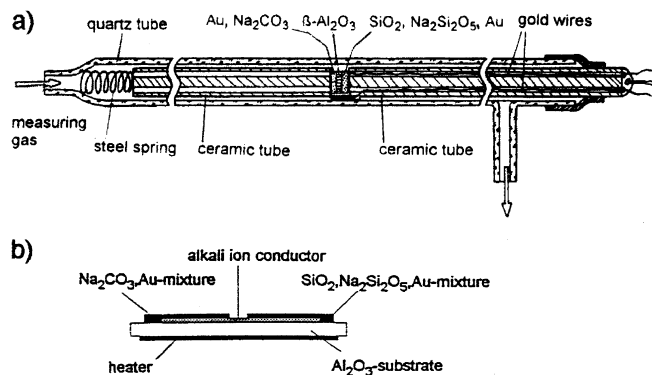
### Aspects of CO<sub>2</sub> sensors with reference electrodes composed of pure solid substances

Sensor construction

In the arrangement of the three main components of the sensors, two forms are realized:

**Table 3** Investigated CO<sub>2</sub> sensor systems with open reference electrodes, composed of pure solid substances

No.	Year	Cell symbol (measuring electrode   solid electrolyte   reference electrode)	ϑ/°C	Overall cell reaction (presumed)	Ref.
1	1986	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> ZrO <sub>3</sub> , ZrO <sub>2</sub> , Au]	325–825	ZrO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> ZrO <sub>3</sub> + CO <sub>2</sub>	[35]
2	1992	Au, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub>   Na <sub>2</sub> Y <sub>2</sub> Zr(PO <sub>4</sub> ) <sub>3</sub> or Na-β-Al <sub>2</sub> O <sub>3</sub>   Na <sub>2</sub> MoO <sub>4</sub> , MoO <sub>3</sub> , Au	320–500	MoO <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> MoO <sub>4</sub> + CO <sub>2</sub>	[7, 36]
3	1992	Au, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub>   Na <sub>2</sub> Y <sub>2</sub> Zr(PO <sub>4</sub> ) <sub>3</sub>   Na <sub>2</sub> WO <sub>4</sub> , WO <sub>3</sub> , Au	380–600	WO <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> WO <sub>4</sub> + CO <sub>2</sub>	[36]
4	1994	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> SnO <sub>3</sub> , SnO <sub>2</sub> , Au]	676–770	SnO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> SnO <sub>3</sub> + CO <sub>2</sub>	[5, 37]
5	1994	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> , TiO <sub>2</sub> , Au]	450–770	6TiO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> + CO <sub>2</sub>	[5, 37]
6	1994	Au, Na <sub>2</sub> CO <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub>   Nasicon   SiO <sub>2</sub> , ZrSiO <sub>4</sub> , ZrP <sub>2</sub> O <sub>7</sub> , Pt	ca. 500	SiO <sub>2</sub> + 3ZrSiO <sub>4</sub> + ZrP <sub>2</sub> O <sub>7</sub> + 3Na <sub>2</sub> CO <sub>3</sub> ⇌ 2Na <sub>3</sub> Zr <sub>2</sub> Si <sub>2</sub> PO <sub>12</sub> + 3CO <sub>2</sub>	[38]
7	1995	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na <sub>2</sub> Y <sub>2</sub> Zr(PO <sub>4</sub> ) <sub>3</sub> or Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , SiO <sub>2</sub> , Au]	450–670	2SiO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> + CO <sub>2</sub>	[7, 39]
8	1995	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> , Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> , Au]	350–750	Na <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ 2Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub> + CO <sub>2</sub>	[6]
9	1996	[Ni, Na <sub>2</sub> CO <sub>3</sub> ], H <sub>2</sub> , H <sub>2</sub> O, CO, CO <sub>2</sub> , N <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , SiO <sub>2</sub> , Ni]	575–750	2SiO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> + CO <sub>2</sub>	This work
10	1996	Au, CO <sub>2</sub> , O <sub>2</sub>   Na <sub>2</sub> CO <sub>3</sub>   Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , SiO <sub>2</sub>   Au	450–650	2SiO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> + CO <sub>2</sub>	[40]
11	1998	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , Na <sub>2</sub> SiO <sub>3</sub> , Au]	590–675	Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ 2Na <sub>2</sub> SiO <sub>3</sub> + CO <sub>2</sub>	This work
12	1998	[Au, Na <sub>2</sub> CO <sub>3</sub> , YSZ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , SiO <sub>2</sub> , YSZ, Au]	450–670	2SiO <sub>2</sub> + ZrO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> ZrSi <sub>2</sub> O <sub>7</sub> + CO <sub>2</sub>	This work
13	1998	[Au, Na <sub>2</sub> CO <sub>3</sub> ], CO <sub>2</sub> , O <sub>2</sub>   Na-β-Al <sub>2</sub> O <sub>3</sub>   [Na <sub>2</sub> Ge <sub>4</sub> O <sub>9</sub> , GeO <sub>2</sub> , Au]	400–720	4GeO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> ⇌ Na <sub>2</sub> Ge <sub>4</sub> O <sub>9</sub> + CO <sub>2</sub>	This work

**Fig. 1** Standard cell voltages  $U_0$  for various CO<sub>2</sub> sensors, calculated thermodynamically [41] or determined by evaluation of measurements [5], with vertical marks at the temperatures of the phase transitions**Fig. 2a, b** Solid state systems for the determination of CO<sub>2</sub>. **a** Arrangement of disks under spring pressure in a quartz tube [7, 42]. **b** Cross section of a planar CO<sub>2</sub> sensor [8]

1. The round discs are pressed together by springs in a tube heated from the outside (see e.g. Fig. 2a) and
2. The layers are on a planar target with the heater on the rear side (see e.g. Fig. 2b).

Both forms have been described in detail with their advantages and disadvantages for cell no. 7 (Table 3) [8].

For the planar design, the long-term stability of thin carbonate layers is generally problematic, due to the creeping property and the volatility of alkali carbonates (see below). To cope with the creeping, a special carbonate barrier between the electrodes was proposed [43]. Using discs permanently under spring pressure ensures good contacts and also long-term stability during gradual evaporation of the carbonate.

The discussed galvanic cells are reaction cells for which the temperature coefficients of the cell voltage are substantially larger than for concentration cells. For example, at the CO<sub>2</sub> concentration in normal air (365 vol ppm CO<sub>2</sub>), and at a cell temperature of 650 °C, this coefficient of a CO<sub>2</sub>, O<sub>2</sub> concentration cell is only

0.375 mV/K, but for the reaction cell with  $\text{SiO}_2$  it is 1.07 mV/K. If high measuring precision is needed, the axially symmetric heating of disc-shaped sensors in a tube is more favorable than the asymmetrical heating of planar arrangements with an electrode openly exposed to the measuring gas.

### Solid electrolytes

Reservations exist for the firstly applied  $\beta$ -alumina (cell no. 1 in Table 3), because for  $\beta$ -alumina ( $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$ ), and for the Na-richer  $\beta''$ -alumina ( $\text{Na}_2\text{O} \cdot 5 \text{Al}_2\text{O}_3$ ), reactions with  $\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  at low temperatures have been frequently described [44, 45]. In principle, every alkali ion conductor should lead to a  $\text{CO}_2$  sensor. Therefore Nasicon ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  in cell no. 6) or a substance similar to Nasicon [e.g.  $\text{Na}_2\text{YZr}(\text{PO}_4)_3$  in cells no. 2, 3 and 7], which is easy to prepare [46], were used. The Nasicon solid electrolytes, however, have not proved as stable in the long term. The measured signals of sensors on a  $\text{SiO}_2$  base with a Nasicon electrolyte fall below the expected cell voltages at temperatures below 540 °C in the course of weeks, and at temperatures above 580 °C within a few days [7]. This is probably caused by continuing chemical reactions of these solid electrolytes with the electrode substances.

Actually, constant signals from sensors on a  $\text{SiO}_2$  base at a constant temperature were obtained only by using  $\beta$ -alumina as the electrolyte. After 55 days the results measured between 600 and 670 °C still lay on a straight line near the thermodynamically calculated curve [7].

It is well known that potentiometric methods are also applicable with modern measuring instrumentation, if the cell resistance is high. Therefore working sensors are also obtained by using pressed discs, in which the  $\text{Na}_2\text{O}$  of  $\beta$ -alumina is depleted or  $\gamma$ -alumina is admixed for reduction of the reactivity [42]. Gastight discs of  $\alpha$ -alumina (an excellent electric isolator) with complete coverage by a  $\beta$ -alumina layer prepared by a known method [47, 48] have proved themselves.

However, the solid electrolyte also may be porous. Noble metal particles (nonconductingly connected with each other) can be introduced into the pores with a diluted noble metal solution to achieve a catalytic effect on the surrounding measuring gas [39].

The  $\text{CO}_2$  sensor function also remains unchanged when  $\beta$ -alumina or Nasicon are completely omitted (cell no. 10). The  $\text{SiO}_2$  is then converted completely to  $\text{Na}_2\text{Si}_2\text{O}_5$  with  $\text{Na}_2\text{CO}_3$  in a layer of the reference system. Since  $\text{Na}_2\text{Si}_2\text{O}_5$  is surely a  $\text{Na}^+$  ion conductor itself, there is therefore  $\text{Na}^+$  ion conduction between the metallic final phases at which the electrode reactions of Eqs. 8 and 9 proceed unchanged. However, without  $\beta$ -alumina between the electrode discs,  $\text{SiO}_2$  is exhausted relatively quickly by the chemical reaction with  $\text{Na}_2\text{CO}_3$ , and the reference system is destroyed.

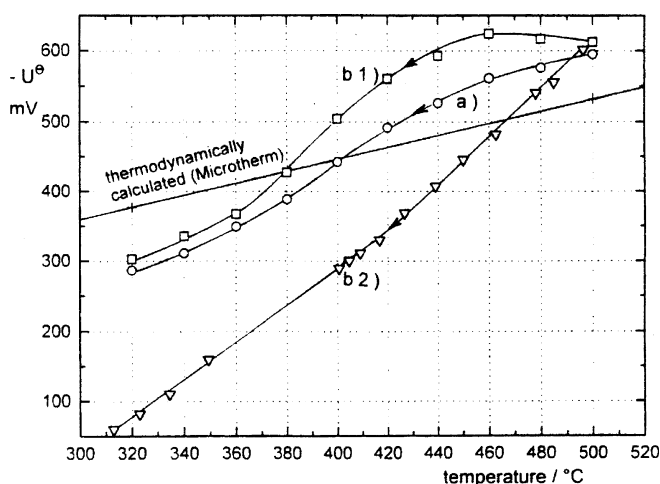
### Reference systems

#### $\text{ZrO}_2$

Galvanic cells with an electrode in which  $\text{ZrO}_2 + \text{Na}_2\text{ZrO}_3$  are used to fix a certain sodium oxide activity at the surface of the solid electrolyte were proposed following a thermodynamic investigation [35] as the first of a new type of sensors for the measurement of  $\text{CO}_2$  [5, 49]. However, cells with this reference system are not suitable for practical applications because  $\text{Na}_2\text{ZrO}_3$  is decomposed chemically at the operational temperature of the sensor in air with a normal  $\text{CO}_2$  concentration. The overall reaction no. 1 in Table 3 proceeds spontaneously backwards in ordinary air.

#### $\text{MoO}_3$

In the reference systems, particles of five phases have to react with each other in the electrochemical equilibrium (see Eq. 9). Therefore, it was suspected that a particularly reactive oxide like  $\text{MoO}_3$  could lead to a  $\text{CO}_2$  sensor utilizable at low cell temperatures. Above 250 °C a quite simple arrangement with  $\text{MoO}_3$  {discs consisting of the solid electrolyte  $\text{Na}_2\text{YZr}(\text{PO}_4)_3$  with gold nets, which were spread with aqueous suspensions, on one side containing  $\text{MoO}_3$  and on the other one containing  $\text{Na}_2\text{CO}_3$  [7, 36], i.e. cell no. 2 in Table 3} actually responds to  $\text{CO}_2$  concentration changes in the surrounding gas. The calculated "standard cell voltages" and their temperature dependence, however, did not agree with the results calculated thermodynamically for the expected overall reaction with  $\text{MoO}_3$  and  $\text{Na}_2\text{MoO}_4$  (curve a in Fig. 3). In the disc arrangement (Fig. 2a) a similar curve results when using  $\beta$ -alumina instead of  $\text{Na}_2\text{YZr}(\text{PO}_4)_3$  (curve b1 in Fig. 3) and a strong alteration at repetition of the measurement (curve b2). From



**Fig. 3** "Standard cell voltages" of a  $\text{CO}_2$  sensor containing  $\text{MoO}_3$  in the reference electrode. Results obtained (a) with the solid electrolyte  $\text{Na}_2\text{YZr}(\text{PO}_4)_3$ , (b) with  $\beta\text{-Al}_2\text{O}_3$  for the measurements 1 and 2. The thermodynamically calculated curve [41] is valid for  $\text{MoO}_3$ ,  $\text{Na}_2\text{MoO}_4$  (cell no. 2 in Table 3)

the literature [50], compounds are known of  $\text{Na}_2\text{O}$  with 1, 2, 3 and 4  $\text{MoO}_3$ . The system shows high sensitivity to  $\text{CO}_2$  concentration changes, but a certain stable standard cell voltage does not exist, probably because of decomposition reactions.

### $\text{WO}_3$

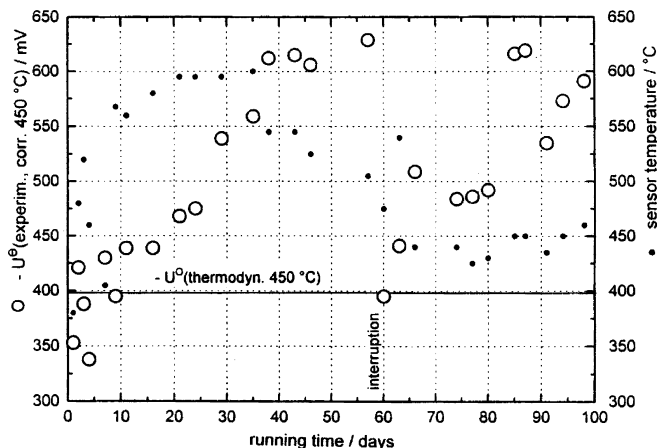
In the simple arrangement described for  $\text{MoO}_3$ , orientating measurements were also carried out with tungsten oxide for more than 3 months in air at temperatures between 380 and 605 °C (cell no. 3 in Table 3). For comparison of the results the “standard cell voltage” for 450 °C was calculated with the thermodynamically expected temperature function. In Fig. 4 the results obtained and the respective operational temperatures of the sensor are shown versus the operation days. High responsivity on changes of the  $\text{CO}_2$  concentration was observed over a long time. However, the “standard cell voltage”, calculated for 450 °C, increased at cell temperatures up to 600 °C and also after an interruption, when the cell was kept constant near 450 °C. Compounds of  $\text{Na}_2\text{O}$  are known with 1, 2, 4 and 8  $\text{WO}_3$  [50]. Evidently, sensors with  $\text{WO}_3$  resemble very much those with  $\text{MoO}_3$ .

### $\text{SnO}_2$

Results concerning the system  $\text{SnO}_2$ ,  $\text{Na}_2\text{SnO}_3$  have been published for the temperature range 675–770 °C (cell no. 4 in Table 3). The authors found that a better performance was achieved using the reference system with  $\text{TiO}_2$  [5].

### $\text{TiO}_2$

The  $\text{CO}_2$  sensor system based on  $\text{TiO}_2$  has been examined between 300 and 750 °C (cell no. 5 in Table 3) in



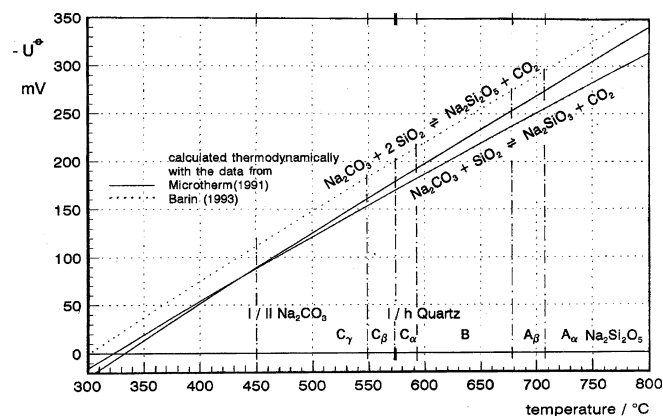
**Fig. 4** “Standard cell voltages” of a  $\text{CO}_2$  sensor containing  $\text{WO}_3$  in the reference electrode (after conversion at 450 °C). The thermodynamically calculated curve [41] is valid for  $\text{WO}_3$ ,  $\text{Na}_2\text{WO}_4$  (cell no. 3 in Table 3)

which Nernstian behavior was found in the range from 0.7 to 1000 mbar  $\text{CO}_2$  partial pressure [5, 6, 51, 52]. Noticeable deviations occurred below 400 °C. The sensor signals were independent of the  $\text{O}_2$  partial pressure, at least above 500 °C. Similar results were obtained when, as well as  $\text{Na}_2\text{Ti}_6\text{O}_{13}$ , not  $\text{TiO}_2$  but the  $\text{TiO}_2$ -poorer sodium compound  $\text{Na}_2\text{Ti}_3\text{O}_7$  coexisted in the reference system (cell no. 8 in Table 3).

### $\text{SiO}_2$

The use of  $\text{SiO}_2$  promises the advantage that  $\text{CO}_2$  measurements should also be possible in strongly reducing gases without the danger of destroying the reference system. The phase diagram of the system  $\text{Na}_2\text{O}-\text{SiO}_2$  [53, 54] and the phase transformations and thermodynamic data of the substances for  $\text{CO}_2$  sensors based on  $\text{SiO}_2$  are well known (Fig. 5). The compound with the highest content of  $\text{SiO}_2$  in this system is  $\text{Na}_6\text{Si}_8\text{O}_{19}$  [55], but this compound only exists between 700 and 800 °C. Below 700 °C,  $\text{Na}_2\text{Si}_2\text{O}_5$  is the sodium silicate with the highest  $\text{SiO}_2$  content.  $\text{Na}_2\text{Si}_2\text{O}_5$  is polymorphous, with different transition phenomena between the modifications [56]. The standard cell voltages calculated on the basis of the data of Barin [57] show a difference from those calculated with the MICROTHERM data bank [41]. The discrepancy is based on differences only in the data for  $\text{Na}_2\text{Si}_2\text{O}_5$ . For the reaction to give  $\text{Na}_2\text{SiO}_3$ , both sources give agreeing curves with a slightly smaller slope than for  $\text{Na}_2\text{Si}_2\text{O}_5$  (see Fig. 5).

For the manufacture of the  $\text{SiO}_2$  reference discs, gold powder and a colloidal  $\text{SiO}_2$  solution or amorphous  $\text{SiO}_2$  (used as purchased according to the German Pharmacopoeia) and dispersed in some water were mixed with the quantity of  $\text{Na}_2\text{CO}_3$  stoichiometrically required for converting about 10% of the  $\text{SiO}_2$  to  $\text{Na}_2\text{Si}_2\text{O}_5$ . After drying, the discs were prepared with a simple press.

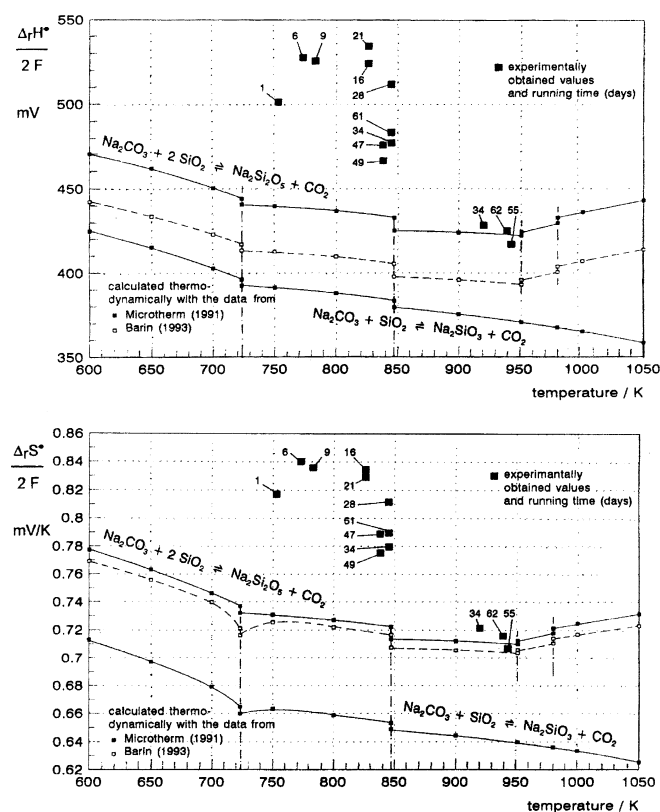


**Fig. 5** Phase transitions and thermodynamically calculated standard cell voltages ( $U^0$ ) for the sensor system  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$

The measurements of the temperature dependence of the “standard cell voltage”, performed between 280 and 750 °C over a period of 1–62 days with  $\beta$ -alumina as the solid electrolyte and with 286 vol ppm  $\text{CO}_2$  in the gaseous phase, yielded too low results below 450 °C [8]. There were considerably scattered results also in the range up to the transformation of the low- to the high-temperature quartz at 574 °C. Results which narrowly followed the curve calculated with the MICROTHERM data occurred only above 574 °C. To decide on the necessary measuring range, the middle straight lines through the “standard cell voltages” obtained in the two temperature ranges were calculated and the enthalpy term and the entropy factor taken from the equation:

$$U\theta = (\Delta_r H \theta / 2F) - (\Delta_r S \theta / 2F)T \quad (13)$$

The results are depicted in Fig. 6a and Fig. 6b. The passed operating times of the sensor are written beside the values obtained; the values are assigned to the temperatures at which the sensor was tempered between the measurements. The results expected thermodynamically were found only in the higher temperature range. Obviously  $\text{Na}_2\text{Si}_2\text{O}_5$  is formed. The system is better

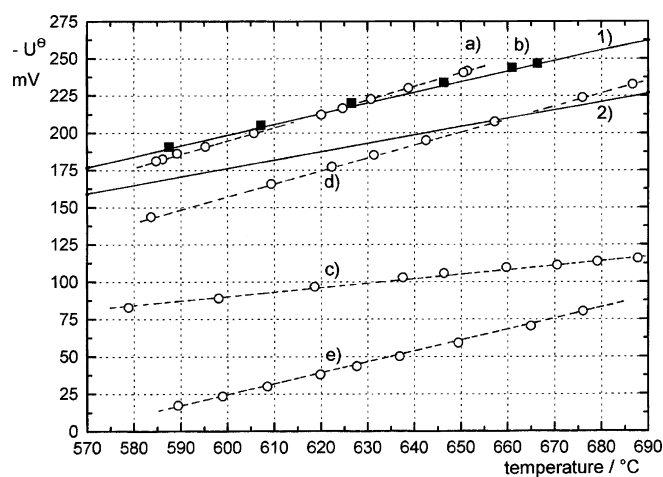


**Fig. 6** The thermodynamically calculated enthalpy parts and entropy factors from the equations for the standard cell voltage of galvanic cells formed with  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$  from 600 to 1050 K and the results obtained from a sensor with  $\beta$ -alumina as the solid electrolyte and with a cell temperature, growing stepwise over 9 weeks, taken from the mean straight line through measuring values  $U\theta(T)$  and drawn against the cell temperature kept previously

described by MICROTHERM than by Barin. In the higher temperature range of 574–678 °C, Eq. 11 is valid with slightly different numbers. With the MICROTHERM thermodynamic data [41] there results:

$$U_{\text{eq}}/\text{mV} = 423.8 - (0.7120 - 0.04309 \ln [\varphi(\text{CO}_2)])T/\text{K} \quad (14)$$

The measurements on the first day of operation yielded “standard cell voltages” on a straight line, which was slightly steeper than the thermodynamically calculated one (line a in Fig. 7), probable because the substances used were not completely in their crystalline state. Results were then observed for a long time near the curve calculated theoretically (line b, Fig. 7). Heating the sensor up to temperatures above 700 °C led quickly to results that did not agree with the thermodynamic expectations, particularly when colloidal  $\text{SiO}_2$  solutions were used (line c, Fig. 7). If the reference discs were separately pre-annealed at 800–820 °C to transform  $\text{SiO}_2$  and  $\text{Na}_2\text{Si}_2\text{O}_5$  into their high-temperature modifications, then the reactivity of the substances was reduced apparently so much that the expected results were not reached (line d, Fig. 7). The same annealing was used to completely convert  $\text{SiO}_2$  with  $\text{Na}_2\text{CO}_3$  to a mixture of  $\text{Na}_2\text{Si}_2\text{O}_5$  and  $\text{Na}_2\text{SiO}_3$ . The cell with that mixture as the reference system (cell no. 11 in Table 3) corresponds to that with the two sodium titanates already examined (cell no. 8 in Table 3). However, the reactivities of the two sodium silicates were obviously strongly reduced by the annealing process and the measured results (line e, Fig. 7) did not reach the thermodynamically calculated standard cell voltages for a sensor with such a reference system (line 2, Fig. 7).



**Fig. 7** “Standard cell voltages” of  $\text{CO}_2$  sensors prepared with  $\text{SiO}_2$  and  $\text{Na}_2\text{CO}_3$ . Results (a) on the first and (b) on the 62nd operating day, (c) in the case of using colloidal  $\text{SiO}_2$  after heating to 750 °C, (d) in the case of using amorphous  $\text{SiO}_2$  and sintering at 820 °C before mounting in the sensor, (e) in the case of forming a mixture of  $\text{Na}_2\text{Si}_2\text{O}_5$  and  $\text{Na}_2\text{SiO}_3$  by using amorphous  $\text{SiO}_2$  and  $\text{Na}_2\text{CO}_3$  and sintering at 820 °C before mounting in the sensor (cell no. 11 in Table 3). The solid lines are calculated thermodynamically for (1)  $\text{SiO}_2$ ,  $\text{Na}_2\text{Si}_2\text{O}_5$  and (2)  $\text{Na}_2\text{Si}_2\text{O}_5$ ,  $\text{Na}_2\text{SiO}_3$



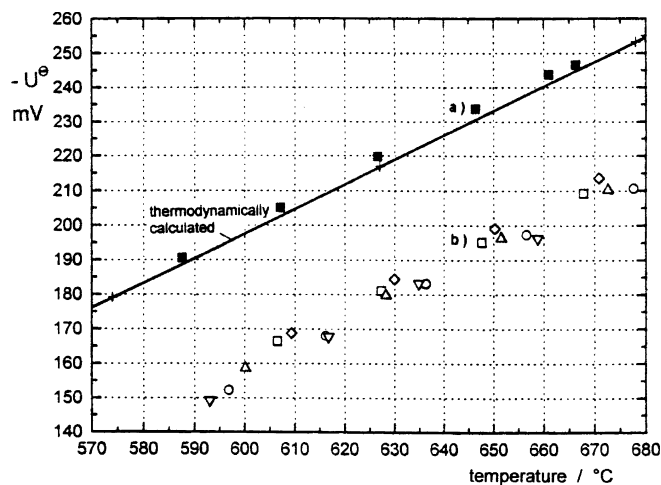


Fig. 8 “Standard cell voltages” of CO<sub>2</sub> sensors with reference electrodes, prepared with SiO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> (a) without and (b) with addition of YSZ (cell no. 12 in Table 3)

Because oxygen plays a role in the reference electrode reaction, it was checked whether the properties of the reference electrode may be influenced favorably by adding an oxide ion conductor. However, the admixture of fine YSZ particles (cell no. 12 in Table 3) led to ca. 40 mV smaller standard cell voltages in several investigations (points b, Fig. 8). YSZ probably reacts with components of the reference system and changes this by the formation of compounds such as Na<sub>2</sub>ZrO(SiO<sub>4</sub>), Na<sub>4</sub>Zr<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub> or Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub>, which were found in the system Na<sub>2</sub>O-SiO<sub>2</sub>-ZrO<sub>2</sub> [58]. No thermodynamic data are available for the calculation of a numerical value equation for CO<sub>2</sub> sensors with YSZ in the reference system. The same is valid for cell no. 6 in Table 3 with a mixture of SiO<sub>2</sub>, ZrSiO<sub>4</sub> and ZrP<sub>2</sub>O<sub>7</sub>, which can react with Na<sub>2</sub>CO<sub>3</sub> forming the used solid electrolyte Nasicon.

The results presented here demonstrate that, in the arrangement and operation of CO<sub>2</sub> sensors, several mistakes can be made which are only detectable by the comparison with results from thermodynamic calculations. On the other hand, it could be seen that under certain conditions the measuring results agree well for a long time with the results calculated thermodynamically. This means that with the investigated sensor system under certain conditions, CO<sub>2</sub> can be measured

driftlessly without calibration on the basis of a thermodynamically well-founded cell voltage equation. In Fig. 9 an example of a typical CO<sub>2</sub> measurement is presented that was obtained using a CO<sub>2</sub> sensor with a SiO<sub>2</sub>, Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> reference electrode.

### GeO<sub>2</sub>

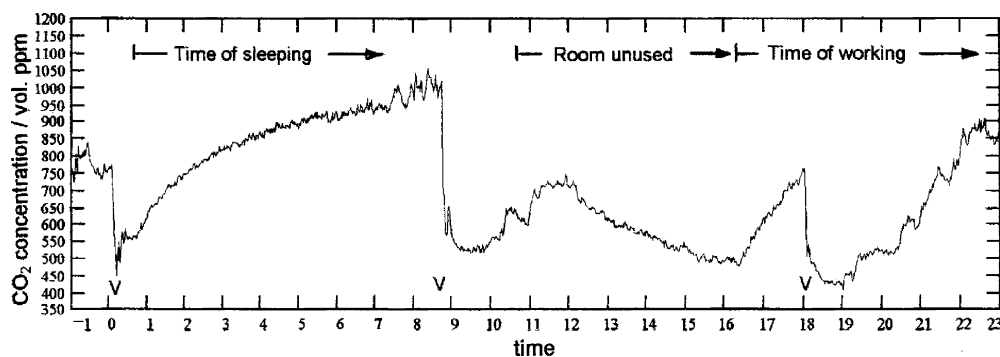
As in other cases, a mixture of GeO<sub>2</sub> with a substoichiometric quantity of Na<sub>2</sub>CO<sub>3</sub> was prepared. In the heating process of the cell (cell no. 13 in Table 3), those sodium compounds are formed that are thermodynamically stable under the given conditions: Na<sub>2</sub>O forms with an excess of GeO<sub>2</sub> the compound Na<sub>2</sub>Ge<sub>4</sub>O<sub>9</sub> and with less GeO<sub>2</sub> the compounds Na<sub>2</sub>Ge<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>GeO<sub>3</sub> [59]. Therefore it is probable that the hygroscopic Na<sub>2</sub>Ge<sub>4</sub>O<sub>9</sub> will be formed. Favorable results were obtained between 400 and 525 °C (Fig. 10). Already at 410 °C a high responsivity to CO<sub>2</sub> was observed. Above 525 °C the “standard cell voltages” deviate from the straight line and above approx. 640 °C changes which indicate phase transformations or composition changes were observed. However, thermodynamic data for sodium germanates are not known so that no check is yet possible on this base.

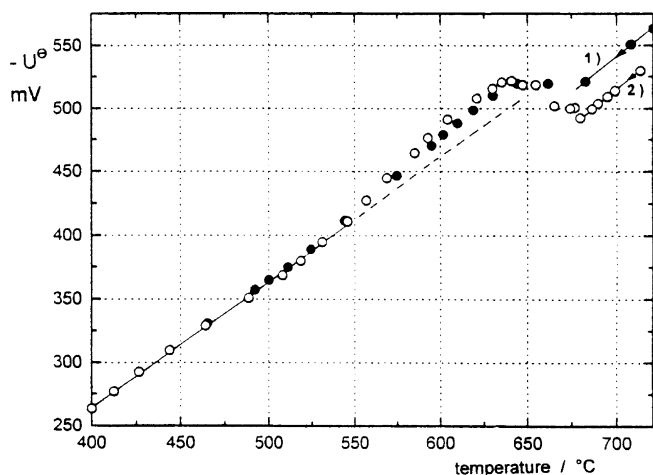
### The measuring electrode

The measuring electrode for CO<sub>2</sub> sensors can be realized with a pressed mixture of gold powder and Na<sub>2</sub>CO<sub>3</sub> and also with compact gold material (e.g. net or sheet) on a pure Na<sub>2</sub>CO<sub>3</sub> body. Without any effect on the sensor signal the sodium ions in the electrode reaction (Eq. 8) are exchanged in one case directly with the solid β-alumina electrolyte and in the other case exclusively with Na<sub>2</sub>CO<sub>3</sub>, which itself is a Na<sup>+</sup> conducting solid electrolyte.

The stability of the measuring electrode is primarily dependent on the persistence of sodium carbonate in resting or flowing measuring gas. For a long time it has been known that Na<sub>2</sub>CO<sub>3</sub> (m.p. 852 °C) decomposes (or volatilizes) at temperatures not expected on the basis of thermodynamic data [60]. A slight decomposition at 400 °C was noticeable after one day (found by titration

Fig. 9 CO<sub>2</sub> concentration in the course of 24 h in the air of a room (60 m<sup>3</sup>) in which a person slept at night, in which nobody stayed during the day and in which a person worked in the evening (V = ventilation of the room by opening a window). Measurements by the author with a self-made tubular CO<sub>2</sub> mini solid electrolyte sensor

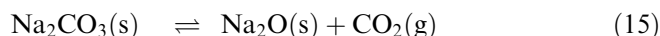




**Fig. 10** “Standard cell voltages” of a CO<sub>2</sub> sensor with a reference electrode containing GeO<sub>2</sub> and sodium germanate (probably Na<sub>2</sub>Ge<sub>4</sub>O<sub>9</sub>, cell no. 13 in Table 3) formed with Na<sub>2</sub>CO<sub>3</sub> during heating to 720 °C on the first and second operating days

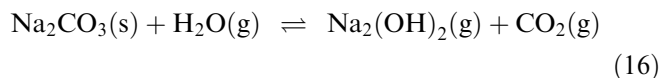
of NaOH after precipitating the carbonate with excess BaCl<sub>2</sub> solution [61].

For the decomposition reaction:



the thermodynamic calculation for 600 °C [57, 62] led to  $\phi(\text{CO}_2) = 2.82 \times 10^{-6}$  vol ppm. Therefore, decomposition under normal air (365 vol ppm CO<sub>2</sub>) cannot be expected.

As the cause of the observed mass loss, the reaction with steam was investigated [60, 61]. H<sub>2</sub>O forms NaOH (m.p. 321.8 °C) that, according to current knowledge, exists as a dimer in the gas state:

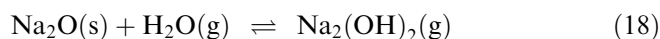


The equilibrium constant for this reaction follows from the thermodynamic data [57] at 600 °C:

$$\begin{aligned} K(600 \text{ }^\circ\text{C}) &= p(\text{CO}_2)p(\text{Na}_2(\text{OH})_2)/p(\text{H}_2\text{O}) \\ &= 1.07 \times 10^{-13} \end{aligned} \quad (17)$$

With that value the equilibrium concentration of Na<sub>2</sub>(OH)<sub>2</sub> above pure Na<sub>2</sub>CO<sub>3</sub> in normal air with 80% humidity at 25 °C (25,006 vol ppm H<sub>2</sub>O) is only  $7.34 \times 10^{-6}$  vol ppm, a value too small for explaining the volatility of Na<sub>2</sub>CO<sub>3</sub> in an air stream.

For Na<sub>2</sub>O (m.p. 920 °C, b.p. 1275 °C, estimated vapor pressure at 727 °C ca.  $10^{-15}$  bar [63]) the following reaction needs to be considered:



In an air stream with 80% humidity at 25 °C the equilibrium concentration over pure Na<sub>2</sub>O at 600 °C ( $K = 0.0402$ ) amounts to 1006 vol ppm Na<sub>2</sub>(OH)<sub>2</sub>. Above the Na<sub>2</sub>O in β-Al<sub>2</sub>O<sub>3</sub> in equilibrium with Na<sub>2</sub>CO<sub>3</sub> (see Eq. 20 below), this concentration is surely much smaller

because there the activity of Na<sub>2</sub>O is considerably smaller than 1. However, an effect of contact with β-Al<sub>2</sub>O<sub>3</sub> on the volatility of Na<sub>2</sub>CO<sub>3</sub> seems possible.

In more recent investigations it was found that the volatility of Na<sub>2</sub>CO<sub>3</sub> is increased substantially in mixtures with BaCO<sub>3</sub> [13]. This observation leads to the assumption that Na<sub>2</sub>CO<sub>3</sub> in a thin layer evaporates more easily than as a compact substance. Alkali carbonates creep over all oxide layers which also exist on all noble metals (and disappear here only under reducing gases). Therefore very thin layers of Na<sub>2</sub>CO<sub>3</sub> are formed permanently at increased temperatures on the surface of admixtures and adjacent solid matter. At present the sublimation pressure of Na<sub>2</sub>CO<sub>3</sub> is not known. It is well known from the thermodynamics of interface equilibria that vapor pressures rise for highly dispersed substances. The undesirable volatilization may be accelerated by reaction of gaseous Na<sub>2</sub>CO<sub>3</sub> according to Eq. 16.

For achieving aims such as high gas perviousness, it is possible that porous particles of MgO or YSZ could be added to the material of the measuring electrode discs without influencing the sensor signal. However, with such additions the discussed volatility affects the long-term operation and the sensor then fails due to high internal resistance.

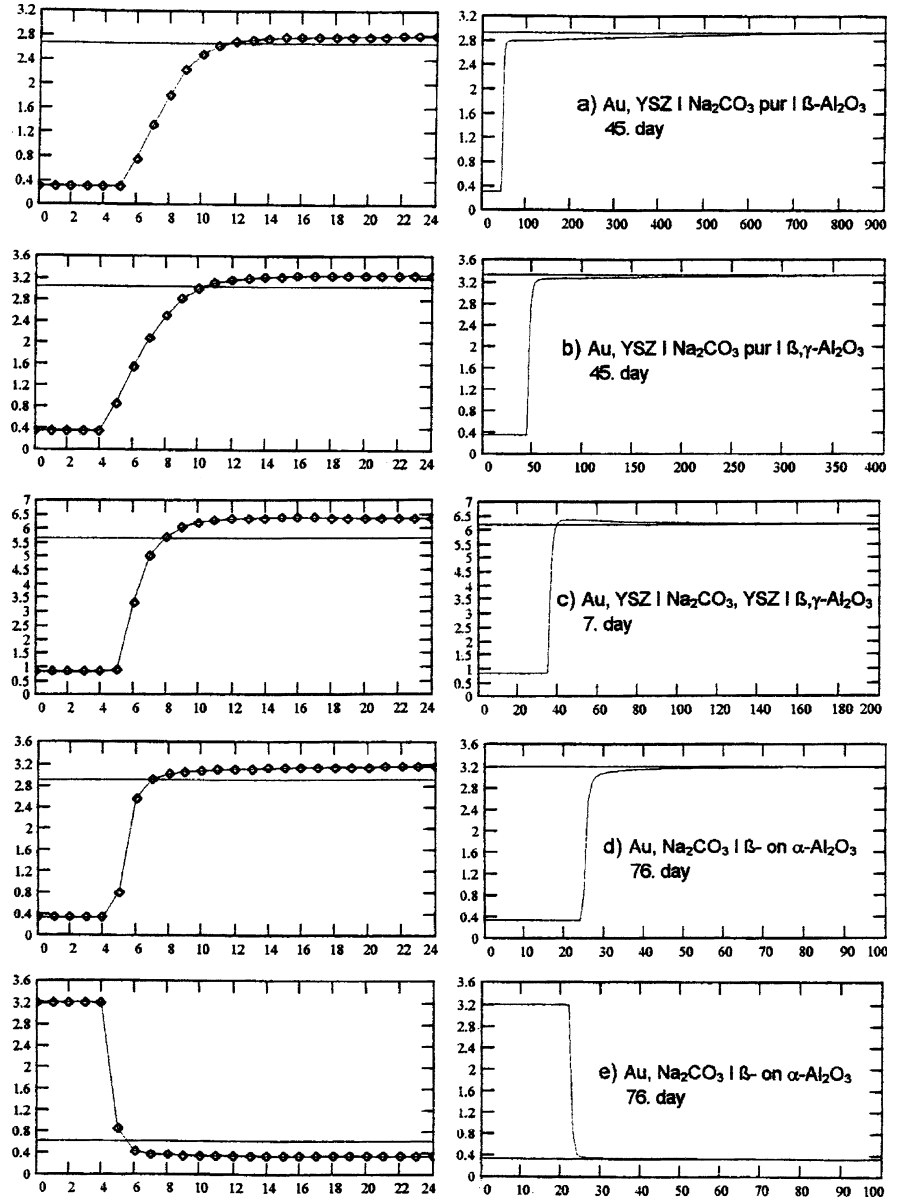
The conductivity of Na<sup>+</sup> ions in the carbonate phase can be increased by approximately two decades by adding 10–20 mol% SrCO<sub>3</sub> [12, 64]. For a sensor with such a mixed carbonate, cell voltages were observed which were strictly on a straight line at heating up or cooling down in the range from 585 to 670 °C. The responsiveness remained high. Because of the reduced activity of the Na<sub>2</sub>CO<sub>3</sub>, the absolute values of the standard cell voltages were, as expected, smaller (less than 10 mV) than in the case of using pure Na<sub>2</sub>CO<sub>3</sub>. In long-term use, particularly in flowing measuring gas, the cell resistance here also increased, because Na<sub>2</sub>CO<sub>3</sub> is lost and SrCO<sub>3</sub> remains with a high resistance.

It is conceivable that the gold particles were covered with a tight layer of the creeping Na<sub>2</sub>CO<sub>3</sub> and due to this the reaction with the gaseous phase is inhibited at the measuring electrode. To keep the junction lines between gold and Na<sub>2</sub>CO<sub>3</sub> accessible to the gaseous phase for a long time, the measuring electrode was built up of two discs consisting of the powder mixtures Au + YSZ and Na<sub>2</sub>CO<sub>3</sub> + YSZ (Fig. 11c).

#### Conditioning period and response time

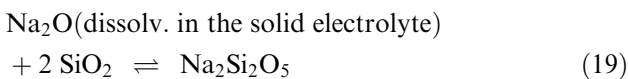
After switching on the heating, CO<sub>2</sub> sensors need a relatively long time before they can be calibrated or used without calibration (see Table 1). Then, if possible, they are kept permanently at the operational temperature. For many practical applications the continuous operation is necessary anyway. However, for devices used only occasionally, a long conditioning period is a disadvantage.

**Fig. 11** CO<sub>2</sub> concentrations measured with differently arranged CO<sub>2</sub> measuring electrodes when the gas is suddenly changed. On the *left side*, CO<sub>2</sub> concentrations measured in 1 s clock frequency are shown (the *line* marks 90% of the whole concentration step). On the *right side*, concentration curves observed up to the final concentration values are shown (here the *line* marks 100% of the concentration step). Time in seconds

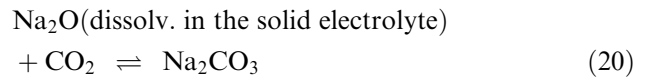


The reason for the long conditioning period is probably the sluggishness of the chemical reactions between the substances in the electrodes and the solid electrolyte. At first, the Na<sub>2</sub>CO<sub>3</sub> incorporated in the reference disc must be exhausted completely. Following this, the chemical equilibria at the interfaces must be established. In the closely related structures of the solid electrolyte β-Al<sub>2</sub>O<sub>3</sub>, the ratio Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> is variable [44, 45]. Na<sub>2</sub>O must be transported through the interfaces of the electrolyte so that, for example in the sensor with SiO<sub>2</sub>, the following chemical equilibria are established:

in the reference electrode:



in the measuring electrode:



Na<sub>2</sub>O must migrate either into or out of the solid electrolyte. The diffusion potential arising from the different mobilities of Na<sup>+</sup> and O<sup>2-</sup> ions in the solid electrolyte and the building up of the double layer charges at the interfaces may be responsible for the slow establishment of a final state. Hence, the cell voltage which is expected thermodynamically on the basis of the overall cell reaction is reached only gradually during the conditioning period.

Establishing the electrochemical equilibrium is independent of the CO<sub>2</sub> concentration on the side of the reference electrode, but, in accordance with Eq. 20, not

on the side of the measuring electrode. Owing to this, effects arise when the  $\text{CO}_2$  concentration changes. At first the electrical potential in the metal of the measuring electrode changes fast in accordance with reaction of Eq. 8 as a result of the changes of chemical potentials in the gaseous phase. Later, slow changes in and on the solid phases follow. If the  $\text{CO}_2$  concentration decreases, the  $\text{Na}_2\text{O}$  activity in the solid electrolyte must increase and  $\text{Na}_2\text{CO}_3$  is consumed. If  $\text{CO}_2$  increases, some  $\text{Na}_2\text{O}$  must leave the solid electrolyte and form  $\text{Na}_2\text{CO}_3$ .

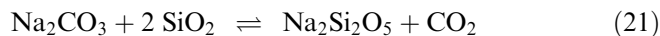
Because of these processes, after a sudden concentration step, about 90% of the following signal change occurs quickly; however, the final value is reached only slowly. Examples are presented in Fig. 11. For realizing a sudden concentration step a special cock was used, which allowed by a quick turn to switch from one flowing gas to another gas while keeping the flow rate constant. In most cases the cell voltages rose to the final value (very slowly in the case of the arrangement used for the results shown in Fig. 11a), but an over-swing to too large values and a gradual reduction was observed also (Fig. 11c). It is remarkable that the different  $t_{90}$  values measured with the used arrangements remained approximately constant over weeks. At one sensor,  $t_{90}$  was smaller than 2 s for months (Fig. 11d and e); other sensors had  $t_{90}$  of 6 s or more (e.g. Fig. 11a and b). Also,  $t_{90}$  was considerably shorter when the  $\text{CO}_2$  concentration was changed from high to low values than in the opposite case (compare Fig. 11d and e).

In investigations of a  $\text{CO}_2$  sensor with a  $\text{TiO}_2$ ,  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  reference electrode [51] the response times (achieved by fast evacuation of the gas chamber from 90 to 60 mbar) were in the range of 1–2 s ( $t_{90}$  ca. 0.8 s).

Clearly, the nature of the electrolyte determines to some extent the response times of the sensors (compare the results obtained with pure  $\beta$ -alumina, depicted in Fig. 11a, and with  $\beta$ - on  $\alpha$ -alumina, depicted in Fig. 11d and e). Further, the response times are influenced by the sensor geometry that determines the purging time during changing the gas, and finally it is the pore structure of the constituents of the measuring electrode and the tight coatings of  $\text{Na}_2\text{CO}_3$  creeping over gold particles that can affect these times. The experimental results are still insufficient for a quantitative description of the response behavior.

#### Cross sensitivities

Because the overall cell reaction is:



only gases which burn in the sensor and deliver  $\text{CO}_2$  should have an influence on the sensor signal. Actually, no essential effect could be found with water vapor, but effects were observed with alcohol vapor in the gas over wine or beer [8].

Also a small amount of  $\text{NH}_3$ -containing air injected in the stream of air passing the  $\text{CO}_2$  sensor caused sharp

changes of the sensor signal (Fig. 12). This cannot be explained on the basis of Eq. 21 but requires the consideration of the electrode reactions (Eqs. 8 and 9). Ammonia burns under consumption of oxygen at the electrodes with different rates, depending on the catalytic properties of the electrode layers. This causes different shifts of the chemical potentials of oxygen at the electrodes and thus their potentials are influenced differently. Consequently, the sensor signal changes when  $\text{NH}_3$  is added to the gas stream. Effects of hydrogen can be interpreted similarly.

The effects of the vapors of petrol, acetone and alcohols, due to different fast burning reactions at the electrodes, overlap with that of the increase of the  $\text{CO}_2$  concentration. Ozone causes an abruptly short effect. Nitrogen oxides disturb the sensor signals in an unclear way.

In contrast to the mentioned gases,  $\text{SO}_x$  and halogen-containing gases cause persistent malfunctions (see Figs. 13 and 14). In the sensor,  $\text{SO}_2$  and oxygen form sodium sulfate and chloroform vapor forms  $\text{HCl}$  and, finally, sodium chloride. Both salts lead to a long-term blocking of the sensor. Figure 14 shows that the sensor after passage of chloroform still reacts to injections of a little air which contains hydrogen, ammonia or petrol. Probably the reaction of Eq. 8 is disturbed only slightly, but reactions at the surface of the solid electrolyte are strongly changed.

To offer protection against interfering gases, it was recommended that a catalyst and a porous body made of  $\text{Na}_2\text{CO}_3$  are arranged in front of the sensor [42]. The

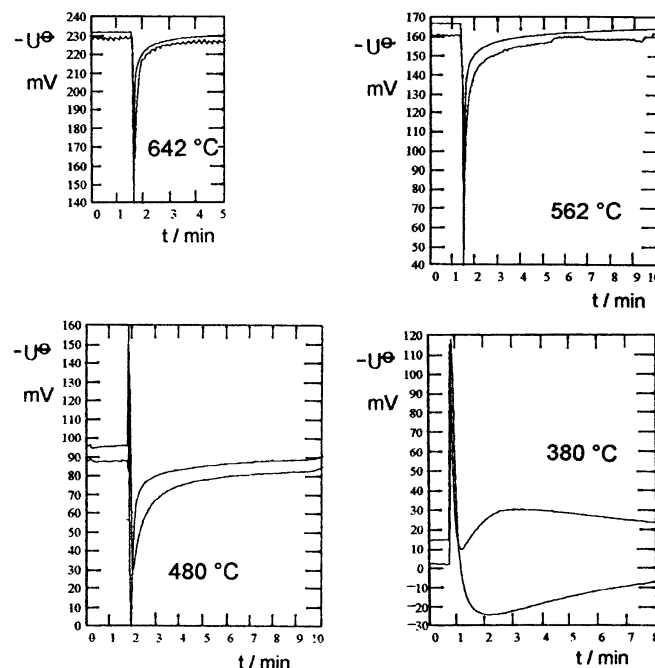
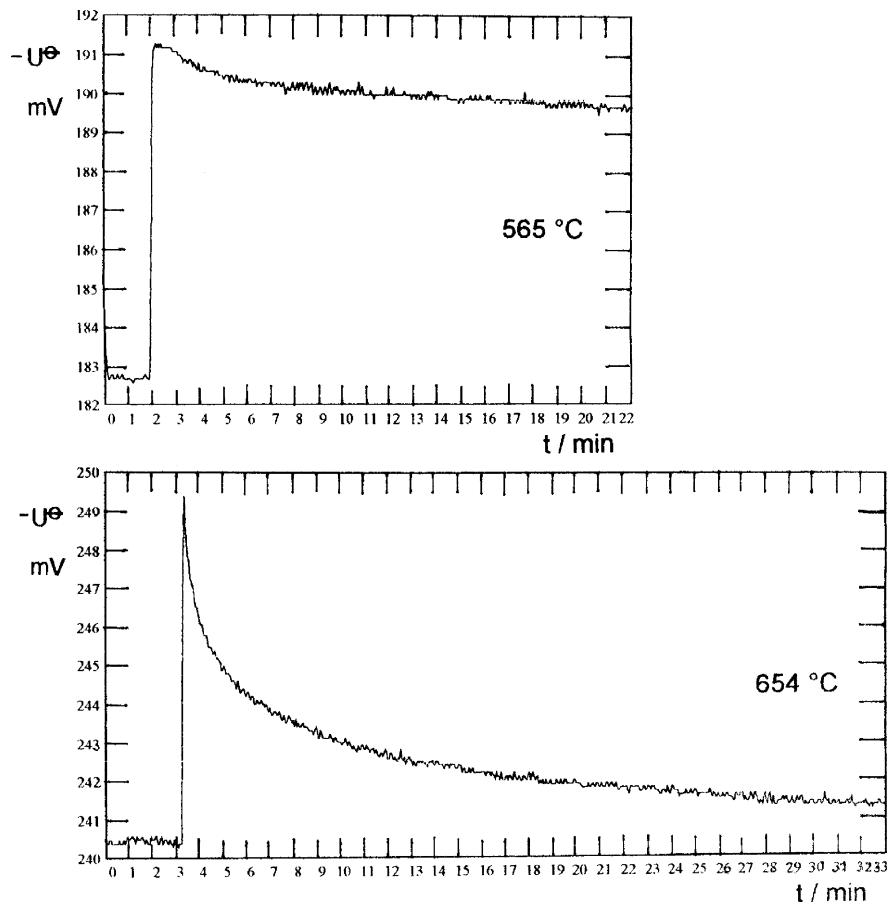
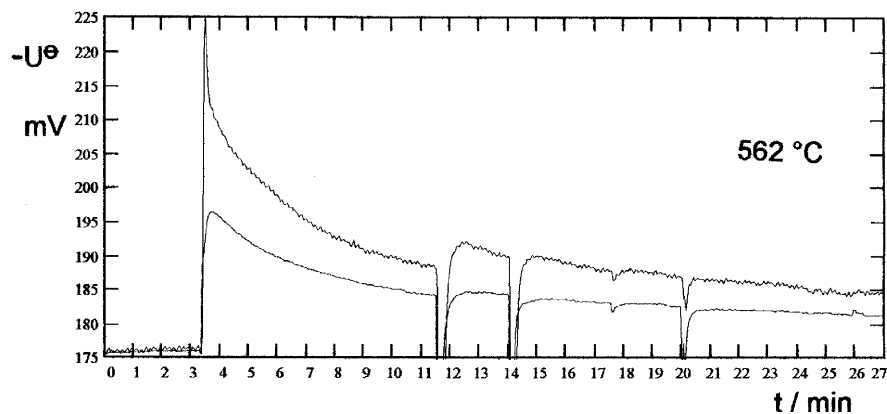


Fig. 12  $\text{CO}_2$  sensor signals for four tests with 0.5 mL  $\text{NH}_3$ -containing air (above an aqueous 25%  $\text{NH}_3$  solution at 22 °C), injected in a stream (2 L/h) of synthetic air with 4.02 vol%  $\text{CO}_2$  (after subtraction of the concentration term)

**Fig. 13** CO<sub>2</sub> sensor signals for tests with 0.5 mL SO<sub>2</sub>-containing air (above a saturated aqueous solution of sodium sulfite at 22 °C), injected in a stream (2 L/h) of synthetic air with 4.02 vol% CO<sub>2</sub> (after subtraction of the concentration term)



**Fig. 14** Signals for two differently aged CO<sub>2</sub> sensors arranged in parallel in a stream (2 L/h) of synthetic air with 286 vol ppm CO<sub>2</sub> (concentration term subtracted) after the injection of 0.5 mL air which stood over pure CHCl<sub>3</sub> at 21 °C, with later additional injections of 0.5 mL H<sub>2</sub> (twice), 0.5 mL NH<sub>3</sub>-containing air and 0.5 mL petrol vapor-containing air



usually small quantities of interfering gases are then oxidized and partly intercepted by the Na<sub>2</sub>CO<sub>3</sub>. The CO<sub>2</sub> formed is negligible in most of the measurement tasks.

### Measurements in reducing gases

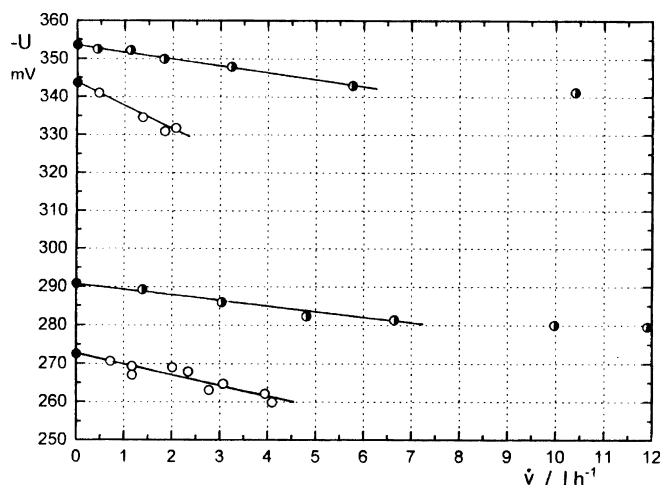
To check whether the sensor based on Na<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub> (Eq. 21) can also be used in reducing gaseous phases, a number of measurements in gas mixtures of CO<sub>2</sub>, CO, N<sub>2</sub> and H<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub> prepared at normal temperature

were carried out. The results of the investigations of cross sensitivities allowed understanding of the special requirements. In these gas mixtures the chemical gas equilibria must be reached in both electrode layers with equal oxygen partial pressures that are extremely small and strongly dependent on the temperature.

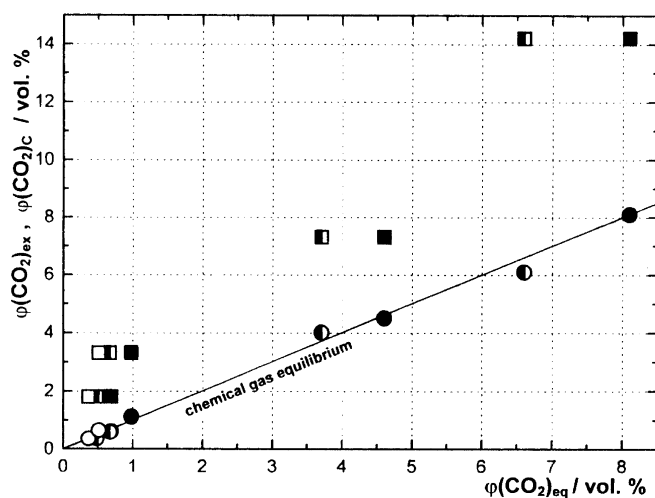
Sensors with gold electrodes did not provide any useful results. The signals were very sluggish under CO, CO<sub>2</sub>. Only with H<sub>2</sub>, and after moistening of the H<sub>2</sub>, N<sub>2</sub> partial stream, did the measuring results come closer to the expectations. However, the sensor signals show a strong dependence on the flow rate of the gas. If the gas

rested, the cell voltage rose quickly because in the hot cell the concentration of  $H_2$  increases and that of  $CO_2$  decreases due to thermal diffusion.

After these experiences a sensor was built with Ni instead of Au powder in the electrodes (cell no. 9 in Table 3). However, the catalytic effectiveness of nickel did not eliminate completely the dependence on the flow rate of the gas. Therefore the cell voltages were measured at different flow rates and extrapolated to quiet conditions. Some results of these investigations are presented in Fig. 15. With the extrapolated values,  $CO_2$  concentrations were calculated and for comparison are put together in Fig. 16 with those in the cold gas and in water-gas thermodynamically calculated for equilib-



**Fig. 15** Cell voltages of a  $CO_2$  sensor in water gas (open circles: without  $N_2$ ; half-closed circles: with 45.8 vol%  $N_2$ ) with various  $CO_2$  concentrations (from above to below: 0.69, 0.98, 4.64, 8.11 vol%  $CO_2$ ), measured at various flow rates of the gas stream at ca. 575 °C, and the extrapolation to the flow rate 0 L/h



**Fig. 16**  $CO_2$  concentrations in the cold gas mixture,  $\phi(CO_2)_c$  (squares), and  $CO_2$  concentrations,  $\phi(CO_2)_{ex}$  (circles), calculated with the values for 0 L/h, extrapolated from measured cell voltages (see Fig. 15) versus the  $CO_2$  concentrations in the equilibrated gas,  $\phi(CO_2)_{eq}$ , at 575 °C (closed symbols), 670 °C (half-closed symbols) and 750 °C (open symbols)

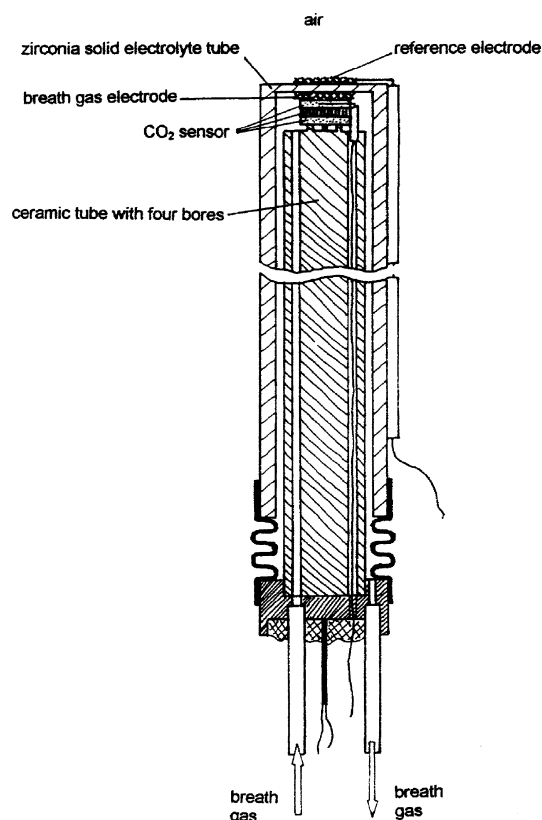
rium. The agreement is quite good. However, whether a sensor arrangement is possible for practical applications, e.g. in furnace gases for hardening processes, is still not clear.

### Problems of breath gas sensors

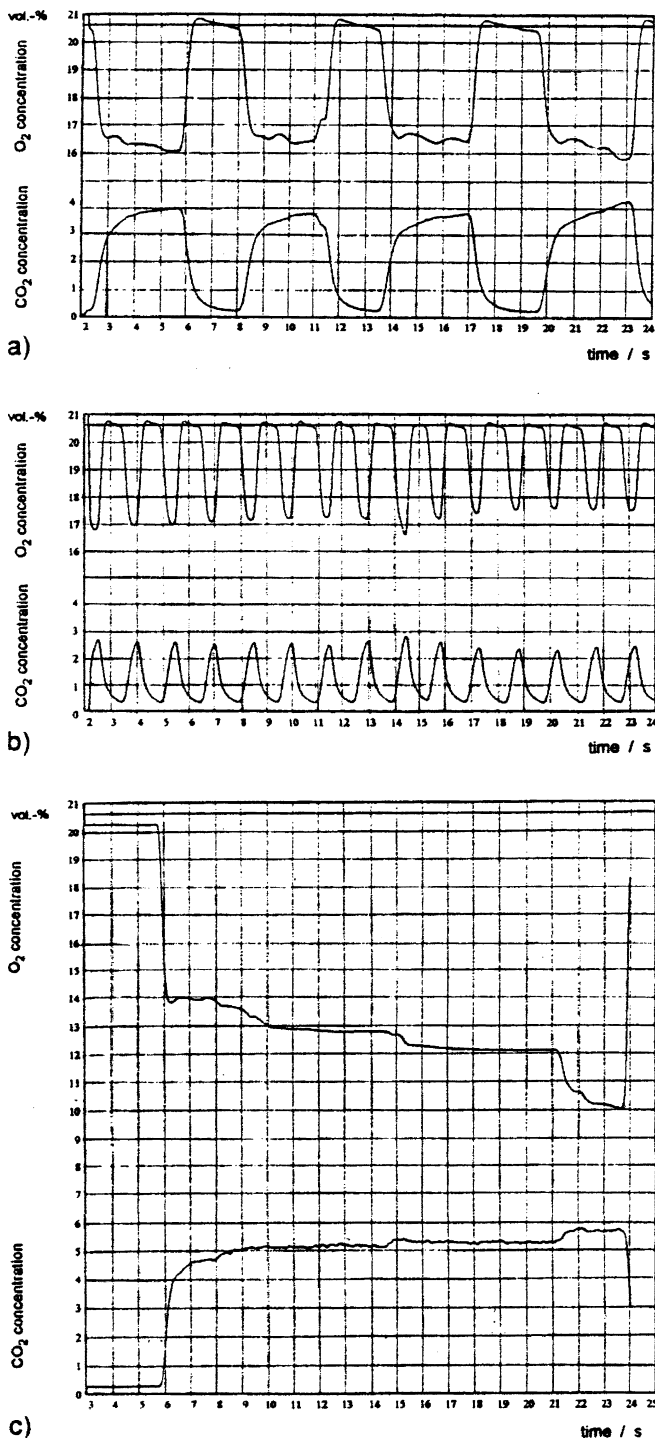
$CO_2$  sensors can be used in breath gas analysis. Measurements of the  $CO_2$  concentration in collected breath gas samples do not offer any problems. At present, for fast simultaneous  $CO_2$  and  $O_2$  measurements in real time in each breath, which is important for medical examinations, e.g. of athletes, divers, mountaineers or airplane staff, the continuously streaming gas samples are supplied in separate ways on separate equipment. The response times of both types of equipment must be compatible with each other.

In 1984, simultaneous measurements of  $CO_2$  and  $O_2$  in streaming breath gas were successfully realized with a combination of a  $CO_2$  concentration cell with an  $O_2$  sensor [12, 65]. However, the necessary equipment [66] was very complicated and not safe to operate practically.

An important simplification is conceivable with the combination of an  $O_2$  and a  $CO_2$  solid electrolyte sensor. Figure 17 shows a suggested construction [67] with which some studies were performed. The sensor could be prepared in a tube made of Nernst mass (YSZ, outer



**Fig. 17** Solid electrolyte arrangement for simultaneous measurements of  $O_2$  and  $CO_2$  [67]



**Fig. 18a–c** Simultaneous measurement of the O<sub>2</sub> and CO<sub>2</sub> concentration in breath. **a** Normal breathing; **b** short-winded breathing; **c** after bated breath during slow exhalation

diameter 8 mm, inner 5 mm and 10 cm long) with a flat thin bottom. The CO<sub>2</sub> sensor, made with discs about 0.4 mm thick and 2.5 mm diameter, were pressed from outside with a steel spring against the bottom which carries the O<sub>2</sub> measuring electrode inside and the air reference electrode outside. The reference electrode of the CO<sub>2</sub> sensor must be situated on the O<sub>2</sub> measuring

electrode because otherwise creeping of Na<sub>2</sub>CO<sub>3</sub> from the CO<sub>2</sub> measuring electrode could harm the O<sub>2</sub> measuring electrode.

The chamber in which O<sub>2</sub> and CO<sub>2</sub> were measured simultaneously by the close electrodes was only a few mm<sup>3</sup> large and could be rinsed out quickly and continuously by a small breath gas partial current (2 L/h) siphoned, for example, from the nose of the test person. Measured curves obtained at different breath frequencies with such an arrangement (already aged) are presented in Fig. 18.

For commercial use, however, no such sensor combinations have been produced. One reason is the high standards that must be met by medical equipment. The necessary heating energy is too large to produce the desired small portable apparatus. It is problematic that, after switching on the equipment, only after about 2 hours can the use start. Furthermore, the best operational temperature for the CO<sub>2</sub> sensor is not optimal for the O<sub>2</sub> sensor and both sensors have a cross sensitivity for traces of organic chemical gas components (e.g. alcohol and acetone), particularly at low temperatures. Until now, the required short response times (ca. 1 s) are not exactly reproducible, particularly with the CO<sub>2</sub> sensor. In continuous operation, damage arises from the loss of Na<sub>2</sub>CO<sub>3</sub>.

However, if certain conditions for the operation of the sensor arrangement and controls with test gas are accepted, it is quite possible to develop, on the discussed basis, a reliable measuring breath gas sensor, considerably cheaper than equipment systems used up to now.

## Conclusions

The establishment of equilibria between alkali carbonates, metals and gaseous CO<sub>2</sub> proceeds fast at temperatures above 400 °C so that it is easy to obtain CO<sub>2</sub>-sensitive electrodes for potentiometric sensors. Long-term stable CO<sub>2</sub> sensors can be prepared with reference electrodes made of pure solid substances on β-Al<sub>2</sub>O<sub>3</sub>. However, obviously only a few substances fulfill the existing requirements. Until now, the systems TiO<sub>2</sub>, Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> and SiO<sub>2</sub>, Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> have proved to be the best. Particularly with regard to the response time and the ageing processes, further investigations are still required.

**Acknowledgements** The investigations were supported by Zirox Sensoren & Elektronik GmbH and the GoMesstechnik in Greifswald with equipment and materials. The author thanks especially Eckhard Brunner and Volker Brüser for valuable cooperation and also the Editor-in-Chief, Fritz Scholz, for helpful discussions and friendly assistance in the completion of the manuscript.

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