Potentiometric CO₂-Sensors with Ion-Conducting Glasses as Solid Electrolytes

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Abstract. Alkali-ion conducting glasses/glass ceramics of the system Me₂O-Al₂O₃-SiO₂ (Me=Li, Na) were applied as solid electrolytes in potentiometric gas sensors to detect CO₂ in the presence of O₂ at increased temperatures. The corresponding Me-Carbonates were utilized as auxiliary electrodes. Sensors using the direct Au-glass contact as a kind of reference electrode (type I), as well as symmetrical sensors with carbonate phase at the reference and measuring electrode (type II - for comparative measurements) were manufactured.

By applying Au as electrode metal, the theoretically expected EMF difference and the observed EMF difference of both sensor types agree quite well with the expected values according to the Nernst equation between 500 and 600 °C (over four orders of magnitude of CO₂ partial pressure (10⁻⁵ - 10⁻¹ bar) at constant O₂ partial pressure (2.1x10⁻¹ bar)). A long time stability of 120 days for sensors of type I with Li glasses has been observed, although evaporation of carbonate phase (Li₂CO₃) was detected under the conditions of sensor application. Sensors of type I (with Li₂CO₃) show thermodynamically unexpected cross-sensitivities to H₂O.

1. Introduction

In many chemical processes CO₂ gas is set free, which is regarded as a main-cause of the greenhouse-effect [1]. To its control and reduction, the cheap and reliable determination becomes more and more urgent. For this assignment potentiometric CO₂ sensors on the basis of solid electrolytes are preferential suitable because they are small, cheap and easily to be manufactured and show quick and reliable responses to CO₂.

Potentiometric sensors based on solid electrolytes, with the same ionic species transferred in the solid electrolyte as detected in the gas atmosphere are declared as sensors of first kind (e.g. λ-probe with stabilized ZrO₂ as solid electrolyte). Solid electrolyte CO₂ sensors with Alkali-carbonate as solid electrolyte are sensors of second kind [2] because the ionic species transferred (Alkali-ion) is different to the species to be detected in the gas atmosphere. Both species are part of the solid electrolyte which separates a measuring and a reference gas atmosphere. These sensor set-ups are applied in the field of CO₂-sensors as gas concentration cells with Alkali-carbonates as solid-electrolytes but there is no possibility of miniaturization [3] [4] [5]. Miniaturization is possible by means of potentiometric solid electrolyte sensors of third kind [2]. Such sensors consist of measuring-electrode, solid electrolyte and reference-electrode. The solid electrolyte transfers e.g. an Alkali-ion species from the reference electrode (constant Alkali-activity) to the measuring electrode. Here, the Alkali-ion reacts with species from the gas atmosphere and forms a new phase. This set-up makes it possible to manufacture cheap and small sensors which can be put in according to the demands.

Normally, crystalline solid ionic conductors are used as membranes in those CO₂ sensors set-ups in order to separate the CO₂ sensitive measuring electrode from the reference electrode. In arrays like these coatings are necessary which separate the surface of the reference electrode from the gas atmosphere of the environment [6] [7]. By applying glasses as solid electrolytes it is possible to use them in the double function of ion conducting diaphragm and coating for the reference electrode. The glassy solid electrolytes can directly take over the
was sintered in the temperature range of sensor application.

\[ \text{type I): Au, CO}_2, \text{O}_2, \text{Me}_2\text{CO}_3 \parallel \text{Me-Si-Al-O-glass} \parallel \text{O}_2, \text{Au} \]  

\[ \text{type II): Au, CO}_2, \text{O}_2, \text{Me}_2\text{CO}_3 \parallel \text{Me-Si-Al-O-glass} \parallel \text{Me}_2\text{CO}_3, \text{CO}_2, \text{O}_2, \text{Au} \]  

Me=Alkali (Li, Na). In sensors of type I, the Au glass/glass ceramics contact zone was used as reference electrode; while in sensors of type II, the gas atmosphere with its constant CO\(_2\) and O\(_2\) partial pressures in equilibrium with Me\(_2\)CO\(_3\) was applied to maintain a constant Alkali activity ("gaseous" reference electrode). Sensors of type II were manufactured for comparing measurements.

The mixing of gases (total pressure 1 bar) was accomplished by electronic mass flow controllers (Tylan general), regulated by computer. By using N\(_2\) as carrier gas, CO\(_2\) test measurements were accomplished over two decades of partial pressure (1x10\(^{-3}\) - 1x10\(^{-1}\) bar or 1x10\(^{-5}\) - 3x10\(^{-4}\)bar) at constant O\(_2\) partial pressure of 2.1x10\(^{-1}\) bar. The total flow was 325 SCCM (Standard Cubic Centimeters) at p(CO\(_2\))<1x10\(^{-1}\) bar and 100 SCCM at p(CO\(_2\)) = 1x10\(^{-1}\) bar, respectively. Subsequently, the gas mixtures were dried by means of P\(_2\)O\(_5\) before they finally reached the PID regulated furnace with the sensor array (temperature range of investigation: 340 to 650 °C). The actual O\(_2\) partial pressure was controlled in a second furnace by means of a \(\lambda\) probe on the basis of cubic stabilized ZrO\(_2\). The sensor testing unit was not suitable to determine the time response behavior for the sensors because of the geometry.

X ray diffraction (XRD) investigations for phase analysis were conducted either by a high temperature diffractometer (Siemens, D5000) or by a room temperature diffractometer (Phillips PW 1400). The determination of the isothermal stability of the carbonate measuring electrodes was accomplished by DTA (Netzsch). SEM photographs (Leitz) of the sensor arrays were recorded at different stages of application.

3. Results and Discussion

Sensors of type I showed that a stable and drift free operation is only possible after a certain time of onset (12-18 d). Sensors with Alkali carbonate as gas sensitive reference electrode and a gas mixture with constant O\(_2\)