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Hydrogen Measuring Probe for Coal Gasification Processes

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Abstract

In the framework of the European R&D program on non-nuclear energy (JOULE I) a research project started in 1990, aiming at in-situ analysis of product gas produced by coal gasifiers. Our contribution in the project deals with the development of solid electrolyte based electrochemical sensors. In this paper the design of the hydrogen measuring probe is presented together with the first emf-measurements in an Ar/H_2 atmosphere and in a simulated coal gasification atmosphere, while the latest results obtained in a real gasifier are discussed as well.

1. Introduction

In the current run for a clean environment, the coal consuming power production plants are forced towards a clean coal technology. The Integrated Coal Gasification Combined Cycle (IGCC) is presently one of the most attractive options for the conversion of coal into electricity as it shows a minimal environmental hazard and optimal economical conditions combined with a high energy efficiency [1]. The optimisation of the electricity production however, requires an adequate process control based on the knowledge of the gas composition inside the reactor. On-line measurements would quickly provide information on sudden changes in the reactor atmosphere, so suitable adjustments of the fuel supply and gasification agents can be made. A direct analysis of the composition under actual process conditions is however not possible, because of the severe and aggressive environment usually existing inside a gasifier.

In view of these issues, a joint project between KEMA (NL), ECN (NL), TU Delft (NL) and VITO (B) was started. The objective of the project is to develop an on-line gas analysis method that allows to measure the gas composition downstream of a gasifier. Two different approaches are selected. One is the development of a gas sampling and gas analysis system for measuring the main gas components [2]. The other one is the

development of on-line electrochemical sensors. This paper is especially devoted to this last option.

2. Solid state Nernst Type gas sensors

Zirconia based sensors are widely accepted in industry for the electrochemical determination of the oxygen activity in the flue gases from combustion processes. Specific advantages of this type of sensor are its accuracy and sensitivity, the rugged construction, the potential of miniaturisation, and the wide concentration range that can be covered [3]. Moreover a high operating temperature can be achieved. Therefore, the same sensing principle was selected for constructing an hydrogen sensor.

Basically, such a Nernst-type sensor consists of a porous *measuring* electrode and a gas or solid state *reference* electrode, separated from each other by a solid electrolyte [4]. Such a cell acts as a concentration cell, where the gas activity at the sensing electrode can be obtained from the open circuit potential E (emf), if a well defined, constant gas activity at the reference electrode is established. This cell potential (or open circuit potential) is related to the concentration (activity) of the active species at the sensing electrode according to the Nernst equation :

$$E = [RT/nF] \ln(P_X/P_{ref})$$

with R the gas constant, F the Faraday constant, T the temperature (K), P_X the partial gas pressure in the sample gas mixture, P_{ref} the reference partial pressure and n the number of electrons involved in the basic electrochemical reaction of the sensor (n=2 for hydrogen and n=4 for oxygen).

3. High temperature hydrogen sensor

3.1. Material aspects

The key element of a high temperature hydrogen sensor is the high temperature proton conductor. After a profound literature investigation the recently developed *Yb-doped strontium cerate* was selected, because of its thermal stability, high protonic conductivity and low conductivity activation energy. The ceramic was synthesised according to the procedure described by Iwahara et al. [5]. Several standard ceramic analysis techniques revealed that the cerate showed no open porosity and that the density was at least 96% of the theoretical density. However it should be remarked that the mechanical strength was rather low, an observation which was also confirmed by other investigations [6]. Therefore, an optimisation of the production route was examined and permitted the density to increase to 99% of the theoretical density and also the mechanical strength improved. Moreover a homogenous perovskite structure and composition was observed throughout the samples and the cerate seemed to be relatively stable for desorption at temperatures up to 900°C in ultra high vacuum. With respect to the shaping of the $SrCeO_3$ solid electrolyte, pellets as well as closed-end tubes with a collar (BOSCH-shape) have been fabricated.

In order to investigate the *electrical properties* of the Yb-doped Sr-cerate pellets, an in-depth impedance spectroscopy analysis was executed in the temperature region 200°C to 950°C in reducing (Ar/H_2 mixtures) as well as in oxidising (air) ambient. More details are presented and discussed in [7]. The measured electrical characteristics of the produced ceramics are comparable with data reported in the literature. Although all transport mechanisms are not yet known in detail, the material should be applicable in a hydrogen sensor.

The *compatibility* of Sr-cerates was first examined in a 100h test in a synthetic coal gasification atmosphere containing Ar, H_2 (5 vol%), CO (0.45 vol%), H_2O (0.08 vol%), and H_2S (32.5 ppm) at 800°C and at atmospheric pressure. Although the specimens remained intact, a change in colour from green to black was detected. This was attributed to the presence of a SrS and CeO_2 corrosion layer of about 7 µm thickness, while the interior of the samples remained unchanged.

Some Sr-cerate pellets were also exposed in the pressurised coal gasifier at CRE (British Coal, Cheltenham, UK) during 15-20 days at around 700°C. However, all samples decomposed into powder due to the combined effect of flying-slag, ash and chemical attack of the aggressive gas. The erosive action of fly ashes can be highly reduced by placing the sensor behind a filter element. This was examined in another experiment, in which specimens were treated in the atmospheric gasifier at ECN for 4 days at temperatures between 300°C and 600°C. The samples were placed behind the dust filter and indeed, the overall shape remained intact. Again a surface layer appeared, which was composed of SrHCl, $SrCO_3$ and CeO_2. In the design of a real measuring probe hydrogen sensor, solutions to the erosion and compatibility problems will be incorporated.

A final material aspect is the realisation of a *ceramic/metal joining*. The basic requirements of this joining are gas tightness by joining $SrCeO_3$ and a metal, better mechanical strength than the strength of $SrCeO_3$, withstanding operating temperatures of maximum 900°C and compatibility with the coal gasification atmosphere. In order to solve this problem, several attempts were made using different joining materials. However, a direct joining between the metal and the Sr-cerate is not yet completely realised.

3.2. Hydrogen measuring probe

Using the results of the material tests, a hydrogen measuring probe, shown in figure 1, was designed and constructed. The sensor is capable to accept sensing elements of the BOSCH-type shape as well as pellet-shaped solid electrolytes. The probe also provides the possibility of encapsulating not only a hydrogen sensor, but any sensor element based on the BOSCH-shape.

Concerning the reference materials to be used, the measuring probe allows the use of a gaseous reference system. The alternative consists of a solid reference material providing a constant hydrogen partial pressure (concentration cell mode), e.g. Th-ThH_2, NbH-NbH_2, etc. or a constant oxygen partial pressure (fuel cell mode), e.g. CeO_2 or In_2O_3-$PrO_{1.83}$-ZrO_2.

In an attempt to eliminate the chemical attack of the vulnerable solid electrolyte by aggressive gas, a protective cap of a non-porous, but hydrogen permeable material is used. As a result of a search for the most suitable material, Pd showed to have a better permeability than other candidate materials (as Nb e.g.). Some questions remain to be answered concerning both the effect of possible recrystallisation of Pd and the

compatibility of Pd with the coal gasification atmosphere, on the lifetime of the protection cap. Moreover this cap induces an increase of the response time of the sensor. According to theoretical calculations a deceleration of about 10 s is expected if a Pd protection cap with a thickness of 0.25 mm is used.

The lack of an accurate metal ceramic joining for closing the sensing tube is bypassed using a gold ring pressed between the metal and the solid electrolyte. A spring in the upper part of the probe produces the necessary strain to ensure a good fitting of the gold ring at high temperature.

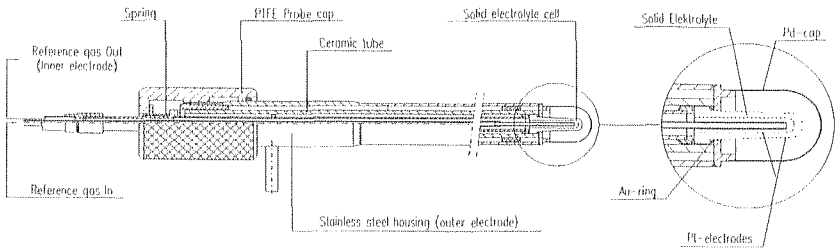

Figure 1 : Design of the hydrogen measuring probe with a gaseous reference system and a thimble shaped solid electrolyte covered with a Pt electrode.

4. Emf measurements

4.1. In H_2/Ar atmosphere

A first test of the probe with a tube-type solid electrolyte was conducted in a flowing, dry Ar/H_2 gas mixture with a fixed hydrogen partial pressure of 2.5 mbar. The hydrogen concentration offered at the reference side was gradually varied from 0.25% to 5% and this gas stream was humidified. Emf measurements were performed at different temperatures. The results are shown on figure 2 and reveal a linear behaviour of the measured emf with the logarithm of the hydrogen partial pressure for each temperature, indicating a Nernstian behaviour. Another feature of these curves is the small offset, varying form 5 mV at 500°C to 30 mV at 900°C (see insert) when the same amount of hydrogen is offered at both sides of the electrolyte. The slopes of the lines are smaller than the theoretical values (RT/2F), a deviation increasing with temperature. Most probably, this phenomenon can be ascribed to electronic conduction of the solid electrolyte [8], combined with a difference in water partial pressure at both sides of the cell.

A similar experiment was performed in a flowing Ar/H_2 gas mixture with a fixed hydrogen partial pressure of 50 mbar. Consequently, the reference hydrogen concentration was constantly lower than (or equal to) the external hydrogen concentration, so the signal was opposite. The results of this test confirmed the conclusions of the previous experiment, indicating a good reversibility of the electrolyte characteristics and a satisfying reproducibility of the measurements.

The reproducibility between different tubes has been tested also. Although again the same tendencies appeared, particularly a better correspondence between the measured

and the expected values at lower temperatures, the deviation of the slopes form the theoretical Nernstian slopes was more pronounced in this experiment.

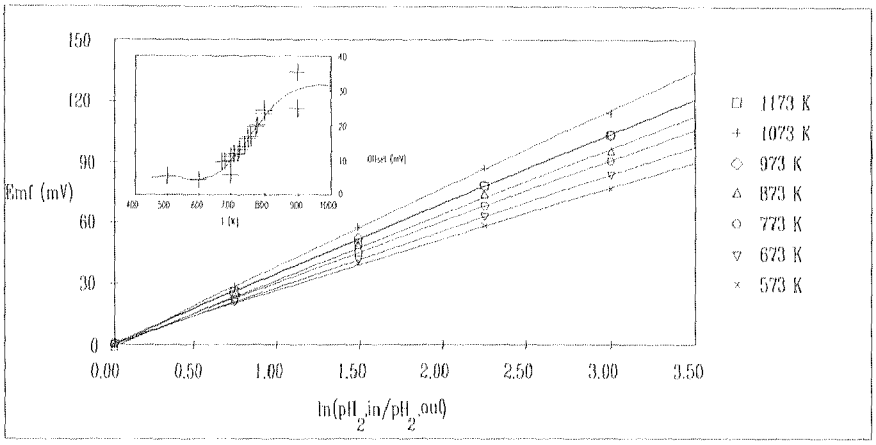

Figure 2 : Emf response of the hydrogen measuring probe with outside hydrogen partial pressure fixed at 2.5 mbar. The offset (see insert) has been subtracted.

Emf measurements were also performed in Ar/H_2 mixtures with a higher H_2 content (5%-100%) and with a fixed reference partial pressure of 2.5 mbar. Here the offset is limited to a few mV, but the slopes of the curves are different from the slopes observed at lower H_2 concentrations.

4.2. In simulated coal gas atmosphere

The hydrogen measuring probe was also examined at 756°C in a diluted simulated coal gas atmosphere, containing Ar (94.5 vol%), H_2 (5 vol%), CO (0.45 vol%) and H_2S (32.5 ppm). Emf measurements were conducted in this gas mixture, while the reference hydrogen concentration inside the probe was gradually changed from 0.25% to 5% H_2.

In a first run, contrary to the external gas stream, the supplied reference gas was dry. The results of these tests show an appreciable offset and a striking deviation from the theoretical curve (figure 3). Nevertheless a linear relationship between the measured emf and the logarithm of the concentration ratio is observed. In the absence of water the Sr-cerate is likely to be reduced, giving rise to deviations of the Nernst equation for a pure concentration cell when only one side is humidified, as different reactions take place at both sides of the solid electrolyte. In view to evaluate the influence of the water in the gas stream a second run was performed in which both the reference gas and the external, synthetic gas stream are humidified to the same extend. Under these circumstances the results show a very low offset and the measured values are situated within the experimental error of the Nernst curve derived for a concentration cell (figure 3). In this experiment the response time of the sensor to changes of hydrogen concentration at the reference side was less than 10 minutes.

From the foregoing experiments it can be derived that the use of a protection cap, which prevents the outside of the electrolyte from being humidified, may cause a certain offset.

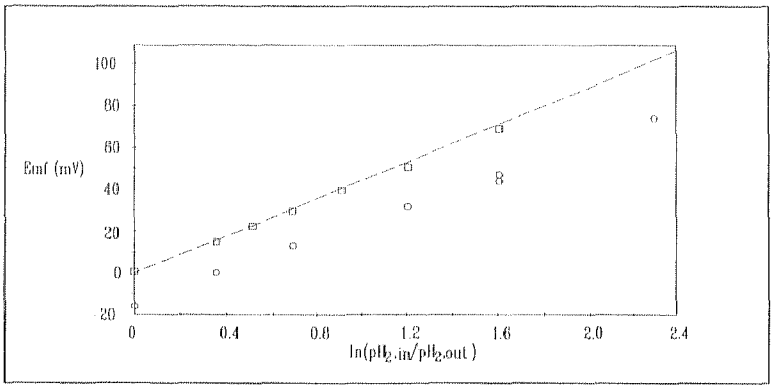

Figure 3 : Emf response of the hydrogen measuring probe in a simulated coal gas atmosphere (5% H2) compared with the theoretical values derived from the Nernst equation (---), only coal gas humidified (O) and both the reference and the coal gas side humidified (□).

4.3. In a gasifier

A hydrogen measuring probe was inserted in the gas stream of an atmospheric gasifier at British Coal. The test section was situated after two cyclones and the local temperature amounted 533°C. The measured emf was acceptable, though in general approximately 25% too low in comparison with the theoretical value deduced form calculations based on the output of a monitor analysing the offgas stream of the gasifier. The signal seemed to be influenced by the water (and O_2) content of the product gas. After being exposed for 24 hours, the probe was still performing well and a visual inspection of the probe afterwards showed that the construction was unaffected. Material tests to determine the effects of the coal gasification atmosphere on the constituents of the sensor are currently continuing.

Conclusion

In this paper, the development of an on-line electrochemical sensor for monitoring hydrogen in coal gasification systems has been described. In an intensive material development program, most important characteristics of the solid electrolyte for an hydrogen sensor were studied. Before the design and construction of a hydrogen measuring probe could be completed, some technical problems had to be solved. The first emf measurements with the hydrogen measuring probe show a Nernstian behaviour, but draw our attention to the importance of the water content in both the reference and

the product gas. The measurements in the atmospheric gasifier at British Coal have proven that the concept of the measuring probe is acceptable, although certain aspects of the sensor such as the metal-ceramic joining, quantification of the influence of steam on the sensor output and the effect of the Pd protection cap on the sensor signal and lifetime, still need further research. Subsequently the sensitivity, accuracy and cross sensitivity have to be examined.

Acknowledgements

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References

[1] Novem, Nederlandse Maatschappij voor Energie en Milieu B.V., Systeemstudie hoge temperatuur gasreiniging bij KV-STEG systemen, Systeemstudie in het kader van het Nationaal onderzoeksprogramma Kolen uitgevoerd door ECN, KEMA, Stork Ketels en TNO. Novem. Ref. nr. 90-310, Dossiernr.8725-21422/500, November 1990.

[2] P. Welberg, P. Alderliesten P., J. Schoonman, F. De Schutter, Development of fuel gas analysis techniques in coal gasification processes, in these proceedings.

[3] F. De Schutter, A. Jacobs, J. Vangrunderbeek, Development of gas sensors for coal gasification processes, Proc. Int. Course and Workshop on Solid State Ionics for Sensors and Electrochromics", Erice (It), July 1992, to be published.

[4] R. Kocache, Solid State Gas Sensors, ed. P. Moseley and B. Tofield, Adam Hilger imprint by IOP Publ. Ltd, Bristol and Philadelphia, 1-16, 1987.

[5] H. Iwahara, H. Uchida, S. Tanaka, High temperature type proton conductor based on $SrCeO_3$ and its application to solid electrolyte fuel cells, Solid State Ionics, N° 9&10, 1021-1026, 1983.

[6] Bonanos N., private communication, 1992.

[7] I. Kosacki, J.M.G. Becht, R. Van Landschoot, J. Schoonman, Electrical Properties of $SrCe_{0.95}Yb_{0.05}O_3$ in Hydrogen Containing Atmospheres, Solid State Ionics 59 (1993), 287 - 296.

[8] A. Jacobs, F. De Schutter, J. Vangrunderbeek, J. Luyten, R. Van Landschoot, J. Schoonman, Development of gas sensors for coal gasification processes, Proc. of the International Conference on Energy Efficiency in Process Technology, Vouliagmeni-Athens, Greece, 19-22 October 1992, 311.

Discussion

Hydrogen measuring probe for coal gasification processes

A. Jacobs, J. van Grunderbeek, H. Beckers, F. De Schutter, J. Luyten, R. Van Landschoot and J. Schoonman

Question: J.A. Moulijn

Your results are encouraging but there must be some problems related to the Pd membrane. It could function as a catalyst, for instance in the formation of methane. Of course, H_2S can poison the catalytic function but you should check this. Do you agree with that?

Answer

When we did experiments in a simulated coal gasification atmosphere, the results have shown that the Nernst law was obeyed and the deviations were minimal. We could not establish if the formation of methane occurred. But I agree that we should investigate the possible catalytic action of Pd. We are also doing a study on other materials which are permeable for H_2.

Question: F. Kapteijn

1. What is the thickness and the response time of the protective Pd cap?
2. Is the recrystallization of Pd a problem, such as in H_2 membrane applications?
3. Due to the presence of the Pd cap one side of the SE cannot be humidified, and a deviation from Nernstian behaviour may result. Can this be solved?

Answer

1. The thickness of the protective Pd cap is in the order of 0.5 mm. The sensor immediately gives a response to a change in H_2 partial pressure, but equilibrium is only reached after 5 to 10 min. However, the protection cap has to be optimized: the dimension should be reduced and the thickness as low as possible. This optimization is planned for the near future.
2. The recrystallization might indeed be a problem, this has to be investigated. We know that some Pd alloys (e.g., Pd-Ag) are much less susceptible to this kind of problems. We still have to investigate further if these alloys can be used.
3. We are aware of the problem. We are going to investigate these ceramic alloys at the end of this year.

Question: H.E. van Dam

1. Pd-catalyzed methane formation should not influence the H_2 concentration inside the cap, as this is thermodynamically controlled (no refreshment of gas inside the tube).
2. Is the assembling of the electrode performed in an oxygen-free environment? Otherwise, moisture content may be undefined due to the reaction $O_2+H_2=H_2O$.

Answer

It is not performed in an oxygen-free environment, so indeed some H_2O may be formed.