Chemical and electrical properties of Yb-doped strontium cerates in coal combustion atmospheres

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This paper describes the development of Yb-doped strontium cerates for use in a hydrogen sensor in coal gasification atmospheres. The first results of a characterization study of the microstructural as well as mechanical properties are presented. A comparison between virgin samples and samples exposed to a synthetic coal gasification atmosphere indicated no deleterious effect by this environment. Also the preliminary results with respect to an electrical characterization confirm this observation and are in agreement with the results of previous investigations.

1. Introduction

In the field of combined cycle power generation systems several advanced coal technologies are considered. However, optimisation of the electricity production with combined cycles requires knowledge of the gas composition inside the reactor.

In the framework of the European efforts on non-nuclear energy production (JOULE), a joint program between the SCK, Mol and the TU, Delft was started to develop a hydrogen sensor for these aggressive atmospheres.

In a first approach a sensor capable of operating at temperatures of about 900°C is envisaged. For this purpose, a galvanic cell using doped cerates as ion conducting element was selected. In this stage, the behaviour of this material in the aggressive atmosphere is of prior importance. Therefore a program was started to test compatibility of the material in a simulated coal gas atmosphere.

In order to synthesize strontium cerate in the form of pellets and bars, the procedure as described by Iwahara et al. [1] was followed. To show the influence of dopant on the defect structure, three different Yb containing compositions are manufactured: SrCeO₄, SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ and SrCe₀.₉Yb₀.₁O₃₋ₓ. After synthesis, the ceramics were characterised in depth using several analysing techniques such as Hg-porosimetry, gas permeability, SEM, TEM, XRD, and ceramography. Finally, also the mechanical properties were measured by performing four point bending tests on the square bars.

In order to measure the electrical properties, an impedance spectroscopy analysis (IS) was performed using a SOLARTRON 1255 frequency response analyser in combination with a SOLARTRON 1286 electrochemical interface at temperatures varying from 373 to 1173 K.

2. Experimental

After the characterisation described above, specimens were exposed at 800°C to a simulated coal gas atmosphere in order to observe the high temperature stability of the component. In order to simulate a coal gas atmosphere, a gas mixture consisting of argon, H₂ (5 vol%), CO (0.45 vol%), H₂O (0.08 vol%) and H₂S, (0.0033 vol%) at atmospheric pressure was used. A calculation of the thermodynamic parame-

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ters at 1073 K yields the following activity values:

\[ P_{O_2} = 1.0 \times 10^{-22}, \]
\[ P_{S_2} = 0.9 \times 10^{-10}, \]
\[ a_C = 0.04. \]

During exposure, specimens were placed in a closed quartz tube of 10 cm diameter mounted in a tube furnace. As the furnace is equipped with three independent heating coils, a temperature gradient of less than 5 K over a length of 10 cm could be obtained. Furthermore, the system is equipped with H₂S-, CO- and H₂-sensors for gas control. A stabilised H₂O content was obtained by leading the gas through a mixture of 90% oxalic acid dihydrate and 10% of anhydrous acid kept in a thermostat at 280 K. The amount of H₂O was continuously monitored by a hygrometer (General Eastern 1100 DP). After an exposure of 100 h, the same material analysis as mentioned above was performed including weight change measurements.

3. Results

3.1. Material properties before exposure

Using Hg porosimetry, a relative density of about 88% td was measured for the Yb-doped cerates and about 82% td for the undoped cerates. In the doped samples, about 12% open porosities were measured (18% in the undoped sample).

Moreover, as the Yb content increases, the specimens show an increasing density. These observations are confirmed by the microscopic investigation of the SrCeO₃-based ceramics. Also a green surface region at the circumference of the specimen was observed.

With respect to the microstructure, SEM analysis of a fractured sample revealed a fracture of a full intercrystalline type with a mean grain size of about 8 μm. This result and the presence of pores was confirmed by a TEM-observation of the microstructure. In addition, as shown in fig. 1, an amorphous phase between the grains was detected. However, it should be mentioned that the amorphous structures did not influence the overall crystal structure of the ceramics, as microstructure XRD-analysis revealed the expected SrCeO₃ structure for all three compositions.

The mechanical properties of specimens before and after exposure and specimens which are one and five times quenched from 900°C are summarised in table 1.

The results of four-point bending tests demonstrate the very low mechanical strength of the specimens. The quenching tests of the specimens, which
were originally performed to provide an indication of the thermal shock resistance, reveal a very deleterious effect. After five times quenching the mechanical strength is nearly reduced to zero.

3.2. Material properties after exposure

After the exposure to the simulated coal-gas atmosphere the specimens remained intact but a change in colour from green (and yellow in the interior) to black could be detected. However, a cross-section of a specimen clearly showed that this colour change did not extend into the inner part of the material, and only the green surface layer mentioned above is transformed into a black one.

The weight differences before and after exposure are very low and dependent on the density of the specimens. There is a small material loss, but the less dense specimens have absorbed some components of the coal-gas atmosphere during quenching. XRD-analysis of the specimens after exposure reveal the existence of SrS and CeO₂ in addition to SrCeO₃. The reaction products SrS and CeO₂ could not be detected in the interior of the sample.

Finally it should be mentioned that the 100 h exposure to the coal-gas atmosphere resulted only in a slight increase of the original strength, probably caused by the surface transformation.

3.3. Impedance measurements

Up to now, IS was performed in air on the SrCe₀.₉₂Yb₀.₀₈O₃₋ₐ specimens only before and after exposure. Impedance spectra were recorded in the temperature range 425 to 930 K, with intervals of ±100 K. At the lowest temperature, three semicircles, indicating the existence of grain boundary effects can be detected. However, due to experimental limitations, only part of these circles could be reproduced at the higher temperatures. IS performed after the exposure, yield almost the same spectra at all temperatures. This is a first indication that the exposure does not alter the electrical properties.

4. Discussion

The detailed evaluation of the microstructural as well as the mechanical properties of the specimens synthesised according to the procedure of Iwahara et

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**Fig. 2.** Arrhenius plot of the temperature dependence of the bulk electrical conductivity for the SrCe₀.₉₂Yb₀.₀₈O₃₋ₐ sample before and after exposure. The results are also compared with the results (refs. [3] and [4]) of other investigations. Insert: Impedance spectrum at 200°C for a specimen before exposure.
al. [1,2] indicate clearly that the preparation route needs further optimisation.

The present results provide a clear indication that the mechanical and electrical properties are practically not affected by an exposure to a simulated coal gas atmosphere.

An interpretation of the IS measurements can be made on the assumption that a dominant bulk conductivity prevails at the higher temperatures. In this case an Arrhenius curve of this bulk conductivity can be constructed and compared with the results of other investigations. As shown in fig. 2, the electrical measurements yield nearly the same results before and after exposure to coal-gas atmosphere. Both data compare very well with the IS data of Scherban et al. [3] and Bonanos et al. [4] for bulk conductivity. The good correlation observed in this figure supports the assumption made. Also the activation energy value of 0.66 eV is in good agreement with the reported values of 0.63 eV [3] and 0.65 eV [4], respectively. To conclude this discussion, it should be mentioned, that in order to prove protonic conduction in low $P_{O_2} (10^{-20})$ atmosphere, as occurring in a fluidised bed gasifier, IS experiments in these atmospheres are necessary.

5. Conclusions

In this study of strontium cerates for use in a hydrogen sensor it is shown that the mechanical and electrical properties are not influenced substantially by exposure to a synthetic coal-gas atmosphere. However, the mechanical properties need to be improved by an optimization of the sintering procedure. Impedance spectroscopy measurements reveal reliable bulk conductivity values. Data in the low $P_{O_2}$ atmosphere are necessary in order to establish the protonic conduction in these circumstances.

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