Proton conductivity in strontium cerates for hydrogen gas sensors in coal gasification systems ☆

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In the framework of the European action on non-nuclear energy (JOULE), an on-line hydrogen Nernst-type gas sensor for coal gasification systems is under development. This electrochemical sensor is based on Yb-doped SrCeO₃ as proton conducting solid electrolyte. With regard to the electrical characterisation, an in depth impedance analysis was performed in reducing as well as in oxidizing atmospheres and the influence on the bulk ionic conductivity and on the electrodes has been studied. Material compatibility in a simulated coal gasification atmosphere has been investigated. Preliminary results of EMF measurements in an air versus hydrogen concentration cell are presented as well.

1. Introduction

During the last decade, doped strontium cerates were recognized to have a high ionic conduction at elevated temperatures [1]. Consequently, these materials were studied more intensively due to the potential application in many novel electrochemical devices such as sensors, advanced fuel cells and steam electrolyzers for hydrogen production. In the framework of the European JOULE program on non-nuclear energy production, a project was started to develop a hydrogen sensor in coal gasification systems. In this joint program between SCK/VITO Mol and TU Delft, SrCe_{0.95}Yb_{0.05}O_{3-α} has been selected as ion conductor. Currently the project is focused on the synthesis and electrochemical characterization of Yb-doped strontium cerate and on the testing of the material in aggressive coal gasification atmospheres. In order to obtain a fundamental characterization of the material, ac impedance spectroscopy (IS) as well as cell measurements in different gaseous atmospheres were performed.

2. Experimental details

In order to synthesize strontium cerates, the procedure of Iwahara [1] was followed. A well determined mixture of SrCO₃ (99.4%, Johnson Matthey), CeO₂ (99.999%, Janssen Chimica) and Yb₂O₃ (99.9%, Fluka Chemie AG) was carefully prepared and calcined at 1673 K for 10 h in air. The calcined oxides were subsequently milled, shaped via cold isostatic pressing and finally sintered at 1823 K for 10 h.

After synthesis, the ceramics were characterized in depth using several analysing techniques such as Hg-porosimetry, gas permeability, SEM, EDAX, XRD and ceramography. Several pellets, having a diameter of 8 mm and a thickness of 1 mm, were characterised by IS. The bottom and the top surface were platinum coated by dc magnetron sputtering of a platinum target in an Ar plasma. The IS measurements were performed using a Solartron 1260 Frequency Response Analyzer in a four terminal set-up. The spectra were recorded in a frequency range from 0.1 Hz to 10 MHz and in a temperature region from 475 K to 1225 K in pure air as well as in hydrogen containing gas mixtures. The impedance spectra were analysed to yield the bulk proton conductivity using the curve-fit computer programme EISCALC [2]. A

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schematic overview of the IS equipment is given in fig. 1.

A hydrogen measuring cell, represented by

in a similar construction as in ref. [3] has been used to perform EMF measurements. Pt/air is used as the reference electrode. The hydrogen concentration could be varied from 0.01 to 34 vol% using Brooks flow meters. Measurements were performed at different temperatures from 773 to 1073 K. The EMF values were recorded using a Keithley 195A DMM.

In order to observe the high temperature stability of the materials in coal gasification systems, specimens were tested in a simulated coal gas atmosphere as described previously [4]. In this reactor, a gas mixture of Ar with 5 vol% H₂, 0.45 vol% CO, 0.08 vol% H₂O and 0.0033 vol% H₂S at 1073 K was used to simulate a coal gasification atmosphere. Starting from the reaction equilibrium constants, a computer code was used to calculate the gas composition (mole fraction) at atmospheric pressure. As a result, the main gas components were calculated to be H₂ (0.905), CO (0.08), H₂O (0.01) and H₂S (0.0006) while a very low oxygen concentration of 2×10^{-19} was calculated.

3. Results and discussion

In previous publications [4,5] the structural char-

Fig. 1. Impedance spectroscopy set-up.

acterisation of the synthesised Yb-doped strontium cerate pellets has been extensively described. The main results are that pellets fabricated according to an optimized production route had a density of at least 90% TD (theoretical density) and no open porosity. Moreover, a homogeneous perovskite structure and composition was observed throughout the pellets. The pellets had however a poor mechanical strength which should be taken into account when developing a prototype electrochemical sensor.

With respect to the electrical characterisation, fig. 2 shows the impedance spectra measured with platinum electrodes in air and different hydrogen concentrations at a fixed temperature of 573 K. The spectra could be fitted with the circuit shown on the insert of fig. 2. The high frequency semicircle is connected with the bulk resistance while electrode polarisation phenomena predominate at low frequencies. At intermediate frequencies, grain boundary polarisation effects are manifest. As can be seen, the major differences between the spectra occur in the electrode effects. In air, the impedance spectra revealed substantial electrode blocking effects. In hydrogen containing atmospheres, a curvature to the real axis is observed with increasing hydrogen concentration and temperature. This difference can be attributed to the hydrogen diffusion through the platinum layer, thereby reducing the electrode block-

Fig. 2. Impedance spectra of a $\text{SrCe}_{0.95}\text{Ce}_{0.05}\text{O}_{3-\alpha}$ (Pt-electrodes) in air and different H₂-N₂ gas mixtures at 573 K.

Fig. 3. Arrhenius curve of the bulk ionic conductivity of a $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ (Pt-electrode) in air and different $\text{H}_2\text{-N}_2$ gas mixtures.

ing effects. Finally it should be remarked that the surrounding hydrogen atmosphere has no effect on the bulk semicircle. Similar results were obtained at the other temperatures.

This observation is also indicated on fig. 3, where the Arrhenius curves of the bulk conductivities, obtained from the IS spectra, are shown at different hy-

drogen concentrations. From these curves, an activation energy of 0.64 eV can be deduced. This value agrees very well with the reported values of 0.63 eV [6] and 0.65 [7]. It should be mentioned that some of these values were recorded in wet (H_2O and D_2O) atmosphere. These observations indicate that the conduction mechanism is more complex than a free migration process or a vehicle mechanism where protons move as a passenger on an oxide species. As this investigation is beyond the scope of this paper, a more detailed study of these phenomena, including Raman spectroscopy and IR reflectivity measurements is in preparation.

After the exposure during 100 h to the synthetic goal gasification atmosphere, the specimens were characterised by XRD, EDAX and by IS. XRD analysis revealed the presence of a SrS corrosion layer on the surface of the pellets, while the interior of the specimen remained unchanged. These results were also confirmed by EDAX. From EDAX mapping in fig. 4, it is clearly seen that a surface layer was formed during exposure. The thickness of the layer was estimated to be about 7 μm . A chemical etching procedure was developed [5] in order to study the microstructure by optical microscopy. The ceramograph

Fig. 4. EDAX mapping of an exposed $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$; the highest concentration of a particular element is found on the brightest spots and vice versa.

Fig. 5. Ceramograph of an exposed $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$.

of fig. 5 shows the typical twin microstructure in the interior and the corrosion layer in a cross section of the pellet. As to the impedance measurements, fig. 6 shows a typical Nyquist plot at different temperatures and confirms a shape identical to the spectra of unexposed samples. An Arrhenius plot of the bulk ionic conductivity yields an activation energy of 0.63 eV, which is equal to the activation energy of an uncorroded specimen within the experimental error.

Concerning the concentration cells, preliminary curves of the cell voltage versus the hydrogen partial pressure obtained at different temperature are presented in fig. 7. For these data, the cells stabilized within 10 s. For a fixed temperature we observed a linear behaviour of the measured emf with the logarithm of the hydrogen partial pressure, indicating a Nernstian behaviour. Nevertheless, it should be remarked that the observed slope does not correspond to $(RT/2F)$ which can be explained by a more complex ion transfer at both sides of the solid electrolyte.

Fig. 6. Impedance spectra of an exposed $\text{SrCe}_{0.95}\text{Ce}_{0.05}\text{O}_{3-\alpha}$ (Pt-electrodes) in 5% H_2 -95% Ar at different temperatures: (A) 526 K, (B) 574 K and (C) 676 K.

Fig. 7. EMF measurements on an air versus hydrogen concentration cell.

Currently, more elaborate tests are ongoing in order to clarify the observations. Furthermore, it should be remarked that the intercept of the curve with the x -axis corresponds to the partial pressure of hydrogen in the ambient air. As can be seen, this reference partial pressure increases with increasing temperature, indicating a further dissociation of moisture at higher temperatures. In order to avoid this, an experimental set-up with a controlled hydrogen partial pressure in both cell compartments is under construction.

4. Conclusions

This paper describes the current state of development of a strontium cerate based hydrogen sensor for coal gasification atmospheres. Electrical characterization of the pellets revealed that the bulk ionic conductivity was independent of the ambient hydrogen partial pressure. However, the electrode characteristics are strongly influenced by the am-

bient hydrogen partial pressure. Furthermore, it could be demonstrated that an exposure to a simulated coal gasification atmosphere resulted in the formation of a SrS surface layer, but the internal electrical properties of the samples remained unaffected. Finally, a hydrogen sensitive cell was constructed and preliminary experiments showed a linear behaviour of the measured emf with hydrogen partial pressure. A very fast response to changing hydrogen concentrations was also observed.

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