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PhD Thesis abstract

„Modifications of the porous microstructure of solid oxide cell flat fuel electrode supports produced by high pressure injection moulding of ceramic mass and experimental studies of the impact of the modifications on the process of water electrolysis in SOE cells"

The subject of this dissertation is microstructural modifications and experimental tests of solid oxide cells operating in the high-temperature water electrolysis mode (SOE). This technology is intended to implement the Power-to-Gas concept for large-scale energy storage. It can be used, for example, to increase the use of installed capacity in renewable energy sources or to improve the flexibility of operation of coal units.

The development of SOE cells as a key element of the electrolyzer is aimed at reducing the electricity input per unit of hydrogen produced in the electrolysis process by reducing losses related to the physical and electrochemical processes taking place inside. The research work carried out was divided into two successive stages: material modifications inside the fuel support of flat SOE cells and electrochemical tests of the impact of the introduced modifications on the operation of the cell. The research hypothesis formulated in the introduction of the work referred to both stages of the work. The material research stage was embedded in the solid oxide cell production technology developed at the Institute of Power Engineering. This technology is based on the high-pressure injection moulding method of ceramic mass for the production of composite, porous fuel substrates from Ni/YSZ cermet. Due to the fact that the substrates produced in this way have a relatively large thickness (~1000 μm), they constitute a potentially significant barrier to the diffusive transport of reagents supplied to and discharged from the electrochemically active sites in the fuel electrode of the SOE cell. Therefore, the aim of this stage of research was to introduce modifications to the established substrate production process according to the mentioned technology in order to obtain improved microstructural parameters, favouring mass diffusion inside the porous structure. These included: open porosity or pore size distribution. Based on a literature review, three material modification methods were identified: increasing the volume addition of pyrolyzable pore-forming material in the ceramic mass, selecting alternative to state-of-the-art pore-forming materials, and reducing the co-sintering temperature of the substrate and electrolyte layers by selecting an alternative electrolyte material. A total number of eleven different fuel supports were manufactured with modified porous microstructures. Microstructural parameters were measured and described using mercury porosimetry, SEM imaging and other techniques. For the needs of the second stage, electrochemical tests, full SOE cells were made on modified fuel supports according to the same preparation of all functional layers. Then, the cells were subjected to comprehensive experimental tests on a dedicated test stand to determine their operating characteristics in the high-temperature water electrolysis mode. The aim of the electrochemical tests was to determine the impact of microstructural modifications made in the cell supports on their performance, in particular the resistance components that could be directly attributed to mass diffusion processes inside the porous structures of the fuel supports. Based on the research results from both stages, the research hypothesis was verified for each of the methods used to modify the production process and the applicability of the results for further work

on the development of solid oxide cell technology carried out at the Institute of Power Engineering was assessed.

Chapter 1 of the dissertation contains an introduction to the work describing the economic background of the development of SOE solid oxide electrolysis technology. The origins of the policy aimed at building an economy based on hydrogen as an energy carrier were outlined and examples of the implementation of this policy in Poland and Europe were described, such as the largest projects for the construction of electrolyzer installations and published government documents containing specific goals for the development of the hydrogen economy. The Power-to-Gas concept was compared with other energy storage methods and the advantages of SOE electrolysis technology compared to other well-established electrolysis technologies (AE and PEME) were detailed. The role of the Institute of Power Engineering in the development of solid oxide cell technology for the implementation of the hydrogen economy in Poland was also mentioned. The second part of chapter 1 defines the purpose and scope of the research included in the dissertation, formulates a research hypothesis and provides detailed research objectives.

Chapter 2 contains a theoretical introduction to high-temperature electrolysis in SOE cells. Fundamental thermodynamic definitions and relations are described. Using a cell diagram, its principle of operation was explained, along with the half-reactions of hydrogen production taking place at the electrodes. A description of the operating areas of the SOE electrolyzer in relation to its thermal management was included. Various definitions of efficiency and types of losses occurring in operating SOE cells are given. The last element of Chapter 2 is a detailed description of the mechanism of water vapor reduction at the three-phase TPB boundary in the fuel electrode of the SOE cell. Based on literature sources, individual reactions constituting the course of electrode processes are listed.

The main part of the literature review for the carried out research is included in chapter 3. An extensive collection of articles focused on the modification of microstructural Ni/YSZ fuel supports for solid oxide cells made using methods belonging to the Sacrificial Template Methods group, in which the porous structure is achieved by the addition of a pyrolyzable material to ceramic mass. The Ni/YSZ substrate forming technology, on which the research in the thesis was based, belongs to the same group of manufacturing methods. The tables summarize microstructural parameters collected from the literature (including open and closed porosity) obtained as a result of various modifications of the production process (including the selection of the pore-forming material and its additive). SEM images of the Ni/YSZ porous microstructures described there are also included. The literature review was supplemented with articles describing microstructural changes in substrates obtained as a result of lowering the co-sintering temperature of the layers and using alternative manufacturing methods to obtain more advanced porous microstructures. The chapter is summarized by listing the novelties of the scientific research conducted for the dissertation in the light of the literature review.

The theoretical foundations of the material and electrochemical measurement techniques used in the research are included in Chapter 4. These were mercury porosimetry and electrochemical impedance spectroscopy EIS. For the EIS technique, the main mathematical relationships, methods for verifying data correctness and analysis techniques such as the distribution of relaxation times DRT and equivalent circuit modelling are listed. The second part of Chapter 4 contains a detailed description of the research procedure for electrochemical measurements of SOE cells. A dedicated measurement station for experimental research is described. The tables list the variables for i-V and EIS measurements and the basic settings for these measurements.

Chapter 5 of the thesis contains a report on all material tests carried out on modified fuel supports for SOE cells. The first part describes the process of producing supports and full SOE cells according to the technology available at the Institute of Power Engineering. Variables such as the selection of pore-forming materials: PMMA, flake graphite and rice starch (with the characteristics of these materials), increasing the addition of pore-forming material to the ceramic mass, lowering the co-sintering temperature of the layers and the methods of implementing the above-mentioned modifications into the substrate production process by high-pressure injection of the ceramic mass are specified. The tables list the parameters of all eleven samples of full SOE cells. The next part of Chapter 5 presents the results of microstructural tests of modified fuel supports of SOE cells, along with discussion and analysis. On the basis of measurement data from mercury porosimetry (open porosity values, pore size distribution charts), SEM images of microstructures of cell cross-sections and additional visual analysis, the impact of modifications introduced into the manufacturing process on changes in the parameters of the porous microstructure of supports important for the conditions of mass diffusion was described.

Chapter 6 is a report on electrochemical tests of eleven SOE cells with modified fuel supports. The introduction to the chapter explains the methodology for analyzing EIS measurement data. A six-element equivalent circuit model was proposed, which was then fitted to EIS measurements. The main criterion for selecting the model was the ability to fit all measurements and clear differences in the time constants of its elements. The rest of the chapter contains a description of the i-V and EIS results and a discussion for each series of compared cells: three series of cells with a variable volume addition of pore-forming material in the support, a series of cells with a variable pore-forming material with the same addition and a series of cells with a variable co-sintering temperature of the layers. The influence of the microstructural modifications of SOE cell supports described in Chapter 5 on their electrochemical performance was determined, including the resistance components directly attributable to diffusion processes.

The last chapter 7 is a summary of the work carried out and presents the main research conclusions, synthesizing conclusions from material and electrochemical tests. For each of the variables introduced in the process of producing cell substrates, the research hypothesis set in the thesis was verified. Additionally, the applicability of the developed microstructural modifications and research methodology for implementation in the development of solid oxide cell technology at the Institute of Power Engineering was assessed. It was found that the most promising direction for improving the microstructure of fuel supports for SOE cells produced using this technology is the use of other alternative pore-forming materials, such as other forms of graphite.

Key words: hydrogen, high-temperature solid oxide electrolysis (SOE), SOEC, water electrolysis, pore formers, fuel electrode, microstructural modifications, high pressure injection moulding of ceramics, electrochemical performance.

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