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Design of open-porous materials for high-temperature fuel cells

T. Wejrzanowski[a,*], S. Haj Ibrahim[a], K. Cwieka[a], J. Milewski[b], K. J. Kurzydlowski[a]

[a] *Warsaw University of Technology, Faculty of Materials Science and Engineering, Woloska 141, 02-507 Warsaw, Poland*
[b] *Institute of Heat Engineering, Warsaw University of Technology, Nowowiejska 21/25, 00-665 Warsaw*

Abstract

Microstructure is one of the major factors influencing material properties. It is especially important for open-porous materials dedicated to catalytic applications, where fraction of pores, their size distribution and specific surface influence the diffusion of reactants and the kinetics of catalytic reactions. In these studies the numerical models of the microstructure of open-porous electrodes for molten carbonate fuel cell (MCFC) are presented. The models presented here simulate fabrication routes for real materials, including mixing of powders, tape casting and sintering processes. The substrate powders are represented by spheres with defined size distribution. Mixing and compaction of powders with polymeric binder is simulated by a granular model implemented in LAMMPS code. In the next step the polymeric phase represented by fine particles and larger porogen addition is removed to form pores. The sintering process is simulated by geometry smoothing, which results in sphere aggregation. The models presented here were compared with micro computed tomography (μCT) 3D images of real MCFC materials. Quantitative analysis of μCT images was performed and it was demonstrated that algorithms used in these studies make it possible to design materials with the desired porous microstructure.

Keywords: Open-porous materials, MCFC, microstructure, modelling

1. Introduction

Molten carbonate fuel cells (MCFCs) may be effectively carbon neutral and emit zero net greenhouse gases when fed with renewable fuels, such as biogas [1]. The carbon dioxide produced on the anode side which is not recirculated to the cathode is simply the result of the carbon-based species that are fed at the inlet. Even if fossil natural gas is used as a fuel, because of the higher efficiency of the MCFC, less CO_2 is emitted since less primary fuel is required to produce a given amount of electricity [2]. In addition, with a radically innovative approach, MCFCs could be used to separate the CO_2 from the flue gas instead, generating power in the process [3]. The MCFC can be used to separate CO_2 thanks to the functional reactions that occur inside the cell: carbonate ions transport CO_2 directly from the cathode to the anode side (see Fig. 1a). Hence, MCFCs offer rich potential to reduce reliance on the already strained power grid, alleviate carbon footprint and provide a source of renewable energy. Most of the key technological and operational issues related with future development of MCFCs are concentrated on materials [4, 5]. The performance, durability and cost (both manufacturing technology and operating costs) can be improved by the application of new materials [6]. Typically, design of new materials is focused on single cell elements (anode, cathode, electrolyte matrix), which can be stacked into a larger device (see Fig. 1b).

The concept of materials design involves mainly the analysis of chemical composition and microstructure effect on the performance and durability of the single cell. However, commercial applications also have to factor in economics. Since MCFCs operate at elevated temperatures (typically~650°C) expensive materials (such as platinum) can be replaced by much cheaper ones (i.e. nickel). Moreover, this temperature is high enough to supply MCFC with natural gas or another fuel, thus the use of pure hydrogen is not necessary [7]. This makes MCFCs very promising from the application point of view.

All the materials for MCFCs are highly porous (open porosity higher than 50%). The pore size distribution must be strictly controlled due to gas flow and electrolyte infiltration phenomena. Optimization of these two effects require significantly different microstructures, which results in a laminate-like concept of electrodes. There must also be a compromise between relatively high gas flow through electrodes and high efficiency of catalytic reactions [8]. The variety of possible modifications, in terms of both chemical composition and

*Corresponding author
Email address: twejrzanowski@inmat.pw.edu.pl (T. Wejrzanowski)

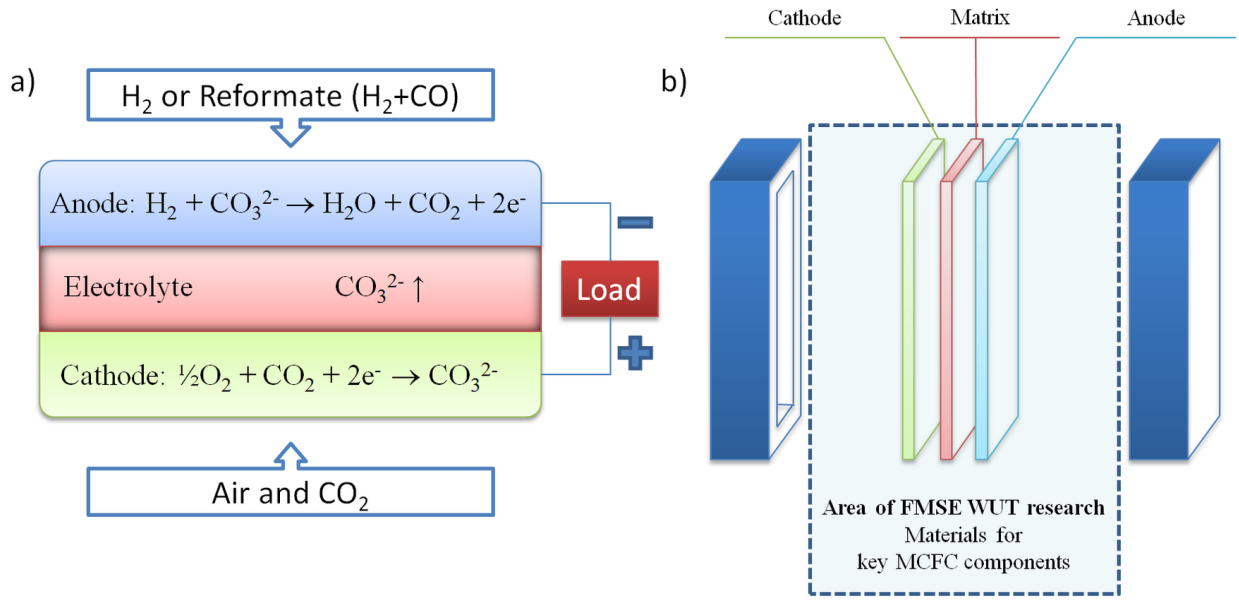

Figure 1: (a): Schematic illustration of the MCFC operation. (b): The main area of interest from the materials science point of view

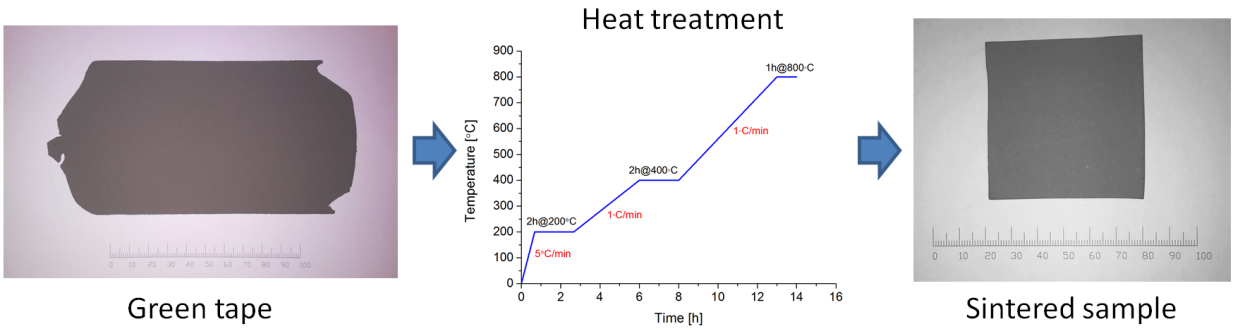

Figure 2: Schematic illustration of the MCFC manufacturing process.

microstructure, open up this field for more extensive studies on the application of novel methods of materials characterization and modeling [9, 10]. In these studies numerical models of the microstructure of open-porous electrodes for molten carbonate fuel cells (MCFC) are presented. The models presented here simulate real materials fabrication routes, including mixing of powders, tape casting and sintering processes. The results of modeling were compared with computed micro-tomography 3D images of real MCFC materials, and further used as feedback for fabrication process optimization. Thus, our materials design studies combine three fundamental areas of materials science: characterization, modeling and manufacturing. Advances in computational science over the past few decades have opened up the vista of applying numerical methods in each of the areas, very often creating a logical sequence in the design of specific materials structure and properties [11, 12].

2. Experimental

2.1. Manufacturing

The fabrication processes applied in these studies typically consist of 3 stages. Initially, a mixture of powders (metallic or ceramic) with polymeric binder and other additives (i.e. porogens) is prepared. Then green tape is produced by the tape casting method. In the last stage of electrodes fabrication green tapes are fired in a reducing atmosphere. A schematic illustration of the manufacturing process is presented in Fig. 2. The initial composition of the slurry, fraction of polymeric phase and size of powders are of key importance for the final structure of the materials for MCFCs. They also decide on the rheology of the slurry, which is important from the technological point of view. The sintering process also needs to be optimized, since it is found to have a significant impact on materials porosity and specific surface.

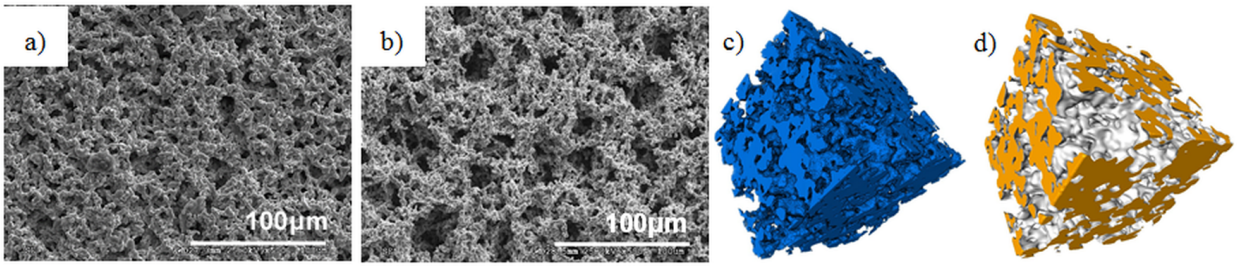

Figure 3: (a): SEM image of the anode. (b): SEM image of the cathode. (c): 3D micro-CT image of the cathode. (d): 3D vector-like model of the cathode microstructure based on micro-CT image

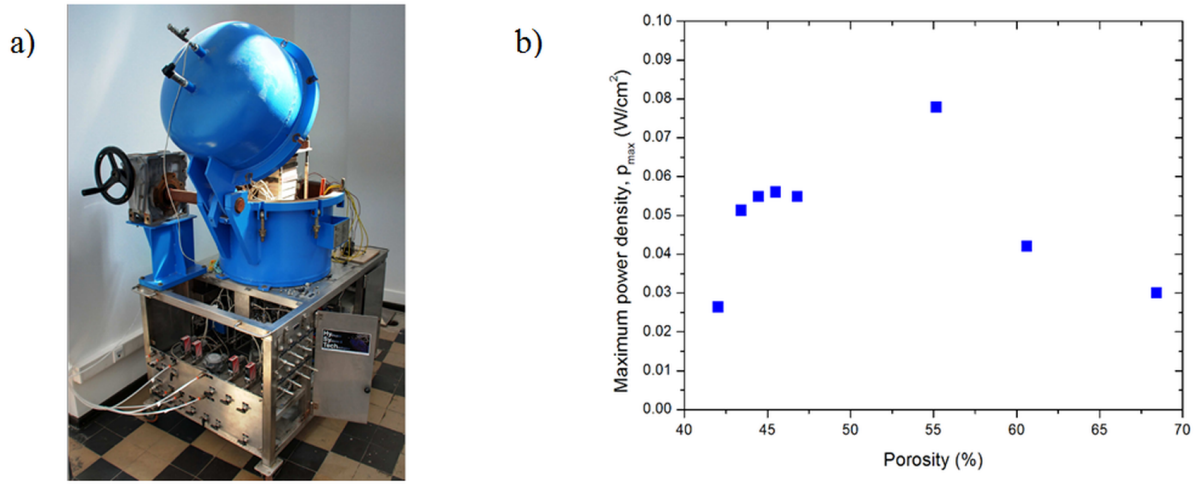

Figure 4: (a): Device for MCFC performance testing. (b): Example of structure-property relationship for MCFC cathodes with different porosity

2.2. Characterization

Both structure and properties of materials are characterized to obtain quantitative structure-property relationships [13, 14]. Scanning electron microscopy (SEM) and X-ray microtomography (μ-CT) are used to analyze the microstructure of MCFC materials (see Fig. 3). These methods (direct) are supported by indirect techniques (i.e. Archimedes density measurements, mercury porosimetry, X-ray diffraction) to study the microstructural parameters such as: porosity (volume fraction of pores), pore size distribution, specific surface, connectivity, etc. Based on micro-CT images numerical models (both raster-like and vector-like) can be created. This data is then used to verify the models, incorporating simulation of the processes taking place during fabrication of the materials. The properties of materials fabricated as part of these studies are examined in performance testing (see Fig. 4). For optimization of a single element (i.e. anode) only this material is replaced (i.e. anode) and others are kept unchanged. This procedure eliminates uncertainty caused by the coincidence of various factors and facilitates the design process.

Table 1: Fitting of the anode model

	Mean pore size μm	S_V 1/μm	Porosity %
μCT model	10.49	0.199	46.93
Representative model	10.67	0.212	48.05
Difference, %	1.7	6.5	2.4

3. Modeling

Numerical models of open-porous materials were generated using multi-step algorithms (see Fig. 5). In these algorithms the quantitative results of characterization of the substrates used for materials fabrication and final porous structures are used. The data consisting of particle size distribution of substrate powders is utilized to create an initial system with polydisperse spheres for MCFC electrodes. Due to the various manufacturing recipes for MCFC anodes and cathodes, different modelling approaches were necessary. For anodes, the slurry was based on a mixture of organic solvent with binder, which were the main factors affecting porosity. In this case, sphere packing implemented as ANSYS APDL script for simulation of the firing process was applied. Generation of spheres and their packing were performed with an algorithm proposed in [15]. Then data containing co-

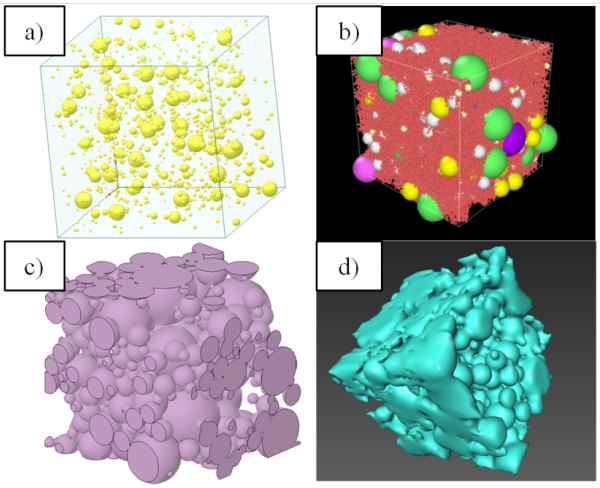

Figure 5: (a): Generation of spheres with given distribution. (b): Packing. (c): Deleting unwanted spheres. (d): Geometry smoothing

ordinates and radii were exported to an ANSYS input file. On the basis of this data, the set of spheres was drawn. The porosity was created by iterative removal of randomly selected spheres and their nearest neighbors, until the desired porosity level was reached. Dilatation of the remaining spheres was applied to create a single volume with connections between spheres. Structural parameters calculated for the models obtained by means of this algorithm and 3D images obtained for real materials (see Fig. 3) were compared, which is a common method of validation for porous structures [16]. It was also required for the purpose of fitting the parameters controlling the generation of structures. The results for anode validation are presented in Table 1. Comparison of simulated models with the real structures has shown that they are sufficiently accurate to predict structural properties of anodes with different porosities.

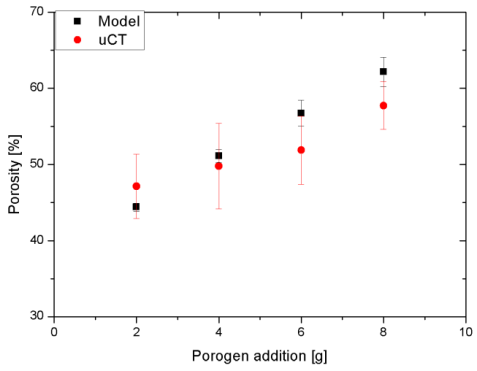

Figure 6: Validation of porosity for cathode model

For a cathode based on inorganic solvent, porogen particles were used to obtain the desired porosity. Thus, another modeling approach was adopted (see Fig. 5) in which porogens and binder were considered as additional small

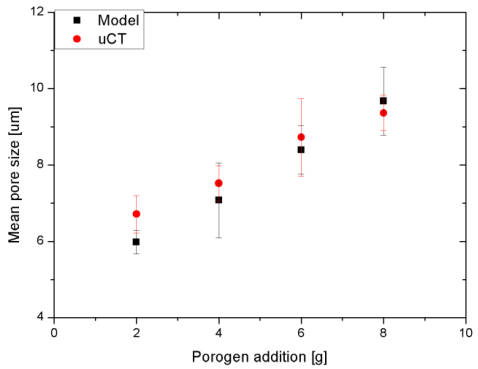

Figure 7: Validation of mean pore size for cathode model

spheres. The system of spheres was based on the fraction of each component added to the slurry, their density and size distribution. To reflect the thermal decomposition of hydrocarbons, porogen particles and polymeric phase in the cathode model were removed during the stage of sphere packing. User defined potentials between spheres with large energy and very small cutoff simulated sintering of the particles. Geometry smoothing was performed to obtain narrow connections between spheres, namely necks in real materials. Models of real MCFC cathode materials were created, based on slurry recipes containing respectively 2, 4, 6 and 8 g of porogen addition. As with the anode, the structures were validated through comparison with μCT images. Results of porosity and mean pore size validation after fitting of structure generation parameters are presented in Figs 6 and 7. The discrepancy associated with the model did not exceed 10% for all specimens. In the light of this fact we can conclude that our methodology makes it possible to model structures based on real slurry mixtures and manufacturing process, which could be invaluable for further optimization of the MCFC cathode material.

4. Summary

In these studies a concept has been applied where three fundamental areas of materials science: characterization, modeling and manufacturing are used to design materials for MCFC. It was proved that this methodology can be applied to create representative models of porous materials fabricated by the tape casting method, where slurry composed of particles suspended in polymer-based mixtures is first casted and then annealed. The tailoring of a wide spectrum of the structure parameters of porous materials enables materials to be designed for application in catalysis and in particular as electrode materials in Molten Carbonate Fuel Cells.

Acknowledgments

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References

[1] J. Milewski, G. Discepoli, U. Desideri, Modeling the performance of MCFC for various fuel and oxidant compositions, International Journal of Hydrogen Energy 39 (22) (2014) 11713–11721.

[2] J. Milewski, Solid oxide electrolysis cell CO–methanation supported by molten carbonate fuel cell – a concept, Journal of Power Technologies 96 (1) (2016) 8–14.

[3] R. Roshandel, M. Astaneh, F. Golzar, Multi-objective optimization of molten carbonate fuel cell system for reducing CO_2 emission from exhaust gases, Frontiers in Energy 9 (1) (2015) 106–114.

[4] J. R. Selman, Molten-salt fuel cells – technical and economic challenges, Journal of Power Sources 160 (2) (2006) 852–857.

[5] E. Antolini, The stability of molten carbonate fuel cell electrodes: a review of recent improvements, Applied energy 88 (12) (2011) 4274–4293.

[6] A. Kulkarni, S. Giddey, Materials issues and recent developments in molten carbonate fuel cells, Journal of Solid State Electrochemistry 16 (10) (2012) 3123–3146.

[7] P. Heidebrecht, K. Sundmacher, Molten carbonate fuel cell (MCFC) with internal reforming: model-based analysis of cell dynamics, Chemical Engineering Science 58 (3–6) (2003) 1029 – 1036, 17th International Symposium of Chemical Reaction Engineering (IS {CRE} 17).

[8] K. Czelej, K. Cwieka, T. Wejrzanowski, P. Spiewak, K. J. Kurzydlowski, Decomposition of activated CO_2 species on Ni(110): Role of surface diffusion in the reaction mechanism, Catalysis Communications 74 (2016) 65–70.

[9] T. Wejrzanowski, J. Skibinski, J. Szumbarski, K. J. Kurzydlowski, Structure of foams modeled by Laguerre–Voronoi tessellations, Computational Materials Science 67 (2013) 216–221.

[10] J. Skibinski, K. Cwieka, T. Kowalkowski, B. Wysocki, T. Wejrzanowski, K. J. Kurzydlowski, The influence of pore size variation on the pressure drop in open–cell foams, Materials & Design 87 (2015) 650–655.

[11] C. R. A. Catlow, G. D. Price, Computer modelling of solid–state inorganic materials, Nature 347 (6290) (1990) 243–248.

[12] C. R. A. Catlow, B. Smit, R. van Santen, Computer modelling of microporous materials, Academic Press, 2004.

[13] T. Wejrzanowski, W. Spychalski, K. Rozniatowski, K. Kurzydlowski, Image based analysis of complex microstructures of engineering materials, International Journal of Applied Mathematics and Computer Science 18 (1) (2008) 33–39.

[14] T. Wejrzanowski, M. Lewandowska, K. J. Kurzydlowski, Stereology of nano–materials, Image Analysis and Stereology 29 (2010) 1–13.

[15] T. Wejrzanowski, J. Skibinski, L. Madej, K. J. Kurzydlowski, Modeling structures of cellular materials for application at various length – scales, Computer Methods in Materials Science 13 (4) (2013) 493–500.

[16] R. Moreno-Atanasio, R. A. Williams, X. Jia, Combining x–ray microtomography with computer simulation for analysis of granular and porous materials, Particuology 8 (2) (2010) 81 – 99.