Modeling of Methane Multiple Reforming in Biogas-Fuelled SOFC and Its Application to Operation Analyses

トラン, ダン, ロン

https://doi.org/10.15017/1866295

出版情報：九州大学, 2017, 博士（工学）, 課程博士
バージョン：

（様式２）

氏　　名　：　TRAN DANG LONG

論 文 名　：　Modeling of Methane Multiple Reforming in Biogas-Fuelled SOFC and Its Application to Operation Analyses
「バイオガス直接供給固体酸化物形燃料電池におけるメタン複合改質反応のモデル化と動作解析への応用」

区　　分　：　甲

論　文　内　容　の　要　旨

This research focuses on solid oxide fuel cell (SOFC) operated at high temperature (700-800 ^{o}C) with the direct feed of biogas, a gaseous mixture of 55–70 vol% CH_4 and 30–45 vol% CO_2 obtained from the anaerobic fermentation of organic matters such as garbage, livestock manure and agricultural residues. When the biogas is supplied directly to SOFC, CH_4 dry and steam reforming simultaneously occur in a porous Ni-based anode material to produce syngas (Methane multiple-reforming (MMR) process). This type of operation is called direct internal reforming (DIR) operation. Biogas-fuelled DIR-SOFC is a promising technology for sustainable development of a rural area abundant in biomass resources.

For the realization of this technology, prior to system development, operating behavior of it has to be fully understood. However, how to model the complex kinetics of MMR process was a big challenge. In this study, from the reforming data obtained in the series of systematic experiments using Ni-based anode-supported cells (ASCs), a MMR model (model parameters) was inductively generated using the approach of artificial neural network (ANN). The developed MMR model can provide the net consumption and production rates of gaseous species (CH_4, CO_2, H_2O, H_2 and CO) involved in the MMR process at arbitrary temperatures and gas compositions. And, it can be applied for different types of Ni-based catalysts by adjusting a correction factor to compensate the differences in catalytically-active surface area.

Computational fluid-dynamics (CFD) calculations, in which mass and heat transports, MMR and electrochemical processes occurring inside the cell were taken into consideration, were conducted for the DIR-SOFC fuelled by biogas. Consistency of the CFD calculation incorporating the MMR model developed in this study (MMR model-incorporated CFD) with the measured performance of SOFC fuelled by CH_4-CO_2 mixture was confirmed through a three-step model validation process consisting of two model-parameter-tuning steps (model fitting steps with the data experimentally obtained under non-DIR and DIR operations) followed by a validity check whether the established-model can reproduce a performance of DIR-SOFC under an arbitrary operating condition. The consistency was not achieved by the conventional approach in literature considering MMR as a sum of CH_4 dry and steam reforming (ignoring the concurrent effect of CO_2 and H_2O on the catalytic CH_4 conversion). The MMR model developed in this study was proved to be able to provide more realistic and meaningful estimations for the DIR-SOFCs.

In order to enhance thermomechanical stability and output power of DIR-SOFC fuelled by biogas, internal reforming rates have to be properly controlled. For this purpose, two advanced DIR concepts, with the anode gas-barrier mask (Concept-I) and with the in-cell reformer using paper-structured catalyst (PSC) (Concept-II), were investigated by the MMR model-incorporated CFD calculation. Two types of 20 × 50 mm^2 ASC, ASC-A and ASC-B, with different thicknesses of anode substrate (Ni-stabilized zirconia) of 950 and 200 μm, respectively, were considered, providing guidelines for selecting a proper cell design depending on the thickness of the anode substrate (in other words the amount of metallic Ni) to obtain a mechanically stable operation with higher power density in the direct feed of simulated biogas mixture ($CH_4/CO_2 = 1$) at 800 °C.

For both ASC-A and ASC-B, by adopting Concept-I which can control mass flux of fuel getting into the porous volume of the anode along fuel flow direction, rapid syngas production at the fuel inlet region was suppressed to have homogeneous temperature distribution over the cell. In comparison to the normal ASCs (Normal), about 20% decrease in the maximum thermally-induced stress was estimated with a slight loss (about 8%) of maximum power density for both ASC-A and ASC-B, indicating that the use of anode gas-barrier mask is effective to reduce the risk of electrolyte fracture. Concept-I was confirmed to be a good choice for getting stable operation of DIR-SOFCs.

For the feed of 200 mL min^{-1} simulated biogas, in the cases of Normal and Concept-I, maximum power densities (P_{max}) with thinner anode substrate (ASC-B) were 1.03 and 0.95 W cm^{-2}, respectively, lower than those with thicker one (ASC-A), 1.17 and 1.08 W cm^{-2}, respectively, reflecting that the degree of catalytic CH_4 conversion is a predominant factor of the performance. In fact, by the application of Concept-II, P_{max} of ASC-A and ASC-B were boosted up to 1.25 and 1.45 W cm^{-2}, respectively, although the risk of electrolyte fracture was increased. The effect of Concept-II was more pronounced for ASC-B with thinner anode substrate, from which H_2O (product of the anodic reaction) was easily drained. As a result, buildup of partial pressure of H_2O within the anode functional layer under high current densities, leading to the decrease in electromotive force, could be suppressed.

This study provided a powerful numerical tool for creating highly efficient and robust DIR-SOFCs operating with biogas.