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Investigation of SOFC material properties for plant-level modeling

Invited Paper

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Abstract: This article describes results of a recent study of SOFC (Solid Oxide Fuel Cell) material properties using a numerical tool. The created model was validated against experimental data collected for two different solid oxide fuel cells. With focus on ionic and electronic conductivities, temperature influence was investigated. Results are presented, compared with available data, and discussed.

Model of a micro-CHP (Combined Heat and Power) unit based on a SOFC stack was used for evaluation of system performance with different cells. On-site generated bio-syngas was considered as a fuel fed for the unit.

The overall system efficiency was analyzed using an Aspen HYSYS modeling environment. Properties of two generic electrolyte materials were implemented in the models for evaluation of a co-generative unit operation. Electrical and overall efficiencies of systems based on those cells were compared and differences were observed. Micro-scale power units with fuel cells are a promising technology for highly efficient distributed cogeneration. As it was concluded, selection of a proper cell is crucial to assure high system efficiency.

Keywords: *SOFC • Modeling • Material properties • Micro-CHP*

1. Introduction

Fuel cell-based systems are of a high attention as a technology capable of providing highly efficient and clean energy. Two main technologies are considered in micro- and small-scale applications, namely the polymer electrolyte membrane fuel cells (PEMFC) and solid oxide fuel cells (SOFC).

High achievable efficiency and limited emissions make those systems a promising technology for sustainable energy generation. This was also noticed by the European Commission, and those systems have been included in the EC directive among other technologies for highly efficient cogeneration [1].

In recent publications, the comparison of a performance of systems based on PEMFC and SOFC can be found [2]. For distributed generation (DG) micro-scale units, SOFC offer a better overall performance in the combined heat and power applications comparing with PEMFC [3]. General concept of a micro-CHP system has been widely discussed during the last decade, so were the system integration and thermal balancing.

Selected units have already reached the proof-of-the-concept stage of development and operated in different locations. In certain markets like Japan, JX Nippon 0.7 kW_{el} unit based on Kyocera SOFC stacks is available for sale, other vendors like Vaillant, Toyota, Topsoe Fuel Cell, Viessmann, Bosch, Baxi, CFCL and Hexis also developed their concepts.

The micro-system with solid oxide fuel cell meets local energy demands and can be easily employed in detached dwellings.

Despite, relatively high capital costs, those units gain public attention, also due to state subsidies introduced to promote

development of the technology. Barriers and potentials of hydrogen-based power systems were also discussed [4].

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Influence of various fuel and different fuel processing technologies were evaluated and can be found in literature [3]. A number of valuable papers present work on multi-level modeling related to micro- and small-scale systems with SOFCs in different configurations. Previous studies were focused on investigations of the thermal and electrochemical issues [5], influence of geometry [6], system integration [7], and performance under different operating conditions [8]. Numerous fuels for SOFC-based power units were considered, including alcohols [9], hydrocarbons [10,11], pure hydrogen [12,13], biogas [14,15], ammonia [16] and dimethyl ether [17]. Utilization of listed fuels requires dedicated fuel processing technology, typically selection is made out of catalytic partial oxidation (CPOX), steam reforming (SR), autothermal reforming (ATR) or combination of thereof [18].

Different approaches were proposed and widely used with focus on particular phenomena. Authors believe that complete understanding of the micro-CHP operation is not possible without investigation of SOFC material properties. A high fidelity numerical simulator of the entire system can be developed once stack parameters are known and well described. Only this knowledge allows for the creation of a versatile modeling tool for steady state and off-design analysis. Due to very limited reports on such studies in available literature, the topic was selected for the current analysis.

The presented work is dedicated to the investigation of solid oxide fuel cell material properties, and evaluation of possible influence on micro-scale power unit performance.

1.1. Previous studies

The main simplification, often found in the literature, is based on an assumption that solid oxide fuel cell electrolytes are only the ionic conductors. Nonetheless it was proved and reported that electronic conductivity is present [19]. For selected materials it can even be dominant, especially were certain dopings are used [20].

Additionally, electronic resistance of SOFC was measured in an inert gas atmosphere in the laboratory facility of the Institute of Power Engineering. Values in order of tens of kΩ were measured using a four terminal ohmmeter at temperatures of 873, 923, 973 and 1023 K for two 5×5 cm cells with active area of 16 cm^2. Each measurement step was preceded by a 45 minute stabilization period. Measurements were performed in two sequences. In the first one ohmic resistance was measured at given temperatures during the heating up of the cell, while the second was done during cooling. Obtained results were comparable as it was expected since no physical cell disintegration was observed. This can be considered as evidence of the electronic conductivity presence.

In the early 1990s Ishihara *et al*. [21] studied perovskite oxides as a potential material for SOFCs. Authors focused on the relation of conductivities to temperature, and possible influence on the cell performance. Increase of electronic conductivity contribution to overall electric conductivity was reported for CeO_2-based systems.

Perovskites performance was compared with bismuth oxide previously studied by Coudhary *et al*. [22]. Higher ionic conductivity and electronic conductivities were reported for the latter. Among interesting experimental studies, work by Cheng *et al*. [23] should be noted for electrical characterization of $Sm_{1-x}Sr_xCoO_3$ (SSC, x=0~0.6) ceramics prepared directly from metal oxide and carbonate powders.

Kawamura *et al*. [24] performed experimental measurements of electrical conductivity in a wide range of temperatures (1173-1573 K) using four the terminal technique, and related partial pressure of oxygen to the property. Separation of the ionic and electronic conductivities was done by using relation in which overall conductivity was a sum of both, where the latter was additionally multiplied by the oxygen partial pressure to the power of -0.25. Their studies revealed electrical conductivity dependence of the composition. It was observed that the increase of CeO_2 content in the CaO doped ZrO_2-CeO_2 is followed by electronic conductivity increase, while ionic conductivity is decreasing at the same time.

Li and Thangadurai [25] investigated electrical properties of Mo-doped CeO_2 materials for SOFC, performing measurement in air, dry N_2, dry O_2, dry H_2 and wet H_2 using Pt electrodes. The authors found that maximum electrical conductivity for the analyzed material corresponds to the temperature of 823 K. Additionally, it was found that $Ce_{0.9}Mo_{0.1}O_{2+\delta}$ exhibits similar electrical conductivity to 10 mol-% Y_2O_3 stabilized ZrO_2 at high temperature. Obtained results may be questionable due to the fact that measurements were performed in oxygen presence. Ceramic material exposed to high temperature tends to operate as an oxygen pump once connected to the voltage. In such a case, distinguishing between ionic and electronic conductivity is not possible anymore.

Indirect investigations of the electrical conductivity were previously done using electrical circuit equivalence to fit the electrochemical impedance spectroscopy response to the physical model [26]. Authors investigated Co-doping, and showed that the indirect method is precise and assures high fidelity. In the case of this

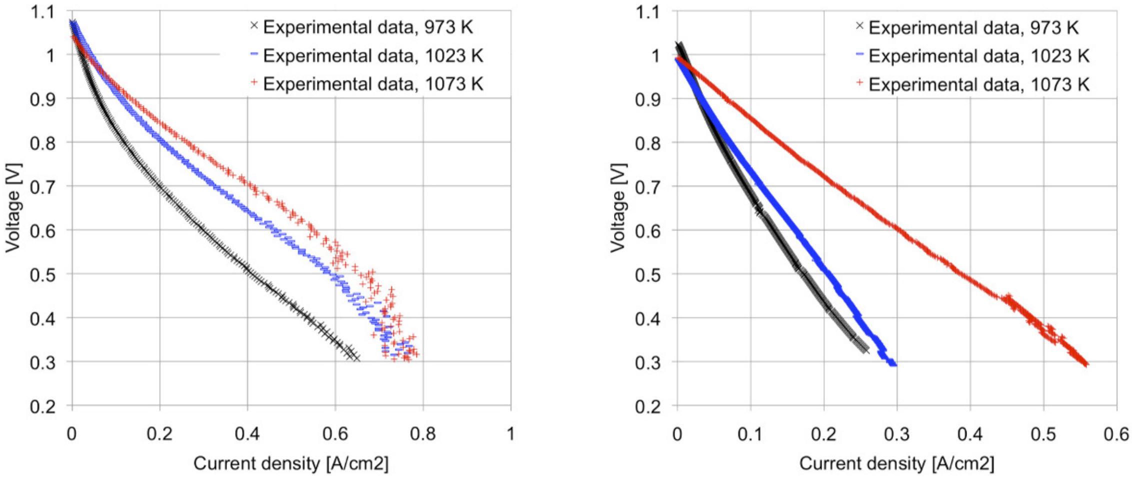

Figure 1. j-V curves collected at three different temperatures (cell no. 1 – left, cell no. 2 – right).

work electrochemical impedance spectroscopy (EIS) measurements were required to provide data for the study.

Correlation of an electrolyte electronic conductivity with temperature can be studied using a numerical model, based on directly measured current and voltage of different SOFCs.

2. Experimental procedure

2.1. Methodology

In the first step, SOFC model based on physical properties was implemented in the modeling environment. For this purpose, equivalent electrical circuit approach for black-box SOFC modeling was employed. This method was previously used by Milewski and Miller [8], with detailed mathematical background available in literature [27,28]. The main advantage of this method over the one described in [26] is that *j-V* curves instead of EIS data are used for computing the electrical properties.

Maximum current of a cell I_{max} is dependent on the molar flow of fuel, Faraday constant, and number of electrons taking part in an electrochemical reaction. As mentioned ealier, SOFC can be fed by various fuels. Hydrogen equivalent $n_{H_{2,equivalent}}$ was proposed to accommodate that fact. In the case of the presented work, only hydrogen was used, therefore, the equivalent molar flow was equal to the real flow of the gas.

For a solid oxide fuel cell electrochemical reaction, maximum current is expressed by formula:

$$I_{\max} = 2F \cdot n_{H_{2,equivalent}} \qquad (1)$$

Where F is the Faraday's constant of 96485.34 [s A mol^{-1}].

Due to the fact, that both analyzed cells had area A_{cell} of 16 cm^2, maximum current, and both resistances, were normalized to 1 cm^2, what can be written:

$$I_{\max} = \frac{2F \cdot n_{H_{2,equivalent}}}{A_{cell}} \qquad (2)$$

Taking into account Eq. 2, SOFC voltage can be now expressed as:

$$E_{SOFC} = \frac{E_{\max} - i_{\max} \cdot r_1 \cdot \eta_f}{\frac{r_1}{r_2}\left(1-\eta_f\right)+1} \qquad (3)$$

In the equation above, two coefficients are present, namely the ionic and electronic area specific resistances r_1 and r_2, respectively. Both can be found using least squares method to fit equation to experimental data.

2.2. Investigation of material properties

2.2.1. Experimental examination

Two different ceramic fuel cells were tested under the same conditions. Market-available anode supported cells were selected, both of the same type, geometry, and electrolyte material. These cells will be referred to as cell no. 1 and cell no. 2, respectively.

Experiments were conducted at three temperature levels: 973, 1023, and 1073 K with constant air and fuel mass flows. High purity hydrogen humidified with 3% water was delivered to the anode compartment, while the cathode was supplied with air. Flow meters were set to 200 mL min^{-1} and 320 mL min^{-1} for the hydrogen and air streams, respectively. Current and voltage measurement were performed for both cells. Collected data is presented in Fig. 1.

As it can be seen, cell no. 1 exhibits a much better performance compared to cell no. 2. The purpose of this comparison was to show how different the performance of the same type of fuel cell can be. Variations can be attributed to different fabrication methods, quality of materials used, porosity and tortuosity of the ceramics, levels of impurities and manufacturing quality.

For the material studies and determination of resistances, cell no. 1 was selected. Obviously, the cell with the better performance should be selected for further studies and modeling of the SOFC-based power system.

2.2.2. Numerical simulation

Material properties were studied by fitting Eq. 3 to measured values of the current-voltage curves for cell no. 1. It was possible to determine material properties by extracting information about change of parameters with temperature from experimental data. Slope of the current-voltage curves, collected at different temperatures, was analyzed. Using a numerical solver, values of coefficients r_1 and r_2 of equation for E_{SOFC} at temperatures 973, 1023, and 1073 K were found. Taking into account thickness of the anode, cathode and electrolyte, cumulative ionic and electronic resistances of the entire SOFC were computed. By this a mean correlation with temperature was obtained. It was assumed that the electrolyte mainly contributes to the electronic resistivity of a SOFC, therefore obtained values were referred only to that layer.

A sufficiently large set of data was collected during experimental campaign, therefore coefficients r_1 and r_2 were found with high accuracy. Moreover, cell voltage predicted by the numerical model was in good agreement with the experimental data. Example of fitting the cell voltage obtained using the model E_{SOFC} to the experimental current-voltage data collected at 1023 K can be seen in Fig. 2.

The method presented in this section allows predicting cell performance under different operating conditions and various fuels. Based on one experimental campaign, *i.e.*, collection of *j-V* curves for one fuel type for at least three different temperatures, it is possible to find global coefficients of equation (3) to be used in the modeling of other SOFC operational states, including off-design [8].

3. Results and discussion

Based on the described methodology, *j-V* data for cell no. 1 were collected at three different operating temperature levels, 973, 1023 and 1073 K. Using a numerical model it was possible to compute coefficients of the Arrhenius equation (Eq. 4) which describes investigated conductivities.

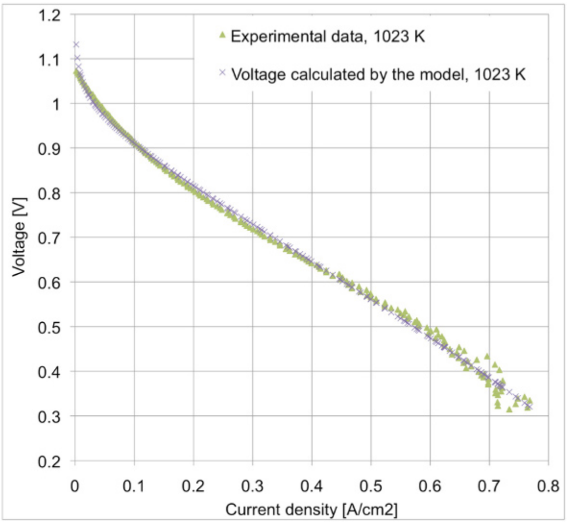

Figure 2. Example of fitting Eq. 3 to experimentally measured current and voltage.

$$\sigma_{i,e} = A_{i,e} \exp\left(\frac{-E_{i,e}}{RT}\right) \tag{4}$$

Where R - universal gas constant 8.31446 [J mol^{-1} K^{-1}], T - temperature [K], $A_{i,e}$- pre-exponential factor, $E_{i,e}$ - activation energy [kJ mol^{-1}].

For the analyzed cell, pre-exponential factors of 9.3594 and 0.0032, and activation energies of 60.7133 and 8.4816 were found for ionic and electronic conductivities, respectively. Obtained functions for both properties are presented on semi-log graphs (Fig. 3).

As expected, ionic conductivity of SOFC material was increasing with an increase in temperature. It was found that electronic conductivity of SOFC material was almost insensitive to the temperature change.
Obtained conductivity functions were plotted against data available in literature. It can be seen (Fig. 4) that ionic conductivity of the analyzed material was in agreement with properties of other SOFC electrolytes. It is also clear that in fact, for certain materials electronic conductivity can be insensitive to temperature change, as it was obtained for the investigated anode supported cell (ASC).

3.1. Model of a micro-CHP system

Model of a micro-CHP system was created in Aspen HYSYS software for the investigation of cell properties on the system performance. The design and optimal fuel processing system were previously developed for bio-syngas fuel [3]. The plant outline was now selected for modeling and optimization of a co-generative system with SOFCs. A stack unit was implemented as a user defined subroutine to assure high flexibility

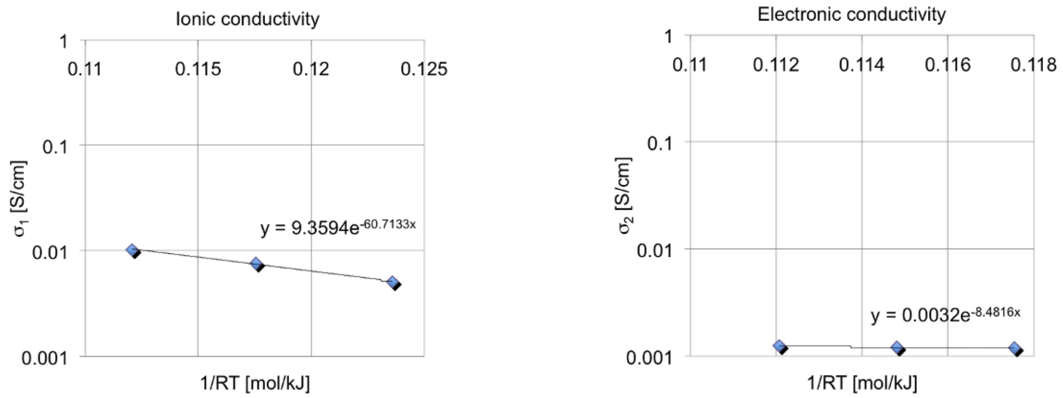

Figure 3. Obtained conductivity functions (ionic – left, electronic – right).

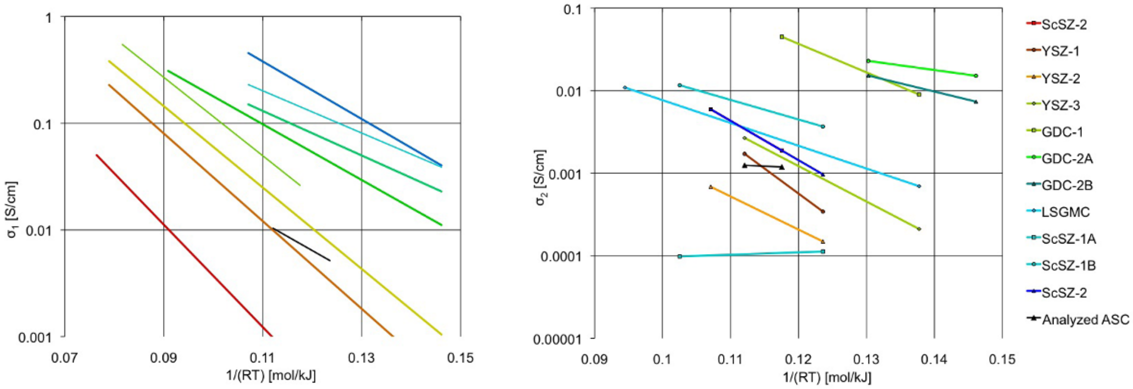

Figure 4. Comparison of conductivities of various SOFC electrolytes (ionic – left, electronic – right).

and versatility. In order to account for findings of the present material studies, two separate modules for ionic and electronic conductivities were employed. Knowing SOFCs properties it was possible to precisely predict stack voltage depending on the operating temperature.

In the model, all major components of the micro co-generative power unit were implemented. Simplified scheme of this system can be seen in Fig. 5. Auxiliary power consumption and thermal loses were estimated and included.

During steady-state operation, air is delivered to the cathode compartments with a conventional blower. The remaining high quality heat of the exhaust gases leaving the afterburner unit is used to preheat cathodic air. This system comprises an additional heat exchanger, which allows heating of the water directed for immediate consumption (hot tap water) or for storage. This additional unit is however not shown in the figure, neither is the storage tank, in order to keep the scheme simple and transparent.

A certain fraction of anodic-off gases is recycled in order to provide a sufficient amount of steam for the reforming process and to maintain the steam to carbon ratio (S/C) of 2.2. Assuring a sufficient amount of steam in the feed steam is required in order to prevent undesirable carbon formation and deposition in the anode compartments of the SOFC stack.

A reformate preheater located on the recycled stream reduces the temperature of the anodic gas to a sufficiently low level for using a conventional recirculation fan. At the same time, fresh fuel premixed with recycled steam is heated up to reformer operating temperature.

A model of the system was created and optimized. As mentioned earlier, two different electrolytes were modeled to evaluate overall unit performance. In the preliminary configuration ceramic fuel cells stacked with an output of 2168 W_{el} was considered.

Under nominal operating conditions, performance varied between the cells. Electrical and overall efficiencies of the system, found for analyzed ASC cell and cell with generic YSZ-3 electrolyte were 43.2%/79.4% and 45.6%/77.2%, respectively. Results indicated that the performance of the micro-CHP unit depends not only on the thermal integration and plant optimization, but also on the selection of a proper cell with desired material

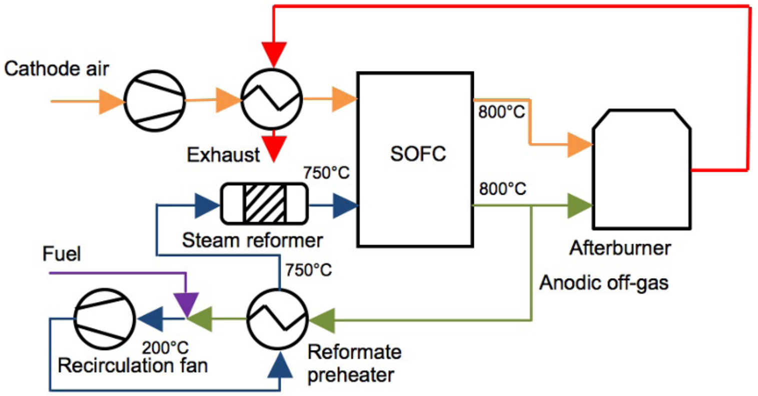

Figure 5. Simplified scheme of analyzed micro-CHP system.

properties. A similar calculation can be performed for all available SOFC electrolytes in order to support the decision on a particular cell selection.

4. Conclusions

The main purpose of this work was to investigate material properties of commercially available SOFC. Obtained ionic conductivity of the analyzed cell was in agreement with data for other materials data available in literature [29-31]. As reported earlier, the temperature influence on the electronic resistance of the investigated cell was not observed. For selected highly porous ceramic materials with mixed ionic-electronic conductivity such behavior might be expected, therefore authors believe that obtained correlation is physically correct. In certain cases such behavior can correspond to metallic materials, and rarely can be attributed to artifacts.

Electronic conductivity of an electrolyte corresponds to electrons current through the electrolyte. It can be measured if no oxygen is applied at both sides of a fuel cell by an ohmmeter. Such an experiment was done and resistance was measured while no load was applied at the fuel cells. In fact, the issue needs a deeper investigation, but as far as the resistance is quite high, it has small influence of the current density-voltage curve.

Obtained results were compared with values calculated and reported previously by Milewski *et al*. [32] for the ionic resistance, and by Nikonowicz and Milewski [33] for the electronic resistance. Good agreement was observed.

In available literature, explicit formulation of conductivity functions can rarely be found. In the work by Pramuanjaroenkij *et al*. [34] an approach similar to the currently presented one was proposed, and interconnect conductivity was included in the mathematical model of SOFC. With focus on the entire cell, conductivity of interconnect was also included. With the present approach it was however not possible to determine its contribution to the overall conductivity of a cell.

Modeling approach, with ionic and electronic conductivities represented by separate functions was previously used by Xie and Xue [35]. In the transient analysis of anode supported cells, separate functions for the two mentioned properties were implemented, as it was done in the work presented in this paper.

The main contribution to the electronic resistance of a solid oxide fuel cell is from the electrolyte, therefore resistivity of different cells can be compared on the electrolyte basis. Influence of structure and cell interconnects might also contribute to the overall cell conductivity [19], but only to a small extent. In general, the electric resistance of the fuel cell components (meshes, manifolds, wires, inter-connectors, *etc*.) need to be as small as possible (it generates ohmic losses in a stack). On the contrast, internal electric resistance of an electrolyte is needed to be as high as possible to stop a shortcut of electrons through the electrolyte, thus it is usually the orders of magnitude higher that an ionic resistance (which should be as low as possible).

In the plant-level modeling this contribution can be withal neglected, and proposed methodology will still provide sufficiently high fidelity.

Additionally, authors implemented the proper methodology for fuel cell stack modeling in the plant-level 0D approach. It must be emphasized, that the created model was based only on the physical properties. No non-physical coefficients were used for the reproduction of experimental data. The proposed technique provides a straightforward method to study material properties without complex and indirect methods. Understanding the conductivity dependence on temperature is of a high attention, especially when performing plant-level modeling.

It was proven, that selection of particular solid oxide fuel cell, i.e. selection of material composition for micro-CHP application must be made with caution. Decision on particular SOFC materials should be based upon investigation of system performance under different operating conditions. Results of the system modeling show that the difference in performance can be of 2.4% point for electrical and 2.2% point for overall efficiencies, respectively.

In the future, the proposed methodology can be used for analysis of off-design operation of SOFC stack, fed by various fuels.

Acknowledgements

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