Fine-Grained YSZ–NiO(Ni) Anode Material

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Reduction–oxidation (redox) cycling of a solid oxide fuel cell (SOFC) due to leakage of a fuel or standby and shutdown cycling is an issue that has attracted the attention of many research groups for a long time. The researchers mainly note the harmful effects of redox cycling on the microstructure of SOFC constituents and search for ways to mitigate or diminish them.

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1. Importance of Studying Electrodes of Solid Oxide Fuel Cells

Renewable energy is a promising source for clean electricity aimed at solving climate change issues [1]. In the reviews of Golkhatmi S.Z. et al. [2], Boldrin P. et al. [3], and Jacobson A.J. [4], it was shown that among the environmentally-friendly devices serving this purpose, solid oxide fuel cells (SOFCs) have significant advantages in efficiency as they employ an electrochemical conversion method of electricity production from direct fuel oxidation. Zamudio-García J. et al. [5] showed that symmetrical SOFCs are ones of the most promising in this field. Recently, many research laboratories are working on the development and improvement of reliable materials for SOFCs as well as on the SOFC design [6][7][8][9][10][11][12]. Along with solid electrolyte and cathode materials [6][10][11][13][14][15][16][17][18][19][20][21][22][23][24][25], great attention is paid to SOFC anode materials [8][12][26][27][28][29]. It is known that fuel loss may occur during operation of a SOFC which usually leads to re-oxidation of the nickel-containing anode [2][30][31][32][33]. Thereafter, reduction in nickel oxide should be performed to reactivate the anode material. These reduction/oxidation (redox) cycles may occur several times during SOFC operation, and thus affect its long-term stability and performance [32][34][35]. Therefore, the understanding of the effects of redox cycling on SOFC behavior, focusing on a nickel/yttria-stabilized zirconia cermet, is essential as it assists in reaching a perfect quality of developed materials for SOFC anodes.

2. Studying the Harmful Effects of the Cyclic Redox Process on Microstructure of SOFC Materials

Wood T. and Ivey D.G. [30] investigated the reaction kinetics and changes in mechanical properties of a SOFC under redox conditions as well as their impact on SOFC performance. Wood A. and Waldbillig D. [36] and Waldbillig D. et al. [37] found that the harmful effects of the cyclic redox process on the microstructure of SOFC materials can be mitigated or diminished using the proposed methods, in particular, the preconditioning treatment to enhance redox tolerance of SOFCs.

In the study of Li J. et al. [38], an effect of moisture on microstructure degradation and mechanical properties of the nanostructured coatings based on yttria-stabilized zirconia (n-YSZ) was studied. The authors found that hydrothermal degradation of the n-YSZ coatings resulted in pores and microcracks and caused the transformation of tetragonal to monoclinic zirconia phase, which in turn, provoked variations in the internal stress. All these microstructural changes were followed by a significant decrease in Young's modulus, flexural strength, and fracture toughness of the n-YSZ coatings.

Mack J.B. et al. [39] studied the evolution of lamellar microstructure of freeze-cast Fe-25Ni foam as material for iron–air batteries operated under conditions of cyclical steam oxidation and hydrogen reduction, and noted the eventual degradation of its internal architecture. The foam was designed as a composite with colonies of parallel lamellae separated by channels to compensate for changes in volume during the cyclical oxidation and reduction in Fe in the battery. The authors proposed a mechanism for developing an outer Fe-oxide scale over Ni during oxidation and Ni acting as a catalyst during reduction with formation of the interdiffused and homogenized Fe-rich shell and the Ni-rich core. They revealed that this cyclic process eliminates both Kirkendall pores and microchannels from the lamellae. Due to Ni alloying, Fe-25Ni foam maintains high active surface area (a channel porosity > 40%) after 10 redox cycles, in contrast to pure Fe foam showing an almost complete loss of the channel porosity.

The redox cycling behavior of lamellar Fe foams with 15 vol% fibers, created by freeze-casting, was studied by Pennell S. and Dunand D. [40]. Long zirconia fibers and long (1–2 mm) and short (0.1 mm) stainless steel fibers were used. The material was undergone to cyclic H_2/H_2O exposure at 800 °C. The authors revealed fiber engulfment as a novel degradation mechanism occurred during redox cycling in this material. As a result, foam architecture changed after the cycling from bridged-lamellar (with evenly distributed porosity) to mixed lamellar/fibrous (with unevenly distributed porosity).

Wang M. et al. [41] designed a dual-layered SOFC anode consisting of a Ni–Fe alloy layer and a Ni–YSZ cermet layer. The cell supported on this anode with straight pore paths exhibited a maximum power density of 1070 $mW \cdot cm^{-2}$ at 800 °C. The SOFC supported on the Ni-YSZ/Ni–Fe dual-layered anode did not degrade during eight redox cycles, whereas the cell supported on the Ni-YSZ single-layered anode failed after the first redox cycle. The reason for the significant improvement in the anode stability was assumed to be the straight pore paths, which allowed for fast gas phase transport. This, in turn, improved the accessibility of electrochemical reaction sites and, as a result, reduced the activation polarization.

3. The Ways to Improve Redox Stability of SOFC Materials

In the study of Chang H. et al. [42], a double-perovskite $Sr_2MoFeO_{6-\delta}$ (SMFO) applied over a Ni-YSZ anode to improve coking resistance in SOFCs operating on methane-based fuels was investigated. This material works as a redox-stable independent on-cell reforming catalyst. It was found that the cell modified with double-layered SMFO–Al_2O_3 has improved performance when fueled with methane-based gas, as compared to a cell without the catalyst layer. In contrast, a more intense coking was revealed in the cell fueled with wet coal-bed gas (CBG), which is attributed to the presence of heavy carbon compounds in CBG. When operated on wet CH_4 at 800 °C, a Ni-YSZ anode-supported cell with SMFO generates a high power output of 1.77 W·cm^{-2} exhibiting improved stability.

Lv H. et al. [43] presented a low-cost and simple dip coating and one-step co-sintering technology to produce a metal supported micro-tubular SOFC with good electrochemical performance at 800 °C. They developed a SOFC sandwich structure containing Sr as “porous 430 stainless steel support|430 stainless steel-SSZ|SSZ|porous SSZ”. It was shown that the structure of the single cell did not degrade as no crack and Sr diffusion were observed after 14 thermal cycles between 600 °C and 800 °C, but the power density was lowered by 19.6%. The relatively fast degradation of microstructure was related to the agglomeration of coarsened Ni and LSM particles.

In the studies of Faes A. et al. [44], Ettler M. et al. [45], Peraldi R. et al. [46], and Mori M. et al. [47], reviews of the effects and parameters influencing redox cycles of the Ni-ceramic anode were presented. The authors described solutions for redox instability taking into account many factors, such as stack design, cell design, new materials, and microstructure optimization. They also exhibited the behavior of Ni-based anode supports with optimized microstructures under redox cycling conditions. In a series of scientific works, a controlled redox cycle was proposed to apply for the enhancement of the redox stability [36][37][44]. The reason for this was the attempt to change the material microstructure. On preconditioned specimens (one redox at 550 °C), a lower decrease in performance (3.2% decrease in voltage at 0.75 A/cm^2 after a redox cycle at 750 °C) was found compared to three times higher decrease in specimens without the treatment. Wood A. and Waldbillig D. [36] proposed the application of the initial controlled redox cycle in various stages of the anode fabrication, namely, on the powder mixture prior to the formation of the green anode, on the sintered anode before insertion in the stack, and in situ in the stack.

Pihlatie M. et al. [48] showed an increase in electrochemical performance after a redox cycle at 650 °C in a symmetrical cell configuration. Moreover, Waldbillig D. et al. [37] and Lang M. et al. [49] announced an increase in performance over short-term redox cycles. They assumed that this is due to the formation of a porous GDC barrier layer between electrolyte substrate and air electrode preventing interdiffusion at the interface.

Similarly to these last works and in contrast to other works, researchers showed in the previous research [27][50][51] that redox may be used as a positive phenomenon for improving long-term stability and performance of ScCeSZ–NiO(Ni) and YSZ–NiO(Ni) anode cermets. For this purpose, a corresponding redox treatment mode was set which comprised of a stage of heating the material in vacuum and intermediate degassing between the stages of reduction and oxidation. Controlled microstructure evolution during reduction and oxidation cycles allowed for the redox-stable microstructure to be obtained. As a result, a significant increase in flexural strength (by about 12–25%) and electrical conductivity (up to an acceptable level) was achieved at 600 °C.

4. The Use of Redox Treatment for Improvement of SOFC Performance

The analyzed above works highlight controversial hypotheses concerning redox effects on microstructure and mechanical properties of Ni-containing anode materials for SOFCs. In the case of a controlled redox mode, significant positive effects may be achieved.

The main aim of the work was to study the mechanical behavior of YSZ–NiO(Ni) anode substrate specimens that underwent the redox treatment in low-temperature (600 °C) and intermediate-temperature (800 °C) modes in comparison with the behavior of as-sintered and one-time reduced specimens. Relation of the mechanical behavior to microstructure and fracture surface morphology of material in the applied modes is to be studied, and an appropriate treatment mode for providing high redox cycling stability of Ni-containing SOFC anode materials is to be found. The main conclusions of the work are as follows: Redox treatment at 600 °C provides an increase in flexural strength and electrical conductivity of YSZ–NiO(Ni) anode cermets, such as the treatment at 800 °C causes formation of a gradient microstructure with lateral cracks initiated on the “near-surface layer/specimen core” interfaces that results in a significant decrease in flexural strength of the material; the mode of redox treatment at 600 °C for 4 h in Ar–5% H_2/air atmosphere can be regarded as promising for preconditioning YSZ–NiO anode ceramics; residual compressive stresses that arose in redox-treated material contributed to an increase in its flexural strength compared to that of other reduced cermets (the values of flexural strength and relative strength were 127 ± 4 MPa and 96 ± 2.5%, respectively); and electrical conductivity was provided at a level of 7×10^5 S/m. These results verify the feasibility of redox technique in appropriate modes for preconditioning Ni-containing SOFC anode materials rather than using a traditional one-time reduction process.

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