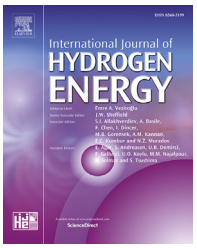
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Degradation of Ni-$Zr_{0.9}Sc_{0.1}O_{1.95}$ anode in $H_2 + H_2O$ at low temperature: Influence of nickel surface charge

D.A. Osinkin [a,b,*]

[a] Institute of High-Temperature Electrochemistry, 620990, Ekaterinburg, 20 Academicheskaya St., Russia
[b] Ural Federal University, 620002, Ekaterinburg, 19 Mira St., Russia

ARTICLE INFO

Article history:
Received 30 July 2017
Received in revised form
22 October 2017
Accepted 9 November 2017
Available online 1 December 2017

Keywords:
Ni-SSZ
Degradation
Long-term test
SOFC
DRT
Point of zero charge

ABSTRACT

The present paper reports on the data of the Ni-$Zr_{0.9}Sc_{0.1}O_{1.95}$ anode polarization resistance long-term test (1500 h) at 600 °C in the wet hydrogen and 30% H_2 + 70% H_2O. The results are presented for two type of anodes: initial and impregnated with ceria. The fast degradation of both types of anodes in 30% H_2 + 70% H_2O was observed. After the long-term tests in 30% H_2 + 70% H_2O at 600 °C, heating and exposure at 900 °C in wet hydrogen leads to the restore of anode performance. At the termination of the 1500 h test, the area polarization specific resistance of Ni-$Zr_{0.9}Sc_{0.1}O_{1.95}$ remained almost unchanged as compared to the initial value, whereas for impregnated anodes the polarization resistance increased three times. The observed phenomena were explained by the OH^- ions adsorption at the positively charged nickel surface. During the long-term tests at 600 °C the electrode microstructure did not change and the significant sintering of highly disperse ceria was not observed.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Degradation processes in solid oxide fuel cells (SOFCs) is a serious problem for a long-term SOFCs application. Deterioration of the functional properties in time is characteristic of all SOFC components: electrolyte, cathode, anode, current collectors, seals etc. There are many factors of different nature that lead to SOFCs components degradation. For example, Schrödla et al. reported about strontium and lanthanum segregation at the $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $La_2NiO_{4+\delta}$ cathodes surfaces, respectively [1]. Strontium segregation at the $La_2NiO_{4+\delta}$ surface was also observed by Zhou et al. [2]. The evaporation of chromium from the FeCr interconnector and nickel from Ni-YSZ anodes during the long-term tests at high temperatures were detected in Refs. [3,4], respectively. Nickel particles sintering in the Ni-based anodes were determined by Simwonis et al. [5], Abdeljawada et al. [6] and Heo et al. [7].

The main reason for the previously mentioned process is the high temperature of SOFCs production and operation. That

* Institute of High-Temperature Electrochemistry, 620990, Ekaterinburg, 20 Academicheskaya St., Russia.
E-mail address: OsinkinDA@mail.ru.
https://doi.org/10.1016/j.ijhydene.2017.11.071
0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

is why to decrease the rate of degradation processes it is necessary to decrease the temperature. The study of new materials, development of production technologies of thin film electrolytes and active electrodes allow decreasing operation temperatures of SOFCs and maintaining their high performances. For instance, the plasma spray [8] and electrophoretic deposition [9] methods were used to produce electrolyte membranes of 26 and 10 μm thickness, respectively, which allowed obtaining high performance of SOFC at medium temperatures. Osinkin et al. report that a single SOFC with a supporting high-active Ni-based anode with a 30 μm thick film electrolyte generates the power density of about 1.3 W cm^{-2} at 700 °C [10]. A decrease in SOFCs operating temperatures has a positive effect on the stability of their characteristics in time, but even at low temperatures degradation processes are present and require further study.

Ni-based anodes are the main SOFC anode material, therefore, there is a diverse data on the study of its degradation. The feature of Ni-based anodes is a fast degradation in atmospheres with high water content [11–13], that are formed and/or are present in the anode chamber at hydrogen-containing fuel oxidation. Chen et al. demonstrated the water influence on the fast Ni-CGO degradation at a low hydrogen concentration and high current density [14]. The increase in the water partial pressure in the gas phase results in the increase of the $Ni(OH)_2$ partial pressure, which has a negative effect on the anode characteristics. Primdahl et al. [15] noted that in hydrogen with water content of 3% at 850 °C the $Ni(OH)_2$ partial pressure was about 10^{-12} atm. Despite a small $Ni(OH)_2$ concentration in gas phase Mogensen et al. [16] suggest a mechanism of Ni-based anode restructuring by formation and decomposition of $Ni(OH)_2$.

In Ref. [17] Perfil'ev et al. reported that the polarization curves of Ni electrode in the $H_2 + H_2O$ have a complex form with an abrupt increase in the inclination angle within the overvoltage region of 0.05–0.15 V. At the overvoltage below 0.05 or above 0.2 V the polarization curve becomes flattened. The potential of Ni electrode, which corresponds to the polarization curve bend, coincides with the minimum capacity of the double-electric layer, i.e. with the point of zero charge of Ni electrode. Kek et al. [18] also observed the presence of double-electric layer capacity minimum for Ni and other metallic electrodes at a definite oxygen activity in the gas phase and temperatures. Therefore, depending on the temperature and oxygen activity in the gas phase the Ni surface may have either positive or negative charge or may be at the point of zero charge. Then we assume that if the Ni electrode surface has a positive change than the adsorption of negatively charged OH^- ions, which concentration increases as the water partial pressure increases, is possible. Papers [19,20] demonstrate that the concentration dependencies of the high-frequency partial polarization resistance of Ni-based electrode in water–hydrogen mixtures change their inclinations at a definite oxygen activity in the gas phase. In Ref. [19] it was assumed that the adsorbed forms of potential defining particles on the electrode surface influence the increase in the electrochemical performance of Ni electrode at the transition from wet hydrogen to gas medium with high water content.

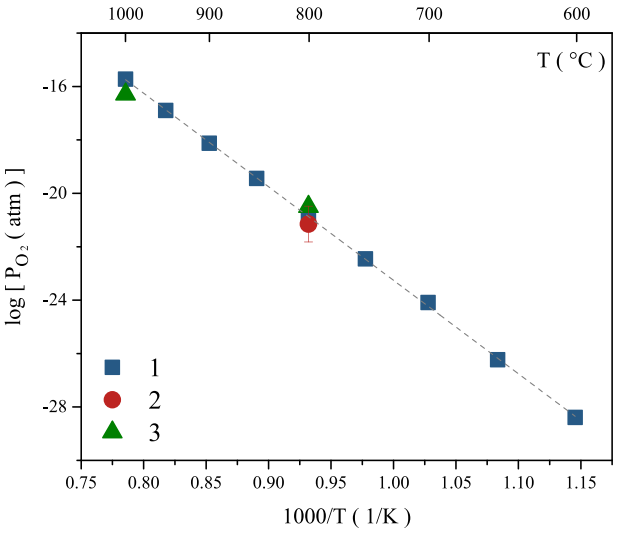


Fig. 1 – Temperature dependencies of oxygen partial pressure in $H_2 + H_2O$. 1 – P_{O_2} corresponds to the point of zero charge of Ni electrode [17], 2 – P_{O_2} corresponds to the Ni electrode electrical double layer capacity minimum [18], 3 – P_{O_2} corresponds to the bend point of concentration dependencies of the high-frequency partial polarization resistance of Ni-based anode [19,20].

Fig. 1 illustrates data taken from papers [17–20]. The oxygen activity, which corresponds to the Ni-electrode zero charge potential [17] at different temperatures was calculated by Eq. (1). The values of oxygen activities, at which observed the minimal value capacity of the Ni electrode double-electric layer, are reported in Ref. [18]. The values of partial oxygen pressures, at which concentration dependencies of the high-frequency partial polarization resistance change their inclination, are reported in Refs. [19,20]. The data is seen to coincide at the same temperature. Therefore, we may assume that the regularities of the high-frequency partial polarization resistance behavior, which was observed in Refs. [19,20], may appear due to the Ni surface charge change.

$$\log Po_2 = \frac{4F(\varphi - \varphi^o)}{RT} \tag{1}$$

where φ – the electrode equilibrium potential, φ^o – the electrode standard potential, R – the universal gas constant, T – the absolute temperature, F – the Faraday number.

Eq. (2) presents the correlation of oxygen (P_{O2}), hydrogen (P_{H2}) and water (P_{H2O}) partial pressures in the water–hydrogen gas mixture:

$$\frac{RT}{4F}\ln\frac{P_{O_2}}{P_{O_2}^{'}} = -1290 + 0.292T - \frac{RT}{2F}\left(\ln\left[\frac{P_{H_2}}{P_{H_2O}}\right] + \frac{1}{2}\ln P_{O_2}^{'}\right) \tag{2}$$

Provided that $P_{H2} = 1 - P_{H2O}$, and $P_{O2}^{'} = 0.21$ atm (oxygen partial pressure in air) Eq. (2) may be simplified to Eq. (3):

$$P_{H_2O} = \left(1 + \frac{A}{\sqrt{P_{o_2}}\cdot\exp[BT^{-1}]}\right)^{-1} \tag{3}$$

where A and B are constants.

Download English Version:

https://daneshyari.com/en/article/7708729

Download Persian Version:

https://daneshyari.com/article/7708729

Daneshyari.com