Solid State Ionics 234 (2013) 1–10

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

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

Electrochemical reduction of NiO in a composite electrode

Qiang Hu *, Torben Jacobsen, Karin Vels Hansen, Mogens Mogensen

Department of Energy Conversion and Storage, Technical University of Denmark, DTU Risø Campus, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ARTICLE INFO

Article history:
Received 28 July 2012
Received in revised form 24 November 2012
Accepted 29 December 2012
Available online 24 January 2013

Keywords:
Electrochemical reduction
Nickel oxide
Impedance spectroscopy
Composite electrode
Oxygen sensor

ABSTRACT

Electrochemical reduction of NiO in a composite electrode along with 8 mol% Y_2O_3 stabilized zirconia (8YSZ) is studied. Voltage sweeps are performed on cells with a counter electrode made from Pt or the composite of $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$ (LSM25) and 8YSZ, but the composite electrode gives a lower overpotential. Microstructures of NiO with different reduction degrees are shown. Electrochemical impedance spectroscopy is carried out during the reduction process. Electrochemical reduction of NiO may need an induction period. When NiO is reduced at a constant voltage the current initially increases, hereafter a decay is observed. The kinetics of electrochemical reduction of NiO can be described by the Avrami equation. In performed experiments the exponent of the Avrami equation is in the range of 0.5–0.7 and the overall rate constant varies from 1.19 to 7.73×10^{-3} and increases with temperature and in particular with the applied voltage. The maximum reaction rate is obtained when 2–11% NiO is reduced. The increasing resistance in NiO reduction can be exclusively ascribed to one arc in impedance spectra.

1. Introduction

Nickel oxide is widely used as a precursor for catalysts and electrodes of electrochemical cells including solid oxide fuel cells [1,2], electrolysis cells [3,4] and oxygen sensors [5,6]. A study on the reduction of NiO has practical importance in preparation of catalysts, in reduction of NiO ores and in fabrication of electrodes for electrochemical devices [7]. The prevailing studies on NiO reduction are carried out with hydrogen [8–12], occasionally carbon [13–15], whereas electrochemical reduction of NiO rarely attracts attention.

Recently we developed an internal reference oxygen sensor (IROS) [5]. The cell is potentiometric and makes use of the equilibrium pO_2 of Ni/NiO as the reference. Fig. 1 shows the schematic structure of an IROS. The cell consists of an internal reference electrode (IRE), an electrolyte, a seal and a sensing electrode (SE). The IRE is sealed hermetically by glass and the binary mixture of Ni/NiO inside the IRE is generated in situ by electrochemical reduction of NiO. The SE can be made from Pt or composite oxides based on $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$ (LSM25) and 8 mol% stabilized zirconia (8YSZ) [5]. Based on the IROS it is possible to carry out a detailed study on the electrochemical reduction of NiO. In this case, the IRE serves as the working electrode and the SE is used as the counter electrode.

To initiate the reduction of NiO a certain voltage is needed. This voltage, on the other hand, depends on the reduction condition such as temperature and the properties of the counter electrode. As NiO is a poor conductor, a composite structure that contains a network of oxide ion conductor is preferable to facilitate the oxide ion transport and extend the triple phase reaction area. Thus, the IRE in this study is composite and includes the well-known oxide ion conductor, 8YSZ [16,17]. During the electrochemical reduction of NiO, the composite structure will change with the reduction degree since the removal of oxide ions causes a collapse of the crystalline of NiO, and the resulting Ni/NiO structure determines the properties of the IRE and consequently the performance of an IROS. Thus, the objectives of this study are: 1) determine the voltage that needed to initiate discernibly the electrochemical reduction of NiO with respect to a specific electrode such as the Pt electrode and the composite electrode of LSM25/8YSZ; 2) study the structure change of the IRE during the electrochemical reduction of NiO; and 3) investigate the influence of the degree of NiO reduced on the performance of an IROS.

2. Experimental

The IRE was made from NiO (Alfa Aesar) and 8YSZ (Tosoh). To achieve a better sintering match among the components of the IRE, and to realize a coherent contact between the IRE and the electrolyte, a mixture containing a calcined and an uncalcined part of both powders, NiO and 8YSZ, was applied. Calcination of 8YSZ was performed at 1100 °C for 2 h and calcination of NiO was performed at 800 °C for 3 h. NiO, calcined NiO, 8YSZ and calcined 8YSZ powders, with a weight ratio of 3:3:2:2, were ball-mill mixed and made into an ink with a terpineol based solvent. The ink was screen-printed on home-made tapes of 10 mol% Sc_2O_3 and 1 mol% Y_2O_3 stabilized zirconia (ScYSZ) and the ScYSZ powder was purchased from Daiichi. The tapes have a size of 10×10 mm^2 and a thickness of ca. 250 μm. The screen printed IRE was sintered at 1350 °C in air for 2 h and

* Corresponding author. Tel.: +45 4677 5609; fax: +45 4677 5758.
E-mail address: qihu@dtu.dk (Q. Hu).

0167-2738/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2012.12.018

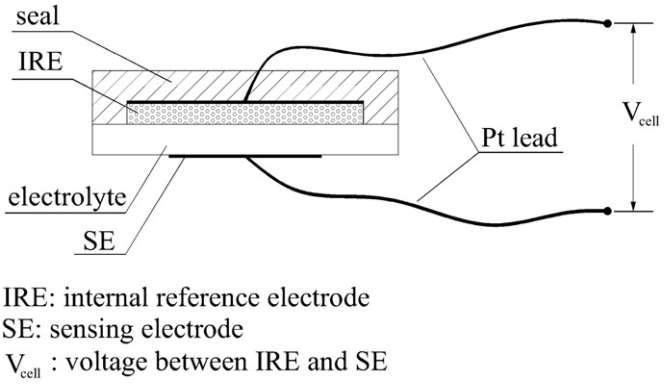

Fig. 1. Schematic structure of an IROS that can be used to study the electrochemical reduction of NiO. In this case the IRE is used as the working electrode and the SE is used as the counter electrode.

the mass of the IRE was found from the weight gain after the IRE preparation.

The SE comprises Pt or the composite oxides of LSM25/8YSZ [5]. Fabrication of the composite sensing electrode (CSE) is based on an ink containing equal weights of LSM25 and 8YSZ. Graphite (Aldrich), used as a pore former, was added into the ink with a weight ratio of 20%. The ink was screen printed onto the electrolyte side opposite to the IRE and sintered at 1050 °C for 2 h. The Pt sensing electrode was prepared by brushing a Pt paste (FERRO) on the side opposite to the IRE, and then heated at 1050 °C for 2 h. The average electrode area was 4×4 mm^2.

A Pt lead used for connection between the IRE and external circuits was adhered to the IRE by Pt paste, followed by a heat treatment at 700 °C for 1 h. After the Pt lead connection, a glass seal comprising SiO_2, 68 wt.%, Al_2O_3, 15 wt.%, and Na_2O, 17 wt.%, was applied. The glass powder was mixed with a polyethylenglycol-containing solution and the resulting slurry was used to cover the IRE. The glass sintering was carried out at 960 °C for 2 h and the cooling rate from 960 °C was 2 °C per minute. According to the calculation of FactSage™ 5.5 [18], the equilibrium potentials of the metal and the corresponding metal oxide that consisted of the glass are at least 600 mV below that of NiO. Thus the oxide constituents of the sealing glass cannot to be electrochemically reduced in the experiments shown in this study. The stability test of more than 5100 h proved that the glass was able to form a hermetic seal for the IRE and the mutual stability of the glass and the IRE [5].

The cells were placed in an alumina test house with an inner diameter of 69 mm, a length of 495 mm, and room for four cells to be tested in one batch. The pO_2 inside the test setup was controlled by mass flow controllers (SLA5850, Brooks) and the source gas species included compressed air, oxygen (N35, Air Liquid) and nitrogen (N48, Air Liquid). The minimum and maximum flow rates of the mass flow controllers were 0.1 and 6 slph (standard liters per hour), respectively. Provided that the electrolyte is an (almost) pure oxide ion conductor, which is the case for ScYSZ, the cell voltage, V_{cell}, the pO_2 at the IRE, p_R, and the pO_2 at the SE, p_S, satisfy the Nernst equation:

$$V_{cell} = \frac{RT}{4F} \ln \frac{p_S}{p_R}. \quad (1)$$

So the pO_2 at the IRE, p_R, can be determined if the pO_2 at the SE, p_S, and the cell voltage, V_{cell}, are known, and vice versa. For example, if the binary mixture of Ni/NiO is not formed within the IRE, then the p_R can be known by measuring the cell voltage, V_{cell}, and setting the p_S by mass flow controllers. On the other hand, if the binary mixture of Ni/NiO is formed the p_R is then well defined by the thermodynamic equilibrium of Ni/NiO and the pO_2 at the SE, p_S, can be determined by measuring the cell voltage. Denoting the potential of IRE versus SE by E_{IRE}, the cell voltage defined by Eq. (1) is in fact equal to the negative potential of the IRE, meaning:

$$E_{IRE} = -V_{cell} \quad (2)$$

followed by a specification of the SE conditions such as pO_2 and temperature.

Voltage sweeps were performed, with a rate of 1, 5, 10 and 20 mV·s^{-1}, respectively, on cells with Pt or CSE as the counter electrode. The voltage sweeps may not be regarded as the real potential sweeps on the IRE since the resistance of the SE was not negligible in the experiments.

IREs were reduced at a constant cell voltage of 0.9 or 1.1 V that corresponded to an E_{IRE} of −0.9 or −1.1 V, well below the equilibrium potentials of Ni/NiO at the relevant conditions. Chronoamperometry was carried out for voltage sweeps and for the reduction of NiO at a constant voltage. From the curve of current versus time the amount of NiO reduced can be determined. Electrochemical impedance spectroscopy (EIS) was performed with a DC voltage applied on the cell. At IRE potentials above the Ni/NiO equilibrium potential the cell was pretreated by application of a DC voltage for 5 min before the impedance spectroscopy was performed. After the pretreatment period the DC current was less than 5 mA. At lower IRE potentials, after formation of the binary mixture of Ni/NiO the cell had immediately a stable and well defined open circuit voltage (OCV), which was very close to the thermodynamic value [5]. In this case the impedance spectroscopy was carried out at the OCV. All of the electrochemical tests were performed with a Solartron 1250 frequency response analyzer combined with a Solartron SI 1287 electrochemical interface. The electrochemical measurement software was Elchemea 6.0 that was developed in-house. The involved thermodynamic calculations were carried out by FactSage™ 5.5 [18].

Electrochemical reduction of NiO was stopped when the desired degree of NiO reduced was reached. The cells were then cooled down at a rate of 5 °C·min^{-1} and then were made into SEM samples. The SEM samples were vacuum embedded in epoxy resin, grounded using SiC paper, polished using 6, 3, and 1 μm diamond paste and then carbon coated to eliminate the surface charging. The samples were observed in a Zeiss Supra 35 field emission gun scanning electron microscope, equipped with a Noran System Six Model 3000 energy dispersive X-ray spectrometer. By energy dispersive spectroscopy (EDS), the particle composition in the IRE can be determined. As samples were all embedded in epoxy resin oxygen is always seen in the EDS analysis.

3. Results

3.1. The structure of IRE before reduction

Fig. 2 shows the microstructure of an unreduced IRE. The particle compositions were determined by energy dispersive spectroscopy as introduced above and the image was taken by a secondary electron detector. The NiO particles, with a smaller average atomic weight, were darker than the 8YSZ particles. The 8YSZ particles were fine, in a size of 1–2 μm, and dispersed among NiO particles. The NiO particles are seen to distribute in the IRE with two major sizes, ca. 10 and 4 μm. Half of the NiO particles in the IRE were calcined before they were used to prepare the IRE. The larger NiO particles in the size of ca. 10 μm should result from the calcination that made NiO particles grow and have a larger size.

3.2. Voltage sweeps

3.2.1. Effects of sweep rate

The first voltage sweeps from 0 to 2 V, corresponding to an IRE potential from 0 to −2.0 V, are shown in Fig. 3(a) and the sweep sections from 0 to 0.6 V are magnified and shown in Fig. 3(b). The sweep curves