Improved Internal Reference Oxygen Sensors Using Composite Oxides as Electrodes

The thesis describes the research on and development of an internal reference oxygen sensor (IROS). The IROS is potentiometric and uses the equilibrium pO2 of the binary mixture of Ni/NiO as the reference pO2. The sensing electrode of the IROS are made from metallic Pt or the composite of (La0.75Sr0.25)0.95MnO3±d(LSM25) and 8 mol % ytria stabilized zirconia (8YSZ), with/without samaria doped ceria (SDC) impregnation. The composite sensing electrodes are verified superior to Pt in terms of a lower polarization resistance and an extended working temperature range. Cell performance is evaluated comprehensively and the evaluation is targeted to the performance indicators that relate closely to the practical application. IROSes show high accuracy, good stability, fast response, good tolerance to thermal and pO2 cycling and easy recoverability when Ni is depleted. Both cell fabrication and performance show good reproducibility. Apart from the excellent performance the IROSes are fabricated by an inexpensive and flexible method. Therefore, the IROSes present in this thesis may be commercialized in the future.

Theoretical investigations on IROS are carried out. The electronic leak of an electrolyte made from 8YSZ is evaluated quantitatively and figures that may be used to design the depletion period of an IROS due to the electronic leak of 8YSZ are provided. One dimensional numerical simulations are performed to study the variation in cell voltage during the process of gas mixing, and the asymmetric behavior in cell response is revealed. The errors in pO2 measurement are analyzed. The temperature dependence of the equilibrium potentials of ten candidates of binary mixtures including Fe/FeO, Pb/PbO, Cr/Cr2O3 are evaluated with respect their use in IROSes that are less sensitive to temperature fluctuations.

Electrochemical reduction of NiO is studied. The kinetics of electrochemical reduction of NiO can be described by the Avrami equation. The electrochemical reduction of NiO may require an induction period. 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. The pO2-dependent part of the resistances of the composite electrodes is determined. SDC impregnation reduces significantly the polarization resistance of the composite of LSM25/8YSZ.

Designs that may extend the application of IROSes are provided. Based on the concepts and fundamentals of the IROS, internal reference sensors that detect other gas species such as hydrogen, chlorine and bromine may be developed.

**General information**
State: Published
Organisations: Department of Energy Conversion and Storage, Fundamental Electrochemistry, Imaging and Structural Analysis
Contributors: Hu, Q., Mogensen, M. B., Hansen, K. V.
Number of pages: 121
Publication date: 2012

**Publication information**
Place of publication: Kgs. Lyngby
Publisher: Department of Energy Conversion and Storage, Technical University of Denmark
Original language: English
Electronic versions:
Thesis_Qiang_Hu_Improved_IROS_Using_Composite_Oxides_as_Electrodes..PDF
Research output: Research › Ph.D. thesis – Annual report year: 2012