Electrochimica Acta 130 (2014) 718–727

Contents lists available at ScienceDirect

Electrochimica Acta

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

Theoretical consideration of Solid Oxide Electrolyzer Cell with zirconia-based electrolyte operated under extreme polarization or with low supply of feedstock chemicals

Jan Pawel Stempien[a,b,*], Qiang Sun[c], Siew Hwa Chan[a,b]

[a] School of Mechanical & Aerospace Engineering, Nanyang Technological University (NTU), 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Energy Research Institute at NTU (ERI@N), Nanyang Technological University, 1 CleanTech Loop #06-04, Singapore 637141, Singapore
[c] Department of Advanced Materials and Nanotechnology, Collage of Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:
Received 24 January 2014
Received in revised form 21 March 2014
Accepted 21 March 2014
Available online 30 March 2014

Keywords:
SOEC
YSZ
Modeling
Electronic conductivity
Co-electrolysis

ABSTRACT

We report on the consequences of operating Solid Oxide Electrolyzer Cell (SOEC) under an extreme electrical polarization or with a low supply of feedstock chemicals. Under such conditions, subsequent switching from dominantly ionic conductivity to mixed conductivity is lowering the cells' Faradic efficiency. We propose a theoretical model, able to accurately predict polarization curve, Faradic efficiency and synthetic fuel production for Zirconia electrolyte-based (8YSZ) cells. To the best of our knowledge this is the first model of SOEC constructed without the assumption of pure ionic conductivity in YSZ. Experimental results from literature were used to extrapolate, fit and validated 8YSZ properties for oxygen partial pressure below 10^{-20} atm. We report a simple fuel map, suggesting design conditions for SOEC, securing the operation with near 100% Faradic efficiency. This consideration suggests strong evidence against a common practice of using Faraday's law to estimate electrolysis yield. Moreover, we speculate that surge of potential difference at high current densities may be due to a switch to the mixed conduction mode, rather than only the concentration loss.

1. Introduction

Pure Zirconium oxide (ZrO_2) is an amphoteric semiconductor with transition from n-type to p-type conductivity under decreasing oxygen partial pressure difference [1]. The conductivity in ZrO_2 is due to defects in its lattice structure [2]. Doubly charged oxygen vacancies allow an ionic transport of oxygen, whereas electrons and holes allow an electronic transport. Altering the defect concentration influences conductivity of a given type. It is known that substituting ions in a semiconductor changes the defect concentration [3]. Adding higher valence cations to an n-type semiconductor causes a decrease in the ionic defect concentration and increase in the electronic defect concentration. The opposite is true for a p-type semiconductor. Doping Zirconium oxide with Yttrium oxide replaces Zr ""cation with Y"' cation and thus increases the ionic conductivity.

Yttria-doped Zirconia, or Yttria-stabilized Zirconia (YSZ), membranes are most commonly used in oxygen sensors [4], oxygen pumps or separators [5], solid oxide fuel cells [6] and solid oxide electrolyzer cells [7]. Apart from changing the oxygen partial pressure difference across the membrane, the lattice defect concentration of YSZ can be also altered by variation of electrostatic potential difference, thus it can be used to relate oxygen partial pressure difference[1] with the electrostatic field, given constant doping level. In the oxygen sensors, concentration of oxygen in investigated gas mixture is estimated from the observed open circuit voltage across the YSZ membrane. Fuel cells generate electrostatic potential difference and current flow, when exposed to difference in chemical potentials of oxygen. Oxygen pump or electrolyzer works reverse to the fuel cell. When exposed to high enough electrostatic potential difference, they generate oxygen partial pressure difference or chemical potential difference, respectively. An electrolyzer additionally facilitates chemical and

* Corresponding author.
E-mail addresses: jan2@e.ntu.edu.sg (J.P. Stempien), mshchan@ntu.edu.sg (S.H. Chan).

[1] Throughout the text we use oxygen partial pressure as a traditional approach. However, we sometimes use oxygen chemical potential when referring to SOEC. SOEC is essentially creating oxygen chemical potential difference, rather than partial pressure difference.

http://dx.doi.org/10.1016/j.electacta.2014.03.102
0013-4686/

Nomenclature

Chemicals

O_O^x	Neutral oxygen at the oxygen site $V_O^{\bullet\bullet}$
$V_O^{\bullet\bullet}$	Double positively charged oxygen vacancy in electrolyte
$Y^{'''}$	Yttrium cation, triple negatively charged
$Y_{Zr}^{'}$	Negatively charged Yttrium at Zirconium site
Y_2O_3	Yttrium oxide
YSZ	Yttria stabilized Zirconia, Zirconium oxide stabilized with Yttrium oxide
8*YSZ*	Zirconium oxide stabilized with 8 mole Yttrium oxide
$Zr^{''''}$	Zirconium cation, quadruple negatively charged
ZrO_2	Zirconium oxide

Abbreviations

OCV	Open circuit voltage
SCV	Short circuit voltage
SOEC	Solid Oxide Electrolyzer cell
SOFC	Solid Oxide Fuel cell
TPB	Triple Phase Boundary

Physical constants and parameters

a	Activity of a chemical specie
c	Concentration
D	Diffusivity [$m^2\ s^{-1}$]
E	Electrostatic potential difference [V]
eV	Electron volt $1.60217657 \times 10^{-19}$ [J]
F	Faraday constant 96485.336521 [$C\ mol^{-1}$]
I	Current [A]
j	Current density [$A\ cm^{-2}$]
N	Specie molar flux [$mol\ s^{-1}$]
k	Boltzmann constant $1.3806488 \times 10^{-23}$ [$m^2\ kg\ s^{-2}\ K^{-1}$]
K	Reaction constant
m	Power exponent
p	Pressure [bar or if other specified]
q	Charge [C]
R	Universal gas constant 8.314462175 [$J\ mol^{-1}\ K^{-1}$]
t	Transport or transference number
T	Temperature [°C or K]
x	Position along electrolyte thickness
z	Carried charge
α	Symmetry factor
γ	Pre-exponential factor for conductivity
δ	Thickness [μm]
η	Overpotential [V]
μ	Mobility [$cm^2\ s^{-1}\ V^{-1}$] or chemical potential [$J\ mol^{-1}$]
$\bar{\mu}$	Electrochemical potential [V]
σ	Conductivity [$\Omega^{-1}\ cm^{-1}$]
φ	Electrostatic potential [V]

Subscripts

0	Refers to equilibrium state
Act	Refers to charge transfer overpotential
Air elect	Refers to air electrode conditions
bulk	Refers to bulk or environment conditions
con	Refers to mass transfer limitation overpotential
e	Refers to electron
eh	Refers to electrons and holes or electronic
Fuel elect	Refers to fuel electrode conditions
h	Refers to hole
i	Refers to ion
k	Refers to k-th specie
O_2	Refers to oxygen
ohmic	Refers to charge movement resistance
SCV	Refers to short circuit voltage
TPB	Refers to triple phase boundary conditions

electrochemical reactions to create oxygen (i.e. hydrogen evolution).

Solid Oxide Electrolyzer Cells (SOEC) attracted an increased attention in recent years due to their ability to recycle combustion products back into usable fuels [8–11]. YSZ electrolyte is the most common choice for high temperature electrochemical cells or sensors. Fuel cells and electrolyzer, regardless still being in the development stage, pose great opportunities for the energy security and sustainability. However, due to the nature of their operation, it is possible to run them in abnormal conditions characterized by extremely high oxygen partial pressure difference [12–15]. Specifically, this refers to the oxygen pumps and the electrolyzers, moderately to the fuel cells. It is hypothesized here that such conditions may occur in SOEC if it is designed incorrectly.

In the SOEC it is traditionally assumed that YSZ is a pure ionic conductor [16–21], thus its Faradic efficiency is always 100%. This assumption is often true in fuel cell mode of operation. However, when operating electrolyzer or oxygen pump[2] with either high electrostatic potential difference or low feedstock chemicals' supply, one can create extremely high oxygen partial pressure difference across the cell. Consequently, switching to mixed or dominantly electronic conduction mode and hence running on low or zero Faradic efficiency. This can be due to the improper design, or when a SOEC is coupled with an intermittent energy source.

Most representative works investigating either running on low feedstock supply or extreme polarization were published by two independent groups in 1998 and 2009. The first group, Pham and Glass [14], investigated the operational characteristics of an oxygen pump based on 8YSZ (zirconium oxide doped with 8-moles of yttrium oxide). The experimental setup considered pumping oxygen from an enclosed volume of gas mixture with low initial oxygen partial pressure. Due to the experiment arrangement, authors arrived in a region of mixed and dominantly electronic conduction. The second group, Schefold et al. [15], performed experiments on several 8YSZ-based SOECs. The group presented that it is possible to operate an SOEC fed with steam with the injected electric current exceeding theoretical value required to convert 100% of the steam. Moreover, the group showed that it is even possible to run the cell with no steam or CO_2 supply at all. They investigated cases of excessive polarization and insufficient feedstock supply. Both groups indicated existence of a short circuit voltage (SCV) in all of the experiments. The values were in the same range of 1.6–1.8 V. Similarly, our in-house experiments showed possibility of injecting electric currents larger than that required for 100% electrochemical conversion of feedstock chemicals, though, no saturation potential difference was observed. Up to date literature only investigated probability of electrochemical decomposing of the electrolyte, however, arriving at mixed conclusions. None of the efforts examined consequences of running the cell under mildly mixed conduction mode. Such effort is made here.

Few models are available in the open literature, describing the transport in a mixed conducting electrolyte. Naefe [22] authored a good review of modeling mixed ionic-electronic conductors. Chan

[2] Electrochemical pump refers to oxygen pumps and electrolyzers, as from electrolyte point of view they are the same device.