



Model for solid oxide fuel cell cathodes prepared by infiltration



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ABSTRACT

A 1-dimensional model of a cathode has been developed in order to understand and predict the performance of cathodes prepared by infiltration of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1.05}\text{O}_{3-\delta}$ (LSC) into porous backbones of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO). The model accounts for the mixed ionic and electronic conductivity of LSC, ionic conductivity of CGO, gas transport in the porous cathode, and the oxygen reduction reaction at the surface of percolated LSC. Geometrical variations are applied to reflect a changing microstructure of LSC under varying firing temperatures. Using microstructural parameters obtained from detailed scanning electron microscopy and simulations of the measured polarization resistances, an expression for the area specific resistance (r_p) associated with the oxygen exchange on the surface of the infiltrated LSC particles was extracted and compared with literature values. A series of microstructural parameter variations are presented and discussed with the aim of presenting specific guidelines for optimizing the microstructure of cathodes prepared by infiltration.

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1. Introduction

A key goal for the research in solid oxide fuel cells (SOFCs) is a lowering of the operating temperature to around 500–750 °C [1], as this will greatly enhance the possibility for SOFC commercialization. Low operating temperature allows the use of cheap ferritic steel supports and interconnects instead of the more common yet comparatively more expensive Ni-based composite supports [2] and LaCrO_3 -based or specialty steel interconnects [3]. In addition, the long term stability of SOFCs is expected to be enhanced with reduced temperature of operation. Several degradation mechanisms such as interfacial diffusion between electrode and electrolyte [4], gradual sintering of the electrode [5], Cr evaporation from the interconnect material and poisoning of the cathode [6], and Sr migration leading to the formation of undesired Sr-related reaction products [7,8] are encountered under long term operation at high temperature. These problems can be minimized with a reduction of the operating temperature. However, the electrochemical performance of the fuel cell electrodes decreases with decreasing temperature. Commonly used electrode materials,

such as Sr-doped lanthanum manganite (LSM) and Ni/yttria stabilized zirconia (YSZ) composites prepared by conventional ceramic processing, do not have a sufficiently high performance at lower temperatures (<650 °C). Thus, it is necessary that new electrode materials with improved electrochemical performance are introduced and/or improved structures of the electrodes are employed. Essential to this search and development is the understanding on how various processes and parameters in electrode development affect the electrochemical performance of SOFC electrodes.

Porous composite electrodes are commonly used in solid oxide fuel cells as the triple phase boundary (TPB) is enhanced and the zone where the electrochemical reactions takes place is extended from the electrolyte. In the case of cathodes, it has been demonstrated that the area specific polarization resistance, R_p , of a lanthanum strontium manganite (LSM) – yttria stabilized zirconia (YSZ) composite cathode is significantly lower than that of a cathode containing LSM only [9,10]. In recent years, it has been demonstrated that significant improvements in cathode performance can be achieved by using composites based on doped ceria, which possesses higher ionic conductivity than YSZ at low temperatures, and a mixed ionic and electronic conducting (MIEC) electrocatalyst material (in contrast to LSM being a predominantly electronic conductor) [11–19]. This allows an extension of the oxygen reduction zone from a narrow band along the TPB to the entire surface of the MIEC due to its higher ionic conductivity [20,21]. Another strategy to obtain improved cathodes is the tuning

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Nomenclature

List of Symbols

a	base radius of an N particle/m
$A_{IC-MIEC}$	specific surface area of the CGO backbone (IC) with the added coating/ $m^2 m^{-3}$
$A_{IC-MIEC}^{particle}$	surface area of one IC particle with MIEC coating/ m^2
A_0	specific surface area based on solid volume/ $m^2 m^{-3}$
A_C	unit area of the cathode/ m^2
A_{coat}	cross sectional area of infiltrate coating/ m^2
$A_{MIEC}(i)$	active surface area of percolated MIEC in segment (i)/ m^2
A_{MIEC}^{sp}	specific surface area of percolated MIEC phase per unit volume/ $m^2 m^{-3}$
$d_{IC,coat}$	diameter of the IC particle with additional coating/m
$D_{O_2-N_2}$	binary diffusion coefficient for oxygen and nitrogen/ $m^2 s^{-1}$
$D_{O_2-N_2}^{eff}$	effective binary diffusion coefficient of oxygen and nitrogen/ $m^2 s^{-1}$
$D_{O_2-N_2,K}^{eff}$	Knudsen diffusion coefficient for oxygen-nitrogen mixture/ $m^2 s^{-1}$
d_{CGO}	diameter of CGO phase/m
d_h	hydraulic diameter for porous electrode/m
d_{IC}	diameter of the ionic conducting (IC) phase/m
d_{LSC}	diameter of LSC phase/m
d_{MIEC}	diameter of the mixed ionic and electronic conducting phase (MIEC)/m
d_p	pore diameter/m
F	Faraday constant
h	height of spherical caps protruding from the coating (called N particles)/m
$I_{i_0}(i-1)$	equivalent current associated with the transport of oxide ions from segment ($i-1$) to segment (i)/A
$I_e(i-1)$	electronic current transported from segment ($i-1$) to segment (i)/A
i_{max}	maximum number of electrode layer segmentation
i_{MIEC}	current generated through the electrode reaction per unit area/ $C m^{-2} s^{-1}$
$J_{N_2}(i)$	molar flux of nitrogen in segment (i)/ $mol m^{-2} s^{-1}$
$J_{O^{2-},IC}(i)$	molar flux of oxide ions in the IC phase into segment (i)/ $mol m^{-2} s^{-1}$
$J_{O^{2-},MIEC}(i)$	molar flux of oxide ions in the MIEC phase into segment (i)/ $mol m^{-2} s^{-1}$
$J_{O_2}(i)$	molar flux of oxygen into segment (i)/ $mol m^{-2} s^{-1}$
k_K	Kozeny constant
L_C	cathode thickness/m
l_{coat}	length of the coating parallel to the CGO electrolyte/m
m	Bruggeman factor
M	particles attached from the infiltrate coating
M_{N_2}	molecular mass of nitrogen/ $kg mol^{-1}$
M_{O_2}	molecular mass of oxygen/ $kg mol^{-1}$
$M_{O_2-N_2}$	average molecular mass/ $kg mol^{-1}$
N	particles protruding from the infiltrate coating
n_{IC}	number fraction of IC particles
n_{MIEC}	number fraction of MIEC particles
N_t	number density of all particles/ $\# m^{-3}$
p	total pressure/Pa
$p_{N_2}(gas)$	partial pressure of nitrogen outside of cathode structure

$p_{O_2}(gas)$	partial pressure of oxygen outside of cathode structure
P_i	probability of an i -phase belonging to a percolated network of the same phase
r	radius of M particle/m
$r_{io,LSC}$	resistance associated with the transport of oxide ions in the LSC infiltrate/ Ω
$r_{p,inj900}$	area specific surface exchange resistance of the infiltrate fired at $T_{max} = 900^\circ C/\Omega m^2$
$r_{p,MIEC}$	area specific resistance associated with oxygen exchange of MIEC phase/ Ωm^2
$R_{el}(i-1)$	electronic resistance for the transport of electrons from segment ($i-1$) to segment (i)/ Ω
$R_{io}(i-1)$	resistance associated with the transport of oxide ions from segment ($i-1$) to segment (i)/ Ω
r_p	area specific resistance associated with oxygen exchange/ Ωm^2
R_p	area specific polarization resistance/ Ωm^2
s	surface area factor
T	temperature/K
t_{coat}	coating thickness, infiltrated electrocatalyst/m
$V(i)$	volume in segment (i)/ m^3
V_{N_2}	diffusion volume for nitrogen
V_{O_2}	diffusion volume for oxygen
x_{N_2}	molar fraction of nitrogen
x_{O_2}	molar fraction of oxygen
y_{coat}	length to travel for the oxide ion through the MIEC towards the IC backbone/m
Z_{i-j}	coordination number between an i -phase particle and a j -phase particle
Z_{IC}	average total coordination number for IC particles
Z_{MIEC}	average total coordination number for MIEC particles

Greek letters

α	ratio between the diameters of IC to MIEC particles
$\Delta x_{(i-1)-(i)}$	distance of segment ($i-1$) and segment (i)/m
ε	porosity of the electrode
η	overpotential/V
η_{el}	electric overpotential/V
η_{io}	ionic overpotential/V
η_{gas}	gas concentration overpotential/V
θ_c	contact angle between particles/ $^\circ$
μ_{N_2}	viscosity of nitrogen/Pa s
μ_{O_2}	viscosity of oxygen/Pa s
$\mu_{O_2-N_2}$	average viscosity of oxygen and nitrogen mixture
σ_i^0	bulk conductivity of phase $i/S m^{-1}$
$\sigma_{el,MIEC}^{eff}$	effective electronic conductivity in the MIEC phase/ $S m^{-1}$
σ_i^{eff}	effective conductivity of phase $i/S m^{-1}$
$\sigma_{io,IC}^{eff}$	effective ionic conductivity in the IC phase/ $S m^{-1}$
τ	tortuosity
ϕ_i	solid volume fraction of phase i
ϕ_{IC}	solid volume fraction of the IC phase
ϕ_{MIEC}	solid volume fraction of the MIEC phase

of the microstructure in order to enlarge the surface area for oxygen reduction. A tuning might be in the form of formation of nanoparticulate electrocatalysts in the electrode. One of the methods to obtain nanoparticulate electrocatalysts is the so-called infiltration or impregnation method [22–25]. The infiltrated nano-sized electrocatalysts have very large surface area and consequently, enhanced surface area for the oxygen exchange reaction.

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