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Computational Analysis of Performance Limiting Factors for the New Solid Oxide Iron-air Redox Battery Operated at 550 °C

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ABSTRACT

In the present study, the effects of discharge and charge current densities, depth-of-discharge, initial porosity of Redox Cycle Unit (RCU), distance between Reversible Solid Oxide Fuel Cell (RSOFC) and RCU, and kinetic rate constant for the Fe_3O_4-reduction reaction on the electrochemical performance of a Solid Oxide Iron-Air Redox Battery (SOIARB) operated at 550 °C have been systematically investigated by a newly developed high-fidelity multi-physics model. The results show explicitly that the battery performance is kinetically limited by the Fe_3O_4-reduction during the charge cycle. The diffusion of Oxygen Shuttle Gas (OSG), *i.e.* H_2-H_2O, through the RCU pores and the gap between RSOFC and RCU is sufficiently fast. The most influential parameters on the performance are found to be the charge current density, depth-of-discharge and rate of Fe_3O_4 reduction. Strategies for design and operation of the SOIARB are subsequently developed with an aim to achieve a balanced energy capacity and cycle efficiency.

1. Introduction

Large-scale and cost effective stationary energy storage is a key to successful implementation of renewable energy into the existing power grid. Sodium-sulfur and redox flow batteries have been traditionally regarded as the promising stationary energy storage technologies for harnessing solar and winds energy. However, these two technologies have not been fully implemented at commercial scale due to obstacles in cost and reliability. Recently, we demonstrated a new dual-functional hybrid fuel-cell/battery system capable of producing power and storing energy with advanced features: solid oxide metal-air redox battery or SOMARB. Since the first laboratory demonstration in 2011 [1], significant experimental progress on SOMARB has been made in the areas of the material properties [2,3], new metal-air chemistries [4–9] and the system design [10–15].

Compared to the productive experimental investigations, the mathematical modeling of the multi-physicochemical processes occurring inside the battery remains underdeveloped. For example, Ohmoti et al., [16] and Guo et al., [17] reported multiphysics models with ignored redox reaction kinetics and simplified battery configurations. To advance the development of modeling in this area, we recently developed a high-fidelity multiphysics model for the new solid-oxide iron-air redox battery (SOIARB) [18,19]. The model combines fundamental theories of mass transport, charge transfer and chemical redox kinetics, and can reasonably predict the electrochemical behavior of a SOIARB. One of the distinctive features of the new model is the application of Johnson–Mehl–Avrami–Kolmogorov (JMAK) [24–27] and Shrinking Core [28,29] theories to simulate the oxidation of Fe and reduction of Fe_3O_4 kinetics occurring inside the redox cycle unit (RCU), respectively. Furthermore, the parameters used in the model were directly derived from the Voltage-Current (V-I) curves and the charge/discharge characteristics obtained from experiments [12], ensuring a high-fidelity analysis and prediction.

In the present study, we apply the developed computational model to systematically analyze the effects of the most important design and operational parameters on the SOIARB's performance, based on which a set of optimization strategies are outlined for future commercial development of the new SOIARB technology. The analysis presented in this work is on a SOIARB operated at 550 °C and has not been reported previously. The selection of 550 °C in this study as the operating temperature is based on the consideration of available experimental data and the desire for

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Abbreviation: DoD, Depth of Discharge; FEM, Finite Element Method; OSG, oxygen shuttle gas; RTE, round-trip efficiency; RSOFC, reversible Solid Oxide Fuel Cell; RCU, Redox Cycle Unit; SOIARB, Solid Oxide Iron-Air Redox Battery; SES, pecific Energy.

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Nomenclature

A	Cross area (m^2)
c	Molar concentration ($mol\ m^{-3}$)
d_{pore}	Diameter of spherical particle of the porous medium (m)
d_p	Pore diameter of the porous medium (m)
D_{ij}	Binary diffusion coefficient for a pair of species i and j ($m^2 \cdot s^{-1}$)
$D_{kn,i}$	Knudsen diffusion coefficient of species i ($m^2 \cdot s^{-1}$)
E	Nernst potential (V)
F	Faraday's constant, 96485 ($C \cdot mol^{-1}$)
G	Gibbs free energy ($J \cdot mol^{-1}$)
J	Operating current density ($A \cdot m^{-2}$)
K	Equilibrium constant
k_D	Reference diffusivity ($m^2 \cdot s^{-1}$)
k_o	Global oxidation rate constant (s^{-1})
$k_{f,I}$	Forward reaction constant in JMAK model (s^{-1})
$k_{b,I}$	Backward reaction constant in JMAK model (s^{-1})
$k_{f,S}$	Forward reaction constant in Shrinking-Core model ($m \cdot s^{-1}$)
$k_{b,S}$	Backward reaction constant in Shrinking-Core model ($m \cdot s^{-1}$)
k_S	Reaction constant in Shrinking-Core model ($m \cdot s^{-1}$)
M_i	Molar weight of species i ($kg \cdot mol^{-1}$)
M	Mean molar weight of gas mixture ($kg \cdot mol^{-1}$)
$m_{Fe,0}$	Initial load of Fe (kg)
N_i	Flux vector of species i ($kg \cdot m^{-2} \cdot s^{-1}$)
N	Avrami exponent
n	Number of electrons (mol)
i_{ict}	Local charge transfer current density ($A \cdot m^{-2}$)
p	Pressure (Pa)
R	Gas constant, 8.314 ($J \cdot (mol^{-1} \cdot K^{-1})$)
R_{c0}	Initial radius of Fe_3O_4 core (m)
r	Reaction rate ($mol \cdot m^{-3} \cdot s^{-1}$)
r_c	Radius of the core in the shrinking core model (m)
R_i	Reaction source term for species i ($kg \cdot m^{-3} \cdot s^{-1}$)
s_i	Stoichiometric coefficient of species i
Sa	Electrochemical reaction active area per unit volume (m^{-1})
T	Temperature (K)
t	Time (s)
V	Cell voltage (V)
x_j	Molar fraction of species j

Greek symbols

σ	Conductivity ($S \cdot m^{-1}$)
ϕ	Potential (V)
η	Overpotential (V)
ρ	Density ($kg \cdot m^{-3}$)
ω_i, ω_j	Mass fraction of species i,j
v_i	Kinetic volume of species i
ε	Porosity
τ	Tortuosity

Subscripts

c	Charge
d	Discharge
e	Electronic
eff	Effective
el	Electrolyte
eq	Equilibrium
i	Ionic
g	Gas
o	Oxygen electrode
h	Hydrogen electrode
react	Reactant
Prod	Product
s	Shrinking core

Superscripts

0	Ideal/Initial

intermediate-temperature operation to achieve long lifetime and high reliability.

2. The SOIARB technology

The solid oxide iron-air redox battery or SOIARB is composed of a reversible solid oxide fuel cell (RSOFC), an iron-iron oxide redox cycle unit (RCU) and an Oxygen Shuttle Gas (H_2-H_2O) chamber in between, as shown in Fig. 1a [18]. The operating temperature of interest for this study is 550 °C, at which Fe/Fe_3O_4 is the prevalent redox couple in the RCU. The 2D axis-symmetric model is shown in Fig. 1b [18]. The details regarding the SOFC materials could be found in our recent publications [24,25].

The RSOFC utilizes its SOFC and SOEC modes to realize electrical discharge and charge, respectively. During discharge, the RSOFC electrochemically consumes O_2 and H_2 to produce H_2O and electricity, while Fe is being oxidized by H_2O produced to form Fe_3O_4 and H_2 to sustain the electrochemical oxidation. During the charge cycle, RSOFC electrochemically splits H_2O into H_2 with external electrical energy supply, while Fe_3O_4 is being reduced back to Fe with H_2 produced and to form H_2O to sustain the electrolysis process. We assume that in RCU, forward reactions occurs for discharge, then backward reactions happen for charge. The electrochemical and chemical reactions occurring within RSOFC and RCU are:

$$\text{At the } O_2\text{–electrode of RSOFC}: \frac{1}{2}O_2(g) + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} O^{2-} \qquad (1)$$

At the H_2–electrode of RSOFC :

$$H_2(g) + O^{2-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} H_2O(g) + 2e^-$$

$$\text{In theRCU}: 4H_2(g) + 3Fe \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Fe_3O_4 + 4H_2(g) \qquad (3)$$

3. The multiphysics model

The multi-physics processes occurring in SOIARB includes: electron/oxygen-ion transport in the RSOFC; electrochemical reactions in RSOFC electrodes; gas diffusion in porous electrodes of RSOFC, open gas chamber and porous RCU bed; redox reactions in RCU bed. The governing equations are summarized in Table 1. The meanings of the symbols used here are listed in the Nomenclature.The convective mass transfer of concentrated species is neglected due to the fact that it is a closed stationary system.

3.1. The boundary/initial conditions

Boundary conditions are given in Table 2. Based on the experimental information, the initial gas mole fraction ratio in the chamber was taken as H_2:H_2O = 0.97:0.03. The initial condition for the reacted mole fraction of Fe is set to $x_{Fe,0} = 10^{-5}$ (a very small number for calculation purpose)..