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.

Keywords: energy storage; solid oxide fuel cell; battery; modeling; Fe_3O_4 reduction

I. 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 2011¹, significant experimental progress on SOMARB has been made in the areas of the material properties^{2, 3}, new metal-air chemistries⁴⁻⁹ and the system design¹⁰⁻¹⁵.

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 Core²⁸⁻²⁹ theories to simulate the oxidation of Fe and reduction of Fe₃O₄ 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 experiments¹², 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 intermediate-temperature operation to achieve long lifetime and high reliability.

II. 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 (H₂-H₂O) chamber in between, as shown in Fig. 1a¹⁸. The operating temperature of interest for this study is 550°C, at which Fe/Fe₃O₄ is the prevalent redox couple in the RCU. The 2D axis-symmetric model is shown in Fig.1b¹⁸. 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 O₂ and H₂ to produce H₂O and electricity, while Fe is being oxidized by H₂O produced to form Fe₃O₄ and H₂ to sustain the electrochemical oxidation. During the charge cycle, RSOFC electrochemically splits H₂O into H₂ with external electrical energy supply, while Fe₃O₄

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:

Fig.1 (a) A schematic illustration of the SOIARB configuration; (b) Finite Element Method (FEM) model of SOIARB (unit: mm)¹⁸.

III. 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.

Table 1 Governing equations used in the model

Governing equations	Mathematical expressions
Charge conservation in RSOFC	$\begin{cases} \nabla \cdot (-\sigma_{e,o/h} \nabla \phi_e) = \pm S_{a,o/h} i_{ict,o/h} \\ \nabla \cdot (-\sigma_{i,o/h} \nabla \phi_i) = \mp S_{a,o/h} i_{ict,o/h} \\ \nabla \cdot (-\sigma_{i,el} \nabla \phi_i) = 0 \end{cases} \quad (4)$
Butler-Volmer equation ²¹⁻²³	$i_{ict} = i_0 \left(\frac{c_{react}}{c_0^{react}} \exp \left(\frac{n\alpha F}{RT} \eta \right) - \frac{c_{prod}}{c_0^{prod}} \exp \left(-\frac{n(1-\alpha)F}{RT} \eta \right) \right) \quad (5)$
Gas species transport ²¹⁻²³	$\frac{\partial(\epsilon \rho \omega_i)}{\partial t} + \nabla \cdot \left(\rho \omega_i \sum_{j=1}^n D_{ij}^{eff} \left(\frac{M}{M_j} \left(\nabla \omega_j + \omega_j \frac{\nabla M}{M} \right) + (x_j - \omega_j) \frac{\nabla p}{p} \right) \right) = R_i$ $M = \left(\sum_i \frac{\omega_i}{M_i} \right)^{-1} \quad (6)$
Source term	$R_{i,RSOFC} = \pm \frac{s_i i_{ct} S_a M_i}{nF}, R_{i,RCU} = \frac{dx_{Fe}}{dt} c_{Fe} (1 - \epsilon_{RCU}) M_i, \quad (7)$ $R_{i,RCU} = \frac{4dx_{Fe_3O_4}}{dt} c_{Fe_3O_4} (1 - \epsilon_{RCU}) M_i$
Binary diffusion	$D_{ij} = k_D \frac{T^{1.75}}{p \left(v_i^{1/3} + v_j^{1/3} \right)^3} \left[\frac{1}{M_i} + \frac{1}{M_j} \right]^{1/2} \quad (8)$
Knudsen diffusion	$D_{Kn,i} = \frac{97}{2} d_{pore} \sqrt{T/M_i}, d_{pore} = \frac{2}{3} \frac{\epsilon d_p}{1 - \epsilon} \quad (9)$
Average Bosanquet diffusion coefficient	$D_{ij}^{eff} = \frac{1}{2} \frac{\epsilon}{\tau} \left(\frac{1}{\frac{1}{D_{ij}} + \frac{1}{D_{Kn,i}}} + \frac{1}{\frac{1}{D_{ij}} + \frac{1}{D_{Kn,j}}} \right) \quad (10)$
Reaction Equilibrium for RCU	$K = \exp \left(-\frac{\Delta G^0}{RT} \right) = \frac{x_{H_2}^4}{x_{H_2O}^4} = \frac{k_f}{k_b} \quad (11)$
Shrinking Core model for Fe ₃ O ₄ reduction ²⁴⁻²⁷	$\frac{dx_{Fe_3O_4}}{dt} = \frac{-3c_g (k_{f,S} x_{H_2O}^4 - k_{b,S} x_{H_2}^4) (1 - x_{Fe_3O_4})^2}{4c_{Fe_3O_4} R_{c0}} \quad (12)$
JMAK model for Fe oxidation ²⁸⁻²⁹	$\frac{dx_{Fe}}{dt} = (k_{f,J} x_{H_2O}^4 - k_{b,J} x_{H_2}^4) N (1 - x_{Fe}) [-\ln(1 - x_{Fe})]^{-\frac{1}{N}} \quad (13)$
Porosity of RCU	$\epsilon = \epsilon_0 + (1 - \epsilon_0) x_{Fe} (1 - x_{Fe_3O_4})_{Fe} \left(\frac{M_{Fe}}{\rho_{Fe}} - \frac{1}{3} \frac{M_{Fe_3O_4}}{\rho_{Fe_3O_4}} \right) \quad (14)$
Pressure in chamber	$p = p_0 \cdot \frac{\epsilon_{anode} V_{anode} + V_{chamber} + \epsilon_{RCU}(t) V_{RCU}}{\epsilon_{anode} V_{anode} + V_{chamber} + \epsilon_{RCU,0} V_{RCU}} \quad (15)$
Depth of Discharge	$DoD = \frac{\iiint x_{Fe} (1 - x_{Fe_3O_4})}{Volume} \quad (16)$

$$\text{Specific Energy} \quad SE = \int_{t_1}^{t_2} \frac{V \times J \times A}{3600 \times DoD \times m_{Fe,0}} \quad (17)$$

$$\text{Round Trip Efficiency} \quad RTE = \frac{SE_d}{SE_c} \quad (18)$$

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).

Table 2 Boundary conditions used in the model

Boundary	Electronic potential	Ionic potential	Stefan-Maxwell diffusion
Dependent Variable	ϕ_e	ϕ_i	ω_j
Air channel/O ₂ electrode	$-\underline{n} \cdot \nabla \phi_e = J_{c/d}$	$-\underline{n} \cdot \nabla \phi_i = 0$	O ₂ :N ₂ :H ₂ O=0.21:0.76:0.03
O ₂ -electrode/electrolyte interface	$-\underline{n} \cdot \nabla \phi_e = 0$	Continuity	$-\underline{n} \cdot \underline{N}_i = 0$
electrolyte/H ₂ -electrode interface	$-\underline{n} \cdot \nabla \phi_e = 0$	Continuity	$-\underline{n} \cdot \underline{N}_i = 0$
H ₂ electrode/Chamber	0 V	$-\underline{n} \cdot \nabla \phi_i = 0$	Continuity
Chamber/RCU	N/A	N/A	Continuity
Other surfaces	$-\underline{n} \cdot \nabla \phi_e = 0$	$-\underline{n} \cdot \nabla \phi_i = 0$	$-\underline{n} \cdot \underline{N}_i = 0$

Note; $\underline{N}_i = -\rho \omega_i \sum_j D_{ij}^{eff} \underline{d}_j$, $\underline{d}_j = \left(\frac{M}{M_j} \left(\nabla \omega_j + \omega_j \frac{\nabla M}{M} \right) + (x_j - \omega_j) \frac{\nabla p}{p} \right)$.

3.2 The Computation and validation

The electronic potential ϕ_e and ionic potential ϕ_i , mass fraction of gas species, ω_j , the reacted fraction ratio x_{Fe}/x_{Fe+O_2} , are computed as a function of time by combining eqs. (4), (5), (6), (12) and (13) with the boundary/initial conditions aforementioned.

The computation was performed with a commercial software package known as COMSOL Multiphysics 4.3 using a workstation equipped with an Intel Core i7-4700MQ processor @2.4GHz and 2.39GHz and 16GB of RAM. The computational domain was discretized by swept mesh and refined until a converged solution was reached. The Direct Solver was applied to solve the transient problem. The modules applied in the model include Electric Currents module, Transport of Concentrated Species module, and General form of **Partial Differential Equations**.

To ensure high fidelity of the model, the exchange current density of RSOFC was extracted from an experimental V-I curve obtained from our previous study²⁰; the results are shown in Fig.2¹⁸. Meanwhile, the reaction rate constants in JMAK and Shrinking Core model were obtained from an experimental Discharge/Charge curve of the battery as a function of time; the results are shown in Fig.3^{12,18}. The physical and chemical parameters obtained are listed in Table 3.

Fig. 2 Validation of V-I curve under 550°C¹⁸.

Fig. 3 Validation of E vs DoD (UFe: Fe utilization) curve¹⁸.

Table 3 Parameters used in the model

Parameters	Values
Atmospheric pressure, p_0	1[atm]
Avrami exponent of JMAK, N	0.28
Charging/Discharging current density, J_c/J_d	100[A/m ²]
Distance between RSOFC and RCU, d	1mm
Diameter of spherical particle, Anode/Cathode, d_p	0.35[μ m]
Electronic conductivity, σ_e	2×10^6 [S/m]
Exchange current density for SOFC, Anode/Cathode i_0^*	75 /15 [A/m ²]
Exchange current density for SOEC, Anode/Cathode i_0^*	11.25 /15 [A/m ²]
Equilibrium reaction constant, K	186
Ionic conductivity, $\sigma_{i,el}^*$	1.15 [S/m]
Initial porosity of RCU, ε_0	0.7
Inlet mole fraction of H_2 $x_{ref,H2}$	0.97
Inlet mole fraction of O_2 $x_{ref,O2}$	0.21
Kinetic volume of H_2 , vh_2	6×10^{-6}
Kinetic volume of O_2 , vo_2	16.6×10^{-6}

Kinetic volume of N ₂ , v_{N_2}	17.9×10^{-6}
Kinetic volume of H ₂ O, v_{H_2O}	12.7×10^{-6}
Loading of Iron, m_{Fe}	0.26[g]
Number of electrons, n	2
Porosity, Anode/Cathode ϵ	0.4/0.3
Permeability of electrodes, κ	$10^{-13} [m^2]$
Radius of Fe ₃ O ₄ particle, R_{c0}	1[μm]
Reference diffusivity, k_D	$3.16 \times 10^{-8} [m^2/s]$
Reaction rate constant of JMAK, $k_{f,J}/k_{b,J}^*$	$10 \times 4.7 \times 10^{-5} / 0.0538 \times 4.7 \times 10^{-5} [1/s]$
Reaction rate constant of shrinking core model, $k_{f,S}/k_{b,S}^*$	$10 \times 3.83 \times 10^{-7} / 0.0538 \times 3.83 \times 10^{-7} [m/s]$
Specific surface area, Anode/Cathode S_a^*	$(1-\epsilon_{a/c}) \times 1.43 \times 10^5 [1/m]$
Temperature, T_0	550[°C]
Tortuosity, Anode/Cathode τ^*	3
Transfer coefficient, α	0.25
Viscosity of air, μ	$4 \times 10^{-5} [Pa \cdot s]$

Note: The parameters with * are adjusted in order to validate the model with the experimental results.

IV. Parametric study on the performance limiting factors

The key parameters of the SOIARB investigated in this study include discharge/charge current density (J_d/J_c), Depth-of-Discharge (DoD), distance between the RSOFC and RCU (d), initial porosity of the RCU (ϵ_0) and the kinetic rate constant ($k_{b,S}$) of Fe₃O₄-reduction reaction. All of the analysis was conducted under an isothermal condition ($T=550^\circ C$), from which performance optimization strategies were developed for the future engineering design and practical operation of this SOIARB. The cut-off voltage for the charge cycle was set as 1.8V in the following discussion.

4.1 The effect of current density

The current density ($J=J_c=J_d$) applied across the RSOFC dictates the dynamic interaction between the RSOFC and the RCU. While the J of the RSOFC can be galvanically controlled, the magnitude of a sustainable cell voltage associated with J depends upon the ability of the RCU to produce sufficient H_2 and H_2O for the discharge and charge cycles, respectively. This is shown in Fig.4, where J -profiles of the RSOFC are depicted as a function of the cycle time. It is taken as positive for discharge cycle, and negative for charge cycle. With $J=100A/m^2$, the discharge cycle lasted 23 hours for a DoD (or Fe utilization as defined below) of 0.6, during which Fe in the RCU was being oxidized to produce H_2 to support the electrochemical oxidation of H_2 at the H_2 -electrode in the RSOFC.

Fig.4 Current density at the RSOFC with DoD=0.6 ($\epsilon_0=0.7$; $d=1mm$) effect on discharge and charge time.

During the charge cycle when Fe_3O_4 in the RCU is being reduced by H_2 to produce H_2O to sustain the electrochemical reduction of H_2O at the H_2 -electrode in the RSOFC, only 17 hours can be maintained before the cut-off voltage at 1.8 volt occurs, reflecting 16% unconverted Fe_3O_4 compared to the initial condition in the RCU and hence a degree of

irreversibility. At higher current density $J=J_c=J_d=120\text{A/m}^2$, the irreversibility becomes even worse; the charge cycle lasted only for 6.5 hours, corresponding to 39% unconverted Fe_3O_4 from the original; at $J=J_c=J_d=150\text{ A/m}^2$, it becomes totally impossible to recharge the battery.

The Depth of Discharge (DoD) of RCU is equivalent to the Fe utilization in this study, which was calculated by integrating the rate of the redox reaction in the whole domain over time, as shown in Table1, equation (16). It is displayed in Fig.5 as a function of the cycle time; it further illustrates the difficulty of recharging the battery at higher J. For a DoD=0.6, the reversibility (or Round-Trip-Efficiency, RTE) is $\sim 73\%$ ($=17\text{h}/23\text{h}$) at $J=J_c=J_d=100\text{ A/m}^2$, but it drops to 33% (6.5h/18.4h) for $J=J_c=J_d=120\text{ A/m}^2$ and becomes completely irreversible at $J=J_c=J_d=150\text{ A/m}^2$.

Fig.5 Volume averaged DoD as a function of cycle time. ($\epsilon_0=0.7$; $d=1\text{mm}$)

The discharge profiles of the cell voltage are shown in the bottom half of Fig.6 as reasonable electrochemical behavior of a battery. The initial instant drop from 1.14 V (the Nernst potential at $H_2/H_2O=0.97/0.03$ of the initial gas composition prior to cycling) to a stabilized current-dependent voltage reflects the chemical equilibrium established between the oxygen shuttle gas (OSG) and RCU. At lower DoDs, the voltage remains relatively flat, implying a good match between J and rate of H_2 production (r_{H_2}), whereas at higher DoDs the voltage begins to bend-over, implying a lowered H_2/H_2O ratio (compared to the equilibrium ratio of 0.79/0.21 with Nernst potential of 1.067 V) in the OSG caused by unmatched r_{H_2} to the demanding J .

The charge profiles under different J shown in the top half of Fig.6 are more revealing. The chargeable time of the battery before reaching a cut-off voltage of 1.8V is significantly reduced with increasing J , indicating the loss of reversibility; the latter is consistent with the results shown in Fig.4 and 5. Comparison of both the discharge and charge cycle profiles strongly suggests that the charge cycle or the reduction kinetics of Fe_3O_4 is the performance limiting step for the battery.

Correspondingly, the profiles of H_2 mole fraction in the RCU as a function of DoD under different J are shown in Fig.7a; it further supports the observation in Fig.6.

During the discharge cycle, the H_2 mole fraction can only maintain the equilibrium concentration of 0.79 at $DoD \leq 0.1$, above which a decrease with DoD is observed. During the charge cycle, only a small fraction of H_2O (complementary to H_2 shown in Fig.7a) is present in the OSG to support the electrochemical reduction and becomes completely depleted at $J=J_c=J_d=150A/m^2$. The inability for the RCU to produce H_2O fast enough to

match the electrolysis J is the root cause of the poor charging performance. Therefore, the reduction kinetics of Fe_3O_4 needs to be further enhanced in the future materials research in order to improve the overall performance of the new SOIARB.

Fig.6 Profiles of cell voltage of the RSOFC during a discharge/charge cycle as a function of DoD under different current densities. ($\epsilon_0=0.7$; $d=1\text{mm}$) (Heavy dashed line is the Nernst potential, 1.14V.)

Since the Nernst potential is directly related to the ratio of $\text{H}_2/\text{H}_2\text{O}$ in the OSG, its profiles should resemble Fig.7a. Indeed, Nernst potential profiles of Fig.7b confirm it in both shape and trending.

Fig.7 (a) Profiles of H₂ mole fraction in the RCU; (b) Nernst Potential of RSOFC during a discharge/charge cycle as a function of DoD under different J . ($\epsilon_0=0.7$; $d=1\text{mm}$)

In summary, the charge cycle is identified as the performance-limiting step of the SOIARB. The root cause for the difficulty to recharge the battery is two folded: 1) the equilibrium composition of the OSG, i.e. $\text{H}_2/\text{H}_2\text{O}=79/21$ at 550°C , is less favorable to the Fe_3O_4 -reduction of the charge cycle; 2) the intrinsic kinetics of Fe_3O_4 -reduction is more sluggish than Fe-oxidation, which has also been implied by the upward charging curve of a 550°C -SOIARB¹⁰. Therefore, improving the kinetics of Fe_3O_4 reduction during the charge cycle is an important task to a commercial development of the SOIARB technology.

4.2 The effect of initial porosity in RCU

Since the molar volumes of Fe and Fe_3O_4 are different, the porosity in RCU will vary with DoD, i.e. the porosity decreases with DoD during the discharge cycle and reversibly increases with DoD during the charge cycle, e.g., the porosity is lowered to 0.475 from the initial $\epsilon_0=0.70$ after exposure to $J=J_c=J_d=100\text{A/m}^2$ and $\text{DoD}=0.6$. The porosity change in RCU during the discharge cycle could affect the mass transport of H_2 and H_2O , thus the performance of the battery.

The effect of ϵ_0 in RCU on battery's performance is shown in Fig.8, where the profiles of cell voltage as a function of DoD during a discharge/charge cycle under $J=J_c=J_d=100\text{A/m}^2$ are depicted for different ϵ_0 . It is evident that ϵ_0 in the range of 0.45 to 0.90 has a little effect on the electrochemical performance of the battery. Very similar trends are also observed for higher J , *e.g.*, 150A/m^2 . This observation implies that the $\text{H}_2\text{-H}_2\text{O}$ diffusion resistance imposed by the reduction in ϵ is negligible for the cases studied.

However, a combined effect from the reduction in ϵ_0 and distance (d) between RSOFC and RCU would affect the chamber pressure (P) as will be discussed in the following section. Therefore, choosing a proper ϵ_0 with a reasonable d is important to a normal operation of the battery.

Fig.8 Profiles of cell voltage as a function of DoD during a discharge/charge cycle with different ϵ_0 in RCU. ($J=J_c=J_d=100\text{A/m}^2$, $d=1\text{mm}$)

4.3 The effect of distance (d) between RSOFC and RCU

The d-value determines the size of the OSG chamber, thus the size of the battery stacks. A greater d can hold more H_2 - H_2O , thus facilitating the electrochemical reactions occurring at RSOFC to reach equilibrium state faster between cycles. It can also serve as a buffer to the pressure variations incurred from volume change in RCU during cycling. However, too wide a distance would increase the mass transport resistance to H_2 and H_2O diffusion and result in a larger stack. On the other hand, too narrow a distance would increase P in OSG chamber, causing operational concerns. Therefore, investigation of the effect of d on the battery's performance and chamber P is necessary.

The profiles of cell voltage during a discharge/charge cycle are shown in Fig.9 as a function of DoD for different d values. It is evident that no significant difference in performance can be discerned for d= 0.1, 1 and 10 mm. Only a small effect is noticed for the charge cycle at d=10 mm (see the inset of Fig.9), which may imply that the diffusion of H_2 and H_2O starts to impact on the establishment of dynamic interaction between RSOFC and RCU.

Fig. 9 Profiles of cell voltage as a function of DoD during a discharge/charge cycle with different distances between RSOFC and RCU. ($J=J_c=J_d=100\text{A/m}^2$, $\varepsilon_0=0.7$)

While the distance may not play an important role in the electrochemical performance of the battery, it could have a significant impact on the pressure inside the OSG chamber due to a decreasing porosity in RCU during the discharge cycle.

Fig.10 shows the variations of porosity with DoD under $J=J_c=J_d=100\text{A/m}^2$. It is evident that the porosity in RCU decreases with DoD, and the rate of porosity reduction also decreases with increasing ε_0 . The reduced free volume in the OSG chamber can cause an increase in P as the oxygen is being continuously added into the chamber during the discharge cycle.

Fig.10 Porosity of RCU as a function of DoD at different initial porosities.

Assuming H_2 and H_2O as ideal gases, the chamber P under $J=J_c=J_d=100A/m^2$ and $\epsilon_o=0.45, 0.70, 0.90$ was estimated as a function of DoD; the results are shown in Fig.11. It is evident from the plot that for a wider distance such as $d \geq 1mm$, the increase in chamber P is relatively small throughout the discharge cycle. However, as d decreases, P increases significantly. On the other hand, higher ϵ_o helps reduce the increase in P, mitigating the effect of d. In general, too high a P may hinder the O^{2-} flux transporting from air-electrode to fuel-electrode by the RSOFC and possibly breach the integrity of the peripheral sealing of the battery. Therefore, optimizing the distance at which the performance and chamber pressure can be best balanced is necessary.

Fig.11 OSG-chamber pressure P (atm) as a function of DoD for different distances between RCU and RSOFC, (a) $\epsilon_o=0.45$; (b) $\epsilon_o=0.7$; (c) $\epsilon_o=0.9$.

4.4 The effect of kinetic rate of Fe_3O_4 -reduction reaction

As aforementioned, one of the root causes for the difficulty to recharge the battery is the sluggish kinetics of Fe_3O_4 -reduction. Increasing the kinetic rate (k_s , from Shrinking Core model) of Fe_3O_4 reduction is, therefore, necessary to improve the overall performance of the battery. From a materials perspective, the simplest way to increase the k_s value is to

increase the surface areas of the RCU materials. This assertion is supported by the Shrinking Core model¹⁸.

The effect of k_s of Fe_3O_4 -reduction reaction (here expressed as $k_s/k_{s,\text{exp}}$, where $k_{s,\text{exp}}$ is the baseline kinetic rate obtained from the experiment) on battery's performance is shown in Fig.12, where the profiles of cell voltage as a function of DoD during a discharge/charge cycle under $J=J_c=J_d=100\text{A/m}^2$ are depicted for different $k_s/k_{s,\text{exp}}$. It is illustrated that as $k_s/k_{s,\text{exp}}$ increases from 1 to 1.25, the unconverted Fe_3O_4 decreases from 16% to 0.15%, significantly improving the reversibility of the battery. A further increase in $k_s/k_{s,\text{exp}}$ can make the cell fully reversible, but the improvement of Round-Trip-Efficiency would be minimal as will be shown as follows. It is important to note that making the charge cycle fully reversible is critical to the cycle life of the battery since accumulation of unconverted Fe_3O_4 over the charge cycles could be the source of long-term degradation.

Fig.12 Profiles of cell voltage as a function of DoD during a discharge/charge cycle with different $k_s/k_{s,\text{exp}}$. ($J=J_c=J_d=100\text{A/m}^2$, $\epsilon_0=0.7$, $d=1\text{mm}$).

V. Performance optimization strategies

Developing strategies to mitigate the slow Fe_3O_4 -reduction kinetics is critically important to the success of SOIARB technology. As previously pointed out, the effects of J_c , DoD and $k_S/k_{S,\text{exp}}$ on the performance of SOIARB are related. In the following, we focus on illustrating the combined effect of J_c , DoD and $k_S/k_{S,\text{exp}}$ on Specific Energy (SE) and Round-Trip Efficiency (RTE) of the battery. To concentrate on the performance-limiting charge cycle, J_d is kept as 100A/m^2 for the discussion and the maximum DoD is chosen as 0.6.

The combined effects of J_c , DoD and $k_S/k_{S,\text{exp}}$ on SE and RTE are shown in 3D surface plots of Figs.13-15. The J_c is purposely selected to be lower than, equal to and higher than $J_d=100\text{A/m}^2$. For $J_c=60\text{A/m}^2$, Fig.13a shows that the charge SE (or SE_c) increases with DoD but decreases with $k_S/k_{S,\text{exp}}$, which are well expected. Clearly, the minimum $\text{SE}_c=1385\text{Wh/kg-Fe}$ is found at $\text{DoD}=0.1$ and $k_S/k_{S,\text{exp}}=4$, the most favorable condition for a reversible charge cycle. The corresponding RTE is plotted in Fig.13b, showing an opposite trend to SE_c in Fig.13a. The maximum $\text{RTE}=0.85$ is observed at $\text{DoD}=0.1$ and $k_S/k_{S,\text{exp}}=4$.

Fig.13 SE_c (Wh/kg-Fe) and RTE as a function of DoD and $k_S/k_{S,\text{exp}}$ with $J_c=60\text{A/m}^2$.

For the case of $J_c=J_d=100\text{A/m}^2$, the 3D surface plots are shown in Fig.14a and b; they follow the same trend as Fig.13a and b, but with higher SE_c and lower RTE, indicating a decrease in reversibility at higher J_c . In fact, there is 16% unconverted Fe_3O_4 at the end of the charge cycle when $\text{DoD}=0.6$ and $k_s/k_{s,\text{exp}}=1$. The best performance is obtained for $\text{DoD}=0.1$ and $k_s/k_{s,\text{exp}}=4$ at which the battery is fully reversible with $SE_c=1472\text{Wh/kg-Fe}$ and $\text{RTE}=0.80$.

Fig.14 SE_c (Wh/kg-Fe) and RTE as a function of DoD and $k_s/k_{s,\text{exp}}$ with $J_c=100\text{A/m}^2$.

For the case of $J_c=140\text{A/m}^2$, the variations of SE_c and RTE with DoD and $k_s/k_{s,\text{exp}}$ remain the same as the previous cases, see the 3D surface plots in Fig.15a and b. It is worth mentioning that SE_c and RTE become much more sensitive to the change of $k_s/k_{s,\text{exp}}$ at higher DoD. In other words, insufficiently high $k_s/k_{s,\text{exp}}$ could result in a sharp decrease in RTE if DoD is operated high.

Fig.15 SE_c (Wh/kg-Fe) and RTE as a function of DoD and $k_s/k_{s,exp}$ with $J_c=140A/m^2$.

To facilitate the understanding of the 3D surface plots shown above, Fig.16 of a 2D plot is further plotted to display the SE_c and RTE as a function of J_c at four extreme conditions: $DoD=0.1$ and 0.6 ; $k_s/k_{s,exp}=1$ and 4 . From Fig.16a, the trend is clear: if k_s is sufficiently high the DoD will have a little effect on SE_c over the entire J_c range. For RTE shown in Fig.16b, the trend is slightly different. The advantage of having higher $k_s/k_{s,exp}$ is only manifested at higher J_c . At lower J_c , the RTE seems to be more impacted by DoD. Having said this, the general trend is still true in that lower DoD and higher $k_s/k_{s,exp}$ would favor a higher RTE for the entire J_c range.

Fig.16 (a) SE_c , (Wh/kg-Fe); (b) RTE as a function of J_c for selected cases.

In conclusion, at low J_c when the reduction kinetics of Fe_3O_4 are not yet performance-limiting, it is more effective to achieve a high RTE by decreasing DoD. To achieve a required energy capacity, a longer charge time is, therefore, needed. At high J_c when the reduction kinetics of Fe_3O_4 becomes performance-limiting, a sufficiently high $k_s/k_{s,\text{exp}}$ is needed to obtain a higher RTE as the effect of DoD becomes less significant.

VI. Conclusions

In the present work, the effects of discharge and charge current densities, depth-of-discharge, initial porosity of RCU, distance between RSOFC and RCU, and kinetic rate constant of Fe_3O_4 -reduction reaction on electrochemical performance of SOIARB have been systematically investigated using a high-fidelity 2D axial symmetric multiphysics model. The results explicitly show that the charge process of Fe_3O_4 -reduction is the performance-limiting step. The initial porosity of RCU and distance between RSOFC and RCU have an insignificant effect on the performance, implying that the H_2 - H_2O diffusion through the chamber and inside RCU bed is not a limiting factor. However, the chamber pressure could be substantially increased if the initial porosity and distance are too small, prompting the need for optimizing these two parameters in engineering design. Finally, charge current density, depth-of-discharge and kinetic rate are shown to have the most significant effect on the specific energy and round-trip-efficiency of the battery. A careful combination of these parameters can lead to a balanced energy capacity and cycle efficiency for the best performance.

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Nomenclature

A , (m^2)	Cross area
c , ($mol \cdot m^{-3}$)	Molar concentration
d_{pore} , (m)	Diameter of spherical particle of the porous medium
d_p , (m)	Pore diameter of the porous medium
D_{ij} , ($m^2 \cdot s^{-1}$)	Binary diffusion coefficient for a pair of species i and j
$D_{kn,i}$, ($m^2 \cdot s^{-1}$)	Knudsen diffusion coefficient of species i
E , (V)	Nernst potential
F , ($C \cdot mol^{-1}$)	Faraday's constant, 96485
G , ($J \cdot mol^{-1}$)	Gibbs free energy
J , ($A \cdot m^{-2}$)	Operating current density
K	Equilibrium constant
k_D , ($m^2 \cdot s^{-1}$)	Reference diffusivity
k_o , (s^{-1})	Global oxidation rate constant
$k_{f,i}$, (s^{-1})	Forward reaction constant in JMAK model
$k_{h,i}$, (s^{-1})	Backward reaction constant in JMAK model
$k_{f,s}$, ($m \cdot s^{-1}$)	Forward reaction constant in Shrinking-Core model
$k_{h,s}$, ($m \cdot s^{-1}$)	Backward reaction constant in Shrinking-Core model
k_s , ($m \cdot s^{-1}$)	Reaction constant in Shrinking-Core model
M_i , ($kg \cdot mol^{-1}$)	Molar weight of species i
M , ($kg \cdot mol^{-1}$)	Mean molar weight of gas mixture
$m_{Fe,0}$, (kg)	Initial load of Fe
N_i , ($kg \cdot m^{-2} \cdot s^{-1}$)	Flux vector of species i

N	Avrami exponent
n , (mol)	Number of electrons
i_{ict} , ($\text{A} \cdot \text{m}^{-2}$)	Local charge transfer current density
p , (Pa)	Pressure
R , ($\text{J} \cdot (\text{mol}^{-1} \cdot \text{K}^{-1})$)	Gas constant, 8.314
R_{c0} , (m)	Initial radius of Fe_3O_4 core
r , ($\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$)	Reaction rate
r_c , (m)	Radius of the core in the shrinking core model
R_i , ($\text{kg} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$)	Reaction source term for species i
s_i	Stoichiometric coefficient of species i
S_a , (m^{-1})	Electrochemical reaction active area per unit volume
T , (K)	Temperature
t , (s)	Time
V , (V)	Cell voltage
x_j	Molar fraction of species j

Greek symbols

σ , ($\text{S} \cdot \text{m}^{-1}$)	Conductivity
ϕ , (V)	Potential
η , (V)	Overpotential
ρ , ($\text{kg} \cdot \text{m}^{-3}$)	Density
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
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Meaning of Abbreviations

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
SE	Specific Energy