Understanding the High-Temperature Solid-Oxide Iron-Air Redox Battery Operated with an Oxygen Shuttle Mechanism: A Computational Study

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In this computational study, we demonstrate the use of a high-fidelity multiphysics model to predict the effects of operational parameters and the performance of a new Solid Oxide Iron-Air Redox Battery (SOIARB) operated at 800 °C. The results show explicitly that the operating current density has the most pronounced effect on the H₂ concentration distribution, Nernst potential, specific energy and round-trip efficiency. The initial porosity in the Redox Cycle Unit (RCU) must be > 0.50 at high current density in order to avoid significant diffusion limitation. Also, the distance between the RSOFC (reversible Solid Oxide Fuel Cell) and the RCU has little effect on the performance of the SOIARB, but has an appreciable effect on the chamber pressure. The simulations indicate that a high round-trip efficiency (RTE) can be achieved at the expense of useful capacity. Enhancement of the electrolysis electro-kinetics of RSOFC and FeO-reduction kinetics of RCU is a key to achieving high capacity with high efficiency.

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Since the first demonstration of oxide-ion-chemistry based anode-supported tubular Solid-Oxide Iron-Air Redox Battery (SOIARB) in 2011,1 significant progress has been made experimentally in the areas of materials identification,2–5 new metal-air chemistries1,6–14 and performance optimization.15–20 In contrast, theoretical understanding of the operating oxygen shuttle mechanisms of the new battery lags behind. In the open literature, only Ohmoti et al.21,22 and Guo et al.23 have reported multiphysics models for the battery. However, neither of them has considered the important time-dependent chemical redox kinetics taking place within the energy storage component, referred to as the Redox Cycle Unit or RCU. To address this problem, we have recently established a high-fidelity multiphysics model with parameters directly validated by experimental results and a chemical redox kinetics model based on Johnson-Mehl-Avrami-Kolmogorov (JMAK) and Shrinking Core theories.24 Integrated with mass transport of H₂-H₂O charge transfer in the Reversible Solid Oxide Fuel Cell (RSOFC) and chemical redox kinetics in the RCU, the new model has been used to simulate the performance of SOIARB at 550 °C with Fe/Fe₂O₃ as the RCU material and H₂-H₂O as the oxygen shuttle gas (OSG).

In this study, we present a computational analysis of a Solid-oxide Iron-air Redox Battery or SOIARB operated at 800 °C by utilizing the same model. At 800 °C, the energy storage redox couple is Fe/FeO according to thermodynamics, which equilibrates with an OSG composition of H₂H₂O = 0.65/0.35 and generates a Nernst potential of 0.97 V vs air. To retain the high fidelity, all the parameters used by this model are directly validated by the experimental data obtained from our lab. This study is primarily focused on investigating the effects of current density, porosity of RCU and distance between RSOFC and RCU on the performance of a SOIARB. Key operational parameters are subsequently identified for future engineering design and practical operation.

Model Construction and Validation

The SOIARB.—The configuration of a SOIARB is shown in Fig. 1a, where the RCU bed consists of a Fe/FeO redox couple synthesized from carbothermic reaction21 and the RSOFC is composed of a 50-μm Sm₀.₅Sr₀.₅CoO₃₋₁/Sm₀.₅CoO₁₋₀.₉ composite O₂-electrode, a 30-μm thick Ce₀.₅Ga₀.₅O₂₋₁/Ni composite H₂-electrode and a 180-μm thick La₀.₃Sr₀.₇Ga₀.₃Mg₀.₁7O₃₋₅ (LSGM) electrolyte membrane. Between the RSOFC and RCU is a space filled with a mixture of H₂ and H₂O referred to as the Oxygen Shuttle Gas (OSG). The O₂-electrode is constantly open to air.

During operation, the RSOFC utilizes its fuel cell and electrolysis modes to realize electrical discharge and charge, respectively, while the RCU stores/releases energy from/to SOIARB through redox reactions. The electrochemical and chemical reactions occurring within the RSOFC and the RCU are:

\[ \frac{1}{2} O_2(g) + 2e^- \xrightarrow{\text{charge}} O^{2-} \]  \[ \text{H}_2(g) + O^{2-} \xrightarrow{\text{charge}} H_2O(g) + 2e^- \]

in the RCU redox reaction: \( H_2O(g) + Fe \xrightarrow{\text{charge}} FeO + H_2(g) \)

The model.—The computational domains corresponding to Fig. 1a are illustrated in Fig. 1b; the model is 2D axis-symmetric. Based on the configuration and electrochemical/chemical reactions aforementioned, the following processes are considered in the model: 1) electron/oxygen-ion transport in the RSOFC; 2) electrochemical reactions at triple phase boundaries in the RSOFC electrodes; 3) gas diffusion through the porous electrodes of the RSOFC; 4) gas diffusion through the open space OSG chamber; 5) gas diffusion through the porous RCU bed; 6) redox reactions in the RCU bed. The governing equations for each of the six processes are given in Table I. The meanings of the symbols used in this computational study are summarized in the Appendix. The convective mass transfer of concentrated species is neglected due to the fact that it is a closed stationary system.

The boundary/initial conditions.—Boundary and initial conditions are necessary to solve the coupled partial differential equations. Since the model is virtually the same as that of 550 °C battery,24 the boundary conditions remain unchanged and are given in Table II. Based on the experimental data, the initial gas composition in the chamber was taken as mole ratio H₂-H₂O = 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 purposes).

The computation.—The electronic potential \( \phi_e \) and ionic potential \( \phi_i \), mass fraction of gas species, \( \omega_j \), the reacted fraction ratio \( x_{Fe}/x_{Fe,0} \).
are computed as a function of time by combining Eqs. 4–6, (12) and (13) with the boundary/initial conditions aforementioned. The time-dependent porosity ($\epsilon$) in the RCU bed is calculated by:

$$\epsilon = \epsilon_0 + (1 - \epsilon_0) x_{Fe} (1 - x_{FeO}) c_{Fe} \left( \frac{M_{Fe}}{\rho_{Fe}} - \frac{M_{FeO}}{\rho_{FeO}} \right)$$

where $\epsilon_0$ is the initial porosity of RCU bed, $M_{Fe}$, $\rho_{Fe}$ and $M_{FeO}$, $\rho_{FeO}$ are the molar mass and density of Fe and FeO, respectively; $c_{Fe} = \frac{M_{Fe}}{\rho_{Fe}}$ is the molar concentration of Fe.

In addition, as porosity ($\epsilon$) varies as a function of time, the pressure of OSG chamber is also subject to change due to the decrease in free

**Table I. Governing equations used in the model.**

| Governing equations                              | Mathematical expressions                                |
|--------------------------------------------------|--------------------------------------------------------|
| Charge conservation in RSOFC                     | $\nabla \cdot (-\sigma_e/o) \nabla \Phi_e = \pm \rho_e/o \nabla \Phi_e$ |
| Butler-Volmer equation                           | $i_{ict} = i_0 \exp \left( \frac{-E_{ict}}{RT} \right) - \frac{c_{out}}{\nu_{prod}} \exp \left( -\frac{E_{ict}}{RT} \right)$ |
| Gas species transport                            | $\frac{d(x_{Fe})}{dt} + \nabla \cdot \left[ \rho \omega_j \nabla \Phi_j \right] + (x_j - \omega_j) \frac{\nabla p}{\rho}$ |
| Source term                                       | $R_{RSOFC} = \pm \frac{\Delta H_{FeO}}{\Delta n} \Phi_{FeO}$, $R_{RCU} = \frac{\Delta H_{FeO}}{\Delta n} c_{Fe}/c_{FeO} (1 - \epsilon_{RCU}) M_i$ |
| Binary diffusion                                  | $D_{ij} = \frac{x_i^2}{p(n_i + \rho_j)} \left[ \frac{\mu_j}{\sigma_{ij}} + \frac{1}{\sigma_{ij}} \right]^{1/2}$ |
| Knudsen diffusion                                 | $D_{Kn,i} = \frac{\nu_i}{\sqrt{\pi M_i}}$ |
| Average Bosanquet diffusion coefficient          | $D_{ij} = \frac{1}{2} \left( \frac{1}{\nu_i} \nabla \Phi_i + \frac{1}{\nu_j} \nabla \Phi_j \right)$ |
| Reaction kinetics model for RCU                  | $K = \exp \left( -\frac{\Delta G_{prod}}{RT} \right) = \frac{x_{Fe}}{x_{FeO}} \frac{\sigma_{FeO}}{\sigma_{Fe}}$ |
| Shrinking Core model for FeO reduction           | $\frac{dx_{FeO}}{dt} = \frac{-3x_{FeO}^{1/2}}{\sigma_{FeO}} (1 - x_{Fe})^{1/2}$ |
| JMAK model for Fe oxidation                       | $\frac{dx_{Fe}}{dt} = (k_f, x_{H2O} - k_{r, x_{H2O}}) [1 - x_{Fe}][1 - \ln(1 - x_{Fe})]^{1 - \frac{3}{4}}$ |

**Table II. Boundary/initial conditions used in the model.**

| Boundary Variable                              | Electronic potential $\Phi_e$ | Ionic potential $\Phi_i$ | Stefan-Maxwell diffusion $\omega_j$ |
|------------------------------------------------|-------------------------------|--------------------------|-------------------------------------|
| Air channel/O2 electrode                       | $-n \cdot \nabla \Phi_e = J_e/d$ | $n \cdot \Phi_i = 0$ | $O_2-N_2 = 0.21:0.76$ |
| O2-electrode/electrolyte interface             | $-n \cdot \Phi_e = 0$ | Continuity | $-n \cdot N_f = 0$ |
| H2-electrode/electrolyte interface             | $-n \cdot \Phi_e = 0$ | Continuity | $-n \cdot N_f = 0$ |
| H2 electrode/Chamber                           | $0 \nabla$ | Continuity | $-n \cdot \Phi_i = 0$ |
| Chamber/RCU                                    | $n \cdot \Phi_i = 0$ | Continuity | $-n \cdot \Phi_i = 0$ |
| Other surfaces                                 | $n \cdot \Phi_i = 0$ | Continuity | $-n \cdot \Phi_i = 0$ |

Note: $N_f = -\rho_i \sum_{j} D_{ij}^{ff} d_j$. 

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volume. This pressure change is calculated by:

$$p = p_0 \cdot \frac{\varepsilon_{\text{anode}} V_{\text{anode}} + V_{\text{chamber}} + \varepsilon_{\text{RCU}} (t) V_{\text{RCU}}}{\varepsilon_{\text{anode}} V_{\text{anode}} + V_{\text{chamber}} + \varepsilon_{\text{RCU}} V_{\text{RCU}}}$$  \[15\]

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 @2.4 GHz and 2.39 GHz and 16 GB 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 PDEs.

The validation.— Both the properties of RSOFC and RCU could significantly affect the overall performance of a SOIARB. 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 study;\textsuperscript{31} the results are shown in Fig. 2. The reaction rate constants in the JM AK and the Shrinking Core models were obtained from an experimental Discharge/Charge curve of the battery as a function of time; the results are shown in Fig. 3.\textsuperscript{11} Depth of Discharge (DoD) or the iron utilization of the RCU was calculated by integrating the rate of redox reaction in the whole domain over time.

From Figs. 2 and 3, it is evident that the simulated results agree well with the experimental data. The uncertainties of voltage predicted from the model vs the experimental data are within ±0.02 and ±0.025 volt for the V-I and charge-discharge curves, respectively. The physical and chemical parameters used are listed in Table III. The parameters marked with “*” are the fitted parameters, which are well within the reasonable range of their physical meanings.

| Table III. Summary of parameters used in the model. |
|---------------------------------------------------|
| Parameters                                      | Values            |
| Atmospheric pressure, $p_0$                     | 1 [atm]           |
| Temperature, $T_0$                              | 800°C             |
| Inlet mole fraction of $H_2$                    | 0.65              |
| $\varepsilon_{\text{H}_2}$                     | 0.21              |
| Inlet mole fraction of $O_2$                    | 0.21              |
| Tortuosity, $\alpha$                            | 3                 |
| Porosity, $\varepsilon$                         | 0.4/0.3           |
| Electronic conductivity, $\kappa$               | $2 \times 10^8$  [S/m] |
| Ionic conductivity, $\kappa_{\text{el}}$        | 5.9 [S/m]         |
| Exchange current density for SOFC, $\sigma_i^{\text{SOFC}}$ | 1662.5/133 [A/m²] |
| Exchange current density for RSOFC, $\sigma_i^{\text{RCU}}$ | 665/226.1 [A/m²] |
| Specific surface area, $\sigma_s$               | $1-(1-\varepsilon_{\text{RCU}}) \times 1.43 \times 10^4$ [1/m] |
| Transfer coefficient, $\alpha$                  | 0.25              |
| Number of electrons, $n$                        | 2                 |
| Viscosity of air, $\mu$                         | $5.5 \times 10^{-5}$ [Pa·s] |
| Permeability of electrodes, $\kappa$            | $10^{-11}$ [m²]  |
| Reference diffusivity, $k_D$                    | $3.16 \times 10^{-8}$ [m²/s] |
| Kinetic volume of $H_2$, $v_{H_2}$              | $6 \times 10^{-6}$ |
| Kinetic volume of $O_2$, $v_{O_2}$              | $16.6 \times 10^{-6}$ |
| Kinetic volume of $N_2$, $v_{N_2}$              | $17.9 \times 10^{-6}$ |
| Kinetic volume of $H_2O$, $v_{H_2O}$            | $12.7 \times 10^{-6}$ |
| Diameter of spherical particle, $d_0$           | $0.35 \mu m$      |
| Loading of Iron, $m_{\text{Fe}}$                | 0.805 [g]         |
| Initial porosity of RCU, $\varepsilon_{\text{RCU}}$ | 0.7               |
| Reaction rate constant of JMAK, $kJ k_b$        | $10 \times 4.7 \times 10^{-5}/5.38 \times 4.7 \times 10^{-5}$ [1/s] |
| Avrami exponent of JMAK, N                       | 0.8               |
| Reaction rate constant of shrinking core model, $kJ k_b$ | $10 \times 4.26 \times 10^{-8}/5.38 \times 4.26 \times 10^{-8}$ [m²/s] |

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

Parametric Study

Based on the validated model, a parametric study was first carried out to understand further the rate-limiting steps of a SOIARB. The discharge/charge current density ($J$), initial porosity of RCU ($\varepsilon_{\text{RCU}}$), and distance between RSOFC and RCU (d) are varied systematically to illustrate their effects on the battery’s performance under an isothermal condition ($T=800\, ^\circ C$). The Specific Energy (SE) and Round-trip efficiency (RTE) are then analyzed under different combinations of the above parameters to provide engineering solutions for achieving a balanced performance of the battery.

The effect of current density.— The current density ($J$) applied on the RSOFC dictates the dynamic interaction between the RSOFC and RCU. At $800\, ^\circ C$, cycle performance of the battery can be significantly improved because of the enhanced redox kinetics inside RCU and electro-kinetics in RSOFC. An improved reversibility is clearly seen in Fig. 4, where the sustainable cycle duration operated under an equal charge and discharge current density can be maintained symmetrically over a wider $J$ range than 550 C-battery.\textsuperscript{24} On the same token, Fig. 5 shows that DoD also varies with cycle duration symmetrically for the same $J$ range (except for 2,000 A/m²). All of these observations suggest that better performance of RSOFC and RCU at higher temperatures significantly improves the battery’s performance toward higher $J$ or rate capacity. This is in stark contrast to 550 C-battery, where the performance was largely limited to low $J$ due to poor RSOFC and RCU performance.\textsuperscript{24}
The discharge/charge profiles of the battery under different J are plotted against DoD in Fig. 6. With \( J = J_c = J_d = 100 \, \text{A/m}^2 \), the cell voltage stays very flat at 0.94 V and 0.99 V for the discharge and charge cycles, respectively. The polarization losses from RSOFC and kinetic impedance from RCU are so small at such a low J that they do not impact on the battery’s performance. As J increases, the effect of polarizations and chemical redox kinetics start to develop in the battery’s performance. A typical feature of the cycle profile at higher J in Fig. 6 is that it bends over at high DoD during the discharge cycle and curves up at low DoD during the charge cycle. At very high J, the charge cycle becomes partially irreversible, implying that the FeO-reduction kinetics or electrolysis electro-kinetics of RSOFC could become a performance-limiting step. Therefore, boosting RCU’s reduction kinetics and reducing RSOFC’s electrolysis resistance are keys to achieving high-rate operation for a high-temperature SOIARB.

The corresponding profiles of averaged H\(_2\) mole fraction (\( x_{H_2} \)) in RCU and OSG chamber as well as Nernst potential of RSOFC during a discharge/charge cycle are plotted against DoD under different J in Fig. 7(a) and 7(b), respectively. At 800°C, the equilibrium composition of the oxygen shuttle gas (OGS) is \( x_{H_2O} : x_{H_2} = 0.35 : 0.65 \), which corresponds to a Nernst potential of 0.97 V vs air. It is seen from Fig. 6 that at low J the equilibrium \( x_{H_2} \) is not disturbed at all. As J increases, however, significant deviation from the equilibrium composition can be discerned at high DoD. Similarly, the Nernst potential profile in Fig. 7 exhibits the same shape and trend as \( x_{H_2} \) due to its close relation with \( x_{H_2} \) through the Nernst equation.

In summary, since the reaction kinetics of RCU and the electrode-kinetics of RSOFC are significantly improved at 800°C, it enables the battery to operate at much higher J compared to 550°C C-battery. The battery can discharge and charge with stable energy at high efficiency under lower J. At higher J, the high energy transfer is achieved in exchange of efficiency due to the losses to kinetic resistance in RCU and polarization in RSOFC. To minimize the trade-off between energy capacity and efficiency, improving chemical kinetics of the FeO-reduction and electro-kinetics of the electrolysis is deemed a key. More discussion will be given in the Performance projection and optimization section.

Figure 4. Simulated cycle duration (h) as a function of current density with a baseline condition: DoD = 0.69, \( \varepsilon_0 = 0.7 \), \( d = 1 \, \text{mm} \).

Figure 5. Simulated volume averaged DoD as a function of cycle duration under different J. (\( \varepsilon_0 = 0.7 \), \( d = 1 \, \text{mm} \)).

Figure 6. Simulated cyclic voltage profiles of SOIARB as a function of DoD under different J. (\( \varepsilon_0 = 0.7 \), \( d = 1 \, \text{mm} \)).

The effect of initial porosity in the RCU.— Since the molar volume of FeO is different from Fe, the porosity of RCU will vary with DoD during cycles. For the discharge cycle, the porosity decreases with DoD as oxidation of Fe occurs, while it increases during the charge cycle as reduction of FeO takes place. Fig. 8 shows the variation of the RCU’s porosity with DoD under different \( \varepsilon_0 \). It is evident that too low a \( \varepsilon_0 \) could lead to a very low end-of-the-discharge porosity, e.g., with \( \varepsilon_0 = 0.42 \), \( J = 1,000 \, \text{A/m}^2 \), \( d = 1 \, \text{mm} \), the resultant \( \varepsilon \) = 0.12 when DoD = 0.69, which would present a serious problem to the gas diffusion. Therefore, for a high DoD and J operation, a high initial \( \varepsilon_0 \) in the RCU is necessary.

The effect of \( \varepsilon_0 \) on battery’s cycle performance is shown in Fig. 9, where the profiles of the cell voltage and averaged \( x_{H_2} \) in the RCU and the OSG chamber are plotted against DoD under different \( \varepsilon_0 \). It is worth mentioning that the nature of Nernst potential being proportional to \( \ln(P_{H_2O}/P_{H_2}) \) not directly to \( P_{H_2O}/P_{H_2} \) implies that it is more sensitive to \( P_{H_2O} \) at higher DoD. It appears that \( \varepsilon_0 \) has little effect on the performance when \( \varepsilon_0 \geq 0.5 \). At \( \varepsilon_0 < 0.5 \), for example, when \( \varepsilon_0 = 0.42 \), an appreciable decrease in voltage is noted in Fig. 9a for DoD>0.4. This is undoubtedly associated with the significantly reduced porosity in the RCU shown in Fig. 8. Correspondingly, the \( x_{H_2} \) profile shown in Fig. 9b depicts a “bend-over” behavior at DoD>0.4, suggesting that increased diffusion resistance by the reduced porosity has negatively impacted the H\(_2\)/H\(_2\)O diffusion.

To illustrate further the created \( x_{H_2} \) gradient by the limited gas diffusion at low \( \varepsilon_0 \), Fig. 10 shows \( x_{H_2} \) distribution along z-axis (the axial symmetric axis) at different \( \varepsilon_0 \). We have chosen to plot the profiles after 10 seconds into the charge mode because of the rapid change in \( P_{H_2O} \) and \( P_{H_2} \) caused by the small button cell modeled. In agreement with Fig. 9, \( x_{H_2} \) distribution varies more appreciably at \( \varepsilon_0 < 0.5 \) than those at \( \varepsilon_0 \geq 0.5 \) for both discharge and charge cycles, further confirming the criticality of the initial porosity of RCU, particularly for high J and DoD operation.

In summary, the initial porosity of RCU should be maintained high enough to avoid the large diffusion-limited kinetic resistance for high J and DoD operation. In addition, the chamber pressure could also be impacted by the combined effect of \( \varepsilon_0 \) and \( d \), which will be discussed in the following sections.

The effect of distance (d) between RSOFC and RCU.— The d value determines the size of OSG chamber, ultimately the size of the entire battery stacks. A wider d can store more H\(_2\)/H\(_2\)O to allow a faster equilibration between RSOFC and RCU, but it can also lead to a greater diffusion resistance. Too small a d could result in pressure
Figure 7. (a) Simulated profiles of H₂ mole fraction in RCU and OSG chamber and (b) simulated Nerst Potential of RSOFC as a function of DoD under different J during a discharge/charge cycle. (ε₀ = 0.7; d = 1 mm).

Figure 8. Simulated volume averaged porosity of RCU as a function of DoD.

increase in the chamber. Therefore, studying the effect of d on the battery’s performance is necessary.

The profiles of cell voltage during a discharge/charge cycle are shown in Fig. 11 against DoD for different d values. Evidently, d in the range of 0.01 mm to 10 mm has little discernable effect on the electrochemical performance of the battery. This observation implies that establishment of the dynamic equilibrium between RSOFC and RCU is sufficiently fast to overcome diffusion resistance of H₂-H₂O raised by widening the gap.

The important impacts arising from reducing d is reflected on the pressure inside the OSG chamber. As oxygen is continuously added into the OSG chamber, they must be converted into oxide in exchange of porosity in RCU. However, if ε₀ is too small, the ability of RCU to absorb oxygen would be limited, resulting in accumulation of oxygen or H₂O in the OSG chamber and subsequently increase in pressure. To illustrate the effect of d on the OSG-chamber pressure (P), we calculated P as a function of DoD assuming that H₂-H₂O is an ideal gas mixture; the results are shown in Fig. 12. As expected, P increases with DoD as the free volume in the OSG chamber decreases. However, the degree of increase depends on ε₀ considerably. At an extreme condition, ε₀ = 0.42 and d = 0.01 mm, P can be as high as 2 atms above the atmosphere at DoD = 0.69. At the baseline condition, ε₀ = 0.70 and d = 1 mm, P is only 0.2 atm above the atmosphere at DoD = 0.69. For the baseline case and operating at lower DoD, the increase in P is much smaller. The predictions presented in Fig. 12 will be valuable in selecting sealing materials and engineering design to prevent breakthrough of gas seals in the stack.

Performance Projection and Optimization

As discussed previously, the reversibility of the battery can be enhanced by operating at a higher temperature. The degree of improvement in the specific energy (SE) and the round-trip efficiency RTE under different conditions is, however, still unknown at this point. In
this section, we focus on quantifying SE and RTE of the battery under different J and DoD, and ultimately provides optimized engineering solutions to design and operation for the battery. SE is calculated by the integration of energy production/consumption over the amount of iron consumed/produced; RTE is determined by the ratio of discharge SE (SE\textsubscript{d}) to charge SE (SE\textsubscript{c}), viz., RTE = SE\textsubscript{d}/SE\textsubscript{c}.

Performance projections.— The variations of SE and RTE with J ranging from 100 to 2,000 A/m\textsuperscript{2} under a baseline condition: d = 1 mm, \(\varepsilon_0 = 0.7\), DoD = 0.69, are shown in Fig. 13. It is evident that SEs of the charge and discharge cycle increases and decreases linearly with J, respectively. This is an expected result since the polarization loss and kinetic resistance increase with J. Correspondingly, the RTE decreases from 0.95 at 100 A/m\textsuperscript{2} to 0.29 at 2,000 A/m\textsuperscript{2}. It is apparent that achieving a higher rate capacity is at the expense of lowering RTE. Increasing the performance of both the RSOFC and the RCU can shift the operating J toward higher value for a given SE and RTE. Finding an appropriate operating J is also a key to achieve a balanced SE and RTE for a specific operation.

Theoretically speaking, decreasing the DoD is another way to improve SE and RTE of the battery. Fig. 14 shows that SE and RTE indeed decrease with DoD, but not as significantly as J. Operating at a very high DoD is, however, not desirable as it may cause a permanent degradation in the RCU when a part of the FeO in the RCU cannot be reversibly converted back to Fe during the charge cycle. Instead, running the SOIARB with low DoD (or Fe unitization) seems to be a reasonable strategy to achieve long lifecycle since Fe is an inexpensive and earth abundant element.

Drastically different from 550\textdegree C-battery previously studied, the kinetic rates Fe redox reactions for 800\textdegree C-battery do not differ considerably. There are two main reasons for this relatively balanced redox reaction: 1) a more balanced H\textsubscript{2}/H\textsubscript{2}O ratio in OSG: 0.65/0.35 for 800\textdegree C vs 0.79/0.21 for 550\textdegree C; 2) an increased rate constant for FeO-reduction due to the abundant defects present in the defective Fe\textsubscript{1-x}O. Therefore, the performance-limiting step for 800\textdegree C-battery is not as obvious as that for 550\textdegree C-battery; the latter performance is completely dominated by the Fe\textsubscript{3}O\textsubscript{4}-reduction kinetics. Nevertheless, we plot the maximum DoD (DoD\textsubscript{max}) allowable to operate as a
Figure 13. Simulated (a) SE (Wh/kg-Fe) as a function of J/1000 (A/m²); (b) RTE as a function of J/1000 (A/m²). (d = 1 mm, ε₀ = 0.7, DoD = 0.69).

function of operating J in Fig. 15 for both charge and discharge cycles. It is apparent that with J increasing from 600 to 2,400 A/m², the allowable DoDmax decreases from 0.94 to 0.77 for the discharge cycle. However, for the charge cycle a lower allowable DoDmax is allowed, for example from 0.91 to 0.32, confirming the reduction kinetics of the charge cycle is still less facile than the discharge cycle. For practical operation, DoD should be maintained well below the values shown in Fig. 15 to avoid irreversibility of the battery.

Performance optimization strategy.— To further indicate the degree of improvement needed for electrolysis electro-kinetics and FeO-reduction chemical kinetics, two 3D surface plots are shown in Fig. 16 for SE-i₀/i₀,exp-k/kexp and RTE-i₀/i₀,exp-k/kexp. Consistent with the aforementioned discussion, i₀/i₀,exp is clearly shown to have a more pronounced impact on SE and RTE than k/kexp. Therefore, improving the performance of RSOFC can lead to a better performance of 800°C-SOIA RB than enhancing the reaction kinetics of RCU.

Fig. 17 depicts a single cycle simulation under a number of extreme conditions. Compared to the baseline performance, simply improving

Figure 14. Simulated (a) SE of discharge (Wh/kg-Fe); (b) SE of charge (Wh/kg-Fe); (c) RTE as a function of DoD under different J. (d = 1 mm, ε₀ = 0.7).

Figure 15. Plot of the simulated maximum DoD allowable to operate as a function of J. (d = 1 mm, ε₀ = 0.7). k = kexp,fit is the rate constant obtained from Fig. 3 for both discharge and charge cycles.
Conclusions

In this work, a high-fidelity multiphysics model has been applied to a SOIARB operated at 800 °C with goal of investigating how the electrochemical performance of SOIARB is affected by current densities, initial porosity of RCU and distance between RSOFC and RCU. The results show that both reduction and oxidation reaction kinetics of RCU are improved significantly compared to the 550 °C-battery, making it possible to operate on higher current density. The initial porosity of RCU has a significant impact on the H2-distribution, thus the performance, if it is <0.50 and/or DoD>0.40. The effect of the distance (d) is generally very small on electrochemical performance, but could be substantial on the OSG chamber pressure if the initial porosity in RCU is low and operational DoD is high. The SE and RTE projected under different conditions suggest that they can be negatively impacted by operating at high current density. To improve the overall performance, particularly at high current density, of the battery, the electrolysis electro-kinetics of RSOFC such as oxygen evolution reaction and FeO-reduction kinetics of RCU need to be further enhanced.

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Appendix

Shrinking Core model.— Shrinking Core model is widely used to correlate the reacted fraction of iron oxide with the kinetic rate. In this article, it is assumed that FeO particles (radius Rc0, remains constant) are uniformly distributed in the solid phase. While FeO is reduced by H2 in the gas phase, a porous layer of Fe is generated on the particle surface. The thickness of Fe grows with time. If the surface reaction is the rate limiting step, the radius of the unreacted core (rc) is governed by:

\[
\frac{drc}{dt} = k_f \left( x_{H_2O} - k_b x_{H_2} \right)
\]

where \( k_f \) is the reversible reaction rate. The fraction of reacted FeO is related to \( r_c \) by:

\[
x_{FeO} = 1 - \exp\left(-\left(\frac{r_c}{R_c}\right)^N\right)
\]

Substitution of \( r_c \) in Eq. (A2) into Eq. (A1) yields

\[
\frac{dx_{FeO}}{dt} = 3k_p \left( x_{H_2O} - k_b x_{H_2} \right) \left(1 - x_{FeO}\right)^{3/2}
\]

This equation has been consistently used throughout our model for calculating the reduction kinetics during the charge cycle.

JMAK model.— The Johnson-Mehl-Avrami-Kolmogorov (JMAK) model has been extensively used to give a phenomenological description of gas-solid heterogeneous chemical reactions. The derivation of the JMAK model is based on the combination of three processes: nucleation, growth and impingement of randomly distributed nuclei. According to the model, the fraction of solid material (here Fe) reacted, \( x_F \), as a function of time at a constant temperature is given by:

\[
x_F = 1 - \exp\left(-k_b t^{N}\right)
\]

Differentiating Eq. (A4) and replacing \( k_b \) by the reversible reaction rate, yields

\[
\frac{dx_F}{dt} = \left( x_{H_2O} - k_b x_{H_2} \right) N (1 - x_F) \left[-\ln(1 - x_F)^{1/3}\right]
\]

List of Symbols

- \( c \) (mol · m\(^{-3}\))
- \( d \) (m)
- DoD

Figure 16. 3D surface plots for simulated (a) SEc=io/io,exp-k/kexp, (b) SEc=io/io,exp-k/kexp and (c) RTE=io/io,exp-k/kexp.

Figure 17. A single-cycle simulation under different \( i_0 \) and \( k \) conditions.

\[
\frac{dx_F}{dt} = \left( x_{H_2O} - k_b x_{H_2} \right) N (1 - x_F) \left[-\ln(1 - x_F)^{1/3}\right]
\]
$d_{pore}$, (m)

D$_p$, (m$^2$·s$^{-1}$)

D$_{gi}$, (m$^2$·s$^{-1}$)

E, (V)

F(C·mol$^{-1}$)

G, (J·mol$^{-1}$)

k$_{act}$, (A·m$^{-2}$)

J$_i$, (A·m$^{-2}$)

K

k, (m$^2$·s$^{-1}$)

k$_{f,j}$, (s$^{-1}$)

k$_{f,s}$, (m$^2$·s$^{-1}$)

k$_{f,f}$, (s$^{-1}$)

k$_{f,g}$, (s$^{-1}$)

k$_{b,s}$, (m$^2$·s$^{-1}$)

K$_p$, (Pa)

k$_f$, (m$^2$·s$^{-1}$)

k$_{b,f}$, (s$^{-1}$)

N$_i$, (mol)

N$_o$, (mol)

N$_p$, (Pa)

R$_i$(J·mol$^{-1}$·K$^{-1}$)

R$_{0,i}$, (m)

r, (mol·m$^{-3}$·s$^{-1}$)

r$_c$, (m)

R$_o$, (kg·m$^{-3}$·s$^{-1}$)

s$_i$

S$_a$, (m$^{-1}$)

T$_f$(K)

t, (s)

$\chi_j$

Diameter of spherical particle of the porous medium

Pore radius of the porous medium

Binary diffusion coefficient for a pair of species i and j

Knudsen diffusion coefficient of species i

Nernst potential

Faraday’s constant, 96485

Gibbs free energy

Local charge transfer current density

Current Density

Equilibrium constant

Reference diffusivity

Global oxidation rate constant

Forward reaction constant in IMAK model

Backward reaction constant in IMAK model

Forward reaction constant in Shrinking-Core model

Backward reaction constant in Shrinking-Core model

Molar weight of species i

Molar of species i

Avrami exponent

Number of electrons

Pressure

Gas constant, 8.314

Initial radius of core

Reaction rate

Radius of the core in the shrinking core model

Reaction source term for species i

Stoichiometric coefficient of species i

Electrochemical reaction active area per unit volume

Temperature

Time

Molar fraction of species j

Greek

$\alpha$

Transfer coefficient in Butler-Volmer equation

Conductivity, (S·m$^{-1}$)

$\sigma$

Potential

$\eta_i$(V)

$\rho_i$(kg·m$^{-3}$·mol$^{-1}$)

Mass fraction of species i/j

Kinetic volume of species i

Porosity

Tortuosity

Subscripts

c

d

e

eff

Charge cycle

Discharge cycle

Electronic

Effective

el

eq

exp

i

g

o

h

react

prod

Electrolyte

Equilibrium

Experiment

Ionic

Gas

Oxygen electrode

Hydrogen electrode

Reactant

Product

Superscripts

0

Ideal/Initial

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