Energy Efficiency of an Intermediate-temperature Solid Oxide Iron-Air Redox Battery

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Abstract

An ASPEN Plus based model is presented for an Intermediate-temperature Solid Oxide Iron-Air Redox Battery (IT-SOIARB) system. The model shows that the energy efficiency of the system can be as high as 83%. Furthermore, the model is used to determine the factors that affect the energy efficiency of the battery. With air as the working fluid, a Heat Exchanger and Thermal Storage Unit are included in the battery system to utilize effectively the heat generated from the

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discharge cycle in the charge cycle. The results show that air utilization (or air mass flow rate) plays a key role in regulating heat flow between the battery components.

KEYWORDS: battery; solid oxide fuel cell; air utilization; efficiency; heat balance

I. Introduction

Large-scale and cost-effective energy storage technology is vitally important to the implementation of a smart grid and renewable energy production. Among many types of energy storage options, Electrochemical Energy Storage (EES) technology is particularly attractive because of its fast response time, high energy capacity, modularity, and low cost. The major form of EES is rechargeable batteries, representative chemistries of which include the well-known lead-acid¹⁻³, Ni-Cd^{4,5}, Ni-MH⁶⁻⁸, Li-ion⁹⁻¹¹, redox flow¹²⁻¹⁴ and Na-S¹⁵⁻¹⁷. For large-scale grid storage applications, only redox flow and Na-S batteries have so far demonstrated the potential to be performance-competent and cost-effective. However, to be commercially viable, these technologies will need breakthroughs in materials discovery and engineering design.

In an effort to develop the next-generation advanced battery technology, we recently demonstrated a new type of battery based on reversible solid oxide fuel cells (RSOFCs)¹⁸⁻²⁰. The core of the technology is the metal-air chemistry, storing and releasing oxygen in/by a metal/metal-oxide chemical bed integrated within a RSOFC operated under fuel-cell and electrolysis modes, respectively. Due to the use of solid oxide and redox materials, the new battery has also been named “Solid Oxide Metal-air Redox Battery” or SOMARB. Compared to other types of batteries, the new battery possesses many distinguishing advantages over conventional redox flow and Na-S batteries: higher energy density, faster charge/discharge rates,

safety, environmental friendliness and scalability, and therefore promises to be a next-generation battery system for large-scale renewable and grid energy storage. Since its first laboratory demonstration in 2011, significant progress has been made in the areas of performance enhancement²¹⁻²⁹, new redox chemistries²⁹⁻³⁴ and computational analysis³⁵⁻⁴¹. However, the ultimate commercialization of the SOMARB technology requires a full understanding of factors affecting system energy efficiency, which has not been addressed in the open literature.

In the present work, we present a system model to analyze the efficiency as well as performance determining factors for a Solid Oxide Iron-air Redox Battery or SOIARB operated at intermediate temperature, collectively IT-SOIARB. To increase the accuracy of the model, the electrochemical sub-model was validated by an experimental V-I curve. To achieve a heat balance between cycles, air was utilized as a working fluid to store, move and transfer heat among the three key components of the system: Heat Exchanger, Thermal Storage Unit (TSU) and IT-SOIARB Unit. The energy efficiency was particularly analyzed as a function of air utilization, current density and air outlet temperature.

II. The IT-SOIARB system

One of the most important thermal characteristics of the IT-SOIARB is the opposite heat signature for the discharge and charge cycles. An efficient utilization of the heat liberated from the discharge cycle (H_2 and iron oxidation reactions) by the endothermic charge cycle (H_2O and iron oxide reduction reactions) can lead to a better energy efficiency. In the present study, a separate air heat exchanger and thermal storage unit (TSU) are included as integrated parts of the system to reuse and capture the heat liberated from the discharge cycle for the charge cycle. Air

is used as the working fluid to store, transport and transfer heat. Fig.1 shows a schematic of the IT-SOIARB system analyzed in this study. The operating temperatures of interest for the study are 550°C for the discharge cycle and 500°C for the charge cycle; at these temperatures the prevalent redox couple in the energy storage Redox Cycle Unit (RCU) is Fe/Fe₃O₄. The operating temperature was assumed to be constant for simplicity.

Fig. 1 A schematic of the analyzed IT-SOIARB system including the Thermal Storage Unit (TSU), (a) discharge cycle; (b) charge cycle. Nomenclature: 1-Redox Cycle Unit (RCU) containing Fe/Fe₃O₄ chemical bed; 2-Reversible Solid Oxide Fuel Cell (RSOFC); 3-Air channel.

The system under analysis consists primarily of an IT-SOIARB stack, TSU, Heat Exchanger and Air Pump. During the discharge cycle, ambient fresh air is first preheated by the hot air exiting from the IT-SOIARB stack. This preheated air then enters the air channel of the IT-SOIARB. This design recovers the waste heat in the exhaust air while delivering O₂ to the cathode for the electrochemical reaction. At the exit of the air channel, the heat-loaded air enters the TSU to store a majority of the process heat for the charge cycle. Clearly, the total molar flow rate of air,

temperature of exhaust air and the capacity of the TSU will have a significant impact on the thermal balance and therefore the energy efficiency of the system. For the charge cycle, the above process flows are reversed as shown in Fig.1 (b). In this case, the preheated air passes through the TSU to extract stored heat before entering the IT-SOIARB stack.

III. Model description

A 5kW/60kWh IT-SOIARB system intended for residential solar panel/battery applications was modeled by using the commercial software known as ASPEN Plus⁴². The simulation flow diagram for the system shown in Fig.1 is illustrated in Fig.2, which contains all the components and functionalities specified in the IT-SOIARB system.

Fig. 2 Process diagram of an IT-SOIARB system: (a) Discharge cycle; (b) Charge cycle. RSOFC: Regenerative Solid Oxide Fuel Cell; RCU: Redox Couple Unit, here is Fe-Fe₃O₄; TSU: Thermal Storage Unit.

In Fig.2, the mass and heat streams are represented by black solid lines and red dashed lines, respectively, while the power input/output streams are represented by magenta solid lines. The heat streams S1 accounts for the heat leakage of the battery during cycles, S4 for the heat stored in TSU during the discharge cycle, S17 for the heat supplied by TSU for the charge cycle, and finally QCA for the heat demand by the charge cycle, or heat released by the discharge cycle. The power terms PA represent the power output from the discharge cycle and input for the charge cycle, respectively.

The commercial system software known as Aspen Plus was selected for the analysis. This software is capable of calculating thermodynamic properties at a defined states of chemical processes. Details of the model construction can be found in the Appendix. The general considerations/assumptions used in the model are:

1. Air is composed of O_2 , N_2 and H_2O , with a composition (mole fraction) of 0.21:0.78:0.01.
2. The reaction occurring in SOIARB is simplified to the overall reaction, as there is no built-in module for the battery in ASPEN Plus.
3. No degradation is considered for the RSOFC or RCU bed, which enables us to treat dynamic discharge/charge as a steady-state process.
4. All the components operate under isothermal and isobaric conditions.
5. The power input/output is calculated by a FORTRAN block, and executed within ASPEN Plus.
6. Heat exchanger and Thermal Storage Unit are represented by a built-in heat exchanger blocks in ASPEN Plus.

3.1 The Chemical and Electrochemical reactions in SOIARB

The reactions occurring in the RSOFC and the RCU can be expressed as follows ³⁸:

Since all of the reactions occur in the same reactor, the following overall battery reaction, which is a summation of eq. (3-1) to (3-2) can be written as:

3.2 Electrochemical sub-model for SOIARB

The cell voltage is critical in determining the heat associated with polarization during the discharge and charge cycles. It is a common practice in the open literature to first validate electrochemical parameters with experimental data, followed by predicting voltage at other operating conditions^{43, 44}. In this model, we applied a Calculator Fortran block function to extract electrochemical parameters from an experimental V-I curve obtained for the RSOFC.

3.2.1 Equations for overpotentials

The stack voltage is determined by:

$$V = \text{OCV} \mp (\eta_{act,an} + \eta_{act,cat} + \eta_{ohm} + \eta_{con,an} + \eta_{con,cat}) \quad (3-5)$$

where OCV is the open circuit voltage; η_{act} , η_{ohm} and η_{con} represent the voltage losses due to activation, ohmic and concentration polarizations, respectively. The subscript “an” and “cat” represent Anode and Cathode, respectively. The “-” sign is for the discharge cycle, and the “+” sign is for the charge cycle.

The OCV of the battery is defined by the Nernst equation for reactions (3-1) and (3-2):

$$OCV = -\frac{\Delta G^0}{2F} - \frac{RT}{2F} \ln \left(\frac{p_{H_2O,h}}{p_{O_2,o}^{0.5} p_{H_2,h}} \right) \quad (3-6)$$

where $p_{O_2,o}$, $p_{H_2,h}$ and $p_{H_2O,h}$ represent the partial pressures of O₂, H₂ and H₂O, in oxygen or hydrogen electrode respectively; ΔG^0 is the change of the standard Gibbs free energy between the products and the reactants. For example, under the operating condition of T=823.15K, $\Delta G^0 = -202.345kJ$, $p_{O_2,o} = 0.21atm$, $p_{H_2,h} = 0.79atm$, $p_{H_2O,h} = 0.21atm$, resulting in a OCV = 1.068V.

The activation polarization, $\eta_{act,an/cat}$, can be determined by the Butler-Volmer equation⁴⁵:

$$J_{ict,an/cat} = 2J_{0,an/cat} \sinh \left(\frac{nF}{2RT} \eta_{act,an/cat} \right) \quad (3-7)$$

Here $J_{0,an/cat}$ and $J_{ict,an/cat}$ are the exchange and local charge transfer current densities in the Anode or the Cathode, respectively (A·m⁻²); n is the number of electrons transferred, (n=1); F is the Faraday constant 96485 (C·mol⁻¹); R is the gas constant 8.314 (J·mol⁻¹·K⁻¹).

The ohmic loss η_{ohm} results mainly from the ionic resistance of the electrolyte:

$$\eta_{ohm} = \frac{1}{\sigma_{i,ele}} \times \delta_{ele} \times J \quad (3-8)$$

Here, $\sigma_{i,ele}$ ($S \cdot m^{-1}$) and δ_{ele} (μm) are the ionic conductivity and thickness of the dense electrolyte, respectively, and J is the operating current density, ($A \cdot m^{-2}$).

The concentration overpotential $\eta_{con,an/cat}$ is governed by:

$$\eta_{con,an/cat} = \frac{RT}{nF} \ln \left(1 - \frac{J}{J_{L,an/cat}} \right) \quad (3-9)$$

where J and $J_{L,an/cat}$ are the operating current density and limiting current density, respectively.

The limiting current density $J_{L,an/cat}$ is calculated by:

$$J_{L,an/cat} = \frac{2F \diamond p_i \diamond D_{eff,mn}}{RT \delta_{e,an/cat}} \quad (3-10)$$

where $D_{eff,mn} = D_{mn} \frac{\varepsilon}{\tau}$ is the effective diffusivity of species m in a gas mixture $m-n$; D_{mn} is the ordinary diffusivity of species m in a gas mixture $m-n$; ε and τ are the porosity and tortuosity of the electrodes, respectively; p_i is the partial pressure of reactant species; $\delta_{e,an/cat}$ is the thickness of anode/cathode electrode.

3.2.2 Validation of Electrochemical sub-model

The electrochemical sub-model including a FORTRAN block for calculating power output and input was developed based on experimental data. To do so, the electrochemical parameters of RSOFC were firstly extracted from an experimental V-I curve (see Fig.3, red circles) obtained

from a button cell in our lab^{46, 47}. All the parameters obtained are listed in Table 1. Excellent agreement between the model predictions and the experimental data is shown in Fig.3.

Fig. 3 Model validation by experimental data (SOEC: Solid Oxide Electrolysis Cell; SOFC: Solid Oxide Fuel Cell.)

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

3.3 Efficiency of the system

The air pumping power is given by:

$$P_{pump} = \frac{\Delta p V_m F_{air}}{\eta_{pump}} \quad (3-11)$$

Here, Δp is the pressure drop through the whole system; η_{pump} is the pump efficiency; V_m is the molar volume of air, ($m^3 \cdot mol^{-1}$); F_{air} is molar flow rate of air, ($mol \cdot s^{-1}$).

The system energy efficiency (η_{energy}), which accounts for the electrical energy generated from the discharge cycle, supplied to the charge cycle and pumping air is given by:

$$\eta_{energy} = \frac{E_d}{E_c + P_{pump} \times h_{cycle} + \blacklozenge Heat} \quad (3-12)$$

where h_{cycle} is the cycle time in hours; $\blacklozenge Heat = Heat_{s17} - Heat_{s4}$ is the external heat needed to maintain the charge cycle at isothermal conditions. Ideally, $\blacklozenge Heat = 0$.

3.4 Air outlet temperature

The air outlet temperature for the discharge cycle is obtained by optimizing the *Design-Spec* block diagram loop shown in Fig.4 while meeting the desired power output “PA” as a criterion:

$$PA = V \times J \times A \quad (3-13)$$

Here V is the cell voltage, (V); J is the operating current density, ($A \cdot m^{-2}$); A is the cross-sectional area of the battery, (m^2).

Fig.4 Optimization block diagram to obtain air outlet temperature (**D**: discharge; **C**: charge)

For the charge cycle, the air outlet temperature is adjusted within the *Design-Spec* block to ensure all the heat stored in TSU during the discharge cycle is fully extracted for the charge cycle:

$$Heat_{S17} - Heat_{S4} = 0 \quad (3-14)$$

If this heat is insufficient, the computation will not converge, which means external heat will be needed by the amount of $\diamond Heat = Heat_{s17} - Heat_{s4}$.

The air utilization ratio R_{air} is an important engineering parameter for operating an efficient IT-SOIARB. The air utilization ratio is related to the air flow rate F_{air} as follows:

$$R_{air} = \frac{F_{O_2} / 0.21}{F_{air}} = \frac{\frac{2}{3} F_{Fe} / 0.21}{F_{air}} \text{ or } \frac{2 F_{Fe_3O_4} / 0.21}{F_{air}} \quad (3-15)$$

where, F_{O_2} , F_{air} , F_{Fe} and $F_{Fe_3O_4}$ are the molar flow rates of O_2 , air, Fe and Fe_3O_4 streams respectively.

IV. Results and discussion

The Energy output/input (kWh) vs theoretical values under different current densities of an IT-SOIARB during the discharge/charge cycle calculated on the basis of the V-I curve shown in Fig.3 are depicted in Fig.5 as a function of J, where $E_d \text{ or } E_c = t \times V \times J \times A$; t is the cycle time, V is cell voltage at J, and A is the effective area of the IT-SOIARB. Because of the polarization losses, the energy output during the discharge cycle (E_d) is lower than the theoretical Gibbs free energy change of the reaction (ΔG): $H_2(g) + 0.5O_2(g) = H_2O(g)$. The energy input during the charge cycle (E_c) is higher than the theoretical ΔG . When $E_c = \Delta H$ (the enthalpy change of the overall reaction $0.75Fe + 0.5O_2(g) = 0.25Fe_3O_4$), the battery becomes thermally neutral. From Fig.5, it is evident that the higher the charging current density (more negative), the less heat

needed ($E_c - \Delta H$) for the charge cycle. No heat is needed for the charge cycle when the operating current density is more negative than -300 A/m^2 , however, the overall efficiency is lower.

Fig. 5 Energy output/input (kWh) vs theoretical values under different current densities.

To maintain a high efficiency, the operating current density should be as small as possible. On the other hand, to satisfy the heat demand of a charge cycle by reusing heat from a discharge cycle, the operating current density should be relatively large. For a given energy capacity, *e.g.* 60kWh for the present study, the cycle time is inversely proportional to the current density. To study the effect of the operating current density on heat balance and energy efficiency, the following three cases are examined:

Case-1: at $J=100 \text{ A/m}^2$ for $h_{\text{cycle}} = 12$ hours for both discharge and charge cycle

Case-2: at $J=150 \text{ A/m}^2$ for $h_{\text{cycle}} = 8$ hours for both discharge and charge cycle

Case-3: at $J=200 \text{ A/m}^2$ for $h_{\text{cycle}} = 6$ hours for both discharge and charge cycle

4.1 Heat stored vs recovered in TSU

As shown in Fig.2, the heat stored in the TSU from a discharge cycle is represented by S4, while the heat recovered from TSU for a charge cycle is S17. The actual heat demand from the charge cycle, QCA, is the heat absorbed by the battery, the difference of which from S17 is the irreversible heat loss. These heat-related quantities are investigated as functions of air utilization and operating current densities. The optimal air utilization would occur when $S4 = S17$.

Fig. 6 shows S4, S17 and QCA as a function of air utilization for Case-1. It is evident that the actual heat demand for the charge cycle, $QCA=5.45kWh$, is only a function of operating current density and independent of air utilization. The heat demand is met by two heat sources: (1) the heat stored in TSU; (2) the heat stored in O_2 product from the battery. The first heat source is the major contributor to the heat supply for the charge cycle. As evident in Fig.6, the heat S17 needed from TSU (Hollow Square) is more than S4 stored in TSU (Solid Square). To meet the heat demand, the heat in the air must be recuperated. In order to balance the heat between the cycles, air utilization must be operated at less than 8%. Since the second heat source is relatively small and plays an insignificant role in the overall heat supply, the heat demand by the charge cycle S17 can be easily fulfilled when the heat stored by the discharge cycle S4 reaches 5kWh.

For air utilization > 10%, S17 of the charge cycle is a constant; this results from a combined effect of air utilization and air outlet temperature. Under such a case, external heat is needed in order to converge the model.

Fig. 6 Heat balance vs air utilization for Case-1

At a higher current density 150A/m^2 , Case-2, Fig. 7 illustrates that the actual heat demand QCA is reduced to 3.92kWh , representing a 28% decrease. As a result, the heat S4 stored in TSU (Solid Circle) converges with the heat S17 needed from TSU (Hollow Circle) at a higher air utilization $\sim 13\%$. In other words, to achieve the heat balance without external heat input, air utilization must be $<13\%$. Operating with an air utilization above 13% would result in unnecessary heat loss due to exhausting hotter air, lowering overall energy efficiency.

Fig. 7 Heat balance vs air utilization for Case-2

At an even higher current density of 200A/m^2 , Case-3, Fig. 8 shows a further lowering of the heat demand $\text{QCA}=2.22\text{kWh}$. Operating at as high as 15% air utilization can meet the heat requirement. At an operating current density $>200\text{A/m}^2$, QCA would no longer be needed. However, the compromise is the much lower cycle efficiency.

Fig. 8 Heat balance vs air utilization for Case-3

4.2 Air Outlet Temperature

4.2.1 Discharge cycle

As aforementioned, air outlet temperature can be an indicator of how well the heat is balanced within the system. It can be determined by optimizing the *Design-Spec* block to meet the energy output PA requirement as described in section 3.4. The actual air outlet temperature reflects the degree of the unutilized heat by the system.

The air outlet temperatures under the three Cases are plotted in Fig.9 as a function of air utilization for the discharge cycle. The total heat balance of the system can be calculated by:

$$\diamond H = t \left(PA + S1 + S4 + \left(C_p \times M_{air} \times F_{air,out} \times T_{air,out} - C_p \times M_{air} \times F_{air,in} \times T_{air,in} \right) \right)$$

(4-1)

where PA and S1 are determined by Fe molar flow, and independent on air utilization. It is evident that increasing air utilization elevates $T_{air,out}$. This is because F_{air} and S4 is decreased by increasing air utilization. For all the cases, the higher the operating current density the higher the $T_{air,out}$. Note that the heat in the air exhaust was not counted in eq. (3-12) for the energy efficiency calculation. If this part of the waste heat can be utilized, especially at higher operating current density, the overall system efficiency can be further improved.

The selection of $\Delta T = 50^\circ\text{C}$ between charge and discharge is based on the consideration whether the induced thermal stress can be acceptable by the industry standard. Lower ΔT would certainly be preferable to minimize the stress, but increase the demand for higher air flow. The latter would result in a higher pressure drop and parasitic power loss.

Fig. 9 Air utilization vs air outlet temperature during the discharge cycle for the three cases studied

4.2.2 Charge cycle

For the charge cycle, the heat stored in the TSU through the discharge cycle is assumed to be 100% reused by the charge cycle. The air outlet temperature is allowed to vary with current density. Fig.10 shows the results for the three cases. For Case-1, external heat is needed to provide sufficient heat for the charge cycle if the air utilization is over 8%. Under such a circumstance, the air outlet temperature varies within ~40-50°C. For Case-2, it is >13% for air utilization when external heat is needed. The air outlet temperature varies within ~45-50°C. For Case-3, no external heat is needed for air utilization ranging from 6 to 20%, yielding air outlet temperature within ~55-60°C.

Fig. 10 Air utilization vs air outlet temperature during the charge cycle

4.3 Overall energy efficiency

The overall energy efficiency is a critical indicator of battery performance, determining the economic potential of the technology. It is calculated by eq. (3-12) and plotted as a function of air utilization in Fig.11 for the three cases. For Case-1, the energy efficiency decreases with air utilization because of the increased demand for external heat as air utilization increases. For Case-2, the energy efficiency peaks at air utilization of 13%, which is consistent with the heat balance shown in Fig.7. For air utilization other than 13%, more energy demand from air pump and external heater would lower the efficiency. For Case-3, the energy efficiency increases gradually with air utilization without peaking within the range studied. The more heat generated under higher operating current density may shift the peak efficiency toward even higher air utilization. Overall, the system energy efficiency is above 70% for the three cases, indicating that IT-SOIARB is an efficient battery technology.

Fig. 11 Total energy efficiency vs air utilization

V. Conclusions

For the IT-SOIARB system analyzed in this study the heat exchanger and thermal storage unit are used as a means of increasing the overall energy efficiency of the system. Air is employed as a working fluid to exchange, move and store heat involved in the battery components. The results show that lower air utilization is needed for low current density operation in order to reach a heat balance and achieve high energy efficiency. The critical air utilizations needed for Case-1 and -2 are 8% and 13%, respectively, above which external heat is needed. For Case-3, no external heat is needed for air utilization less than 20%. The energy efficiency is generally flat with regard to air utilization, but is higher at lower current density. The energy efficiency is shown to be above 70%, indicating that the IT-SOIARB is a promising battery technology.

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Nomenclature

A , (m^2) Cross area of IT-SOIARB
 C_p , ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) Heat capacity
 D , ($\text{m}^2 \cdot \text{s}^{-1}$) Diffusion coefficient
 E , (kWh) Energy input or output
 F , ($\text{C} \cdot \text{mol}^{-1}$) Faraday's constant, 96485
 F_{air} , ($\text{mol} \cdot \text{s}^{-1}$) Molar flow rate of air
 F_{O_2} , ($\text{mol} \cdot \text{s}^{-1}$) Molar flow rate of O_2
 F_{Fe} , ($\text{mol} \cdot \text{s}^{-1}$) Molar flow rate of Fe
 $F_{Fe_3O_4}$, ($\text{mol} \cdot \text{s}^{-1}$) Molar flow rate of Fe_3O_4
 G , ($\text{J} \cdot \text{mol}^{-1}$) Gibbs free energy
 ΔHeat , (kWh) External heat flow provided to SOIARB at charge cycle
 h_{cycle} , (h) Cycle time in hour
 J , ($\text{A} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) Current density
 J_{ict} , ($\text{A} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) Local charge transfer current density
 M_{air} , ($\text{kg} \cdot \text{mol}^{-1}$) Molar weight

n , (mol) Number of exchanged electrons
 OCV , (V) Open circuit voltage
 p , (Pa) Pressure
 P , (kW) Power
 PA Power output/input
 Q , (W) Heat
 QCA Heat stream to/from the battery
 R , (J·(mol⁻¹·K⁻¹)) Gas constant, 8.314
 R_{air} Air utilization ratio
 $S1$ Heat leakage of the battery
 $S4$ Heat stored in TSU for discharge cycle
 $S17$ Heat restored from TSU for charge cycle
 T , (K) Temperature
 V , (V) Voltage
 V_m , (m³·mol⁻¹) Molar volume of air

Greek symbols

σ , (S·m ⁻¹)	Conductivity
ε	Porosity of electrodes,
τ	Tortuosity of electrodes
η , (V)	Overpotential
$\eta_{elec}/\eta_{energy}$	Electric/Energy efficiency
δ , (μm)	Thickness

Subscripts

act	Activation overpotential loss
an	Anode
cat	Cathode
con	Concentration overpotential loss
c	Charge cycle
d	Discharge cycle
e	Electrode
eff	Effective
ele	Electrolyte
i,m,n	Species
L	Limiting
o	Oxygen electrode
ohm	Ohmic loss
h	Hydrogen electrode

Superscripts**0**

Ideal

Meaning of Symbols

IT-SOIARB	Intermediate-temperature Solid Oxide Iron Air Redox Battery
RSOFC	Reversible Solid Oxide Fuel Cell
RCU	Redox Cycle Unit
SOIARB	Solid Oxide Iron-Air Redox Battery
SOEC	Solid Oxide Electrolysis Cell
TSU	Thermal Storage Unit

APPENDIX

A 5kW/60kWh IT-SOIARB system intended for residential solar panel/battery applications was modeled by using ASPEN Plus. The simulation flow diagram for the system shown in Fig.1 is illustrated in Fig.A1, which contains all the components and functionalities specified in the IT-SOIARB system. In the following, a detailed description of Fig.A1 is provided. Terms in italics represent the actual ASPEN Plus terminology.

Fig. A1 An IT-SOIARB system represented by ASPEN Plus simulation flow diagrams: (a) Discharge cycle; (b) Charge cycle. (Blue solid line: air stream; black solid line: Fe/Fe₃O₄ stream; green solid line: power input/output; red dashed line: heat stream.)

A1. The heat exchanger for preheating air

The inlet cold air (stream “AIR”) shown in Fig.A1 for the IT-SOIARB stack under operation is first preheated by the hot exhaust air exiting from the TSU (stream “S3”). The heat exchange process is modeled in ASPEN Plus by a rigorous heat exchanger module *Heatx* (labeled as “Recuper”). Utilization of exhaust heat to raise the temperature of the inlet air is expected to improve the overall system efficiency. The temperature of the exhaust air stream “S1”, heat stored in TSU, and operating current densities can be optimized to ensure sufficient heat supply for the charge cycle.

A2. The IT-SOIARB in the discharge mode

Since there is no built-in module for IT-SOIARB in ASPEN Plus, we used a separator module *Sep* (labelled as “O2 electrode”) and an equilibrium reactor module *Rgibbs* (labeled as

“Discharge H2 electrode”) to simulate the battery behavior in conjunction with a heat stream (QCA) from the “HE1” - a temperature exchanger module *Heater* in ASPEN Plus, to the “Discharge H2 electrode” to maintain the same temperature for the two electrodes. The RCU is included in H₂ electrode.

A2.1. Oxygen supply

The inlet cold air (stream “AIR”) is heat-exchanged with the hot exhaust air (stream “S3”), and then enters the O₂ electrode to provide oxygen for the electrochemical reaction. The latter is modeled by a separator module *Sep* (labelled as “O2 electrode”) and a temperature exchanger module *Heater* (labelled as “HE1”). A fraction of oxygen (determined by the air utilization) from the inlet cold air is separated in the “O2-electrode” and enters the “Discharge H2 electrode” to oxidize Fe. An ASPEN Plus Calculator was used to calculate the molar flow rate of stream “O2” from the feed Fe molar flow rate based on mass balance $F_{O_2} = \frac{2}{3} F_{Fe}$. The heat absorbed by the air stream exiting the battery in the discharging mode is represented by a heat stream (labelled as “QCA”) from the “HE1” to the “Discharge O2 electrode”. The heat QCA is quantified by equalizing the temperatures of the exhaust air stream (labeled as “CAIR”) and the H₂ electrode outlet (labeled as “FE3O4”).

A2.2 Electrochemical reaction at the H₂ electrode

To simulate the electrochemical reactions inside the IT-SOIARB, an equilibrium reactor module *Rgibbs* (labelled as “Discharge H2 electrode”) was used. The overall reaction, shown in eq.(3-4), is considered to be in equilibrium at a given temperature, *viz.* 550°C, for this study. Material stream “O2” (O₂ from O₂-electrode) and “FE” (iron in the chemical bed) are supplied to the

reactor to produce material stream “Fe₃O₄” (iron oxide in the chemical bed), stream “PA”, “S1” and “QCA”; the stream “PA” represents power output of the discharge cycle, P_d ; “S1” is heat loss of the reactor, P_{loss} ; the stream “QCA” is the heat liberated by the IT-SOIARB to air stream.

A3 The IT-SOIARB in the charge mode

Because the backward reaction of eq.(3-4) occurring during the charge cycle is not spontaneous and “Fe₃O₄” is the only chemical supply, a different reactor type is selected for the charging unit, *Rstoic* (labeled as “Charge H₂ electrode”), to simulate the charging reaction. This module is more appropriate when the reaction stoichiometry and conversion are known, which is the case for the charging reaction.

The product O₂ separated from Fe enters “O₂ electrode” and mixed with hot air “CAIR”. The heat transferred from O₂-electrode to H₂-electrode is represented by heat stream “QCA”, which connects “Charge H₂ electrode” and “HE1”. Because our goal is to reuse the heat generated during the discharge cycle for the charge cycle, there must exist a temperature gradient in the battery between cycles in order to transfer heat. We assume that the operating temperature of charge cycle is at 500°C, whereas it is 550°C for the discharge cycle.

A4 The Thermal Storage Unit (TSU)

Due to the opposite heat flow between the discharge and charge cycles, a thermal storage unit (TSU) is included in the system to assist in reusing the heat generated during the discharge cycle for the charge cycle. The heat stored or reused by air is represented, respectively, by heat stream “S4” for the discharge cycle or “S17” for the charge cycle, which connects “HE2”, a second heat exchanger, to “TSU”. To ensure an efficient heat-transfer, we assume that the operating temperature of the TSU is at 525°C.

During the discharge cycle, the hot air “CAIR” from the battery with a temperature of 550°C passes through “HE2” to store part of the heat (S4) in “TSU” and exits with a temperature of 525°C. During the charge cycle, the preheated air “S2” enters “HE2”, which extracts all the heat stored in S17 of “TSU”. The hot air “CAIR” then delivers some heat to the battery by Heat Stream “QCA” that connects “HE1” and “Charge H2 electrode”. The heat stored or reused by S4 of the discharge cycle or S17 of the charge cycle can be calculated by:

$$Q_{S4/S17} = C_p \times M_{air} \times F_{air} \times (T_{SOIARB} - T_{TSU}) \times h_{cycle} \quad (A-1)$$

where, M_{air} and F_{air} are the molar weight and molar flow rate of air; C_p is the heat capacity of air; T_{SOIARB} and T_{TSU} are the operating temperatures of the SOIARB and TSU, respectively; h_{cycle} is cycle time in hour.

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Table 1 Summary of parameters used in the FORTRAN model

Parameters	Values
Atmospheric pressure, P_0	1[atm]
Cross-sectional area of SOIARB, A	35[m ²]
Exchange current density, Anode/Cathode, J_0^*	400 /400 [A/m ²]
Effective diffusion coefficient H ₂ -H ₂ O, $D_{\text{eff,h2h2o}}$	5.4×10 ⁻⁴ [m ² /s]
Effective diffusion coefficient O ₂ -N ₂ , $D_{\text{eff,o2n2}}$	1.21×10 ⁻⁴ [m ² /s]
Heat loss of SOIARB stack, Q_{loss}	2%
Ionic conductivity, $\sigma_{\text{i,el}}^*$	0.4 [S/m]
Molar fraction of H ₂ , $x_{\text{ref,H2}}$	0.79
Molar fraction of O ₂ , $x_{\text{ref,O2}}$	0.21
Porosity of electrodes, ε	0.3
Tortuosity of electrodes, τ	4
Temperature of Discharge/Charge cycle, T_0	550/500[°C]
Thickness of electrolyte, δ_{ele}	180[μm]
Thickness of O ₂ /H ₂ electrode, δ_e	50/30[μm]