Performance of Solid Oxide Iron-Air Battery Operated at 550°C

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The “Metal-air” batteries have the potential to offer high specific energy without the need to store oxygen for the “metal-oxygen” chemistry. The modern “metal-air” batteries, either primary or secondary, have primarily employed two types of ionic conductors as the electrolyte: cation conductors (e.g., Li+-conductor for “Li-air”) or anion conductors (e.g., alkaline OH−-conductor for “Zn-air” and “Fe-air”).1–4 Despite exhibiting high initial specific energy, these batteries typically suffer from fast decay in performance upon cycling, resulting in very poor round-trip efficiency and short cycle-life. Evidence gathered from in-situ spectroscopic and microscopic studies explicitly reveals air-electrode and electrolyte as the primary sources of performance degradation: clogging of air-pathway by the formation of condensed oxides,5 precipitation of carbonate in the air-electrode catalyst’s pores,6,7 and evaporation/decomposition of liquid electrolytes.6–10

Recently, we demonstrated a new type of high-temperature “metal-air” battery based on reversible solid oxide fuel cell (RSOFC) and redox-couple energy storage unit.11–15 The RSOFC consists of a perovskite-structured oxide air-electrode, a solid oxide-ion electrolyte and a Ni-based fuel-electrode. The redox-couple energy storage unit is comprised of a pair of metal/metal-oxide. The dual functionality of a RSOFC, i.e., fuel-cell and electrolyzer modes, is utilized in the new “metal-air” battery as the means of discharging and charging, respectively, while the chemical energy are simultaneously stored in the metal/metal-oxide redox couple through a H2/H2O mediated redox reaction. During operation, the air-electrode reactions involve only reduction and evolution of gaseous O2, making air-pathway clogging no longer an issue. In addition, solid oxide-ion electrolytes are known to be stable in a broad range of gas mixtures and in contact with a variety of oxides.16–18 Therefore, this new all solid-state “metal-air” battery is free of the problems faced by the conventional liquid-electrolyte based “metal-air” batteries. Furthermore, by inheriting all the merits of the solid oxide fuel cell technology, it is well-suited for large-scale stationary grid energy storage.

While the high operating temperature is an advantage to promote high conductivity in the electrolyte and fast reaction kinetics in electrodes and redox-couple, it also presents challenges to the durability and cost of the battery. Therefore, an optimal temperature window that can best balance kinetics, durability and cost is needed. For the development of RSOFC, a well-accepted temperature window is within 550–650°C where reasonably fast kinetics can be maintained with improved durability and reduced cost.

Selection of the same operating temperature window for the solid oxide “metal-air” battery (SOMAB) is also beneficial to the energy storage. As the temperature decreases, the maximum theoretical specific energy (MTSE) becomes higher, and more importantly the coarsening of fine metal-particles in the redox-couple can be mitigated, thus extending the lifetime of a SOMAB. Fig. 1 shows the comparison of MTSE and EMF of Fe-FeO and Fe-Fe3O4 redox couples, two suitable energy storage materials for the solid oxide “iron-air” battery. According to the Fe-O phase diagram, the former is thermodynamically stable at t > 600°C, whereas the latter is only stable at t ≤ 600°C. It is evident from Fig. 1 that the Fe-FeO redox couple at t ≤ 600°C possesses a higher EMF and MTSE than those of Fe-Fe3O4 stable at t > 600°C. A much higher discharge capacity (~1,000 mAh/g) has indeed been experimentally observed on Fe-FeO as the redox-couple at 600°C,19,20 although it was H2 not electricity used to recharge the battery.

A key to the success of such an intermediate-temperature (IT) SOMAB is to retain the kinetic performance of both RSOFC and redox-couple in the battery. While there has been significant progress made in recent years in the area of IT-RSOFC, which can be beneficial to the development of the IT-SOMAB, information on the kinetics of H2-H2O mediated metal/metal-oxide redox reaction is rather scarce in the literature.

In this study, we report that the performance of IT-SOMAB operated at 550°C can be enhanced by either applying redox-active catalyst or increasing the surface area of active redox-couple particles in the energy storage unit. From the obtained results, the effects of catalysts and reactive surface areas on the redox kinetics of Fe-FeO are discussed.

Experimental

Synthesis of Fe-Fe3O4 redox couple.—The baseline Fe-Fe3O4 redox couple in the IT-SOMAB was derived from a precursor synthesized by a chemical co-precipitation method. An aqueous solution containing 0.1 M Fe(NO3)3·9H2O (Alfa Aesar, 98.0–101.0%) and ZrO(NO3)2·4H2O (Alfa Aesar, 99.9%) was peptized by (NH4)2CO3, precipitating out Fe and Zr hydroxides simultaneously. The use of ZrO2 is intended to mitigate the coarsening of Fe-particles during operation. The atomic ratio of Fe:Zr in the starting aqueous solutions was prepared in such a way that the Fe/Zr ratio in the final mixture was at 42.5:1. To ensure a full precipitation of all the cations in the solution, the molar ratio of (NH4)2CO3 and Mn2+ = 2:3. The precipitates were then filtered, washed, dried and finally calcined at 600°C for 2 h. The formation of the desirable oxides Fe2O3 and ZrO2 was confirmed by X-ray diffraction with no impurity phase. The prepared powders were then mixed with a pore former, pressed into small granules and finally sintered in air at 1000°C for 1 hour. Thus fabricated granules possess an averaged porosity of ~70% and a BET surface area of ~127 m2/g.

To study the effect of catalyst on the redox kinetics of Fe-Fe3O4, CeO2 nanoparticles were dispersed into the aforementioned Fe2O3/ZrO2 granules by solution infiltration technique. To be
are then removed, followed by drying at RT which the porous ZrO₂ pellets were immersed. During the soaking, the solution was first mixed with Triton-X100 (3 wt%) in DI water, into which the porous ZrO₂ pellets were immersed. After approximately a half-hour holding to allow the mixture to settle at 600 °C in air for 1 h. The final weight pickup was estimated around 4.5%.

The effect of surface area of active metals on the redox kinetics was also investigated. To acquire fine particles of Fe, an aqueous solution of Fe(NO₃)₃ was infiltrated into a commercial porous ZrO₂ catalyst support (Alfa Aesar, surface area: 51 g/m²) using a modified one-step infiltration procedure. Specifically, a 2 M Fe(NO₃)₃ aqueous solution was first mixed with Triton-X100 (3 wt%) in DI water, into which the porous ZrO₂ pellets were immersed. During the soaking, the solution was gradually heated to 80 °C while the air trapped in the porous ZrO₂ pellets was driven out of the solution, allowing the maximum loading of Fe into the pores of ZrO₂. When no bubbles were visible and the solution finally became viscous, the ZrO₂ pellets filled with Fe(NO₃)₃ were then removed, followed by drying at RT and finally calcining at 600 °C for 2 h. The final weight gain in terms of Fe was estimated to be 10%.

Battery assembly.— A simple planar button cell configuration was employed for all the battery tests in this study, schematic of which is shown in Fig. 2. The RSOFC consisted of a Sr-and Mg-doped LaGaO₃ (LSGM) electrolyte, Sr-and Co-doped LaFeO₃ (LSCF) air-electrode and Ni-CeO₂ based fuel electrode, all homemade in our lab. The active cell area was 1.30 cm². Table I summarizes the composition and thickness of the functional components in the RSOFC. The active redox couple material Fe₂O₃-ZrO₂ was situated below the surface of fuel-electrode (not in contact). The active Fe loading was controlled within 0.6–0.7 grams for each test. Not shown in Fig. 2 is the homemade glass seal used to seal the battery. For more experimental details, readers can refer to our previous publications.

Battery characterization.— At the beginning of a test, the Fe₂O₃-ZrO₂ granules were first exposed to a mixture of 5%H₂-N₂ during heating. Once reached the melting temperature of the sealing glass around 650 °C, a pure H₂ was then introduced to fully reduce Fe₂O₃ into metallic Fe. After approximately a half-hour holding to allow the glass to settle, the temperature was then gradually ramped down to the testing temperature of 550 °C. The Fe₂O₃-ZrO₂ redox couple was created in-situ by applying a small discharge current from the RSOFC. To ensure the attainment of Fe₂O₃ redox couple without over-oxidizing the Fe, the EMF of the RSOFC was closely monitored during the electrochemical oxidation by intermittently switching between the discharging and OCV states. As soon as the EMF reached 1.067 volts, the theoretical Nernst potential for the Fe₂O₃-ZrO₂ equilibrium, the electrochemical oxidation was stopped, and the system was ready for the charge-discharge cycles. During the cycles, the reaction gas H₂-H₂O was also circulated in a closed-loop to homogenize the concentration of the reactants. To prevent water condensation, all pipelines were heat-wraped and kept at 110 °C.

A Solartron 1260/1287 Electrochemical System was employed to characterize the electrical performance of the battery with software modules such as OCV-t, impedance spectroscopy, potential-dynamics, galvanic-dynamics and galvanic cycles.

The microstructures of RSOFC and redox couple, either pre-tested or post-tested, were examined with a field-emission scanning electron microscopy (FESEM, Zeiss Ultra) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. The post-tested samples contained a majority of Fe mixed with ZrO₂ as a result of being cooled down in 5%H₂-N₂ protective gas.

Results and Discussion

The performance of the baseline battery.— The baseline battery contains the pellets of Fe₂O₃-ZrO₂ redox-couple prepared from the coprecipitation method described above. Fig. 3 shows the cycling performance characterized under the conditions of t = 550 °C, J = 10 mA/cm² and n = 10 continuous 2-h discharge and 2-h charge cycles. The current density necessary to achieve a meaningful cell voltage was largely limited by the performance of the RSOFC operated at this low temperature.

The discharge specific energy (DSE) was calculated from the amount of Fe consumed by the oxygen flux (or current density) from the RSOFC, averaging 892 Wh/kg-Fe. Similarly, the charge specific energy (CSE) was averaged to be 2,203 Wh/kg-Fe, yielding a round-trip efficiency of 40.5%. It should be noted that the normalization of the specific energy to the amount of Fe consumed by the oxygen flux allows for a direct comparison with the MTSE, difference of which reveals the scale of the battery’s inefficiency. The
obtained DSE is evidently lower than the MTSE = 1,360 Wh/kg · Fe calculated from \( \Delta G_f \) (550°C) of the iron-oxygen reaction \( 3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4 \). This difference (DSE amounts to 65.6% of MTSE) reflects the degree of energy loss to the electrical polarizations of RSOFC and kinetic resistance of Fe/Fe\(_3\)O\(_4\) redox couple. Indeed, the RSOFC for the test employed a thick LSGM electrolyte membrane (350 \( \mu \)m, see Table I) and electrode materials that have not been fully optimized for operating at 550°C. With the use of electrode-supported thin-film electrolytes and more active electrode (particularly air-electrode) materials, the energy loss is expected to be lesser and efficiency to be higher.

The low round-trip efficiency is another sign of energy loss and irreversible redox kinetics. It is known that the total cell resistance of a RSOFC operating under “electrolysis” mode has a tendency to be greater than that of “fuel-cell” mode, which can result in a reduced round-trip efficiency. On the other hand, the lower kinetic rate of Fe\(_3\)O\(_4\)-reduction to Fe than the oxidation of Fe to Fe\(_3\)O\(_4\) also decreases the round-trip efficiency. Overall, the 550°C CF Fe / Fe\(_3\)O\(_4\) battery has ample rooms to further improve its specific energy and efficiencies by optimizing the components of RSOFC (e.g., use of new cell materials and optimization of microstructure) and promoting the redox kinetics (e.g., use of catalysts, use of fine-particle active metals).

Performance of the battery with CeO\(_2\)-added Fe-Fe\(_3\)O\(_4\) redox couple.— As a means of promoting the redox kinetics, nanoparticles of CeO\(_2\) were incorporated into the microstructure of Fe-Fe\(_3\)O\(_4\) as a catalyst, testing result of which is shown in Fig. 4. The battery was cycled for 10 times under the conditions of \( t = 550 \)°C, \( J = 10 \) mA/cm\(^2\) and cycle duration of 2 hours. Compared to Fig. 3 of the baseline battery, the improvement is evident in discharging cycle: higher and more stable voltage. The DSE reached 1,026 Wh/kg · Fe, yielding a round-trip efficiency of 52.2% when compared to the CSE = 1,971 Wh/kg · Fe. These results represent a 15% and 29% improvement in specific energy and round-trip efficiency, respectively, over the baseline battery. It also appears that there was no apparent performance decay over the 10 continuous repeated charge-discharge cycles.

The promotion of redox reaction kinetics by CeO\(_2\) has been well documented in the literature.\(^{24-27}\) The mixed valence of Ce\(^{4+}/\text{Ce}^{3+}\) in low partial pressures of oxygen contributes additional catalytic activity to the primary Fe-Fe\(_3\)O\(_4\) redox reaction. Previous studies have also reported that Ce can retain the redox activity of Fe-oxides for repeated redox cycles.\(^{24}\) On the other hand, nanoparticle catalysts can boost the rate of redox reaction by increased reactive area. Fig. 5 shows the morphologies of CeO\(_2\) nanoparticles before and after tests. The original particle sizes of CeO\(_2\) particles were \( \sim 50 \) nm, and increased to approximately \( 60 \) nm after testing. Although the finely dispersed CeO\(_2\) nanoparticles appear to have been sintered, the adherence of CeO\(_2\) to the Fe/ZrO\(_2\) backbones seems to have little effect on the catalytic activity of CeO\(_2\) as suggested in Fig. 3.

Performance of the battery with nanoparticle Fe-Fe\(_3\)O\(_4\) redox couple.— The active metal Fe in the form of nanoparticles supported on porous ZrO\(_2\) substrate was also evaluated as the energy storage medium, result of which is shown in Fig. 6. The battery was operated at the same condition as the CeO\(_2\)-catalyzed battery of Fig. 4. Compared to Fig. 3 of the baseline battery, the improvement is also notable.

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**Figure 3.** The performance of the baseline battery operated at 550°C for 10 continuous cycles with single-cycle duration of 2 hours under a current density of 10 mA/cm\(^2\); (a) E vs charge capacity; (b) averaged specific energy vs number of cycles.
Figure 4. The performance of the CeO$_2$-catalyzed battery operated at 550°C for 10 continuous cycles with single-cycle duration of 2 hours under a current density of 10 mA/cm$^2$; (a) $E$ vs charge capacity; (b) averaged specific energy vs number of cycles.

Figure 5. SEM images of CeO$_2$ nanoparticles inside Fe-based energy storage unit before (a) and after (b) tests.
Figure 6. The performance of the battery with nanoparticle active Fe supported on porous ZrO$_2$ operated at 550°C for 10 continuous cycles with single-cycle duration of 2 hours under a current density of 10 mA/cm$^2$; (a) $E$ vs charge capacity; (b) averaged specific energy vs number of cycles.

The DSE reached 1,012 Wh/kg·Fe, yielding a round-trip efficiency of 59.9% with CSE = 1,695 Wh/kg·Fe. These results represent 13% and 48% improvement in specific energy and round-trip efficiency, respectively, over the baseline battery. When compared to Fig. 4 of the CeO$_2$-catalyzed battery, the major improvement is the lowered charging voltage, which is also the reason for the higher round-trip efficiency.

The issue of the nanoparticle redox couple is the poor cycle stability. This is likely caused by the thermal coarsening of these nanoparticles, resulting in a gradual loss of reactive surface area. The morphological change of the Fe nanoparticles in Fig. 7 seems to support this assertion by showing the flaking morphology of Fe$_2$O$_3$ precursor before the test and a cluster of sintered Fe-grains after the test.

**A general discussion on the sources of performance degradation.**—Besides thermal coarsening of the active metal particles during operation, another source of battery performance degradation arises from the RSOFC itself. Fig. 8 shows an example of AC impedance spectra of the baseline battery before and after cycling at 550°C. It is evident that the polarization area-specific-resistance (ASR) of the cell increased significantly after the test. In our previous study, it has been shown that “vapor transport and condensation” phenomenon could be a mechanism leading to an increase in fuel-electrode ASR. Therefore, developing a stable fuel-electrode for RSOFC is equally important in the future research.
An ongoing effort to improve the overall performance of the battery.—We are currently working to improve the performance of RSOFC and redox kinetics of Fe-based energy storage. Fig. 9 shows the preliminary result of a most recently tested battery with thinner electrolyte, lower electrode resistance and better redox kinetics. To achieve the first two, a LSGM electrolyte membrane of 180 μm thick was screen-printed with a high-activity Sm0.5Sr0.5CoO3-δ-Sm0.2Ce0.8O1.9 cathode28 and a similar anode as the baseline battery. To further improve the anode performance, we also performed twice infiltrations of a Ni(NO3)2-Gd(NO3)3-Ce(NO3)3 solution (Ni:Gd:Ce = 0.70:0.24:0.06) into the anode structure. The results of Fig. 9 are very promising. Under the testing conditions of t = 550°C, J = 10 mA/cm² and cycle duration of 10 minutes, the newly developed battery yielded a DSE of 1,237 Wh/kg·Fe, which is up to 91.0% of MTSE, and a round trip efficiency of 82.5%, when compared with the CSE = 1,500 Wh/kg·Fe. The improved battery performance is a direct result of lowered ASRs of the RSOFC as is shown in Fig. 10. The initial ASR of the RSOFC is only 40% of the RSOFC used in the baseline battery. After cycling, the ASR increased only $5\Omega \cdot \text{cm}²$, much less than $53\Omega \cdot \text{cm}²$ observed in the post-tested RSOFC of the baseline battery. We will report more detail about this new development in the future.
Conclusions

The performance of three types of solid oxide “iron-air” batteries have been evaluated at 550°C in this study. The baseline battery comprised of Fe-Fe3O4 redox couple mixed with the ZrO2 as a sintering inhibitor show a low discharge specific energy and round-trip efficiency. The second battery using the same Fe-Fe3O4 redox couple but infiltrated with CeO2 nanoparticles exhibit a 15% and 29% improvement in discharge specific energy and round-trip efficiency over the baseline battery, respectively. The third battery using nanoparticle active Fe supported on a porous ZrO2 substrate demonstrate 13% and 48% higher specific energy and round-trip efficiency, respectively, than the baseline battery. These improvements reflect the beneficial effects gained from enhanced catalytic activity offered by catalyst and increased reactive surface area derived from nanoparticles. An issue to the latter is the poor long-term cycle stability due to the coarsening of the nanoparticles under operating conditions.

Despite the improvements presented, the useable specific energy, round-trip efficiency and cycle stability of the battery remain to be further improved. An area that can lead to a significant advance in performance lies in the RSOFCs. Thin-film electrolyte and high performance and stable electrode materials in RSOFCs is currently being tested in our laboratory with a goal to achieve higher specific energy, round-trip efficiency and better cycle stability. The preliminary results show that the discharge specific energy can reach 91.0% of the maximum theoretical specific energy with a round trip efficiency of 82.5%.

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References

14. X. Zhao, N. Xu, X. Li, Y. Gong, and K. Huang, accepted, to be published in ECS Trans. (Volume 50), 2013.