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Reducing the Cost of Zinc-Oxygen Batteries by Oxygen Recycling

Zhao Yan,[a, b] Jianxin Gao,[a] Min Liu,[a] Erdong Wang,*[a] Gongquan Sun*[a]

Abstract: With the increasing demand of energy storage towards renewable energy technologies, electrochemical systems with low-cost, high safety levels, and low environmental impact are critically needed. Zinc-air/oxygen batteries, which were always considered to be cheap, are losing their competitive advantages due to the poor cyclic performance and energy efficiency. Herein, we report an effective strategy of oxygen recycling which reduces the cost of oxygen to as low as 0.2 ¢ kWh^{-1} per cycle. With the use of oxygen, the performance of zinc-oxygen batteries is largely increased with the maximum power density of 290 mW cm^{-2}, stable cycling for more than 1500 cycles with an average energy density of 60% and elimination of carbonates. A 1kW/1kWh zinc-oxygen battery system is also integrated and exhibits a satisfactory energy efficiency of 58% and a high working power density of 75 mW cm^{-2}.

Recent years, there are great developments of renewable energy technologies due to the fast increasing worldwide electricity demand along with the requirement for clean energy and environmental protection.[1-2] However, the fluctuation and uncertainty of renewable energy sources, such as solar and wind, bring significant challenges for the electric grid.[3] Thus, economical and efficient electrochemical energy storage technologies are critically needed.[4] Among a great variety of technologies, zinc-air/oxygen batteries have attracted considerable interest as a possible candidate for energy storage solutions due to their low cost, abundant reserves and perfect safety.[5-10] However, very less zinc-air/oxygen systems[11-12] were developed in recent years for the reason that the cyclic performance and energy efficiency were still unsatisfactory, which lead to a great increment in capital cost (one-time setup cost) and running cost.

Cyclic performance of zinc-air/oxygen batteries was mainly restricted by three reasons: (i) formation of zinc dendrite, which lead to electrical short-circuit,[5, 13-14] (ii) corrosion of oxygen electrode caused by high potential in charge process which lead to the deactivation of electro-catalysts towards oxygen reduction reaction[15], (iii) formation of carbonate which destroy the structure of positive electrode.[16-17] As to the energy efficiency, the main cause is the slow kinetic of oxygen reduction and evolution and the use of air instead of oxygen in the discharge process.[18] In terms of these issues, much effort has been focused on the development of new electro-catalysts and electrolytes. Wang *et al*. reported a bifunctional catalyst ($Co_3FeS_{1.5}(OH)_6$) for zinc-air battery[19] and cycled for 36 h at 2 mA cm^{-2} with the voltage gap less than 0.84 V. Hao et al. synthesized Co@NCNTs with a better activity,[6] the voltage gap decreased to 0.81 V at 5 mA cm^{-2}. The catalyst of $CoO_{0.87}S_{0.13}$/GN developed by Chen and co-workers[20] showed a much stable cycling over 320 h with 0.77 V voltage gap at 20 mA cm^{-2}. Fu et al.[21] introduced quaternary ammonia-functionalized nanocellulose (QAFC) membrane for zinc-air battery, which cycled for over 35 h with oxygen gas containing 20 000 ppm CO_2. However, zinc-air/oxygen batteries with high cyclic performance and energy efficiency are still full of challenges.

In our recent studies, we proposed an effective three-electrode zinc-air/oxygen battery[22] with separated oxygen reduction reaction (ORR) electrode and oxygen evolution reaction (OER) electrode in order to avoid the corrosion of ORR electrode. With intentional arrangement of the positions and areas of these three electrode, the cyclic performance can be greatly extended.

To further improve the cyclic performance and energy efficiency of zinc-air/oxygen batteries, oxygen should be used instead of air aiming at higher discharge voltage and the elimination of the formation of carbonates. Unfortunately, the oxygen is too expensive for the energy storage systems where the cost is a vital factor. The dosage of oxygen for a 10 MWh zinc-oxygen energy storage system is around 2100 Nm^3 day^{-1} (1 cycle per day), where the Pressure Swing Adsorption (PSA) Oxygen Generator become the most efficient oxygen supply method with suitable scale and lowest cost.[23-24] However, the cost of oxygen still reaches to 30 ¢ Nm^{-3},[25-28] which leads to 6 ¢ kWh^{-1} increment per cycle for the energy storage system. According to the review of Yang *et al.*,[4] the cost of electricity storage needs to be comparable to that of traditional electricity generating at a cost as low as 8-10 ¢ kWh^{-1} per cycle. Therefore, the cost of oxygen in zinc-oxygen battery is urgent to be reduced

In this communication, we proposed an efficient oxygen recycling strategy in zinc-oxygen battery due to the fact that the the amount of oxygen generated from charge process is equal to that required for discharge process with the same charge/discharge capacities. Therefore, the cost can be reduced substantially for the following aspects: (i) the cost of oxygen supply decreases for that the complex PSA oxygen generator can be replaced by a simple air compressor; (ii) the enlarged energy efficiency reduced the running cost; (iii) the extended cyclic stability reduced the capital cost. With some satisfying results in single prototyped batteries, a kW-class zinc-oxygen battery system was integrated to verify the practicability of three-electrode zinc-oxygen battery and oxygen recycling.

The significance of oxygen instead of air towards zinc-air/oxygen batteries were investigated in detail. As shown in Figure 1a, i-V curves of zinc-air/oxygen batteries were recorded with different gas feed. Obviously, the battery with oxygen exhibits a much higher performance with the maximum power density of 290 mW cm^{-2}, nearly double of that from the battery fed with air. More seriously, the CO_2 in the air may destroy the structure of the ORR electrode which lead to severe effects towards the performance and stability of zinc-air batteries. Figure 1b presents the comparison of zinc-air/oxygen batteries with the feed of oxygen and mixture of O_2-CO_2. The discharge voltage plateau drops severely from 1.25V to 0.71V with the feed of O_2-CO_2 (10% CO_2). The performance can't recover after the gas feed changes to O_2, which means an irreversible destroy

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is caused by CO_2. To evaluate the stability of zinc-air/oxygen batteries, charge-discharge cycles were performed with different gas feed (Figure 1c, typical charge-discharge profiles are shown in Supplementary Figure S1). Under condition of oxygen, the battery provides a remarkable stability for more than 1500 cycles. The average energy efficiency reaches to around 60%, which is still a perfect result in zinc-air/oxygen batteries (Supplementary Table S1). In contrast, the energy efficiency of the battery fed with air decays rapidly with only 55% at 700th cycle.

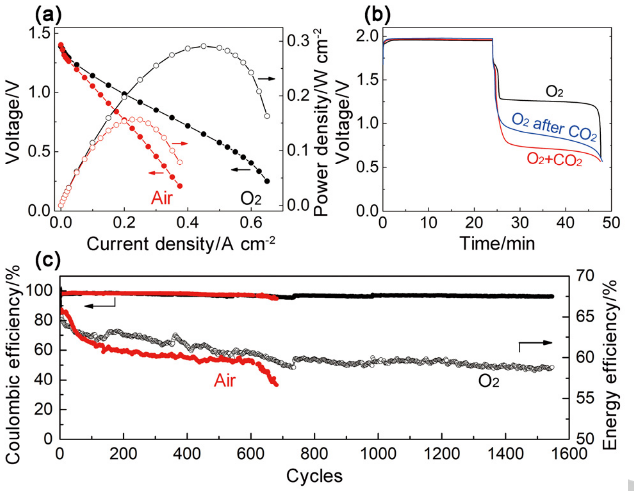

Figure 1. Comparison of zinc-air/oxygen batteries with different gas feed. a) Polarization and b) charge-discharge curves. c) Cyclic performance at 20 mA cm^{-2} (~48 min for 1 cycle).

The morphology of ORR electrodes was characterized with scanning electron microscope and shown in Figure 2a-b. A layer of irregular particles are formed on the catalyst layer of ORR electrode after discharged with the feed of 10% CO_2. Element analysis shows that the major component of this layer might be $KHCO_3$ or K_2CO_3, which demonstrates that the formation of carbonate may be the cause of the degradation of ORR electrodes. The specific compositions of the catalyst layer of these two electrodes were further confirmed by X-ray diffractometer (XRD) and infrared spectroscopy (IR). The XRD patterns in Figure 2c suggests that a new phase of $KHCO_3$ (PDF: 12-0292) exists in the ORR electrode after discharge with O_2-CO_2. IR data of ORR electrode also exhibits the characteristic absorption peaks of $KHCO_3$ according to the Spectral Database from National Institute of Advanced Industrial Science and Technology (AIST), Japan (Supplementary Figure S2).[29-31] In detail, the weak peaks at 2948 and 2617 cm^{-1} represent the bending of O-H···O and the O-H stretching. Two strong bands at 1629 and 1400 cm^{-1} can be assigned to C=O stretching and the in-plane bending of O-H···O. The peak appearing at 1006 cm^{-1} is attributed to the C-O stretching and the weak shoulder at 978 cm^{-1} represents the out-of–plane bending of O-H···O. The peaks at 829 and 703 cm^{-1} can be assigned to out-of-plane bending mode of the CO_3 skeleton and the in-plane bending of C=O, respectively. All these results reveal that carbonates are formed with the feed of CO_2 containing gas, which may lead to the destruction of ORR electrode and finally decrease the performance of zinc-air/oxygen batteries. Therefore, for longtime applications such as energy storage systems, oxygen becomes a better reactant than air.

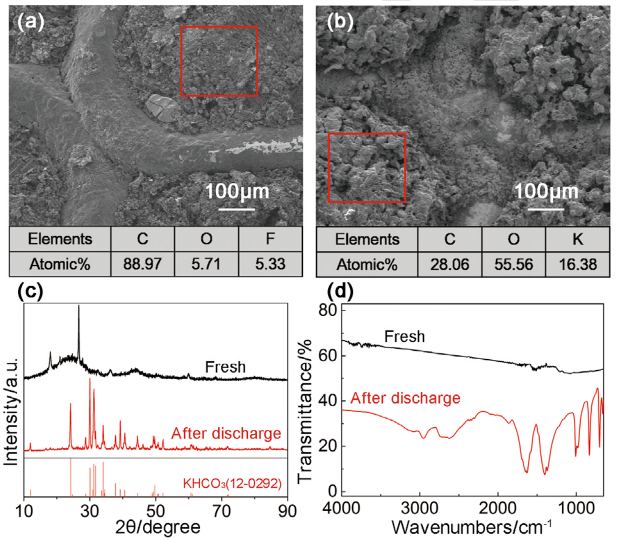

Figure 2. Physical characterization of ORR electrodes. a,b) SEM images and element contents before (a) and after (b) discharge. c) XRD patterns and d) infrared spectra of catalyst layers of these two electrodes.

However, oxygen is too expensive for energy storage systems although the use of oxygen brings delectable effects on the performance and stability of zinc-oxygen batteries. Therefore oxygen recycling is of great importance in zinc-oxygen energy storage systems. In the first stage, a single prototyped battery with oxygen recycling module was designed and evaluated. As illustrated in Figure 3a, in the charge process, oxygen was collected from a three-electrode zinc-oxygen battery and pumped into a collecting apparatus through the flow field of ORR electrode. Oxygen is pumped into the flow field again in the discharge process to support the oxygen reduction reaction. Figure 3b shows the volumes and collection efficiencies of oxygen recycling in 30 charge-discharge cycles. The collection efficiency is increased with the cycles and an average efficiency of 96.6% is obtained in 30 cycles. The satisfactory result indicates that the cost of oxygen can be reduced to around 3.4% of pure oxygen supply, i.e. 0.2 ¢ kWh^{-1}, which is acceptable in the zinc-oxygen energy storage systems. The performance of zinc-oxygen battery with recycled oxygen was recorded and presented in Figure 3c. The zinc-oxygen battery exhibits stable charge-discharge curves with a high discharge voltage plateau of 1.23 V. The coulombic and energy efficiencies reach 98% and 63%, respectively, which demonstrates that the strategy of oxygen recycling is feasible in zinc-oxygen battery.

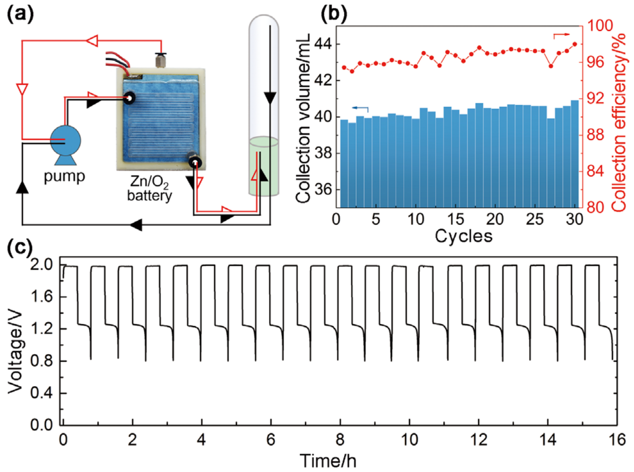

Figure 3. Oxygen recycling results of zinc-oxygen battery. a) Schematic diagram of oxygen recycling system. The red lines (△) show the oxygen collection during charge process, the black lines (▲) show the oxygen supply in the discharge process. b) Collection volumes and corresponding efficiencies of oxygen recycling in 30 cycles. c) Cyclic performance of zinc-oxygen battery with oxygen recycling.

With the satisfying results in prototyped batteries, a 1kW/1kWh zinc-oxygen battery system was integrated. Figure 4a shows the design of this system, which is comprised of two zinc-oxygen battery modules (500W/500Wh) and a battery management system (BMS). Each battery module (Figure 4b) is made up of 24 single batteries (6 in series and 4 in parallel) connected by 6 electric relays to switch the ORR electrodes. Several pipelines are installed to collect and supply oxygen for charge and discharge processes. The charge-discharge curves at different current density were conducted and presented in Figure 4c. Energy efficiency reaches 63% and 58% at the current density of 10 and 20 mA cm^{-2}. When the current density increases to 75 mA cm^{-2}, which is comparable to that of vanadium redox flow batteries (VRB), the discharge voltage remains ~6V, which achieves a remarkable power density of ~75 mW cm^{-2}. Figure 4d illustrates the voltage (U), current (I) and power (P) curves during the charge-discharge test. At these cycles, the average charge power is around 620W, while the constant power discharge at 500W lasts for nearly 1h. The coulombic efficiency remains ~80% while the energy density decreases obviously to ~39% due to the severe polarization of oxygen electrodes. Moreover, the cost of the integrated 1kW/1kWh zinc-oxygen battery system is estimated based on the price of key materials and summarized in Table 1. The total cost of zinc-oxygen battery system reaches as low as \$131 kWh^{-1}, which is much cheaper than traditional electrochemical energy storage systems, such as Na/S, Zn/Br and VRB. This study gives primary results of kilowatt-class zinc-oxygen battery system with comparable current density towards energy storage. Further investigation are urgently demanded to enhance the activity and stability of ORR and OER electrodes and the reliability of zinc-oxygen system.

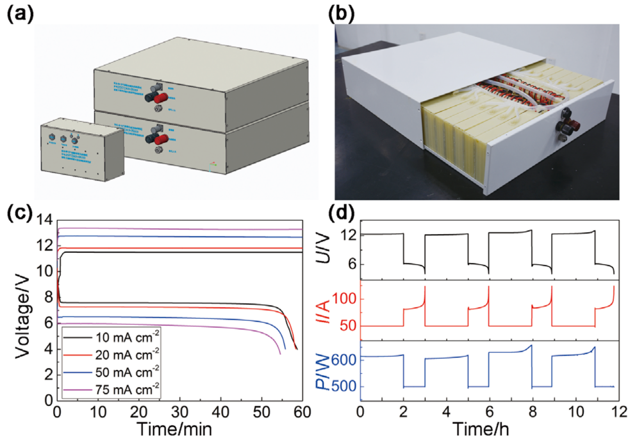

Figure 4. Primary results of the 1kW/1kWh zinc–oxygen battery system. a) Design of the zinc–oxygen battery system. b) Photograph, c) charge-discharge curves and d) cyclic results of a 500W/500Wh zinc-oxygen battery module.

Table 1. Cost estimation of the integrated 1kW/1kWh zinc-oxygen battery system

Materials	In 1kW/1kWh system[a]	Unit price	Price
OER electrode	1.3m^2	\$24 m^{-2}[b]	\$31.2
Cu foam	1.3m^2	\$13.7 m^{-2}[c]	\$17.8
ORR electrode	1.3m^2	\$38.5 m^{-2}[d]	\$50
KOH	23.8kg	\$1 kg^{-1}	\$23.8
ZnO	4.1kg	\$2 kg^{-1}	\$8.2
	Total		\$131

[a] 1.0 V @ 75 mA cm^{-2}. [b] This price is estimated from Ref.[22]. [b] Price of Cu foam (780 g m^{-2}) is estimated based on the price of Ni foam (\$12 m^{-2} @ 320 g m^{-2}) and raw materials (\$6.9 kg^{-1} for Cu and \$11.1 kg^{-1} for Ni). [c] This price is estimated from the materials in homemade ORR electrode.

In summary, we have successfully demonstrated an effective strategy to reduce the cost of zinc-oxygen batteries by oxygen recycling. The practicability of oxygen recycling is confirmed with an average collection efficiency of 96.6% in 30 charge-discharge cycles in a zinc-oxygen battery, which not only reduces the running cost of oxygen to 0.2 ¢ kWh^{-1}, but also cuts down the capital cost of complex oxygen generator. With the use of oxygen instead of air, the performance of zinc-oxygen batteries is largely increased with the maximum power density of 290 mW cm^{-2}, stable cycling for more than 1500 cycles with an average energy density of 60% and elimination of carbonates. Based on the delectable results, a 1kW/1kWh zinc-oxygen battery system is integrated, which exhibits a satisfactory energy efficiency of 58% at the current density of 20 mA cm^{-2} and a high working power density up to 75 mW cm^{-2}. Further extensive effort should be paid to the development of ORR and OER electrodes with high activity and stability and the technology of system integration. Nevertheless, this work provides a new insight into cost reduction of zinc-oxygen batteries by oxygen recycling, which is certain to promote their applications in energy storage systems.

Experimental Section

Fabrication of zinc-oxygen battery

Zinc-oxygen battery was fabricated with copper foam as the current collector of the negative electrode, NiFe layered double hydroxides coated nickel foam (NiFe-LDH/NF, detailed method was stated in ref.[22]) as the OER electrode in the charge process and commercial available air electrode (MetAir®, QuantumSphere) as the ORR electrode in the discharge process. Aqueous solution of 8.5 mol L^{-1} KOH with the additive of 1.0 mol L^{-1} ZnO was used as electrolyte. The relative position of these three electrodes was ORR-Zn-OER in order to reduce the effect on the discharge process. The effective area of copper foam was 5cm×5cm, while the area of ORR and OER electrodes were designed to be a little larger (6cm×6cm) and smaller (4cm×4cm) than the copper foam to eliminate zinc accumulation during cyclic test.

Physical Characterization

The morphology of ORR electrode was examined by JSM-7800F scanning electron microscope (SEM). XRD patterns of the catalyst layer of ORR electrodes were collected at MiniFlex 600 diffractometer using Cu Ka radiation at a scanning rate of 5° min^{-1}. IR spectra were measured by Nicolet 6700 FTIR spectrometer with the wavenumber range from 4000 cm^{-1} to 650 cm^{-1}.

Electrochemical Measurements

Electrochemical measurements of the prototyped zinc-oxygen batteries were carried out using a battery testing system (Neware Electronics, Shenzhen) at the current density of 20 mA cm^{-2}. The charge process was set stop at a fixed capacity of 200 mAh, and the discharge process was set stop at the cut-off voltage of 0.6 V.

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Keywords: zinc-oxygen battery • oxygen recycling • running cost • carbonate formation • kilowatt-class system

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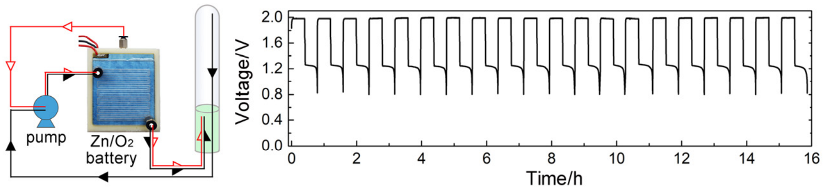

Reducing by recycling! An effective strategy of oxygen recycling is proposed, which reduces the cost of oxygen to as low as 0.2 ¢ kWh^{-1} per cycle. With the use of oxygen, the performance of zinc-oxygen batteries is largely increased with stable cycling for more than 1500 cycles with an average energy density of 60%. A modular 1kW/1kWh zinc-oxygen battery system is also integrated and exhibits a satisfactory energy efficiency of 58%.

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