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A Horizontal Three-Electrode Structure for Zinc-Air Batteries with Long-Term Cycle Life and High Performance

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Limited cycle life is a main reason preventing the large-scale application of electrically rechargeable zinc-air batteries. With the aim of increasing cycle life, a novel three-electrode zinc-air battery in a sandwich arrangement was designed and fabricated. The cycle life was evaluated by charge-discharge cycling tests with 100 cycles at high operational current density (40 mA cm^{-2} and 80 mA cm^{-2} for charging and discharging, respectively) for performance testing. A maximum power density of 105 mW cm^{-2} was achieved at current density of 150 mA cm^{-2}. The average columbic efficiency, depth of discharge and energy efficiency were 90%, 73% and 42%, respectively. A longer cycling test for 1000 cycles approximately 1917h cycling duration at a current density of 20 mA cm^{-2} was also achieved and voltage decay for charging and discharging was 13% and 12%, respectively. The results demonstrate that a horizontal tri-electrode structure for zinc-air batteries is advantageous for achieving increased cycle life while exhibiting high power density, high depth of discharge and excellent charge-discharge cycling performance, which provide promising applications of zinc-air batteries for electric vehicle and grid-scale energy storage.

Keywords: Zinc-air batteries, Three-electrode, Horizontal placement, Cycle life

1. INTRODUCTION

Interest has been growing recently in electrically rechargeable zinc-air (Zn-air) batteries because of their obvious advantages, such as intrinsic safety, low cost, high energy density, and negligible toxicity [1, 2]. However, the batteries' limited cycle life has restricted their large-scale application in electronic devices and electric vehicles. The button cells used in hearing-aid devices are generally the only mature Zn-air batteries currently produced. Other Zn-air batteries under development have their electrodes arranged vertically in a stack [3-5]. This often results in gravity

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effect, a non-uniform deposit of zinc on the electrode in the vertical axis. In the alkaline solution, zinc prefers to accumulate on the lower portion of the zinc electrode during charging, causing battery capacity to weaken and the battery may become short circuit. This is one reason for zinc-air battery's limited cycle life and 270 cycles（testing 90 hours in total）is the maximum cycle life reported up to now for electrically rechargeable zinc-air batteries in an aqueous alkaline solution [6]. The uneven distribution of zinc deposits, dendrite growth, and physical deformation can have a more significant impact on batteries' performance than cathode catalysts [7-11]. Therefore, zinc anodes have increasingly been studied and recent research has centered on controlling dendrite formation by pulsing the charging current or using ionic liquid and organic as additives in the electrolyte solution [12-14].

Most recent research on rechargeable Zn-air batteries has concentrated on the preparation and evaluation of bifunctional electrocatalysts for the air cathode because of its simpler cell structure [7, 15–21]. Using a bifunctional electrocatalyst to simplify the batteries' configuration often results in shorter cycle life, because the evolution of oxygen during charging can lead to mechanical catalyst loss and air electrode corrosion [15, 22]. This is another reason for zinc-air battery's limited cycle life. To avoid the drawback arose from using a bifunctional electrocatalyst, a vertical three-electrode structure was employed for zinc-air batteries and a total of 200h cycling duration at 20 $mAcm^{-2}$ and 120h cycling duration at 5-15 $mAcm^{-2}$ were obtained[23, 24]. Obviously, these are far from enough for application. However, a longer cycle life is tough to be achieved owing to the fact that uneven deposition of zinc on anode during the charge-discharge cycling course still exists in this vertical mode [24].

To overcome the short life time associated with bifunctional catalysts and the gravity effect in a vertical zinc electrode structure, we designed and fabricated a novel tri-electrode Zn-air battery arranged horizontally with the oxygen evolution reaction (OER) electrode on top, air electrode at the bottom, and zinc electrode between them. It is the first time that the combination of horizontal placement and three-electrode design has been used to our knowledge. A horizontal framework can fundamentally eliminate the gravity effect on the zinc anode, greatly relieving the negative influences of dendrite growth and electrode deformation during charge-discharge(C-D) cycling. With the structure of OER electrode detached from air electrode and arranged at the top position, oxygen generated during charging can easily diffuse to the air that fundamentally averts catalyst loss and physical and chemical destruction to air electrode caused by the generated oxygen. The three-electrode structure is also an excellent choice to avoid difficult construction of diffusion channels for oxygen passing in and out during cycling which is the main cause for air cathode's physical degradation especially under high operational current density. Besides, materials for the OER electrode can be obtained from the mature water electrolysis industry which can facilitate to accelerate the commercialization of zinc-air batteries [25]. In this study, we propose a horizontal tir-electrode configuration to improve zinc-air batteries' performance, especially the cycle life and performance durability, and prove the feasibility in two kinds of running condition.

2. EXPERIMENTAL

2.1 Preparation and evaluation of zinc-coated carbon felt electrode

To investigate gravity effect and the influence of electrode placement, the electrochemical deposition of zinc onto carbon felts was conducted using two electroplating cells. The two electrodes were placed together in both a horizontal and a vertical arrangement. For plating the vertical cell, a piece of porous conductive carbon felt (thickness = 3 mm) was immersed in an AR grade ethanol ultrasonic bath for 5 minutes followed by air drying, then the felt was coated with zinc through electroplating for 5 minutes with a plating current density of 10 mA cm^{-2} in an aqueous alkaline solution made by dissolving 0.4M ZnO in 6M KOH. During electro-deposition, the anode (zinc plate, thickness = 1 mm) and the cathode (carbon felt) were kept vertically parallel in the solution. For plating the horizontal cell, a piece of carbon felt was prepared with the same approach described above except that the anode and cathode were retained horizontally parallel instead of vertically parallel during electrodepositing. The cathodes that resulted from both the vertical and horizontal methods were then characterized using a Merlin scanning electron microscope (SEM) instrument (Zeiss Company, Oberkochen, Germany) to compare the difference of zinc morphology on the felts.

2.2 Cell fabrication and electrochemical testing

Cell #1: An electrically rechargeable three-electrode Zn-air battery arranged in a horizontal orientation was designed and assembled (Fig.1). The three-electrode Zn-air battery consists of three parts: OER electrode (ruthenized titanium net, thickness = 2 mm) on top, air electrode (QSI-Nano Gas Diffusion Electrode, QuantumSphere Inc., Santa Ana, CA, USA) on the bottom, and a zinc electrode fixed between them. The current collector for the zinc electrode was porous copper foam (thickness = 1.5 mm, PPI = 90). The distance (controlled by rubber washer) from the zinc electrode to the air electrode and OER electrode was 1.5 mm and 3 mm, respectively. A double electrode groove was used to hold the zinc electrode and the OER electrode, and the air electrode was set close to the lower surface of the groove. The three electrodes were packaged to form a single cell through a frame made of PVC material, forming a chamber to hold the alkaline electrolyte. The working size of the electrodes is $25cm^2$. 45mL alkaline electrolyte made by dissolving 0.5M ZnO in 6M KOH was used for the single cell and the OER electrode was submerged in electrolyte. The OER electrode and zinc electrode were connected in a circuit during charging, and the air electrode was connected with the zinc electrode when discharging. Charge-discharge(C-D) cycling tests were conducted by charging for 1 h at current density of 40 mA cm^{-2} and discharging until the cut-off voltage of 0.9 V was reached at current density of 80 mA cm^{-2}. The anodic and cathodic polarization curves were obtained: charged or discharged for 300 s at different current densities and the steady-state cell voltage value were recorded. Both the C-D cycling data and polarization data were collected through a CT2001B Battery Testing System (LANHE Company, Wuhan, Hubei, China). The testing device is a modified version which has three pairs of testing electrodes: two positive electrodes and one communal negative electrode. So the electrochemical testing for three-electrode cells can be easily fulfilled especially for long-term cycling test with the modified device.

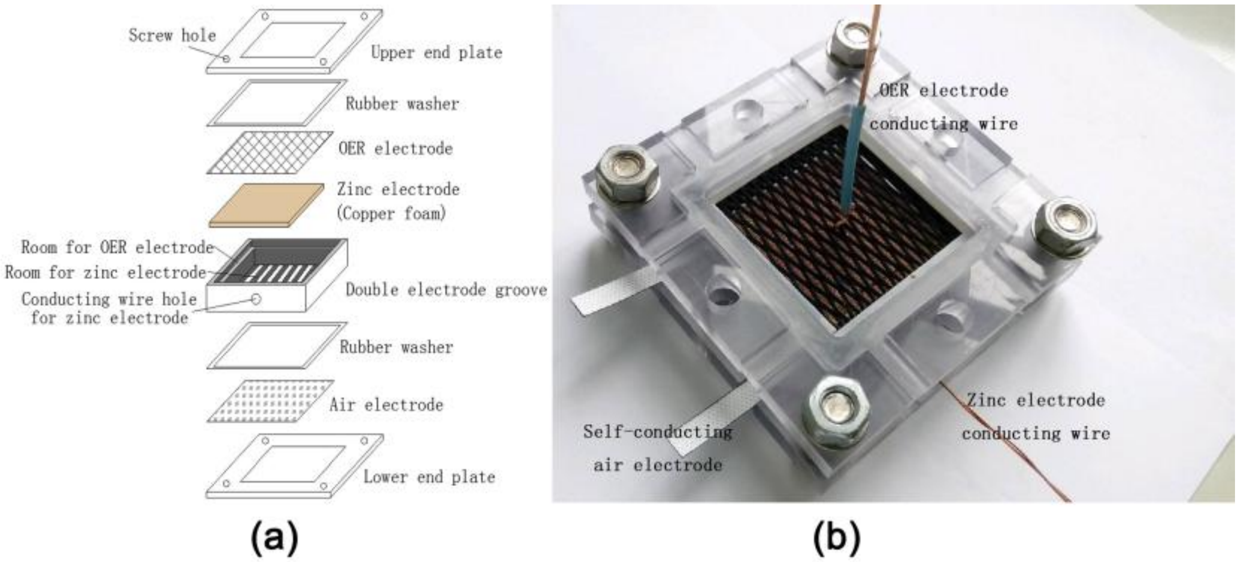

Figure 1. The horizontal three-electrode zinc-air battery: (a）Schematic diagram of cell structure and (b) picture of the three-electrode zinc-air battery.

Cell #2: The cell was fabricated the same as cell #1 except that the alkaline electrolyte was made by dissolving 0.4 M ZnO in 6 M KOH. C-D cycling tests were performed by charging for 1h at current density of 20 mA cm^{-2} and discharging at the same current density until the cut-off voltage of 0.9 V was reached. Polarization curve and C-D cycling data were once again obtained using the modified CT2001B device.

Cell #3: The cell was manufactured the same as cell #2 other than a smaller distance between the zinc electrode and air electrode, namely that the two electrodes were clingy to each other. Before each discharging course carried out at different current density, 0.5 Ah equivalent of zinc was deposited on the zinc electrode at current density of 20 mA cm^{-2}. The experimental data were acquired by the modified CT2001B machine.

3. RESULTS AND DISCUSSION

The SEM images in Fig. 2(a)–(c) show that the lower portion of the carbon felt collected more deposited zinc than the upper portion when the anode and cathode were kept vertically parallel in the solution during deposition. It can be expected that for a Zn-air battery arranged vertically, zinc deposit tends to accumulate at the bottom of the zinc electrode, causing deformation of the electrode and leading to fading capacity or a short circuit. As a result, the battery fails prematurely. The situation was different in the case of the horizontal experiment. As shown in Fig. 2 (d)–(f), no excessive accumulation of zinc was present. Gravity effect enabled zinc to deposit uniformly on the carbon felt, preventing dendrite accumulation. The negative impact of gravity can be totally alleviated by arranging the anode and cathode assembly horizontally.

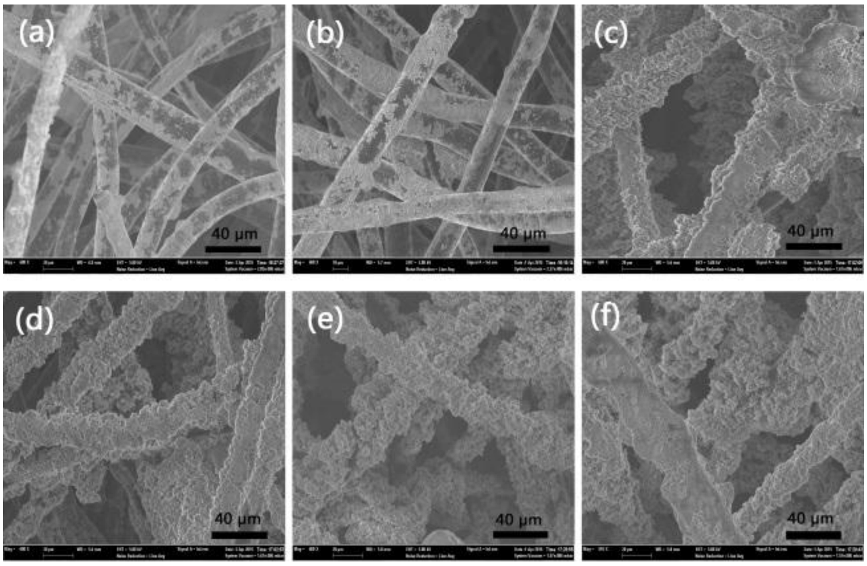

Figure 2. Comparison of SEM images for electrochemical plating behaviors of zinc on carbon felt; (a), (b) and (c) are zinc-plated carbon felts at the top, middle and bottom portion with vertical cell; (d), (e) and (f) are zinc-plated felts at the top, middle and bottom portion with horizontal cell.

Based on our findings, three single cells were manufactured according to the horizontal three-electrode design illustrated in Figure 1. The electrode working area of the cell we fabricated is 25cm^2 which is close to the size of an actually applicable single cell compared with most reported tiny lab cell for the evaluation of catalyst [23, 26-28]. Fig. 3(a) exhibits the cathodic and anodic polarization curves for cell #1. The cell charging voltage increased by 0.24 V while the current density increased from 2 to 100 mA cm^{-2}. Cell voltage decreased by 0.8 V as current density rose from 2 to 170 mA cm^{-2} for the discharge process. The cell resistance including the kinetic polarization resistance, the ohmic resistance and the concentration polarization resistance was roughly estimated to be 4.1 $\Omega\cdot$cm^2 for the discharging process and 2.4 $\Omega\cdot$cm^2 for the charging process. This manifests a small cell resistance for zinc air battery system [29-30]. The polarization curve also implies that ohmic resistance was responsible for the most losses. Performance could be increased by reducing ohmic resistance, perhaps by lowering the distance between the two electrodes or increasing the electrolyte conductivity. Battery testing result for cell #3 in Fig. 4(d) has verified this point. In cell #3, a smaller distance between the zinc electrode and air electrode leads to an improved discharging performance than that in cell #1 and cell #2 when compared under the same current density. Figure 3(b) shows that the current density increase was accompanied by a power density increase, which peaked at 105 mWcm^{-2} at 150 mA cm^{-2}. Figure 3 (c) compares the cell voltages of the first and the 100th C-D cycles, when charging at 40 mA cm^{-2} and discharging at 80 mA cm^{-2}. Cell #1 experienced a mild increase in voltage during charging, on average 3.7% (from 2.13 to 2.21 V), and a 2.0% drop in cell voltage (from 1.00 to 0.98 V) for the discharging process. During each C-D process, the charging capacity (1000mAh) was about 83% of the rated capacity (1200mAh) which is determined by the amount of ZnO dissolved in electrolyte. The C-D cycling can run repeatedly as long as we control the charging capacity to avoid zinc deposits layer forming a short-circuit with the OER electrode and the depth of discharge (DOD) managed by cut-off voltage to avoid overdischarge. Figure 3(d) shows the total 100 C-D cycling curve of cell #1 and the corresponding average columbic efficiency, DOD and energy efficiency were 90%, 73% and 42%, respectively (Fig. 3 (e, f)). These results indicate that the Zn-air battery with horizontal three-electrode structure exhibited long-term stability, even under high operating current density and DOD [31]. This demonstrates that air electrode's physical degradation, namely catalyst loss caused by oxygen evolution, uneven depositing and deformation of the anode can indeed be suppressed to a certain extent with this novel design.

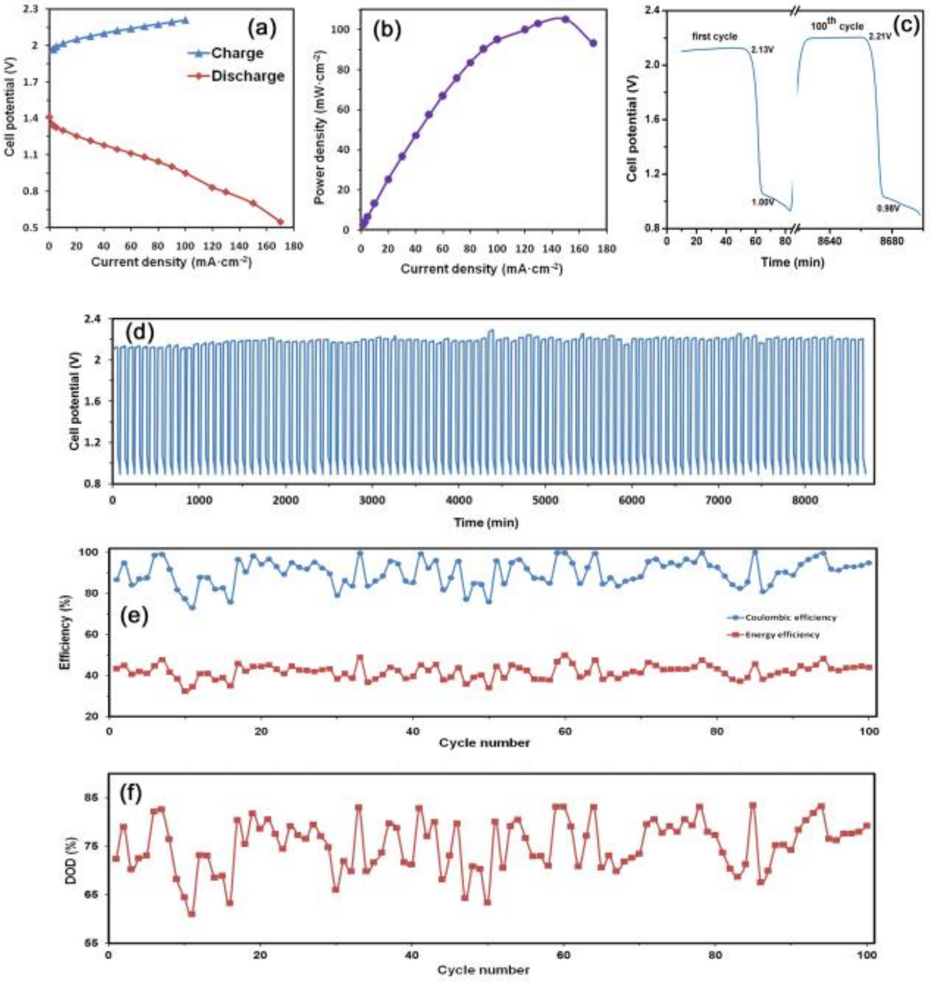

Figure 3. Battery testing results for cell #1: (a) anodic and cathodic polarization curves; (b) power density curve, (c) the enlargement of the first and the 100th cycles; (d) 100 C-D cycles; (e) the coulombic and energy efficiencies during the 100 C-D cycles; (f) DOD change during the 100 C-D cycles.

Battery testing results for cell #2 and cell #3 are showed in Fig.4. For cell #2, the charging capacity was 500mAh and the DOD set up was about 50% during each C-D cycle. The cell #2 has run 1000 C-D cycles approximately 1917h, which is far over all published results tested in similar conditions in table.1. For these reasons, the horizontal three-electrode configuration can obviously improve the cycling performance, especially cycle life and durability of zinc-air batteries. Fig. 4(a) exhibits the cathodic and anodic polarization curves at its initial state and after 1000 cycles for cell #2. During the 1000 C-D cycles, the cell resistance increased from 3.1 $\Omega\cdot cm^2$ to 8.6 $\Omega\cdot cm^2$ and 3.2 $\Omega\cdot cm^2$ to 3.6 $\Omega\cdot cm^2$ for the charging process and discharging process, respectively. Figure 4(b) displays the cycling performance of cell #2.

Table 1. Cycling performance of zinc air batteries and comparing with this stdy.

Air cathode	Charge-discharge current density	Cycling performances	Reference
bifunctional electrocatalysts	5 mA cm^{-2}	270 cycles for ~90 h	6
bifunctional electrocatalysts	20 mA cm^{-2}	100 cycles for ~16.7 h	17
bifunctional electrocatalysts	8 mA cm^{-2}	50 cycles for ~8.3h	26
bifunctional electrocatalysts	17.6 mA cm^{-2}	75 cycles for ~12.5h	32
bifunctional electrocatalysts	15mA cm^{-2}	60 cycles for ~14h	33
bifunctional electrocatalysts	25 mA cm^{-2}	20 cycles for ~1.7 h	34
bifunctional electrocatalysts	20 mA cm^{-2}	50 cycles for ~33.3 h	35
Vertical three-electrode	20 mA cm^{-2}	20 cycles for ~200h	22
Vertical three-electrode	5-15 mA cm^{-2}	~10 cycles for ~120h	24
Horizontal three-electrode	Charging at 40 mA cm^{-2}, Discharging at 80 mA cm^{-2}	100 cycles for ~145 h	This study
Horizontal three-electrode	20 cm^{-2}	1000 cycles for ~1917 h	This study

Within 1000 C-D cycles, the charging phase experienced an average increase of 13% in cell voltage (from 2.10 to 2.37 V) and the discharging process experienced a reduction of 12% in cell voltage (from 1.14 to 1.00 V), very steady performance which is consistent with the polarization curves. Result in Fig. 4(d) reveals the relationship between cell capacity and cell voltage with respect to discharge current density. And the cell voltage increases with decreasing current density, which fits in with the polarization curves. Arranging electrodes horizontally improved cell durability, extending the usable C-D life of batteries when compared with the current state of the art. These results prove the feasibility of the horizontal three-electrode configuration.

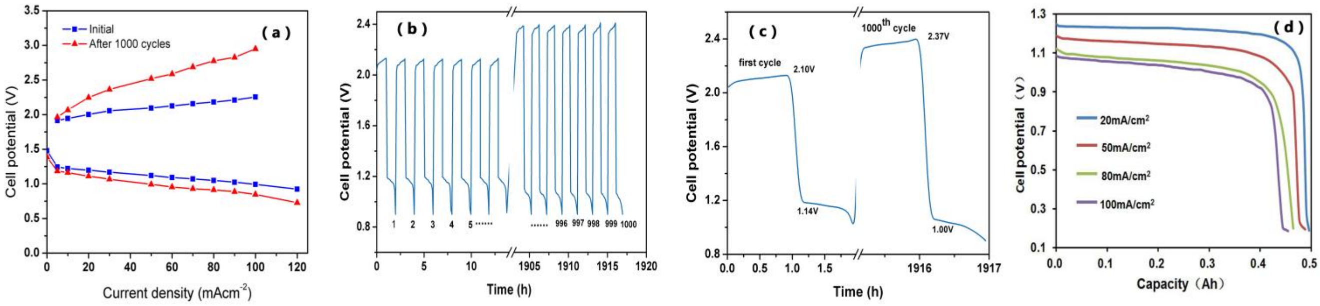

Figure 4. Results for cell #2: (a) cathodic and anodic polarization curves at its initial state and after 1000 cycles; (b) 1000 charge-discharge cycles; (c) the enlargement of the first and the 1000th cycles; and result for cell #3: (d) the relation between the cell capacity vs. cell voltage.

4. CONCLUSIONS

A novel electrically rechargeable three-electrode Zn-air battery featuring elements arranged horizontally with an actually applicable single cell size was designed, fabricated, and tested. A long-term test of 1000 charge-discharge cycles approximately 1917h cycling duration with mild decay demonstrated the rationality and feasibility of this novel structure, and a maximum power density of 105 mWcm^{-2} was achieved at a current density of 150 mA cm^{-2}. The cycle life and duration of zinc-air batteries in alkaline electrolyte using this novel structure have been extremely enhanced. A good energy efficiency and high depth of discharge were also achieved under high operational current density during 100 charge-discharge cycles. These results indicate promising practical applications of zinc-air batteries in area such as electric vehicle and grid-scale energy storage. The polarization curve reveals that ohmic resistance was responsible for the most losses of cell potential. Thus the cell performance can be further improved by reducing ohmic resistance, for instance, by lowering the distance between the two electrodes or increasing the electrolyte conductivity. In the future, we plan to develop an electrically rechargeable Zn-air battery stack similar in configuration to what has been reported here.

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