Long-Life, High-Voltage Acidic Zn–Air Batteries

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Low-cost, high-energy-density batteries have been intensively pursued in recent years to electrify transportation and facilitate the efficient use of renewable energy sources.\[3\] In this regard, metal–air batteries are receiving world-wide attention as they are powered by a high-energy metal anode and an inexhaustible, low-cost air cathode.\[2\] Particularly, Zn–air batteries (ZABs) are regarded as a more practical metal–air battery system due to their low cost, safety, rechargeability, and good stability of Zn in aqueous solutions.\[11\] However, the current ZABs suffer from problems such as low cell voltage (≈1 V), carbonate formation in the air electrodes, as well as dendritic problem and zincate loss at the Zn anode.\[4\] Breakthrough innovations are needed to solve these problems before rechargeable ZABs could become commercially viable.

The low cell voltage of current ZABs is determined by the electrolyte used. In most cases, an aqueous 6–7 m KOH solution is used to achieve the optimum ionic conductivity and good oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics.\[5\] The theoretical cell voltage is 1.65 V based on the Nernst equation,\[6\] but the working potential is usually ≈1 V,\[10\] which is only one half or one third of the operating cell voltage of aprotic (≈2.5 V)\[7\] or aqueous Li–air batteries (≈3.5 V).\[8\] Acidic electrolytes offer a higher redox potential for the ORR, leading to an increase in the overall voltage of metal–air batteries.\[9\] The acidic electrolytes also eliminate the carbonate clogging problem, which arises from the reaction of CO₂ in air with an alkaline electrolyte. However, metallic Zn undergoes violent hydrogen evolution in acidic solutions. Therefore, acidic Zn–air batteries (AZABs) are not possible without a proper protection of the Zn anode.

The dendrite problem in ZABs mainly arises from the dissolution and migration of the battery discharge product, zincate (Zn(OH)₂)\[4\]. On charging the Zn–air batteries, zincate is reduced to metallic Zn, which is plated on the Zn metal anode. However, the reduced Zn is not plated on the same location at the electrode surface where it came from. The nonuniform Zn plating leads to the growth of dendrites, which accumulate during cycling and eventually lead to a short circuit of the cell. Although the use of a solid electrolyte will not avoid the formation of dendrites, it can block the dendrites from short circuiting the cells. In addition, the use of a solid electrolyte could also enable the use of an acidic electrolyte in metal–air batteries, increasing the cell voltage.\[10\] However, a Zn–ion solid electrolyte, which can be operated at room temperature, has rarely been reported.\[11\]

The rechargeability of ZABs requires bifunctional catalytic activity of the air cathode: ORR and OER. The requirements for the active sites and electrochemical environment for ORR and OER are so different that it is very difficult to achieve high activity for both reactions within one material. For example, ORR prefers hydrophobic sites, which form a three-phase (solid catalyst, liquid electrolyte, and air) interface. In contrast, OER prefers hydrophilic sites to maximize the contact between the catalyst and the electrolyte. Recently, a “decoupled” design of bifunctional air electrodes has attracted much attention.\[12\] By dividing the ORR and OER functions into two different electrodes, which are optimized for ORR and OER respectively, high cell efficiency as well as long cycle life could be achieved. However, the decoupled design has mainly been pursued with alkaline metal–air batteries, and no such design has been reported for acidic metal–air batteries.

We report here AZABs with decoupled air electrodes, which is promising to eliminate the problems of conventional Zn–air batteries. The prototype AZABs are composed of a Zn-metal anode, an alkaline anode electrolyte, a NASICON-type Li-ion solid electrolyte (LTAP), an acidic phosphate buffer catholyte, and a decoupled IrO₂ thin films grown onto a Ti mesh (IrO₂@Ti) for OER and a commercial Pt/C catalyst on a gas diffusion layer (GDL) for ORR. The Li-ion solid electrolyte LTAP separates the alkaline anode electrolyte and the acidic catholyte and provides ionic channels. LTAP does not serve as a direct Zn²⁺-ion conductor, but as a Li⁺-ion “messenger” to achieve the charge balance on both sides of an AZAB.\[13\] The decoupled OER electrode is carbon-free and binder-free, ensuring good mechanical integrity in the high-voltage oxidizing environment. The decoupled ORR electrode is isolated during the high-voltage charge process, minimizing the problem of catalyst dissolution and oxidation.\[14\] During cell operation, a high discharge voltage close to 2.0 V could be achieved at a low current density. The acidic catholyte also eliminates the persistence problem of CO₂ ingestion associated with alkaline electrolytes. In addition, the solid electrolyte provides the possibility of blocking Zn dendrite from reaching the cathode, greatly improving the battery safety. Moreover, although the soluble discharge product zincate will still form on the anode side, the solid electrolyte will keep the zincate in the anode chamber, decreasing the mass transport barrier and facilitating zincate reduction upon charge. The assembled AZABs achieve a high voltaic efficiency of 81% at 0.1 mA cm⁻². The cell could also be cycled for hundreds of hours in the ambient air environment without significant degradation.

**Figure 1** shows the discharge and charge mechanism of an AZAB based on an alkaline anode electrolyte and an acidic catholyte. During discharge, oxygen (O₂) from air diffuses into the porous air electrode, gets reduced, and combines with...
phosphoric acid (H$_3$PO$_4$) to form phosphate dihydrogen ions (H$_2$PO$_4^-$) and H$_2$O. At the anode side, Zn is oxidized and combines with hydroxide ions (OH$^-$) to form zincate (Zn(OH)$_4^{2-}$). Zincate tends to decay into zinc oxide (ZnO) and water (H$_2$O) after reaching its solubility limit. To balance the charge in the anode electrolyte and catholyte, Li$^+$ ions in the anode electrolyte diffuse back to the anode through the solid electrolyte. At the anode side, Zn(OH)$_4^{2-}$ is reduced into Zn and OH$^-$. While Zn is plated on the Zn anode, OH$^-$ combines with Li$^+$ ions to form LiOH. It is worth mentioning that any protons diffusing through the solid electrolyte will neutralize the anode electrolyte and even corrode the Zn metal at the anode side. However, this possibility has been excluded by a recent study, which concluded that protons can be absorbed on the LTAP surface but cannot go through it.\cite{15} This is due to the fact that protons form a strong bond with nearby oxygen upon absorption onto LTAP, which leads to a large energy barrier for proton diffusion. The energy barrier of Li$^+$ ions (0.79 eV) is much lower than that of protons (3.21 eV). Thus, the proton conductivity in LTAP at room temperature can be neglected.

The decoupled OER electrode was made of IrO$_2$ nanoparticles deposited onto a Ti mesh (IrO$_2$@Ti) with the overall morphology shown in Figure 2a–d. The anodic electrodeposition was carried out with a three-electrode half-cell setup in an ice bath as shown in Figure S1a in the Supporting Information.\cite{16} The corresponding anodic voltage profile is shown in Figure S1b in the Supporting Information. As shown in Figure 2a, the wire diameter of the Ti gauze is \approx 130 µm. A thin layer of IrO$_2$ was deposited onto the mesh wires, like a tree skin, which is shown in Figure 2b. As we zoom in on the IrO$_2$ coating, we find that the coating is full of micro cracks, which enhance the infiltration of electrolyte into the catalyst layer. A high-resolution scanning electron microscopy (SEM) image is shown in Figure 2d. The IrO$_2$ coating is actually made of numerous IrO$_2$ nanoparticles with a size of $<20$ nm. This particle size is in agreement with the IrO$_2$ particles in the prepared IrO$_2$ colloid solution as shown in the transmission electron microscopy (TEM) images in Figure S2 in the Supporting Information. The obtained IrO$_2$ film is amorphous as reported in the literature and proven by the TEM images (no crystalline planes are observed) in Figure S2 in the Supporting Information.

In addition, the absence of peaks in the X-ray diffraction (XRD) pattern in Figure S3 in the Supporting Information also supports the amorphous nature. The small particle size and amorphous feature of the deposited IrO$_2$ provide a large amount of highly active sites toward OER in acidic solutions.\cite{17} Previously, decoupled bifunctional air electrodes have been mostly reported in alkaline solutions.\cite{18} As far as we know, this is the first report of decoupled bifunctional air electrodes in acidic metal–air batteries. Ti is chosen as the current collector here due to its.

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**Figure 1.** Schematic illustrations of the a) discharge and b) charge mechanism of an acidic Zn–air battery.

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good stability and inertness in acidic solutions. IrO$_2$ is used as the OER catalyst since it is the most stable and active catalyst in acidic solutions found so far.$^{[19]}$

X-ray photoelectron spectroscopy (XPS) analysis was conducted to study the oxidation states of IrO$_2$ films on Ti gauze as shown in Figure 2e,f. In Figure 2e, the iridium signal exhibits two different peaks with the binding energies of 62.0 and 65.0 eV, which could be assigned to, respectively, Ir$^{4+}$ 4f$^{7/2}$ and 4f$^{5/2}$. At the same time, there are two doublets located at 63.1 and 66.2 eV, which are believed to be caused by the existence of higher-oxidation-state iridium.$^{[21]}$ This is also supported by the analysis of the O1s peak shown in Figure 2f. The additional doublet peak is around 531.5 eV, which is $\approx 1$ eV higher than the main peak located at 530.5 eV. Another evidence for excess oxygen (higher-oxidation-state iridium) is that the quantitative analysis of the XPS peaks shows the atomic ratio of Ir and O in the film is 21:79.

The electrochemical performance of the synthesized IrO$_2$@Ti in phosphate buffer was tested with a three-electrode half-cell as described in our previous report.$^{[22]}$ The counter and reference electrodes were, respectively, a Pt flag and saturated calomel electrode (SCE). From the linear sweep voltammetry (LSVs) shown in Figure 3a, we can see that the Ti gauze shows nearly zero current density within a wide potential range of 0.1–1.8 V versus SCE. This indicates the negligible OER activity of Ti in the phosphate buffer electrolyte as well as its good stability, which are the important characteristics of current collectors. However, after a thin layer of IrO$_2$ (0.27 mg cm$^{-2}$) was deposited onto the Ti gauze, the anodic current increased sharply beyond the onset potential around 1.2 V versus SCE. The current density at 1.8 V versus SCE is $4000 \times$ higher than that of Ti gauze, proving the ultra-high activity of IrO$_2$@Ti in the phosphate buffer electrolyte. A prolonged deposition time (20 000 s) was tried, leading to an increased loading of $\approx 1$ mg cm$^{-2}$. However, the electrode did not perform well since the IrO$_2$ layer started to peel off the Ti substrate due to internal tension as shown in Figure S5 in the Supporting Information.

To further study the reaction mechanism, the Tafel plots based on the LSVs were calculated and plotted in Figure 3b. The Tafel slope of Ti is large around 357.4 mV dec$^{-1}$, which indicates the poor intrinsic activity of Ti metal toward OER in acidic solution.

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**Figure 2.** a–d) Low and high-resolution SEM images of IrO$_2$@Ti. e,f) Ir 4f and O 1s peaks of IrO$_2$@Ti.
While for IrO$_2$@Ti, the Tafel slope at a low current range is as low as 121.8 mV dec$^{-1}$. The Tafel slope increases sharply in the high-current range (>100 mA cm$^{-2}$), which may be due to the accumulation of oxygen bubbles on the electrode, blocking the contact between the catalyst and the electrolyte.[23] The stability of IrO$_2$@Ti was tested by chronopotentiometry at a current density of 0.5 mA cm$^{-2}$ as shown in Figure 3c. As can be seen from Figure 3c, the charge potential quickly rises to $\approx$1.14 V versus SCE upon charging. The charge potential is almost constant for more than 250 h without observable degradation.

The high intrinsic activity and durability of IrO$_2$@Ti is critical to the high cell efficiency and stability of AZABs.

The AZABs were assembled with a polished Zn plate anode, a 0.5 M LiOH + 1 M LiNO$_3$ anode electrolyte, a NASICON-type LTAP, a 0.1 M H$_3$PO$_4$ + 1 M LiH$_2$PO$_4$ cathode electrolyte, and Pt/C + IrO$_2$@Ti decoupled air electrodes. 0.5 M LiOH + 1 M LiNO$_3$ was used as the anode electrolyte to create an alkaline environment for the Zn metal anode and provide good compatibility with the solid electrolyte.[24] The discharge and charge voltage profiles at 0.5 mA cm$^{-2}$ are shown in Figure 4a. A current density of 0.5 mA cm$^{-2}$ was applied since it has been the most standard current density for batteries with the LTAP solid electrolyte.[25] Although the open-circuit voltage is as high as 1.8 V, the initial discharge voltage is $\approx$0.9 V, which is even lower than the operating voltage of conventional ZABs ($\approx$1 V). In addition, we found the cell could only be cycled for eight cycles and it suffered from fast degradation afterwards. Since the air electrodes and solid electrolyte were quite successful in our hybrid Li–air batteries with stability of more than hundreds of hours,[26] the problem is most likely due to the Zn anode.

To study the stability of Zn anode in the 0.5 M LiOH + 1 M LiNO$_3$ electrolyte, a pristine Zn plate was immersed in a solution composed of 0.5 M LiOH + 1 M LiNO$_3$. Upon immersion, the bright and shining Zn foil became dull and dark within several minutes, indicating a fast chemical reaction. After 2 D, the Zn foil was taken out from the solution, washed with ethanol and dried, and tested by XRD as shown in Figure 4b. In Figure 4b, most of the peaks correspond to Zn(OH)$_2$ and Zn, indicating the chemical reaction between Zn metal and LiOH + LiNO$_3$ electrolyte. In addition, we also observed several minor peaks associated with ZnO, which might be due to the dehydration of Zn(OH)$_2$ upon drying. The morphology features of Zn metal after immersion in LiOH + LiNO$_3$ were observed by SEM as shown in Figure 4c. By comparing these two images, we could see that a thick layer of crust has formed on the Zn metal surface, which is shown to be mostly Zn(OH)$_2$ from the XRD pattern in Figure 4b. This thick layer may be the main problem leading to fast cell degradation in the full cell. The insulating Zn(OH)$_2$ covers up the metal surface and prevents contact between the electrolyte and Zn metal anode, leading to a low initial discharge voltage and cell failure after around 30 h of cell operation. After analyzing the passivation layer on the Zn-metal anode, we believed the main problem arose from the LiNO$_3$ additive in the anode electrolyte, which is quite oxidative. The passivation layer on Zn-metal surface is both electronically and ionically insulating, cutting off the contact between Zn metal and the electrolyte and stopping the cell reaction.

To eliminate the adverse effects of LiNO$_3$, we used only 0.5 M LiOH as the anode electrolyte. To study the compatibility of Zn metal with LiOH, a pristine Zn plate was immersed into 0.5 M LiOH. After 2 D, the Zn plate still maintained a shiny appearance, indicating the good stability of Zn metal in 0.5 M LiOH. We also conducted SEM and XRD characterizations of the Zn plate after removing it from 0.5 M LiOH, and the data are shown in Figure 5a,b. It can be
Figure 4. a) Typical cycling voltage profiles of AZABs with the 0.5 M LiOH + 1 M LiNO₃ anode electrolyte. b) XRD pattern (Zn JCPDS No. 65-3358, ZnO JCPDS No. 65-3411, and Zn(OH)₂ JCPDS No. 38-0358), and c) SEM image of a Zn plate after immersing into 0.5 M LiOH + 1 M LiNO₃ for 2 D. d) SEM image of a pristine Zn plate.

Figure 5. a) SEM image and b) XRD pattern of a Zn plate after immersing into 0.5 M LiOH for 2 D. c) LSV and power density of AZAB with a 0.5 M LiOH or 0.5 M LiOH + 1 M LiNO₃ anode electrolyte. d) Rate capability of AZAB with a 0.5 M LiOH anode electrolyte and Pt/C + IrO₂ bifunctional air electrodes.
seen that no observable passivation layer formed on the surface of Zn plate. The XRD pattern in Figure 5b also shows pure Zn metal with no impurities. Again, we assembled the AZABs with 0.5 M LiOH instead of 0.5 M LiOH + 1 M LiNO₃ as the anode electrolyte. The linear scanning voltammetry and calculated power densities are shown in Figure 5c. The AZABs with the LiOH anode electrolyte exhibited a higher open-circuit voltage (≈2.1 V) than the ZAB with the LiOH + LiNO₃ anode electrolyte (≈1.8 V). Further increase in the cell voltage can be achieved by increasing the acidity of the catholyte (increasing the cathode potential) and alkalinity of the anolyte (decreasing the anode potential). However, the pH value should be well controlled to avoid any significant corrosion of the solid electrolyte. The maximum power density is also much higher when LiNO₃ is eliminated from the anode electrolyte. The discharge and charge profiles of AZABs at different current densities are shown in Figure 5d. The catalysts involved are conventional Pt/C + IrO₂ bifunctional catalysts. We could see that at a current density of 0.1 mA cm⁻², a high discharge voltage of ≈1.92 V is achieved, which is even 0.27 V higher than the theoretical cell voltage of conventional ZABs (1.65 V). The charge voltage at 0.1 mA cm⁻² is ≈2.37 V, leading to a high cell efficiency of ≈81.0%. It should be mentioned that the working current density of the developed AZABs is smaller than conventional ZABs due to the much larger cell resistance associated with the thick solid electrolyte. Further improvements on cell efficiency and rate capability can be made by using a solid electrolyte with higher ionic conductivity and reduced thickness. Although expensive Pt/C and IrO₂ are used here to demonstrate the concept, alternative low-cost catalysts are possible for ORR and OER in the acidic electrolyte. For example, cobalt–polypyrrole (Co–PPY–C) and iron-based (Fe/N/C) catalysts have been reported to possess high ORR performance comparable to that of Pt/C in acidic fuel cells.²⁷ MnO₄⁻, PbO₂, and their derivatives have also been explored as stable OER catalysts in an acidic electrolyte.²⁸

The cycling voltage profiles of AZABs with a 0.5 M LiOH anode electrolyte and Pt/C + IrO₂@Ti decoupled air electrodes are shown in Figure 6. Since the decoupled bifunctional air electrodes are utilized in the cells, two sets of curves (red for discharge and black for charge) are present in the figure, representing the discharge and charge voltage profiles. In total, 50 cycles are present, with no observable degradation in cell performance, indicating the high stability of the developed AZABs. The initial round-trip overpotential is 0.98 V, contributing to a high cell efficiency of 63.7%. After 50 cycles (200 h operation), the round-trip overpotential increased slightly to 1.00 V, which corresponds to a cell efficiency of 62.3%. The cell voltage, power density, and cycle life could be further improved by increasing the ionic conductivity and chemical stability of the solid electrolyte.

In summary, the developed AZABs not only possess a higher cell voltage than conventional ZABs, but also demonstrate good stability upon cycling in the ambient environment. The incorporation of a solid electrolyte solves some of the persistent problems with conventional ZABs, such as CO₂ ingestion, cell short circuit by dendrites, zincate loss, and low cell voltage. Furthermore, the study represents the first report on using decoupled bifunctional air electrodes for acidic metal–air batteries. We believe this new configuration of Zn–air batteries will bring new hope to solve the persistent problems of rechargeable Zn–air batteries toward practical applications. The methodology adopted here could also be applied to a broad range of systems with other anodes like Fe and Al.

**Experimental Section**

**Chemicals and Materials:** Potassium hexachloroiridate (K₂IrCl₆, Strem Chemicals, Inc), iridium oxide (Alfa Aesar), oxalic acid (H₂C₂O₄·2H₂O, Fisher Scientific), potassium carbonate (K₂CO₃, Fisher Scientific), titanium gauze (Ti, 80 mesh, Alfa Aesar), titanium wire (0.031 inch diameter, McMaster-CARR), phosphoric acid (H₃PO₄, Fisher Scientific), lithium dihydrogen phosphate (LiH₂PO₄, Fisher Scientific), Zn plate (OnlineMetals), potassium hydroxide (KOH, 85.3%, Fisher Scientific), lithium hydroxide monohydrate (LiOH·H₂O, Fisher Scientific), lithium nitrate (LiNO₃, 99%, Acros Organics), Pt/C
(20 wt. %, Johnson Matthey), and acetylene black (AB) were purchased and used as received.

Anodic Electrodeposition of Iridium Oxide Films on Ti Gauze (IrO@Ti): IrO@Ti was synthesized by an anodic electrodeposition method as reported in the literature.[15] K$_2$IrCl$_6$ (0.2 mmol) and H$_2$C$_2$O$_4$ (1 mmol) were dissolved in water (30 mL) in a beaker and stirred for about five min. Then K$_2$CO$_3$ (5 mmol) was added into the mixture to adjust the pH value to ~10. Afterwards, more water (20 mL) was added into the solution and kept stirring at 35 °C for 9 D until a dark blue solution (IrO$_2$ colloid) was formed. The IrO$_2$ colloidal solution was poured into a three-electrode glass cell in an ice bath. The working electrode was a rectangular-shaped Ti gauze with a width of 1 cm. It was inserted into the solution about 1 cm deep (depositing area 1 cm$^2$). The reference and working electrodes were, respectively, an SCE and a Pt wire. A fixed anodic current of 35 mA was applied to the working electrode, leading to a current density of 35 μA cm$^{-2}$. The deposition time was set to be 5000 s (0.27 mg cm$^{-2}$).

Characterization: The morphology features of the IrO$_2$@Ti, Ti gauze, and Zn plates were studied with a Hitachi S-5500 STEM. IrO$_2$ colloid particles were observed with a JEOL 2010F TEM at 200 keV. The XRD data was collected with a Philips X-ray diffractometer equipped with Cu Kα radiation at a scan rate of 0.03 s$^{-1}$. XPS data were collected with a Kratos Analytical spectrometer.

Electrochemical Characterization: The intrinsic catalytic activity and stability of IrO$_2$@Ti and Ti gauze were studied by LSV and chronopotentiometry in a three-electrode half-cell with a SCE reference electrode, a Pt flag counter electrode, and a phosphate buffer electrolyte (1 M LiH$_2$PO$_4$ catholyte). The OER electrode was IrO$_2$@Ti with the electrode area cut to 0.76 cm$^2$ to fit into the cell. The OER electrode was Pt/C (20 wt%, 1 mg cm$^{-2}$) nanopowder sprayed onto a gas diffusion layer with 20 wt% LithION binder (Ion Power, obtained with a current density of 0.5 mA cm$^{-2}$) and used as received.

Zn-air Battery Tests: The acidic Zn-air batteries were assembled with a layered battery mold, which is similar to our hybrid Li-air batteries.[10] The anode side was a Zn plate connected to a Ti wire as the current collector. The electrolyte system contained three parts: 2 mL of 0.5 M LiOH or 0.5 M LiOH + 1 M LiNO$_3$ anode electrolyte, a LTAP (Li$_{1+x}$Ta$_2$O$_6$Al$_{3-y}$Si$_{2-x}$O$_{12}$) membrane (0.15 mm thick, 1 × 10$^{-4}$ cm$^{-1}$, 0.76 cm × 0.76 cm, OHARA Inc., Japan), and 2 mL of 0.1 M H$_2$PO$_4$ + 1 M LiH$_2$PO$_4$ catholyte. The OER electrode was IrO$_2$@Ti with the electrode area cut to 0.76 cm$^2$ to fit into the cell. The OER electrode was Pt/C (20 wt%, 1 mg cm$^{-2}$) nanopowder sprayed onto a gas diffusion layer with 20 wt% LiH$_2$PO$_4$ binder (Ion Power, USA). For the bifunctional Pt/C+ IrO$_2$ air electrodes, Pt/C and IrO$_2$ nanopowder were sprayed on the gas diffusion layer with the loadings of 1 mg cm$^{-2}$ + 1 mg cm$^{-2}$. Polarization curves were recorded with a scan rate of 10 mV s$^{-1}$. Discharge-charge experiments were conducted with an Arbin BT 2000 battery cycler with a 5-min rest time between each discharge and charge period, which was set to be 2 h. For the cell with decoupled air electrodes, two independent Arbin channels were used to collect the discharge and charge data alternatively with a 5-min rest time between each discharge and charge period.

Supporting Information: Supporting Information is available from the Wiley Online Library or from the author.

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