Perspective

Magnetic zinc-air batteries for storing wind and solar energy

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SUMMARY
With the consensus on carbon peak and neutrality around the globe, renewables, especially wind and solar PV will grow fast. Correspondingly, the batteries for renewables would be scheduled to meet the requirements of performance, lifetime, cost, safety, and environment. Rechargeable zinc-air battery is a promising candidate for energy storage. However, the lifetime and power density of zinc-air batteries remain unresolved. Here we propose a concept of magnetic zinc-air batteries to achieve the demand of the next generation energy storage. Firstly, an external magnetic field can effectively inhibit dendrite growth of the zinc depositing layer and expel H2 or O2 bubbles away from the electrode's surface, extending the battery life. Secondly, magnetic fields can promote electrons, ions, and O2 transfer, enhancing power density of zinc-air batteries. Lastly, four schemes to generate magnetic fields for zinc-air batteries are exhibited to fulfill battery energy storage demand of high performance and long service life.

INTRODUCTION
The global call for carbon peak and neutrality will spur rapid growth in the field of renewables. Wind and solar PV play a great role among renewables to meet the challenge of environmental pollution (Kruitwagen et al., 2021; Wiser et al., 2021). An appropriate energy storage technique is needed to satisfy unstable characteristics of power generation. Furthermore, energy storage devices are also required to achieve peak-shaving of the electrical grid and energy management flexibility of distributed storage (Wei et al., 2021).

As a low-carbon energy storage device, the batteries are more suitable for microgrid energy storage or end users to stabilize power quality and local industrial or commercial services to regulate peak load. Lead-acid batteries (Lopes and Stamenkovic, 2020) and vanadium redox flow batteries (Lourenssen et al., 2019) have low specific energy, short lifetime, and environmental pollution, which are difficult to meet current demand. As for the next generation energy storage, high specific energy of the batteries is one of important criteria. Sodium sulfur batteries (Wang et al., 2020a, 2020b) need to use the vacuum insulation technology at the working temperature of 300–350°C. Lithium-ion batteries (Turcheniuk et al., 2018) take risks of hidden safety, high cost, severe degradation under extreme conditions, and the batteries’ energy storage is insufficient for social needs. In comparison, metal-air batteries have higher specific energy, effectively improving the intelligent management of electric energy. Metal-air batteries are composed of metal electrode, electrolyte, and air electrode, where oxygen involved in the reaction is not stored in the batteries but drawn directly from the surrounding air (Wang and Xu, 2019). Exactly, iron-air batteries have the lowest cost among metal-air batteries but low specific energy. Metal elements of lithium-air, sodium-air, and potassium-air batteries are more active and use high cost aprotic electrolyte, and reaction products are easy to cause air electrode porosity blockage and thus prevent subsequent reaction, resulting in battery failure (Bruce et al., 2012). Aluminum-air, magnesium-air batteries are generally used as primary batteries, which have serious self-discharge and are difficult to dispose of discharging products.Remarkably, zinc-air batteries have the advantages of good electrochemical reversibility, high specific energy, environmental compatibility, and rich resources (Liu et al., 2020).

The development trend of wind and solar PV needed for carbon emission reduction is illustrated in Figure 1, exhibiting the next generation battery techniques of energy storage accompanied by renewables (IEA, 2021). Zinc-air batteries will be a promising candidate superior to lithium-ion batteries in terms of safety, cost, and performance. A typical zinc-air battery comprises zinc electrode, the electrolyte, and air...
electrode, among which interfacial coupling stability either at the side of the air electrode or zinc electrode influences output performance of the battery. As such, dendrite growth of zinc electrodes and sluggish kinetics of air electrodes severely restrict the lifetime and power density of zinc-air batteries. Dendrite growth of electrodeposited zinc can be suppressed by means of physical separation (Yuan et al., 2018; Higashi et al., 2016), composition, structural modification (Parker et al., 2017; Zheng et al., 2019; Parker et al., 2017; Zheng et al., 2019; Huang et al., 2020), electrolyte flow, and multiple fields coupling (Zhang et al., 2019; Li et al., 2018; Zuo et al., 2021; Zhao et al., 2021). Oxygen redox polarization may be reduced by way of catalytic materials and micro-nano structure (Dionigi et al., 2020; Yang et al., 2020; Gorlin and Jaramillo, 2010; Gong et al., 2009), and performance degradation of air electrode because of oxygen bubbles erosion and carbon corrosion can be alleviated by means of self-supported sulfurization structure (Radehnamad et al., 2021) and electrospinning process (Chen et al., 2019). However, the problems of cycle life and power of zinc-air batteries remain unresolved. Most solutions can only improve the battery performance or lifetime to a certain extent, meanwhile these measures may cause other negative effects.

According to our previous works, external magnetic fields cannot only control zinc morphological change but also promote oxygen transfer and redox reactions, which can improve the cycling performance of zinc-air batteries. In consideration of electromagnetic coupling properties, especially unsteady electric fields like wind or PC renewables may pay the way for magnetic field generation. More importantly, adsorption characteristics of magnetic fields can be used to absorb metal catalysts instead of carbon material of air electrodes, avoiding carbon corrosion at high currents. Therefore, uncovering electromagnetic induced

| Type                  | Lithium-ion batteries (Jiao et al., 2021) | Zinc-air batteries (Shinde et al., 2021) |
|-----------------------|-------------------------------------------|----------------------------------------|
| Specific energy       | <200 W h kg⁻¹                            | ~500 W h kg⁻¹                          |
| Security              | Hazardious                               | Safe                                   |
| Extreme conditions    | Severe attenuation                       | Strong adaptability                    |
| Efficiency            | ~90%                                      | ~75%                                   |
| Cost                  | Expensive                                 | Cheap                                  |

Figure 1. Expected application of zinc-air batteries for clean energy storage to meet the demands of carbon peak and carbon neutrality.
Phenomena, understanding action mechanisms of magnetic fields, and designing magnetic zinc-air batteries are the objectives of this Perspective, which are of great importance for designing the next generation battery with high power density and long cycle life.

**Effects of unsteady electric field**

Hydrogen evolution reaction (HER) always occurs in accompaniment with metal electrodeposition, and hydrogen would stay within the depositing layer, leading to pore defects of metal deposits. For instance, the bump phenomenon appears in the process of electrodeposited zinc at the current density of 100 mA cm$^{-2}$, as shown in **Figure 2A**, which is mainly caused by hydrogen bubbles adsorption on the electrode.

**Figure 2. Effects of electric/magnetic fields**

(A) H$_2$ bubbles staying within the zinc depositing layer (Wang et al., 2020a, 2020b; Tsai et al., 2002).
(B) The compacted morphology of zinc at pulse currents (Wang et al., 2014).
(C) Free diffusion movement of oxygen bubbles creates movement in the electric field (Wang et al., 2016).
(D) Swirl motion of oxygen bubbles in electromagnetic fields (square electrolytic bath) (Wang et al., 2016).
(E) Directional transfer of oxygen bubbles in electromagnetic fields (rectangular cell) (Wang et al., 2016).
(F) Dendritic morphology of electrodeposited zinc in the electric field (Wang et al., 2015).
(G) Granule morphology of electrodeposited zinc in electromagnetic field (Wang et al., 2017).
(H) Charging voltage of a zinc-air battery in the magnetic field (Wang et al., 2018).
(I) ORR polarization curves of L10-PtFe NF before/after magnetization (Lu et al., 2020)
surface and zinc deposits upon these bubbles. In addition, zinc dendrites inevitably grow in alkaline solution at large currents (Oxley and Fleischmann, 1965), and cyclic plating/splitting, electron transfer ability, and limited diffusion of ions further promote dendrite growth, giving rise to short circuit of zinc based batteries. Pulse currents to a certain extent can provide additional time for free diffusion of ions and hydrogen bubbles detached from the depositing layer, demonstrating that the compacted morphology of depositing zinc can be obtained in an unsteady electric field (Figure 2B). Renewables like wind and solar PV electricity generation are frequently subjected to weather conditions, producing the fluctuating electric field. Amazingly, employing the unstable properties of solar or wind energy as charging zinc-air batteries is able to inhibit dendrite growth and bubbles coalescence.

Effects of magnetic field

Bubble growth and bubbles coalescence during OER/HER are bound to affect the following reaction at the electrode surface, increasing ohmic resistance, and energy dissipation. When a magnet is brought closer the electrode, gas bubble movements would be changed, as shown in Figures 2C, 2D, and 2E, displaying that the direction of gas bubbles in motion depends on magnetic poles (N/S), and disturbance intensity of gas bubbles is mostly proportional to the strength of the electromagnetic fields. In such, external magnetic fields can inhibit bubble growth and drive the bubbles away from the reaction sites, which is facilitated to promote oxygen evolution reaction (OER) and metal electrodeposition. An example of zinc electrodeposition in Figures 2F and 2G, illustrating that the granular morphology of electrodeposited zinc is obtained and looks sturdy in the magnetic field, whereas the dendritic morphology of zinc deposits gets formed and appears to be porous and loose without magnetic field. More importantly, directional movements of the bubbles in the magnetic field can enhance ion transfer, minimizing the concentration gradient. It is noted that varying electric field offers ions much time to diffuse naturally, whereas the magnetic field forces ions to transport in the electrolyte. Consequently, the applied pulsation currents and magnetic field all can reduce concentration polarization of ions, and the external magnetic field is more effective for enabling the process. As shown in Figures 2H and 2I, magnetic field can reduce charging voltage of a zinc-air battery because of oxygen bubbles detached from the electrode surface, and the ORR activity of magnetized L10-PtFe(M) NF is superior to that of both L10-PtFe NF and pure Pt film because of enhancement of oxygen adsorption ability.

Mechanisms of magnetic field on oxygen redox reactions

The oxygen molecules involved in the reduction reaction would be restricted to the non-catalytic area in the presence of magnetic moment perpendicular to oxygen molecular bond. Ferromagnetic catalyst after magnetism has a lower localized magnetic field in comparison to before magnetism (Figure 3A), encouraging the oriented chemisorption of paramagnetic oxygen toward the catalyst surface (Lu et al., 2020). Electron transfer ability between the catalyst and the chemisorbed reactants would be increased in the magnetic field (Zeng et al., 2018), as shown in Figure 3B, where electron transfer is mainly determined by the transition probability (Ren et al., 2021), and ferromagnetic delocalization and exchange interactions is favorable to transport charge, reducing Gibbs energy (Gracia et al., 2018; Aaboubi et al., 1990; Bund et al., 2003). Spin exchange between the ferromagnetic catalysts and the adsorbed oxygen reactants would occur, as illustrated in Figure 3C, inducing spin-dependent conductivity, reducing the rate-limiting bonding energies, and promoting the generation of parallel spin aligned oxygen by quantum spin-exchange interactions (Ren et al., 2021). Figure 3D displays that the ferromagnetic catalyst with spin alignment would thermodynamically promote OER, and the overpotential of triplet oxygen production is reduced by 200 mV in the magnetic field (Ren et al., 2021). OER includes ionic absorption and oxidation of hydroxyl ions, and O2 formation and adsorption at the electrode surface. Oxygen bubbles during OER would move at a certain direction in the magnetic field, illustrating that oxygen bubbles turn right when the N pole of the magnet is toward the air electrode, and these bubbles turn left when the S pole of the magnet is toward the air electrode. Directional movement of oxygen bubbles is stemmed from buoyancy and Lorentz force (Wang et al., 2020a, 2020b). Because ions would accumulate near the electrode at the action of electric field, ions around the bubbles give rise to ionic current when these bubbles are rising (Figure 3E), which can produce Lorentz force in the magnetic field and act on the bubbles. In addition, uniform distribution of magnetic domains in the magnetic field is conducive to hydrogel ions adsorption on electrode surface and promotes electron transfer, increasing local current density on the electrode surface (Garcés-Pineda et al., 2019; Qian and Bau, 2005). Figure 3F shows that physical resistance and reaction polarization during OER becomes low with increase of magnetic field intensity because of oxygen bubbles desorption and increase of current. Therefore, magnetic fields can enhance mass transfer and reduce polarization, promoting oxygen redox reactions.
Strategies for constructing magnetic zinc-air battery

In view of the above mentioned, magnetic field can improve electrode-electrolyte interfacial coupling, including removal of bubbles adhered onto the electrode, inhibition of dendrite growth, and reduction
concentration polarization of ions. More importantly, magnetic field can also accelerate electron transfer between ferromagnetic catalyst and the reactants. To establish magnetic zinc-air batteries for storing energy, four schemes are proposed in the following:

(1) Cylindrical electrodes placed within Maxwell or Helmholtz coils generate a uniform magnetic field. A structure of electromagnetic generator is shown in Figure 4A, noting that discrete electrodes are designed for fabricating zinc particles with the help of magnetic field, suppressing dendrite growth and avoiding dead zinc (Ma, 2015).

(2) Unsteady electric field of wind/solar energy would be converted into magnetic field according to Maxwell’s electromagnetic theory. Magnetic zinc-air batteries will be employed as a promising energy storage carrier of these new energy resources (Figure 4B), utilizing wavy characteristics of electric field to bring about magnetic field beneficial for charging.

(3) Air electrode magnetization, magnetic materials can be selected as catalysts supporter. Here we propose a coronary structure of catalyst, namely magnetic bead is applied as the core, and ORR/OER bifunctional catalysts are automatically absorbed upon magnetic bead (Figure 4C). Three-dimensional structure induced by a micro-nano magnet cannot only increase the active area of the catalysts but also directly change electron spin and orbital of the catalyst itself.

(4) Zinc-air batteries with external magnetic field (Wang et al., 2018). A permanent magnet needs to be placed at the external side of the batteries for improving interfacial coupling between electrode and electrolyte and promoting ions/electrons transfer, which is simple and convenient to disassemble and not subjected to climatic environment (Figure 4D).
CONCLUSIONS
Zinc-air batteries have received much attention in the fields of energy storage and power supply because of their high energy density, economic applicability, good safety, and environmental compatibility. The renewables, especially wind and solar PV will be applied on a large scale to meet the demand for carbon peak and neutrality in the near future. This perspective highlights the effects of magnetic field on dendrite growth and bubbles adsorption, acting mechanisms of magnetic field on oxygen redox reactions and design strategies for establishing magnetic field, which can offer an idea for designing future zinc-air batteries.

Increasing power density and extending cycle life of zinc-air batteries will be available for energy storage techniques. Future developments in zinc-air batteries should concentrate on optimization of electrode structure and composition. For air electrode, carbon materials need to be replaced by magnets for avoiding carbon corrosion, ORR/OER catalysts can be designed in accordance with spin and orbital theory of computational simulation, and uniform distribution of nanoscale catalysts loaded upon the magnets may be designed and fabricated by means of program-controlled technologies, achieving precise regulation of catalyst active sites. As for oxygen transport at large currents, the magnetic field for zinc-air batteries is required to be further intensified by way of electromagnetic conversion at the zinc electrode as well as the integrated structure of magnetic air electrode. Overall, building a magnetic field of zinc-air batteries that is composed of magnetic zinc electrode and magnetic air electrode is a key direction for improving the performance of the batteries.

Limitations of the study
ORR/OER mechanisms in the magnetic field need more analyses and discussions. The authors will revisit this topic again somewhere in the near future.

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AUTHOR CONTRIBUTIONS
K.W. conceived the concept of this study and completed the writing and revision of the paper. Y.Z., M.W., H.W., P.Z., Z.C., and N.S. collected and analyzed the data.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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