REVIEW

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A brief review on solar charging of Zn–air batteries

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This brief review reveals the possibility of solar charging of Zn–air batteries. It describes the various configurations that have been adopted in order to employ solar radiation to directly charge Zn–air batteries, paying particular attention to simple constructions with a minimum number of components. Solar charging is differentiated from solar batteries, which are based on a different concept and mainly depend on the variation of the redox level of added electrolytes.

Introduction

The intermittent nature of renewable energy resources as well as the expansion of mobile electronics and mobile energy demand necessitate parallel development of efficient and low-cost energy storage devices. Batteries are of course the obvious and direct means of energy storage and supply. Li-based batteries are the best known and currently in use devices; however, the cost of Li and some environmental and safety concerns have led to the study of other types of batteries. Zn–air batteries are among the most interesting for several reasons: Zn is abundant in the earth crust, therefore, not expensive and does not introduce any environmental or safety issues. Zn has been used to make a few different types of battery, for example, Zn–I$_2$ and ZnBr$_2$, Zn–Ni(OH)$_2$, Zn–air, *etc.*[1,2] One interesting feature of these batteries is that they are based on aqueous electrolytes,[2] which offers a further environmental advantage. In the present work, we will focus on Zn–air batteries, the most interesting and the most popular of all Zn-based batteries.[2–14] Zn provides a relatively high theoretical specific energy which mounts up to 1086 W h kg^{-1} and theoretical specific capacity[15] of 820 A h kg^{-1}. Zn–air batteries are in principle rechargeable, as it will be analysed here below. Therefore, they may be used to store electric energy. It is always possible to charge a Zn–air battery by using electricity from the grid or by combining it with a renewable energy source.[16] This possibility is practical but involves additional connection circuitry and substantial energy losses. Most interesting is the integration of the light conversion component with the electricity storage component in one single device. This possibility has been studied in several recent works and their results are summarized in the present work.

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Operation principle of Zn–air batteries

A schematic illustration of the components of a Zn–air battery is given in Fig. 1. It is made of a Zn foil anode and a gas-diffusion cathode both in contact with an alkaline electrolyte. Zn is oxidized to Zn(OH)$_4^{2-}$ which is finally decomposed to ZnO, liberating 2 electrons. Electrons move through an external circuit, thanks to a favourable potential difference with the cathode and there they assist oxygen reduction reaction. Oxygen comes from the air, hence the Zn–air functionality. The overall theoretical voltage produced by the battery is 1.65 V but because of losses it is usually 0.3–0.4 V lower. The chemical reactions involved are the following:[17]
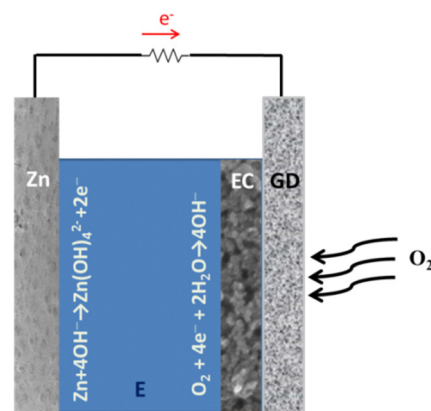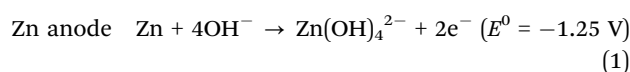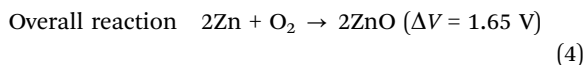
$$\text{Zn anode} \quad \text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \ (E^0 = -1.25 \text{ V}) \quad (1)$$
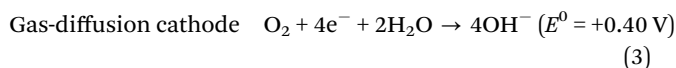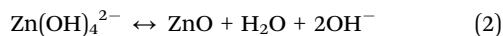

Fig. 1 Schematic illustration of a simple Zn–air battery functioning in the discharging mode: Zn is the zinc foil anode, GD the gas-diffusion electrode (cathode), EC the electrocatalyst deposited on the GD electrode and *E* the electrolyte.

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2OH^- \qquad (2)$$

Gas-diffusion cathode $\quad O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \; (E^0 = +0.40 \text{ V})$
$$(3)$$

Overall reaction $\quad 2Zn + O_2 \rightarrow 2ZnO \; (\Delta V = 1.65 \text{ V})$
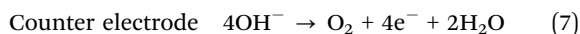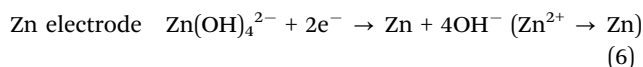$$(4)$$

All these reactions as well as the corresponding potentials are written for an alkaline electrolyte, which is the most common case.

Fig. 1 shows a cell with only one compartment but it is possible to separate the anode from the cathode compartment with an ion-transfer membrane. Reaction (3) is a 4-electron oxygen reduction reaction (ORR) which can take place in the presence of a powerful electrocatalyst. In the lack of such an electrocatalyst, another ORR might take place leading to the production of hydrogen peroxide:

$$O_2 + 2e^- + H_2O \rightarrow H_2O_2 + 2OH^- \; (E^0 = -0.15 \text{ V})$$
$$(5)$$
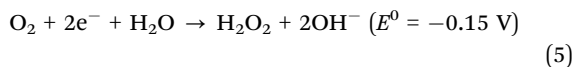
Even though, hydrogen peroxide hardly survives in an alkaline electrolyte, it may be harmful to the battery and will produce a lower overall voltage ($\Delta V = 1.10$ V); therefore, a good electrocatalyst is necessary for better battery performance.

Charging of the Zn–air battery corresponds to the reversal of reactions (1)–(3):[4]

Zn electrode $\quad Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^- \; (Zn^{2+} \rightarrow Zn)$
$$(6)$$

Counter electrode $\quad 4OH^- \rightarrow O_2 + 4e^- + 2H_2O \qquad (7)$

Charging then of the Zn–air battery means reproduction of Zn at the zinc electrode and oxygen evolution at the gas-diffusion electrode. The minimum electric bias necessary to achieve these reactions is 1.65 V. In reality, it is higher than 2 V[15,16] due to losses and mainly due to the overpotential necessary to achieve the energetically difficult 4-electron oxygen evolution reaction (OER). Various approaches have been adopted in order to decrease this large electric bias.[15–34] They will be reviewed here below.

Bifunctional and photo-assisted electrocatalysts for ORR and OER

In the most common case of a rechargeable Zn–air battery, the cathode electrode is the host of the oxygen reduction reaction in the discharging mode and the oxygen evolution reaction in the charging mode. A straight forward approach, in order to facilitate both charging and discharging functionalities, is to employ an electrode loaded with a bifunctional electrocatalyst capable of carrying out both ORR and OER. There have indeed been published several such cases. Benchmark electrocatalysts for both reactions are, of course, noble metals such as Pt or Ru/ Ir oxides.[35] However, these electrocatalysts are rare, therefore, expensive and do suffer of some serious problems such as agglomeration or contamination. For this reason, researchers have made a huge effort for developing noble metal substitutes. Electrocatalysts for OER and ORR are of course applicable not only to metal–air batteries but also to a broad range of other devices, notably fuel cells and electrolysers. Bifunctional OER and ORR electrocatalysts may be divided into two major categories: metal free and transition metal-based electrocatalysts.[35] However, no clear distinction can be made between the two categories since a large number of works simply refer to electrocatalysts which are made of materials chosen from both categories.

Metal-free electrocatalysts are those based on various carbon nanostructures: graphene, carbon nanotubes, biochar-derived activated carbon or simple graphite nanoparticles. Even though, graphene and carbon nanotubes remain always popular,[36–38] in recent years, there is a strong interest expressed towards carbon electrocatalysts obtained by pyrolysis of carbon-rich substrates including biomass-derived wastes.[39–48] The three principal properties of any electrocatalyst are electric conductivity, high active surface and presence of active sites which facilitate electron transfer from the solid to the liquid phase. Carbon based materials are conductive, except of course in rare crystalline forms like diamond, and when appropriately treated they are porous and have high active surface. The third property may be obtained by doping. Usual dopants of metal-free electrocatalysts are N, P, F, B and S. For this reason, most recent works focus on doping porous carbon.[36–41,43,45,48] These metal free bifunctional electrocatalysts sometimes outperformed noble metal electrocatalysts and provided long time stability under recyclyning of Zn–air batteries and a small ΔV gap between charging and discharging.[39] Biochars obtained by pyrolysis of biomass and further treated with KOH at high temperature obtain a hierarchical porous structure of very high active surface.[49] Such materials have so far received small attention as OER/ORR electrocatalysts[40,42,50,51] but it is expected that they will become much more popular in the near future. Their hierarchical micro–meso–macro-porous structure (cf. Fig. 2) creates a balance between the need for high active surface and the ability of electrolyte diffusion through the pores and this offers advantage to these materials which may prove effective in their role as electrocatalysts.

Transition metal-based materials are the most studied OER/ ORR electrocatalysts.[35,52] In reality, transition metal-based electrocatalysts always come in combination with carbon, therefore, this case actually concerns hybrid electrocatalysts.[6,53–63] Hybrid materials exploit the high active area of porous carbon and the enrichment with active sites offered by the presence of metals. Metals come in as metal particles,[56,61,62] alloys,[55,57,59] oxides[60] or two-metal oxides, like perovskites[54,58] or spinels.[53,54,63] Spinel oxides are of particular interest for the following reason. Spinels are oxides of two metals with a homonymous crystalline structure, for example, ACo_2O_4, where A = Mn, Co, Ni, Cu, Zn.[63] Substitution of A, in terms of element and percentage, leads to a regulation of the Co^{3+}/Co^{2+} ratio, therefore to optimization of the OER/ORR capacity of the electrocatalyst.[63] The same approach is also adopted in the case of perovskites, which are also oxides of two metals, for example $LaMnO_3$,[58] with a different crystalline form from that of the spinels. Again, the combination of two metals allows the regulation of the redox state of the active component in each case resulting in electrocatalyst optimization. There are works that report the employment of such electrocatalysts in
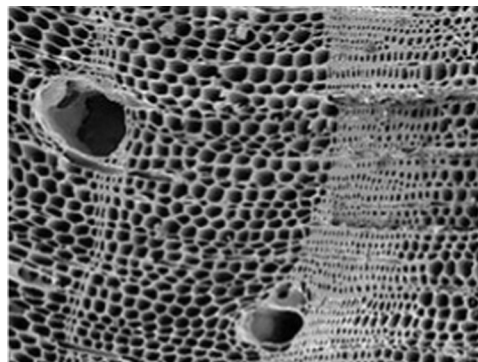
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Fig. 2 A typical SEM image of biochar.

Zn–air batteries that have outperformed noble metal electrocatalysts, again providing cycling stability and a small ΔV gap between charging and discharging.[54] Similar approach is also adopted in the case of metal alloys, for example NiFe alloys.[57] The combination of the two metals also allows regulation of their redox state. Metal alloys are more vulnerable to agglomeration and corrosion. For this reason, they are combined with N-doped carbon. The presence of N provides conditions for metal stabilization.

There is a class of bifunctional electrocatalysts which are photoactive.[15,22,23,25,26,29,31,32,34] One such case, is spinel-type Co_3O_4 which has a direct and indirect band gap in the range 2.2 to 1.35 eV,[15] therefore, it absorbs visible light. Co_3O_4 was employed as electrocatalyst in the air (cathode) electrode of Zn–air batteries and it was observed that the current produced under illumination was 30% larger than in the dark.[15] Similar behaviour was also observed with another spinel-type photo-electrocatalyst,[29] $NiCo_2S_4$, as well with a combination of $Ni_{12}P_5$ with nitrogen-doped carbon nanotubes.[22] In general, photoactive materials combined with the air electrode do result in improving the redox properties of a bifunctional electrocatalyst. However, an organic polymer semiconductor, polytritheophene, affected only ORR and had small effect on OER.[25] Ref. 6,10 are review papers with a detailed analysis on bifunctional electrocatalysts.

The above discussion shows that an efficient bifunctional electrocatalyst deposited on the air electrode of a Zn–air battery, can facilitate both ORR during battery discharging and the OER during battery charging. A benchmark of electrocatalyst bifunctionality is the small potential difference between galvanostatic charging and discharging and its stability through several charge–discharge cycles,[54] as already said. Nevertheless, there is an additional and different approach in dealing with Zn–air battery charging. So far the focus was placed on the electrocatalytic efficiency of the air-electrode. It is also possible to separate the two functions, *i.e.* the ORR from the OER, in different electrodes and substitute the energetically difficult OER by other processes, as will be detailed in the following section.

Solar charging of Zn–air batteries

Spatial separation of the charging from the discharging process opens the possibility for solar charging of the Zn–air battery.[16–20,33]

Fig. 3 shows a set up for such a case. This time, the cell consists of three electrodes and two compartments separated by an ion-transfer membrane. On the left is a transparent photoelectrode carrying a mesoporous photocatalyst. On the right is an air electrode which carries an ORR electrocatalyst. Zn electrode is in the middle. The two compartments can be filled with the same or different electrolytes. When functioning in the discharging mode, the cell operates as a regular Zn–air battery according to reactions (1)–(4). In the charging mode, the Zn electrode becomes the cathode, receiving electrons and reversing reaction (1), according to reaction (6). Metallic Zn is then deposited on the Zn electrode. These reducing electrons come from the photoanode which produces photogenerated charges by absorption of photons. Photons are absorbed by the photocatalyst generating electrons and holes. Holes oxidize water or, preferably, a sacrificial agent added in the electrolyte of the photoelectrode compartment. Therefore, electron–hole recombination is prevented and electrons are free to move through an external circuit and reach the Zn cathode and produce metallic Zn according to reaction (6). This corresponds to battery charging. The energy for charging comes directly from light; therefore, it may come from sun, hence solar charging. The advantage of this photoelectrocatalytic charging is that OER is in this case substituted by photocatalytic degradation of a sacrificial agent, which is much easier than the OER.[16] Such a solar charging model of Zn–air batteries has been applied in ref. 16–20. As a photocatalyst has been used mesoporous titania sensitized in the visible with CdS and CdSe photosensitizers. The bias necessary for solar charging is very small and in certain cases is zero.[18] This means that a Zn–air battery can be charged simply by exposing it to solar radiation.[18] The sacrificial agent can be any waste of biomass[16] or industrial origin.[18] This introduces an additional environmental benefit which may be exploited by the above process.

Even in the absence of any sacrificial agent, photoelectrocatalytic charging is still more efficient as far as the OER[23] is concerned, for the following reason. In the absence of a sacrificial agent, photogenerated holes oxidize water and produce O_2, *i.e.* OER is obtained photocatalytically.[23] The valence
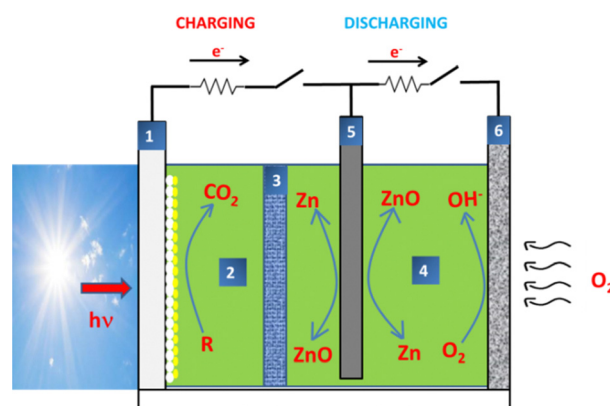
Fig. 3 Schematic illustration of a Zn–air battery with two compartments, three electrodes and separate discharging and solar charging functions: (1) photoelectrode carrying photocatalyst; (2) electrolyte of the photoelectrode compartment; (3) separation membrane; (4) electrolyte of the Zn compartment (5) Zn electrode and (6) air-electrode.

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band potential, which is approximately the potential of the photogenerated holes, is usually much more positive that the OH^-/O_2 potential (reaction (3)), *i.e.* 0.40 V in an alkaline electrolyte. Indeed, the valence band of a few characteristic semiconductor photocatalysts in alkaline environment is approximately located at: titania (+2.2 V); CdS (+1.0 V); $BiVO_4$ (+1.5 V), *etc.* Therefore, they are positive enough to facilitate photocatalytic water oxidation and OER.[12,14,23,33] Thus the photocatalytic process eliminates the problem arising with the overpotential for OER.

The driving force which moves photogenerated electrons towards the metal cathode must overcome the opposite bias generated by the presence of the electrolyte. In most cases, both the electrolyte in the photoelectrode compartment and the electrolyte in the Zn compartment are alkaline electrolytes. Therefore, the potential of reaction (1), and (6) is −1.25 V. The conduction band, for example, of photosensitized titania is located around −1.0 V in an alkaline electrolyte. In order then to overcome the opposing bias it is necessary to apply an external bias of at least 0.25 V, in reality, a bit larger. However, when aliphatic alcohols (and other fuels) are used as sacrificial agents, because of a phenomenon called "current doubling", which is due to injection of electrons by the oxidized fuel into the conduction band of titania, its electronegativity is increased.[64] This limits the potential difference and makes the need for external bias much smaller. Thus in Ref. 16 the bias tended to zero for small charging currents and never overpassed 0.5 V for larger currents.

The band structure of other photocatalysts may not be as favourably located and the necessary external bias is then much larger.[23] It is concluded, that with the above photoelectrocatalytic system, it is possible to solar-charge a Zn–air battery with minimal energy expenditure.

The disadvantage with the cell of Fig. 3, if any, is the need for employing 3 electrodes. If instead of three, two electrodes are used,[23] as in Fig. 4, solar charging is possible with a small external bias but discharging in the same device would

necessitate for the photoelectrode to act as an air electrode. Indeed, during charging, the photoanode produces electrons which carry reduction reactions (6) on the metal cathode. During discharging, Zn becomes the anode while the photoelectrode becomes the cathode, *i.e.* the air electrode. This is not at all efficient with a simple photoelectrode. This matter has been dealt with several studies.[2,12,13,23,32,33,65−71] Solar charging with the cell of Fig. 4 is in many ways associated with photo-assisted promotion of OER/ORR electrocatalysis discussed in the previous section.[15,22,23,25,26,29,31,32,34] OER is presently substituted by photocatalytic oxidation of water or, preferably, an added sacrificial agent. The main issue remains ORR on the photoelectrode. This problem can be partially solved by adding a ORR co-catalyst.[19] However, it remains an open question calling for further research.

In most cases related with Zn–air batteries, no issues arise with electrolyte, since the employed electrolyte is more or less a standard alkaline electrolyte. This is not the case with other type of batteries, for example, potassium metal batteries[72] or the redox batteries described in the next section.[73−76] Nevertheless, the composition of the electrolyte may play a role concerning Zn dendrite formation. Solar charging as well as any electric charging process faces a common problem of dendrite growth during metal Zn deposition.[7,21,24,27,77−83] Dendrite growth limits battery life and for this reason measures must be undertaken, such as use of mechanical obstacles, choice of the electrolyte, additives in the electrolyte, additives on the Zn surface *etc.*, in order to prevent dendrite growth. Table 1 gives a collection of recent publications and lists a series of methods which have been undertaken in order to prevent dendrite growth. Nevertheless, the low tension applied between the photoelectrode and the Zn electrode during solar charging may limit dendrite growth. This is a matter of investigation. An example of Zn deposition images following solar charging can be seen in Ref. 16.

Fig. 4 Schematic illustration of discharging and solar-assisted charging of a Zn–air battery made of a photoelectrode (left) and a Zn electrode (right).

Solar batteries

The term solar battery refers to a different configuration and operation principle from that of the above described solar charging or photo-assisted electrocatalysis. A solar battery may be schematically represented by Fig. 5. It is made of two compartments separated by an ion-transfer membrane.[69] The compartment on the left comprises two electrodes, a photoelectrode and a counter electrode, in contact with an electrolyte containing a redox couple C_{ox}/C_{red} (catholyte). The compartment on the right comprises one electrode, the anode, in contact with an electrolyte containing a redox couple A_{ox}/A_{red} (anolyte). Preferably, the redox potential of C is more positive than that of A. The photoelectrode can be a transparent electrode bearing a semiconductor photocatalyst. Upon absorption of photons, electron–hole pairs are generated. Holes are consumed by oxidizing $C_{red} \rightarrow C_{ox}$ and thus lowering the potential to more positive levels. Electrons move to the anode through an external circuit and reduce $A_{ox} \rightarrow A_{red}$ raising the
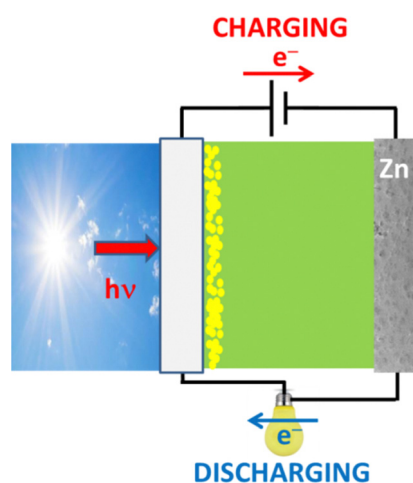
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Table 1 List of recently applied methods to prevent dendrite growth

Method	Ref.
porous nano-$CaCO_3$ coating	21
ZnO/graphene oxide coating	24
Synthesis of Zn-sponge electrodes	27
Preparation of a Zn–Sn alloy	77
Application of a magnetic field	78
Use of quasi-solid state CO_2-decorated highly conductive cellulose electrolyte	79
LDH-Array@PVA Gel Electrolyte and MXene/Zn Anode	80
Deposition of Zn on brass	81
Sn hollow microspheres on Zn and gel polymer electrolyte	82
Sn–Cu/reduced graphene oxide coating	83

potential to more negative levels. This operation corresponds to photo-assisted charging of the battery. In the discharging mode, electrons move from the anode to the counter electrode. The bias for this current flow is provided by the difference in the redox potential between the two electrolytes. Variants of the solar battery of Fig. 5 may involve a cathode electrode on the left side and a photoelectrode with a counter electrode on the right side or involve a tandem configuration with photoelectrodes on both sides.[69] It is also possible to drop the counter electrode and use only a photoelectrode combined with an anode (or cathode) electrode.[8] Most recently, the solar battery structure is further simplified by very effective 2-electrode configurations, such as the so-called photoelectrochemical redox battery of Ref. 73. The main difference with the devices of Fig. 3 and 4 is the fact that a solar battery contains redox species which reversibly store or release electrochemical energy by regressing between different redox levels. In the case of Zn–air batteries, for example, oxygen is consumed irreversibly during discharging while charging may not necessarily reproduce the consumed oxygen. Theoretically, the two cases are similar but in practice may be very different.

The first solar batteries were developed in the seventies using CdSe and Ag_2S/Ag as photoelectrode and anode electrode respectively, together with a polysulfide electrolyte.[74] The redox potential of the polysulfide electrolyte is −0.69 V while that of

Ag_2S/Ag is −0.45 V, therefore, their combination is thermodynamically favorable.[69] Since then, this field has enormously evolved and has produced a large number of publications which cannot be efficiently managed by this brief review. Nevertheless, it is worth mentioning some recent studies on solar batteries, not necessarily involving Zn. One such remarkable case is an all-vanadium photoelectrochemical flow cell, which combines a vanadium redox flow battery with a photoelectrochemical flow cell[75] as well as the above mentioned photoelectrochemical redox battery.[73] Utilization of all-vanadium redox couples[76] certainly simplifies solar battery construction possibilities.

Conclusions and perspectives

The present brief review has shown that it is possible to use solar energy to charge a Zn–air battery by employing a photoelctrochemical cell integrating both the solar conversion and energy storage components.

The main challenge in this type of integrated devices is the need for an external bias to overcome part of the opposing bias created by zinc electrode. An obvious suggestion is to employ a tandem electrode structure which may eliminate the need for an external bias, even though, this will necessitate additional components.
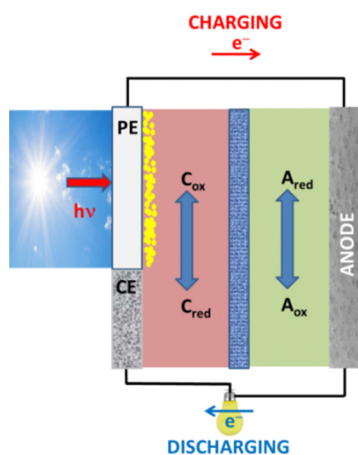
It is expected that research on bifunctional electrocatalysts will continue to lead the pace, as it is shown in recent publications.[84–87]

The problem of Zn dendrite formation during solar charging needs to be further elaborated since the related conditions present several particularities. Zn dendrite formation during battery charging depends on the applied voltage and the ensuing current. In the case of solar charging, the applied voltages are relatively small; therefore, dendrite formation in those cases needs specific elaboration.

Finally, solar charging of Zn–air batteries is so far distinguished from solar batteries which are based on photoelectrochemical redox functionalities.

Fig. 5 Schematic Illustration of a solar battery: (PE) photoelectrode; (CE) counter electrode. C (Catholyte) and A (anolyte) represent redox couples of different redox potential.

Conflicts of interest

There are no conflicts to declare.

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