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Introduction to Metal–Air Batteries: Theory and Basic Principles

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Nowadays, energy is the power engine that sustains the operation of our society. In the energy field, we are confronted with a daunting challenge caused by the gradual depletion of fossil fuel. To secure a safe and sustainable energy supply, renewable energies such as solar and wind have been developed. However, these energies are geographically limited and intermittent, thus calling for reliable electrical energy storage (EES) system for stable and efficient power delivery. Simultaneously, the growing number of transportation vehicles has made the development of reliable EES system a task of urgency. Among various EES systems, rechargeable batteries are the most promising to meet these needs thanks to their high energy density and high energy efficiency [1]. Among them, the lithium-ion battery (LIB), which is operated on the basis of intercalation mechanism, has played an important role in our society in the past two decades [2]. However, the low energy density of LIB has restricted its application as the energy supplier of next generation. Under this circumstance, the development of metal–air battery has provided a solution benefitting from its much higher energy theoretical energy density than that of LIB.

In contrast to the closed system of LIB, the metal–air battery are featured with an open cell structure, in which the cathode active material, oxygen, coming from ambient atmosphere. In general, the metal–air battery consists of metal anode, electrolyte, and porous cathode. Metals such as Li, Na, Fe, Zn, etc. can be used as anode materials in metal–air batteries. And the theory and battery electrochemistry will be briefly discussed on the basis of metal–air battery with different metallic anodes in the following section, which will be discussed in detail in the following chapters.

1.1 Li–O_2 Battery

Of all rechargeable metal–air batteries, the Li–O_2 battery (usually the aprotic Li–O_2 battery) possesses an ultrahigh theoretical energy density and is a promising EES. The theoretical energy density of the Li–O_2 battery can be

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around 11 586 Wh kg^{-1} based on the mass of Li metal alone. When the mass of Li and Li_2O_2 is involved, the theoretical energy density of the Li–O_2 battery is still as high as 3505 Wh kg^{-1}, which is much higher than that of LIB [3]. The exceptionally high energy density of Li–O_2 battery mainly originates from two aspects. First, oxygen, the cathode material, is sourced from outside environment rather than being stored within the battery, thus helping to reduce the weight of the assembled cell. Second, during discharge, the lithium anode can deliver an extremely high specific capacity and rather low electrochemical potential (−3.04 V vs standard hydrogen electrode (SHE)), ensuring a desirable discharge capacity and a high operation voltage, respectively [4]. The history regarding the development of Li–O_2 battery is introduced briefly as follows. The first prototype of Li–O_2 battery was reported by Semkow and Sammells [5]. In 1996, a Li–O_2 battery with polymer-based electrolyte was introduced by Abraham [6]. During the following couples of years, Read et al. have carried out relevant researches in the Li–O_2 field, and Bruce has demonstrated the rechargeability of the system [7–9]. Since then, numerous efforts have been devoted into the Li–O_2 field along with success of varying degrees. Currently, there are four types of Li–O_2 batteries under investigation, which can be categorized on the basis of the applied electrolyte species (aprotic, aqueous, hybrid, and all solid-state electrolytes) [10]. All the four types of lithium–air batteries use lithium metal and oxygen (air) as anode and cathode active materials, respectively. Their fundamental electrochemical reaction mechanisms are closely associated with the electrolytes used. Simultaneously, the schematic illustration of these four types of Li–O_2 batteries is provided in Figure 1.1, being able to provide the readers with an easy access to their configuration.

Compared with the Li–O_2 batteries with aqueous, hybrid, and solid-state electrolytes, the researches on the Li–O_2 battery has taken the dominant place. So in the following section, all the discussion is around the Li–O_2 battery with aprotic electrolyte. A typical Li–O_2 battery consists of a lithium-metal anode, a porous carbon cathode, and a separator saturated with aprotic electrolyte, which is shown in Figure 1.1. In principle, the Li–O_2 chemistry is based on the following conversion reaction: [11]

$$2Li + O_2 \leftrightarrow Li_2O_2 \quad E^0 = 2.96\,V \text{ vs } Li^+/Li \tag{1.1}$$

The ideal operation of a Li–O_2 battery is based on the electrochemical formation (discharge) and decomposition (charge) of lithium peroxide (Li_2O_2). The reduction proceeds through the following general steps:

$$O_2 + Li^+ + e^- \rightarrow LiO_2 \tag{1.2}$$

$$LiO_2{}^* + Li^+ + e^- \rightarrow Li_2O_2 \tag{1.3}$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \tag{1.4}$$

It is worthy to note that the growth process of Li_2O_2 is very complicated. Currently, two models of O_2 reduction have been proposed, including surface-growth model and solution-growth model. During discharge, O_2 undergoes a one-electron reduction to generate $O_2{}^-$. In the surface-growth model,

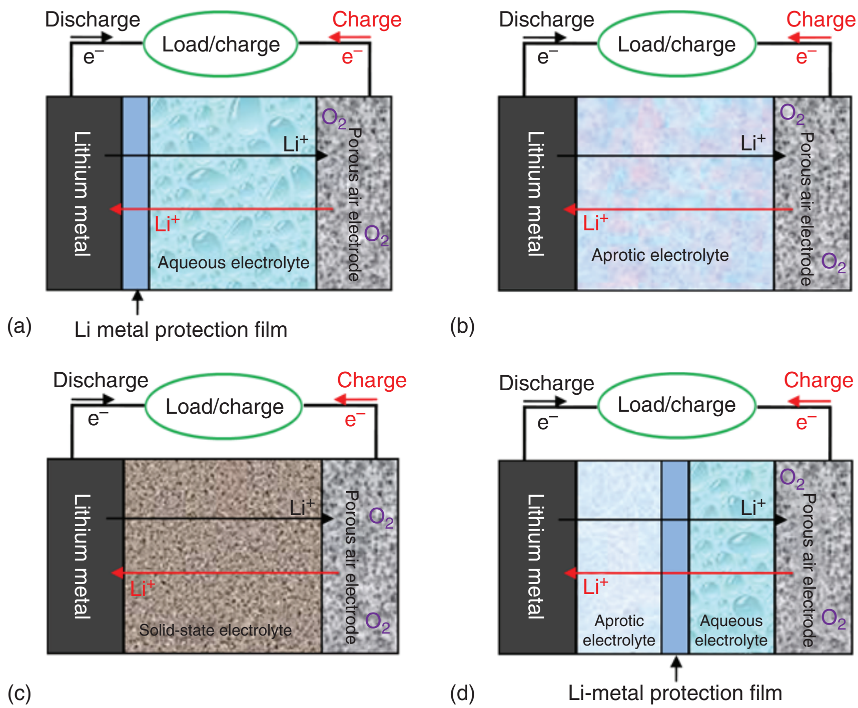

Figure 1.1 Schematic illustration of Li–O_2 battery based on (a) aqueous electrolyte, (b) aprotic electrolyte, (c) solid-state electrolyte, and (d) hybrid electrolyte.

the superoxide species (O_2^{-*} and/or LiO_2^*, where * indicates surface-adsorbed O_2^- and LiO_2) adsorb on the cathode surface and undergo a second reduction, forming Li_2O_2 thin films (thickness <10 nm) on the cathode surface, severely passivating the cathode and limiting the maximum battery discharge capacity [12, 13]. In contrast, in the solution-growth pathway, the generated LiO_2 is dissolved in the electrolyte, which undergoes disproportionation, ultimately forming large Li_2O_2 toroidal crystals of variable sizes (typically <2 μm) [14–16]. Clearly, the reaction pathways can be affected by the solubility of LiO_2 in the electrolyte, which can be decided by the equilibrium between LiO_2 adsorbed on the electrode and LiO_2 dissolved in the electrolyte solution. Such an equilibrium is listed below: [17]

$$LiO_2^* \leftrightarrow Li_{(sol)}^+ + O_{2(sol)}^- + \text{ion pairs} + \text{higher aggregates} \tag{1.5}$$

According to Johnson et al. [18], at high discharge voltages (low discharge overpotentials) and in solvent with high donor number (DN), such as 1-methylimidazole (Me-Im, DN = 47), the Li^+ or Li^+-containing species is solvated, and the equilibrium (1.5) is displaced to the right, yielding mainly soluble LiO_2. While in low DN solvents, such as CH_3CN (DN = 14), the solvation is weaker, and the equilibrium lies to the left, resulting in surface-adsorbed LiO_2 being dominant. In the latter case, the LiO_2^* disproportionates or undergoes a second reduction to Li_2O_2 on the electrode surface, whereas in the former pathway, disproportionation of LiO_2 in solution dominates, precipitating Li_2O_2. Similarly, Aetukuri et al. have prompted a solution-based mechanism with trace amount of electrolyte additives, such as H_2O, which increases the solubility of LiO_2 with the O_2^- acting as a redox mediator [19]. In addition, the reaction pathways can be affected by other factors such as current density, the cathode adsorption ability, etc. [20, 21] As a typical example, in 2013, Xu et al. have promoted the solubility of superoxide into the electrolyte with Pd nanocrystal [21]. In his research, two kinds of cathodes including hollow spherical carbon (HSC) deposited onto carbon paper (CP) cathode (HSC deposited onto CP) and palladium (Pd)-modified HSC deposited onto CP cathode (P-HSC deposited onto CP) are prepared. In the P-HSC deposited onto CP cathode, the strong binding of superoxide (O_2^- or LiO_2^*) with the carbon defect sites traps the superoxide on the cathode surface (a short diffusion path), leading to a poor superoxide availability on the prismatic crystal faces (a preferred nucleation site) and gives rise to the observed toroid aggregates for Li_2O_2. In contrast, in the P-HSC deposited onto CP cathode, the Pd nanocrystal surfaces are considered to be less sticky than carbon surfaces riddled with dangling bonds, which can weaken the binding of the generated superoxide to the substrate, thus enhancing the diffusion of the superoxide molecules away from the cathode surface, favoring the nucleation and crystallization of Li_2O_2 on the preferred prismatic crystal faces and leading to nanosheet-shaped structure growth.

The charge process of Li–O_2 battery involves the electrochemical decomposition of Li_2O_2 formed on the air electrode, which is accompanied by several metastable states. In a similar case to the discharge process, the charge process of Li_2O_2 decomposition is also very complicated, involving many steps. In this aspect, several points such as surface delithiation and bulk oxidation of Li_2O_2 proposed by Gallant [22], the promoted one-electron charge reactions [23], etc. have been provided. Of note is that these achievements are insufficient to clarify the intrinsic mechanisms involving the discharge and charge, thus calling for more relevant efforts.

Although the study on the Li–O_2 batteries has been ongoing over the past decade, they have been hindered from commercialization due to several practical challenges. First is the sluggish reaction kinetics that lead to a high charge overpotential, thus inducing electrolyte decomposition. The second problem is the poor conductivity of Li_2O_2. Catalysts have been incorporated to promote the formation of amorphous Li_2O_2, whose conductivity is better than that of crystalline Li_2O_2. The third problem is the high oxidative ability of these species, degrading cathode and electrolyte to give parasitic products, which can passivate the active sites. In this aspect, various strategies have been proposed to enhance the chemical stability of carbonaceous cathode and fabricated noncarbonaceous cathodes. In addition, various kinds of catalyst have been applied to accelerate the reaction kinetics. Simultaneously, the selection of highly stable electrolyte is also required. Of note is that the oxygen and ionic conductivity of the electrolyte are also parameters that can affect the battery performances. After all, a Li–O_2

battery with high performance depends on the interplay between the anode, the electrolyte, and the cathode rather than each in isolation.

1.2 Sodium–O_2 Battery

As mentioned in the above section, the Li–O_2 battery is viewed as a promising energy supplier of next generation. However, this battery suffers from terrible problems, including poor efficiency and low rate capability, which have restricted its practical application. Particularly, the serious charge overpotential over 1 V, the main reason for the low efficiency, also accelerates the degradation of the electrode and electrolyte. Under this circumstance, the Na–O_2 battery is viewed as a promising alternative of Li–O_2 battery, thanks to the merits of Na–O_2 battery compared with the Li–O_2 battery. In light of previous reports, the main advantage of a Na–O_2 battery is its much lower charge overpotential than that in typical Li–O_2 batteries. Simultaneously, in contrast to lithium, sodium resources are unlimited everywhere, and sodium is one of the most abundant elements in the Earth's crust [17].

In 2011, the first Na–O_2 battery with molten sodium anode is reported by Peled et al. [24] However, this battery is operated at above 100 °C, thus limiting its practical application in our daily lives. Luckily, later in 2012, a Na–O_2 battery constructed at room temperature is reported by Janek's group [25]. Since then, the researches in Na–O_2 battery conducted at room temperature have been surging. Currently, the Na–O_2 batteries can be split into two categories according to the used electrolyte, including nonaqueous and aqueous electrolyte [26]. It is worthy to note that the researches on the aprotic Na–O_2 battery have taken the dominant place, based on which all the discussions mentioned below are all around nonaqueous Na–O_2 battery. In a common configuration, the Na–O_2 battery comprises a sodium-containing anode (currently Na metal), a sodium-conducting organic electrolyte, and an air cathode. Unlike the cell chemistry in the Li–O_2 battery, where the targeted discharge product is only Li_2O_2, the discharge products in the Na–O_2 battery at least include Na_2O_2 and NaO_2. In detail, during discharge, the sodium metal anode is electrochemically oxidized to produce Na^+ ions, which migrates across the electrolyte to reach the cathode. Simultaneously, the oxygen gas (O_2) dissolved in the electrolyte is reduced to form superoxide species (O_2^-) or peroxide species (O_2^{2-}), generating sodium superoxide (NaO_2) or sodium peroxide (Na_2O_2), respectively. Upon charge, the generated NaO_2 or Na_2O_2 is decomposed with the release of O_2 and Na^+.

In terms of cell chemistry, the free enthalpy of formation of $\Delta_f G(Na_2O_2) = -437.5\ kJ\ mol^{-1}$ [27]. The standard open cell potential for the formation of Na_2O_2 is estimated to be $E(Na_2O_2) = 2.33$ V. And the theoretical energy density of a Na–O_2 battery based on Na_2O_2 can be ~1600 Wh kg^{-1}. In 2013, Li et al. reported the application of nitrogen-doped graphene nanosheets (N-GNSs) as cathode catalyst in the Na–air battery, which has promoted the formation and decomposition of Na_2O_2 [28]. In their study, N-GNSs displayed a discharge capacity two times greater than their pristine counterpart, as well as superior electrocatalytic activity as a cathode material for sodium–air batteries. The enhanced performance of N-GNSs is attributed to the active sites introduced by nitrogen doping. In another case, Liu et al. reported the formation of Na_2O_2 nanosheets, which grow on the $NiCo_2O_4$ nanosheets fabricated on Ni foam [29]. In this research, the Na–air battery based on the $NiCo_2O_4$ nanosheets exhibits an initial discharge capacity of 1762 mAh g^{-1} with a low polarization of 0.96 V at 20 mA g^{-1}.

In the pursuit of a Na–O_2 battery with excellent performances, the Na_2O_2 is not the desirable discharge product. Generally, the battery with Na_2O_2 shows poor reversibility and high overpotentials, similar to the problems in recharging Li–O_2 batteries [24, 30, 31]. In response, the generation of NaO_2 rather than Na_2O_2 should be promoted, given the fact that the charge and discharge overpotentials can be reduced to less than 200 mV when NaO_2 forms [32, 33]. From the thermodynamic point of view, NaO_2 is less stable than Na_2O_2. With a free enthalpy of formation of $\Delta_f G(NaO_2) = -437.5\ kJ\ mol^{-1}$, the formation of NaO_2 is energetically rather similar to that of Na_2O_2, with a small energy difference of only 12 kJ mol^{-1} [27]. This small difference is also expressed by the quite close standard open cell potentials, $E(NaO_2) = 2.27$ V and $E(Na_2O_2) = 2.33$ V. Theoretical calculations indicate that the relative thermodynamic stability of NaO_2 and Na_2O_2 depends on the crystallite size; nanosized NaO_2 appears to be more stable than Na_2O_2 of equal size, and nucleation of NaO_2 might thus indeed be favored [34, 35]. So far, various researches regarding the formation and decomposition of NaO_2 are reported. These products have been shown to have different morphologies: NaO_2 in micron-scale cubic shapes, nanorods, and conformal films.

Just like the case in Li–O_2 battery, it is critical to gain insights into the oxygen reduction kinetics in the presence of Na ions and the nucleation and growth mechanisms of discharge products. In 2015, Vitoriano et al. reported the rate-dependent effects on the size and distribution of the discharge product [35]. In addition, the type of solvent can affect the discharge reactions as well. In the report by Luntz et al. [36], strong solvent–solute interactions in long-chain ethers shift the formation of NaO_2 toward a surface process, resulting in submicrometric crystallites. In contrast, short chains, which facilitate desolvation and solution precipitation, promote the formation of large cubic crystals (c. 10 μm). In addition, the current rates are also reported to affect the growth of NaO_2 [35]. At low rates, the entire thickness of the carbon nanotube (CNT) carpet was more homogeneously covered with faceted nanoparticles. While at high rates, micron-sized cubes were formed on the top and bottom interfaces between the CNT carpet and electrolyte. In fact, nucleation and growth under electrochemical conditions are complex processes [37], and future mechanistic studies are required to obtain a more coherent picture. For these considerations, relevant discussions are only provided here.

Apart from the mentioned controversies, there is a general agreement in literature that Na–O_2 batteries can be a good alternative to overcome some of the drawbacks of Li–O_2 batteries. Thus, their promising electrochemical performance could open new opportunities beyond LIB. However, the development of sodium–air battery is still at its infancy, and more efforts are necessary to realize its practical application.

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