Recent Developments for Aluminum–Air Batteries

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Received: 28 June 2019 / Revised: 30 January 2020 / Accepted: 30 March 2020 / Published online: 9 May 2020
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Abstract

Environmental concerns such as climate change due to rapid population growth are becoming increasingly serious and require amelioration. One solution is to create large capacity batteries that can be applied in electricity-based applications to lessen dependence on petroleum. Here, aluminum–air batteries are considered to be promising for next-generation energy storage applications due to a high theoretical energy density of 8.1 kWh kg^{-1} that is significantly larger than that of the current lithium-ion batteries. Based on this, this review will present the fundamentals and challenges involved in the fabrication of aluminum–air batteries in terms of individual components, including aluminum anodes, electrolytes and air cathodes. In addition, this review will discuss the possibility of creating rechargeable aluminum–air batteries.

Keywords Aluminium air battery · Metal air battery · Anode · Air cathode · Secondary battery

1 Introduction

Climate change has become an acute environmental problem, and one of the main causes is the tremendous amounts of CO_2 gas emitted due to the explosion of human population and activity. One method to combat climate change is to suppress the consumption of petroleum as an energy and material resource through the development of renewable and sustainable energy sources for electric vehicles (EVs) and electrical energy storage systems. In terms of EVs, vital factors to assess market potential are the driving range as well as the vehicle price. Based on this, the development of low-cost batteries with high energy potential is a dominant research topic. Currently, the lithium-ion battery (LIB) is considered to be the most advanced and practical technology to be developed from small- to large-scale secondary batteries. However, the cost of LIBs is dependent on the cost of raw materials, including cathode and anode active materials, separators and electrolytes. In addition, the widespread adoption of LIBs in EVs is hindered by drawbacks such as safety concerns, limited driving ranges, slow charging times

and heavy battery packs [1]. Moreover, the energy density of LIB cathodes ranges from ~ 140 to 350 mAh g^{-1} for oxide cathodes and 370 to over 2000 mAh g^{-1} for anodes depending on the material (i.e., graphite and silicon), leading to LIB cell capacities ranging from ~ 100 to 250 Wh kg^{-1} , which are insufficient to meet the high energy and power density demands of modern EVs [2]. And although tremendous efforts have been undertaken to improve LIBs to provide greater energy capacity [3, 4], alternative strategies have also been proposed involving the creation of novel rechargeable batteries with sufficient theoretical energy densities for future applications [5]. Here, metal–air batteries have been intensively investigated over the last decade because of their high energy density and capacity as well as their relatively low costs in which the theoretical energy density of metal–air batteries can be 2- to 40-fold greater than that of LIBs. And of these different types of metal–air batteries, Li, Na, K, Zn, Mg, Fe, Si and Al air batteries have all been studied [6, 7] with each metal possessing advantages and drawbacks for use as anode electrodes. (Table 1 presents the voltage, theoretical specific capacity and energy density of typical metal–air batteries.) In general, metal–air batteries are composed of a metal anode, an air cathode and an appropriate electrolyte and possess high theoretical energy due to an open configuration in which oxygen can be directly absorbed from surrounding air. And among different types of metal–air batteries, Li–air batteries possess the highest theoretical energy density (11140 Wh kg^{-1}) [8]. However,

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Table 1 Comparison of various metal–air batteries with individual electrochemical properties

Metal air battery	Theoretical specific energy Wh kg ⁻¹ (including oxygen)	Theoretical specific energy Wh kg ⁻¹ (excluding oxygen)	Calculated open circuit voltage (V)
Calcium–air	2990	4180	3.12
Germanium–air	1480	7850	1.00
Iron–air	1431	2044	1.30
Aluminium–air	4300	8140	1.20
Lithium–air	5210	11140	2.91
Sodium–air	1677	2260	2.30
Magnesium–air	2789	6462	2.93
Potassium–air	935	1700	2.48
Zinc–air	1090	1350	1.65
Tin–air at 1000 K	860	6250	0.95

rechargeable Li–air batteries are difficult to obtain because of issues such as the blocking of air cathodes by discharge products as well as the instability of Li in humid environments that necessitates hermetical sealing in which Li metal is easily oxidized under ambient atmosphere. Alternatively, Al, Mg (2.20 Ah g⁻¹) and Zn (0.82 Ah g⁻¹) are all economically and environmentally friendly, abundant and relatively safe metals and in particular, Al is able to be recycled in large quantities in the modern world [9–11]. In addition, Al–air batteries possess a high theoretical voltage (2.7 V) and an energy density (8.1 kWh kg⁻¹) that are second only to Li of the various metal–air batteries and are large enough to be considered for next-generation rechargeable batteries. The basic structure of primary Al–air batteries is composed of an Al anode, an air cathode and an appropriate electrolyte and in general; the electrolytes used for primary Al–air batteries are aqueous solutions of sodium hydroxide (NaOH), potassium hydroxide (KOH) or sodium chloride (NaCl) [12] in which electrochemical reactions in alkaline electrolytes at the electrodes can be expressed as follows [13]:

As for neutral pH electrolytes such as sodium chloride, the reaction of Al is not completely clear due to mixed species on the Al surface, which can combine metallic Al–Al₂O₃–Al(OH)₃–H₅AlO₄, and other chlorinated complex species. And by taking the latter into account, the most extended and accepted reaction is described as follows [14]:

Al–air batteries were first proposed by Zaromb et al. [15, 16] in 1962. Following this, efforts have been undertaken to

apply them to a variety of energy storage systems, including EV power sources, unmanned aerial (and underwater) vehicle applications and military communications [17–20]. And in 2016, researchers demonstrated that an EV can drive over 3000 km with the use of an Al–air battery that weighed ~100 kg. Despite this, Al–air batteries still possess many challenges prior to practical application, such as the accumulation of byproducts [Al(OH)₃ and Al₂O₃] that can suppress Al–air battery electrochemical reactions. Based on all of this, this review will discuss the challenges associated with Al–air battery components including electrolytes, anodes and air cathodes to create better Al–air batteries. In addition, the possibility of rechargeable Al–air battery technologies will also be presented.

2 Electrolytes

The electrolyte is a main component of Al–air batteries, and the following section will present both aqueous and non-aqueous electrolytes used in these systems as well as additives that can influence battery properties. As for ionic liquid and deep eutectic solvent-based electrolytes for Al–air batteries, they are discussed in detail in the rechargeable Al–air battery section of this review.

2.1 Aqueous Electrolytes

Water-based aqueous electrolytes can be classified depending on their pH values as acidic (pH 2–7), neutral (pH 7) and alkaline (pH 7–13). Alkaline solutions such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) solutions are the most common electrolytes developed for use in Al–air batteries, and KOH-based electrolytes are more preferable than NaOH because of their higher ionic conductivity, lower viscosity, higher oxygen diffusion coefficient and faster reaction kinetics [21] in which an Al–air battery using

combination of the KOH alkaline electrolyte and the silver manganate nanoplate air cathode has recently been reported to be able to provide large specific cell capacities [22]. NaCl, a salt water electrolyte, has also been intensively studied for use as an Al–air battery electrolyte because of its abundance and safety in which if used, can provide a battery potential in the range of ~ 0.65 – 1.1 V for pure Al anodes. Previous studies have also noted the effects of NaCl concentration and battery operating temperature on the redox potential of Al anodes [23]. However, researchers have also reported that NaOH and KOH aqueous solutions can produce higher redox potentials in conjunction with Al anodes, which is one advantage of using alkaline solutions instead of salt water solutions (NaCl) [24]. Furthermore, researchers have demonstrated that dendrite formation on anodes and byproduct formation on cathodes can be suppressed through the use of acidic electrolytes such as hydrochloric acid and sulfuric acid [25]. Unfortunately, the use of acidic solutions can also result in corrosion issues for Al–air batteries.

2.2 Electrolyte Additives

Aqueous electrolytes face critical issues involving dendrite formation, electrode corrosion and hydrogen gas evolution. To address these issues, corrosion and hydrogen gas inhibitors can be used in which the basic mechanism of corrosion inhibitors is the adsorption of inhibitor molecules onto Al anode surfaces to suppress corrosion reactions. Based on this, various electrolyte additives have been actively studied. Here, Zn^{2+} , Sn^{3+} and In^{3+} ions have been studied as additives for neutral salt water solutions [26–28], whereas polyethylene glycol and ZnO have been used as additives for alkaline conditions [29]. For example, Wang et al. [29] demonstrated that the corrosion rate of Al anodes can be suppressed by mixing polyethylene glycol and ZnO additives with KOH aqueous electrolytes and Liu et al. [30] reported that the addition of CMC (carboxymethyl cellulose) and ZnO can also suppress the corrosion rate of Al anodes in which the self-corrosion of Al anodes in a NaOH alkaline electrolyte solution can be delayed. Here, these researchers suggested that the carboxyl group of the CMC can bind to anode surfaces strongly and interact with Zn^{2+} ions to allow for the formation of a complex film on the anode surface, thus stabilizing it (Fig. 1). Researchers have further reported that some inorganic additives can effectively prevent Al anode corrosion, although other studies have shown that inorganic chemicals such as chromates, vanadates, borates and hexafluoride silicates do not have significant inhibitory effects [31]. Moreover, organic additives can also effectively prevent Al anode corrosion [24, 32]. For example, Zhang et al. [33] tested three dicarboxylic acids including succinic acid, adipic acid and sebacic acid as additives for alkaline electrolytes and found that these three acids lessened

Fig. 1 Schematic of corrosion protection for AA5052 alloy anodes immersed in NaOH containing: **a** CMC, **b** ZnO and **c** CMC/ZnO. Reprinted with permission from Ref. [30]. Copyright 2016 Elsevier B.V.

hydrogen evolution and confirmed that adipic acid is the most effective anode corrosion inhibitor. Researchers have also reported that some aromatic carboxylic acids can also be effective in the suppression of Al corrosion in alkaline solutions through the adsorption of carboxylic groups onto Al surfaces and that similar effects can be observed in other metals under acidic conditions [34]. Furthermore, Mahmoud et al. [32] reported the influence of imidazole derivatives on the inhibition of Al corrosion in a 0.5 M HCl solution and suggested that the N atoms of the imidazole group can bind to Al surfaces to suppress corrosion. Interestingly, Wang et al. [35] suggested that amino acid and rare-earth metal complexes such as L-cysteine and cerium nitrate can also suppress Al anode corrosion and hydrogen gas evolution by forming a complex film on anode surfaces in a 4 M NaOH alkaline solution and Wang et al. [36] applied a KOH solution in water with methanol as an electrolyte for comparison

and found that the methanolic KOH solution delayed anode corrosion and that corrosion rates increased as the solution water content increased. Kang et al. [37] also reported that calcium oxide and L-aspartic can suppress the corrosion of Al anodes in NaOH alkaline media. Overall, all of these results suggest that various types of Al corrosion and hydrogen gas evolution inhibitors exist and can have practical use. More recently, Hopkins et al. [38] also created a new Al–air battery system using non-conducting oil instead of a liquid electrolyte during battery standby and reported significant Al anode corrosion suppression effects (Fig. 2).

2.3 Solid Electrolyte

Solid-state Al–air batteries are ideal because of their robustness, thermal stability and possible prevention of electrolyte

leakage. Based on this, polymer-based electrolytes have been reviewed for their use in Al–air batteries [39, 40]. For example, Tan et al. [41] investigated acrylamide-based polymer gels (Fig. 3) and Ma et al. [42] applied a solid electrolyte composed of acryl resin containing inorganic materials including Sn, Zn and In in an Al–air battery combined with an air–cathode material composed of iron carbide. Di Palma et al. [43] also used xanthan and κ -carrageenan as hydrogel additives and found that these additives were conductive toward Al ions in which the performances of these additives were compared and their conductivities were in the order: the 1 M KOH liquid electrolyte < xanthan 8 M KOH < κ -carrageenan 8 M KOH. Furthermore, Peng et al. [44] studied a new type of all-solid-state fiber-shaped Al–air battery with high energy density and Mori et al. [45] prepared an all-solid-state Al–air battery with deep eutectic

Fig. 2 Oil displacement method. **a** Schematic of a conventional flowing electrolyte metal–air battery, **b** schematic of the constructed oil displacement system for a flowing electrolyte metal–air battery. Here, the electrolyte is continuously pumped during operation and if not in use, oil is pumped to displace the corrosive electrolyte for a specified duration, **c** schematic of the constructed oil displacement system if not in use with a magnified view of the interface of the metal electrode and the separator, **d** voltage versus time for on–off cycling of a primary Al–air battery with **a** the conventional cell design and **(b, c)** the constructed cell design. Current densities of 150 mA cm^{-2} were drawn for 5 min with 24- or 72-h pauses during which no current was drawn. The conventional cell stopped operating at the start of day 3, yielding an energy density of $0.40 \pm 0.07 \text{ Wh g}_{\text{Al}}^{-1}$. Reprinted with permission from Ref. [38]. Copyright 2018 American Association for the Advancement of Science

Fig. 3 Schematic of a metal–air battery with a freestanding polymer gel electrolyte. Reprinted with permission from Ref. [41]. Copyright 2018 Elsevier B.V.

solvents. Despite these results, however, solid-state electrolytes can also increase battery resistances, which can result in lowered battery capacities as compared with those fabricated by using liquid-form electrolytes. Based on this, further studies need to be carried out to create high-performance solid-state Al–air batteries.

3 Anode Materials

Al anodes in Al–air batteries have been intensively studied because of their critical impact on performance in which main goals are to prevent corrosion and hydrogen evolution as well as to improve electrochemical properties such as electrolyte current density. Based on this, this section will describe the effects of pure Al anodes and alloy anodes of different metals with Al. In addition, this section will also discuss the influences of additives and coating materials on Al anodes.

3.1 Pure Al

In general, pure Al can exhibit better anodic performances than Al anodes with impurities. For example, Cho et al. [19] used 99.5% purity Al (2N5 commercial grade Al) as an Al anode in an Al–air battery with a NaOH alkaline electrolyte and found that the battery performance of 2N5 Al was inferior to that of 4 N high-purity Al (99.99%) because of the existence of a complex impurity layer that can reduce the discharge voltage. However, Wen et al. [46, 47] studied the effects of combining other metals with Al and found that Al–Mg–Ga–Sn–Mn anodes were more active than Al, Zn or Al–Mg–Ga–Sn anodes in which self-corrosion rates were found to be in the order: $\text{Al} < \text{Al–Mg–Ga–Sn–Mn} < \text{Al–Mg–Ga–Sn} < \text{Zn}$. In addition, these researchers also observed that Al–air batteries based on Al–Mg–Ga–Sn–Mn anodes can provide higher operating voltages and anodic utilization as compared with those using other anodic materials. In a further study, Pino et al.

[48] compared commercial Al alloys including Al 2000, Al 2000 clad and Al 7000 as anodes in alkaline electrolytes and found that Al 2000 was ideal because it can exhibit higher open-circuit potentials, better anode efficiency and minimal corrosion rates. Furthermore, Mutlu et al. [49] investigated the effects of Al anodes treated with Cu through chemical and electrochemical processes on battery performance and found that Cu can improve anode efficiency by promoting the dissolution of Al according to battery reactions. Moreover, Ocon et al. [17] confirmed that carbon-treated commercial Al alloy anodes can achieve discharge rates up to three times higher than those without carbon on anode surfaces (Fig. 4).

For normal Al–air batteries, several issues exist, including: (1) the formation of byproducts such as Al_2O_3 and $\text{Al}(\text{OH})_3$ on electrode surfaces that can suppress Al–air battery electrochemical reactions, (2) hydrogen evolution resulting from parasitic corrosion reactions on Al surfaces and (3) the formation of corrosion products such as $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_3$ [50]. This parasitic chemical side reaction can be expressed as:

and can induce passivation and corrosion on Al anode surfaces to further suppress electrochemical reactions and often occurs in electrodes containing aqueous electrolytes. Furthermore, this passivation film is mainly composed of Al_2O_3 and $\text{Al}(\text{OH})_3$ and can induce positive shifts in the corrosion potential of Al electrodes, which can cause failure in corresponding Al–air batteries [17].

From a morphological point of view, Fan et al. [51, 52] studied the effects of grain size on Al anodes and found that the electrochemical properties of Al anodes are related to grain size in which finer grain-sized anodes demonstrated suppressed hydrogen evolution, improved electrochemical activity and increased anodic utilization in alkaline electrolytes. As for crystallinity, Fan et al. [53] also investigated the electrochemical properties of polycrystalline Al including

Fig. 4 Schematic of Al accumulation in Al–air batteries with and without carbon treatment. Reprinted with permission from Ref. [17]. Copyright 2016 Elsevier B.V.

Al (001), (110) and (111) single crystals and reported that the electrochemical properties of Al anodes were closely related to crystallographic orientation in alkaline electrolytes in which the (001) crystallographic plane demonstrated good corrosion resistance, but the (110) crystallographic plane was more sensitive. And as a result, Al (001) single crystals displayed higher anode efficiency and capacity density, proving that the control of the crystallographic orientation of Al anodes is a viable method to improve the performance of Al–air batteries using alkaline electrolytes (Fig. 5).

3.2 Al Alloys

Despite their promising characteristics, pure Al materials are unstable as anodes in Al–air batteries and a common method to improve electrochemical property involves the

use of Al alloys. Based on this, numerous studies have been conducted to create better performance Al anodes by mixing Al with other metals such as Mn, Mg, Bi, In, Sn, Zn, Ga and Ti. And thus far, Al–Ga, Al–Sn, Al–Zn and Al–In alloys have been actively developed and have shown relatively high Al anode performances [23, 26, 54–57]. For example, Jingling et al. [58] investigated the electrochemical and corrosion performances of Al–0.5Mg–0.1Sn–0.02In–0.1Si and Al–0.5Mg–0.1Sn–0.02Ga–0.1Si alloys in both NaCl and NaOH electrolytes and found that the electrochemical properties of the Al–0.5Mg–0.1Sn–0.02Ga–0.1Si alloy were better in a 2 M NaCl solution, whereas the Al–0.5Mg–0.1Sn–0.02In–0.1Si alloy exhibited better performances in a 4 M NaOH solution. In another example, Ma et al. [59] reported that Si was effective at decreasing self-corrosion rates in which the anode properties of Al–Mg–Sn

Fig. 5 Effects of crystal orientation on Al anodes of Al–air batteries in alkaline electrolytes. Reprinted with permission from Ref. [53]. Copyright 2015 Elsevier B.V.

based alloys were examined. Here, these researchers reported that a Mg–6%–Al–3%–Zn–1.0%–In alloy was an optimal anode material for both cathodic protection and as a source of power.

In terms of the effects of individual elements, researchers have reported that Ga can suppress the formation of oxide film passivation in chloride solutions by becoming activated on Al surfaces and Sn can enhance Al anode dissolution rates and reduce corrosion rates [12]. Furthermore, Zn has been reported to be able to suppress hydrogen evolution on Al anodes by enhancing hydrogen evolution reaction (HER) potential and decreasing anode deterioration [60] and In can increase hydrogen evolution overpotential. For example, Sun et al. [61] reported that the addition of 0.5 wt% In to Al anodes can result in lowered corrosion rates and higher anodic efficiency as compared with pure Al. Here, this type of Al is referred to as a sacrificial anode, which can generally suppress the formation of passivating layers on Al surfaces. Furthermore, researchers have reported that further improvements in Al–air battery properties can be obtained by covering Al anodes with oxides or carbonaceous film layers [62–67].

4 Air Cathode

The properties of Al–air batteries are largely influenced by air–cathode catalytic materials, making air cathodes vital components. In general, an air cathode is composed of a current collector, a gas diffusion layer and a catalyst. Here, a current collector is normally composed of a stainless steel or Ni metal mesh and functions to transfer electrons and electricity and to connect to external electrical circuits [61, 68, 69]. Recently, Ti and Mo metals as well carbon meshes have also been used to prevent corrosion, especially from AlCl_3 -based electrolytes in rechargeable Al–air batteries. In terms of gas diffusion layers, they allow metal–air batteries to not only absorb air from ambient atmosphere but also seal batteries to prevent the leakage of liquid electrolytes, making their careful preparation a necessity. And in general, gas diffusion layers are usually composed of carbon or catalytic materials as well as hydrophobic binders such as polytetrafluoroethylene (PTFE) [70, 71]. As for catalytic materials in air cathodes, they can greatly influence the properties of corresponding metal–air batteries. And although carbon and manganese-based materials have often been applied as catalysts, many challenges associated with the use of other catalytic materials remain unresolved as described in the following section. Overall, however, catalytic materials are often mixed with binders and printed or placed onto current collectors in which the main chemical reaction catalyzed is the oxygen reduction reaction (ORR) [8, 10, 72]. Because air cathodes can greatly affect the properties of metal–air

batteries, they must be optimized. This can be achieved by enhancing ORR, reducing carbonate and byproduct formation, preventing electrolyte evaporation and avoiding air–cathode flooding [21].

4.1 Al–Air Battery Electrochemical Reactions in Aqueous Electrolytes

The following reactions occur in the aqueous electrolyte of metal–air batteries during discharge [73]:

Anode:

Air cathode:

The following reactions occur during charge:

Air cathode:

Although metal reduction reaction is feasible in Zn–air batteries with KOH aqueous electrolytes, the reduction of Al^{3+} to Al is generally not possible in aqueous electrolytes in the case of Al–air batteries [24, 74]. However, if ionic liquid and deep eutectic solvent-based electrolytes are used in Al–air batteries, metal reduction reaction becomes possible. Rechargeable Al–air batteries are discussed in more detail in Sect. 5.

And based on Eq. (6), ORR is the critical cathodic reaction in Al–air batteries in which in aqueous electrolytes, ORR proceeds through a multi-electron chemical reaction that occurs at the cathode with two main possible pathways, including the transfer of 2e^- to produce peroxide (H_2O_2) and the production of water through direct 4e^- transfer as expressed by the following equations [75]:

Direct 4e^- pathway:

2e^- pathway:

Here, the 4e^- pathway is preferable because the 2e^- pathway produces H_2O_2 , which is detrimental to air–cathode materials.

4.2 Catalysts

Because catalysts can greatly influence the properties of metal–air batteries, their improvement is of great interest. And because the reaction kinetics of ORR is often slow due to overpotentials [76], optimized catalysts that can reduce overpotentials and enhance ORR are vital for metal–air batteries and Al–air batteries. Based on this, numerous studies have been conducted to explore viable ORR catalysts, including precious metals and alloys, metal macrocyclic compounds, carbonaceous materials, transition metal oxides, chalcogenides, etc. (Fig. 6) [7, 13, 77–79].

4.3 Noble Metals and Alloys (Pt-Based Catalysts)

Noble metals including Pt, Pd, Au and Ag have all been actively investigated because they can exhibit strong catalytic activities in metal–air batteries as well as in fuel cells due to the vacant state of the unoccupied d-orbitals, allowing them to be able to readily absorb reactant molecules [80–83]. And because activity is largely affected by the surface atomic configuration and the electron level state, the modification of electronic states can improve the catalytic activity of precious metal catalysts. Overall, Pt has been the most extensively studied noble metal catalyst in the past decades because of its excellent catalytic activity. Here, researchers have focused on catalytic activity and its dependence on Pt particle size and crystallographic facets [84, 85] in which the binding strength between Pt atoms and reactant species

Fig. 6 I - V / I - P curves of Al–air batteries with different ORR catalysts. To evaluate the catalytic activities of different catalysts, Al–air batteries using LAM ($\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$), (LAM)-0 ($x=0$), LAM-30 ($x=0.3$), LSM-30 ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) and Ag as ORR catalysts were measured and their I - V / I - P curves are shown. The maximum power density (P_{max}) of the battery using high-purity Al (99.99%) as the anode with the LAM-30 catalyst can reach 230.2 mW cm^{-2} , which is the highest among the four batteries. Reprinted with permission from Ref. [78]. Copyright 2011 Royal Society of Chemistry

can determine ORR catalytic activity on different crystallographic facets in the order: $\text{Pt}\{100\} < \text{Pt}\{110\} < \text{Pt}\{111\}$ [86, 87].

And although many challenges exist in the use of Pt catalysts, including the regulation of facet distribution and control of particle size, they are overshadowed by the essential problem arising from the high cost and scarcity of Pt as a limited natural resource. Therefore, the preparation of efficient Pt-based catalysts with minimal Pt loading is vital. One effective method is the deposition of Pt onto catalytic supports with large surface areas such as carbon (Fig. 7) [88–90]. In addition, Wang et al. [91] reported that the catalytic activity of Pt metal alloys can be higher than that of pure Pt as a result of an interesting phenomenon involving electronic ligands and compressive strain in which Pt lattices can be decreased and Pt d-orbital filling can be altered by incorporating transition metal atoms with different electronegativities into Pt lattice structures, allowing for higher catalytic activities than that of pure Pt. Furthermore, as other metals are mixed or doped with Pt metal catalysts, catalytic activities become dependent on the particle size, structure, chemical composition and electronic structure of these metals [92–96]. Based on this, researchers have incorporated Co, Fe, Ni, Ti and V into Pt structures to investigate their effects on Pt alloys. And in the case of a Pt–Ni alloy, a 9 nm octahedral Pt–Ni catalyst demonstrated optimal catalytic performances [97] and octahedral Pt–Ni nanoparticles possessed stronger ORR activities as compared with cubic structured Pt–Ni nanoparticles, suggesting that catalytic activity depends on both catalyst size and crystalline structure [98]. Despite these performances, however, catalytic activities can deteriorate during long-term ORR processes because of the weak durability of mixed transition metals. To address this, researchers have proposed core–shell-type

Fig. 7 Electrodeposited Pt sub-nanoclusters on pristine and N-doped single-walled carbon nanotubes (SWCNTs) as bifunctional cathodes for Li-O_2 batteries. Reprinted with permission from Ref. [88.] Copyright 2016 American Chemical Society

catalysts to prevent damage to transition metals on catalyst surfaces and to reduce Pt consumption in which in this configuration, Pt can only be used at the surface of the catalyst [99–106].

4.4 Transition Metal Oxides

Although Pt and other metal-mixed or doped Pt alloy catalysts possess excellent ORR catalytic activities, their practical use in metal–air batteries and polymer electrolyte fuel cells is limited due to high costs and low natural abundance. As a result, tremendous efforts have been undertaken to explore alternative catalysts with high performance and low costs. Here, catalysts based on transition metal oxides are good options because of their high abundance and low costs. And based on this, early transition metal elements such as Fe, Mn, Co and Ni have been actively studied. For example, Mn-based oxides have been studied intensively as electrocatalyst materials because they possess relatively high ORR activities [107–114]. And because the valence states of Mn can exist as Mn(II), Mn(III) and Mn(IV), many manganese oxides can be obtained, including MnO, Mn₃O₄, Mn₅O₈, Mn₂O₃, MnOOH and MnO₂ [115]. These multiple options for the valence and crystal structures of these transition metal oxides can provide great potential to create high-performance non-precious metal catalysts. And although the chemical composition of the various manganese oxides is identical to that of MnO₂, different orientations can exhibit different catalytic activities because of differences in electrical conductivity and intrinsic tunnel size in the order: α -MnO₂ > δ -MnO₂ > γ -MnO₂ > λ -MnO₂ > β -MnO₂ [116]. Researchers have also reported that the ORR activity of MnO₂ can also differ based on morphology, including nanoflakes, nanowires and hollow spheres and attributed this to the differing amounts of Mn³⁺ on the surfaces of variable morphology [117, 118]. Other transition

metal oxides, such as iron oxides [119], copper oxides [120], titanium oxides [121], cobalt oxides [122], nickel oxides [123] and cerium oxides [124], have also been studied in terms of their ORR activity, and researchers have reported that Co₃O₄ is a promising catalytic material among these transition metal oxides because of its high catalytic activity and low costs [125–130] in which the catalytic activity of Co₃O₄ depends on its corresponding crystalline facets and is in the order: (111) > (100) > (110) due to surface Co²⁺ ions [131]. Researchers have also reported that transition metal oxide catalysts possess low electrical conductivities, including Mn- and Co-based oxide catalysts and therefore, these catalysts are often combined with carbon-based support materials to enhance electrical conductivity for practical use [132–140].

Perovskite oxides (ABO₃, A is a rare-earth metal and B is a transition metal) are a crystal structure of metal oxides that can exhibit bifunctional catalytic activity for both ORR and oxygen evolution reaction (OER) as catalysts. The ORR mechanism of perovskites is complex, and various factors such as surface absorption and electric conductivity can influence catalytic activity. Here, researchers have reported that ORR activities increased in the order of LaCoO₃, LaMnO₃, LaNiO₃, LaFeO₃ and LaCrO₃ among LaMO₃ (M = Ni, Co, Fe, Mn, and Cr) (Fig. 8) [141] and that a combination of individual perovskite catalysts such as LaNiO₃ and LaMnO₃ can produce synergetic effects to allow for good bifunctional catalysts by combining the high conductivity of LaNiO₃ with the high ORR catalytic property of LaMnO₃ [142]. Takeguchi et al. [143] also used a Ruddlesden–Popper-type layered perovskite (RP-LaSr₃Fe₃O₁₀) as a reversible cathode catalyst for both ORR and OER and reported an equilibrium potential of 1.23 V with negligible overpotentials in which its ability to remove oxygen was suggested to be one of the reasons that both reversible ORR and OER were achieved with good efficiency.

Fig. 8 Current voltage curves of Al–air batteries prepared with air cathodes composed of different perovskites, including LaCoO₃, LaMnO₃, LaNiO₃, LaFeO₃ and LaCrO₃. Reprinted with permission from Ref. [141]. Copyright 2012 American Chemical Society

Among transition metal oxide crystalline structures, spinel oxides (AB_2O_4) are also promising catalysts. Spinel oxides possess a cubic close-packed lattice structure with oxide anions in which one-eighth of the tetrahedral sites are occupied by A atoms and half of the octahedral sites are occupied by B atoms [144]. For example, $CoMn_2O_4$ has shown promise as a bifunctional catalyst for both ORR and OER in alkaline solutions [145]. And along with the above-mentioned perovskite catalysts and other transition metal oxides, spinel oxides also suffer from intrinsically low electrical conductivities and therefore are also commonly applied in combination with conductive carbon-based materials (Fig. 9) [146–155].

4.5 Carbonaceous Nanomaterials

Carbonaceous nanomaterials such as graphite, graphene and carbon nanotubes are promising metal-free ORR catalysts or supports because of their high electronic conductivity, large specific surface areas, environmental acceptability and corrosion resistance [156–161] and can be classified by their dimensional structure, including 0D fullerene, 1D carbon nanotubes, 2D graphene and various 3D nanostructured materials. As a result, carbon nanomaterials have been reviewed extensively and their catalytic activities have been

studied in terms of the intermolecular charge-spin redistribution for ORR/OER/HER and in fuel cells [144].

4.6 Carbon Nanotube and Graphene-Based Nanocomposites

The structure of graphene involves one-atom-thick planar sheets composed of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice and recently; graphene has been intensively studied as an ORR catalyst in which significant catalytic activity improvements have been observed without the use of large quantities of Pt or noble metals [162–167]. In addition, Co_3O_4 and graphene composite catalysts have also shown high catalytic activities, demonstrating the possible synergetic chemical coupling effect between Co_3O_4 , N and graphene toward enhanced ORR and OER [168, 169]. A combination of Mg and graphene has also been reported to be a promising material that can produce high performances in which Kosasang et al. [170] prepared a reduced graphene oxide and manganese oxide composite catalyst and reported a dominant $4e^-$ pathway mechanism. As for carbon nanotubes (CNTs), they can be used as good support materials for catalysts because of their high specific surface areas, porous structure and high conductivity (Fig. 10) [171–174]. For example, Yoon et al.

Fig. 9 TEM and HRTEM images of **a, b** LMO/rGO and **c, d** LMO/N-rGO. The insets of **b, d** are selected area electron diffraction (SAED) patterns. Reprinted with permission from Ref. [149]. Copyright 2015 Elsevier B.V.

Fig. 10 **a** Schematic of the formation of MnO₂/CNTs, **b** XRD patterns of MnO₂, CNTs and MnO₂/CNTs, **c** crystal structure of tunnel MnO₂. TEM images of **d**, **e** MnO₂ and **f**, **g** MnO₂/CNTs. **h** N₂ adsorption isotherms and the inset is corresponding surface areas of MnO₂

and MnO₂/CNTs. XPS spectra of MnO₂/CNTs **i** Mn 2p and **j** O 1s. **k** Schematic of OER and ORR processes catalyzed by MnO₂/CNTs. Reprinted with permission from Ref. [173]. Copyright 2019 American Chemical Society

[134] applied a Co₃O₄ and CNT composite as a Li–air battery air cathode and reported high discharge capacities and low over-voltages, demonstrating the promising performance of the CNT/Co₃O₄ composite as a Li–air battery air electrode. In another study, Ni et al. [175] prepared a manganese oxide and CNT composite as a Li–air battery air cathode and reported enhanced catalytic activities and the formation of confined Li₂O₂ particles that can reduce the charge potential of Li–O₂ batteries due to the synergistic effects of the intrinsic catalytic activity of MnO₂ and the fewer oxygen functional groups on the catalyst surface.

4.7 Metal–Nitrogen–Carbon and Heteroatom-Doped Carbon

Metal–nitrogen–carbon materials are regarded as excellent low-cost ORR catalysts with high performances and generally involve metals such as Ni, Co, Fe, Mn, Cr and V. These materials are usually prepared by pyrolyzing N-rich metal complexes with carbon or by using metal salts, carbon and N-rich precursors as raw materials [176]. Here, the catalytic activity of these M–C–N catalysts is largely influenced by

M and N precursors as well as pyrolysis temperatures in which appropriate pyrolysis temperatures are in the range of 700–900 °C. In alkaline media, the activity of M–C–N catalysts (M is V, Cr, Mn, Fe, Co or Ni) follows the order: Co > Ni > Mn > V > Cr, whereas in acidic media, the order follows: Fe > Co > Cr > Ni [177]. And although the mechanisms of active sites in M–N–C catalysts remain unknown, M–N moieties and N dopants that exist in carbonaceous materials are proposed to be the cause of high ORR catalytic activities [178].

Aside from N-doped carbon, the heteroatom-doping of carbon materials is another method to create carbonaceous catalytic materials with high efficiency in which B, S, P and F are generally used as dopants. In addition, the use of N as a mixed hetero-dopant is another method to create carbonaceous catalytic materials in which by introducing these dopants into carbon, resulting materials will possess large structural disorder and large amounts of heteroatom functionalities that can enhance ORR activity (Fig. 11) [179–183]. Furthermore, the introduction of heteroatoms into carbonaceous materials can allow for O–O bond breakage through the control of oxygen

Fig. 11 Schematics of the fabrication of **a** N/O bi-doped and **b** N/O/S/P tetra-doped few-layer carbon nanosheets. Reprinted with permission from Ref. [183]. Copyright 2018 Royal Society of Chemistry

binding energy, which will result in the creation of carbon active sites adjacent to heteroatoms [184]. Based on all of this, Paraknowitsch et al. [185] and Cui et al. [186] provided excellent reviews on the recent progress made in the development of B-doped, P-doped and S-doped carbon materials for fuel cell applications. Moreover, Niu et al. [187] developed an easy preparation process to fabricate flexible, porous and well-dispersed metal-heteroatom-doped carbon nanofibers through the direct carbonization of electrospun Zn/Co-ZIFs/PAN nanofibers (Zn/Co-ZIFs/PAN). Here, the obtained Zn/Co and N co-doped porous carbon nanofibers as carbonized at 800 °C (Zn/Co–N@PCNFs-800) presented good flexibility, a continuous porous structure and an ORR catalytic activity superior to that of commercial 20 wt% Pt/C based on the onset potential (0.98 V vs. RHE), the half-wave potential (0.89 V vs. RHE) and limiting current density (-5.26 mA cm^{-2}). Kim et al. [188] also incorporated various types of heteroatoms, including single dopants of N, B and P as well as multiple dopants involving B–N and P–N into a carbon matrix and reported that doping with N decreased the bonding between P and C in the matrix, whereas the use of multiple dopants induced the formation of additional

active sites for ORR, which further enhanced both the ORR activity and stability of the resulting catalyst.

4.8 Carbon Quantum Dots

Carbon quantum dots and graphene quantum dots are small carbon nanoparticles (less than 10 nm in size) that possess various unique properties and can exhibit unusual chemical and physical properties due to their strong quantum confinement and edge effects [189]. As a result, these nanomaterials have found use in a growing number of fields over the last few years. However, the development and application of carbon-based quantum dots are not yet mature, especially in terms of electrocatalysis. Despite this, the numerous oxygen-rich functional groups on the surface of these carbon-based quantum dots can disrupt electroneutrality and produce abundant amounts of positively charged active sites that are useful for O_2 surface adsorption. In addition, active sites on the edges of carbon-based quantum dots can enhance ORR. For example, Liu et al. [21] prepared surface-like multidimensional carbon-based quantum dots with O- and N-rich functional groups and reported that the resulting material possessed superior electrocatalytic activity for ORR and Zhang et al. [190] investigated the use of

carbon-based quantum dots as ORR catalysts and suggested that the size of N-doped GQDs can affect ORR in which the adsorption strength of ORR intermediates, the reaction free energy of the rate-determining step and the overpotential can all increase with increasing N-doped GQD sizes. These researchers also reported that N-doped GQDs with the smallest size possessed the smallest overpotential and the highest ORR catalytic activity (Fig. 12), demonstrating the size effect of N-doped GQDs on ORR catalytic activity. In another study, Tam et al. [191] synthesized B-doped graphene quantum dots (BGQDs) through the hydrothermal treatment of glucose as the precursor in the presence of boric acid and investigated the effects of different types of B–C bond species on ORR catalytic activity to clarify the origin

of the electrochemical reduction of O_2 . In addition, these researchers also prepared a composite of reduced graphene oxide and BGQDs (G-BGQDs) as a metal-free electrocatalyst for ORR and reported that the G-BGQD composite exhibited significantly enhanced electrocatalytic activities, including a positive onset potential and a high current density with a one-step, $4e^-$ pathway toward ORR that were comparable to commercial Pt/C catalysts. Furthermore, these researchers reported that among various B–C bond structures in the BGQDs, the graphite-like BC_3 structure was considered to be an important site for ORR because it improved the electric conductivity and electrocatalytic activity of the BGQDs as determined through DFT. Overall, these results demonstrated that both synthesized BGQDs

Fig. 12 Favorable adsorption structures of ORR intermediates on **a** $C_{23}H_{12}N$, **b** $C_{53}H_{18}N$ and **c** $C_{95}H_{24}N$. Reprinted with permission from Ref. [190]. Copyright 2018 Royal Society of Chemistry

and carbon-based quantum dots as metal-free catalysts are inexpensive, efficient electrocatalysts to replace Pt-based catalysts for ORR and other electrochemical applications.

4.9 Metal–Organic Frameworks

Metal–organic frameworks (MOFs) are synthesized by linking inorganic and organic units with strong bonds, and the corresponding flexibility with which the geometry, size and functionality of the constituents can be varied has led to more than 20000 different MOFs having been reported and studied within the past decade. In addition, organic units that are ditopic or polytopic organic carboxylates (and other similar negatively charged molecules) can be linked to metal-containing units to yield architecturally robust crystalline MOF structures with typical porosity 50% greater than that of MOF crystal volumes. Moreover, the surface areas of these MOFs typically range from 1000 to 10000 m² g^{−1} and greatly exceed those of traditional porous materials such as zeolites and carbons. Furthermore, MOFs with permanent porosity are more extensive in their variety and multiplicity than any other classes of porous materials. And as a result of these aspects, MOFs are ideal candidates for the storage of fuels (hydrogen and methane), capture of carbon dioxide and catalysis applications as well as for use as electrodes in fuel cells and metal–air batteries [192] (an extensive review on the application of MOFs as ORR catalysts can be found in Ref. [193]). Despite these advantages, however, the low intrinsic electronic conductivity of MOFs remains an obstacle hindering utilization as electrodes. To address this, Gonen et al. [194] synthesized benzene tricarboxylic acid–based MOFs inside activated carbon (AC) with four different first-row transition metals, including Mn,

Fe, Co and Cu and electrochemically analyzed the resulting MOFs@ACs based on their catalytic activity. Here, these researchers found that the MOFs@AC catalysts were conductive and active for ORR in alkaline environments and that Mn-MOF-based @AC exhibited the best performance with an onset potential of 0.9 V versus RHE and an almost 4e[−] mechanism. In another study, Zhao et al. [195] also prepared a newly designed mixed-node MOF catalyst Co_xFe_{1−x}-MOF-74 (0 < x ≤ 1) as a highly efficient electrocatalyst for OER in alkaline media and reported a remarkably low overpotential (280 mV at a current density of 10 mA cm^{−2}), a small Tafel slope (56 mV dec^{−1}) and high faradic efficiency (91%) (Fig. 13), in which the catalyst delivered a current density of 20 mA cm^{−2} at 1.58 V for overall water-splitting reaction. These researchers also used aluminum terephthalate as an air cathode for an Al–air battery and again obtained promising results [196].

4.10 Single-Atom Catalysts

Single-atom catalysis has arguably become the most active frontier in heterogeneous catalysis. And with recent advances in practical synthetic methodologies, characterization techniques and computational modeling, numerous single-atom catalysts (SACs) have been studied that exhibit distinctive performances for a wide variety of chemical reactions. Because SACs possess well-defined active centers, unique opportunities exist for the rational design of novel catalysts with high activity and stability. And considering certain practical applications, researchers can often design suitable SACs. As a result, this field has developed rapidly and has produced promising catalyst leads [197]. For example, Zang et al. [198] prepared single Co atoms anchored on

Fig. 13 A newly designed mixed-node MOF catalyst, Co_xFe_{1−x}-MOF-74 (0 < x ≤ 1) that can act as a highly efficient electrocatalyst for OER in the alkaline solution. Reprinted with permission from Ref. [195]. Copyright 2018 American Chemical Society

porous N-doped carbon nanoflake arrays from a Co-MOF precursor followed by the removal of unwanted Co clusters, which resulted in the attachment of well-dispersed Co single atoms to the carbon network through N–Co bonding and additional porosity and active surface areas as created by the removal of Co metal clusters. Here, these researchers reported that the single Co atom catalyst demonstrated lower OER overpotential and much higher ORR saturation current as compared with electrocatalysts containing excess Co nanoparticles, demonstrating that Co metal clusters were redundant in driving both OER and ORR (Fig. 14). And based on this bifunctional electrocatalytic activity and mechanical flexibility, these researchers assembled this electrocatalyst on carbon cloth as an air cathode in a solid-state Zn–air battery and obtained good cycling stability (2500 min, 125 cycles) as well as a high open-circuit potential (1.411 V). In another study, Jia et al. [199] synthesized N-doped porous carbon with atomic-level dispersion of Fe–N_x species and reported that the obtained Fe/N co-doped carbon nanocage ORR electrocatalyst exhibited a comparable half-wave potential (0.82 V) and higher limiting current density as compared with commercial Pt/C electrocatalysts. These researchers also used the obtained electrocatalyst in an air electrode of an assembled Zn–air battery and obtained a specific capacity of 705 mAh g^{−1} at 5 mA cm^{−2} and negligible voltage loss after continuous operation for 67 h. Here, these researchers attributed the superior performance of the Fe/N co-doped carbon nanocages to the porous structure and synergetic effects of the atomically dispersed Fe–N_x species and N-doping.

4.11 Nitrides and Carbides

Nanostructured metal carbides and nitrides have attracted much attention because of their active properties in various

areas such as magnetism, biomedicine, electrocatalysis and environmental applications. In general, the intrinsically harsh characteristics of carbides and nitrides make their synthetic protocols difficult, especially at the nanoscale; however, they can usually result in improved performances in specific applications. For example, He et al. [200] used TiN as an ORR catalyst in a Li–air fuel cell with a non-aqueous/acidic aqueous hybrid electrolyte and extensively investigated the electrochemical properties of the TiN-based catalyst and the single cell and concluded that TiN possessed considerable electrochemical catalytic activity for Li–air fuel cells in weak acidic media. Lin et al. [201] also prepared a bifunctional electrocatalyst consisting of manganese iron binary carbide (Mn_xFe_{3−x}C) nanoparticles anchored on

Fig. 15 A robust bifunctional electrocatalyst consisting of manganese–iron binary carbide (Mn_xFe_{3−x}C) nanoparticles armored by N-doped graphitic carbon (Mn_xFe_{3−x}C/NC). Reprinted with permission from Ref. [201]. Copyright 2019 American Chemical Society

Fig. 14 Single Co atoms anchored on porous N-doped carbon as efficient Zn–air battery cathodes. Reprinted with permission from Ref. [198]. Copyright 2018 American Chemical Society

N-doped graphitic carbon ($\text{Mn}_x\text{Fe}_{3-x}\text{C/NC}$) (Fig. 15) in which the synthesis involved the facile pyrolysis of a trimetallic (Fe, Mn, Zn) zeolitic imidazolate framework. Here, these researchers reported that the incorporation of Mn modulated the electronic properties of Fe_3C and the surrounding carbon to enhance both ORR and OER activities. In addition, these researchers also suggested that $\text{Mn}_x\text{Fe}_{3-x}\text{C}$, which is well protected by carbon layers, can display high resistances to oxidation and corrosion. And as a result, the assembled Zn–air battery exhibited a large peak power density (160 mW cm^{-2} at 250 mA cm^{-2}) with an energy density of up to 762 mWh gZn^{-1} , a high open-circuit voltage of 1.5 V and an impressive long-term stability of over 1000 cycles.

Lin et al. [201] also used TiN and TiC as active materials for air cathodes in rechargeable Al–air batteries with promising results.

5 Rechargeable Al–Air Batteries

Aside from the use of Al–air batteries as primary batteries, studies have also been conducted to explore the possibility of creating rechargeable Al–air batteries. In general, the creation of rechargeable Al–air batteries is challenging and can provide large breakthroughs in this field because Al possesses a large theoretical capacity. And

Fig. 16 Cyclic voltammograms of Al–air batteries for each air–cathode material (the air–cathode material is listed in the figures). Reprinted with permission from Ref. [202]. Copyright 2017 Royal Society of Chemistry

although many researchers have reported the creation of rechargeable Al-ion batteries, few studies have reported rechargeable Al–air batteries. Despite this, researchers are actively researching rechargeable Al–air batteries, particularly using ionic liquid or deep eutectic solvents as electrolytes (Fig. 16) [13, 196, 202, 203]. Al–air batteries that use chloroaluminate ionic liquid as the electrolyte exhibit Lewis acid–base chemistry comparable to Brønsted acidity in water, and similar to the control that proton concentration exerts over chemistry and electrochemistry in aqueous solutions, chloroacidity is the major determinant of speciation, reactivity and electrochemistry in ionic liquids. As for Al–air batteries, the composition of the melt determines chloroacidity in which as the chloride donor undergoes stepwise Lewis acid–base reactions with acidic AlCl_3 , chloroaluminate anions form according to the following equilibrium reactions:

Here, at <0.5 mol fraction of AlCl_3 in the room temperature liquid melt, the only anions present in significant quantities are Lewis bases Cl^- and AlCl_4^- , making the melt basic. And at AlCl_3 mol fractions greater than 0.5, as was used in our study, the only anions present in appreciable amounts in the liquid were AlCl_4^- and Al_2Cl_7^- . This is a crucial factor because the electrodeposition of Al can only occur from Al_2Cl_7^- through the following reaction [204]:

Therefore, it is hypothesized that Al_2Cl_7^- can function as a charge carrier in Al–air batteries. The overall electrochemical reactions in aqueous solution electrolytes are described in the above section and for rechargeable Al–air batteries, suitable ionic liquids must be applied as an electrolyte in the battery to permit the deposition of Al [205]. Overall, the theoretical voltage of Al–air batteries with an ionic liquid-based electrolyte can be speculated in which the following reactions occur upon discharge:

Anode:

And the following reactions may occur upon charge:

Anode:

Cathode:

Based on this, the theoretical voltage should be 3.24 V (cell potential = anodic potential + cathodic potential). However, the actual voltages of rechargeable Al–air batteries using ionic liquid-based electrolytes are lower than 3.24 V and detailed chemical reaction mechanisms remain to be determined in future studies to elucidate overpotentials as caused by electrolytes, electrode bulk resistances and interfacial resistances [202]. As for aqueous electrolytes and protic solvents, ORR proceeds through a multi-electron chemical reaction that occurs at the air cathode of Al–air batteries with two main possible pathways, including the transfer of 2e^- to produce peroxide (H_2O_2) and the production of water through direct 4e^- transfer as described in a previous section. In general, 1-ethyl-3-methylimidazolium chloride (EMImCl) has been used as an electrolyte for Al–air batteries. However, because EMImCl is an aprotic solvent, ORR is difficult to achieve due to the lack of protons in the solvent [206]. In addition, the effects of humidity (water) need to be considered with the use of EMImCl due to it being a hydrophilic ionic liquid, which can absorb humidity (water) from ambient atmosphere and cause water to be present in the electrolyte, leading to corresponding Al–air batteries absorbing water from surrounding ambient atmosphere and reactions 11 and 12 occurring at the air cathode.

In terms of electrocatalysts, bifunctional electrocatalysts are ideal for rechargeable Al–air batteries and various bifunctional electrocatalysts such as Pt, noble metal, metal nitride and carbide catalysts are active for ORR through the 4e^- pathway. As for carbonaceous materials, they proceed through the 2e^- pathway and therefore, corresponding air–cathode catalysts need to be carefully selected to prepare high-performance Al–air batteries. As examples, Sun et al. [207] prepared a gelled ionic liquid by complexing EMImCl with AlCl_3 through Al electrodeposition in their Al-ion battery and reported promising results and aside from ionic liquid-based electrolytes, Nakayama et al. [208] managed to deposit and dissolve Al in non-corrosive sulfone-based electrolytes (Fig. 17). Furthermore, Gonzalo et al. [209] reported a stable electrogenerated superoxide ion in a phosphonium-based ionic liquid in the presence of water that led to a chemically reversible O_2/O_2^- redox couple instead of the usually observed disproportionation reaction and Gelman et al. [205] developed a primary Al–air cell based on an oxygen and water-stable 1-ethyl-3-methylimidazolium oligo-fluorohydrogenate electrolyte $[\text{EMIm}(\text{HF})_{2.3}\text{F}]$ that delivered 140 mAh cm^{-2} . Wang et al. [210] also reported a rechargeable Al–air battery based on 1-butyl-3-methylimidazolium

Fig. 17 I - V curve of an Al-air battery with sulfone-based electrolytes. Reprinted with permission from Ref. [208]. Copyright 2015 Royal Society of Chemistry

Fig. 18 **a** Al-air battery discharge profiles at different current densities of 0.1 (the black square); 0.25 (the red circle); 0.5 (the green up-based triangle); 1 (the cyan diamond) and 1.5 mA cm⁻² (the blue down-based triangle). **b** Al-air battery discharge (0.5 mA cm⁻², the square in magenta) in inert atmosphere. Reprinted with permission from Ref. [210]. Copyright 2016 American Chemical Society

Fig. 19 **a** SEM micrograph of electrodeposited Al on Au formed after potentiostatic polarization for 1 h in [MoeMIm]Cl/AlCl₃ (40/60 mol%) at a potential of -0.35 V at 100 °C. **b** XRD patterns of electrodeposited Al layers obtained at 20 and 100 °C. Reprinted with permission from Ref. [211]. Copyright 2014 Elsevier B.V.

chloride with aluminum triflate as a metal salt (Fig. 18). Moreover, Bogolowski et al. [206] recently used a Pt/C gas diffusion electrode (GDE) to show the feasibility of creating an electrically rechargeable Al-air battery at a 100 mA cm⁻² current density for 15 cycles (200 h) in a 1:1.5 EMImCl/AlCl₃ electrolyte. However, the charge/discharge cycle in this battery was limited to 3 h each, which represented a reversible capacity of 300 mAh cm⁻² and is only 0.4% of the theoretical capacity for anode-normalized Al foil. Here, these researchers attributed the poor cell reversibility to trace amounts of residual water.

More recently, deep eutectic solvents such as acetamide- and urea-based eutectic solvents have also been investigated for use in Al-air batteries because of their cheaper material cost and ease of preparation (Fig. 19) [211, 212]. For example, some urea- and acetamide-based deep eutectic solvents developed by Abood et al. [213, 214] have shown appreciable reversible activities for Al deposition/stripping (Fig. 20)

Fig. 20 First 10 cycles of Al deposition/stripping in AlCl₃ (1:1.5) containing **a** EMImCl, **b** acetamide, **c** urea on pyrolytic graphite foil and **d** comparison of the tenth cycle of each cell at room temperature. Reprinted with permission from Ref. [214]. Copyright 2018 Elsevier B.V.

in which amide groups can react with AlCl₃ and build positively charged complexes and negatively charged tetrachloroaluminate anions according to the following reaction:

And although the exact ion species or charge carriers for Al–air battery systems remain unclear, it is assumed that AlCl₄⁻ or Al₂Cl₇⁻ is the charge carriers. In addition, Katayama et al. [215] suggested that in the case of Al–air batteries with an electrolyte composed of a mixture of AlCl₃, 1-butyl-3-methylimidazolium chloride and bis(trifluoromethylsulfonyl)amide, the charge carriers should be either AlCl₄⁻ or Al₂Cl₇⁻ and that as Al₂Cl₇⁻ concentrations decrease, the concentration of AlCl₄⁻ increases as confirmed by Raman spectroscopy. Agiorgousis et al. [216] also excluded the possibility of Al³⁺ cations acting as charge carriers and instead suggested AlCl₄⁻ anions as possible charge carriers and Angell et al. [217] claimed that both Al₂Cl₇⁻ and AlCl₄⁻ existed in the AlCl₃–urea ionic liquid analog electrolyte. Anyway, the creation of efficient rechargeable Al–air batteries would be a great achievement and has large impacts

because the theoretical capacity of Al–air batteries is much larger than that of Li-ion batteries.

6 Conclusion

Al–air batteries possess great potential for practical application due to their large energy capacity and in this review, Al–air batteries with Al anodes, electrolytes and air cathodes have been discussed and the possibility of creating rechargeable Al–air batteries has been presented. Overall, the focus of the development of pure Al and Al alloy anodes is the prevention of self-corrosion and byproduct formation. As for electrolytes, they are critical components determining the rechargeability potential of Al–air batteries. Electrolyte additives are also an important issue because they can suppress corrosion and hydrogen evolution to improve electrochemical properties. Furthermore, various solid electrolytes have been investigated despite poorer energy capacities as compared with liquid electrolytes due to bulk and interface impedance between electrodes and solid electrolytes. In terms of the ORR, this is the rate-determining critical

process in Al–air batteries because of its sluggish reaction kinetics in comparison with electrochemical reactions at the anode. As a result, air–cathode materials are also critical components that can significantly influence overall battery properties. And although Pt-based catalysts are the most promising catalytic materials for ORR, their high cost and resource scarcity hinder application. Therefore, Pt alternatives have been extensively explored and involve the application of other transition metals to either fully or partially replace Pt. Furthermore, metal oxide catalysts including perovskites, spinel crystalline materials, metals and nitrogen as well as heteroatom-doped carbonaceous catalytic materials have also shown promise. Moreover, studies have shown that non-oxide materials such as metal nitrides, carbides, carbon-based quantum dots, MOFs and single-atom catalysts can also be used as next-generation catalytic materials that possess high ORR activity. Overall, because the theoretical capacity of Al–air batteries is much larger than that of Li-ion batteries, the creation of rechargeable Al–air batteries is of great importance and can be used in the design of smart grid energy systems. These rechargeable Al–air batteries can also potentially be applied in electricity-based vehicles to promote an environmentally friendly future.

Acknowledgements The author wishes to express thanks to Dr. Hideki Yoshioka and Mr. Kazuo Sakai for their helpful discussions.

Compliance with Ethical Standards

Conflict of interest The author has no conflict of interest.

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- functional materials for rechargeable batteries, solar cells, fuel cells, quantum dots, metal organic frameworks, catalysts, etc.

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