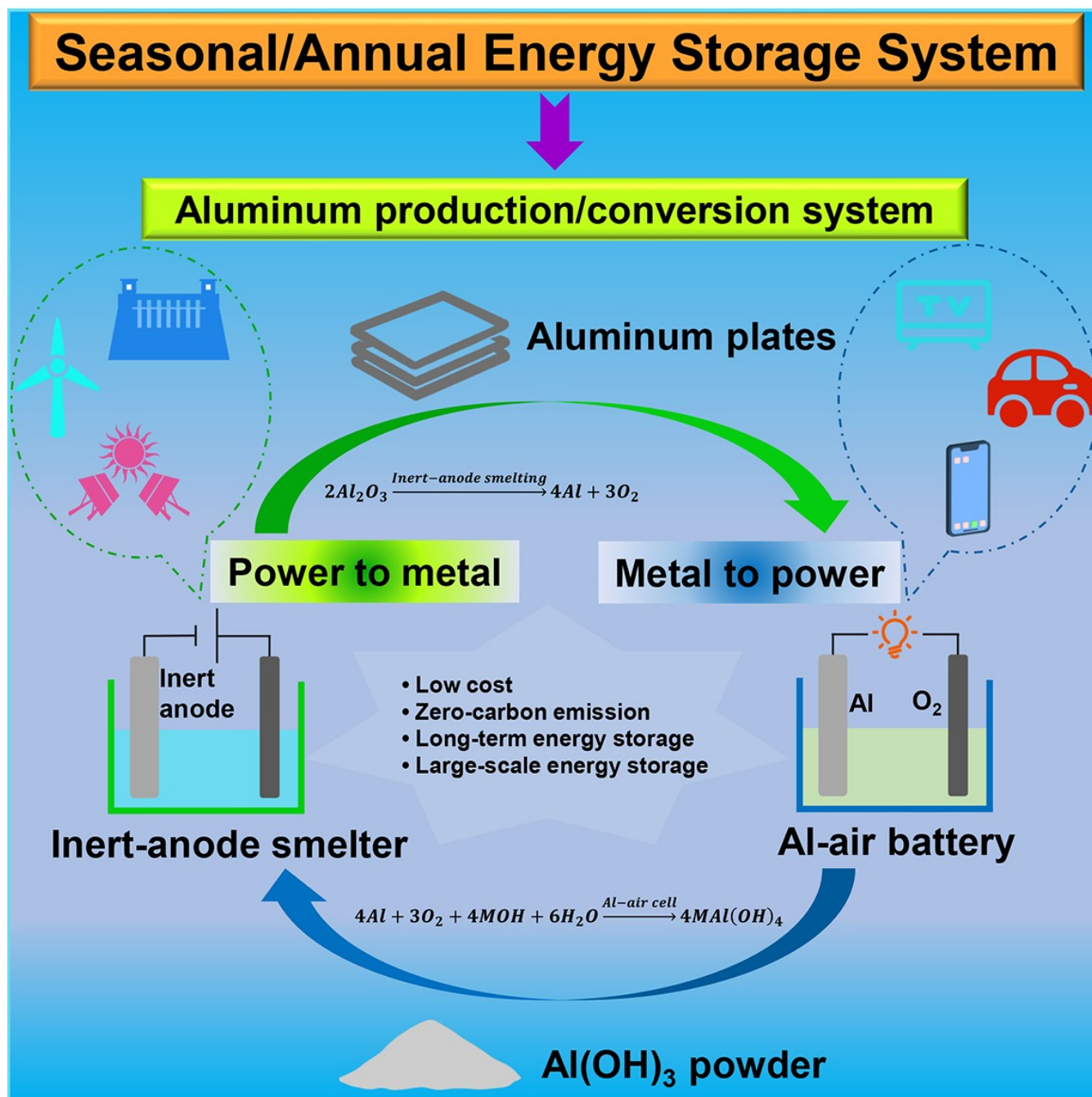


Al–Air Batteries for Seasonal/Annual Energy Storage: Progress beyond Materials

Cheng Xu,^[a, b] Xu Liu,^{*[a, b]} Olga Sumińska-Ebersoldt,^[a, b] and Stefano Passerini^{*[a, b, c]}



Cost-effective and zero-carbon-emission seasonal/annual energy storage is highly required to achieve the Zero Emission Scenario (ZES) by 2050. The combination of Al production via inert-anode smelting and Al conversion to electricity via Al–air batteries is a potential option. Although playing an important role in this approach, Al–air batteries, however, suffer from limited specific energy and inefficient collection of the discharge product. Herein, an important progress in addressing these issues is summarized, emphasizing the importance of

non-material, but rather process-related aspects. First, a recently reported approach allowing controllable collection of discharge product and electrolyte regeneration is presented. Next, the importance of cell design in addressing the obstacles of Al–air batteries is emphasized. Subsequently, the impact of operational parameters on improving electrochemical performance of Al–air batteries is summarized. Last, a perspective on future research directions is proposed.

1. Introduction

Societal rapid development is accompanied by an increasing consumption of fossil fuels.^[1] However, such non-sustainable resources with limited abundance cannot fulfill the future's vast energy needs. Moreover, fossil fuels utilization unavoidably produces CO₂, SO_x, and NO_x, leading to a series of environmental issues, e.g., greenhouse effect and acid rain.^[2] The realization of a decarbonized economy requires the increase of energy (electricity) generated from renewable energy sources (RES), e.g., solar and wind power, which, however, suffer from seasonal/annual energy fluctuations.^[3] The implementation of sustainable, low-cost, and large-scale storage systems that can balance these fluctuations is urgently required, but still full of challenges.

In this context, the combination of Al production via inert-anode smelting (power to metal) and Al conversion to electricity via Al–air batteries (metal to power), namely, Al production/conversion system (APCS), is a potential option as illustrated in Figure 1. With the electricity generated from RES, Al₂O₃ can be electrochemically converted to metallic Al, which is the energy carrier to be stored. In fact, the Al smelting process can be realized with no CO₂ emissions when the carbon anode in the conventional Hall–Héroult technology is replaced with inert anodes, e.g., metal, oxide, or cermet anode.^[4,5] The electricity can be released again via electrochemical oxidation of the stored Al metal in Al–air batteries. Due to the earth abundance, low cost, and easy storage of Al metal,^[6,7] as well as the high energy density of Al–air batteries (8100 Wh kg_{Al}⁻¹),^[8,9] one can find that such a combination allows long-term energy storage with zero emission of greenhouse gases.

Although Al–air batteries may play a very important role in this seasonal and annual energy storage approach, two main issues of this battery technology need to be addressed for the realization of APCS with high round-trip energy efficiencies (RTEs).^[10] The first one is the limited energy conversion efficiency of Al metal into Al(OH)₃ (later transformed into Al₂O₃ for reuse in Al production), which is determined by the effective Al utilization and the cell discharge voltage. The spontaneous chemical reaction of Al metal in alkaline electrolytes leads, in fact, to H₂ evolution and thus low coulombic efficiencies (although the evolving H₂ could be collected and utilised). Additionally, the polarization occurring at both the Al metal anode and the air cathode leads to low cell discharge voltage, i.e., low voltage efficiency. Both hurdles contribute to the low specific energy and RTE of Al–air batteries. The second issue is the difficulty in collecting the discharge product,^[11] e.g., MAI(OH)₄ (M = Na, K) and/or Al(OH)₃. In alkaline electrolytes, the typical discharge product MAI(OH)₄ is highly soluble, converting to the Al(OH)₃ precipitate only at very high concentrations, i.e., when its solubility limit is reached. However, reaching the solubility limit inside the cell results in the precipitation of the solid product in the cell itself, causing the formation of an inert coating on the Al electrode as well as the clogging of the positive air electrode, which reduces the RTE even further. Therefore, these two aspects crucially affect the RTE of an APCS.

To solve these obstacles, Al–air batteries have been extensively studied in the past decades, but mainly from the materials aspects,^[12] including cathode catalysts for oxygen reduction reactions,^[13–15] doped Al metal anode to suppress self-corrosion,^[16–20] and electrolytes additives for more protective electrolyte/electrodes interphase,^[21–25] which have been systematically reviewed in previous literature.^[12] However, little attention has been placed on factors beyond materials, actually affecting the energy density delivered by Al–air batteries, particularly the RTE of an APCS.

Herein, the recent progress of Al–air batteries for the development of high-RTE APCS targeting seasonal/annual energy storage is summarized focusing on the non-material aspects. These include a recently reported approach allowing the ease removal of the discharge product (Al(OH)₃), resulting in its easy collection for the power to metal step and the electrolyte regeneration. Following, the impact of cell's design on the electrochemical performance of Al–air batteries is reviewed together with the importance of the operational parameters. Finally, a perspective on future research directions is proposed.

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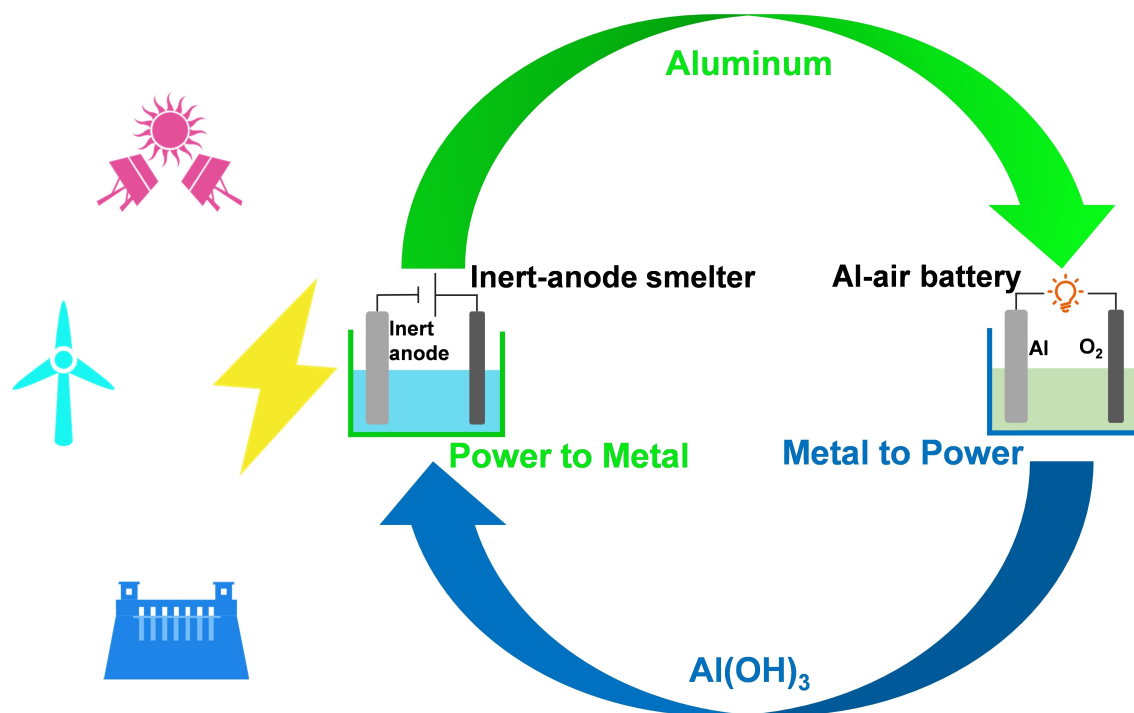
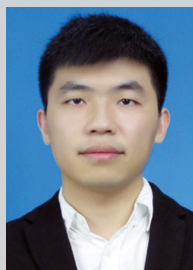
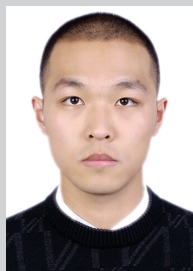


Figure 1. Schematic of the combination of Al–air batteries and inert-anode based Al electrolysis: Al production/conversion system.



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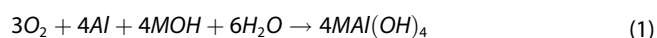


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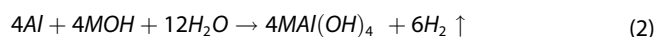
2. Discharge Product Control and Electrolyte Regeneration

Inert-anode based Al smelter and Al–air batteries are relatively independent devices, but they are connected by the input and output of materials. In fact, Al is the anode for Al–air batteries, of which the discharge product ($\text{Al(OH)}_3/\text{Al}_2\text{O}_3$) is the raw material for the Al electrolysis in carbon-free smelters. The smooth combination of these two processes is the key to close the loop for the realization of APCS.

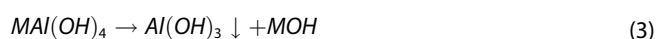
Alkaline solutions are the most commonly used electrolytes for Al–air batteries, owing to their low cost, high ionic conductivity, and fast oxygen diffusion and reaction kinetics when compared with acidic and neutral electrolytes.^[26] The electrochemical reaction of Al–air batteries with alkaline electrolytes can be described by equation (1).^[27]



Water is consumed during discharge according to equation (1) and, as such, it is necessary to supplement it along the process. In addition to the electrochemical reaction, Al also chemically reacts with alkaline electrolytes as described by equation (2), i.e., self-corrosion of Al metal anodes.



As described by equations (1) and (2), the metal aluminate (MAI(OH)_4) is the product generated from both the electrochemical and the chemical reactions. Upon discharge, MAI(OH)_4 accumulates in the electrolyte, reducing the OH^- concentration and, in turn, reducing the ionic conductivity, decelerating the electrochemical reaction kinetics, decreasing the cell voltage as well as specific energy.^[28] When the solubility of MAI(OH)_4 in the electrolyte is reached, the formation of insoluble Al(OH)_3 occurs according to (3).



It has been reported that Al(OH)_3 could precipitate on the surface on AMAs and air cathodes with the further reaction blocked.^[29] Moreover, the uncontrolled deposition of Al(OH)_3 leads to the plugging of cell components as well as difficulties in its collection for the use in further Al production. The use of flowing electrolyte to mitigate the voltage decay and prolongs the discharge lifespan of Al–air cells has been already reported,^[30] but the beneficial effect was only associated to the larger volume of the employed electrolyte. Nonetheless, upon time the OH^- concentration decreases and the MAI(OH)_4 concentration gets close to its solubility in the electrolyte, making the increased electrolyte volume approach only temporarily beneficial. To recover the cell performance, the discharge product MAI(OH)_4 must be removed to recover OH^- , i.e., the electrolyte needs to be regenerated.

Very recently, Xu *et al.* proposed a seeded precipitation process to remove the KAl(OH)_4 from the electrolyte, taking

advantage of the decreasing KAl(OH)_4 solubility for decreasing temperatures.^[28] For example, when the KAl(OH)_4 saturated electrolyte at 50 °C is cooled and kept at 20 °C for 24 and 72 h in the presence of 1 wt.% Al(OH)_3 as the seed, around 52% and 72% KAl(OH)_4 can be converted to Al(OH)_3 as shown in Figure 2a. This allows the removal of the discharge product and its efficient collection, e.g., outside of the cell. Meanwhile, the OH^- anion in the aluminate anion (KAl(OH)_4) is released back into the electrolyte, enabling the full recover of the Al–air battery kinetics. As a result, the regeneration of the electrolyte via the seeded precipitation process enables recovering the decayed voltage and specific energy (Figure 2b,c). This approach has been scaled-up into an Ah-level prototype Al–air cell operating at 50 °C. As displayed in Figure 2d,e, the voltage and specific energy decreased upon discharge (0–24 h). However, after electrolyte regeneration via the seeded precipitation process, the cell voltage and specific energy were effectively recovered. The battery operation generates heat by Joule effect, while the electrolyte regeneration is carried at lower temperature. Designing the system with two electrolyte tanks, one in operation and one under regeneration (i.e., cooling), there is no need to interrupt the Al–air cell operation.

3. Cell Design

Cell design is important for improving the energy density of Al–air batteries. In spite of static electrolyte, Al–air primary batteries employing a flow electrolyte benefit of improved performance when properly combined with auxiliary systems.^[30] For example, flowing the electrolyte through a gas separation unit could enable to collect the hydrogen released from the self-corrosion of AMAs.^[31]

Liu *et al.* proposed double-face flow Al–air batteries, i.e., each side of AMA is faced with an air cathode, as schematised in Figure 3a.^[32] Compared with the static electrolyte battery, the flow Al–air battery exhibits prolonged discharge life due to the removal of the by-product deposition on the electrodes (Figure 3b).^[32] Although a similar discharge voltage was observed for conventional single-cathode and dual-cathode Al–air batteries (Figure 3c), the specific energy delivered by the latter system was 3595.4 Wh kg^{-1} , i.e., approximately twice that of the former (1807.6 Wh kg^{-1}), even when tested at the same cathodic current density. This is attributed to the highest current density applied at the negative electrode, which effectively reduces the self-corrosion of AMAs.^[28,32]

Apart from this, the cell design with flowing electrolyte enables addressing the issue of Al–air batteries when the battery is at the idle state (Figure 4a). In fact, the AMAs soaked in the electrolyte would continuously react with the alkaline electrolyte according to equation (3), exacerbating the Al self-corrosion and H_2 production. To avoid this problem under open-circuit, an oil displacement Al–air cell was developed to replace the alkaline electrolyte between the electrodes and remove the residual electrolytes on the surface of Al anode and separator (Figure 4b,c).^[33] The mass change of AMAs in alkaline electrolyte and oil at open-circuit is displayed in Figure 4d,e. Six

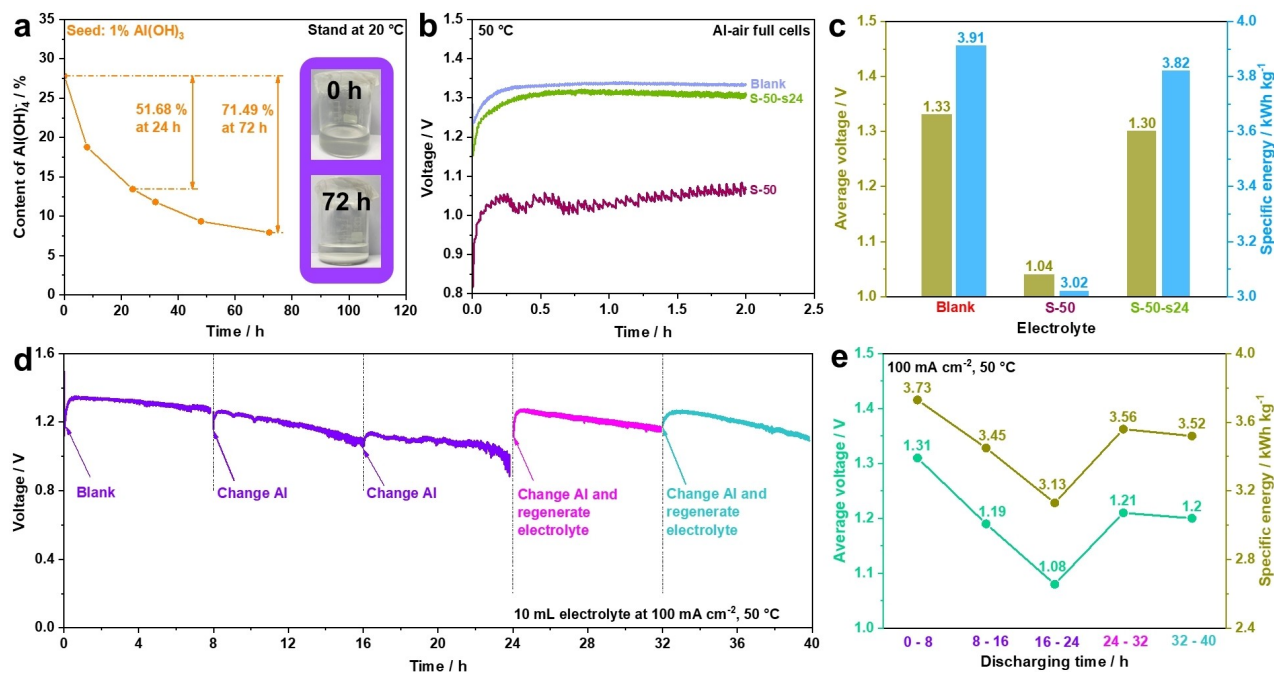


Figure 2. (a) Aluminate content in the electrolyte during the seeded precipitation process. (b) Galvanostatic discharge curves at 100 mA cm^{-2} and 50°C of Al–air full cells employing as electrolyte the 4 M KOH solution freshly made (Blank) and after saturation with KAl(OH)_4 (S-50), and regeneration by resting at 20°C for 24 hours (S-50–s24), and (c) corresponding average voltage and specific energy based on the mass of consumed Al. (d) Voltage evolution of Al–air cells. The Al electrode was consumed after 8 h and therefore replaced with a new one. The same cathode was used for the whole measurement. The electrolyte reached saturation after discharging for 24 h, after which was regenerated via the seeded precipitation process. Such an electrolyte regeneration was conducted again after 8 h discharge. (e) Average voltage and specific energy of the Al–air cell in the five discharge periods.^[28]

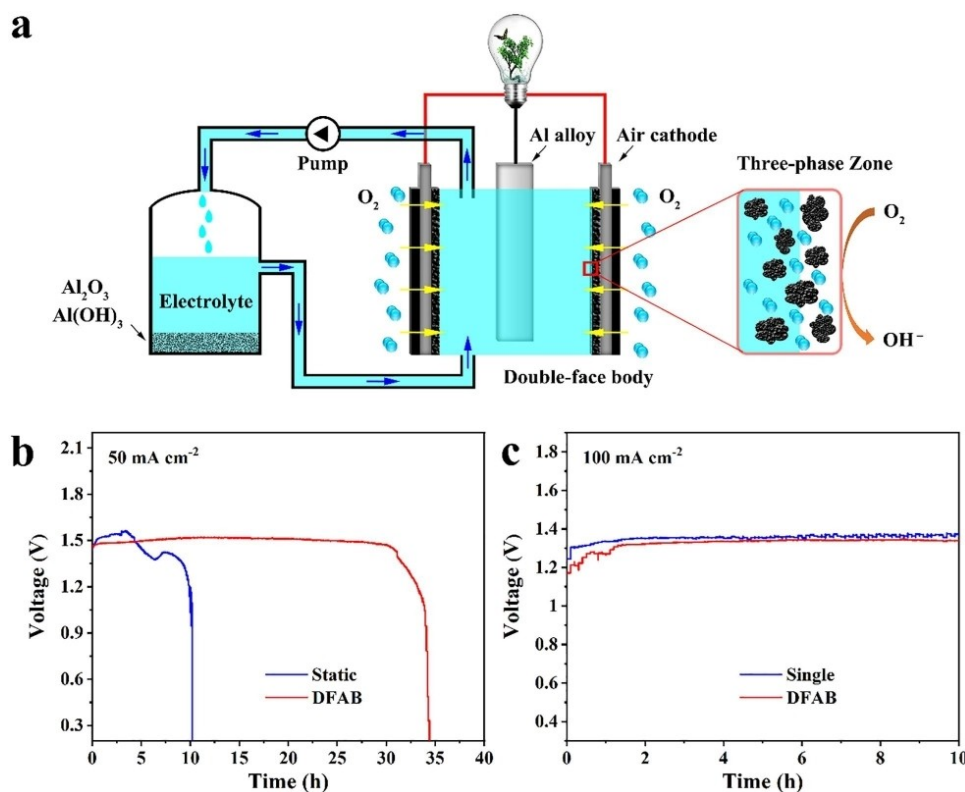


Figure 3. (a) Schematic diagram of the DFAB. Discharge curves of (b) static single- and dual-cathode flow Al–air batteries at 50 mA cm^{-2} , (c) single- and dual-cathode flow Al–air battery at 100 mA cm^{-2} (reproduced from ref.^[32]).

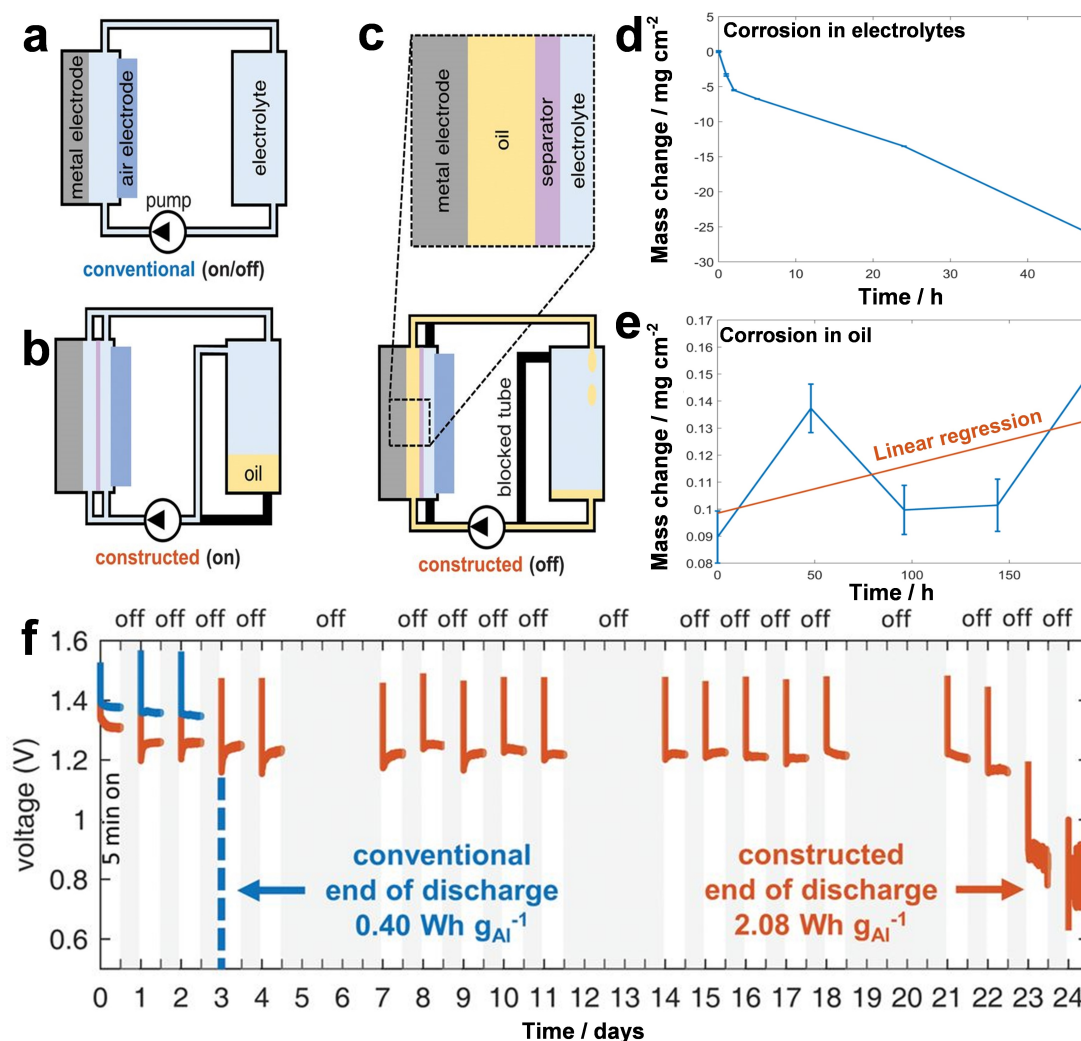


Figure 4. (a) Schematic of a conventional flowing electrolyte Al–air battery. (b) Schematic of the constructed oil displacement system for a flowing electrolyte Al–air battery. The electrolyte is pumped during operation, but oil is pumped to displace the corrosive electrolyte when the cell is not discharged. The magnified view in (c) shows the multi-phase interface between AMA and the electrolyte. Six independent measurements of Al foil mass change in (d) electrolyte and (e) oil at 20 °C. (f) Voltage versus time for on-off cycling of Al–air batteries with (a) and (b) cell design.^[33]

independent measurements indicate a lower mass change of Al in oil, proving that the introduction of the oil effectively limits Al-self corrosion at open-circuit. The on-off cycling of Al–air cells using the above mentioned cell designs (Figure 4a–c) is shown in Figure 4f. The discharge of the cell was paused for 24- or 72-hours after 5-mins discharging at the current density of 150 mA cm⁻². The conventional cell stopped operating after 2 days, while, by contrast, the cell with oil displacement system lasted more than 24 days, yielding an energy density of 2.08 kWh kg_{Al}⁻¹.

Besides, a hybrid system combining an Al–air battery with a hydrogen–air fuel cell has been proposed to improve the overall RTE.^[34] The hydrogen generated from the self-discharge of AMAs can be utilized as the fuel for the hydrogen–air fuel cell, which leads to the enhancement of the system delivered energy by more than 40%.

4. Optimization of Al–Air Batteries Operational Parameters

The specific energy of Al–air batteries is determined by the anode utilization and the polarization arising from both the electrodes. As mentioned earlier, the research and development attention has focused on the development of the relevant materials for the anode, cathode, and electrolytes. However, for a given Al–air battery, the selection of suitable operative parameters in specific cell design is important for the delivery of high performance. Wen et al. systematically screened the effect of current density, test temperature, electrolyte flow rate, and O₂ source, on the specific power and energy efficiency of Al–air batteries.^[14] As shown in Figure 5a, the cell voltage shows the expected decreasing trend with the increase of the current density. The resulting bell-shaped, power density trend is caused by the opposite effects of the accelerated electrochemical reaction and decreased voltage.^[12,35] Additionally, the

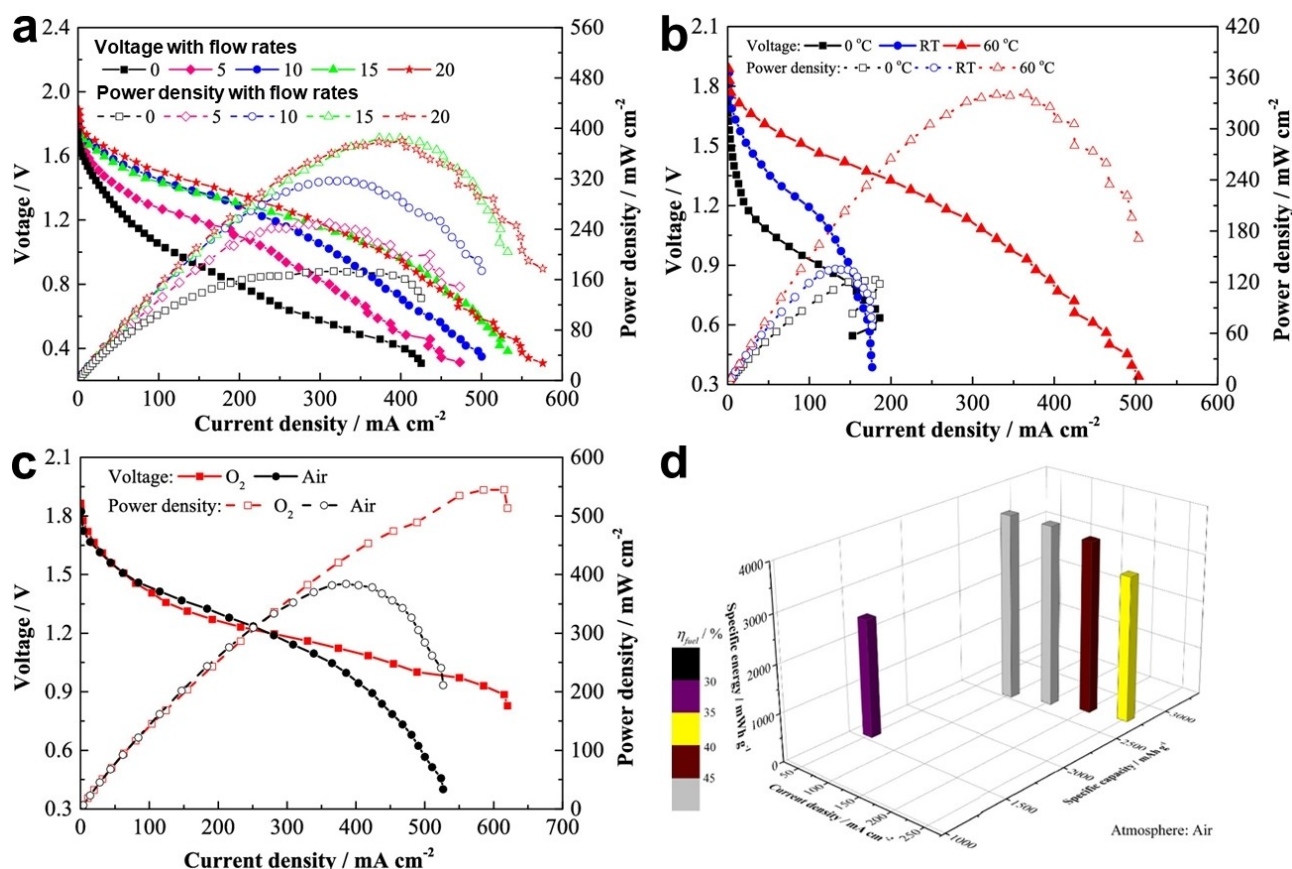


Figure 5. (a) Polarization and power density curves of Al–air batteries at different current densities with different electrolyte flow rates, and (b) at different temperatures. (c) Voltage and power density vs current density of the batteries in air and O₂ atmospheres. (d) Discharge curves of the batteries for various discharging current density in air atmosphere.^[14]

voltage increases with the electrolyte flow rate, due to the larger dissolution of O₂ inside the electrolyte and, consequently, the amount of O₂ getting in contact with the cathode catalysts. The operative temperature may also promote the reaction kinetics reducing the overpotential as shown in Figure 5b.^[14] The highest power density is reported for the temperature set at 60 °C resulting in a current density of ~350 mA cm⁻². Furthermore, Al–air batteries working in ambient air exhibit similar performance to those supplied with pure O₂ at current densities below 300 mA cm⁻² (Figure 5c).^[14] Considering the high cost of pure O₂ and system operability, ambient air is a better choice for Al–air batteries. With the optimized parameters discussed above, Wen et al. reported a specific energy of 3.88 kWh kg_{Al}⁻¹ at 100 mA g⁻¹ (Figure 5d).

5. Conclusions and Perspectives

The combination of a low-cost, high-energy-density Al–air battery with inert-anode-based Al electrolysis is a promising approach to address the seasonal/annual, but also day/night, energy storage needs with neat zero carbon emission. The performance of such a sustainable energy storage cycle, i.e., achieving high-RTE APCS, can be improved by optimizing the

Al–air battery system beyond the mostly investigated materials aspects.

Inspired by this, further exploration is worth being conducted. Although the developed seeded precipitation allows the aluminate removal and electrolyte regeneration, it is quite time-consuming. A wider operation temperature range is required to make it more efficient. Besides, the effect of the seeded process on the electrolyte species, e.g., SnO₃²⁻, remains unknown. In case of a consumption of the additive during the precipitation process, its effect on the performance of regenerated electrolytes and AMAs produced with the collected aluminate is crucial for the specific energy of Al–air batteries at more practical occasion. To utilize the seeded precipitation process, the cells need to operate at temperatures higher than room temperature.

The cell design needs to integrate more functions. Since the self-corrosion and energy inefficiency during the electrochemical operation lead to simultaneously heat release, cell design to maintain the operating temperature at the optimal state and even utilize the released heat is vital for the overall energy utilization. For the seeded precipitation process, the device can automatically work without manual efforts would be important for practical use. It is essential to implement procedures for detecting and adjusting the variable components of the electro-

lyte to ensure the optimal concentration of additives. Additionally, it has been demonstrated that the operation temperature and other operative conditions have significant effect on the specific energy density of Al–air batteries. Therefore, the operative factors could be rebalanced in the newly designed cell to pair conventional Al–air batteries and the seeded precipitation process.

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Conflict of Interests

The authors declare no competing interests.

Keywords: Al–air batteries · annual/seasonal energy storage · inert-anode smelting

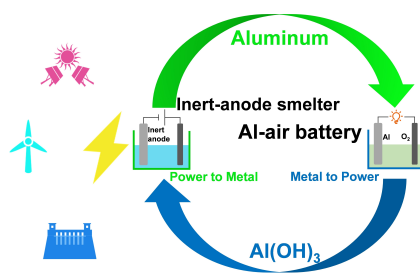
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REVIEW

The combination of Al production via inert-anode smelting (power to metal) and Al conversion to electricity via Al–air batteries (metal to power) is a promising approach for seasonal/annual energy storage systems. The recent progress of Al–air batteries beyond materials, including the removal of discharge-products, and impacts from operational parameters together with cell designs on electrochemical performance are summarized and discussed.



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Al–Air Batteries for Seasonal/Annual Energy Storage: Progress beyond Materials