The Pitfalls in Nonaqueous Electrochemistry of Al-Ion and Al Dual-Ion Batteries

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The quest for cost-effective and TWh-scale stationary energy storage systems has caused a surge of research on novel post-Li-ion batteries that consist solely of abundant chemical elements. Nonaqueous Al batteries, inter alia, are appealing as an inexpensive electrochemical technology owing to the high natural abundance of aluminum. A critical assessment of the literature on Al batteries, however, points to numerous misconceptions in this field. The latter is primarily linked to the false assessment of the charge storage redox reactions occurring upon cycling of Al batteries. To ensure the constructive progress of Al batteries, in this essay, the current scientific understanding of the operational mechanisms of two commonly studied Al battery systems, Al-ion and Al dual-ion batteries are summarized. Furthermore, the main pitfalls in interpretation and reporting of the electrochemical performance of Al cathode materials and cell-level energy densities of Al batteries are clarified along with core challenges currently limiting their development. Toward this end, the subject of the charge storage balancing of Al dual-ion batteries is discussed.

1. Introduction

Presently, the effective replacement of fossil fuels by alternative renewable sources of energy (other than hydropower) represents a major technological challenge worldwide. From this perspective, stationary batteries are considered as an ultimate solution for balancing the rapidly rising energy consumption (electrification of the mobility and building sectors) with the intermittent nature of renewable sources (e.g., solar and wind energy). Nonetheless, lithium-ion batteries (LIBs) are the most advanced technology widely deployed in the mobility and portable electronics sectors, the uneven distribution of known reserves of lithium significantly diminishes the economic appeal of LIBs for TWh-scale stationary energy storage.[1] Moreover, the CO₂-footprint and social impacts of LiBs are inherently dominated by other materials it is made of—foremost transition-metal oxide (Ni, Co) cathodes.[2] Toward finding sustainable energy storage electrochemistries, the last decade has seen a surge of reports on Al batteries as an inexpensive electrochemical technology. Aluminum has several essential advantages such as natural abundance, high volumetric/gravimetric charge storage capacity (8046 mAh cm⁻³/2980 mAh g⁻¹), and sufficiently low redox potential.[3–9] Besides, Al can be safely electrodeposited and stripped, as compared to metallic Li, Na, or K.

Although a great deal of attention of scientists to Al batteries is certainly a primary prerequisite toward their progress, the detailed assessment of publications in this field unveils severe issues as a result of an insufficient examination of their operational mechanism. Truthfully, numerous reports on Al batteries fail to explain actual redox chemistry upon charge/discharge and this has implications on the reporting of the specific charge storage capacity of Al cathode materials and cell-level energy density of Al batteries. In an attempt to capture the attention of the researchers to this matter and to secure further development of Al batteries, in this essay, we overview in detail operational principals of two mostly reported nonaqueous Al systems such as Al-ion and Al dual-ion batteries (AIBs and ADIBs). The particular emphasis of this work is given on the assessment of the correct charge storage mechanism of these types of batteries and on the appropriate reporting of their electrochemical performance. Additionally, we discuss the common mistakes made by researchers in this field and cover the topic of charge storage balancing of ADIBs.

2. Working Principle of Al-Ion and Al Dual-Ion Batteries

The conventional configuration of AIB consists of Al foil as a negative electrode, an Al electrolyte supporting efficient Al deposition/stripping redox reactions and the positive electrode being reduced/oxidized with concomitant intercalation and deintercalation of Al⁺ ions upon discharge and charge, respectively. The most widely used Al electrolyte is a mixture of aluminum chloride and other chlorides consisting of an...
organic cation such as 1-ethyl-3-methylimidazolium chloride (EMIM), 1-butyl-3-methylimidazolium chloride, and 1-methyl-3-propylimidazolium chloride. As a result of the acid–base reaction between Lewis acid ($\text{AlCl}_3$) and Lewis base ($\text{Cl}^-$), the mixture of salts gets a liquid at room temperature, subsequently forming a room-temperature ionic liquid widely denoted as RTIL. At equal molar amounts of Lewis acid and base, RTIL is composed of $\text{AlCl}_4^-$ anions that are charge-balanced with organic cations. However, an excess of Lewis acid over Lewis base results in the formation of both $\text{AlCl}_4^-$ and $\text{Al}_2\text{Cl}_7^-$ ions. Importantly, the electroplating of aluminum occurs through the reduction of $\text{Al}_2\text{Cl}_7^-$ ions, or in other words only in acidic chloroaluminate melts (an excess of $\text{AlCl}_3$).\[30-39\]

With respect to $\text{Al}^{3+}$ ion storage, various materials have been explored so far as positive electrodes, such as metal oxides,\[20–32\] sulfides,\[33–40\] selenides,\[41–43\] Prussian blue analogs,\[44,45\] phosphates,\[46\] carbides,\[47\] molybdates,\[48\] vanadates,\[49\] sulfur,\[50,51\] iodine,\[52\] and oxygen.\[53] It should be noted, however, that although these cathode materials were studied as potential hosts for $\text{Al}^{3+}$ ions, the mechanism of $\text{Al}^{3+}$ ion storage is reported scarcely. In fact, similar to Mg-ion batteries, the intercalation of multivalent $\text{Al}^{3+}$ ions, being much smaller than Li-ions, was shown to be hindered by the strong Coulombic interaction with the anionic sublattice of an intercalation host.\[54\] Namely, the polarizing power (i.e., the tendency of the nearby anions to become polarized by the cation) of $\text{Al}^{3+}$ is six times greater than that of $\text{Li}^+$ ($10.68$ e Å$^2$ vs $17.3$ e Å$^2$).\[55\] Consequently, the majority of reported cathodes demonstrated low charge storage capacity, low average discharge voltage versus $\text{Al}^{3+}/\text{Al}$, high polarization upon charge and discharge, as well as short cycle life. In general, the proposed redox reactions for the AIB with cathode denoted as AM (active material) can be presented as follows (Figure 1a)\[1,2\]

On the negative side: $\text{Al} + 7\text{AlCl}_4^- \leftrightarrow 4\text{Al}_2\text{Cl}_7^- + 3\text{e}^-$ \hspace{1cm} (1)

On the positive side: $\text{AM} + 4x\text{Al}_2\text{Cl}_7^- + 3x\text{e}^- \leftrightarrow \text{Al}_x\text{AM} + 7x\text{AlCl}_4^-$ \hspace{1cm} (2)

Contrary to the rocking chair AIBs, where the active cationic species $\text{Al}^{3+}$ (in the form of $\text{Al}_2\text{Cl}_7^-/\text{AlCl}_4^-$ ions) are shuttled between cathode and anode upon discharge and charged, ADIBs have a different operation mechanism, as displayed in Figure 1b. In short, the basic arrangement of ADIBs consists of a carbonaceous (graphite, zeolite-templated carbon (ZTC), or graphene) or organic cathode, metallic aluminum foil placed at the anode side of the battery and chloroaluminate ionic liquid melt. ADIBs work as a battery system utilizing reversible intercalation/insertion of the $\text{AlCl}_4^-$ anions into the positive electrode upon oxidation (charge). Concurrently, the reduction of $\text{Al}_2\text{Cl}_7^-$ ions occurs, resulting in the formation of metallic aluminum (electroplating) at the negative electrode of ADIBs. The operating principle of ADIBs can be depicted by the following half-reactions (Figure 1b)\[1,2\]

On the negative electrode: $4\text{Al}_2\text{Cl}_7^- + 3\text{e}^- \leftrightarrow 7\text{AlCl}_4^- + \text{Al}$ \hspace{1cm} (3)

On the positive electrode: $\text{AM} + x\text{AlCl}_4^- \leftrightarrow (\text{AlCl}_4)_x\text{AM} + x\text{e}^-$ \hspace{1cm} (4)

It should be stressed that taking into consideration the very fact that electrodeposition of Al occurs only in acidic compositions (in the presence of $\text{Al}_2\text{Cl}_7^-$, but not $\text{AlCl}_4^-$ ions), the amount of $\text{Al}_2\text{Cl}_7^-$ ions, and consequently the mass/volume of the chloroaluminate melt, should be balanced with the cathodic capacity. For one electrodeposited aluminum atom, three $\text{AlCl}_4^-$ ions are concomitantly intercalated/inserted into the cathode. Subsequently, the charging terminates when solely $\text{AlCl}_4^-$ anion left in the ionic liquid melt (equivalent to neutral melt formulation, $\text{AlCl}_4^-$:EMIMCl = 1) or conversely, when the maximum cathodic capacity is reached. As follows from the operational mechanism of ADIB, contrary to “rocking-chair” AIBs there is no reversible flow of $\text{Al}^{3+}$ ions or any other Al ions from the positive to the negative electrodes upon charge and discharge. For that reason, it is incorrect to call ADIB an “Al-ion battery.” In fact, the electrochemical energy storage mechanism of ADIBs is far more different from the operational principle of “rocking-chair” AIBs. Specifically, $\text{Al}_2\text{Cl}_7^-$ ions are depleted from the ionic liquid melts upon the charge, concomitantly changing its acidity (Figure 1b). In the case of AIBs, however, the composition of the ionic liquid electrolyte remains stable upon cycling (Figure 1a). Furthermore, the presence of Al foil at the negative electrode is not required because any current collector with deposited thin Al layer as a seed film for the initial aluminum plating might be sufficient. In this context, chloroaluminate ionic liquid melt of ADIBs must be seen as an anolyte (i.e., liquid anode) being reduced upon charge rather than Al electrolyte used “rocking-chair” AIBs. The dependence
of the theoretical capacity of chloroaluminate ionic liquid anolytes on their acidity \( r \) is represented as follows:

Volumetric \( C_{\text{an}} \) = \( \frac{F x (r - 1) \rho}{r M_{\text{AlCl}_3} + M_{\text{XCl}}} \) (mAh g\(^{-1}\)) \hspace{1cm} (5)

Gravimetric \( C_{\text{an}} \) = \( \frac{F x (r - 1)}{r M_{\text{AlCl}_3} + M_{\text{XCl}}} \) (mAh g\(^{-1}\)) \hspace{1cm} (6)

where \( F = 26.8 \times 10^3 \) mAh mol\(^{-1}\) (the Faraday constant), \( M_{\text{AlCl}_3} \) is the molar mass of AlCl\(_3\) in g mol\(^{-1}\), \( M_{\text{XCl}} \) is the molar mass of Cl\(^-\) source (for example, 1-ethyl-3-methylimidazolium chloride) in g mol\(^{-1}\), \( x = \frac{3}{4} \) (moles of electrons needed to reduce 1 mol of the Al\(_2\)Cl\(_7\) anions), \( r \) is the AlCl\(_3\):XCl molar ratio, and \( \rho \) is the density of the chloroaluminate ionic liquid melt in g mL\(^{-1}\). Thereby, for \( r = 1.3 \) and \( r = 2 \), volumetric and gravimetric capacities of AlCl\(_3\):EMIMCl equal 24 Ah L\(^{-1}\), 19 mAh g\(^{-1}\), and 63 Ah L\(^{-1}\), 48 mAh g\(^{-1}\), respectively. Importantly, the uppermost molar ratio \( r \) between AlCl\(_3\) and EMIMCl at which liquid still forms is \( \approx 2:1 \). At higher molar ratios, excess of the aluminum chloride precipitates. Considering the volume/mass of the chloroaluminate ionic liquid melt, the theoretical cell-level charge-storage capacity of ADIB can be calculated as follows (only including capacities of the cathode and the chloroaluminate melt):\(^{[7]}\)

\[
\text{Volumetric } C_{\text{cell}} = \frac{C_{\text{an}} C_{\text{c}}}{C_{\text{an}} + C_{\text{c}}} \frac{F x (r - 1) C_{\text{c}} \rho}{F x (r - 1) + C_{\text{c}} (r M_{\text{AlCl}_3} + M_{\text{XCl}})} \text{ (mAh mL}^{-1}\text{)} \hspace{1cm} (7)
\]

\[
\text{Gravimetric } C_{\text{cell}} = \frac{C_{\text{an}} C_{\text{c}}}{C_{\text{an}} + C_{\text{c}}} \frac{F x (r - 1) C_{\text{c}}}{F x (r - 1) + C_{\text{c}} (r M_{\text{AlCl}_3} + M_{\text{XCl}})} \text{ (mAh g}^{-1}\text{)} \hspace{1cm} (8)
\]

where \( C_{\text{cell}}, C_{\text{c}}, \) and \( C_{\text{an}} \) are the capacities of the cell, the cathode, and the anolyte; in mAh mL\(^{-1}\) or mAh g\(^{-1}\). Detailed derivation of Equations (7) and (8) can be found in ref. [7].

The implications of acidity \( r \) of chloroaluminate ionic liquid melts on the theoretical energy density of ADIBs using carbonaceous or organic cathode materials are demonstrated on Figure 2a (experimental data points). Besides, Figure 2a shows calculated cell-level energy densities of ADIBs (curves) computed from Equation (8), assuming that the voltage of ADIB equals 2 V irrespective the acidity. In accordance with Figure 2a, capacities of cathode and chloroaluminate ionic liquid anolyte (confined by the acidity of \( r \) of chloroaluminate ionic liquid) contribute to the energy density of ADIBs. Importantly, the analysis of all published data on ADIBs\(^{[6,61–73,87,97,98]}\) revealed that the highest theoretical energy density of \( \approx 65 \) Wh kg\(^{-1}\) was reported for ADIBs comprising kish graphite cathode with the capacity of 142 mAh g\(^{-1}\) (average discharge voltage of 1.79 V) and chloroaluminate bionic liquid melt with the acidity of \( r = 2 \).\(^{[72]}\) It should be emphasized, however, that majority of literature on ADIBs render studies on chloroaluminate ionic liquid melts with a quite low acidity \( r = 1.3 \). This evokes strict limitations on the energy density of ADIBs, which can not exceed 30 Wh kg\(^{-1}\), no matter how high is the capacity of graphite cathode (Figure 2a).

We stress that completely different calculations of theoretical energy density are applied for ADIBs taking into consideration the volumetric/gravimetric capacities of the Al anode (8046 mAh cm\(^{-2}\)/2980 mAh g\(^{-1}\)) and cathode, excluding Al-ion electrolyte. In ADIBs, chloroaluminate ionic liquid melt acts exclusively as a transmitter of the Al\(^{3+}\) ions, therefore, not contributing to the energy density calculations. Therefore, the gravimetric and volumetric capacity of ADIBs can be calculated using conventional equation (see ref. [7] for derivation details):\(^{[99]}\)

\[
\text{Volumetric or Gravimetric } C_{\text{cell}} = \frac{C_{\text{c}} C_{\text{an}}}{C_{\text{c}} + C_{\text{an}}}
\]

Figure 2. a) Comparison of the calculated (curves) and experimental (data points) cell-level energy densities of ADIBs consisting various carbonaceous\(^{[6,63–87]}\) and organic\(^{[5,88]}\) cathode materials. The curves are computed from Equation (8), which describes the dependency of the energy density versus cathode capacity at various values of \( r \) assuming an average discharge voltage of 2 V. The experimental energy density points of ADIBs are calculated using Equation (8) and reported voltages and capacities of cathodes at specific acidity of chloroaluminate melt. b) The comparison of cell-level energy densities of ADIBs comprising various cathode materials such as V\(_2\)O\(_5\), TiO\(_2\), MoS\(_2\), TiS\(_2\), NiS, CuS, and S\(^{[56,91–96]}\). The experimental energy density points of ADIBs are calculated using Equation (9) and reported voltages and capacities of cathodes.
where \( C_{\text{cell}}, C_a, \) and \( C_{\text{cat}} \) are the capacities of the cell, the cathode and Al anode; in mAh g\(^{-1}\) or mAh mL\(^{-1}\). To determine the energy density of AIBs or ADIBs, the \( C_{\text{cell}} \) value is multiplied by the average discharge voltage \( \langle V_{\text{cell}} \rangle \) of the battery, \( E_{\text{cell}} = C_{\text{cell}} \cdot \langle V_{\text{cell}} \rangle \). The latter can be determined by dividing the area under a discharge curve by the discharge time. Using Equation (9) as well as reported voltages and capacities of various oxide and sulfide cathode materials, one can show that the cell-level energy densities of studied AIBs fall in the range of 90–305 Wh kg\(^{-1}\). The highest reported values of \( \approx 1400–1500 \text{Wh kg}^{-1} \) were measured for S cathodes. It should be noted, however, that Al–S batteries are characterized by poor cyclic stability not exceeding 20–50 cycles.\(^{[100]}\) The cell level energy densities of AIBs composed of various cathode materials are summarized in Figure 2b. Notably, for assessment of the realistic capacity of both AIBs and ADIBs, \( C_{\text{cell}} \) should be decreased by 25–50% considering the weight of separator, current collectors, and packaging (depending on the battery design) or any other nonactive battery components required for battery operation.

Interestingly, aside from conventional chloroaluminate ionic liquid melts, it has been shown that other chloroaluminate formulations such as AlCl\(_3\)/NaCl\(^{[101,102]}\) or AlCl\(_3\)/LiCl/KCl\(^{[86,103]}\) fully inorganic melts can be used in ADIBs as cost-efficient alternatives. In this regard, because of the lower molar mass of alkali chlorides, the theoretical charge storage capacity of inorganic melts is higher than for ionic liquid melts of the same acidity. Furthermore, aluminum anolyte based on inorganic molten salts are low-cost and possess low viscosity and high ionic conductivity at melting temperatures, which improves the kinetics of AlCl\(_{4}^-\) insertion/deinsertion processes at the positive electrodes of ADIB. We note that from a perspective of large-scale industrial application, the high melting point of inorganic molten ADIBs should not be considered as a significant drawback as the exhausted heat from industrial processes.\(^{[101]}\)

Apart from chloroaluminate ionic liquid and inorganic melts, deep eutectic solvents (DESs), also named as ionic liquid analogs (ILAs), were recently tested in AIBs and ADIBs.\(^{[16,17,104]}\) In a similar fashion to chloroaluminate ionic liquid melts,\(^{[14]}\) DESs can be represented as liquids composed of an oxygen donor amide (Lewis base), such as urea, and metal halide (Lewis acid). Thereby, AlCl\(_3\)-urea DES can be prepared by the exothermic reaction between AlCl\(_3\) and urea

\[
2\text{AlCl}_3 + 2 \text{Urea} \rightarrow \text{AlCl}_2 + [\text{AlCl}_2(\text{Urea})_2]^+ \tag{10}
\]

Comprehensive studies of DESs using NMR\(^{[105–107]}\) and Raman\(^{[105,107–109]}\) spectroscopies revealed that Al\(_2\)Cl\(_7^-\) anions are not present in the AlCl\(_3\)-urea DESs with an AlCl\(_3\)/urea = 1 molar ratio formulation. However, at higher acidities of AlCl\(_3\)-urea melts, the amount of Al\(_2\)Cl\(_7^-\) ions concomitantly increases as compared with the quantity of the AlCl\(_4^-\) anions. It is worth noting that Al electrodeposition from AlCl\(_3\)-urea DESs takes place only in acidic compositions (AlCl\(_3\)/urea > 1.1), accompanying a decrease and increase of the concentration of AlCl\(_3^-\) and AlCl\(_4^-\) anions, accordingly.\(^{[108]}\) Similar findings have also been reported for other AlCl\(_3\)-amide DESs.\(^{[109]}\) Thereby, electrodeposition/stripping reactions of aluminum in AlCl\(_3\)-urea DESs can be described similar to RTILs

\[
4\text{AlCl}_3 + 3e^- \leftrightarrow 7\text{AlCl}_2 + \text{Al} \tag{11}
\]

Importantly, it has been experimentally demonstrated that the highest acidity \( (r) \) of the AlCl\(_3\)-urea DES, equals \( \approx 1.5.\(^{[105]}\) In this context, using the concentration of AlCl\(_3^-\) ions in AlCl\(_3\)-urea DES reported in ref. \( [108] \), the theoretical capacity of AlCl\(_3^-\)urea DES at \( r = 1.4 \) can be assessed at the level of 20–21 mAh g\(^{-1}\). AlCl\(_3\)-Me-urea and AlCl\(_3\)-Et-urea melts at \( r = 1.4 \) possess similar capacities of \( \approx 16 \) and 18 mAh g\(^{-1}\), respectively.

It should be underlined that Al electroplating/stripping (Al\(^{3+}\)/Al redox potential in AlCl\(_3\)-EMIMCl) was revealed to occur at 2 V versus Na\(^+/\)Na (i.e., \( \approx 0.7 \text{V} \) vs standard hydrogen electrode (SHE) and 2.3 V vs Li\(^+/\)Li), whereas the chloroaluminate ionic liquid melt starts to oxidize at \( \approx 4.5 \text{V} \) versus Na\(^+/\)Na (1.8 V vs SHE and 4.8 V vs Li\(^+/\)Li).\(^{[77]}\) These measurements were conducted employing specially designed cell consisting of a \( \beta \)-alumina solid electrolyte and Na metal reference electrode inserted in 1 m NaClO\(_3\) in propylene carbonate. Interestingly, these findings allow assessing the redox potentials of reported cathode materials for AIBs and ADIBs on the absolute scale, allowing the comparison with Li-ion or Na-ion electrochemistries (Figure 3). In this context, one can determine that the reason for the low overall voltage of AIBs and ADIBs is a low redox potential of Al\(^{3+}/\)Al in chloroaluminate melts compared to aqueous media. In fact, the shift of the Al\(^{3+}/\)Al redox potential of Al plating/stripping in chloroaluminate melts significantly decreases the overall energy density of both AIBs and ADIBs.

3. The Interpretation and Reporting of Data on AIBs and ADIBs

In our view, the most frequently observed issue leading to errors in data reporting on Al batteries is the incorrect classification of their charge storage mechanism. The very first matter
of concern, which should be addressed is whether the cathode material stores charge through the accumulation of Al\textsuperscript{3+} or AlCl\textsubscript{4}\textsuperscript{-} ions. To distinguish between these two types, one should first determine the content of Cl and the kind of Cl-species in the active material upon charge and discharge. First, this requires removal of excess chloroaluminate anolytes by a suited solvent. Subsequently, Al-species must be characterized by diverse methods such as \textsuperscript{27}Al solid-state nuclear magnetic resonance,[6] Raman,[67] X-ray photoelectron,[83] Auger electron,[63] X-ray absorption, and energy-dispersive X-ray spectroscopies.[90] The presence of the AlCl\textsubscript{4}\textsuperscript{-} species in charged cathode would clearly point to the dual-ion storage mechanism. Care must be taken when choosing the solvent for removing the excess ionic liquid and any physically absorbed Al-chloride species. For instance, many solvents that can solubilize the excess ionic liquids, such as acetonitrile, methanol, toluene, pentane, tetrahydrofuran, hexane, and trichloroethylene, can easily reduce cathode (i.e., chemically discharge it),[6] thereby depleting the amount of intercalated AlCl\textsubscript{4}\textsuperscript{-}. Tetrachloromethane (CCl\textsubscript{4}), however, is an oxidatively stable solvent capable of removing such ionic liquids.[6] Only when a charge storage mechanism is revealed, electrochemical half-reactions can be written and hence formulas for calculating the theoretical charge-storage capacities can be deduced. This is particularly critical for ADIBs, where incorrect, usually far overestimated, cell-level energy densities are often reported due to omission of the anolyte capacity from the calculations. Additionally, while conventional cathode materials of AIBs and ADIBs such as MoS\textsubscript{2}, S\textsubscript{8} and graphite are easily distinguishable from one another, there is an increasing number of materials displaying electrochemical charge storage mechanisms that are neither purely Al\textsuperscript{3+} nor AlCl\textsubscript{4}\textsuperscript{-}. This often leads to confusion among researchers during the analysis and reporting of data. It is usually attributed to the fact that the large addition of carbonous materials, required for the preparation of electrodes (for instance in the case of sulfur cathode), causes the extra capacity contribution from the AlCl\textsubscript{4}\textsuperscript{-} ion storage, eventually resulting in incorrect reporting of the intrinsic Al\textsuperscript{3+} ion capacity of cathodes for AIBs. Apart from that, to ensure proper electrochemical measurements, it is crucial to use the electrochemically stable cell components of AIBs and ADIBs such as cell casing, separator and sealing.

4. Charge-Storage Balance in ADIBs

Eventual commercialization of any kind of battery requires fulfilment of stringent requirements, of which one is optimal balancing of the cathode and anode quantities. For instance, in commercial Li-ion batteries, there exist only a small excess (\(-10\%\)) of an anode material (graphite) with respect to the quantity required to accept all Li-ion from the cathodic material upon full charge (capacity-matched cell). In this specific case, the anode excess serves to avoid the risk of lithium metal plating, a severe aging and safety-deteriorating process.[111] Importantly, any imbalance of the active materials as well as all nonactive materials (electrolytes, separators, casing) reduce the achievable energy density, which in the case of best Li-ion batteries is \(\approx 50\%\) of theoretical value.[112] These considerations are equally important for ADIBs.

For ADIBs too, the maximal theoretical energy density corresponds to the case of a capacity-balanced cell—when anolyte quantity matches the charge-storage capacity of the cathode in a fully charged state. Thus far, reports on ADIBs presented the results obtained with heavily imbalanced cells, typically with the high excess of anolyte. Such cathode-limited cells are well suited for accessing the performance of novel cathode materials. In this regard, we recommend authors to report the excess of used anolyte. Another important consideration is assessment of the rate-capability (power density) of ADIBs. Such measurements, i.e., capacity versus current density, are also usually conducted with cathode-limited cells. The results are usually very impressive, seen as a good retention of cathodic capacity at high current densities of up to 100 A g\textsuperscript{-1} (full charge in 4 s) owing to the fast intercalation of chloroaluminate ions. At these high current densities, graphene based cathodes can retain up to 100% of the low-rate capacity (120 mAh g\textsuperscript{-1}) and for very long cycling (250 000 cycles).[74] At the same time, much less attention is paid to the anode(anolyte)-limited and balanced cells. In ref. [62], with \(\approx 40\%\) surplus of cathode a rather small anolyte capacity of just 10–14% from theoretical value was measured at a current density of 1 A g\textsuperscript{-1} and close to theoretical value at lower current densities (20 mA g\textsuperscript{-1}). This drastic difference was observed in a broad range of acidity (\(r = 1.3–2\)). We thus conclude that it is critical to use anolyte-limited or balanced cells in reports on novel anolytes to assess their capacity. Overall, it is imperative to describe the quantities of active materials (cathodes, ionic liquids) in the experimental sections.

5. Summary and Outlook

With respect to the AIBs, a significant difference exists in comparison to monovalent Li-ion electrochemistry. Reversible intercalation of Al\textsuperscript{3+} cations, which are smaller than Li\textsuperscript{+} ions, was revealed to be far harder due to Coulombic interaction with the lattice of the host cathode. The most pressing need is therefore exploration of novel cathode materials with the aid of material discovery platforms, which combine machine learning, computation chemistry, high-throughput experimentation, and data collection.

While the literature on AIBs and ADIBs has flourished in recent years, the development of their commercially competitive prototypes lags far behind. Among diverse types of Al batteries, Al–graphite DIBs have the highest technology readiness level for deployment in stationary energy storage owing to their low cost, relatively high energy densities of up to \(\approx 70\) Wh kg\textsuperscript{-1} (at the cell-level),[7] and high cycling stability (thousands of cycles).[67] Al–graphite DIBs can potentially last for tens of years with daily deep cycling due to the highly reversible AlCl\textsubscript{4}\textsuperscript{-} intercalation into the graphite cathode and efficient anodic Al plating/stripping. The capital cost of Al–graphite DIBs was recently assessed by Albufera Energy Storage (ALION project, 1 Ah cell prototype) to be on the level of \(\approx 0.03\) € kWh\textsuperscript{-1} per cycle,[113] which is on par with the goal set by the European Union in Strategic Energy Technology Plan 2030 (<0.05 € kWh\textsuperscript{-1} per cycle).[114]

As to the ADIBs, we have to stress that chloroaluminate melts employed in ADIBs are not only the ion-conductive
electrolytes, but a capacity- and rate-limiting, electrochemically active battery components (anolytes). ADIBs can thus be considered as a half-liquid energy storage technology. The excess amount of liquid anolyte, above that needed for matching the cathode capacity, must be minimal but sufficient for attaining the targeted power density and for ensuring long cyclability of the battery. Finding this optimal balance is specific to the active materials used and the design of cells and batteries. Drastic fluctuations in the volume of the liquid phase during the battery operation (unlike to rocking-chair-type batteries such Li-ion batteries) must be factored into the design of the cell.

With regard to the main pitfalls in interpretation and reporting of data on nonaqueous AIBs and ADIBs, they are as follows: 1) the use of improperly washed electrodes from electrolytes that has a direct impact on revealing the charge storage mechanism of Al batteries; 2) the use of electrochemically unstable (active) cell components, such as current collectors, cell casing, separator, and sealings. Their electrochemical activity upon cycling leads to incorrect reporting of the charge storage capacity of cathode materials and, consequently, the energy density of AIBs and ADIBs; 3) the electrochemical measurements of ADIBs in a cathode-limited configuration for the evaluation of power density of ADIBs.

Importantly, we have to stress that first two discussed pitfalls on nonaqueous Al systems should also be considered when reporting on aqueous AIBs.

Another major practical issue for both AIBs and ADIBs is the high corrosivity of Al electrolytes (anolytes). For example, stainless steel is rapidly corroded by the chloroaluminate melts and hence cannot be used for battery casing. Unlike Li-ion batteries, where the Al foil is a ubiquitous choice for current collector at the cathode side, other conductors shall be tested as current collectors in AIBs and ADIBs such as titanium carbide, and vanadium carbide and vanadium nitride. Moreover, additional research should be carried out to mitigate or fully suppress the corrosion of Al foil with chloroaluminate electrolytes at the anode side. A promising avenue is also to reduce Al plating/stripping redox potential, which for chloroaluminate melts is ≈1 V higher (≈−0.7 V vs SHE) than in aqueous media (≈−1.66 V vs SHE). Any decrease in Al\(^{3+/4+}\) potential will translate into higher cell voltage and hence higher energy densities for both AIBs and ADIBs. Al-batteries are often tagged as an extremely cost-competitive solution, owing to the low cost and simple manufacturing of the presently used components. It remains uncertain whether these cost benefits will be retained once all herein discussed issues are resolved.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Al dual-ion batteries, Al-ion batteries, aluminum, stationary energy storage

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