t present, the replacement of fossil fuels by alternative CO₂-emission-free energy sources, such as solar and wind, is substantially hindered by the lack of low-cost and large-scale energy storage technologies. Although lithium-ion batteries (LIBs) represent the most mature and widely deployed electrochemical energy storage technology for mobility and portable electronics, the uneven worldwide distribution of known lithium reserves and the high production costs greatly reduce the economic appeal of LIBs for large-scale stationary storage.¹⁻⁵ In this regard, inexpensive Al–graphite dual-ion batteries (AGDIBs) have attracted great attention over the past few years.⁶⁻⁻²⁶ With energy densities of 30–70 Wh kg⁻¹, AGDIBs are suitable for stationary storage.²⁷⁻⁻³⁰ The constituents of AGDIBs include highly abundant elements (H, O, N, C, and Al) and are easy to manufacture. While recent research efforts on AGDIBs have been mainly focused on testing various graphite cathodes, further progress of this technology is inherently limited by the low charge storage capacity of the chloroaluminate ionic liquids used as anolytes (often but incorrectly called electrolytes). In this Viewpoint, we discuss the critical interplay between the capacity of the anolyte and the energy density of AGDIBs along with their measurements at different current densities.

The basic configuration of an AGDB contains a graphite cathode, AlCl₃-EMIMCl (1-ethyl-3-methylimidazolium chloride) ionic liquid anolyte, and metallic aluminum current collector, as demonstrated in Figure 1a. AGDIBs operate as an electrochemical energy storage system by employing the reversible intercalation of AlCl₄⁻ anion species into the positive graphite electrode upon charging (i.e., the oxidation of the graphite network). Concurrently, the aluminum electroplating reaction takes place on the negative side of AGDIBs. The working principle of AGDIBs can be represented by the following cathodic and anodic half-reactions during charging:

**On the negative electrode**

\[ 4\text{AlCl}_4^- + 3e^- \leftrightarrow 7\text{AlCl}_4^- + \text{Al} \]  

**On the positive electrode**

\[ x\text{C} + \text{AlCl}_4^- \leftrightarrow x\text{C}_n(\text{AlCl}_4^-) + xe^- \]  

The chloroaluminate ionic liquid anolyte used in AGDIBs is defined as a mixture of aluminum chloride and other chlorides countered by a bulky organic cation, such as 1-ethyl-3-methylimidazolium chloride (EMIM) or 1-butyl-3-methylimidazolium chloride (BMIM). As a result of the acid–base reaction between AlCl₃ (Lewis acid) and Cl⁻ (Lewis base), the solid mixture liquefies at room temperature, forming AlCl₄⁻ anions that are charge-balanced with asymmetric organic cations, such as EMIM⁺. The chloroaluminate ionic liquid with an excess of AlCl₃ over EMIMCl is composed of both AlCl₄⁻ and Al₂Cl₇⁻ ions. Importantly, only AlCl₄⁻ ions enable the electroplating of aluminum, which, therefore, occurs only in acidic chloroaluminate melts (i.e., an excess of AlCl₃).³¹⁻⁴⁰ Consequently, the specific charge storage capacity of the acidic melt is a function of the concentration of AlCl₄⁻ ions in the ionic liquid. Electroplating, and consequently the charging process, stops when no AlCl₄⁻ ions remain in the ionic liquid, at which point the melt becomes neutral (AlCl₃:EMIMCl = 1). The highest molar ratio (r) of AlCl₃ and EMIMCl that forms an ionic liquid is ca. 2:1. AlCl₃ does not dissolve in the chloroaluminate melts at higher molar ratios. In this context, we note that the mechanism of AGDIBs is substantially different from the operation of “rocking-chair” metal-ion batteries: there is no unidirectional flow of Al³⁺ ions from the cathode to the anode and vice versa. In fact, the Al species are depleted from the chloroaluminate ionic liquid during the charge of AGDIBs and are being consumed by both electrodes (Figure 1a). Notably, the electrochemistry of AGDIBs is not restricted to AlCl₃/EMIMCl ionic liquids. Other possible ionic melts have also been recently tested in AGDIBs, such as AlCl₃/1-methyl-3-propylimidazolium chloride (MPIMCl),⁴¹ AlCl₃/benzyltriethylammonium chloride (TEBACl),⁴² AlCl₃/1,2-dimethyl-3-propylimidazolium chloroaluminate (DMPICl),⁴³ AlCl₃/NaCl,⁴⁴ and AlCl₃/LiCl/KCl⁴⁵ or AlCl₃/urea/EMIMCl,⁴⁶ AlCl₃/urea,⁴⁷⁻⁴⁹ and AlCl₃/Et₃N/NaCl.⁵⁰⁻⁵¹

Figure 1b illustrates the impact of acidity (r) on the charge storage capacity of the chloroaluminate ionic liquid anolyte. The
theoretical capacity of the ionic liquid \((C_{\text{an}})\) as an anolyte, considering its whole mass/volume, can be calculated as follows:

Gravimetric

\[
C_{\text{an}} = \frac{Fx(r - 1)}{rM_{\text{AlCl}_3} + M_{\text{ACl}}} \text{ (mAh g}^{-1}\text{)}
\]  

(1)

Volumetric

\[
C_{\text{an}} = \frac{Fx(r - 1)\rho}{rM_{\text{AlCl}_3} + M_{\text{ACl}}} \text{ (mAh mL}^{-1}\text{)}
\]  

(2)

where \(F = 26.8 \times 10^3\ \text{mAh mol}^{-1}\) (the Faraday constant), and \(x = \frac{3}{5}\) (number of electrons used to reduce 1 mol of the \(\text{Al}_2\text{Cl}_7^{-}\) ions); \(M_{\text{AlCl}_3}\) is the molar mass of \(\text{AlCl}_3\) in g mol\(^{-1}\), \(M_{\text{ACl}}\) the molar mass of the \(\text{Cl}^{-}\) source (for example, EMIMCl) in g mol\(^{-1}\), \(r\) the \(\text{AlCl}_3:\text{ACl}\) molar ratio, and \(\rho\) the density of the chloroaluminate-based anolyte in g mL\(^{-1}\).

The theoretical gravimetric charge storage capacities of \(\text{AlCl}_3:\text{EMIMCl}\) ionic liquids equal, for instance, to 48 mAh g\(^{-1}\) and 19 mAh g\(^{-1}\) for \(r = 2\) and \(r = 1.3\), respectively. These capacities determine and limit the overall energy density of AGDIBs, as previously pointed by us\(^7\)\(^\text{-}\)\(^5\)\(^9\) and others.\(^5\)\(^2\)\(^\text{-}\)\(^5\) To the best of our knowledge, it had not been verified whether these capacities are achievable experimentally, i.e. whether \(\text{Al}_2\text{Cl}_7^{-}\) ions can be fully depleted for \(\text{Al}\) electroplating at practically relevant experimental conditions. For this, the anolyte-limited cell must be assembled, that is, the cell with the significant excess of graphite cathode. On the contrary, the commonly reported AGDIB tests employ an up to 10-fold excess of anolyte (or even higher). We note that such a 10-fold anolyte access can be recalculated into an impractical overall charge-storage capacity of the cell (<5 mAh g\(^{-1}\)). In the anolyte-limited cell, depletion of \(\text{Al}_2\text{Cl}_7^{-}\) ions \(r\) will eventually cause a drop in the potential at the negative electrode of the battery. It is thus also important to conduct tests in a three-electrode configuration in order to differentiate between changes in the potentials originating at positive and negative electrodes.

Following these considerations, we prepared an anolyte-limited full cell, in which an excess of graphite flakes was used in combination with the anolyte, i.e. having roughly an order of magnitude higher cathodic capacity in comparison to that needed to match the theoretical charge storage capacity of the anolyte. AGDIBs were assembled using a three-electrode cell
composed of a glassy carbon current collector, graphite flake cathode, Al foil reference electrode, separator impregnated with chloroaluminate ionic liquid anolyte, and Al foil current collector (Figure 2a). The cells were cycled between 2.5 and 0.1 V vs Al^{3+}/Al. An example of the electrochemical measurement at a current density of 60 mA g$^{-1}$ is shown in Figure 2b using a chloroaluminate ionic liquid with a molar ratio of 2.0. In these measurements, the simultaneous acquisition of the potential profiles of both positive and negative electrodes was recorded, in addition to that of the full cell.

As follows from Figure 2b, the voltage profile at the negative electrode ($E_{CE}$) remains relatively stable during charging for 15 min, with a small overpotential of up to 200 mV. However, upon further charging, this voltage drops sharply when the Al plating process ends. The plating termination is also indicated in the pronounced deviation (not shown). The green line shows the theoretical voltage profile at the positive electrode ($E_{CE}$), however, is relatively stable for the full charging cycle. In contrast to the anolyte-limited cell, the voltage profiles at the negative electrode ($E_{CE}$) for the graphite-limited cell are relatively stable during the entire charge, with a minimal overpotential of ∼50 mV (Figure 2c). As indicated above, the graphite-limited cell configuration is used for the assessment of the charge storage capacity of graphite in the majority of research studies on AGDIBs.

Using the ionic liquid formulations with $r = 1.3$--2.0, we performed rate capability measurements of anolyte-limited full cells at different current densities ranging from 5 A g$^{-1}$ to 20 mA g$^{-1}$. Figure 3a presents the galvanostatic curves of the anolyte with $r = 2$ during charging (see Figure S1 for details). The electrochemical data for $r = 1.3$ and 1.8 are shown in the Supporting Information (Figures S2 and S3). Figure 3b summarizes these results in terms of the obtained charge storage capacities at different current densities. The results reveal two major points. First, a more acidic anolyte yields a higher anolyte capacity. For instance, the charge storage capacity of the most commonly used anolyte with $r = 1.3$ is ca. 21 mAh g$^{-1}$ at 20 mA g$^{-1}$. In contrast, the anolyte with the highest acidity ($r = 2.0$) possesses a capacity of ca. 46 mAh g$^{-1}$. These results point to the fact that the highest energy density of the AGDIBs can be obtained using a 2.0 molar ratio, and therefore, future works on AGDIBs should be focused on the most acidic formulations. Second, the charge storage capacity of the anolyte is highly dependent on the applied current density. For instance, at a high current density of 1 A g$^{-1}$, minimal charge storage capacities are obtained (ca. 10--14% from theoretical values). The latter point is reflected in the pronounced deviation of the voltage profiles at the negative electrode at high current densities (Figures 3a and S1--S3). Conversely, minimal polarization is observed at the graphite positive electrode. These results indicate that the frequent statements regarding the high power density of AGDIBs need to be taken with care. Specifically, we note that at high current densities the energy density of AGDIBs is expected and originated from the rate capability limitations of the chloroaluminate ionic liquid anolyte when its acidity (concentration of Al$_2$Cl$_7$) is drastically reduced. In fact, our observations show that the charge storage capacities of the anolyte significantly deviate from the theoretical value at charge current densities greater than 20 mA g$^{-1}$.

In conclusion, we reiterate that commonly reported tests of AGDIBs employ large excess of ionic liquid anolyte (cathode-limited cells) and, despite nominally dealing with full cells, do not provide correct and practically relevant information on achievable energy and power densities, as well as cycling stability, energy and Coulombic efficiencies of these batteries. At best, such tests yield the theoretical capacities and other characteristics of the cathode material only, similar to, for instance, Li-ion half-cell tests of novel cathodes (with thick Li foil as a counter electrode). We further note that ionic liquids used in AGDIBs are not just electrolytes (ion-conductors) but represent an electrochemically active, capacity- and rate-limiting battery component. It is also apparent that future work should focus on finding ways of minimizing the amount of this anolyte toward the capacity-matched quantity, ideally with just ca. 10% of the excess anolyte, without sacrificing the power density and cyclability of the battery. Most likely, a successful solution to this problem will be based on a radically new battery design, vastly different from that employed in commercial Li-ion batteries and nearly all tests of new battery materials. All these advancements will need to come at low capital costs in order to retain the overall cost-competitiveness that is commonly attributed to AGDIBs (based on low costs of electrochemically active constituents). Similar considerations apply also to other nonrocking-chair batteries, such as magnesium–sodium and magnesium–lithium dual-ion batteries.

Kostiantyn V. Kravchyk orcid.org/0000-0001-6149-193X
Carlotta Seno
Maksym V. Kovalenko orcid.org/0000-0002-6396-8938

ACS Energy Lett. 2020, 5, 545–549

http://dx.doi.org/10.1021/acsenergylett.9b02832

Aluminum chloride financially supported by Innosuisse - Swiss Innovation Agency.

REFERENCES


Kovalenko, M. V.; Searles, D. J.; Wang, L. Unlocking the potential of commercial carbon nanofibers as free-standing positive electrodes for flexible aluminum-ion batteries. J. Mater. Chem. A 2019, 7 (25), 15123−15130.


Acknowledgments

This research is part of the activities of SCCER HaE, which is financially supported by Innosuisse - Swiss Innovation Agency.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.9b02832.

Additional electrochemical data (PDF)

Author Information

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsenergylett.9b02832.

Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS. The authors declare no competing financial interest.

Received 10 May 2019. Accepted 10 June 2019. Publication Date: 18 June 2019.


