ACS Energy Letters
Cite This: ACS Energy Lett. 2019, 4, 2124−2129
http://pubs.acs.org/journal/aelccp

Avoiding Pitfalls in Rechargeable Aluminum Batteries Research

Rechargeable aluminum (Al) batteries have become an attractive topic in recent years driven by the quest for battery technologies beyond lithium. Al has excellent theoretical specific capacity (2980 mAh g^{-1}) and volumetric capacity (8040 mAh cm^{-3}) as a battery anode, although high-voltage Al batteries can be difficult to achieve due to its relatively high anodic potential. A typical rechargeable Al battery is composed of an Al metal anode, a deep eutectic solvent electrolyte, and a cathode capable of reversible electrochemical reaction with the Al-containing species in the electrolyte. Al metal is likely the only viable choice as the anode. Therefore, the electrochemical reaction at the anode is reversible Al deposition−stripping. To date, the only (without ambiguity) electrolytes that can facilely enable Al deposition−stripping at room temperature are deep eutectic solvents composed of aluminum halides (aluminum chloride $AlCl_3$ or aluminum bromide $AlBr_3$) and the corresponding halides with organic cations such as imidazolium, pyridinium, and ammonium.[1] The discovery of this type of electrolyte is attributed to the electrodeposition community in the pursuit of the electrochemical plating of Al.[2,3] It is well-known that only a Lewis acidic electrolyte, in which the molar ratio between $AlCl_3$ (or $AlBr_3$) and organic halide is higher than 1, can reversibly deposit and strip Al. The active species responsible for Al deposition is the Lewis acidic chloroaluminate anion $Al_2Cl_7^-$.[3] The other major chloroaluminate anion existing in the electrolyte is $AlCl_4^-$, which is not active in Al deposition. On the other hand, it is known to be prone to electrochemical oxidation to evolve chlorine (Cl_2).[3] $AlCl_4^-$ also is reported to be capable of intercalating into the layers of graphitic carbons,[4,5] which have attracted significant attention as the cathode material in rechargeable Al batteries.

Although there have been a few studies reporting new Al electrolyte systems,[6−9] due to the readiness of (or a lack of alternatives to) the deep eutectic electrolytes, current Al battery investigations are mainly focused on cathode materials. The performance of some representative cathode materials for rechargeable Al batteries is compared in the Supporting Information. The deep eutectic chloroaluminate electrolytes play an essential role in cathode material investigations, but it is also extremely important to understand the interference and even misleading results caused by their use. The problems of the chloroaluminate electrolytes originate from their intrinsic properties: low anodic stability, i.e., generation of chlorine or other active side products during charge, and electrochemically enhanced corrosivity. Investigators must carefully design and execute the experiments as well as rigorously interpret the data to obtain the true results. In the following sections, we discuss some pitfalls that may be overlooked in the research on rechargeable Al batteries, as illustrated in Figure 1.

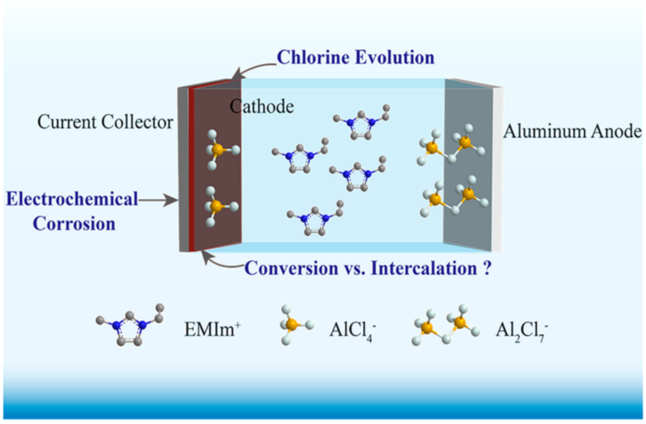

Figure 1. Illustration of the potential issues overlooked in rechargeable aluminum battery research.

Selection of Current Collectors. Selecting suitable cathode current collectors is of fundamental importance because most of the studied metals can be (electrochemically) corroded in deep eutectic chloroaluminate electrolytes, and the corrosive current can be mistaken as the current from battery reactions, as demonstrated by Reed and Menke in the case of stainless steel.[10] To demonstrate the importance of a suitable current collector, the electrochemical properties of a number of conductive substrates were analyzed in a representative deep eutectic electrolyte composed of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) with a molar ratio of 1.3:1. The electrolyte was prepared by mixing ultrapure anhydrous $AlCl_3$ with [EMIm]Cl, which was first dried at elevated temperature under vacuum for 24 h in an argon-filled glovebox. A thoroughly polished Al foil was used as the anode, a piece of dried cotton wool soaked with the electrolyte was used as the separator, and the cathode was the bare current collector being tested. To eliminate potential interference, customized Swagelok-type cells with polyether ether ketone (PEEK) body and glassy carbon (GC) rod electrodes were used. Polytetrafluoroethylene (PTFE) was not selected for the cell body due to our previous finding that fluorinated polymers may not be electrochemically inert in the deep eutectic chloroaluminate electrolyte.[11] The entire Swagelok cell contained no metal parts in contact with the electrolyte. A drawing and digital image of the Swagelok-type cell and the experimental details can be found in the Supporting Information.

Figure 2 shows the galvanostatic reduction and oxidation of the current collectors, denoted as discharge and charge, respectively, to be consistent with battery study. The corresponding cyclic voltammetry (CV) analysis are shown

Received: June 16, 2019
Accepted: August 2, 2019

DOI: 10.1021/acsenergylett.9b01285
ACS Energy Lett. 2019, 4, 2124−2129

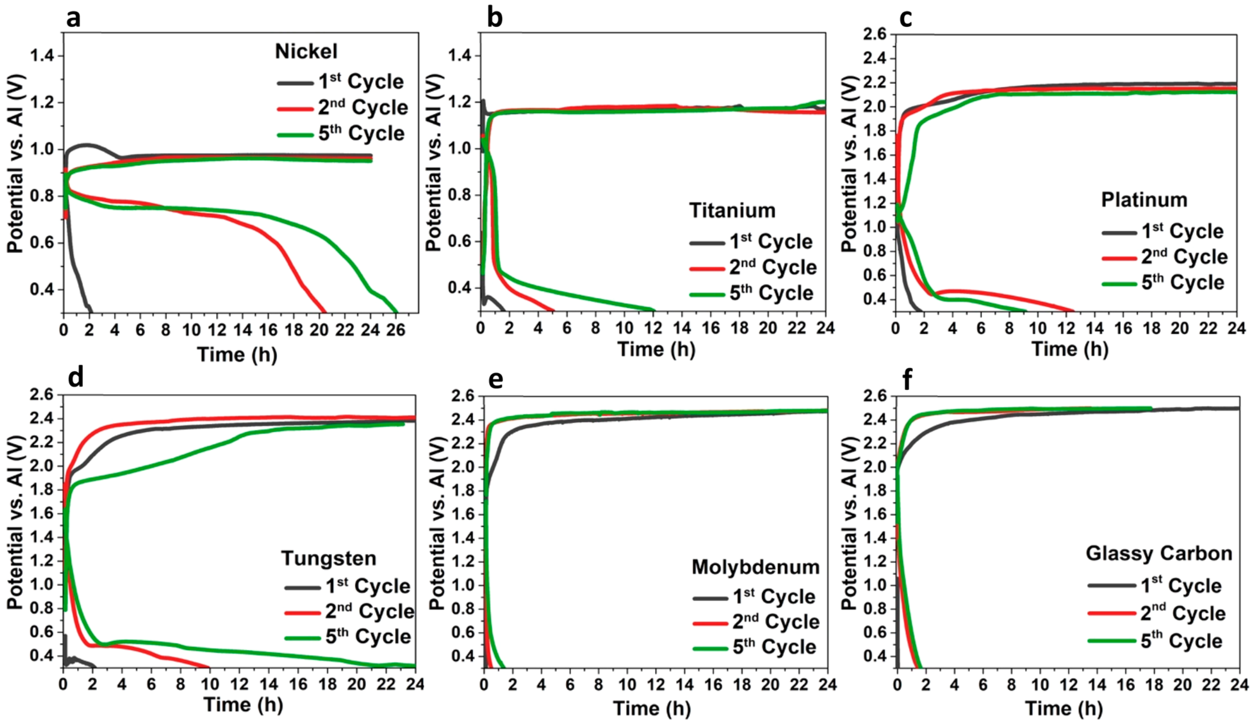

Figure 2. Galvanostatic discharge−charge (reduction−oxidation) curves of various conductive substrates including (a) nickel, (b) titanium, (c) platinum, (d) tungsten, (e) molybdenum, and (f) glassy carbon versus aluminum under a current of 1.78 × 10^{-2} mA cm^{-2} at room temperature.

in the Supporting Information. The galvanostatic experiments started with a discharge current of 1.78 × 10^{-2} mA cm^{-2}. All current collectors except GC and molybdenum (Mo) showed a short discharge potential curve for approximately 2 h before reaching the cutoff potential at 0.3 V versus Al. If we assume that the areal loading of the material of interest was 1 mg cm^{-2}, the artificial "capacity" from the first discharge would be around 35 mAh g^{-1} even if the material is completely inert. This false capacity may be related to the native oxide layer on the surface of the metal substrates and the cathodic decomposition of the electrolyte. It is also worth noting that this artificial discharge capacity is very sensitive to the moisture content of the electrolyte. As shown in the Supporting Information, the discharge curve is much longer on the GC surface in an $AlCl_3$-[EMIm]Cl electrolyte not dried under vacuum. The side reaction could be the electrochemical reduction of water to produce hydrogen and hydroxyl anions. The cathodic decomposition of the deep eutectic chloroaluminate electrolytes is worth thorough investigation.

Even more significant than the false discharge potential curve, the first charge resulted in a very pronounced potential plateau on all substrates with different onset points. The lowest plateau occurred with the nickel (Ni) substrate at approximately 1.0 V versus Al, which is clearly due to the electrochemical oxidation (corrosion) of Ni because it is much lower than the potential of chloride oxidation (chlorine generation). Furthermore, the electrochemical oxidation of Ni resulted in a distinct discharge plateau at 0.8 V versus Al in the subsequent discharge with a high apparent capacity and repeatability. Although Ni demonstrates some interesting electrochemical behavior, which may be worth further investigation, it is clear that Ni and Ni-containing alloys cannot be used as current collectors to study any active cathode materials. This statement is also true for titanium (Ti), platinum (Pt), and tungsten (W), although these metals appear to have better resistance to electrochemical oxidation with higher charge plateaus. Nevertheless, the electrochemical oxidation of unstable substrates can lead to significant false discharge capacities from ∼150 to ∼400 mAh g^{-1} with a current of 1.78 × 10^{-2} mA cm^{-2} (under the assumption of 1 mg cm^{-2} loading of material of interest).

The most stable substrates among those tested are Mo and GC, which displayed oxidation plateaus above 2.4 V versus Al with onset potentials at 1.8 and 2.0 V, respectively. The 2.4 V plateau is due to the chlorine generation of reaction 1, and it is the upper limit of the stable window of the deep eutectic chloroaluminate electrolytes.

$$4AlCl_4^- - 2e^- \rightarrow 2Al_2Cl_7^- + Cl_2 \qquad (1)$$

It is also worth noting that the chlorine generation reaction does not induce any noticeable artificial discharge reactions on either Mo or GC surfaces. This indicates that Mo and GC can be cathodically stable even in the presence of chlorine. Therefore, one can conclude that Mo and GC are suitable current collectors to study cathode materials. Moreover, to avoid any potential interference, the best practice would be to keep the upper cutoff potential well below the 2.4 V limit versus Al. As the next section demonstrates, a high surface area of the cathode structure may promote side reactions even at potentials lower than 2.4 V versus Al. In addition to Mo and GC, titanium nitride and chromium nitride were also reported to be stable in deep eutectic chloroaluminate electrolytes.[12] In that same study, the authors also reported W to be more anodically stable than Mo and GC, a result inconsistent with that of our study. This finding indicates that the stability of the current collector is quite sensitive to experimental conditions, although Mo, GC, or W current collectors appear to be the better choices regardless. We suggest investigators to always

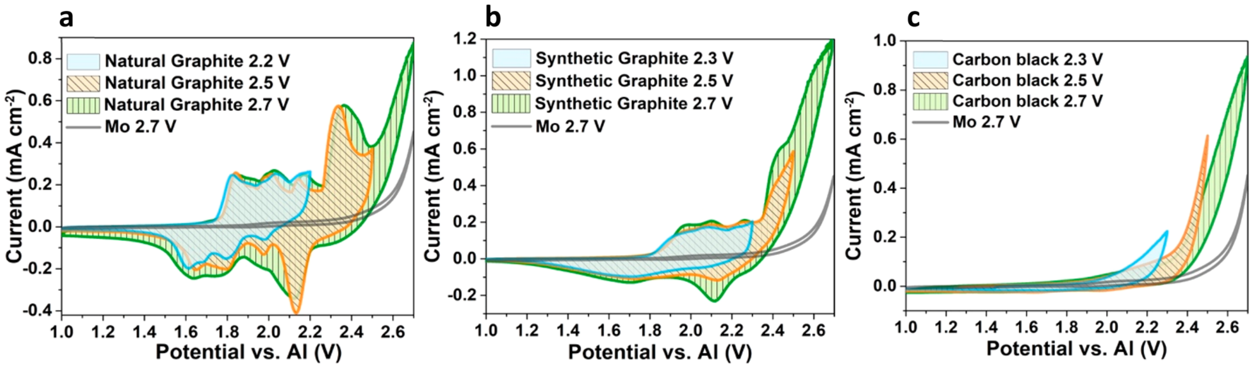

Figure 3. CV scans of various carbon materials including (a) natural graphite, (b) synthetic graphite (carbon paper), and (c) high-surface-area amorphous carbon nanoparticles versus Al under a scan rate of 0.2 mV s^{-1} at room temperature.

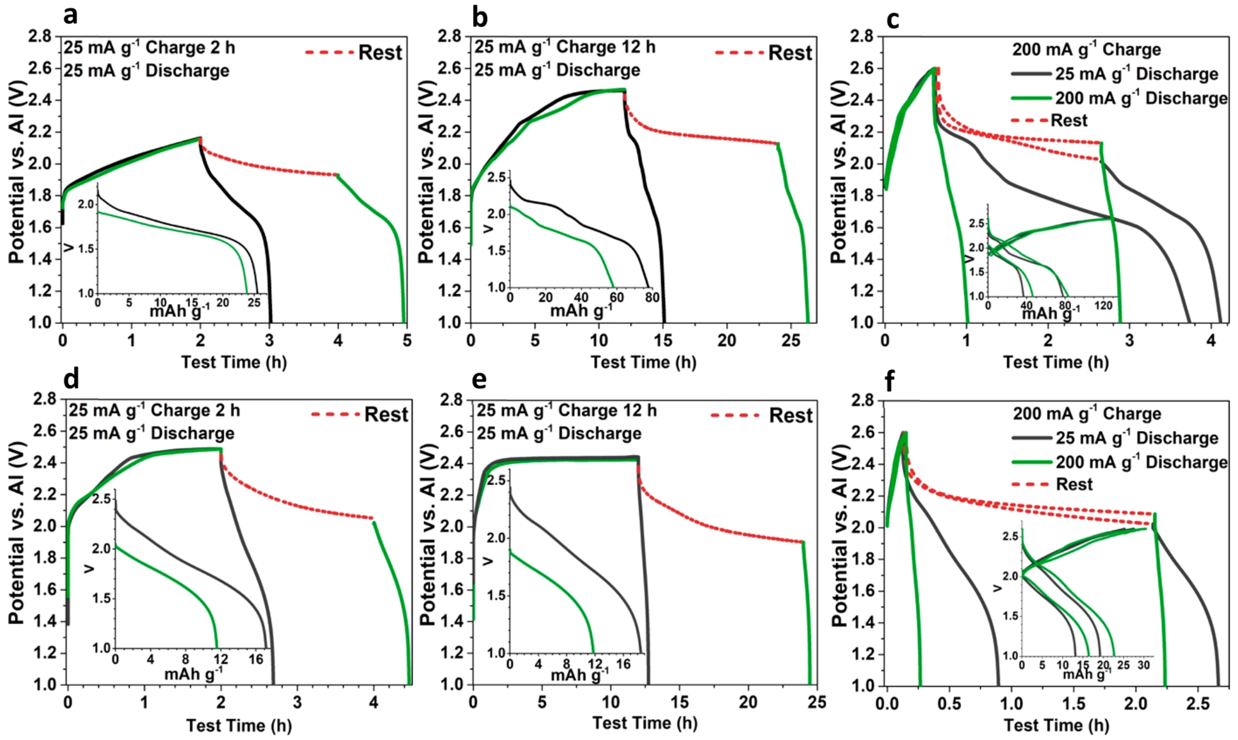

Figure 4. Different galvanostatic charge and discharge profiles (first cycle) of natural graphite (a−c) and synthetic graphite (d−f) at room temperature. The insets display the discharge potential profiles and capacities.

test "blank" electrodes (bare current collectors) as a reference while avoiding contact between the electrolyte and the usual suspects such as stainless steel, Ni, Ti, Pt, etc.

Ambiguities Concerning the Carbon Cathode Materials. The most promising cathodes for rechargeable Al batteries are graphite or graphene-based materials, which have been under intensive investigations motivated by Lin et al.'s work reporting $AlCl_4^-$ reversibly intercalating into the interlayers of graphitic carbons with high voltage, good capacity, excellent C rate, and cycle stability.[4] However, it is our intention to raise the awareness of certain potential points of contention regarding carbon cathode materials. As demonstrated in the current collector study, chlorine generation occurs at approximately 2.4 V versus Al. Because the current used to determine the chlorine generation was fairly low at 1.78×10^{-2} mA cm^{-2}, no considerable concentration polarization would be generated. Therefore, 2.4 V versus Al should be close to the thermodynamic potential (with an activation overpotential) of chlorine generation in the deep eutectic chloroaluminate electrolytes. On the other hand, the charge-cutoff potential in most of the publications on carbon cathode materials is higher than or very close to 2.4 V versus Al. Thus, the possible generation of chlorine during the charging process on carbon cathodes is a legitimate concern.

Figure 3a displays the CV scan of natural graphite (3.5 mg cm^{-2} loading) versus Al. Three anodic potential limits including 2.2, 2.5, and 2.7 V versus Al were selected to illustrate the evolution of the redox reactions of natural graphite. The graphite was coated on a Mo current collector; therefore, the CV scan of the bare Mo current collector is also shown in the plot for reference. Three pairs of reversible redox peaks appear within the CV window between 1.0 and 2.2 V versus Al, and one more pair of reversible peaks with high peak current appears when the window is extended to 2.5 V. These peaks were assigned to different stages of $AlCl_4^-$ intercalation into graphite in the literature. However, disagreement exists concerning the specific stage numbers obtained from X-ray diffraction and Raman spectroscopic characterizations.[13−16] When the anodic scan is extended to 2.7 V versus Al, a high-current oxidation peak appears but without a reversible reduction peak. This peak clearly coincides with the chlorine generation peak indicated by the scan curve on the bare Mo current collector. The CV scans on synthetic graphite with 7.0 mg cm^{-2} loading (Figure 3b) demonstrate the same behavior but with less defined peaks. It is worth noting that the synthetic carbon that we used was carbon paper, which is a common current collector used in studies of Al cathode materials. Figure 3c shows the CV scans on amorphous carbon (carbon black) (1.8 mg cm^{-2} loading) with a high surface area of 1100 m^2 g^{-1}. It is interesting to see that amorphous carbon, lacking a periodic graphitic structure, hardly shows reversible redox peaks. However, it indeed shows pronounced and irreversible oxidation peaks. This observation has two indications: that it is possible that some portion of the apparently reversible oxidation peaks (charging process) in natural graphite and synthetic graphite is irreversible and that high surface area may promote this irreversible oxidation mechanism(s), which may be universally true for all high-surface-area materials.

The complexity of the electrochemical processes on carbon is further illustrated in the galvanostatic charge−discharge experiments. Figure 4a−c shows the charge−discharge cycles of natural graphite. It is worth mentioning that one of the proclaimed merits of carbon cathodes is their capability of extremely fast charging and discharging with very high specific current. However, it is necessary to utilize a low current to study intrinsic electrochemical properties to avoid the concentration polarization imposed by high currents. Furthermore, utilizing low currents does not alter the reaction mechanisms. For these reasons, a relatively low (compared to the values reported in the literature) specific current of 25 mA g^{-1} was used. As shown in Figure 4a, the natural graphite cathode was charged for 2 h to reach a charge capacity of 50 mAh g^{-1}, which is consistent with the typical discharge capacity reported for natural graphite cathodes. The potential of the cathode was noted to have nearly reached 2.2 V versus Al after 2 h of charging. However, the immediate discharge with the same specific current demonstrated a discharge capacity of only 25 mAh g^{-1}, a nearly 50% irreversibility. In another experiment, the cathode was allowed to rest for 2 h after the same charging process, and the following discharge demonstrated a capacity of 24 mAh g^{-1}. This is clear evidence supporting the CV data in Figure 3: some reaction(s) in the charging process is irreversible, even at a potential well below that of chlorine generation. As shown in Figure 4b, we charged the natural graphite for 12 h under 25 mA g^{-1}, and it reached the chlorine generation potential plateau at 2.45 V versus Al. The immediate discharge under 25 mA g^{-1} demonstrated a capacity of 78 mAh g^{-1}, significantly lower than the charge capacity. In a separate experiment, the same charging process was followed by a 12 h rest before discharge, upon which the discharge capacity decreased to 58 mAh g^{-1} along with the disappearance of the higher discharge plateau (inset of Figure 4b). This observation raises another key problem of the carbon cathode, which is severe self-discharge. To date, there has been only one study to our best knowledge showing self-discharge behavior of Al batteries with graphite electrodes but without mechanism investigation.[17] In fact, the plateau of chlorine generation can be overcome (or, more accurately, masked) by use of a higher specific charge current due to concentration polarization. As shown in Figure 4c, the natural graphite cathode charged under 200 mA g^{-1} could reach 2.6 V versus Al (the set upper cutoff potential) without showing the plateau. The charge capacity is approximately 130 mAh g^{-1} (inset of Figure 4c). However, the discharge, under either 25 mA g^{-1} or 200 mA g^{-1}, still only delivers a capacity of 80 mAh g^{-1}, a nearly 40% irreversibility. After a 2 h rest, the discharge capacity decreased to approximately 40 mAh g^{-1}, confirming the severe self-discharge behavior. The synthetic graphite cathode in Figure 4d−f basically demonstrates identical behaviors. An additional abnormal observation is that fast discharge demonstrates higher capacity than slower discharge does, which can also be seen in the literature.[4] One possible explanation (and perhaps the only rational explanation) is the kinetic competition between the chemical self-discharge reaction(s) and the electrochemical discharge reaction: if the electrochemical discharge is not under mass transfer limitation and intrinsically fast, enforcing a high discharge current can indeed "win" over a kinetically slower chemical self-discharge. This could be the reason that the irreversibility of carbon cathodes has not been widely noted in the literature because many reports emphasized high charge−discharge rates.

Hopefully we have made a clear case that what really happens at carbon material cathodes is more complicated than the simple intercalation of $AlCl_4^-$. We speculate that the charging of graphitic carbon cathodes in the deep eutectic chloroaluminate electrolytes is a process consisting of a number of simultaneous and intertwined mechanisms. The electrochemical processes on carbon cathodes must be thoroughly scrutinized to prove the feasibility of this Al−carbon rechargeable battery technology. It is difficult to expect a practical battery while risking chlorine evolution during operation. There is little doubt that graphitic carbons indeed host intercalated species, as demonstrated by X-ray diffraction and Raman characterizations, but whether the intercalated species is only $AlCl_4^-$ needs to be examined. An interesting question that has not been answered is why an intercalation reaction with a fairly large intercalating species ($AlCl_4^-$), whose rate capability is typically limited by the solid-state diffusion of the intercalating species in the host structure, allows extremely fast charge and discharge. Actually, in the early studies of using graphite as the cathode material for rechargeable Al batteries (represented by the study by Gifford and Palmisano[18]), chlorine was proposed to be the intercalated species in graphite. Chlorine intercalation into graphite from chloride-containing electrolytes was also recently reported by Yang et al.[19] Considering the chlorine generation potential in close proximity of the charging potential, the irreversible charge capacity, and the severe self-discharge behavior, it is a reasonable hypothesis that chlorine is involved in the intercalation and may not be stably hosted.

Other Issues in Al Battery Research. In addition to the above concerns about carbon cathode materials, there are also issues with other types of cathode materials, specifically transition metal oxides and sulfides. The rationale for the selection of metal oxide and sulfide cathode materials in current literature is mainly based on the understanding of how these materials behave as cathodes for Li-ion batteries. However, one must recognize that Al-ion electrochemistry is drastically different from Li-ion electrochemistry. The Coulombic interaction of the Al-ion is tremendously stronger than that of the Li-ion due to its trivalency, which can make the intercalation of Al-ions in metal oxides and sulfides extremely difficult if not impossible.[20]

To date, the only material to have been unambiguously proven as a host structure for reversible Al-ion intercalation is Chevrel-phase molybdenum sulfide (Mo_6S_8).[21−23] However, the Al-ion intercalation in Mo_6S_8 is attributed to the very unique crystal structure of the Chevrel-phase molybdenum chalcogenides, which could be a singular case for Al-ion intercalation. To demonstrate Al-ion intercalation, unambiguous crystallographic data would be the most convincing, but they are generally absent in current literature. Spectroscopic techniques identifying the change of oxidation state of the transition metals in the cathode materials cannot be used as the sole means to claim intercalation chemistry. For instance, X-ray photoelectron spectroscopy (XPS) is one of the widely used methods to characterize the metal oxide and sulfide cathodes before and after electrochemical reaction with Al. However, XPS is essentially a surface chemical analysis method to identify the oxidation states of the surface elements only. Even if change of an oxidation state was detected, XPS data could not distinguish the origin between intercalation and simple redox. Furthermore, the surface chemistry may not represent the bulk properties. In fact, if electrochemical reactions indeed occurred in the metal oxides or sulfides (more likely in sulfides due to the more polarizable sulfide anion) in Al batteries, the mechanism would more likely be simple redox reactions of the transition metals. Another problem with transition metal oxide and sulfide cathodes is their chemical compatibility with the deep eutectic chloroaluminate electrolytes, a problem that has been completely overlooked in current literature. One of our recent studies (currently under review) clearly indicates that vanadium pentoxide (V_2O_5), a widely investigated potential cathode material for rechargeable Al batteries, dissolves in and reacts with deep eutectic chloroaluminate electrolytes at different Lewis acidities to generate new vanadium compounds. Iron sulfide (FeS_2) was also reported to be soluble in the chloroaluminate electrolytes,[24] but unfortunately, the species resulting from the dissolution were not identified. It is reasonable to speculate that V_2O_5 and FeS_2 may not be the only two metal oxides/sulfides that can dissolve in deep eutectic electrolytes. Therefore, testing the compatibility between potential cathode materials and electrolytes should be mandated practice in these investigations.

Summary and Outlook. Rechargeable Al batteries are both scientifically intriguing and challenging. At the research's current infancy stage, the fundamental mechanisms of Al electrochemistry, not performance, should be the emphasis of the research community. For experimental investigations, rigorous experimental setup, execution, and data interpretation without prejudgments are very important. False positive results can be generated from unsuitable current collectors or impure electrolytes, as demonstrated in this work. The electrochemical properties of cathode materials such as graphitic carbons, transition metal oxides, and sulfides are yet another area demanding thorough and unbiased scrutiny.

It is also clear that most of the problems and discrepancies in current Al battery research originate from the use of complex deep eutectic chloroaluminate electrolytes. They are fundamentally different from the known Li and Mg electrolytes using either salts with weakly coordinating anions or organomagnesium complexes. The chloroaluminate electrolytes are also corrosive, expensive and have the risk of chlorine generation; thus, it could be challenging to use these electrolytes in real devices. Therefore, new Al electrolytes, which are inexpensive, chemically and electrochemically stable, and active-chloride-free, should be the priority of future research on rechargeable Al batteries. As the only rational choice for anode, Al should be investigated with the focus on the deposition−stripping efficiency and the Al/electrolyte interface phenomenon. On the cathode side, transition metal oxides and sulfides may be scientifically interesting (to investigate the reaction feasibility and mechanisms) but suffer from the combination of low capacity and low reaction potential. Cathode materials that could have real application impact are conversion-type materials such as chalcogens. From the practical point of view, rechargeable Al batteries cannot and should not compete with Li-ion batteries for the high-end markets such as passenger electric vehicles and personal electronics. Therefore, investigation on cell design and operation conditions for specific applications that do not require high-capacity batteries could be a new direction for rechargeable Al batteries.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b01285.

> Performance comparison of representative cathode materials, experimental section, drawing and digital images of the Swagelok-type cells, galvanostatic discharge profiles on glassy carbon using $AlCl_3$-[EMIm]Cl electrolyte with and without proper drying, and CV scans of various conductive substrates including Ni, Ti, Pt, W, Mo, and glassy carbon (PDF)

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Notes

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for financial support from the U.S. National Science Foundation (NSF) CAREER program through Grant Number CBET-1751929. We also thank Mr. Dylan Harter for designing and fabricating the Swagelok-type cells used in this work.

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