State of the Art of Rechargeable Aluminum Batteries in Non-Aqueous Systems

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The main challenges to implement sustainable energy storage technologies are the utilization of earth-abundant recyclable materials, low costs, safe cell reactions and high performance, all in a single system. Aluminum batteries seem to cover these requirements. However, their practical performance is still not comparable with the state of the art high performance batteries. A key aspect to further development could be the combination of aluminum with charge storage materials like conductive polymers in non-aqueous electrolytes taking advantage of the properties of each material. This review presents the approaches and perspectives for rechargeable aluminum-based batteries as sustainable high-performance energy storage devices.

The storage of electricity is a key component in the drive to a sustainable energy society. However, current energy storage devices, like high performance lithium-ion batteries, have constrained raw material resources, difficult recycling process and danger of flammability. Far less attention has been directed to the use lightweight aluminum based batteries in non-aqueous systems as aluminum has lower cost, is more abundant and is safer than lithium. Furthermore, its specific capacity of 2980 mAh g^{-1} and volumetric capacity of 8040 mAh cm^{-3}, respectively, are higher than lithium.[1]

The number of studies on rechargeable aluminum-based batteries in non-aqueous systems has increased 10-fold in the last decade (Figure 1). Therefore, it seems appropriate and timely to review the state of the art and the implementation of novel ideas and approaches made for rechargeable high performance aluminum-based batteries and reflect on the perspectives, challenges and limitations that these relatively new systems face.

Gifford et al. described this novel battery system in 1988 with aluminum and graphite as the negative and positive electrodes respectively, in a Lewis acidic chloroaluminate ionic liquid at room temperature. Chloroaluminate anions intercalated into the graphite electrode reaching 64 Wh kg^{-1} specific energy at 1.7 V discharge voltage over 150 cycles and 80–90% coulombic efficiency.[2] The same idea was taken up several years later by various research groups[1,3–5] using different oxides, sulfides and zeolites materials as intercalation electrodes.[6–13] More recently the introduction of conductive polymers (CP) as intercalation electrode sets a further development with great potential for a rechargeable aluminum hybrid battery-capacitor energy storage system.[14,15]

Current Status- Conventional Aluminum Based Batteries with Aqueous Electrolyte

A number of primary battery compositions like Al-MnO$_2$, Al-AgO, Al-H$_2$O$_2$, Al-S, Al-FeCN and Al-NiOOH[16] in aqueous electrolyte have been reported. Al-air batteries are characterized by low cost, sustainability and high theoretical specific energies 8100 Wh kg^{-1},[17] which are higher than the theoretical values of some lithium-ion batteries (600 Wh kg^{-1}).[18] The theoretical specific energy does not consider the weight of the oxygen electroactive species for the positive gas diffusion electrode (GDE) electrode because the battery utilizes oxygen from the atmosphere.[19] In practice, aluminum-air batteries based on aqueous systems are still characterized by the slow kinetics of the oxygen reduction reaction, even if the aluminum alloy used, is highly active. In addition, the use of air from the environment seems to be problematic due to the presence of nitrogen and carbon dioxide that could passivate the GDE catalyst. Furthermore, the parasitic corrosion and a passivation of the aluminum electrode, except in very high concentrated alkaline electrolytes, lowers the cell voltage and consequently the battery performance.[20,21]

In general, the use of aqueous electrolytes enables only primary aluminum batteries because the aluminum re-deposition occurs at a more negative potential (-1.66 V vs. SHE[20]) than the hydrogen evolution. Secondary aluminum-based batteries are only possible in non-aqueous electrolytes with larger electrochemical stability window.

Future Needs and Prospects

Introduction of non-aqueous electrolytes.—Secondary batteries can be realized due to the reversible deposition and dissolution of aluminum in non-aqueous electrolytes like molten salts NaCl-AlCl$_3$ or NaCl-KCl-AlCl$_3$[22,23] or ionic liquids (quaternary ammonium species).[24] In non-aqueous electrolytes the passive oxide layer found on the aluminum electrodes, is not formed[1,15,17] while the electrochemical stability window enables the deposition of aluminum and the realization of higher cell voltages.[21] In contrast to high temperature molten salts, ionic liquids are liquid at room temperature.[24]

Ionic liquids are widely promoted as green solvents or designer electrolytes, which are water free salts, consisting of weakly coordinated complex ions liquid below 100°C, or at room temperature. At least one ion has a delocalized charge and one component is organic, which prevents the formation of stable crystal lattices.

The main attraction of the ionic liquids is their characteristic wide electrochemical stability window, usually from 4.5 to 6.0 V. This is more than three times larger than aqueous solutions with maximum of 1.3 V making them suitable for high-performance electrochemical energy storage devices with electroactive species with redox potentials outside the stability window of water.[11,12] Furthermore, most ionic liquids show a high thermal stability, non-flammability, non-volatility and a low vapor pressure, offering a much lower toxicity and higher safety in comparison to organic solvents. The substituents of the organic component and the counter-ion, influence the ionic liquid properties like melting point, viscosity, conductivity and solubility.[25–27]

Ionic liquids such as 1-ethyl-3-methylimidazolium, 1,3-di-n-butylimidazolium, 1-butylpyridinium, triazolium, or alphatic onium cation[27] in combination with chloroaluminate anions can reach a potential window of up to 6 V. In addition, their melting point is around room-temperature with an electric conductivity of 10 mS cm^{-1},[28] which is within the order of magnitude of most aqueous electrolytes.

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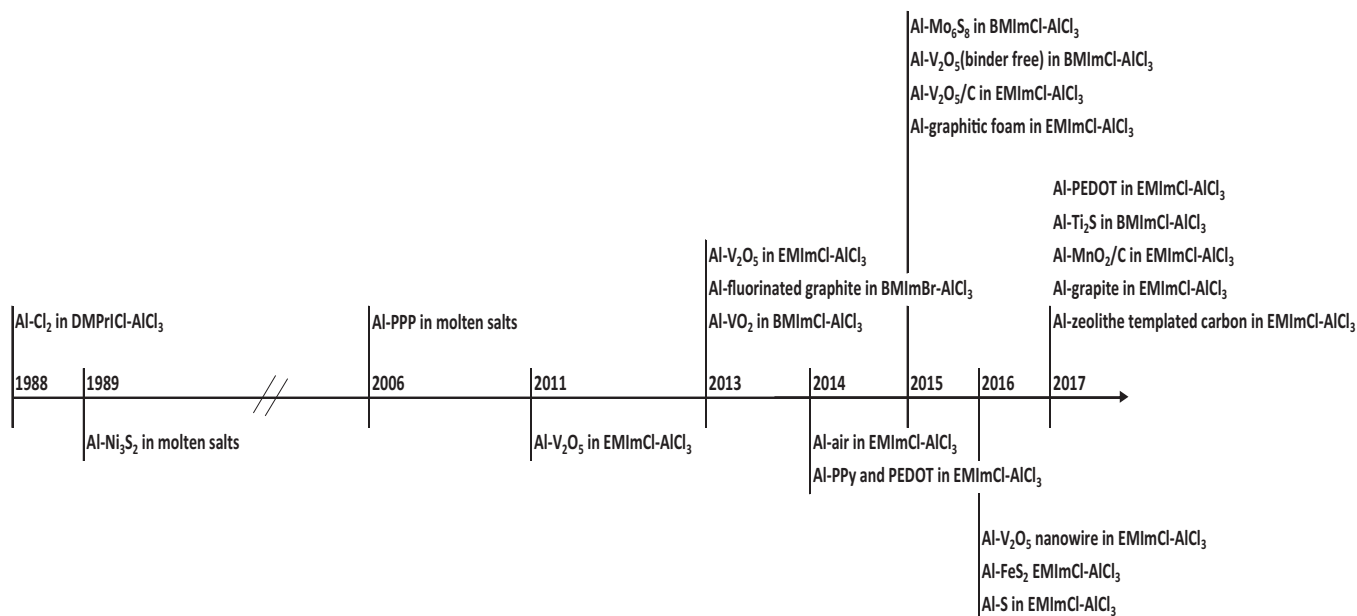[z]E-mail: T.Schoetz@soton.ac.uk

Figure 1. Timeline of significant rechargeable aluminum-based batteries in non-aqueous systems.

Chloroaluminate based ionic liquids are mostly hygroscopic.[29] Moisture can decompose them or decrease the potential window. For example 3 wt% of water could decrease the anodic and cathodic potential window from 6 V to 3 V.[27] In contrast to non-chloroaluminate systems, which are mostly Lewis neutral, chloroaluminate ionic liquids can change their acidity by varying the molar composition of the anion and cation components to basic, neutral or acidic, changing their conductivity and viscosity.[30]

The deposition and dissolution of aluminum in quaternary ammonium chloroaluminate based ionic liquids has a current efficiency from 85% to 100%.[29,31,32] The typical morphology of deposited aluminum on glassy carbon, tungsten, platinum or aluminum is granular, circular and cluster structures with high adhesion. The repeated deposition and dissolution of aluminum caused only an increase of the microcrystalline surface roughness. Dendrite growth was only observed at high current densities over 100 mA cm^{-2}.[1,5,15,21,32,33] The electrodeposition of aluminum on glassy carbon, tungsten and platinum electrodes follows an instantaneous mechanism with diffusion controlled growth, in contrast, the deposition on aluminum electrodes has kinetic limitations.[32]

The deposition (charge reaction) and dissolution (discharge reaction) of aluminum (Equation 1) at the negative electrode is only possible in a Lewis acidic chloroaluminate ionic liquid, containing $Al_2Cl_7^-$.[24]

$$4Al_2Cl_7^- + 3e^- \overset{charge}{\underset{discharge}{\rightleftharpoons}} Al + 7AlCl_4^- \qquad [1]$$
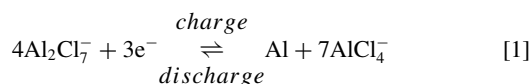
The heptachlorodialuminate $Al_2Cl_7^-$ anion forms when the molar ratio N, of $AlCl_3$ to the ionic liquid cation is higher than 0.5 (Lewis acidic). An excess of the cation and a molar ratio of $AlCl_3$ lower than 0.5 leads to a Lewis basic ionic liquid, owing to the presence of free halide ions (Equation 2).[34] A Lewis neutral composition consist of the same molar ratio of $AlCl_3$ and EMImCl (N of $AlCl_3$ is 0.5).

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad [2]$$
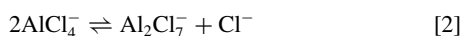
The properties of the different compositions of an EMImCl-AlCl$_3$ ionic liquid differ with their acidity. A Lewis acidic composition has the highest density (acidic 1.39 g cm^{-3}, basic 1.26 g cm^{-3} and neutral 1.29 g cm^{-3}), but only a medium conductivity (acidic 15 mS cm^{-1}, basic 6.5 mS cm^{-1}, neutral 23 mS cm^{-1}) and viscosity (acidic 14 mPa s, basic 47 mPa s, neutral 18 mPa s).[26,27] In comparison, the Lewis neutral composition is characterized by the highest conductivity whereas the Lewis basic composition by the lowest.

Charge-storage materials as positive electrodes in rechargeable aluminum batteries.—Ionic liquid electrolytes, improve the stability and life-time of batteries in contrast to aqueous or organic solvents.[6,35,36] Proof of concept studies demonstrate that the performance of rechargeable aluminum batteries with an ionic liquid electrolyte can be improved by introducing an active charge-storage material as the positive electrode. Charge-storage materials can reversible intercalate aluminum-anion species of the ionic liquid electrolyte like 1-ethyl-3-methylimidazolium chloride (EMImCl-AlCl$_3$) or 1,3-di-n-butylimidazolium bromide (BImBr-AlCl$_3$). Typical positive electrodes include porous and three-dimensional materials like graphite,[1,3–5] zeolites,[37] oxides,[7–11,38] sulfides[12,39] and sulfur[13]) (Table I). Another type of positive electrode materials include conductive polymers[14,15,40] which also store anions to compensate their positive charges created during the oxidation of the polymer backbone. The aluminum battery systems with graphite, zeolites, sulfides and oxides show high reversibility, cycle stability, constant electrochemical behavior and coulomb efficiencies >95%.

Aluminum batteries with oxides as the positive electrode show a very high specific discharge capacity. However, low cell voltages and strongly sloping discharge plateaus for oxide, sulfide and zeolite template carbon electrodes, indicated capacitive behavior problems, making it difficult to define the specific energy and power characteristics. In addition, the oxides have a strong electrostatic interaction with the doping anions, which complicate the reversible intercalation mechanism.

Porous three-dimensional graphitic-foam[4] and pyrolytic graphite[1] electrodes are also promising; at the graphitic foam positive electrode, the $AlCl_4^-$ ions are intercalated and de-intercalated between the graphite layers while the metallic aluminum electrode oxidizes to $Al_2Cl_7^-$ during the discharge cycle and is reduced back to aluminum during the charge cycle. This type of battery shows a high discharge cell voltage of ~2 V and its specific energy (40 Wh kg^{-1}) is only comparable to lead acid and nickel-metal hydride batteries, which is less than half of the specific energy of high performance batteries like lithium-ion (180 Wh kg^{-1}[18]).

When using graphite electrodes, there is a partial irreversible intercalation of anions, especially during the initial charge and discharge cycles. After the first cycles, the capacity remains stable without a

Table I. Battery components (positive/negative electrodes and electrolyte) and characteristic battery values (measured cell voltage, specific capacity, energy and power) for rechargeable aluminum batteries with a charge-storage material as positive electrode.

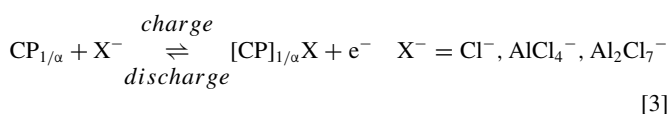| Positive electrode	Negative electrode	Electrolyte	Average cell voltage/V	Specific discharge capacity/Ah kg^{-1}	Specific energy/Wh kg^{-1}	Reference
Graphite	Al foil	Lewis acidic EMImCl-AlCl$_3$	1.7–2	70–148	40–64	1–5
Zeolite-templated carbon	Al foil	Lewis acidic EMImCl-AlCl$_3$	Sloping ~1.05	n/a	64	37
Oxides, sulfides	Al foil and plate	Lewis acidic BMImCl- and EMImCl-AlCl$_3$	Sloping ~0.7–0.5	46–273	40–90	7–12,38,39
PPy on glassy carbon	Al foil	Lewis acidic EMImCl-AlCl$_3$	Sloping above ~1	30–100	46	14
PEDOT on glassy carbon	Al foil	Lewis acidic EMImCl-AlCl$_3$	Slightly sloping above ~1	30–100	44	14
PEDOT on glassy carbon	Al plate	Lewis acidic EMImCl-AlCl$_3$	Slightly sloping above ~1	84–282	84–282	15
PAn on platinum	Al rod	Lewis acidic BPCl-AlCl$_3$ and EMImCl-AlCl$_3$	< 1.6	45–68	n/a	40

significant drop in performance. It is assumed that an activation process and adaption of the graphite structure takes place within the first cycles causing partial irreversibility.[4]

Battery systems based on a conductive polymer and aluminum.— Conductive polymers like poly(thiophene) (PEDOT), poly(pyrrole) (PPy) and poly(aniline) (PAn) have the ability to store high amounts of charge while acting as capacitor and battery simultaneously.[15] These hybrid battery-capacitors combine the oxidation/reduction faradaic process of the conductive polymer and the non-faradaic behavior of doping/de-doping anions into the polymer. The non-faradaic charges stored depends on the thickness and porosity of the conductive polymer and is therefore and important parameter of the material. Hybrid battery-capacitors are potentially positive electrode materials for high performance batteries, which require high capacities and cell potentials.

The use of conductive polymers as anion intercalation material has already been demonstrated in lithium-ion batteries showing high coulombic efficiencies of up to 99% and energy densities (280–420 Wh kg^{-1}).[15] There are few studies of conductive polymers coupled with aluminum, as the positive and negative electrodes respectively, in the ionic liquids 1-ethyl-3-methylimidazolium chloride (EMImCl-AlCl$_3$)[14] and 1-butylpyridinium chloride (BPCl-AlCl$_3$) showing energy densities between 44–282 Wh kg^{-1} (Table I).

The charging reaction (Equation 3)[15] of the positive polymer electrode is characterized by the change from neutral to positively charged state of the conductive polymer (CP) electrode and the simultaneous insertion of anions (X$^-$) (anion doping). The amount of doped anions is defined as degree of doping α from 0 to 1 and describes the number of monomer units in the polymer that accommodate one doping anion. The conductive polymer oxidizes during the charging cycle generating positively charged centers that are neutralized by the anions of the chloroaluminate ionic liquid (Cl$^-$, AlCl$_4^-$, Al$_2$Cl$_7^-$). The nature of the anion doping species depends on the composition of the chloroaluminate ionic liquid (Table I). During the discharge reaction (Equation 3),[15] the positive electrode releases the anions to the electrolyte converting the conductive polymer back to the uncharged/neutral state.

$$CP_{1/\alpha} + X^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} [CP]_{1/\alpha}X + e^- \quad X^- = Cl^-, AlCl_4^-, Al_2Cl_7^-$$

[3]

The reversibility of the charge and discharge reaction depends significantly on the positive electrode and could take place within a potential window of 2.6 V vs. Al/Al(III) for polythiophene and polypyrrole.[14] Over-oxidation of the polymer at high anodic potentials leads to a degradation of the conductive polymer due to nucleophilic attack of the ionic liquid, while high negative cathodic potentials enable the doping of cation (n-doping) of the conductive polymer.[41] The doping/de-doping reaction occurs at different electrode potentials, which are important for the charge and discharge cell voltage of the battery. The doping/charge and de-doping/discharge electrode potentials are preferred to be as positive as possible in order to be far from the aluminum deposition/dissolution process but close to each other to increase the cell potential and the performance of the battery.

The synthesis path of the conductive polymer influences the cycle stability of the battery. Conductive polymers films prepared chemically with a binder, show lower cycle stability and reversibility than those synthesized at constant current or potential electrolysis on vitreous carbon.[14] In addition, the polymerization media, aqueous or non-aqueous, has a significant influence on the reversibility and degradation. The films synthesized in aqueous electrolytes can suffer damages if small amount of water remains in the structure because the hygroscopic chloroaluminate ionic liquid can form hydrochloric acid during cycling, which could cause detachment of the film from the substrate. For example, a detached polythiophene was observed as blue cloud-like film.[15] A better approach is the direct synthesis of the conductive polymers in chloroaluminate ionic liquids.[14] The films show high reversibility and high mechanical stability than those prepared in aqueous solutions or conventional organic solvents like acetonitrile.[41,42] The surface structure of an electro-polymerized polythiophene film on a planar vitreous carbon substrate appears as granular agglomerate structures both in aqueous and ionic liquid electrolytes.

Quartz crystal microbalance studies consistently show that a mixture of anionic species of the ionic liquid intercalates into the conductive polymer during electro-polymerization and cycling. Larger anion species like AlCl$_4^-$ and Al$_2$Cl$_7^-$ could have a significant influence on the capacity and stability of the conductive polymer because they could remain trapped into the polymer structure if the pores are too small and impede the reversible shuttling of the doping anions. It is also reported that the conductive polymer is affected by swelling due to the size of the anions of the chloroaluminate ionic liquid.[14,15,38,40] The swollen polymer films could offer higher porosity and ability to accommodate bulky anions. Moreover, three-dimensional conductive polymer electrodes with a high surface area are suggested to create more space as well as higher number of doping positions and accommodate more doping anions, which will increase the capacity and the specific power of the battery system.[15]

Conclusions

Aluminum based batteries using non-aqueous electrolytes like ionic liquids at room temperature are promising alternatives for high performance batteries.

The main characteristics of these systems are:

(a) The deposition and dissolution of aluminum at the negative electrode in a Lewis acidic chloroaluminate ionic liquid has been studied in detail and shows high reversibility and microcrystalline depositions, which do not cause dendrite growth avoiding short circuit the battery.

(b) Several charge-storage materials like graphite, zeolites, oxides, sulfides and conductive polymers have been reported. However, positive electrodes based on graphite, oxides and sulfides are characterized by low specific capacity or low and sloping cell voltages, whereas conductive polymers show higher specific capacities and specific energies.

(c) The influence of the type of conductive polymer positive electrode on the battery performance needs further studies to address the effect of different substrate materials and preparation methods.

(d) A major challenge in this system is the intercalation of bulky anions in the conductive polymer, which decrease the cycle stability of the conductive polymer. Therefore, the preparation of conductive polymer-carbon composites on three-dimensional substrates seems promising due to their larger surface area that could potentially accommodate a higher number of intercalation anions, leading to a higher electrode capacity and battery performance.

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