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EUROPEAN **TECHNOLOGY**
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INTRODUCTION

Being the one-stop shop for battery research in Europe, Batteries Europe includes outstanding researchers in its experts' community who produce scientific content on a regular basis, contributing to and improving the knowledge pool on batteries.

For this reason, the Platform has decided to highlight a few articles produced by its stakeholders on topics that can be of interest to the battery research community, starting from the Journal of Power Sources, whose editor-in-chief is Stefano Passerini, co-chair of Batteries Europe Working Group 1.

The Journal of Power Sources is the journal for researchers and technologists interested in all aspects of the science, technology and applications of sources of electrochemical power. Please find below a collection of articles written by Batteries Europe experts and published in this medium.

CHALLENGES OF TODAY FOR NA-BASED BATTERIES OF THE FUTURE

Overview

Na-based batteries potentially allow reducing costs and improving sustainability compared to present Li-based technologies. Various concepts such as Na-ion, Na/O₂, Na/S or Na all solidstate batteries are under development, with distinct degree of technological readiness, key performance indicators and challenges. The present work aimed at highlighting the most promising materials employed by these technologies and identify the main challenges to be addressed to render these technologies complementing alternatives to Li-based technologies. A realistic comparison of key performance indicators for Na-ion and Li-ion cells is included.

Major R&I Challenges to be addressed

Despite the evident benefits of replacing Li by Na in terms of cost and sustainability, reaching a competitive cost/kWh figure compared to present and next generation LIBs remains a tough challenge. Na is a larger and heavier element compared to Li, and its higher standard reduction potential reduces the available voltage window, leading to an overall penalty in terms of energy density. This is only partially compensated by the possibility to use Al foil current collector on the anode side, compared to the more expensive and heavier Cu foil required for Li-based batteries to avoid Li-Al alloying. For the more mature Na-ion technology, whose best performing materials should allow to approach the performance of the present LIB technology, improving cycling stability and Coulombic efficiency are the major challenges. Competing with next generation Li-ion batteries would however require the more disruptive Na/O₂, Na/S and all solid-state concepts to substantially gain in maturity.

Future perspective and potential application for this battery chemistry

Na-ion could be competitive with present and future Li-ion cells generation for applications requiring a power-oriented design, where sustainability is more important than energy density; or in case of a cost increase of Li-ion batteries related to critical materials availability. Progress in materials development coupled to the low-cost, green, and sustainable philosophy of Na-based batteries are expected to make this technology industrially appealing in the nearfuture.

Publication Title: Challenges of today for Na-based batteries of the future: From materials to cell metrics

Publication Authors: I. Hasa, S. Mariyappan, D. Saurel, P. Adelhelm, A.

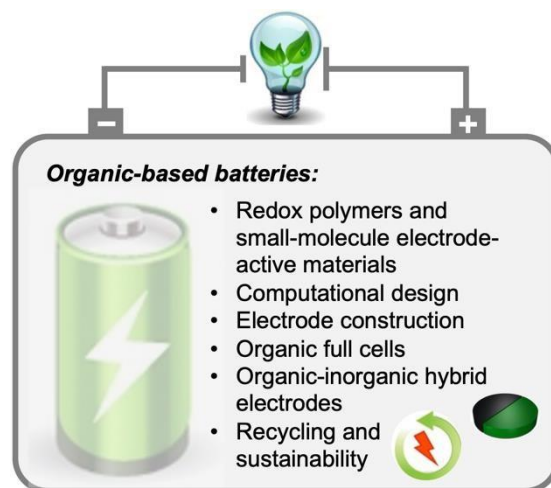
Y. Kuposov, C. Masquelier, L. Croguennec, M. Casas-Cabanas.

Publication Link: <https://doi.org/10.1016/j.jpowsour.2020.228872>

A PERSPECTIVE ON ORGANIC ELECTRODE MATERIALS AND TECHNOLOGIES FOR NEXT GENERATION BATTERIES

Overview

Rechargeable batteries based on organic active materials have great potential for future energy storage solutions, which are greener and more sustainable. This review article highlights selected, recent advances in this field and aims to provide an overview of the state-of-the-art and to give future perspectives. This includes polymeric and small molecule (solid) electrodeactive materials, computational design, electrode construction, realization of all-organic batteries, organic-inorganic hybrid electrodes, and recycling and sustainability aspects.



Major R&I Challenges to be addressed

While many high-performing organic electrode materials have been reported, there is still much potential for further improvement of their electrochemical performance, but also on other aspects such as electrode construction, the design of full and all-organic cells, and on recycling.

Future perspective and potential application for this battery chemistry

Organic materials possess a lower environmental footprint and toxicity compared to conventional inorganic metal oxides. They are composed of abundant elements (i.e. C, H, O, N, and S) and can be produced in more eco-friendly processes. Their high structural designability allows for facile tuning of the electrochemical properties. These are likely the major advantages of organic materials compared to competing technologies.

Publication Title: A Perspective on Organic Electrode Materials and Technologies for Next Generation Batteries

Publication Authors: Birgit Esser, Franck Dolhem, Matthieu Becuwe, Philippe Poizot, Alexandru Vlad, Daniel Brandell

Publication Link:

<https://www.sciencedirect.com/science/article/pii/S0378775320311186?dgcid=author>

MISSING PUZZLES AND PERSPECTIVE OF RECHARGEABLE MAGNESIUM BATTERIES FROM THE CURRENT STATUS

Overview

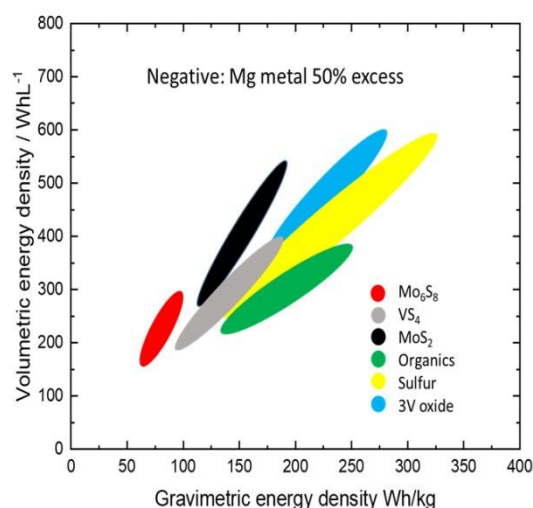
Rechargeable magnesium batteries are considered as a potential battery technology that can find an application in the different areas of the portable energy storage sectors. Their electrochemical characteristics are at least in theory comparable with those of current Li-ion batteries. This is enabled by using thin metal foils and high-energy cathode materials together with the compatible electrolyte enabling high efficiency. Currently, only a few cathode materials promise possible commercialization. Chevrel phases, transition metal sulfides, and redox-active organics can be cycled for hundredths of charge/discharge cycles while cyclability of the batteries based on the transition metal oxides or sulfur cathode is vague and should be improved on the laboratory scale. Most advanced cathode materials were used for the calculation of the volumetric energy densities and gravimetric energy densities assuming realistic conditions with optimized electrode thicknesses and loadings, electrode porosity, and optimized electrolyte quantity.

- low TRL activities with a focus on different cell components and understanding interfaces and interphases, including passivation of the surface, formation of uneven deposits, or formation of dendrites;
- stable electrochemical cycling of the magnesium foil coupled with the high voltage cathode materials or with a sulfur cathode;
- development of novel electrolyte formulations coupled with novel/improved cathode materials. Weakly coordinating salts are considered currently, however stripping and deposition efficiency and oxidative stability should be further improved.

Future perspective and potential application for this battery chemistry

Rechargeable magnesium batteries are considered sustainable battery chemistry, based on materials with high abundance in the earth's crust. Their development is still on the laboratory

Major R&I Challenges to be addressed



Correlation between volumetric and gravimetric energy densities of different cathodes coupled with pure magnesium metal with 50 wt.% excess. Cathode loading between 1-4 mAh cm⁻².



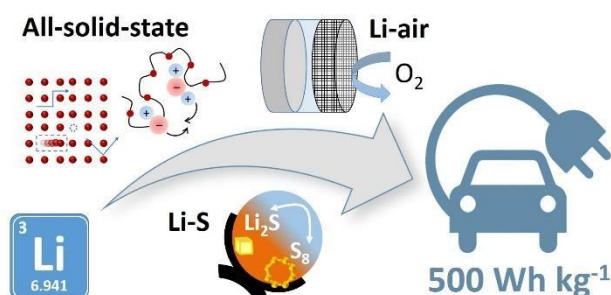
level with some attempts to prepare small prototype cells. This is due to complicated chemistry and a lack of understanding of interfacial problems. Some additional breakthroughs on the field of 3V inorganic cathode material or the field of sulfur cathodes are required to confirm calculations, which suggest energy density higher than 300 Wh kg^{-1} and 600 Wh L^{-1} . The major advantage of the given technology is related to the predicted price parity compared to Li-ion batteries and the sustainability avoiding critical elements such as lithium, graphite, copper, cobalt, and nickel.

Publication Title: Magnesium batteries: current picture and missing pieces of the puzzles

Publication Authors: Robert Dominko, Jan Bitenc, Romain Berthelot, Magali Gauthier, Gioele Pagot, Vito Di Noto

Publication Link: <https://www.sciencedirect.com/science/article/pii/S0378775320313240>

CURRENT STATUS AND FUTURE PERSPECTIVES OF LITHIUM METAL BATTERIES



Overview

Lithium Metal Batteries are a family of rechargeable battery chemistries where metallic Li is reversibly plated/stripped at the negative electrode. Owing to its very low reduction potential (-3.040 V vs. SHE) and high theoretical capacity (3861 mAh g⁻¹), Li

Implementing Lithium metal anodes is crucial to achieve next generation high energy rechargeable batteries.

metal is considered

the “holy grail” anode material for high energy density batteries (>500 Wh kg⁻¹). On the positive electrode,

this can be couple with either next generation high capacity conversion materials such as Sulfur (Li-S batteries) or Oxygen (Li-O₂ or Li-air batteries), as well as with lithiated cathodes such as the layered Li transition metal oxides from the current generation of Lithium-ion Batteries (e.g., NCM 811). In the latter case, the Li provided by the cathode can be plated onto a lithophilic anode current collector during the first charge in a so-called “anodefree” cell. The electrolyte can either be based on liquid organic solutions (carbonates, ethers, ionic liquids, etc) or solid-state conductors (e.g., polymeric or inorganic) and its composition tuned according to the requirement of each specific battery chemistry.

Major R&I Challenges to be addressed

Among all known challenges of Li metal batteries, the main issues hindering their widespread commercialization are two: safety and cyclability. Although many parameters can affect these properties, they can all be somehow related to: (i) the formation/disappearance of the full volume, and (ii) the high chemical reactivity of metallic Li. Establishing a chemo-mechanically stable Li/electrolyte interface is therefore crucial in order to enable safe and long-lasting high energy batteries. In this respect, the development of novel electrolytes and Li protection strategies will have a decisive role.

Future perspective and potential application for this battery chemistry

Lithium metal batteries are considered particularly appealing for automotive applications (EV). However, while well performing prototypes have been demonstrated at the laboratory scale, the transition to large cell formats suitable for EV application presents technical challenges associated, e.g., with handling, manufacturing and assembly of ultra-thin Li and solid electrolyte separator layers.

Publication Title: Current status and future perspectives of lithium metal batteries

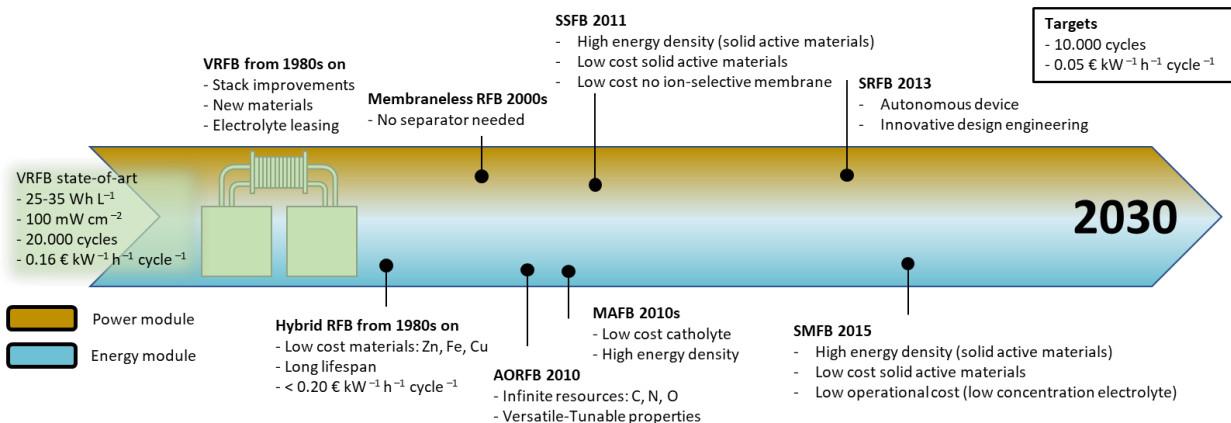
Publication Authors: A. Varzi, K. Thanner, R. Scipioni, D. Di Lecce, J. Hassoun, S. Dörfler, H.

Altheus, S. Kaskel, C. Prehal, S.A. Freunberger.

Publication Link: <https://doi.org/10.1016/j.jpowsour.2020.228803>

REDOX FLOW BATTERIES: STATUS AND PERSPECTIVE TOWARDS SUSTAINABLE STATIONARY ENERGY STORAGE

Overview



State-of-the art of RFBs, timeline and strategies

Redox Flow Batteries (RFBs) can be defined as

battery concept alternative to static batteries, e.g. conventional LIBs, that relies on a particular system architecture that allows decoupling of power and energy. Thus, active species are contained in external tanks, typically as a solution, defining the energy density of the system. Those are pumped by the flow system through the stack, where the electrochemical conversion takes places, and therefore this second element defines the power of the system.

This electrochemical reactor is constituted by two half-cells, where typically, a carbon-based material serves as electrode, and an ion conductive polymeric membrane acts as physical separator between half cells.

It is to say, that RFBs term comprehends a variety of technologies, mainly sorted according to the chemistry behind the electrochemical process.

The mentioned modular design, which is a clear advantage for scalability and maintenance purposes; and the competitive cost, mainly relying on the long-life cycling, are the main features of those batteries.

Aqueous systems, despite the energy density limitation linked to lower cell voltage, are the best option based on their technical, economic and safety advantages. Indeed, all flow aqueous systems as all-VRFBs (all vanadium RFB) stand as state-of-the-art and have reached the market, together with some other hybrid (flow/non-flow) approaches, mainly ZBFB (ZincBromine RFB).

Major R&I challenges to be addressed

Redox flow batteries are, according to their properties, ideal for stationary application and therefore objectives are defined in terms of durability (10.000 charge-discharge cycles) and cost (0.05 €/kWh/cycle).

Availability and cost of active materials has been identified as the main limitation of currently commercialized batteries. Vanadium has been classified as strategic material, not available in European countries. Besides, electrolyte is by far the component with a higher contribution to the total cost of the battery and therefore a decrease on the cost of the active material will dramatically impact the cost of the battery itself. Among multiple alternatives being explored organic materials and earth abundant inorganic compounds, as iron and copper, are excellent based on potential low cost and low toxicity as compared to vanadium or bromine. However, durability is still a limitation to be solved due to the low stability of active species.

Aiming at boosting the limited energy density of those batteries, scientific community is devoting efforts to, in addition to the already mentioned non-aqueous systems, the use of solid electroactive materials. Thus, solid mediated flow batteries (SMFBs), where the solid materials are confined in the external reservoirs, are considered as a promising approach to easily surpass 50 Wh/L limit, while overcome drawbacks related to previously proposed semisolid flow batteries (SSFBS).

Other innovative concepts aim at removing the physical barrier between electrolytes as an approach to diminish the cost of the battery. Currently explored in microfluidic batteries, this technology requires of further investigation on reactor designs.

Future perspective and potential application for this battery chemistry

RFBS with lifetimes over 20 years, low LCOS (Levelized Cost of Storage) values and inherent modular design that eases industrialization and maintenance; are ideal for their implementation for large-scale grid storage. Efforts devoted to development of new materials will serve to improve cost-competitiveness of those batteries whilst enable large deployment to asset global demand of energy storage.

Publication Title: Redox flow batteries: Status and perspectives towards sustainable stationary energy storage

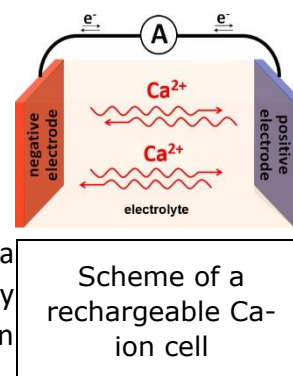
Publication Authors: Eduardo Sánchez-Díez, Edgar Ventosa, Massimo Guarnieri, Andrea Trovo, Cristina Flox, Rebeca Marcilla, Francesca Soavi, Petr Mazur, Estibaliz Aranzabe, Raquel Ferret.

Publication Link: <https://doi.org/10.1016/j.jpowsour.2020.228804>

EMERGING CALCIUM BATTERIES

Overview

Aprotic calcium-based battery chemistries can theoretically achieve performance of interest, not far from that of lithium-based ones. Calcium is a divalent, abundant and cheap alkaline earth metal with an extraordinarily strong oxidative ability. In comparison to other elements under study for battery applications, calcium is the multivalent metal with the most negative redox potential (i.e., 2.87 V vs SHE for the Ca^{2+}/Ca couple) and ionic radius very similar to Na^+ , a cation that is easily intercalated/deintercalated in/from a variety of materials. The research in the field is still in its infancy. The practical realization of rechargeable Ca batteries still relies on the identification of suitable electrode and electrolyte materials.



Major R&I Challenges to be addressed

The choice of active electrode materials and their coupling with the electrolyte sets the theoretical limits in voltage and energy density but also affects the kinetics (power), cycle life and safety. While Ca metal is by far the most promising anode material for this technology, its electrochemistry is rather complex (e.g., a very stable and resistive solid electrolyte interphase is formed between calcium metal and the electrolyte, hindering Ca^{2+} diffusion) and, due to low coulombic efficiency, it is still far from meeting the expectations for commercial applications. However, different calcium-based anode materials, such as calcium-metal alloy, are becoming of interest for Ca-ion batteries.

Future perspective and potential application for this battery chemistry

Ca-based batteries may disclose remarkable innovations and technological breakthrough, either from a fundamental scientific point of view or from an application perspective. Particular voltage/capacity combinations with realistic Ca-cell materials, would provide both gravimetric and volumetric energy densities higher than targeted values at cell level by year 2030 ($400 \text{ Wh}\cdot\text{kg}^{-1}$ and $>1000 \text{ Wh}\cdot\text{L}^{-1}$). With the abundance and lower cost of Ca ($5\text{-}50 \text{ \$}\cdot\text{kg}^{-1}$ vs $100 \text{ \$}\cdot\text{kg}^{-1}$ of Li metal), cost and resources advantages may also be expected for Ca metal batteries. Overall, it is considered a future emerging technology particularly advantageous from a techno-economic point of view for large scale stationary applications.

Publication Title: Emerging calcium batteries

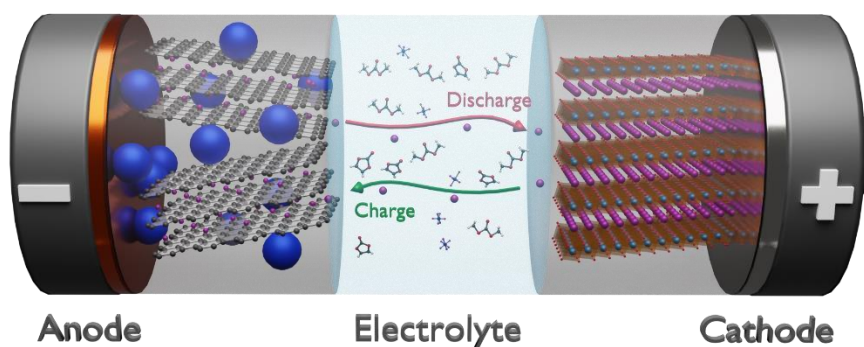
Publication Authors: Lorenzo Stievano, Iratxe de Meatza, Jan Bitenc, Carmen Cavallo, Sergio Brutti, Maria Assunta Navarra

Publication Link: <https://www.sciencedirect.com/science/article/pii/S0378775320311794>

LITHIUM-ION BATTERIES – CURRENT STATE OF THE ART AND ANTICIPATED DEVELOPMENTS

Overview

Lithium-ion batteries are the leading electrochemical energy storage technology for a wide range of applications, including small-scale devices such as mobile phones and laptops as well as large-scale devices like (hybrid) electric vehicles and stationary storage – not least owing to the continuous improvement of the cell design and cell components. The general principle of lithium cations moving back and forth between the two electrodes through the electrolyte appears rather simple at first glance, but the careful design and alignment of all cell components to achieve high energy and power densities requires eventually a comprehensive understanding of the system as a whole, especially given the great variety of potentially suitable inactive and active materials.



Scheme of a state-of-the-art lithium-ion cell, comprising a silicon/graphite negative electrode, a liquid organic electrolyte, and a lithium transition metal oxide positive electrode.

Major R&I Challenges to be addressed

In addition to further improvements concerning the gravimetric and volumetric energy and power density of lithium-ion cells to $300 \text{ Wh kg}^{-1}/900 \text{ Wh L}^{-1}$ and $1,000 \text{ W kg}^{-1}/2,000 \text{ W L}^{-1}$, respectively, and beyond, also the charging time, cycle life, safety and recycling have to be further enhanced – while simultaneously decreasing the cost to less than 50 Euro per kWh.

Future perspective and potential application for this battery chemistry

Lithium-ion batteries are expected to remain the leading battery technology for applications that need high energy and power densities in the near- to mid-term future. In fact, it is and will be a great challenge for any alternative battery chemistry to compete in terms of cost per kWh. Nonetheless, the tremendous success of this technology has also raised awareness of the potential bottlenecks, particularly the worldwide availability of critical elements and



compounds, highlighting the utmost importance of efficient recycling technologies and further advances in developing truly sustainable fabrication processes and in-/active cell components.

Publication Title: Lithium-ion batteries – Current state of the art and anticipated developments

Publication Authors: Michel Armand, Peter Axmann, Dominic Bresser, Mark Copley, Kristina Edström, Christian Ekberg, Dominique Guyomard, Bernard Lestriez, Petr Novák, Martina Petranikova, Willy Porcher, Sigita Trabesinger, Margret Wohlfahrt-Mehrens, Heng Zhang

Publication Link: <https://www.sciencedirect.com/science/article/pii/S0378775320310120>

RECENT DEVELOPMENTS AND FUTURE PERSPECTIVES OF ANIONIC BATTERIES

Overview

The necessity to enhance the energy densities and independency from expensive materials, have collectively called for search of new battery chemistries beyond Lithium. Precisely, anion shuttle dependent new battery chemistries; mainly chloride ion batteries (CIB) and fluoride ion batteries (FIB), bid promising characteristics. These batteries make use of chloride/fluoride-containing electrode materials, as a source of the shuttle ion (figure 1). Under a load, the positive electrode undergoes reduction, from which, chloride/ or fluoride ions will be removed and reacts with anode, followed by a reverse reaction upon charge. For CIBs, there are a wide range of metal chlorides which are applicable as positive electrode materials, such as MCl_x , $MOCl_x$, where M can be any of the d-block elements and x =number of Cl^- ions. The common metal chloride electrode materials are $CoCl_2$, VCl_3 , $BiCl_3$, while metal oxychloride candidates are $VOCl$, $BiOCl$, $FeOCl$ ¹. The most

cyclable candidates are layered double hydroxide (LDH) materials, e.g: NiFeCl LDH. For FIB's, cathode materials are transition metal-based fluorides (e.g: BiF_3 , CuF_2 , FeF_3). The electrolytes can be divided into two main categories: Liquid and solid electrolytes. The carbonate, etherbased organic solvents or ionic liquids coupled with chloride/ or fluoride conducting salts are used as liquid electrolytes. Fluorite-type (CaF_2 based) and tysonite-type (LaF_3 based) F^- ion conductors are also investigated as solid electrolytes for FIBs². The metallic lithium, zinc and magnesium are the anode materials employed in initial investigations for both CIB and FIB's.

Major R&I Challenges to be addressed

The major challenges of CIB's include, the solubility of metal chlorides in organic solvents, which limits the suitability of electrode materials. To tackle this issue, designing a liquid/or solid electrolyte, that can showcase a predominant chloride ion conductivity, without affecting cathode structure, is secondary hurdle. From the FIB point of view, development of intercalation-based cathodes and efficient electrolyte that offers facile F^- ion transport are the main challenges.

Future perspective and potential application for this battery chemistry

Anionic batteries are storage devices that offer high energy density compared to Li-ion batteries, but require continual research efforts to realise its efficacy. With intercalation type cathode, and in combination with a high conducting stable electrolyte, Cl^-/F^- based anionic batteries could reach a technical level, e.g., for stationary applications.

References: 1. F. Gschwind *et al.* Eur. J. Inorg. Chem., 2017: 2784-2799.

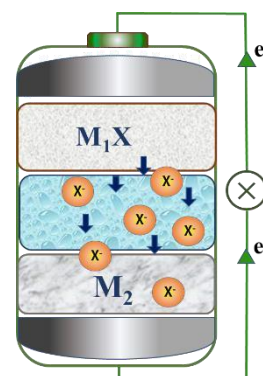


Figure 1: The schematic diagram of anionic battery in discharge mode: M_1X = metal chloride / or fluoride cathode and M_2 is Metallic anode.



2. F. Gschwind *et al.* Journal of Fluorine Chemistry 182 (2016) 76–90.

Publication Title: Recent developments and future perspectives of anionic batteries

Publication Authors: Guruprakash Karkera^a, M Anji Reddy^b, Maximilian Fichtner^{a,c}

Publication Link: <https://www.sciencedirect.com/science/article/pii/S0378775320311812>

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AN OVERVIEW AND PROSPECTIVE ON AL AND AL-ION BATTERY TECHNOLOGIES

Overview

Aluminum batteries are considered an appealing electrochemical energy storage system because of aluminum's natural abundance, high charge storage capacity ($2980 \text{ mAh g}^{-1} / 8046 \text{ mAh cm}^{-3}$), and the sufficiently low redox potential of Al^{3+}/Al . Several electrochemical storage technologies based on aluminum have been proposed so far ^[1,2]. The TRLs of most Al systems proposed so far ranges from 1 to 2. Only Al-air and Al-graphite dual ion cell (AGDIB) can be placed at slightly higher TRLs of 3 to 4. An elevated theoretical energy density characterizes Al-air cells 8.1 kWh kg^{-1} (practical value does not exceed 900 Wh kg^{-1}). In comparison, AGDIBs can provide an energy density comparable to lead-acid/Ni-MH batteries (65 Wh kg^{-1}) ^[2].



Major R&I Challenges to be addressed

The severe corrosion of aluminum alloys in alkaline electrolytes limits the practical application of Al-air batteries. Moreover, $\text{Al}(\text{OH})_4^-$ poor solubility leads to cathode clogging ^[3]. Additionally, Al-air cells are non-rechargeable batteries, which is a clear disadvantage. However, a closed value chain where Al_2O_3 is formed as the discharged product in the cell and then regenerated to Al-metal via electrodeposition of molten salts is a possible solution. However, this production method is energy-consuming and generates significant quantities of CO_2 .

Low-cost AGDIBs are the most mature secondary Al-battery technology, considered appealing for stationary energy storage applications. ALBUFERA ENERGY STORAGE evaluated the cell's cost, assessed on the developed 1 Ah cell prototype, at about 0.153€. The main limitation of AGDIBs is the relatively low energy density ($\leq 65 \text{ Wh kg}^{-1}$). Similar to all dual-ion electrochemical systems, AGDIB electrolytes (anolytes) are electrochemically active and rate-limiting battery components ^[4]. An additional drawback of AGDIB is the elevated corrosivity and reactivity of chloroaluminate melts electrolyte ^[5]. The development of electrolyte compositions with reduced reactivity can contribute to a breakthrough for this technology. The use of chlorine-free systems can be a valuable route to follow ^[6].

Future perspective and potential application for this battery chemistry

Overall, the overview of Al-batteries shows that there is a considerable gap between Al battery systems and Li-ion technology. The evaluation suggested that it will be highly challenging for Al-batteries to reach KPIs close to Li-ion systems. However, Al-batteries can offer several advantages over the more mature Li-ion technology, and after proper maturation, they can find their application niche. The most suitable application for Al-battery technology will be stationary storage due to the expected low cost and high sustainability of Al-based systems.

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Publication Title: An overview and prospective on Al and Al-ion battery technologies

Publication Authors: Elia Giuseppe Antonio, Kostiantyn V. Kravchyk, Maksym V. Kovalenko, Joaquín Chacón, A.W. Holland, R.G.A. Wills

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