A review of halide charge carriers for rocking-chair and dual-ion batteries

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Abstract
This review discusses how halide ion species have been used as charge carriers in both anion rocking-chair and dual-ion battery (DIB) systems. The anion rocking-chair batteries based on fluoride and chloride have emerged over the past decade and are garnering increased research interest due to their large theoretical energy density values and the natural abundance of halide-containing materials. Moreover, DIBs that use halide species as their anionic charge carrier are seen as one of the promising next-generation battery technologies due to their low cost and high working potentials. Although numerous polyatomic anions have been studied as charge carriers, the use of single halide ions (i.e., F$^-$ and Cl$^-$) and metal-based superhalides (e.g., [MgCl$_3$]$^-$) as anionic charge carriers in DIBs has been considerably less explored. Herein, we provide an overview of some of the key advances and recent progress that has been made with regard to halide ion charge carriers in electrochemical energy storage. We offer our perspectives on the current state of the field and provide a roadmap in hopes that it helps researchers toward making new advances in these promising and emerging areas.

KEYWORDS
charge carrier, dual-ion battery, halide, rocking-chair battery, superhalide

1 | INTRODUCTION

The pressing challenges of global warming and environmental pollution fundamentally threaten the well-being and security of the entire global population. The necessity is crystal clear to shift away from fossil fuels as the primary energy resources that are unsustainable. Unfortunately, the electricity generated from renewable energies such as solar and wind is inherently intermittent, where the energy generation is not always aligned with the demand. This intermittency is incompatible with the current grid infrastructure and can even cause catastrophic grid failures in extreme circumstances.$^{1,2}$ The solution to this challenge is to equip the grid with storage batteries that can effectively capture energy surplus during peak generation and deliver it to the grid when the demand for electricity surpasses generation. Without safe, efficient, and inexpensive storage batteries, a shift toward renewable energy will be difficult.

The need for better batteries comes from the grid, the rapid market growth of electric vehicles, and more...
powerful portable electronics that demand safer energy storage systems with high energy densities. Among the available secondary battery technologies, four rechargeable chemistries have seen significant commercial applications: lead–acid, nickel–cadmium, nickel–metal hydride, and Li ion. None of the first three batteries show potential to fill the grid storage gap and to electrify transportation. In contrast, Li ion batteries (LIBs) are seen as the most promising candidates for many applications due to their high energy densities and long cycle life. Unfortunately, LIBs suffer from significant issues surrounding their safety, toxicity, and resource availability. Therefore, to meet the demand, the continuous development of novel battery systems that incorporate the use of under-explored charge carriers and new operating mechanisms represents a solution.

A conventional LIB is an example of a cation rocking-chair battery (RCB) in which the Li⁺ cation acts as a shuttle between cathode and anode. The reactions occurring at cathode and anode during charging of a typical LIB with LiCoO₂ and graphite as the cathode and anode, respectively, can be represented by the following equations:

\[
\text{At cathode: } \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- , \quad (1)
\]

\[
\text{At anode: } x\text{Li}^+ + xe^- + C \rightarrow \text{Li}_x\text{C} , \quad (2)
\]

\[
\text{Overall cell reaction: } \text{LiCoO}_2 + C \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C} . \quad (3)
\]

Lesser explored battery operation mechanisms include the anion RCB, dual-ion battery (DIB), and reverse dual-ion battery (RDIB) (Figure 1). Analogous to the cation RCB, anion RCBs function using a single anion as a shuttle. During discharge, the charge of anion migrates from the cathode to the anode through the electrolyte. Upon charging, the reverse process occurs. Examples of anion RCBs include halide ion batteries (XIBs), that is, fluoride ion batteries (FIBs) and chloride ion batteries (CIBs). Typically, a transition metal halide is used as the cathode and another metal is the anode. The reactions occurring at cathode and anode during the charge of a typical XIB with F⁻ as the charge carrier and CuF₂ and La as the cathode and anode, respectively, can be represented as follows:

\[
\text{At cathode: } \text{CuF}_{2-x} + x\text{F}^- \rightarrow \text{CuF}_2 + xe^- , \quad (4)
\]
At anode: \( \text{LaF}_x + xe^- \rightarrow \text{La} + x\text{F}^- \),

(5)

Overall cell reaction: \( \text{CuF}_{2-x} + \text{LaF}_x \rightarrow \text{La} + \text{CuF}_2 \).

(6)

These systems are particularly attractive due to their high theoretical energy densities. Moreover, the natural abundance of halide materials provides a plethora of possible inexpensive redox couples. Nonetheless, anion RCBs employing halide ions as charge carriers have just started to be developed over the past decade and are still in the fledgling stages of research with vast opportunities. In particular, new electrode materials amenable to reversibly hosting halide ions and novel electrolytes with high halide ion conductivities are expected to significantly advance the XIB research.

DIBs and RDIBs represent another two battery operation mechanisms in which both cations and anions are used as charge carriers. Different from RCBs, DIBs and RDIBs operate via an accordion-like mechanism. In DIBs, during discharge, anions and cations are released from the cathode and anode, respectively, to the electrolyte (Figure 1C). Upon charging, the ions migrate back from the electrolyte and are reincorporated into their respective electrodes. The reactions occurring at cathode and anode during charging of a typical DIB with graphite electrodes and Li\(^+\) and PF\(_6^-\) as the cation and anion charge carriers, respectively, can be summarized as follows:

At cathode: \( C + x\text{PF}_6^- \rightarrow (\text{PF}_6)_x\text{C} + xe^- \),

(7)

At anode: \( C + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C} \),

(8)

Overall cell reaction: \( C + C + x\text{Li}^+ + x\text{PF}_6^- \rightarrow \text{Li}_x\text{C} + (\text{PF}_6)_x\text{C} \).

(9)

For RDIBs, the cation and anion storage sequence is flipped (Figure 1D). During discharge, cations and anions are incorporated into the cathode and anode, respectively. Upon charging, the charge carriers return to the electrolyte solution. Therefore, the reactions occurring during charging at an Na\(_{0.44}\)MnO\(_2\) cathode and a BiF\(_3\) anode for an RDIB with Na\(^+\) and F\(^-\) as charge carriers can be represented by the following equations:

At cathode: \( \text{Na}_{0.44}\text{MnO}_2 \rightarrow \text{Na}_{0.44-x}\text{MnO}_2 + xe^- + x\text{Na}^+ \),

(10)

At anode: \( \text{BiF}_3 + xe^- \rightarrow \text{BiF}_{3-x} + x\text{F}^- \),

(11)

Overall cell reaction: \( \text{BiF}_3 + \text{Na}_{0.44}\text{MnO}_2 \rightarrow \text{Na}_{0.44-x}\text{MnO}_2 + \text{BiF}_{3-x} + x\text{F}^- + x\text{Na}^+ \).

(12)

In both DIBs and RDIBs, the ionic charge carriers are supplied only by the electrolyte, where the electrolyte must, therefore, be considered as a part of the active mass. In recent years, DIBs have attracted considerable attention due to their potential cost-effectiveness, high working potentials, and environmental friendliness. These features make DIBs attractive next-generation energy storage candidates for both grid applications and potentially portable electronics. Of particular interest is the anion (de)insertion at the cathode, which endows DIBs with characteristically high discharge voltages and thus potentially high energy densities.

A number of reviews have come out in the past few years, providing comprehensive analyses on DIBs and the progress made thus far. To date, most DIBs have used polyatomic ions (e.g., PF\(_6^-\), BF\(_4^-\), TFSI\(^-\), ClO\(_4^-\), etc.) as their anionic intercalants. In this paper, we choose to focus our discussions of DIBs and RDIBs on those that have used single halide ions and metal–halide complex ions (i.e., metal-based superhalides) as their anionic ion species. Besides chloroaluminates, these classes of charge carriers are underexplored, and there are many more metal-based superhalides that should be investigated as potential anionic intercalants for DIBs.

The goal of this paper is to review how halide species have been used as charge carriers in rechargeable battery systems. We will present a summary of halide charge carriers in both anion RCB (i.e., XIB) and DIB systems. A particular emphasis is placed on recent updates in these fields and a roadmap for future research directions is proposed to avail new advances.

## 2 | HALIDE CHARGE CARRIERS FOR ANION RCBS

### 2.1 | Fluoride Ion Batteries

#### 2.1.1 | Overview of FIBs

The FIB is a fairly new electrochemical system that involves the use of the fluoride anion as a charge carrier. A typical working principle of an FIB can be expressed by the reaction below, in which M\(_c\) represents the metal used in the cathode, M\(_a\) represents the metal used in the anode, and \( n \) represents the number of fluoride ions in the formulas of electrodes:

\[
m\text{M}_c\text{F}_n + n\text{M}_a \rightleftharpoons m\text{M}_c + n\text{M}_a\text{F}_m.
\]

(13)

During discharge of the cell, de-insertion of fluoride ions takes place at the cathode and insertion of fluoride occurs at the anode. Upon charging, the reverse process occurs. Although primary cells based on fluoride transfer were developed nearly half a century ago, rechargeable batteries using fluoride ion as a charge carrier were...
introduced much more recently. The first proof-of-principle of a secondary FIB was reported by Reddy and Fichtner in 2011, which employed a solid-state electrolyte, a metal fluoride as cathode, and metallic cerium as anode. Since then, a number of papers have come out exploring different pairs of electrodes and electrolytes for rechargeable FIBs. Owing to the highly electronegative feature of fluorine, fluoride ions can operate in a large electrochemical stability window. In addition, the chemical formation of metal fluorides from fluorine and metal precursors is often associated with large changes in Gibbs free energy that endows FIBs with high theoretical voltages. These features, along with the global abundance of fluoride-containing materials, make FIBs attractive alternative energy storage systems. That being said, rechargeable FIBs are still in the early stages of investigation, and there is much more work that needs to be done before they can reach their full potential. In the following sections, we provide a brief overview of the research that has been done regarding FIB electrode materials and electrolytes. We also discuss the primary challenges currently surrounding FIB development and offer our perspective on the state of the field and future research directions.

2.1.2 FIB electrode materials

As stated above, one of the main appeals of the FIB system is the large theoretical voltages and high volumetric energy densities that can be obtained when transition metal fluoride cathodes are paired with alkaline-earth or rare-earth metal anodes. Many metal fluorides are bivalent or trivalent, which could allow for multielectron redox reactions and thus high specific energies. In fact, the theoretical energy density values of FIBs are expected to reach as high as 5000 Wh·L⁻¹, based on the electrodes alone, which is considerably larger than those of the state-of-the-art battery systems. Nonetheless, the research on FIBs is still at its early stage, and there are many electrochemical couples (the pairs of cathode and anode) that have yet to be explored. Gschwind et al. have published an excellent review that includes an in-depth theoretical screening of possible FIB materials as well as an assessment of associated safety and toxicity concerns. Readers are encouraged to see this review when considering new FIB anode and cathode systems.

At present, there are two main categories of FIB electrode materials: conversion-type electrodes, which typically operate via the reversible formation of metal fluoride/metal, and insertion-type electrodes, which operate via the reversible (de)insertion of F⁻ ions inside a host lattice. Although the conversion-type electrodes are widely available and possess large theoretical energy density values, they typically suffer from poor cycling stability and structural degradation. The insertion-type materials are promising toward improving the cyclability issues but are considerably less explored and possess significantly lower theoretical capacities and energy densities.

The vast majority of rechargeable FIBs reported thus far have used a metal fluoride cathode and metal anode, with a particular emphasis placed on demonstrating the feasibility of the electrode systems. In the first proof-of-concept study, Reddy and Fichtner tested a few metal fluorides (BiF₃, SnF₂, CuF₂, and KBiF₄) as cathode materials with Ce metal as the anode. It is worth noting that as BiF₃ and CuF₂ are not good electron conductors or fluoride conductors, it was necessary for these materials to be mixed with the solid electrolyte (i.e., La₀.₉Ba₀.₁F₂.₉ solid solution) and conductive carbon, so that their electrochemical performance can be measured. SnF₂ and KBiF₄, on the contrary, are good fluoride ion conductors; thus, mixing with conductive carbon alone was deemed sufficient. In addition, in the case of the BiF₃ cathode, two different material compositions were tested on the basis of different ball milling conditions. Ball milling BiF₃, carbon black, and La₀.₉Ba₀.₁F₂.₉ together at 150 rpm for 12 h yielded a simple nanocomposite, whereas increasing the mechanical milling speed to 600 rpm for 12 h led to the formation of a tysonite-type solid solution.

As far as the anode is concerned, Ce metal was regarded as a good starting point, as the fluorinated state (i.e., CeF₃) can act as a fluoride conductor by itself. Using ex situ X-ray diffraction (XRD), Reddy et al. gained mechanistic insights into the cycling behavior at each of the cathodes. Fluoride extraction of the cathode was successfully demonstrated by the appearance of XRD peaks associated with metallic Bi and metallic Sn after...
the first discharge of the electrodes of BiF₃ and SnF₂, respectively (Figures 2C and 2D). The XRD patterns clearly confirmed the reactivity of CuF₂; however, no peaks associated with metallic copper could be observed after discharge likely due to the initial amorphous nature of CuF₂. Through this study, Reddy et al. successfully demonstrated the feasibility of secondary batteries based on fluoride shuttle and opened up the field of research on rechargeable XIBs.

After the pioneering work of Reddy et al., most FIB papers have followed suit by also using metal fluoride/metal as the electrochemical couple. Unfortunately, many of these FIBs experience significant capacity decay in the initial cycles due to the large volume changes seen at either electrode during fluoride transfer.⁸,²⁴–²⁶ These volume changes can result in structural collapse as well as the loss of mechanical contacts between electrodes and the solid-state electrolyte.

Besides the FIB electrodes operating on the basis of conversion reactions, more recently, oxide intercalation-type compounds have been explored as FIB electrodes. Ruddlesden–Popper-type (AO(ABO₃)ₙ) compounds, including La₂NiO₄ and Sr₂TiO₃F₂, were investigated.²⁹,³⁰ Schafarzikite-type Fe₀.₅M₀.₅Sb₂O₄ (M=Mg or Co) and perovskite-type BaFeO₂.₅ have also been studied for electrochemical fluorination.³¹,³² Very recently, Hartman and Mishra³³ calculated different intercalation-type electrodes for FIBs with first-principles density functional theory (DFT). Their calculations found that layered electrodes (e.g., Ca₃N and Y₂C) are extremely promising anode materials and can provide voltages up...
to $-2.86$ V versus the La$_2$CoO$_4$F cathode. Druffel et al.\textsuperscript{34} further explored electrochemical fluorination of electrodes using first-principles methods. Their results demonstrate that the removal of anionic electrons from the Y$_2$C electrode structure and subsequent fluorination to Y$_2$CF$_2$ occur without any oxidation or reduction of the host lattice. Moreover, the activation barrier for electron–fluoride exchange was calculated as only 196 meV and negligible volume expansion was determined, demonstrating the potential of electrodes as a new class of electrodes for anion shuttle batteries. Fluorine-intercalated graphite has also recently been explored as a cathode for FIBs.\textsuperscript{35} However, upon increasing the F content, the C–F bonds transition from ionic to covalent and can thus not be considered as an intercalation-type electrode.

It should be noted that the potentially large energy densities associated with FIBs are somewhat sacrificed by using inorganic intercalation-type materials as compared with metal fluorides. Nonetheless, topotactic intercalation of fluoride ions is one of the most promising approaches toward solving the significant cycling issues. This study area is very new, and it is expected that many more intercalation-type compounds will be amenable to electrochemically hosting F$^-$ ions.

### 2.1.3 FIB electrolytes

FIBs can be categorized into two main types: high-temperature fluoride ion batteries (HTFIBs), which employ solid-state electrolytes that require elevated temperatures to operate, and room-temperature fluoride ion batteries (RTFIBs), which typically use liquid electrolytes and can operate at room temperature.\textsuperscript{7} The first proof-of-principle FIBs were HTFIBs operating at 150°C, which use three different nanocrystalline tysonite-type La$_{1-y}$Ba$_y$F$_{3-x}$ solid solutions as the electrolyte.\textsuperscript{8} Ultimately, the La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ solid solution with a conductivity of $-2.0 \times 10^{-4}$ S·cm$^{-1}$ was selected for the FIB tests. The authors note that the tysonite MF$_3$ (M=La, Ce) and fluoride MF$_2$ (M=Ca, Sr, Ba)-type structures are well-known as high-temperature fluoride conductors. Indeed, materials with fluoride-type (Fm-3m) and tysonite-type (P-3c1) structures have largely been seen as the most promising solid-state FIB electrolytes.\textsuperscript{5,7,20,21,36–38}

Rongeat et al.\textsuperscript{21} provided an in-depth analysis of the ionic conductivities of HTFIB electrolytes based on fluoride-type barium fluoride salts doped with lanthanum (Ba$_{1-y}$La$_y$F$_{2+x}$). The ionic conductivity of fluoride-type structures is known to originate from intrinsic anti-Frenkel pairs (anion vacancies combined with anion interstitials). Although pure fluoride-type structures tend to show fairly low conductivities, increasing the number of point defects through homogeneous and/or heterogeneous doping (by creating interfaces with defects or providing fast diffusion paths) has been shown to improve ionic conductivity.\textsuperscript{31} In Rongeat et al.’s work, doping fluoride-type barium fluoride salts with trivalent La$^{3+}$ ions was found to enhance the fluoride ion conductivity. Further improvements in ionic conductivity were demonstrated by providing conduction paths along the grain boundaries through the preparation of nanocrystalline materials. The composition of Ba$_{0.6}$La$_{0.4}$F$_{2.4}$ had the highest ionic conductivity ($1.9 \times 10^{-4}$ S·cm$^{-1}$ at 160°C) and was successfully demonstrated as an electrolyte in an FIB using BiF$_3$/Li as the cathode/anode.

Soon after their report on fluoride-type Ba$_{1-y}$La$_y$F$_{3+x}$ electrolytes, Rongeat et al.\textsuperscript{38} provided an in-depth analysis of the ionic conductivity of tysonite-type La$_{1-y}$Ba$_y$F$_{3-y}$ (0 ≤ $y$ ≤ 0.15) prepared by ball milling. Contrary to what was found for the fluoride-type electrolytes, the presence of grain boundaries was found to be detrimental to the ionic conductivity of the tysonite-type La$_{1-y}$Ba$_y$F$_{3-y}$ solid solutions. The ionic conductivity of fluoride in tysonite-type structures is known to originate from a vacancy mechanism via intrinsic Schottky defects. Using a combination of AC and DC conductivity studies, Rongeat et al. determined that the presence of grain boundaries partly blocks the ionic conductivity originating from the migration of vacancies through the structure. As such, sintering experiments were employed to reduce grain boundaries and bring about grain growth. Figure 3A shows the improved and diminished ionic conductivities obtained for tysonite-type La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ and fluoride-type Ba$_{0.9}$La$_{0.1}$F$_{2.4}$, respectively, after sintering treatment. These studies by Rongeat et al. represent significant pioneering work done on analyzing the fluoride ion conduction mechanisms in HTFIB electrolytes. Understanding how the fluoride ion conduction mechanisms vary in the presence or absence of grain boundaries has great impacts on the optimization of fluoride- and tysonite-type electrolytes for future HTFIB research.

Another approach to improve fluoride ion conductivity in HTFIB electrolytes involves the preparation of thin films.\textsuperscript{39} In the early HTFIB studies, the high thickness of the solid-state electrolyte layers (700–800 µm) caused high ionic resistance. Additional resistance was likely caused by the poor interparticle contacts between the electrode and electrolyte. Taking into account these issues, Zhang et al.\textsuperscript{40} developed tysonite-type La$_{1-y}$Ba$_y$F$_{3-y}$ (0 ≤ $y$ ≤ 0.15) thin-film electrolytes in an attempt to reduce the electrolyte thickness and resistivity. These 5–6 µm-thick thin films, prepared by a sol–gel spin-coating method, demonstrated the
highest fluoride conductivity of $8.8 \times 10^{-5} \text{S}\cdot\text{cm}^{-1}$ at 170°C. Although lower than the conductivity found for the same electrolyte composition prepared by ball milling, the overall $F^-$ ion resistance was significantly reduced by this thin-film approach due to its minuscule thickness. Thin-film electrolytes were successfully demonstrated in FIB cells using either Cu or Bi as the cathode and MgF$_2$ as the anode. Although initial discharge capacities of 76 and 66 mAh·g$^{-1}$ were obtained for the Cu and Bi cathodes, respectively, the capacity faded rapidly in the following cycles. It is expected that more effective approaches toward improving electrode–electrolyte contacts will be necessary for HTFIB electrolytes to be successfully implemented.

The large volume changes associated with fluoride hosting in the electrodes will also need to be addressed. In this pursuit, approaches that have been used to prevent volume expansion and improve structural integrity in other electrode systems, such as sulfur or silicon, should be explored. Design techniques such as nanoconfinement, fabrication of three-dimensional (3D) and one-dimensional structures, shape-preserving core–shell designs, and graphene composites could all be promising. For further discussion on advances in HTFIB electrolytes, readers are encouraged to see Zhao et al.’s review on halide-based materials and chemistry for secondary battery systems. In addition, Patro and Hariharan have provided an overview of solid-state fluoride ion-conducting materials and a discussion of the various techniques that can be used to influence their ionic conductivity values.

Besides HTFIBs, there have also been advances in the realm of RTFIBs. The development of electrolytes that can operate under ambient conditions is critical for the...

**FIGURE 3** (A) Arrhenius plot of the conductivities obtained for ball-milled and sintered samples of tysonite-type La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ and fluorite-type Ba$_{0.6}$La$_{0.4}$F$_{2.4}$ electrolytes. Reproduced with permission: Copyright 2014, American Chemical Society. (B) Schematics of neopentyl-substituted alkylammonium fluoride salts: Np$_1$F (top) and Np$_2$F (bottom). (C) Fluoride ion conductivities of Np$_1$F/BTFE and Np$_2$F/BTFE electrolytes at various concentrations. (D) Fluoride transport numbers and ionic conductivities for 0.75 M Np$_1$F/BTFE and 0.75 M Np$_2$F/BTFE electrolytes. Reproduced with permission: Copyright 2018, The American Association for the Advancement of Science. BTFE, bis(2,2,2-trifluoroethyl) ether; Np, neopentyl
practical applications of rechargeable FIBs to be achieved. Unfortunately, there exist a few significant hurdles that need to be addressed for RTFIB electrolytes such as low ionic conductivity and narrow electrochemical stability windows.\textsuperscript{3,7,25,48,49} Nevertheless, considerable advances are starting to be made in this area. The first proof-of-principle RTFIB was reported by Darolles et al.\textsuperscript{50} in US patent 9166249. Therein, an ionic PbF\textsubscript{2}/PANI electrochemical couple, an initial discharge dissolved Li\textsuperscript{+} ions in the electrolyte were assessed and charge performance was reported, and the cycling capacity of 103 mAh·g\textsuperscript{-1} was obtained. Unfortunately, only the first galvanostatic discharge cycles were demonstrated for the electrolyte of 0.75 M NH\textsubscript{4}HF\textsubscript{2} and Li metal as the anode. Noticing significant challenges associated with cathode dissolution, they designed a Cu@LaF\textsubscript{3} core–shell nanostructure to protect the active Cu from dissolution and prevent electrolyte decomposition. This architecture was found to be useful, and seven charge–discharge cycles were demonstrated for the Cu@LaF\textsubscript{3} cathode in 1 M Np\textsubscript{F}/BF\textsubscript{4} electrolyte at a current of 10 μA. This report was pioneering in its use of a completely nonaqueous liquid electrolyte for room-temperature fluoride ion cells. Still, the reported Coulombic efficiencies, energy efficiencies, and energy densities need to be improved. Although finding new electrolytes with similar properties as BTFE represents a monumental challenge, we are hopeful that more discoveries will be made along this line. In addition to improving the features of HTFIBs, substantial work is done by Davis et al.\textsuperscript{53} who reported a room-temperature fluoride ion-conducting electrolyte with high ionic conductivity based on dry tetraalkylammonium fluoride salts dissolved in partially fluorinated ethers. Specifically, they chose to use neopentyl (Np)-substituted alkylammonium fluorides as the salts, as the branched Np chain improves solubility and lacks β-hydrogens (Figure 3B). The lack of β-hydrogens is key, as it prevents decomposition of F\textsuperscript{−} to HF\textsubscript{2} and thus greatly improves the stability of the electrolyte. When using bis(2,2,2-trifluoroethyl) ether (BTFE) as a solvent, they were able to form electrolytes with ionic conductivities akin to those seen in traditional LIB electrolytes (10\textsuperscript{−3} to 10\textsuperscript{−2} S·cm\textsuperscript{-1}) (Figure 3C). In addition, a high F\textsuperscript{−} transport number of 0.53 was obtained for the electrolyte of 0.75 M N,N,N,N-trimethyl-N-neopentylammonium fluoride (Np\textsubscript{F}) in BTFE (Figure 3D). The authors demonstrated the cycling of Bi, Pb, Cu, Ce, and Ca conversion-type electrodes using Pt as the counter electrode. Noticing significant challenges associated with cathode dissolution, they designed a Cu@LaF\textsubscript{3} core–shell nanostructure to protect the active Cu from dissolution and prevent electrolyte decomposition. This architecture was found to be useful, and seven charge–discharge cycles were demonstrated for the Cu@LaF\textsubscript{3} cathode in 1 M Np\textsubscript{F}/BTFE electrolyte at a current of 10 μA. This report was pioneering in its use of Np\textsubscript{F} and Li metal as the anode.
needed on the development of FIB electrolytes that can operate at room temperature. Although considerable work is being done toward solid-state electrolytes for both HTFIBs and RTFIBs, it seems that liquid electrolytes are the best bet toward tackling the challenges associated with loss of interparticle contacts. Table 1 shows a summary of some of the representative pairs of cathode/anode and electrolyte that have been reported for rechargeable FIBs.

### 2.2 Chloride Ion Batteries

#### 2.2.1 Overview of CIBs

Rechargeable batteries using chloride ion as the charge carrier were first reported by Fichtner's group in 2014. Since then, considerable strides have been made in the field of rechargeable CIBs. The basic working principle of the proof-of-concept rechargeable CIBs involves the use of chloride ion as a shuttle between a metal chloride/metal electrochemical couple in a chloride-containing electrolyte. During discharge of the system, chloride ions are released from the cathode and transported to the anode through the electrolyte. Upon charging, the reverse process occurs. As a new technology, CIBs are particularly attractive due to the large variety of abundant chloride-containing materials. This abundance of materials leads to a wide array of possible electrochemical couples with high theoretical energy density values approaching those of Li/S batteries (~2800 Wh·L⁻¹). In recent years, a considerable number of new electrodes and electrolytes for chloride shuttle have been presented. Nonetheless, research on CIBs is still in its infancy and substantial improvements to performance will be needed before the practical applications can be achieved.

#### 2.2.2 CIB electrode materials

Similar to FIBs, electrode materials for CIBs can also be categorized into two main types: conversion type and

| TABLE 1 | Pairs of cathode/anode and electrolyte for some of the representative reports on rechargeable FIBs |
|-------------------------|-------------------------|-------------------------|-------------------------|
| Cathode/anode | Electrolyte | Electrolyte conductivity (S·cm⁻¹) | Capacity after cycling (mAh·g⁻¹) | Number of cycles | References |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| High-temperature FIBs |
| BiF₃/Ce | La₀.₉Ba₀.₁F₂.₉ | ~2.0 × 10⁻⁴ (150°C) | 50 | 38 | [8] |
| BiF₃/Li | Ba₀.₄La₀.₆F₂.₄ | 1.9 × 10⁻⁴ (200°C) | ~37 | 2 | [21] |
| Cu/MgF₂/C | La₀.₉Ba₀.₁F₂.₉ thin film | NA | 23 | 20 | [41] |
| CuF₂/La | La₀.₉Ba₀.₁F₂.₉ | ~2.0 × 10⁻⁴ (150°C) | 40 | 23 | [24] |
| LaSrMnO₄/Pb–PbF₂ | La₀.₉Ba₀.₁F₂.₉ | NA | ~30 | 1 | [27] |
| LaₓCoO₄/Pb–PbF₂ | La₀.₉Ba₀.₁F₂.₉ | NA | ~8 | 50 | [28] |
| LaₓNiO₄.₁₃/Zn–ZnF₂ | La₀.₉Ba₀.₁F₂.₉ | NA | ~28 | 220 | [29] |
| Room-temperature FIBs |
| BiF₃/Zn | BaSnF₄ | 3.5 × 10⁻⁴ | 61 | 20 | [25] |
| Bi/PbF₂/Pb | 0.35 M MPPF in TMPA-TFSA | 2.5 × 10⁻³ | ~0.01 mAh | 5 | [49] |
| BiF₃/Pt | 0.5 M CsF and 0.25 M LiBOB in tetraglyme | 1.31 × 10⁻³ | 189 | First discharge | [54] |
| BiF₃/Li | 0.05 M NH₄HF₂-doped PEG in 2:1 MeCN-DMC | 2.1 × 10⁻³ | | | [51] |
| 4-hydroxy-TEMPO/BiF₃ | 0.8 M aqueous NaF | 5.17 × 10⁻² | 89.5 (based on anode mass) | 85 | [52] |
| Cu@LaF₃/Pt | 1 M Np₁F in BTFE | ~2.8 × 10⁻³ | ~66 | 7 | [53] |

Note: Specific discharge capacity is based on the active mass of the cathode alone, unless otherwise specified.

Abbreviations: BTFE, bis(2,2,2-trifluoroethyl) ether; FIB, fluoride ion battery; LiBOB, lithium bis(oxalato)borate; MeCN-DMC, acetonitrile-dimethylcarbonate; Np, neopentyl; PEG, polyethylene glycol; TMPA-TFSA, N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide.
insertion type. The most widely studied electrodes for CIBs are conversion type with high theoretical energy densities but relatively poor cyclability. In the past few years, insertion/intercalation-type electrodes, such as layered double hydroxide (LDH) materials, have also emerged for CIBs and have demonstrated a superior cycling performance.

The vast majority of CIBs investigated thus far have featured the use of transition metal chloride/metal or transition metal oxychloride/metal electrochemical couples. Figure 4A shows the enticingly high theoretical energy densities that can be achieved through potential CIB electrochemical couples. When compared with the volumetric energy densities of other battery systems, the motivation to increase research efforts on CIBs becomes apparent. Furthermore, the relative abundance of active materials for CIB electrodes makes the system an attractive alternative to current state-of-the-art rechargeable LIBs, which are known to suffer from resource availability issues.

The first proof-of-principle rechargeable CIB utilized CoCl₂, VCl₃, and BiCl₃ as cathode active materials and lithium metal as the anode. Therein, using ionic liquids as electrolytes, it was successfully demonstrated that chloride ion moves from cathode to anode during discharge and from anode to cathode during the subsequent charging process (i.e., chloride shuttle). Unfortunately, the authors encountered a problem of cathode active material dissolution in the electrolytes, which is noted as a possible explanation for the lower-than-expected capacities. Furthermore, many metal chlorides are known to be soluble in conventional electrode-preparatory solvents such as N-methylpyrrolidone (NMP).

Lewis acidic transition metal chlorides are known to react with chloride-containing Lewis bases to form highly soluble complex ions. Noticing the challenge of cathode dissolution, Zhao et al. proposed the use of metal oxychlorides (e.g., BiOCl, FeOCl, SnOCl₂, etc.) as electrode active materials for CIBs. Metal oxychlorides are considerably less soluble in many solvents due to the strong binding between metal cations and the Lewis basic O²⁻ anions. In their study, Zhao et al. demonstrated chloride shuttle in BiOCl/Li and FeOCl/Li electrochemical couples. Using a combination of XRD, high-

![Figure 4](https://example.com/figure4.png)

**Figure 4** (A) Comparison of theoretical specific and volumetric energy densities of various possible chloride ion battery electrochemical couples. Electrochemical performances of the (B) FeOCl/Li and (C, D) BiOCl/Li CIB systems. Reproduced with permission: Copyright 2013, Wiley.
resolution transmission electron microscopy (HRTEM), and scanning transmission electron microscopy with corresponding Cl L-edge electron energy loss spectroscopy, the mechanistic reversible transfer of Cl\(^-\) in each of the layered structures was characterized. The BiOCl cathode was found to lose chloride ion and quickly transform to a mixture of amorphous Bi\(_2\)O\(_3\) and Bi metal during discharge of the cell. Chloride ion returned to the cathode, and BiOCl was reformed during the subsequent charging stage. Similarly, the FeOCl cathode was found to lose Cl\(^-\) during discharging of the cell, forming FeO, and recover Cl\(^-\) during the subsequent charging step, reforming FeOCl. Figure 4B–D demonstrates the electrochemical performance of the BiOCl/Li and FeOCl/Li systems, respectively.\(^5^7\) The BiOCl cathode showed a reversible capacity of ~60 mAh·g\(^{-1}\) that is nearly 60% of its theoretical capacity (103 mAh·g\(^{-1}\)). The charge/discharge curves for the FeOCl cathode showed an initial discharge capacity of 158 mAh·g\(^{-1}\) (~63% of the theoretical capacity). The capacity of the FeOCl cathode faded significantly in the next few cycles before stabilizing around 60 mAh·g\(^{-1}\), which was ascribed to possible loss of electrical contacts between the active material and conductive carbon additive.

These encouraging results indicated the promise of metal oxychlorides as cathode materials for rechargeable CIBs. Indeed, many of the rechargeable CIB studies succeeding this study have followed suit and employed the use of metal oxychlorides as cathode active materials.\(^5^8\)–\(^6^6\) Again, it should be emphasized that rechargeable CIB research is still in its infancy, and there are potentially many more chloride materials capable of hosting chloride ions. Therefore, there exist vast opportunities to explore new cathode materials for chloride shuttle beyond transition metal chlorides and metal oxychlorides. For a detailed analysis on theoretical calculations and considerations to take into account when screening possible CIB electrochemical couples, readers are encouraged to see Gschwind et al.’s review\(^6\) on CIBs.

Structurally, LDHs possess a number of features that make them attractive CIB cathode material candidates. First, the two-dimensional LDH interlayer gallery may potentially provide LDHs with superb anion intercalation–deintercalation features. Furthermore, LDHs with a large variety of interlayer anions are known to have high anionic conductivity values of ~10\(^{-2}\) S·cm\(^{-1}\).\(^6^7\)–\(^6^9\) Yin et al.\(^6^9\) synthesized a CoFe LDH with chloride ions occupying the interlayer space (CoFe–Cl LDH) and demonstrated its performance as a new cathode material for CIBs. Figure 5A shows a schematic of the CoFe–Cl LDH structure with a Co/Fe ratio of 3:1. The structure consists of positively charged sheets of edge-sharing FeO\(_6\) and CoO\(_6\) octahedra with chloride anions in the interlayer regions. The CoFe–Cl LDH was found to undergo a unique topochemical transformation during the charge/discharge processes.
During discharge, the reduction of Co$^{3+}$/Fe$^{3+}$ to Co$^{2+}$/Fe$^{2+}$ occurs and chloride ions migrate from the LDH cathode to the oxidized lithium metal anode. Upon charging, the chloride ions are reintercalated into the LDH gallery accompanied by the oxidation of Co$^{2+}$/Fe$^{2+}$ back to Co$^{3+}$/Fe$^{3+}$.

These charge/discharge processes were found to occur with a very slight expansion/contraction of the LDH basal spacing, respectively, as evidenced by XRD. The unique topochemical transformations during cycling endow the CoFe–Cl LDH with excellent reversible Cl$^-$ ion storage properties and superb electrochemical performance. Figure 5B,C show the energy storage performance of the CoFe–Cl LDH CIB at a current rate of 100 mA·g$^{-1}$. A maximum discharge capacity of 239.3 mAh·g$^{-1}$ was obtained during the second cycle and a stable capacity of ~160 mAh·g$^{-1}$ was retained over 100 cycles. Unfortunately, as can be seen in Figure 5B, a significant average overpotential over ~1.0 V was observed. In addition, rate performance was not mentioned, and the use of expensive cobalt is another potential downside. The poor energy efficiency may possibly be ascribed to strong interactions between Cl$^-$ ions and the positively charged sheets. It is worth noting that the CoFe–Cl LDH did not exhibit any structural changes during the galvanostatic charge/discharge (GCD) process, which indicates its high chemical and structural stability as compared with the metal chloride/oxychloride cathodes used in previous reports.

After the work on CoFe–Cl LDH, Yin et al. continued their exploration of LDH materials for rechargeable CIBs and reported the use of a trimetallic NiVAl LDH with interlayer Cl$^-$ (Ni$_2$V$_{0.9}$Al$_{0.1}$–Cl LDH) as a new high-performance CIB cathode. The Ni$_2$V$_{0.9}$Al$_{0.1}$–Cl LDH was found to possess an ultralong cycle life of >1000 cycles at 200 mA·g$^{-1}$ with a capacity higher than 113 mAh·g$^{-1}$ (Figure 6A). To date, this long cycle life (~57 days) far exceeds that of all other reported CIBs. Using a suite of structural characterization, kinetic investigations, and theoretical calculations, the authors were able to attribute the excellent performance to three key features. First, through the use of synchrotron X-ray absorption near-edge structure, it was found that vanadium undergoes multivalent redox activity (V$^{3+}$/V$^{5+}$) upon intercalation/deintercalation of Cl$^-$ ions. Second, the Al$^{3+}$ was found to enhance the LDH's structural stability via a pinning effect, which helps suppress local structural distortion and improves the cyclability of Ni$_2$V$_{0.9}$Al$_{0.1}$–Cl LDH. And lastly, the electronic configuration of Ni$^{2+}$ seems to make vanadium much more susceptible to valence state changes. These three features work in tandem to give Ni$_2$V$_{0.9}$Al$_{0.1}$–Cl LDH excellent

![Figure 6](image-url)
storage performance. Unfortunately, similar to the CoFe–Cl LDH, NiVAl–Cl LDH possesses a fairly large overpotential (~0.75 V) and somewhat low average discharge potential (~1.65 V) at 200 mA·g⁻¹ (Figure 6B). That being said, the removal of cobalt from the structure provides a considerable improvement in terms of cost and environmental impact. Along the same line, Han’s group has also demonstrated high-performance CIBs using NiMn–Cl and NiFe–Cl LDHs as cathode active materials.⁷¹,⁷²

These recent works on LDH materials highlight the opportunity that the exploration of new chloride-hosting electrodes can help solve the most challenging and persistent problems associated with rechargeable CIBs. In particular, the negligible volume change associated with Cl⁻ (de)intercalation into LDH materials demonstrates how new Cl⁻ intercalation materials could mitigate the longstanding stability issues. Venturing further beyond the traditional CIB electrode materials will be necessary for the continued development of rechargeable CIBs.

Besides transition metal chlorides (or metal oxychlorides) and LDH materials, a few papers have also reported the use of chloride-doped organic polymers as cathode active materials for CIBs.⁷³,⁷⁴ Conductive polymers have been widely studied as electrodes for alkali/alkaline metal ion batteries and have distinct advantages pertaining to their structural tunability, design flexibility, and abundance of chemical elements (e.g., C, H, O, N, and S).⁷⁵,⁷⁶ In 2017, Zhao et al.⁷³ reported a chloride-doped (chloride-hosting) polymer, polypyrrole chloride (PpyCl), for use as a CIB cathode material. Specifically, a nanostructured PpyCl@carbon nanotubes (PpyCl@CNTs) composite was synthesized via chemical oxidative polymerization using FeCl₃·6H₂O as the oxidant. When employed as a cathode in a CIB with Li metal as the anode and 0.5 M 1-butyl-1-methylpiperidinium chloride (PP₄Cl) in 1-butyl-1-methylpiperidinium bis(trifluoromethane)sulfonimide (PP₄TFSI) as the electrolyte, the PpyCl@CNT demonstrated a high discharge capacity of 118 mAh·g⁻¹ and slow capacity decay with >90 mAh·g⁻¹ reversible capacity retained after 40 cycles at 10 mA·g⁻¹. An average discharge potential of ~2.6 V was observed. Using X-ray photoelectron spectroscopy (XPS) analysis, the reversible electrochemical reactions based on the redox of nitrogen species and chloride ion deintercalation/intercalation in PpyCl were revealed. Along somewhat similar lines, following the research on PpyCl@CNTs, Zhao et al.⁷⁴ reported the use of chloride-doped polyaniline/carbon nanotubes (PANI/CNTs) as a new CIB cathode material. Similar to the PpyCl@CNT, the PANI/CNTs cathode was found to reversibly store chloride ions via redox reactions associated with the nitrogen species in the PANI. The as-prepared PANI/CNTs composite with 50 wt% CNTs (denoted as PANI/50CNTs) delivered a maximum reversible capacity of 80 mAh·g⁻¹ at 10 mA·g⁻¹ with a high Coulombic efficiency of 99% and good cycling stability.

Following the results of these studies, it can be expected that many more chloride-doped conductive polymers and organic molecules will be suitable CIB electrode materials, considering the highly tunable nature of organic structures. In addition, the design flexibility and stability of organic/polymer materials offer potential solutions for overcoming many of the challenges associated with other, more traditional, CIB active materials.

Similar to the cathodes, there has been relatively little diversity as far as anodes are concerned for CIBs. The vast majority of rechargeable CIBs reported thus far have employed the use of lithium metal as the anode with a few papers also exploring the use of other metals such as magnesium, zinc, tin, and bismuth.⁶,⁶²,⁶⁴,⁷⁷,⁷⁸ A key advantage of CIBs is the lack of metal plating on the anode and the obviated dendrite formation at the anode due to chloride shuttle. This feature improves the safety of CIBs and makes them a particularly attractive system for large-scale energy storage. It is worth noting that the solubility of LiCl in the electrolyte will be a key descriptor of the anode’s performance. On the contrary, aqueous CIBs have used metal oxychlorides (BiOCl and Sb₂O₅Cl₂) as anodes paired with silver as the cathode.⁷⁹–⁸¹

The lack of diversity in electrode materials used for CIBs represents a clear opportunity for the exploration of new cathodes and anodes for chloride shuttle. Exploring new combinations of electrode materials and electrolytes will be essential for CIBs to reach their full potential. As stated previously, research on electrode materials for CIBs is still very much in its infancy, and there are significant challenges to overcome. Finding new electrode materials that are suitable for hosting Cl⁻ ions with high capacity and long cycle life will significantly enhance the development of rechargeable CIBs. We will continue to talk about Cl⁻-hosting electrode materials in the section of DIBs.

2.2.3 | CIB electrolytes

One of the largest challenges associated with CIBs is the development of electrolytes with high chloride ion conductivity that can operate at room temperature. Since the first proof-of-principle rechargeable CIB was reported by Fichtner’s group, the majority of CIBs have employed ionic liquids as the electrolytes. In the initial CIB research, Zhao et al.⁹ used an electrolyte composed of a mixture of binary
ionic liquids consisting of 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) in a 1:3 volume ratio. The addition of [BMIM][BF₄] to the electrolyte helped reduce the viscosity and allowed for much higher chloride mobility than was found for pure [OMIM][Cl]. Although they encountered possible dissolution of the cathode active materials in the electrolyte, Zhao et al. managed to demonstrate reversible performance of the chloride shuttle in CoCl₂/Li, VCl₃/Li, and BiCl₃/Li electrochemical couples using this binary ionic liquid as the electrolyte. Following this study, a number of other aprotic chloride ionic liquids have been used, including those with cations of piperidinium, quaternary ammonium, and pyrrolidinium. The high chloride ion conductivity, large electrochemical stability window, compatibility with Li metal, and high level of safety have made these ionic liquids the electrolytes of choice for CIB applications.

Venturing beyond ionic liquids, a few papers have dealt with the use of aqueous electrolytes for rechargeable CIBs. The first aqueous rechargeable CIB was reported by Chen et al. in 2017. Therein, a BiOCl anode was paired with a silver cathode in 1 M aqueous NaCl electrolyte. During charging of the battery, chloride ions are released from the BiOCl anode, transported through the aqueous NaCl electrolyte, and incorporated into the silver cathode to form AgCl. A stable capacity of 92.1 mAh·g⁻¹ was maintained for 45 cycles (~20.7 h) at a current rate of 400 mA·g⁻¹. Following these results, Hu et al. reported another rechargeable aqueous CIB using the same electrolyte of 1 M NaCl. This system was similar to that of Chen et al.'s in that it employed an analogous working mechanism with a metal oxychloride material (Sb₂O₃·Cl₂) as anode and silver as cathode. More recently, Zhang et al. synthesized a novel bismuth–carbon nanotube anode through the thermal reduction of a Bi–metal organic framework under a hydrogen atmosphere. When paired with an AgCl cathode and NaCl (1 M) electrolyte, the system maintained a stable capacity of 51.8 mAh·g⁻¹ over 1000 cycles at 1200 mA·g⁻¹. In each of these aqueous CIBs, 1 M NaCl has been the electrolyte of choice; however, it will be very surprising if NaCl is the optimal electrolyte. Other inorganic or organic chloride salts may bring about interesting properties through their interactions with the electrodes, for example, suppressing the dissolution of the electrodes. Clearly, there is a lack of diversity in terms of aqueous electrolytes that have been explored for rechargeable CIBs.

The meager amount of research on aqueous CIBs likely stems from the possible dissolution of active materials, incompatibility with reactive metal anodes, for example, Li, and the inherent limitations associated with the potential stability window of the electrolyte solvent, that is, water. This presents an opportunity to uncover a plethora of new aqueous electrolytes for the chloride shuttle. In particular, it is expected that highly concentrated water-in-salt electrolytes (WiSEs) can open up new avenues for reducing the solubility of transition metal chloride electrodes while simultaneously mitigating issues of water electrolysis. However, it should be noted that an increase in the concentration of Cl⁻ ions in the electrolyte also increases the likelihood of chlorine gas evolution by reducing the onset potential of Cl⁻ oxidation. These factors will have to be taken into account when designing new aqueous chloride electrolytes.

In addition to aqueous and ionic liquid electrolytes, a number of papers have come out in recent years exploring all-solid-state CIBs. Gschwind et al. spurred research toward room-temperature solid-state CIBs by suggesting the use of polymer electrolytes to help prevent electrode dissolution. Therein, three chloride-conducting membranes based on gelatin, polyvinyl chloride (PVC), and polyvinylidifluoride-hexafluoropolymer (PVDF-HF) were explored as quasi-solid-state polymer CIB electrolytes. Each air-stable membrane was combined with a chloride salt containing a large ammonium counterion and tested in a rudimentary battery setup consisting of pieces of Zn as anode and either CuCl₂·4H₂O, PANI, or BiCl₃ as the cathode. In these studies, tetraethylammonium chloride was mixed with gelatin; octyltrimethylammonium chloride was mixed with PVC; tetrabutylammonium chloride was mixed with PVDF-HF. Electrochemical impedance spectroscopy (EIS) measurements revealed that the PVC-based electrolyte had the lowest Cl⁻ ion conductivity (~10⁻⁷ S·cm⁻¹) of the three. The gelatin and PVDF-HF electrolytes possessed considerably higher conductivities of about 10⁻⁴ S·cm⁻¹. Only first discharge performance was reported for these systems and the cyclability remains unknown. Still, Gschwind et al.'s results demonstrated the feasibility of quasi-solid-state polymer membrane electrolytes for use in CIBs.

Following the introduction of chloride-conducting membranes for CIBs, Zhao's group reported a solid polymer electrolyte for chloride shuttle consisting of a poly(ethylene oxide) (PEO) matrix, tributylmethylammonium chloride (TBMACl) salt, and succinonitrile (SN) as the plasticizer. The as-prepared electrolyte (denoted as PEO₁₋TBMACl₁₋SN₃) was thoroughly characterized on the basis of composition and found to have high electrochemical stability. Using EIS, the PEO₁₋TBMACl₁₋SN₃ electrolyte showed conductivities of 10⁻⁵ to 10⁻⁴ S·cm⁻¹ in the 298–343 K temperature range. By pairing this solid polymer electrolyte with a Li/FeOCl anode/cathode, Chen et al. successfully
demonstrated the first-ever all-solid-state rechargeable CIB.\textsuperscript{58} Considering the high electrochemical stability of the electrolyte, it would be interesting to evaluate its performance with other electrode materials (e.g., transition metal chlorides and Cl\textsuperscript{−}-doped conductive polymers).

Very recently, Zhao’s group demonstrated another all-solid-state rechargeable CIB using the inorganic halide perovskite of CsSnCl\textsubscript{3} as an electrolyte.\textsuperscript{78} Therein, Xia et al. used mechanical milling and subsequent mild heat treatment to prepare the CsSnCl\textsubscript{3} perovskite (Figure 7A). The cubic CsSnCl\textsubscript{3} had been a well-known Cl\textsuperscript{−} conductor with a high ionic conductivity of \( \sim 1 \text{ mS cm}^{-1} \) at 100°C, but up until this study, its electrochemical stability remained unknown.\textsuperscript{9,83,84} In addition, the conductivity of CsSnCl\textsubscript{3} had been shown to decrease around room temperature as a result of a gradual transformation from the cubic to monoclinic phase.\textsuperscript{84} Xia et al. found their as-prepared cubic CsSnCl\textsubscript{3} to be stable with no phase transformation for more than 3 months at 298 K. It is worth noting that the as-prepared perovskite electrolyte demonstrated a high room-temperature ionic conductivity of \( 3.6 \times 10^{-4} \text{ S cm}^{-1} \), which is considerably higher than those obtained from other solid-state CIB electrolytes. Furthermore, a large electrochemical stability window of \( \sim 6.1 \text{ V} \) was achieved (Figure 7C). Many of these attractive features were ascribed to the defects introduced into the structure during its preparation. Abundant nanograins, tin vacancies, and lattice strain endowed the CsSnCl\textsubscript{3} with enhanced structural stability. Lastly, Xia et al. demonstrated the practicality of the electrolyte for chloride shuttle in cells with either SnCl\textsubscript{2}/Sn or BiCl\textsubscript{3}/Bi electrochemical couples. To the best of our knowledge, these three studies, by Gschwind et al., Chen et al., and Xia et al., represent the only work done on all-solid-state rechargeable CIBs, to date.

Considering the significant electrode dissolution issues that have been encountered in CIB research, solid-state electrolytes certainly seem like a good direction. In addition, the use of solid-state electrolytes could reopen research on intriguing inorganic CIB electrode materials that were found to be highly soluble in ionic liquid electrolytes. Overall, the vast majority of CIBs have used ionic liquid-based electrolytes. There have also been a few reports exploring aqueous and solid-state CIBs; however, the research is limited. It is expected that further investigation of these less conventional electrolytes

![Figure 7](image_url)

**Figure 7** (A) A schematic of the preparation of the CsSnCl\textsubscript{3} perovskite solid-state electrolyte. (B) Nyquist plots of the CsSnCl\textsubscript{3} electrolytes showing the high chloride ion conductivity of \( 3.6 \times 10^{-4} \text{ S cm}^{-1} \) when cooled to 298 K. (C) Linear sweep voltammetry scan of the cubic CsSnCl\textsubscript{3} electrolyte at 298 K, demonstrating an electrochemical stability window of \( \sim 6.1 \text{ V} \).\textsuperscript{78} Reproduced with permission: Copyright 2020, American Chemical Society\textsuperscript{78}
will bring about further innovations and possibly open up a new paradigm for the rechargeable CIB field.

3 | HALIDE CHARGE CARRIERS FOR DIBS

The DIBs have emerged as a promising next-generation energy storage system. First introduced by McCullough et al. in 1989, DIBs are fundamentally different from RCBs, where upon charging of a typical DIB, cations are intercalated into the anode and anions are intercalated into the cathode. Upon discharge, the ions leave their respective electrode hosts and return to the electrolyte (Figure 1C). Recently, a novel variation of the DIB, dubbed as a “reverse dual-ion battery,” has been demonstrated, in which the cation and anion storage sequences are flipped (Figure 1D). The feature of anion intercalation/deintercalation at the cathode often allows DIBs to operate at high potentials. Moreover, unlike conventional RCBs, based on Gibbs free energy, the potential of DIBs is dependent on the electrolyte solvent and the anion charge carrier.

As such, the choice of anionic intercalant is critical to the performance of a DIB and should not be taken lightly. So far, the vast majority of DIBs have used polyatomic ions as their anionic intercalants. Numerous reports have come out exploring a variety of anionic intercalants for DIBs, including PF$_6^-$, BF$_4^-$, AlCl$_4^-$, FSI, TFSI$^-$, ClO$_4^-$, and DFOB$^-$ among others. Single halide ions (i.e., F$^-$, Cl$^-$, etc.) represent a fairly underexplored group of anionic intercalants for DIBs. In addition, besides chloroaluminate species, alternative metal-based superhalides, such as Mg–Cl and Zn–Cl superhalides, have just started to be investigated. Therefore, we choose to focus our discussion on DIBs and RDIBs to those that have used single halide ions and metal-based superhalides as their anionic charge carriers. In the following sections, we discuss these classes of halide-based anionic intercalants and their use in DIB systems. We also identify knowledge gaps that exist in this area in the hope that it helps make new advances for halide charge carriers in DIBs.

3.1 | Single halide ion charge carriers for DIBs

There are very few reports describing DIB systems that operate with single halide ions as the anionic charge carrier. This likely has to do with the fact that DIBs have traditionally been designed with graphite as both cathode and anode. The electrochemical insertion of a single halide ion (i.e., F$^-$) into graphite is associated with such a high potential that most aprotic electrolyte solvents would decompose. However, the recent exploration of new electrode materials and electrolytes is engendering the discovery of new DIBs that employ single halide ions (e.g., F$^-$, Cl$^-$) as charge carriers.

Very recently, our group demonstrated highly reversible storage of chloride ions in the compact structure of Mn$_3$O$_4$ after the initial irreversible insertion of Zn$^{2+}$. This new mechanism, dubbed counter-ion insertion (CII), illustrates a new way of designing high-performance Cl$^-$-hosting electrodes. Although it seems counterintuitive that compact metal oxide structures can be amenable to hosting anions, Jiang et al.’s previous results have challenged this assertion, showing that the Mn$_3$O$_4$ structure can readily store NO$_3^-$ or SO$_4^{2-}$ ions with high reversibility in aqueous electrolytes. A number of other studies have also explored the insertion of polyatomic anions (e.g., ClO$_4^-$, CO$_3^{2-}$, etc.) in a variety of metal oxides. Motivated by these results, we explored the Cl$^-$-hosting capabilities of the Mn$_3$O$_4$ cathode in a highly concentrated WiSE of 20 M ZnCl$_2$ + 5 M NH$_4$Cl with Zn metal as the anode. Interestingly, it was found that the initial irreversible reductive insertion of Zn$^{2+}$, forming Zn$_{0.2}$Mn$_3$O$_4$, transformed the chemical structure, such that it allowed for reversible chloride storage in the subsequent cycles. Using an electrochemical quartz crystal microbalance, we were able to confirm chloride as the primary charge carrier after the initial irreversible insertion of Zn$^{2+}$ (Figure 8A). In addition, the Zn$^{2+}$-trapped Zn$_{0.2}$Mn$_3$O$_4$ exhibited a large chloride storage capacity of over 200 mAh·g$^{-1}$ at a high operation potential of >1.6 V versus Zn$^{2+}$/Zn (Figure 8B). It is worth noting that the enormous hysteresis that can be seen in the first cycle further suggests that the initial reductive Zn$^{2+}$ insertion is irreversible. The minimal extent of polarization and high reversibility seen in subsequent cycles indicate that chloride is the only charge carrier at the cathode.

These attractive features are unprecedented for halide storage in aqueous electrolytes. Figure 8C shows the generic CII mechanism in which the initial irreversible insertion of A-ions into a metal oxide (MO$_x$) allows for the resulting structure to host B-ions of opposite electric charge. This mechanism, which allowed for highly reversible Cl$^-$ storage in a DIB and the formation of a new ionic compound equivalent to Zn$_{0.2}$Mn$_3$O$_4$Cl$_{1.7}$, represents a new methodology for the development of novel chloride-hosting electrodes. It is expected that this methodology will be used for the electrosynthesis of many novel compounds never-before-seen by the scientific community that can be used for DIBs, CIBs, and other energy storage technologies.
Besides chloride, a new RDIB was recently demonstrated using fluoride as the anionic charge carrier. Therein, Zhang et al. described a novel aqueous RDIB operating on reversible fluoride and sodium storage at the anode and cathode of BiF₃ and Na₀.₄₄MnO₂, respectively.¹² Using 0.₈ M aqueous NaF as the electrolyte, an initial fluoride storage capacity of ~₁₂₃ mAh·g⁻¹ was obtained at the BiF₃ anode. The capacity decayed significantly in the following initial cycles, but a stable capacity of ₄₇.₂₈ mAh·g⁻¹ was obtained after ₄₀ cycles with a Coulombic efficiency of ₉₉% at ₁₀₀ mA·g⁻¹. Reversible storage of F⁻ by the BiF₃ anode was confirmed using ex situ XRD and XPS. The authors noted that significant volume changes and possible structural collapse associated with fluoride-transfer-caused phase transformations were likely responsible for the capacity decay. The oxidation of Bi to BiF₃ occurs with a considerable volume expansion of ~₁₃₄%, which has also been seen as a challenge for all conversion-based electrodes.

To address the poor cycling performance and stability issues at the BiF₃ electrode, Hu et al.⁹³ engineered a hybrid electrode of bismuth nanoparticles dispersed in a matrix of carbon nanotubes (Bi@CNTs). When used in an identical battery configuration with ₀.₈ M NaF as electrolyte and Na₀.₄₄MnO₂ as the cathode, the Bi@CNTs demonstrated improved electrochemical performance and stability. Unfortunately, similar to the first aqueous FIB, the possibility of HF or bifluoride formation in the electrolyte is not discussed in either of these systems. Nonetheless, they demonstrated the feasibility of using F⁻ as an anionic charge carrier for DIBs, which is valuable to the development of new energy storage systems.

Wang’s group made a significant advance when they recently reported on a new halogen conversion-intercalation chemistry for DIBs.⁹⁴ Although the battery is considered by the authors belonging to rocking-chair type, because Li⁺ ions are extracted from the cathode, we still consider its chemistry for DIBs for the sake of emphasizing the work’s values for the DIB area. Therein, Yang et al. prepared a composite graphite cathode containing equimolar amounts of lithium chloride and lithium bromide salts, that is,
(LiBr)$_{0.5}$(LiCl)$_{0.5}$-graphite (LBC-G). Using a highly concentrated water-in-bisalt (WiBS) electrolyte, a hydrated LiBr/LiCl layer formed on the surface of the LBC-G electrode. This hydrated LiBr/LiCl layer served to accelerate the halogen redox reactions and simultaneously confine all the halide anions to the graphite cathode. Upon charging, the oxidized Br$^0$ and Cl$^0$ were sequentially intercalated into the graphite host, as can be seen by the following two redox reactions:

$$\text{LiBr} + C_n \rightleftharpoons C_n[\text{Br}] + \text{Li}^+ + e^-,$$  \hspace{1cm} (14)

$$\text{LiCl} + C_n[\text{Br}] \rightleftharpoons C_n[\text{BrCl}] + \text{Li}^+ + e^-.$$  \hspace{1cm} (15)

The intercalations of bromine and chlorine species were found to occur between 4.0 and 4.2 V and 4.2–4.5 V versus Li$^+$/Li, respectively. Upon discharge, the reverse process occurred, in which Cl$^0$ and Br$^0$ were successively reduced and deintercalated from the graphite host. The reduced halides then recombined with the free Li$^+$ ions to form LiCl/LiBr on the surface of the cathode.

This unique conversion-intercalation mechanism manages to combine the high energy densities of conversion reactions with the excellent reversibility of intercalation mechanisms. On the basis of the total mass of the LBC-G composite, a highly reversible gravimetric discharge capacity of 243 mAh·g$^{-1}$ (based on the mass of graphite plus LiCl and LiBr) was achieved at an average potential of ~4.2 V. It should be noted that in the literature of DIBs, the mass of charge carriers is usually not considered when calculating the capacity of the cathode materials. It is worth noting that the highly concentrated WiBS electrolyte containing 21 mol·kg$^{-1}$ (m) LiTFSI and 7 m LiOTf is essential for extending the oxidation potential of water and allowing for the reversible halide redox to occur without electrolyte decomposition. Yang et al. assembled full cells by combining this LBC-G composite cathode with a graphite anode passivated by a highly fluorinated ether polymer gel. Impressively, an estimated specific energy density of ~460 Wh·kg$^{-1}$ (based on the total mass of the cathode and anode) can be expected for such a full cell, which is comparable to that of the state-of-the-art nonaqueous LIBs. Even when considering the mass of the electrolyte, the full cell still achieves an impressive gravimetric energy density of ~304 Wh·kg$^{-1}$. This novel chemistry represents a significant advance in the design of high-performance DIBs that use halide ions as charge carriers.

It should also be noted that DIB systems using single halide ions as anionic charge carriers have the potential to be used in a wide variety of desalination and ion removal applications. Single halide ions represent the most attractive anionic charge carriers for DIBs due to their small sizes and mass. These batteries offer the potential of developing new systems with extremely high energy density. As more electrodes and electrolytes are explored, it is expected that many DIBs using F$^-$ and Cl$^-$ as anionic intercalant will start to be reported.

### 3.2 Metal-based superhalide charge carriers for DIBs

The term “superhalogen” has been used to describe complex halide radicals due to their comparatively high electron affinity values. Superhalides, the anions of superhalogens (e.g., PF$_6^-$, BF$_4^-$, AlCl$_4^-$, etc.), are some of the most studied anionic intercalants for DIBs. In particular, PF$_6^-$, BF$_4^-$, and imide-based anions (e.g., FSI$^-$, TFSI$^-$, etc.) have all been studied extensively. More recently, chloroaluminates (e.g., AlCl$_4^-$, Al$_2$Cl$_7^-$) have begun to be explored as charge carriers in DIBs. However, the use of other metal-based superhalides (e.g., Mg–Cl and Zn–Cl superhalides) as charge carriers is still a relatively uncharted research area. Further exploration of novel metal-based superhalides as anionic charge carrier will be necessary to the advancement of DIB research.

#### 3.2.1 Chloroaluminate ions for DIBs

In part due to the comparably low diffusion energy barrier of AlCl$_4^-$ in graphite (0.012–0.029 eV), the study of chloroaluminates as anionic charge carriers for DIBs has been gaining momentum. Lin et al. made a significant advance when they reported on an Al/graphite DIB that uses chloroaluminates as the anionic intercalant. Therein, they explored the use of two novel graphitic cathode materials (pyrolytic graphite foil and three-dimensional graphitic foam) paired with aluminum metal as the anode. During discharge, the battery operates via the dissolution/stripping of Al$^{3+}$ at the anode and the simultaneous de-intercalation of chloroaluminates from the cathode. When using 3D graphitic foam as the cathode and an ionic liquid of ~3:2 AlCl$_3$/1-ethyl-3-methylimidazolium chloride as the electrolyte, a capacity of ~60 mAh·g$^{-1}$ was achieved at an extremely high current rate of 75 C. Impressively, this capacity was maintained for more than 7500 cycles without decay. Using Raman spectroscopy, both AlCl$_4^-$ and Al$_2$Cl$_7^-$ superhalides were found to be present in the electrolyte at a ratio of ~2.33 [AlCl$_4^-$]:[Al$_2$Cl$_7^-$]. Characterization demonstrated that AlCl$_4^-$ superhalide was the species predominantly intercalated between graphite layers during the charge process. At the anode side, during charge, Al$_2$Cl$_7^-$ superhalide transforms into metallic Al...
and AlCl₄⁻. Upon discharge, the reverse process happens.

The impressive results demonstrated by Lin et al. encouraged numerous additional works using AlCl₄⁻ as an anionic intercalant in DIBs. Many of these works provided in-depth analyses of the intercalation mechanisms of chloroaluminate anions into graphite. Wang et al.¹¹³ used Raman spectroscopy to identify two different (de)intercalation processes of AlCl₄⁻ into a natural graphite cathode at two discharge plateaus. Moreover, they improved upon the performance of the previously reported AlCl₄⁻ DIB by demonstrating a significant increase in capacity from ~66 to ~100 mAh·g⁻¹. Various theoretical studies have also examined the intercalation behavior of AlCl₄⁻, pointing to a number of energetically favorable configurations depending on the testing conditions.¹¹⁴⁻¹¹⁶ Zhang et al.¹¹² explored how changes in size along the graphitic ab plane and c direction affect AlCl₄⁻ intercalation chemistry. Therein, using an ionic liquid of AlCl₃ in 1-methyl-3-propylimidazolium as the electrolyte, they demonstrated that decreases in the graphite c direction improve the charge transfer and kinetics of chloroaluminate superhalides. In addition, increases in the size of the ab plane were found to enhance cycling stability by improving graphite’s flexibility. With some exceptions, the majority of research done on chloroaluminate superhalides for DIBs have employed graphite carbon as the cathode. This makes sense, considering the attractive high operation potential and inexpensive features of graphite. Nonetheless, the use of other chloroaluminate hosts should be explored. Also, more electrolytes that contain AlCl₄⁻ and Al₂Cl₇⁻ anionic species should be formulated.

3.2.2 | New metal-based superhalides for DIBs

Besides chloroaluminates, the use of other metal-based superhalides as anionic intercalants in DIBs is just emerging as an area of research. Very recently, our group demonstrated the feasibility of using Mg–Cl superhalides as charge carriers for DIBs.¹¹⁷ Therein, Kim et al. achieved reversible oxidative insertion of Mg–Cl superhalides into a graphite cathode using a highly concentrated aqueous deep eutectic solvent (DES) electrolyte. In the aqueous DES electrolyte, composed of 9 m MgCl₂ and 30 m choline chloride (ChCl), the Mg²⁺ cations were found to be mostly coordinated as Mg–Cl superhalides (i.e., [MgCl₃(OH)₂]⁻ and [MgCl₄]²⁻).
It should be noted that we extend the definition of superhalides to include metal–X complex ions (Figure 9A). A record-high initial anion storage capacity of 151 mAh·g\(^{-1}\) was obtained. Although the cathode’s capacity faded rapidly to ~50% in the first 25 cycles, a stable capacity of ~70 mAh·g\(^{-1}\) with an average Coulombic efficiency of 99% was maintained for the next 275 cycles (Figure 9B). Interestingly, HRTEM images indicate that the insertion of Mg–Cl superhalides into graphite introduces turbostratic sites rather than the formation of staged GICs (Figure 9C,D). It is worth noting that this study represents the first research work on Mg–Cl superhalide charge carriers for electrochemical anion storage. Therefore, new electrolytes consisting of Mg–Cl superhalides and the hosting electrodes are expected to receive further attention for reversibly hosting these novel charge carriers.

Zhang et al.\(^{118}\) found that Zn–Cl superhalides are the primary anionic species solvated in a highly concentrated WiSE of 30 m ZnCl\(_2\). Motivated by this knowledge, Wu et al.\(^{13}\) defined RDIB with a system that employed Zn–Cl superhalides as the anionic intercalant. Upon discharge, Zn\(^{2+}\) cations were inserted into the cathode and Zn–Cl complex anions were hosted by the anode. Wu et al. used a nanocomposite consisting of ferrocene (Fc) encapsulated in microporous activated carbon as the anion-hosting anode and a Zn-insertion Prussian blue, Zn\(_3\)[Fe(CN)\(_6\)]\(_2\), as the cathode. The electrochemical processes at either electrode can be described by the half reactions below:

At anode: \(2\text{Fc} + [\text{ZnCl}_4]^{2-} \rightleftharpoons 2[\text{Fc}]^+ + [\text{ZnCl}_4]^{2-} + 2\text{e}^-\), \(\text{(16)}\)

At Cathode: \(\text{Zn}^{2+} + 2\text{e}^- + \text{Zn}_3[\text{Fe}^{III}(\text{CN})_6]_2 \rightleftharpoons \text{Zn}^{2+} \cdot \text{Zn}_3[\text{Fe}^{II}(\text{CN})_6]_2\) \(\text{(17)}\)

It is worth noting that when using 30 m ZnCl\(_2\) as the electrolyte, the ferrocene anode was able to deliver a high anion storage capacity of ~106 mAh·g\(^{-1}\), which corresponds to roughly 73% of the theoretical capacity (Figure 10A). In addition, the use of 30 m ZnCl\(_2\) WiSE was found to increase the cation-insertion potential at the cathode and also simultaneously lower the anion-insertion potential at the anode. The negative shift in anion-(de)insertion potential can be explained by the Nernst equation for the half reaction at the anode:

\[ E = E^0 - \frac{RT}{2F} \times \ln \left( \frac{a_{\text{anion}}}{c_{\text{anion}}} \right) \]

\[ E = E^0 - \frac{RT}{2F} \times \ln \left( \frac{q_{\text{anion}} \times \gamma_{\text{anion}}}{c_{\text{anion}}} \right) \] \(\text{(18)}\)

In 30 m ZnCl\(_2\), the anion activity, \(a_{\text{anion}}\), is dramatically higher than in more dilute electrolytes due to the much higher concentration \(c_{\text{anion}}\) and increased activity coefficient \(\gamma_{\text{anion}}\) of the anion. Although numerous studies have
shown increased cation-(de)insertion potential in WiSEs, to the best of our knowledge, this is the first report showing how a WiSE can cause a negative potential shift for anion (de)insertion.

Using Zn-based superhalides as charge carriers, Guo et al. reported another DIB using [ZnCl4]2− as the anionic intercalant. Therein, a nitrogen-doped microcrystalline graphene-like carbon was investigated as the anion-hosting cathode. When cycled in 30 m ZnCl2 electrolyte, this carbon cathode was found to reversibly store [ZnCl4]2− superhalides by both electrical double layer adsorption and ion insertion (Figure 10C). It should be noted that in the highly concentrated ZnCl2 WiSE, the water content is only a mere 19.7 wt%. This high concentration raises the onset potential of oxygen evolution reaction in the aqueous electrolyte and allows for the reversible (de)insertion of anions into the carbon cathode at a high-potential of 1.85/1.95 V versus Zn2+/Zn (Figure 10B). Tang’s group has also demonstrated that the use of a locally ordered graphitized carbon (LOGC) cathode can improve superhalide anion storage capacity as compared with traditional graphite cathodes. The LOGC cathode was found to reduce anion–anion repulsion and offer additional capacitive anion storage sites, thereby improving the anion diffusion kinetics and lowering the corresponding diffusion potential.

Hong et al. demonstrated another intriguing DIB system, operating with Zn–I superhalides as the anionic charge carriers. Using a WiSE of 15 m ZnCl2 plus 5 m KI, highly reversible plating of iodine was observed on a carbon fiber paper current collector, delivering a substantial capacity of 4 mA·h·cm−2. The speciation of the WiSE was probed using wavelength-tunable femtosecond stimulated Raman spectroscopy combined with first-principles calculations. Interestingly, the electrolyte was found to contain [Zn(OH)2]2+, [ZnCl4(OH)2]4−, and [ZnI4(OH)2]4− species. On the basis of DFT calculations, three primary species containing Zn2+ and I− ions were identified: [ZnI3(OH)2]2−, [ZnI5(OH)2]3−, and [ZnI4]2−. A very small quantity of free iodide ions (9.25 × 10−3 M) was also present in the electrolyte solution. This lack of free iodide is essential to the performance of the cathode, as it helps prevent the dissolution of the plated iodine as triiodides. Instead of free iodide ions, Zn–I superhalides (i.e., [ZnI4(OH)2]2−) serve as the charge carrier for plating iodine at the cathode. When pairing this I2 plating cathode with Zn metal as the anode, a new type of DIB mechanism was demonstrated. Dubbed as a “dual-plating battery” (DPB), this novel mechanism operates via the reversible plating/stripping of anions (I−) and cations (Zn2+) at the cathode and anode, respectively. Different from traditional DIBs, DPBs do not require a cathode framework to host anions and are thus not limited by the mass of the electrodes.

These reports demonstrate the immense utility of highly concentrated electrolytes. By using new formulations of WiSEs or DESs, it is expected that many more superhalide charge carriers can be identified for anion storage. In addition, the unique properties of high-concentration electrolytes, such as widening operation potentials and reducing active material dissolution, could be extremely beneficial to halide batteries. In a sense, this field has just emerged and is wide open with ample research opportunities. Moreover, the use of superhalides as charge carriers should not be limited only to applications in DIBs. Anion RCBs that employ superhalides as the charge carrier should be explored as well.

To help further contextualize the current research done on halide charge carriers for energy storage, Table 2 provides a summary of some of the key performance metrics reported for various anion rocking-chair and dual ion battery systems.

4 SUMMARY AND ROADMAP

The natural abundance of halide-containing materials, as well as improved safety characteristics, provides these batteries with distinct advantages over conventional, state-of-the-art LIBs. Of the battery operation mechanisms that employ halide ions as charge carriers, anion RCBs (i.e., XIBs) and DIBs show great potential. Nonetheless, these fields are only just starting to be explored, and many advances need to be made before these battery technologies can be successfully implemented. Below, we provide our perspective on each of these battery operation mechanisms and identify promising future research directions.

4.1 Anion RCBs with halide ion charge carriers

As far as XIBs are concerned, it is clear that a major issue lies within the volume changes and structural instability that occurs during halide ion conversion reactions at either electrode. This structural instability has seemingly caused researchers to move away from using transition metal halides as cathodes and instead look toward more stable/rigid F− and Cl− hosts. Indeed, using intercalation-type electrodes (e.g., layered oxides, LDHs, etc.) as halide ion hosts rather than conversion-type electrodes has seen considerable success in recent years. Nevertheless, a sacrifice is usually made in terms of theoretical energy density when these intercalation-type...
| Halide charge carrier | Electrode | Electrolyte | Average potential $^a$ | Specific capacity (mAh·g$^{-1}$)$^b$ | Energy density (Wh·kg$^{-1}$)$^c$ | Capacity retention, cycling life | References |
|-----------------------|-----------|-------------|------------------------|---------------------------------|---------------------------------|---------------------------------|------------|
| Anion rocking-chair batteries | | | | | | | |
| Fluoride (F$^-$) | BiF$_3$ | La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ | 2.15 | 190 | 107 | 26%, 38 | [8] |
| | BiF$_3$ | Ba$_{0.6}$La$_{0.4}$F$_{2.4}$ | 2.15 | 110 | 236 | N/A | [21] |
| | CuF$_2$ | La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ | 2.4 | 360 | 96 | 11, 23 | [24] |
| | BF$_3$ | BiSnF$_4$ | 0.3 | 56 | 17 | 100%, 20 | [25] |
| | La$_2$NiO$_{4.13}$ | La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ | 1 | 30 | 30 | 93%, 220 | [29] |
| | | TEMPO | NaF (aq) | 0.6 | 150 | 90 | 60%, 85 | [52] |
| Chloride (Cl$^-$) | BiCl$_3$ | [OMIM][Cl] | 2.34 | 179 | 418 | N/A | [9] |
| | FeOCl | PP–TBMACl–SN$_3$ SPE | 2.1 | 160 | 126 | 37%, 30 | [57] |
| | FeOCl/CMK-3 | PP$_{14}$Cl–PP$_{14}$TFSI | 2.1 | 200 | 336 | 80%, 30 | [60] |
| | VOCl | PP$_{14}$Cl–PC | 1.5 | 189 | 170 | 60, 200 | [63] |
| | VOCl | PP$_{14}$Cl–PP$_{14}$TFSI | 1.35 | 101 | 80 | 60%, 53 | [64] |
| | FeOCl/PANI | PP$_{14}$Cl–PP$_{14}$TFSI | 2.1 | 120 | 206 | 82%, 50 | [65] |
| | Sb$_2$O$_5$Cl$_2$ | PP$_{14}$Cl–PC | 1.45 | 100 | 94 | 65%, 100 | [66] |
| | CoFe–Cl LDH | BpyCl–PP$_{14}$TFSI–PC | 1.75 | 240 | 280 | 67%, 100 | [69] |
| | Ni$_2$V$_{0.9}$Al$_{0.1}$–Cl LDH | BpyCl–PP$_{14}$TFSI–PC | 1.75 | 312 | 197 | 36%, 1000 | [70] |
| | NiMn–Cl LDH | Bpy$_{14}$Cl–PC | 1.65 | 285 | 214 | 45%, 150 | [71] |
| | NiFe–Cl LDH | Bpy$_{14}$Cl–PC | 1.38 | 350 | 280 | 18%, 800 | [72] |
| | BiOCl (anode) | NaCl (aq) | 0.54 | 153 | 50 | 60%, 45 | [79] |
| Dual-ion batteries | | | | | | | |
| Chloride (Cl$^-$) | Zn$_{0.2}$Mn$_3$O$_4$ | ZnCl$_2$ (aq) | 1.6 | 210 | 300 | 90%, 50 | [88] |
| | LBC-G | WiBS gel | 4.2 | 127 | 385 | 74%, 150 | [94] |
| | | | | | | | |
| Chloride, bromide (Cl$^-$, Br$^-$) | | | | | | | |
| | | | | | | | |
| PF$_6^-$ | Graphite | LiPF$_6$-EC/EMC | 2.7 | 60 | 108 | 67, 50 | [99] |
| | Coronene | LiPF$_6$-EC/EMC | 3.9 | 40 | 156 | 100%, 4000 | [100] |
| | | NaPF$_6$-EC/DEC | 3.2 | 100 | 77 | 80%, 5000 | [101] |
| | Graphite | NaPF$_6$-EC/DEC | 4.5 | 55 | 247 | 100%, 100 | [105] |
| | | | | | | | |
| FSI$^-$ | Graphite | Py$_{14}$FSI/LiFSI | 4.2 | 40 | 150 | 91%, 1000 | [107] |
| | | | | | | | |
| TFSI$^-$/FSI$^-$ | Graphite | WiBSE | 2.25 | 110 | 200 | 80%, 200 | [108] |
| | | | | | | | |
| Mg–Cl superhalide | Graphite | MgCl$_2$–ChCl (aq) | 1.1 | 150 | 82 | 50, 280 | [117] |
| | | | | | | | |
| ZnCl$_2^{2-}$ | Carbon | ZnCl$_2$ (aq) | 1.85 | 130 | 151 | 63%, 800 | [121] |
| | Zn–I superhalide | Carbon paper current collector | | | | | |
| | | Carbon | ZnCl$_2$ + KI (aq) | 1.1 | 211 | 232 | ~100%, 500 | [122] |
| Reverse dual-ion batteries | | | | | | | |
| ZnCl$_2^{2-}$ | Ferrocene (anode) | ZnCl$_2$ (aq) | 0.9 | 30 | 27 | N/A | [13] |
| F$^-$ | BiF$_3$ (anode) | NaF (aq) | 0.8 | ~76 | 38 | 62%, 40 | [92] |
| | Bi@CNTs (anode) | NaF (aq) | 0.23 | ~150 | 25 | 73%, 80 | [93] |

Abbreviation: WiBSE, water-in-bisalt electrolyte.

$^a$Average potential is against the reference electrode included in the respective reference.

$^b$Specific capacity is that of the first reversible discharge capacity.

$^c$Energy density is calculated using the capacity of the electrode, the cell voltage versus the counter electrode, and the active mass of cathode only at the end of the reported cycle life.
electrodes are used. In addition, the cost associated with intercalation-type electrodes tends to be considerably higher than that of simple inorganic halide salts that can be used for conversion-type reactions. Therefore, we believe that significant efforts should be placed on engineering new electrode architectures, especially nanocomposites and novel 3D current collectors, that can improve the stability of these conversion-type electrodes. Much can be learned from the development of sulfur electrodes in Li–S batteries.42,43,45,46

In terms of the nanostructured electrodes, for FIBs, core–shell architectures have been demonstrated as one effective approach toward mitigating metal fluoride dissolution.53 For CIBs, besides Zhao et al.'s proof-of-principle report, almost all research works have moved away from the use of simple metal chlorides as cathode active materials. Although metal chlorides can easily react with chloride-containing Lewis bases to form highly soluble complex ions (e.g., [CoCl₄]²⁻, [FeCl₄]⁻), they are still highly attractive due to their low cost and large theoretical energy densities. Therefore, it is suggested that engineering these simple salts to be less soluble is extremely important to the field. The use of new solid-state electrolytes may also be helpful toward preventing dissolution; however, the loss of interparticle contacts due to volume change may present another challenge. Moreover, finding a solvent that can be used for washing electrodes for ex situ measurements without dissolving active material is critical to advancing CIB research and gaining a better understanding of the electrochemical processes occurring at each electrode.

For CIBs, the reactions occurring at metallic anodes should also be examined in more depth. When using metallic Li as an anode, the mechanism of LiCl formation should be studied thoroughly and the solubility of Li⁺ ions, that is, of LiCl, in the electrolyte should be addressed. Although some papers have considered the possibility of Li⁺ acting as a co-shuttle, the majority of research has focused primarily on reactions occurring at the cathode. Despite the fact that metallic Li is extremely attractive as an anode due to its high electropositivity, the continued exploration of other anode materials is crucial to helping avoid stagnation in this field. It should also be re-emphasized that a major appeal of XIBs is the lack of dendrite formation at metallic anodes, which provides these batteries with potentially improved safety over systems that involve metal ion plating.

Similar to the anodes, there is a relative lack of diversity in terms of electrolytes used for CIBs. Besides ionic liquids, the use of aqueous electrolytes and solid-state electrolytes is only just emerging. In particular, the aqueous CIBs that have been demonstrated have all employed 1 M NaCl as electrolyte. Therefore, there exist vast opportunities for aqueous Cl⁻-conducting electrolytes to be explored. It is suggested that highly concentrated WiSEs and DESs can be attractive candidates due to their potential of increasing the stability window of water and stopping the dissolution of active materials. Unfortunately, one downside to CIBs as compared with FIBs is the lower onset potential of chlorine gas evolution (1.36 V vs. standard hydrogen electrode [SHE]) as contrasted with the higher onset potential of fluorine gas evolution (2.87 V vs. SHE). This especially needs to be taken into consideration when higher concentrations of Cl⁻ ions are present in the electrolyte, thereby further lowering the onset potential of chlorine gas formation.

For FIBs, significant and impressive work has been done on solid-state F⁻-conducting electrolytes. Unfortunately, less progress has been made in terms of liquid electrolytes. To prevent the loss of electrode–electrolyte interparticle contacts, the use of liquid or gel electrolytes seems to be the most promising solution. However, finding solvents that can dissolve fluoride salts but that do not also simultaneously form fluorohydrogenate species represents a herculean task. That being said, the discovery of novel ionic liquids and solvents that do not generate bifluoride species will be monumental in advancing FIB research.

### 4.2 DIBs with halide charge carriers

The use of F⁻ and Cl⁻ ions as anionic charge carriers in DIBs has only very recently started to be explored. This can likely be ascribed to the fact that graphite has traditionally been used as the cathode for most DIB studies and has not been seen as amenable to the facile electrochemical hosting of single halide ions. Therefore, we suggest the exploration of more novel electrolyte materials for DIBs. In particular, we have recently demonstrated that metal oxides may act as amenable halide ion hosts.88 In addition, electrode materials used for halide ion RCBs (e.g., metal oxychlorides, LDHs, etc.) may also serve as good cathodes for DIBs. Simple organic compounds and polymer materials are another interesting and underexplored approach. The exploration of new electrolytes (e.g., ionic liquids, DESs, WiSEs, etc.) may also significantly impact this area.

As for the use of metal-based superhalides as charge carriers, there exists a plethora of new research opportunities. Besides the use of chloroaluminate species in DIBs, the exploration of other metal-based superhalides as charge carriers is a fairly untapped research direction. Transition metal-based superhalides, such as Fe and Mn, should be
explored. Many new electrolytes should also be examined beside conventional ionic liquids. Our recent reports on Mg–Cl and Zn–Cl superhalides demonstrate the utility of highly concentrated WiSEs and DESs for forming metal-based superhalides. It is expected that further exploration of these electrolyte systems will greatly enhance progress in this field. It is also expected that the use of unique ion insertion techniques such as CII and ionic drilling could help improve the reversibility of superhalide (de)insertion. In addition, computational studies may be extremely useful in screening electrode materials amenable to hosting metal-based superhalides.

In summary, it is clear that the use of halide ion species as charge carriers for electrochemical energy storage is an exciting and burgeoning field. The research on rechargeable systems that use halide ions as charge carriers is about four decades behind research on LIB systems. As such, it is expected that significant advances will occur in this field over the coming years. Although there are still some significant hurdles that must be overcome, we hope that this review provides researchers with a summary of the key advances and recent progress in these areas. We also hope that this review acts as a catalyst to incite more research along these directions.

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