Introduction to the Chemistry of Alternative Battery Technologies: Survey of Liquid Electrolytes in Next Generation, Fluoride-Ion Batteries

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Abstract: Lithium-ion batteries (LIBs) are central in modern life, where they are found in products from smartphones to laptops to electric vehicles. The demand for efficient and sustainable batteries is higher than ever, with the predicted depletion of lithium sources after 2050 [1-3]. As an alternative to LIBs, next-generation fluoride-ion batteries (FIBs) are now being studied since fluorine is more abundant than lithium. While the majority of FIBs reported use solid electrolytes, liquid electrolytes are of interest for room-temperature applications and they are the focus of this article. This article begins by providing a concise background on specific concepts of battery chemistry that can be used as a basis to expand micro/nanotechnology education curricula to include alternative battery technologies. Key points on defining battery components, battery capacity, and redox reactions at play (including differences between redox reactions in LIBs vs FIBs) are presented. A survey on recent developments of liquid electrolytes in FIBs is derived, where three chemical strategies for designing liquid electrolytes for FIB are determined. This analysis of FIB liquid electrolytes studied so far provides a perspective to holistically improve room-temperature FIBs by tailoring the anode, cathode, and electrolyte combination. Ultimately, the survey of literature developed in the article can have an exemplary role in bibliographic research on alternative battery technologies for students in secondary, two-year, or four-year higher education institutions.

Keywords: chemical education, lithium batteries, fluoride batteries, electrolytes

Introduction

In today's world, energy storage devices are everywhere, from smartphones, laptops, electric vehicles, and power tools. With the increase in technology, the demand for an efficient and sustainable battery is higher than ever. Following the 2019 Nobel Prize in Chemistry to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino, "for the development of lithium-ion batteries," the advancement of novel battery materials is still, more than ever, a hot topic. Lithium-ion batteries (LIBs) have become the top choice for portable electronics. This was preceded by decades of research, starting from their first academic pursuit in the 1970s by the 2019 Nobel Laureates, their first commercial use by Sony in 1991[4], and many years of optimization since then. This has allowed them to attain their current state-of-the-art high energy density, specific power, and cycling ability, making them the most common energy storage systems in the market and in our daily lives.

As a result, it is paramount to integrate the basics of battery chemistry and battery materials into the micro/nanotechnology education of two-year and four-year colleges, especially with the ease of accessibility of these consumer products and the developments in relevant environmental policies. As battery chemistry is an interdisciplinary field, the instruction of various chemistry and engineering subfields can incorporate fundamental battery chemistry topics to be included in course curriculums related to electrochemistry, crystal structure/crystallography, materials chemistry, organic chemistry, and chemical engineering technology [5-11].

While LIBs are the prevailing battery technology today, their high demand has resulted in a depletion of metal lithium resources, which are low in abundance [1]. This means that new generational batteries must be developed to replace LIBs and allow modern life to function with the continuously high technological demand. Other key metal elements used in LIBs are also low in abundance-availability and are highly expensive to mine, such as cobalt and nickel [12]. This issue has motivated research for next-generation battery technologies that are more sustainable and efficient than LIBs. Current research on secondary battery technologies includes sodium batteries [13], magnesium [14], calcium [15], aluminum [16], chloride [17], and fluoride [18]. Fluoride-ion batteries (FIBs) are a highly attractive class of alternative battery technology where monovalent F^- anions

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have a similar size/ionic radius to Li+ cations. FIBs are of particular importance because they pose sustainable alternatives to lithium, as F- anions are mined from the fluorspar mineral CaF2, a naturally occurring mineral that is abundant on Earth (**Figure 1**) [19, 20]. From **Figure 1**, the global production of fluorine is over 3.5 million tons per year, towering above the production (and consequently availability) of lithium by nearly two orders of magnitude [20]. The massive abundance of fluorine, along with this well-established supply chain are promising for the development of FIBs as a low-cost and sustainable alternative to LIBs. In addition, theoretically, FIBs can even outperform lithium batteries with energy density in the range of 550 Wh/kg for FIBs versus 300 Wh/kg for current LIBs [19]. The majority of battery research has been developed with cations serving as the working ions in batteries since scientists have established the fundamental principles for them and have a better understanding how to harness the electrochemical properties in the respective batteries. In contrast, much is unknown about harnessing anions as working ions in batteries. While LIBs operate with Li+ working cations, FIBs operate with alternative F- working ions inhering different (electro)chemistry from cationic working ions, that has yet to be elucidated and requires fundamental research.

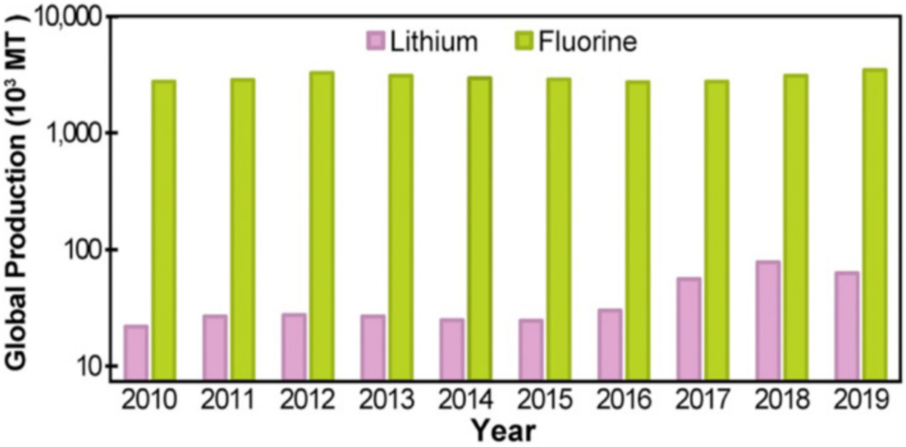


Figure 1. Global production of fluorine and lithium from 2010 to 2019, adapted from Reference [20].

Key Points of Battery Chemistry as Learning Objectives for Developing Lecture Lessons

A key for students' understanding of battery operation is based on understanding the redox processes at play. A battery produces electrical and chemical energy through electrochemical reactions that happen simultaneously at two electrodes, termed the anode and the cathode. An oxidation reaction releases electrons into the external circuit, while a reduction reaction consumes the electrons at the opposite electrode. The gain and loss of electrons is charge balanced by ions that conduct through the electrolyte, which is electronically insulating. The oxidation and reduction reactions that happen respectively at the electrodes are called half reactions. The sum of the two half-reactions together equals the full redox reaction of the battery. If the half-reactions are irreversible, the battery can only be discharged once. Otherwise, if the half-reactions are reversible, then the battery is rechargeable.

Rechargeable batteries are essential because they are vital components in modern-day technology, including electronic devices, electric vehicles, etc. With a rechargeable battery, the same battery can be reused without swapping it with a new one when it "dies," reducing the number of batteries needed. That way, less harm is done to the environment, and helps maintain resources. For any reversible battery, its performance and stability are what is essential. Rechargeable batteries can run into complications such as stability, cycling efficiency (conducting many discharge and charge cycles), high energy density, and manufacture compatibility.

In a rechargeable battery, the electrodes are separated with an electrolyte that transfers ions back and forth between the two electrodes through an external circuit, causing the battery to charge and discharge. The anode is the electrode where oxidation occurs during the discharge, and the cathode is the electrode where reduction occurs. The mnemonics "An Ox" and "Red Cat" can be used as a helpful way to remember this convention. **Figure 2** illustrates a LIB during discharge, where chemical energy is converted into electrical energy spontaneously, leading to the movement of electrons from the anode to the cathode. During charge, the electrical energy is converted into chemical energy upon applying a voltage to the battery. Now, the oxidation reaction occurs at the cathode and the reduction reaction at the anode (**Figure 2**). Although the opposite reaction occurs at each electrode, the scientific terminology keeps the designation of the electrodes (anode and cathode) as defined for the spontaneous discharge reaction.

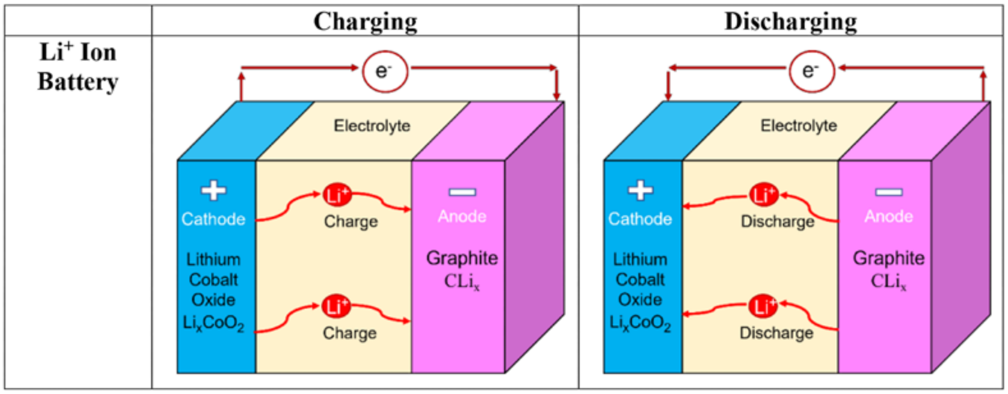


Figure 2. General electrochemical reactions scheme in Lithium-Ion Batteries (LIBs).

The most commercially successful rechargeable Li-ion batteries consist of two electrodes, usually a layered lithium transition metal oxide electrode (LiCoO2) as the cathode and a graphite electrode as the anode (**Figure 2**). Upon charging, the lithium cations travel via the electrolyte from the LiCoO2 cathode to the graphite anode with the simultaneous movement of electrons. The LiCoO2 cathode is oxidized during the charging process, while the graphite anode gets reduced. The oxidation of the cathode is accompanied by delithiation, while the reduction of the anode is accompanied by lithiation. The reverse process will occur upon discharging, and the (negative) graphite electrode will be oxidized, thus losing an electron. Delithiation of the anode occurs as lithium ions are removed and travel to the cathode. The (positive) LiCoO2 electrode will be reduced, thus gaining the electron, and it is lithiated. The redox reactions happening in a lithium-ion battery system upon discharge (**Equation 1**) are as followed:

$$\text{Anode: } CLi_x \rightarrow C + xLi^+ + xe^-$$

$$\text{Cathode: } xLi^+ + Li_{1-x}CoO_2 + xe^- \rightarrow Li_{1-x}CoO_2$$

$$\text{Cell: } CLi_x + Li_{1-x}CoO_2 \rightarrow C + Li_{1-x}CoO_2$$

The cell potential or voltage (E°cell) measures the potential difference between two half-reactions in a battery cell. As the value of E°cell of a redox reaction becomes greater, the driving force of electrons through the system also becomes greater, thus making it more likely that the reaction will proceed more spontaneously. E°cell is measured in volts (V). The overall voltage of the cell (E°cell) is equal to the half-cell potential of the reduction reaction (E°red) plus the half-cell potential of the oxidation reaction (E°ox): E°cell = E°red + E°ox. The standard reduction potentials of many half-reactions are tabulated in Table 1. When viewing a standard potential table, the higher the half-reaction is on the table, the higher its possibility as an oxidizing agent.

Table 1. Standard reduction potentials of selected half-reactions.

Reduction Half-Reaction	Standard Reduction Potential (V)
$F_2(g)+2e^- \rightarrow 2F^-(aq)$	+2.87
$Fe^{3+}(aq)+e^- \rightarrow Fe^{2+}(aq)$	+0.77
$2H^+(aq)+2e^- \rightarrow H_2(g)$	**0.00**
$Na^+(aq)+e^- \rightarrow Na(s)$	-2.71
$Li^+(aq)+e^- \rightarrow Li(s)$	-3.04

The battery capacity or energy density of a battery is a measure of the charge by the battery, and it represents the maximum amount of electrical energy that can be extracted from the battery under specific conditions. The theoretical capacity of a battery rarely matches the practical, actual battery capacity because multiple factors take place primarily (i) related to the internal battery characteristics: active material (that makes up the battery), practical function as an electrode, the age the battery, etc. and (ii) related to the external battery characteristics: the history of the battery functioning, the charging or discharging regimes of the battery and the temperature.

The battery capacity is determined by the mass of active material contained in the battery. In the case of **Equation 1**, the active material of the cathode is LiCoO2. The gravimetric specific capacity of a compound employed as an electrode is given by the following, **Equation 2**:

$$\textit{Specific Capacity} = \frac{F \times x \times n_e}{3.6 \times M}$$

F: Faraday constant, 96485 (Coulomb/mol)

x: number of working ions

ne: Number of electrons involved in each reaction

M: Molecular weight of compound

The theoretical specific capacity can be calculated based on **Equation 2** for the case of LiCoO2 in our discussion, assuming 1e− oxidation per formula unit, as follows:

$$\textit{Specific Capacity for LiCoO2} = \frac{96485\,(\frac{\mathrm{c}}{\mathrm{mol}}) \times 1 \times 1}{3.6\,(\frac{\mathrm{c}}{\mathrm{mol}}) \times 97.87} = 273.85\ \mathrm{mA\,.\,h/g}$$

The key terms of specific battery capacity and battery cell voltage (E°cell) are essential in identifying a material suitable to act as an electrode (anode or cathode). As mentioned, the battery cell voltage (E° cell) is determined by the potential difference between the cathode and the anode. The anodes in LIBs are made from materials such as graphite, silicon, and silicon oxides that can act as hosts for Li cations to be delivered by the cathode. Since only specific materials have been employed as anode in commercial LIBs, the anode materials have a more limited range of cell potentials. Hence, the cathode materials are the key electrode determining the battery's voltage and capacity. The cathode materials in LIBs contain varying amounts of Li in their compound's structure, as seen in **Equation 1**. The higher the Li content (x) in the cathode, the larger the battery capacity.

Finally, as preluded, the electrolyte is a fundamental component of a battery, and it is vital for the functioning of a battery. The electrolyte promotes the movement of ions from the cathode to the anode on charge and in reverse on discharge, enabling the battery to be conductive. Ions are electrically charged atoms that have lost or gained electrons. There are countless electrolytes that scientists have developed for LIBs in the last half-century. Usually, electrolytes of LIBs consist of soluble salts in liquid, polymers, solid ceramics, or molten salts [21]. A liquid electrolyte solution consists of the electrolyte solvent and supporting electrolyte salt. The electrolyte salt is responsible for the ionic conductivity of the overall electrolyte solution, and the electrolyte solvent is responsible for dissolving the electrolyte salt. The ionic conductivity (σ) of an electrolyte solution is a measure of its ability to conduct electricity, and its unit of measurement is Siemens per meter (S/m). The higher the ionic conductivity, the more ions can pass through at a given time, improving the battery capacity at higher discharge rates.

Fluoride Ion Batteries; An Alternative Battery Technology

Having provided a brief overview of the fundamental aspects of battery chemistry, employing the ubiquitous lithium-ion batteries as a reference, we will now expand upon the next generation, alternative battery technology of fluoride-ion batteries.

Both LIBs and FIBs consist of an anode, cathode, and electrolyte. However, how electrons and ions are transferred within a battery differs between the two technologies. Since Li+ ions are cations, they travel to the same electrode the electron travels to. On the other hand, FIBs have F- anions, and those anions travel to the opposite electrode that the electrons are traveling to. Hence, the working principles of the redox processes in FIB (Figure 3) are opposed to LIB since now the working ion is an anion.

During the discharge process of a FIB, electrons are generated at the anode, travel through an external circuit, and reach the cathode. This process causes oxidation of the anode and reduction of the cathode. It also leads to fluorination of the anode and defluorination of the cathode. Charge neutrality is assured by the transport of F- anions through the electrolyte. The opposite occurs for the charging process in a FIB, where electrons are generated at the cathode and reach the anode. This process causes oxidation of the cathode and reduction of the anode. It also leads to fluorination of the cathode and defluorination of the anode. Overall, the movement of electrons and anion charge carrier movements are opposite. The redox reactions happening in a fluoride-ion battery system upon discharge (Equation 3) are as followed:

$$\text{Anode: } xF^- + M' \rightarrow M'F_x + xe^-$$

$$\text{Cathode: } xe^- + MF_x \rightarrow M + xF^-$$

$$\text{Cell: } MF_x + M' \rightarrow M'F_x + M$$

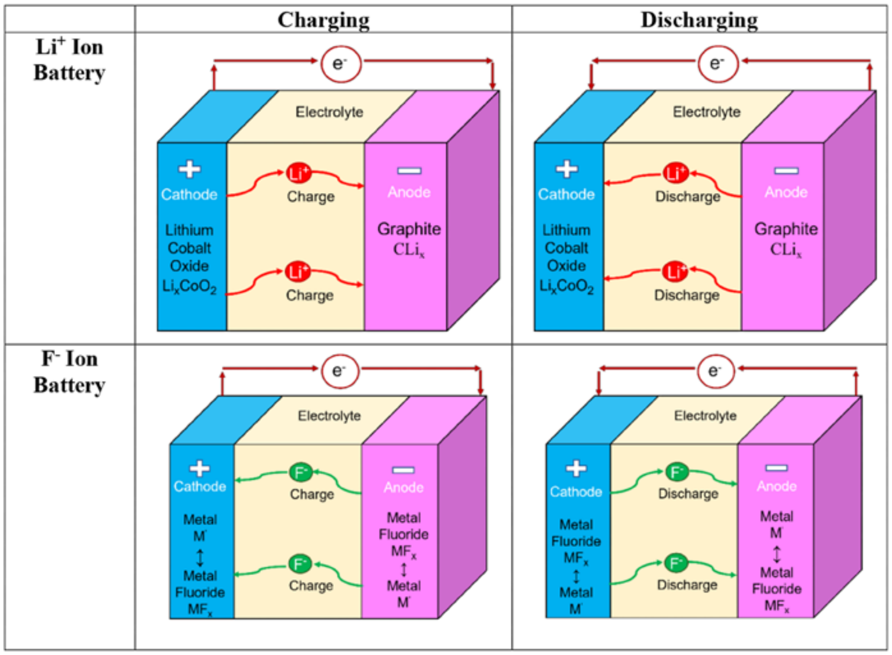


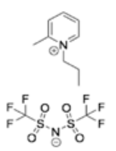
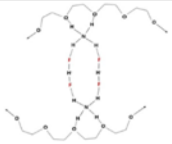
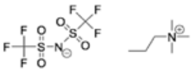
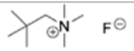
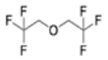
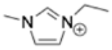
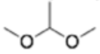
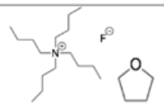
Figure 3. Comparative scheme of electrochemical reactions happening during charge and discharge in (i) Lithium-Ion Batteries (LIBs) and in (ii) Fluoride-Ion Batteries (FIBs), highlighting the movement of the electrons and the working ions during the electrochemical reactions.

Research on FIBs has accelerated since their inception in 2011 [18]. Since then, the majority of FIBs that have been studied employ solid-state electrolytes that require elevated temperatures to operate at around 150ºC [19, 20, 22-25] complicating their application in many daily devices. In addition, liquid electrolytes display higher ionic conductivity than solid electrolytes, thus enabling batteries that can perform more efficiently. Hence, it is of interest to use liquid electrolytes for room-temperature batteries. The following section will discuss current research progress on liquid electrolytes for FIBs, as there has not yet been an established liquid electrolyte for FIBs. At the same time, this survey of the current literature on liquid electrolytes in FIBs can serve as an example of research work that can be conducted by students interested in alternative battery technologies.

Discussion

A primary difference between LIBs and FIBs is the preparation of their liquid electrolytes. The liquid electrolytes for LIBs typically consist of lithium salts such as LiPF6 dissolved in organic solvents. However, in the case of FIBs, metal fluoride salts (e.g., KF, CsF) are not soluble in non-aqueous and organic aprotic solvents. Based on the literature, there are three general strategies for preparing fluoride-ion conducting liquid electrolytes: (i) mixing organic fluoride salts into ionic liquids, (ii) dissolving fluoride salts in organic or aqueous solvents, including the use of anion acceptors and (iii) employing electrolytes that can contain F- ions in true anhydrous form, without transformation of F- into HF2- upon dissolution in solvent. We provide an assessment of recent work on liquid electrolytes in FIBs, concisely summarized in Table 2 with an outline of the anode, cathode, and liquid electrolyte materials to analyze comparatively the developments and improvements of liquid electrolytes for next-generation FIBs.

Table 2. Survey of current liquid electrolytes in FIB with structural formula and electrochemical characteristics.

Electrolyte, Electrolyte Salt, Anion Acceptor (AA)	Structural formula of electrolyte solvent	Ionic conductivity σ (S/cm) at 25°C	Stability-window (V)	Anode/Cathode	Reference
0.1 M TMAF/MPPTFSI	$C_{11}H_{14}F_6N_2O_4S_2$ 	1×10^{-3}	–3.5 to 4.0 (vs. Ag/Ag^+)	PbF_2 /PANI	[26]
0.02 M NH_4F_2-doped PEG		2.1×10^{-3}	—	Mg/BiF_3	[27]
0.35 M MPPF/TMPA-TFSA	$C_8H_{16}F_6N_2O_4S_2$ 	2.5×10^{-3}	0 to 0.7 (vs. Pb/PbF_2)	PbF_2/Bi	[28]
CsF, FBTMPhB, G4	$C_{18}H_{22}BF$	—	–2.2 to –0.3 (vs. BiF_3/Bi)	Pt/BiF_3	[29]
0.75 M Np1F/BTFE	 $(CF_3CH_2)_2O$ 	7.9×10^{-3}	0.7 to 4.8 (vs. Li/Li^+)	Pt/Cu@LaF_3	[30]
$[C_2C_1im][(HF_2)_{2.3}]$	$C_6H_{11}N_2^+$ 	1×10^{-1}	–0.3 to 0.7 (vs. CuF_2/Cu)	CuF_2/Cu- CuF_2	[31]
1 M $LiPF_6$ in EC/DME	$C_3H_3O_4$  $CH_3CH(OCH_3)_2$ 	—	0 to 3.0 (vs. Mg/MgF_2)	Mg -MgF_2 /BiF_3 Mg - MgF_2 /SnF_2	[32]
0.8 M Aqueous NaF	$Na^+ F^-$	—	0 to 1.5 (Ag/AgCl)	NMO/BiF_3	[33]
Aqueous CsF	$Cs^+ F^-$	$15.2\ 10^{-3}$	1.9 to 5 (vs. Li/Li^+)	Pb -PbF_2/ Pb-PbF_2 symmetric cell	[34]
TBAF/THF		-	-	Bi -BiF_3/ $CsMnFeF_6$	[35]

The first category of liquid electrolytes for FIBs we will discuss is ionic liquids. An ionic liquid is salt in a liquid state with a melting point below 100ºC [36]. Ordinary liquids like water consist of electrically neutral molecules, while ionic liquids consist of charged ions. Ionic liquids have found wide application as electrolytes for LIB and other battery technologies as a result of their stability, less toxicity, low vapor pressure, and low viscosity that allows favorable ion mobility [36, 37]. As a salt, ionic liquids consist of cations and anions. One of the most common anions in ionic liquids is the bistriflimide group, (formally bis(trifluoromethanesulfonyl) amide or bis(trifluoromethane)sulfonimide) with the chemical formula [(CF3SO2)2N]- abbreviated as TFSI or TFSA [38]. This anion is significant for LIB where LiTFSI is a common electrolyte for lithium batteries and poses as a safer alternative to LiPF6 [39]. From the TFSI anion, ionic liquid electrolytes for FIB draw inspiration for research. An ionic liquid electrolyte for FIB composed of tetramethylammonium fluoride (TMAF) supporting electrolyte salt and 1-methyl-1-propylpiperidinium bis(tri-fluoromethanesulfonyl) imide (MPPTFSI) as the electrolyte solvent was reported with a conductivity of 1.0 mS/cm [26]. In the ionic liquid: 1-methyl-1-propylpiperidinium bis(tri-fluoromethanesulfonyl)imide (MPPTFSI) serving as the electrolyte, the MPP+ species are cationic, and the TFSI- species are anionic. The reported FIB cell with this electrolyte solution TMAF/MMPTFSI was able to perform only two cycles of charge/discharge (**Table 2**) [26]. Another related report studied the electrolyte solution consisting of the organic fluoride salt, 1-methyl-1-propylpiperidinium fluoride (MPPF), and the ionic liquid N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA/TFSA) as seen in **Table 2** [28]. This electrolyte solution MPPF in TMPA/TFSA with a concentration of 0.35 M was studied to demonstrate a conductivity of 2.5 mS/cm at room temperature. The full-cell assembly utilizing the electrolyte MPPF in TMPA/TFSA demonstrated a few cycles of charge/discharge [28]. Lastly, a fluorohydrogenate ionic liquid: [C2C1im][(HF2)2.3], composed of fluorohydrogenate [HF2]-n anions and 1-ethyl-3-methylimidazolium cations (C2C1im) was reported to exhibit a significantly high conductivity of 100 mS/cm at room temperature, much higher than the prior two electrolytes discussed in this paragraph [31]. In this case, the FIB cell was capable of performing ten reversible cycles of charge/discharge with the [C2C1im][(HF2)2.3] electrolyte (**Table 2**). However, there was gradual performance degradation of this FIB cell as the gravimetric specific capacity of the CuF2 cathode decreased significantly from 500 mA.h g-1 at the first cycle to 264 mA.h g-1 at the 10th cycle. This issue of fully utilizing the specific capacity of a cathode material with liquid electrolytes at room temperature is an existing challenge in developing liquid electrolytes for FIBs.

The second category of liquid electrolytes for FIBs is dissolving fluoride salts in organic solvents. This is the standard preparation method for most liquid electrolytes in FIBs thus far. Initial work on the synthesis of anhydrous, quaternary ammonium salts showed their solubility in tetrahydrofuran (THF) solvent [40, 41]. Quaternary ammonium salts have the structure [NR4]+, where R is an alkyl group or an aromatic group. They are ammonium derivatives where the N atom has a positive charge. Recently, a paper studied the inorganic crystalline compound CsMnFeF6 as a cathode material for FIBs using tetrabutylammonium fluoride (TBAF) in THF as a liquid electrolyte [35]. On the other hand, liquid polymer electrolytes have also been explored as electrolytes for FIB. One of the first reports of FIB utilizing polymer electrolytes was the optimized polymer-based electrolyte: polyethylene glycol (PEG) doped with ammonium bifluoride (NH4F2), with its structural formula depicted in **Table 2** [42]. The chemical rationale for preparing the electrolyte solution of NH4F2 in PEG was to trap NH4+ cations within the extended network of hydrogen bonding in PEG, allowing F- anions into a solution for fluoride conduction [42]. This electrolyte solution of 0.02 M concentration was employed in a cell demonstrating ionic conductivity of 2.1 mS/cm at room temperature. This cell exhibited a good first discharge capacity but could not cycle reversibly. Regarding polymer systems as fluoride ion electrolytes, poly(ethylene)oxide system was studied as a solid polymer electrolyte for FIBs, composed of poly(ethylene) oxide polymer, LiF salt, and trimethoxyboroxine [43].

Furthermore, within the scope of dissolving fluoride salts in organic solvents, there has been a large amount of work from the research groups of Takeshi Abe and Zempachi Ogumi that utilize organic compounds termed “anion acceptors” [29, 44-50]. An anion acceptor is a compound with a positive charge (cation) that can easily bond with anions-compounds with a negative charge. As mentioned, due to the limited solubility of metal fluoride salts in organic aprotic solvents, Abe and Ogumi proposed the addition of the organic compounds named anion acceptors that contain electropositive elements (e.g., B, P, Si). These anion acceptors act as solvating additives to help dissolve the fluoride salt in an organic solvent. The main anion acceptors that have been investigated are phenylboranes [29, 44-50]. A representative example of an electrolyte solution with anion acceptors is bis[2-(2-methoxy ethoxy)ethyl] ether (otherwise known as tetraglyme, abbreviated as G4) as the electrolyte solvent with the addition of CsF and a boron-based anion acceptor: fluorobis (2,4,6-trimethylphenyl) borane (FBTMPhB) (Table 2) [29]. The anion acceptor FBTMPhB enhanced the solubility of CsF in the tetraglyme solution by reducing the cation–anion interaction between Cs+ and F-. An important observation is that these studied phenylborane anion acceptors were shown to dissolve F- anions from the active cathode material. The dissolution of the cathode material deteriorates the integrity of the electrodes and, thus, the stability of the electrode to last a long time.

Lastly, within this second category of FIB liquid electrolytes, fluoride salts in aqueous solutions can consist as a subcategory of dissolving metal fluoride salts in solvents [33, 51]. A study employing a NaF salt solution as a liquid electrolyte to assemble a FIB cell was studied [51]. The electrochemical data demonstrated stable battery cycling performance, where the authors claim at least 85 cycles of charge/discharge [51]. This year, it was reported that an aqueous CsF electrolyte solution exhibited high solubility, an incredibly high room-temperature conductivity of 152 mS/cm, and (electro)chemical stability, which has been absent in most FIB liquid electrolytes [34]. **Figure 4** depicts comparatively the ionic conductivity and electrochemical stability window of select FIB liquid electrolytes [34]. The electrochemical stability window is the voltage cell potential window in which the electrolyte is stable electrochemically and does degrade to produce byproducts. The high (electro)chemical stability window of 3.1 V of this aqueous CsF electrolyte solution is promising in enabling high operating voltage electrodes that can be maintained stable [34]. Moreover, it is encouraging that the initial cycling performance of FIB cell in a concentrated solution of the aqueous CsF electrolyte demonstrated high retention of its capacity, permitting a more stable cycling performance of FIB at room temperature [34]. Also, it showed suppression of the dissolution of the electrode materials, providing a positive trajectory for the reversible cycling of FIB in liquid electrolytes.

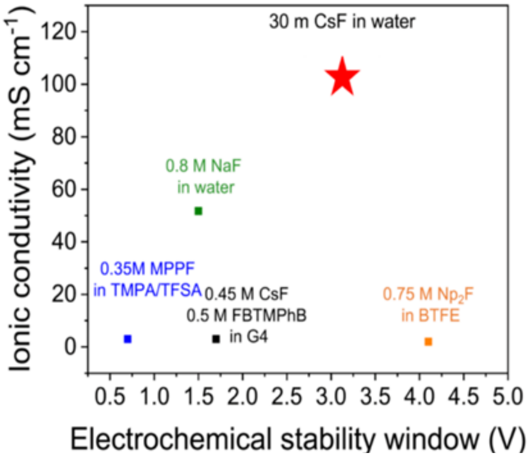


Figure 4. Performance comparison of ionic conductivity and electrochemical stability of selected liquid electrolytes in FIB, adapted from Reference [34].

Finally, our discussion of the literature on liquid electrolytes in FIB culminates with the third category of developing liquid electrolytes, focused on liquid electrolytes that are impervious to protonation of F- ions. The design of liquid electrolytes containing a high concentration of chemically stable F- ions is a challenge in chemical synthesis and electrochemistry, as F- ions are extremely reactive with solvent protons resulting in the formation of bifluoride ions (HF2–) [52]. HF2– lead to electrochemical side-reactions happening upon battery charge/discharge that give electrochemical responses that can be confused to be from the active electrode materials. These electrochemical side reactions deteriorate the battery's performance. One of the few liquid electrolytes to function at room temperature without HF2– formation upon proper handling is the electrolyte solution: Np1F/BTFE where Np1F is N,N,N-trimethyl-N-neopentylammonium fluoride and BTFE is bis(2,2,2-trifluoroethyl) ether [30]. The lack of β-hydrogens is primarily important for preventing decomposition towards the formation of HF2–. The 0.75 M Np1F/BTFE electrolyte solution displayed high ionic conductivity of 7.95 mS/cm (**Table 2**) and a wide electrochemical stability window around 4 V at room temperature. Nevertheless, when subjected to electrochemical cycling using different metallic electrodes (Cu, Pb, Bi, Ce, and Ca), significant dissolution of the electrodes into the electrolyte was observed, resulting in poor performance [30]. Through the engineering of the electrode, a CuF2@LaF3 core−shell nanoparticle was fabricated, encapsulating the electrodes within the thin layer of LaF3 [30]. This fabricated battery cell made up of the modified electrodes and the Np1F/BTFE liquid electrolyte was able to cycle reversibly at room temperature, although with a gravimetric capacity of around 60 mA h g-1, which is eight times less than the theoretical capacity of CuF2 (528 mA h g-1), indicating an incomplete reaction occurred at the electrodes.

In summary, FIBs are an emerging, sustainable technology that employs highly abundant fluorine instead of lithium, eliminating the dependence on strained metal sources and drastically reducing the cost of energy storage devices. Liquid electrolytes display higher ionic conductivity than solid electrolytes, thus enabling efficient batteries with high energy density. The ability to have FIBs operating at room temperature is highly appealing for commercial applications. Yet, much fundamental research still needs to be pursued to have identifiable principles of efficient and stable liquid electrolytes for FIBs. In this discussion, we have analyzed and developed the ongoing research progress of liquid electrolytes for FIBs. We distinguish three general chemical strategies for designing liquid electrolytes for FIBs. While FIBs have been at an infant stage since their inception almost a decade ago, they are a compelling next-generation battery technology that offers much promise for sustainable batteries. Future research for tailoring the electrolyte chemistry of FIB should also focus on battery safety and manufacturing compatibility that merge the interdisciplinary collaboration of chemists, material scientists, and engineers.

Perspective of a Student from a Community College

The survey of literature developed in the article can have an exemplary role in bibliographic research work on alternative battery technologies for students in secondary, two-year, or four-year higher education institutions. First, one can identify which alternative battery technology to focus on learning (e.g., sodium batteries, magnesium batteries). Within the broader field of alternative battery technology, there is a significant amount of research conducted by scientists on each component of the alternative battery technology (anode, cathode, and electrolyte) component. Instructors and students can work together to determine which component or concept of that battery technology they would like to dive into deeper, as a result expanding dynamic micro/nanotechnology education curricula.

The current research was conducted within the Caltech Connections program, an outreach program that pairs graduate students and postdoctoral scholars from Caltech as mentors with undergraduates from local community colleges. The following paragraph from co-author Pablo A. Romero reflects on his research experience in this outreach program:

> *Besides seeing all the state-of-the-art lab equipment throughout my time at Caltech Connections, I was profoundly impressed by the dedication and time my mentor Dr. Vasileiadou, put into her research and mentorship. Some aspects of battery research I enjoyed were electrode fabrication and battery assembly. It was also the first time I had ever used a glove box, which was pretty remarkable. There was also a great amount of time spent reading the scientific literature on battery chemistry. This included starting off with old and progressing to current literature on Lithium-Ion Batteries, along with Fluoride-Ion Batteries. Throughout the 6-month program, much of the literature read was analyzed and reproduced in the lab. Ipso facto, I feel more confident in my abilities to analyze and interpret scientific literature and, of course, being inside a lab.*
>
> *Additionally, reading papers on battery electrolytes is very dense, but focusing on the chemical molecules (highlighted in the papers' figures) helped connect the compounds to knowledge from my previous chemistry courses. Even though it was my first time in a research lab, I felt comfortable asking Dr. Vasileiadou any questions that came to mind. My questions were always greeted with a detailed answer that made sense to me, and I will always appreciate Dr. Vasileiadou for that.*

Conclusion

In this article, an introduction to battery chemistry is briefly developed to provide background on expanding curriculums toward including alternative battery technologies. The principal topics of battery chemistry are outlined that can be used as learning objectives to develop lecture lessons or research projects for students in secondary, two-year, or four-year higher education institutions. Following the foundation of principal topics in battery chemistry, a concise and comprehensive survey is presented of current literature of liquid electrolytes in FIBs. Our survey here on the literature of liquid electrolytes in FIBs is an example of bibliographic research work in alternative battery technologies, which targeted student groups can undertake. We identify three chemical strategies for designing liquid electrolytes for FIB: (i) mixing organic fluoride salts into ionic liquids, (ii) dissolving fluoride salts in organic or aqueous solvents, (iii) employing electrolytes that can contain "naked" F- ions in true anhydrous form. A comparative table is generated, including the anode, cathode, and liquid electrolyte materials from our discussion, providing a compass for the future pursuit and design of suitable liquid electrolytes for FIB. This discussion and analysis of liquid electrolytes studied so far in FIBs extends perspective on how to improve room-temperature FIBs holistically by tailoring the anode, cathode, and electrolyte combination.

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