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COMPARISON OF RECHARGEABLE BATTERY TECHNOLOGIES

Melissa Morris and Sabri Tosunoglu

Florida International University
Department of Mechanical and Materials Engineering
Miami, FL USA

ABSTRACT

As processing power and sensors improve, electronic devices require increasing amounts of power. Unfortunately, battery capacities are increasing at a much slower rate. This creates a bottleneck for miniaturization and operational time of portable devices. This is especially an issue in products such as smart phones that are in almost constant use as well as mobile robotics where high-current actuators demand a significant amount of power. Traditional commercial batteries can quickly become depleted or are too slow to charge; thus, severely limiting their functionality. This paper explores all common commercial as well as many investigational rechargeable battery types. After exploring these options, various battery technologies are evaluated in order to provide insight into current and emerging choices for a wide variety of applications.

INTRODUCTION

Batteries are devices that convert chemical energy to electrical energy. This allows for both energy storage as well as a direct method of producing of direct current (DC) electricity. The electrical energy is created through an electrochemical oxidation reduction (redox) reaction within the battery [1]. When connected to a load, batteries will produce electrical energy until the reactants are depleted. Batteries can be classified into four groups:

1. *Primary Cells:* These can be discharged only once and are then discarded or recycled after this single use. Primary batteries are commonly used in consumer electronics such as cameras and toys.
2. *Secondary Cells:* These can be easily recharged. Secondary batteries be used as back-up or temporary augmentation for another power source, such as in vehicles or laptop computers. They can also be used as the sole energy source instead of primary cells in order to reduce waste or to avoid physically changing the battery when depleted. In addition to replacement of primary cells in many applications, these batteries are commonly the primary energy source for cell phones and tablet computers.

3. *Reserve Batteries:* Unlike the “active” batteries above, these have one component, such as the electrolyte, separated to avoid chemical deterioration. These batteries can be stored for long periods and then activated as needed. These are typically seen in weapon systems.
4. *Fuel Cells:* These are considered a battery by some sources (such as [1]) but not by others (such as [2]). Either way, they differ in that a fuel cell is supplied fuel from outside of the reaction chamber and will continue to function as long as fuel is supplied. They do however function through a redox reaction like batteries and unlike most capacitors [3].

This survey will focus primarily on secondary cells (also referred to as rechargeable batteries). These are of primary interest in most current device designs in order to minimize the need for physical interchange and also to reduce waste. Fuel cells, while similar, have not matured to a point for use in mobile electronics and mechatronic devices and so are only briefly noted. Rechargeable batteries can be used both for augmentation or emergency loads and as the main source of power.

All batteries consist of a positive electrode (cathode), a negative electrode (anode) and an ionic conductor (electrolyte). Many cells also have a separator that physically keeps the electrodes from shorting, but allows ions to flow [3]. These components together form a cell. Most batteries can be classified either as a wet cell if the electrolyte is liquid, or a dry cell if the electrolyte is a gel or solid. Multiple cells may be stacked together and packaged to form a battery [4], though this term is also commonly used when referring to a single cell, especially when packaged for consumer use [1]. To follow common convention, the terms are also used interchangeably in this paper when the differentiation is not critical.

Batteries function by converting ion transfer into electron transfer. When a battery is discharged through a load, negative ions (anions) flow through the electrolyte to the anode. Here, electrons become loose due to the oxidation of the anode. The electrons then flow through the load and back to the battery at the cathode. The

cathode experiences a reduction reaction as the electrons are gained and positive ions (cations) flow to the cathode through the electrolyte [1]. Charging of the cell involves simply reversing this process by connecting a power source instead of the load. This power source must be DC in order to be compatible and leave a net charge within the cell. These processes are depicted in Figure 1.

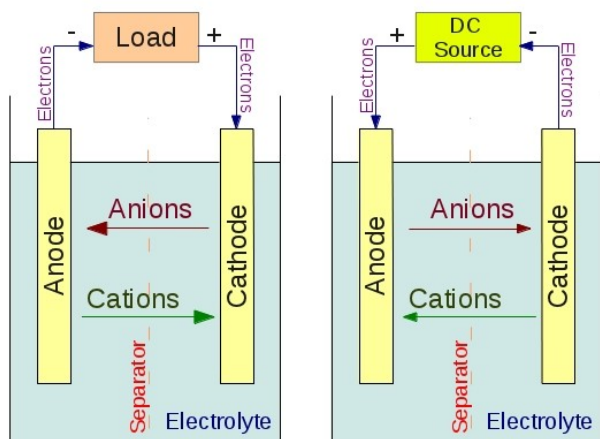


Figure 1. Basic Battery Operation

Over the next several sections, various rechargeable battery technologies are explored. There are hundreds of types of rechargeable batteries. To restrict the scope, this survey concentrates only on the most notable types commonly used or currently showing the most promise in future usage. These are explored by categorizing them by their base electrolyte material. Afterwards, some general observations are noted.

LEAD-ACID BATTERIES

The lead-acid battery was developed by Raymond Louis Gaston Planté in 1860 [5]. This became the basis for the first usable rechargeable battery. Despite other forms of rechargeable batteries, the lead-acid battery is still very common in a wide range of applications [6].

Lead-acid batteries are either flooded or valve-regulated [7]. Flooded lead-acid batteries are composed of lead plates serving as electrodes that are immersed in water and sulphuric acid. These batteries require some maintenance due to the loss of hydrogen over time. Valve-regulated lead-acid batteries, on the other hand, are sealed and have a pressure-regulating valve to keep air from getting into the cells. However, sealed lead-acid batteries are more expensive and have a shorter life than flooded batteries [7]. These batteries can have a liquid or gel electrolyte.

Full power can be delivered by this type of battery extremely quickly. This makes them ideal for uses where a large amount of power may suddenly be needed – which is why they are used for electrically starting internal combustion engines in most vehicles. Lead-acid batteries should be charged slowly, however.

The cost of lead-acid batteries is the lowest of all rechargeable battery types for the amount of power

delivered. This is yet another reason why lead-acid batteries remain so common and also why they are preferred in many common large-capacity applications.

The depth of discharge of lead acid batteries can vary from around 20% for 'starting' batteries to 80% for 'deep cycle' batteries. They have an open circuit voltage of up to 2.1 V [8], but battery voltage decreases with discharge. Both power and energy of a lead-acid battery is increased by increasing the surface area of the electrode. These batteries are candidates for large and medium-scale robots, but their short cycle life may outweigh their low cost when used constantly [4]. Because of these issues, the battery shape and size is usually dictated and cubic. However, some types of sealed lead acid batteries can have more customized shapes.

Problems with these batteries include sensitivities to temperature that affect both the life of the battery and cycle life [7]. The batteries are wet cells and should never be frozen. In addition, it is best for them to be charged slower when used in warmer climates. They also have to be stored charged to ensure best performance when they are again needed. Since they have a rapid self-discharge rate of 3-20% per month, these batteries should not be stored unmaintained for long periods of time. Protective measures for acid are needed when handling these batteries, particularly those that are not sealed. The acid levels must be maintained and they need to be charged in ventilated areas. Next, these batteries can be very heavy due to lead and other components. They add weight to any application and also must be disposed of in an environmentally-conscious way. Finally, these batteries have a relatively short cycle-life. They require replacement after only a couple of hundred charge-discharge cycles.

ALKALINE BATTERIES

Rechargeable alkaline batteries can be classified into four principle types. The first type has a nickel oxide cation electrode and an iron anode and are commonly referred to as nickel-iron batteries. The second type also have a nickel oxide cation electrode, but the anode is composed of cadmium so that these batteries are commonly called nickel-cadmium (NiCd or NiCad) batteries [9]. More recently, nickel-hydrogen and the commercially successful nickel-metal-hydride (NiMH) batteries have found favor for many applications.

Thomas Edison developed a useful version of a nickel-iron battery in 1901 [10]. Nickel-iron batteries have double the specific energy of lead-acid cells, are rugged, have a long life cycle at deep discharges (80% depth of discharge) and can handle fairly high discharge rates [9], [11]. However, they do not perform as well as lead-acid batteries at low temperatures and they can be damaged by high temperatures [4]. In fact, they can be charged very quickly, but only if they do not get heated in the process. In addition, nickel-iron cells have a relatively high self-discharge rate due to high corrosion and gassing on the leads causing poor efficiency [9]. These batteries are therefore not widely used anymore, though they used to be preferred for large vehicles due to their robustness [10]. Some research is being done on

this type of battery to make them maintenance-free, provide better performance, and be more attractive through the use of a starved-electrolyte and sealed package [11].

Unlike nickel-iron batteries, nickel-cadmium batteries are widely used and still widely researched. They were invented by Waldemar Jungner in 1899 [10]. NiCd batteries have a lower specific energy than nickel-iron, but otherwise perform better and do not suffer from the other problems of nickel-iron cells. In addition, they have a constant discharge voltage, can be continuously overcharged (especially if vented) – though this is not recommended, and are very reliable [9]. They can also be made into many shapes and sizes through different manufacturing techniques [9]. They are acceptable for use in high-temperature applications [7]. These are not used more often because they cost ten times as a lead-acid battery and because of environmental concerns when disposing of cadmium [9]. They also have memory effects which cause gradual reduction in capacity if they are not fully discharged and charged during every cycle [7]. Like lead-acid batteries, NiCd batteries are available vented or sealed [7]. Vented batteries allow oxygen and hydrogen gases to be released in the case of overcharging or rapid discharging in order to make the battery safer and less expensive [7]. However, sealed batteries can be used in any orientation for prolonged periods without any leakage or drying [9].

Nickel-hydrogen batteries were designed as a replacement for nickel-cadmium batteries. However, due to the high cost of obtaining and storing the hydrogen, these batteries are only used in space applications. They are of interest because they have a very high specific energy (50 Wh/kg) and very long life cycle even under deep discharging [9]. They are also not susceptible to cadmium whisker development as with NiCd batteries, which has caused numerous system failures in government systems including ones in space [12]. They are also tolerant to overcharging and voltage reversal [1].

To overcome the cost and storage problems with hydrogen, nickel-metal-hydride cells were developed. They are in some ways similar to nickel-cadmium batteries, but they have some advantages including more power. In addition, memory effects can be reduced when quick charging is used. However, the batteries also must be frequently discharged or the memory effect may appear. Hydrides store hydrogen within their physical structure. The hydrogen can later be extracted for use in the battery. A common hydride is an alloy based on nickel, aluminum, and rare earth metals though there is another based on titanium and zirconium [10]. Other hydrides exist, but are not explored here. NiMH cells show the most promise for an aqueous electrolyte cell [13] [14].

Nickel-zinc is another type of alkaline-based battery under investigation. It is briefly mentioned here because it shows promise and outperforms lead-acid as well as other alkaline-based batteries in many ways. However, it is not in production due to the solubility of zinc in potassium hydroxide [10]. It simply can not sustain enough cycles for commercial success. There are

other alkaline-electrolyte batteries, such as silver oxides. These include silver-zinc batteries and silver-cadmium batteries [1]. Though their high energy density is attractive, they are very expensive and have short life cycles so that they are not currently of interest for most applications. There is also the zinc-alkaline-manganese dioxide battery. This battery proved to have a short cycle life and be difficult to recharge, so these are also not of current interest [1].

Alkaline-based batteries have a more stable voltage over their discharge range than lead-acid batteries. Nickel-iron and nickel-hydrogen cells have an open circuit voltage of about 1.5 V when fully charged [9]. NiCd and NiMH on the other hand have an open circuit voltage of about 1.2 to 1.3 V, though this stays nearly constant through most of the discharge [9]. This means that most commercially used alkaline rechargeable batteries have voltages less than the primary alkaline counterparts. For this reason, more batteries may be needed in series if a rechargeable alkaline replaces a primary alkaline in any application. Nickel-zinc, should it prove commercially feasible, is an excellent substitute with an open circuit voltage of 1.6 V [10].

All alkaline-based batteries are sensitive to temperature. They typically perform best in the range of -20 to 40 °C.

LITHIUM BATTERIES

Lithium is attractive because it is the lightest metal, and thus produces lighter batteries. It also has a high specific capacity and specific energy [9]. Lithium is not used with an aqueous electrolyte to avoid undesired chemical reactions [9]. Lithium in metal form is not used in rechargeable batteries because it forms dendrites that tear through the separator and cause the electrodes to short [9]. Instead, rechargeable lithium batteries use lithium ions spread within a carbon anode (when charged) or oxide cathode (when discharged) [9].

This technology holds a lot of promise, but does not yet completely replace alkaline batteries. This is due to several reasons. The first is a higher cost. Other issues are in charging characteristics discussed later.. However lithium-ion batteries do not depend as much on the charge current and so can tolerate more simplistic chargers and a wider range of charge sources.

The lithium-ion cell was invented in 1979 and provides an open circuit voltage of up to 4 V [15]. Using lithium as an ion rather than a metal solved the recharging problems of dendrite growth. Still, the battery does not do well if overcharged or heated and can lose capacity if either of these events occur [9]. Advantages include a relatively low self-discharge rate, no memory effect, and high energy [4]. Reducing the depth of discharge increases the cycle life of the battery, as does not fulling charging the battery. For example, at 100% depth of discharge (DOD), 3,000 cycles are expected while at 40% DOD over 20,000 cycles are possible [1]. Due to cost and safety considerations, lithium-ion technology is used primarily for small consumer electronics [16] and has only slowly and recently been debuting in vehicles and other high-power applications

[17]. Even in consumer electronics, the use of this battery technology is sometimes limited by the high cell voltage, which is more than double the typical alkaline primary cell voltage [18].

Since lithium-ion batteries are expensive mostly due to the use of cobalt and nickel, substitutions for these two metals are being considered. The use of manganese is being investigated, but so far it is not proving to be extremely stable [9]. Loss of charge capacity and chemical issues were reported in early work [19]. More recent work is showing improvements, but mostly at room temperature since performance quickly decreases as the temperature increases [17]. In addition, research is being done on other altered chemistries such as using aluminum-silicon-graphite anodes in place of carbon for increased safety and energy density [20]. This study showed that silicon was useful in improving the energy capacity with some reduction in cell degradation caused by internal reactions.

Lithium-sulfur was heralded as the next trend in batteries both for energy density and safety [19]. However, it did require a control circuit and does not seem to have advanced as quickly as hoped. Recently there were still reports of trouble in achieving the expected power, maintaining the charge, and maintaining chemical stability [21]. Work was done on the electrolyte [22] as well as adding a coating to the electrodes [23], but the capacity decreased with time. The later paper did show that carbon was helpful in slowing the reaction, however. More recent work suggests that wrapping the cathodes in graphene has proven effective in slowing or even stopping the loss of capacity [24].

The use of nanostructures is also a trend in the research of lithium-ion technology. One paper describes work using nanospheres of titanium-dioxide-carbon to produce a lithium-ion cell of only 1.5 V [18]. This would allow lithium-ion rechargeable batteries to be used in nearly all consumer electronics. Nanocomposite spheres of sulfur-carbon are being investigated to improve lithium-sulfur technology mentioned above in an by optimizing surface area contact [25]. These spheres could also be used to buffer internal mechanical strains and improve cycle life against this type of failure [26]. Silicon nanowires, not spheres, are suggested as the best way to incorporate silicon in a lithium-sulfur cell by another group of researchers [27].

Other lithium-ion technology utilizes iron-phosphate. Early work didn't report much success; in fact, the carbon seemed to have a negative effect [28]. However, a more recent paper describes the manufacture of a foam that becomes a three-dimensional substrate for this battery technology [29]. The use of this foam and a copper-tin anode showed significant stabilization of the lithium-sulfur cell.

Lithium polymer batteries hold some promise as well. These work acceptably if the polymer is thin enough and the cell is made large enough to account for the limited current density [9]. The polymer acts as a solid electrolyte when it is embedded with liquid electrolyte [8]. It allows for almost solid-electrolyte

performance while maintaining the cell at room temperature [30]. Electroactive polymers such as Nafion can be used with a lithium compound to create a rechargeable battery. An early one was reported in literature, but it suffered severely from self-discharge as does other similar technology [31]. Metals other than lithium can be used as well, but even after investigating numerous substances, lithium is still favored for investigation despite the self-discharge and cell degradation drawbacks [32].

SODIUM BATTERIES

Sodium batteries are of interest because of their low mass, non-toxicity, and low-cost due to the abundance of sodium [9]. These batteries have a potential for high specific energy and are mostly being considered for grid-storage applications. They are, however, also capable of explosion, so care in their use must be taken such as not using an aqueous electrolyte [9]. They have a high operating temperature, so use outside of large stationary applications will be limited.

One of the most promising sodium batteries is the sodium-sulfur (NaS) battery. It has a very high energy density, a long life, low maintenance, and high efficiency [33] [34]. The electrolyte must be kept above 270°C, however, which can take energy and create thermal management issues [33].

Another type is a sodium-nickel-chloride battery. It was developed in Africa and was dubbed the ZEBRA battery [9]. It is able to operate at slightly lower temperatures than the NaS battery, but still quite high at 175 to 400 °C. The battery is cell-failure tolerant, which makes it more robust. This is a beneficial feature to make this battery feasible since the electrolyte is ceramic and may be prone to cracking [35]. This battery type is being proposed for electric vehicle use, but no actual tests have been performed to date.

FLOW BATTERIES

Flow batteries can also be considered as a type of fuel cell or a battery - fuel cell hybrid [9]. Though they run on an external fuel source, they are charged and discharged like a battery.

Vanadium Redox flow batteries are the most common flow batteries found in literature. These are composed of vanadium ions in sulphuric acid. A pump controls the flow from each of two tanks – one with the positive vanadium ion electrolyte and another from the negative vanadium ion electrolyte. Vanadium redox flow batteries offer a fast response and high overload capacity. They can also be fully discharged without decreasing the life of the battery. These batteries have low power densities, but are not suited for small-scale energy [7]. As with sodium batteries, stationary grid-storage applications are their current target application. There are working batteries of this type in use for grid storage. As with other battery technologies, some improvement is achievable with respect to capacity losses, though the battery does well at producing electrical energy [36].

Another popular flow battery in literature is the zinc-bromine (ZnBr) flow battery. This battery is

basically a fuel cell with bromine stored in an external tank within the battery [9]. It works much like the flow battery above. Like the vanadium battery, the ZnBr battery can be fully discharged without a reduction to the life of the battery. It also does not have any memory effect and has a large energy density [7]. This battery can be made smaller than a vanadium battery, but it is still only suitable for larger-scale mobile robotics. It was successfully tested in a Chrysler vehicle, but there were concerns about safety and system complexity [37].

A third type of flow battery is the polysulphide-bromide (PSB) flow battery. This battery has an open circuit voltage of 1.5 V. It has a wider range of operating temperatures as well [7].

There are some other flow batteries under investigation, but their future is currently uncertain. One is an alkaline single flow zinc-oxide battery. This battery depends upon composite electrodes with nanostructures. However, it is not fully functional as of the last reported research [39]. Another battery mentioned here briefly is the single zinc-nickel battery [40]. This particular configuration shows a lot of chemical instability and so isn't at all promising in its current state. However, future advancements could hold more promise.

OTHER BATTERIES

Some batteries do not fit into any of the categories above. One class of batteries is metal-air batteries. These are of interest because they are not expensive and are environmentally friendly. However, recharging is difficult [38]. A specific example is the zinc-air battery. A rechargeable version was developed that uses mechanical charging rather than electrical. In this process, the battery is disassembled and rebuilt. Recharging can therefore occur in a few minutes, but involves some technical ability [9]. These cells have high specific energy, but relatively low specific power.

Another metal-air battery is the aluminum-air battery. It has an theoretical voltage of 2.7 V and an very high energy density (8.1 kWh/kg for the metal) [41]. The authors making the theoretical calculations determine that this type of battery can provide the same range in an electric vehicle as cars get with internal combustion engines. Like the zinc-air battery, the cost of materials is relatively low, making this an interesting area for research. Iron-air is another battery type with a cell voltage of 1.3 V, but this one does not hold much favor as iron tends to rust in this environment and so stability is an issue [1]. Other possible metals include lithium (3.4 V), cadmium (3.4 V), and Magnesium (3.1 V).

Although a fuel cell is technically not the same as a rechargeable battery, some brief comments will be noted here since recent research shows some promising developments for primary and secondary battery replacement in electronic and mobile devices. Most current fuel cells must be kept in an upright position and are also rather large when considering the fuel cell, fuel tanks and control system. This is to maintain the proper pressures of fuel and water being pumped throughout. However, miniaturizing the fuel cell allows passive flow systems such as capillary action to control the fuel cell

and it can be used in any orientation [42]. These tiny fuel cells expand the use of fuel cells to applications as small as MEMS technology.

Though not a battery, ultra capacitors can sometimes be beneficial when used in conjunction with batteries. Ultra capacitors function like other capacitors with charges stored on two parallel plates. They have a very long life cycle, high efficiency and a high power density (they can very quickly respond to supply energy as well as be quickly recharged). The problem is that they have a lower energy density than batteries and so they can not provide as much power for a given size [43]. They can be very useful in providing additional power during short bursts for low power applications.

DISCUSSION

The previous sections have given an overview of the major types of rechargeable batteries currently in use and on the horizon. Technical details of the most important types are summarized in Table 1 to provide a side-by-side comparison of some important features.

Rechargeable battery selection in general depends upon several factors. These include mechanical and chemical stability, storage capability, operation temperature, self-discharge rate, discharge curve features, cost, safety, recharge capability, cycle life, charge time and overcharge/overdischarge protection [3]. Within these considerations are factors such as the maximum voltage, maximum current, running time, charging time, and depth of discharge. Some battery properties are interrelated. For instance, increasing the depth of discharge (the amount the battery is drained of power) will decrease the number of cycles that most batteries can last [7].

If a battery is to be used on a portable device, the size and weight are critical factors to consider. The battery is typically the limiting factor in size reduction of portable consumer electronics, for instance. In addition, the weight of the battery often adds a significant weight to the system and thus increases power usage in self-propelled applications.

If the application will be upgrading or swapping with primary batteries or cells, then battery voltage becomes an issue. Since commercially available secondary alkaline cells have significantly lower voltages than their primary cell counterparts, modified lithium-ion batteries or other emerging technology will best serve this need. Otherwise, provisions need to be made for including extra cells in series and parallel to obtain the desired voltage and current.

As with any system component, factors such as availability, assembly and manufacturability, aesthetics, integration, and support infrastructure (for electrical charging and disposal/replacement procedures) are all important considerations as well. In addition to traditional manufacturing and economic considerations, the environmental and global impacts are also important considerations. Studies have been done investigating the environmental impact and recycle-ability of various

battery types. One study in Europe [44] found that salt-based batteries tend to have the least amount of impact with lithium-ion technology being a good environmentally-conscious compromise when sodium-batteries are not well suited. Lead-acid, nickel-cadmium and nickel-metal-hydride all have a more significant environmental impact. Since not all countries have battery recycling infrastructure set-up for all battery types [45], this can mean lots of contaminants end up in landfill

and thus water and food supplies. Still, recent work has improved the recycle-ability of lead-acid batteries by recovering more lead and sulphates [46]. In addition, investigations were performed in China [47] and India [48] to develop a method of recovering cadmium other heavy metals from batteries. Advances such as this can equalize this aspect of battery selection.

Table 1. Comparison of Key Characteristic of Rechargeable Battery Technologies

	Specific Energy (Wh/kg)	Specific Power (W/kg)	Cell Voltage (V)	Cycles	Life (years)	Maximum Depth of Discharge	Self-Discharge Rate	Efficiency
Lead-Acid	35-50 [9]	150-400 [9]	2.1 [1]	250-1,000 [7]	5 years [7]	20-80% [1]	2-8%/month, some 20-30%/month [1]	75-85% [7]
Nickel-Iron	50-60 [9]	80-150 [9]	1.5 [9]	2,000 [10]	20 years [11]	80% [10]	20-40%/month [1]	
Nickel-Cadmium	30-60 [9]	80-150 [9]	1.2 [9]	1,000 to 50,000 [7]	10-15 years [7]	60-80% [1]	5-15%/month [1]	60-70% [7]
Nickel-Hydrogen	50 [9]	220 [9]	1.4 [1]	1500-6000 [1]	15 years [1]	-	Very high except at low temperatures [1]	-
Nickel-Metal-Hydride	60-80 [9]	200-300 [9]	1.2 [9]	300-600 [1]	2-5 years [1]	-	15-25%/month [1]	-
Nickel-Zinc	70 -100 [9]	170-260 [9]	1.6 [10]	up to 500 [10]	-	100% [1]	<20%/month [1]	-
Lithium-Ion	80-180 [9]	200-1000 [9]	3.05 [9]; 4.2 [1]	3,000 [1]	5+ years [1]	100% [1]	2-10%/month [1]	-
Sodium-Sulfur	150-240 [9]	230 [9]	2.71 [9]	2,500 to 40,000 [7]	-	100% [7]	-	86-89% [7]
ZEBRA	90-120 [9]	130-160 [9]	2.58 [9]	-	-	-	-	-
Vandium Redox Flow	0-30 [9]	100 [9]	1.2 [7]	10,000 [7]	7-15 years (estimated) [7]	100% [7]	-	85% [7]
Zinc-Bromine Flow	65-85 [9]	90-110 [9]	1.8 [7]	2,000 [7]	-	100% [7]	-	75-80% [7]
Zinc-Air	200 [9]	100 [9]	1.6 [1]	300 [38]	-	-	-	50% [38]

CONCLUSION

This paper has reviewed the major types of rechargeable batteries available. In addition, many investigational batteries were discussed. For the most part, battery selection and use involves a trade-off between cost, power and size. However, advances are making this technology more diverse and robust. It can be expected that more choices will be available as research progresses.

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