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CURRENT STATE-OF-THE-ART OF ELECTROCHEMICAL BATTERIES FROM A USERS POINT OF VIEW

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Abstract

This paper will present a description of some of the battery types (couples) on the market, energy densities, and recycle lives. The possibility that some of these could be used in the transportation industry will be explored. Speculation of future battery development will be discussed.

1.0 INTRODUCTION

Most individuals' contact with electrochemical batteries comes on below freezing weather. Two factors have brought the battery increased attention. First, development of electrochemical batteries has been accelerated by the Aerospace industry applications. Second, since the current petroleum energy crunch of the world, alternates to the internal combustion engine (ICE), such as the battery-powered electrical car, have received attention. Many couples are possible, as noted by reviewing a college chemistry book.

However; not all of them are practical. In the next section, some of the presently available battery types are defined along with existing characteristics.

2.0 TYPES OF BATTERIES

2.1 LEAD - ACID

2.1.1 Design

The lead $-$ acid battery is composed of a series of "positive" and "negative" lead plates immersed in a solution of water and sulfuric acid. The charge/discharge equation is as follows:

CHARGING
\n2Pb
$$
SO_4 + 2H_2O
$$

\n $PD + PbO_2 + 2H_2SO_4$
\n $QB + 2H_2SO_4$

In actual construction, the positive plate has many grids comprised of lead dioxide. The negative plate has many pockets filled with spongy lead. Both are of flat construction. Improved design techniques are currently under investigation which, hopefully, will improve the characteristics described in paragraph 2.1.3. One, in particular, is going to a tubular construction of the positive plate.

2.1.2 Characteristics

The lead acid battery is capable of high current drains for short periods of time (over 400 amps for starting and internal combustion engines). Other typical characteristic curves are shown in figure 1. Other current state-of-the-art characteristics are as follows: (1)

12 watt — hours/pound (2 hr rate) 400 — 450 cycles (2 hr rate)

2.1.3 Applications

Of course, the most popular use of the lead-acid battery is for the automobile. Other lesser-known usages includes standby power for railroad switching, trolling motors, emergency power for the tram cars that parallel the Queens Boro Bridge (from Manhattan to Roosevelt Island), and electric buses on Roosevelt Island. (2) Of course, countless other applications could be listed for this widely utilized battery.

Future applications — it is most probable that the main usage for the lead-acid battery in the near term will remain as it is today $-$ as the "car battery".

However, research is in progress to upgrade the lead-acid battery for an increase in cycle life and improved energy density. Specifically, the research is directed towards tubular construction for the positive electrode. (3) This concept allows for a lighter battery thru use of lightweight plastic tubes that hold the active material in place.

2.2 ZINC-AIR

2.2.1 Design

The zinc-air battery consists of a group of cells interconnected as the designer desires (parallel, series, etc.). Each cell consists of a zinc annode that fits inside a cathode grid with catalyst thru which the air or oxygen flows. The electrode reactions are: (4)

Zinc Annode: Zn + 2(OH $^{-}$) $-$ Z_n 0 + H₂ 0 + 2e $^{-}$ Oxygen Cathode: $\frac{1}{2}0_2$ + H₂0 + 2e = 2(OH)⁻ Overall Reaction: $Zn + \frac{1}{2}0$ ₂ – $Zn0$

One design technique investigated was that of "mechanically" rechargeable zinc air cells in which the expended zinc annode is merely removed and replaced with another "fresh" one. The expended annode is then recycled. Another technique consisted of a closed system where oxygen is used instead of air.

2.2.2 Characteristics

Some projected characteristics of a mechanically rechargeable type zinc-air battery are as follows:

Capacity: 100 watt-hours/pound (max) Output: 150 amp-hours (max) Life: 125 cycles (max)

2.2.3 Applications

Early in the development of the zinc-air battery (circa 1970), military usage was envisioned. Currently, very little research is underway in the United States. Therefore, it is impossible to predict a future application for the zinc-air battery.

2.3 SILVER OXIDE - ZINC BATTERIES

2.3.1 Background

The silver oxide-zinc system, commonly referred to as the silver-zinc (Ag-Zn) battery, has been the workhorse in the missile and aerospace field. This system has held the position of primary power source since the onset of the industry. The Ag-Zn system possesses relatively high energy densities, and is capable of providing the high power requirement usually characteristic of space and missile applications. New inorganic ceramic separators are being developed to increase the ''wet-life'' and "cycle-life" capabilities of the Ag Zn couple. Cell capacity ranging from fractional ampere-hours (A-Hr) to hundred of A-Hr have been realized. Batteries with normal separator systems (i.e. hemp fiber, asbestos, cellophane, polyethylene, etc.) provide wet-life and cycle-life expectancies from one to two years and up to 150 cycles, respectively. Moreover, batteries with ceramic separators have projected wet-life and cycle-life targets of five to ten years and greater than 500 cycles!

2.3.2 Design

The Ag-Zn battery is a wet alkaline system. Each cell consists of separated, alternate silver and zinc plates in a potassrum hydroxide (KOH) electrolyte solution. The specific construction of the battern is dictated by the application with high/low discharge rate, auto/manual activation, sealed/ vented cells, and primary/secondary power being some of the variables. Separator systems range from a single wrap for high rate, short life jobs to multiple wraps or ceramic separators for long life, rechargeable applications. Similarly, the cell pack construction may vary from a large number of thin plates for high rate of discharge and low capacity, to a few heavy plates for the opposite electrical effect. Mercury treatment of the negative zinc plate is used to control unwanted gassing during discharge, but at a price of reduced negative plate efficiency. Discharge is accomplished by reduction of silver oxide to silver with a corresponding oxidation of the zinc to zinc hydroxide as noted in the following full cell

reaction: $Ag0 + Zn + H_20 - A_g^+ + Zn (OH)_2$

Battery construction may consist of individual cells bussed together or be arranged in monoblock form. The monoblock construction is used primarily for auto-activated batteries having a common manifold and electrolyte reservoir. These auto-activated batteries are usually provided with five to ten percent excess electrolyte so as to insure proper wetting. Any remaining electroyte is then dumped into a sump containing a fiberous cotten (webbed) material. The wet-life expectancy of an auto-activated battery is usually limited by (1) self discharge due to intercell leaking through the common electrolyte manifold plus (2) individual cell wet-life degradation from silver migration and growth of dendrites.

2.3.3 Characteristics

The silver zinc couples are fairly well defined with an extensive amount of development test data and literature available. Unfortunately, no one battery exists off-the-shelf for every application in the space and missile industry. Each battery design is tailored to meet the environmental and load conditions imposed by the specific mission. The charge efficiency of a Ag-Zn system is nearly 100% on a A-Hr basis at room ambient. The dynamic resistance (ΔR) of the Ag-Zn couple is a function of state of charge, charge control, temperature and age. This parameter has been under heavy scrutiny over the past years in order to determine if knowledge of ΔR can predict the state of cell conditions. Supporting this concept is test data that has indicated that wet Ag-Zn cells left on standby in a charged mode over long periods of time be subjected to a voltage conditioning pulse prior to applying critical loads due to increased Δ R probably caused by the reduction of the AgO on the surface of the silver plates to A_{g2}O. The resistivity of AgO is 10 ohms-cm; Ag 1.6x10—6 ohm-cm and A_{g2}O 10⁸ ohm-cm!

2.3.4 Application

The Ag-Zn battery has been the main power source for most of the missile and space primary power requirements. This system has been so reliable that even major space programs utilizing fuel cells and/or other rechargeable systems (e.g. solar array and N1-CAD batteries) have used Ag-Zn batteries to insure adequate power for recovery. Reliability and high energy density and rate are positive points for the Ag-Zn system, but at the moment life and cost for commercial application are the major prohibiting factors.

2.4 LITHIUM SYSTEMS

2.4.1 Background

The lithium couple has for many years been recognized as having one of the highest theoretical energy efficiency known. A great number of lithium systems have been under development over the last ten years with the most promising couples listed in Table I. But it hasn't been until the last four to eight years that these battery systems have been in production. The newness of the systems in conjunction with the relatively low discharge rate of the lithium systems presently developed and the fact that most missile and aerospace systems are medium to high rate types, has caused users in the industry to hesitate in taking advantage of these highly efficient couples.

In spite of these unfamilar conditions great interest has been generated in the military communications area for utilization of the lithium sulfur dioxide (Li S0₂) system in radio and transmission equipment. Moreover, the missile and aero space industries have been observing with great interest the development of the lithium system since mos* of the vehicle systems are weight and volume critical. Hesitation also exists with the safety of the lithium systems. Lithium is a highly active/combustible material and reacts violently with water. Five parts per million (PPM) acetonitrite of SO_2 and (AN) organic solvent are toxic, with 10 PPM $SO₂$ inducing a suffocating and irritating effect,

2.4.2 Design

The construction of lithium cells go from button to prismat'c to jelly roll with both primary and reserve cells being produced. Since lithium is extremely active with water, they must be non-aquerous "dry" systems. The cells consist of (1) a highly pure lithium anode, (2) a polypropelene, nonwoven weberal, pelon, etc., spearator, and (3) a cathode and electrolyte. For instance, in the Li/SO₂ and Li/SOCL₂ systems the electrolyte is the cathode with a carbon substrate onto which SO₂ and SOCL₂ are reduced providing cathode current collector. The electrolyte in all lithium systems consist of lithium salts dissolved in a non-aqueous ion transport solution. Each cell is constructed with a case rupture vent so to preclude any possible explosive condition. In this way a controlled orderly vent at an internal pressure between 400 to 450 psig is provided.

2.4.3 Characteristics

Due to the relatively poor conductivity of the non-aqueous electrolyte, lithium couples are relatively low rate systems with a normal dicharge rate being C/100. At this capacity/100 rate, energy densities of 250 watt-hours (W-Hr)/Kg are attainable. At the full capacity discharge rate, 140 W-Hr/Kg and 35 W-Hr/Kg can be achieved at ambient and -30°C temperature, respectively. The conductivity of the lithium couples are good compared to other dry systems and thus

Characteristics	Li/SO ₂	Li/SOCL ₂	Li/CF	Li/V ₂ O ₅	Li/CuCL ₂
Cathode	$SO2$ Reduced on C	SOCL ₂ Reduced on C	$(CF_x)_n$ & C	V_2O_5 &C	CuCL ₂
Electrolyte	IM LIBR:AN:SO ₂	1.5 M LIALCL ₄ : SOCL ₂	1M LiBF _A /BL + THF	2M $LiAgFg$ + 4M LiBF _R /MF	$LiCL + ALCL3$
Reaction	2 Li + 2 SO ₂ \longrightarrow $Li_2 S_2 O_4$	4 Li + 2 SOCL ₂ \longrightarrow 4 Li CL + $\bar{S}0_2$ + S	$n \times Li + (CF_x)_n$ n X LiF + nC		
Voc (Open Ckt)	2.9 to 3.05 V	3.6 to 3.7 V	2.9 to $3.0V$	3.42	3.15V
Avg Plateau Voltage	2.6 to 2.76 V @ 1.4 ma/cm ² 2.42 V @ 15 ma/cm ² 1.8 to 2.0 V @ 30 ma/cm ²	3.35 to 3.4 V @ 3 ma/cm ² 2.4 V @ 20 ma/cm ²	2.6 V $@.65$ ma/cm ² $2.5 \vee 0.162$ ma/cm ² 2.4 V @ 3.9 ma/cm ²	3.23V $@0.4 \text{ ma/cm}^2$ 3.14 V @ 1.0 ma/cm ²	2.52 V @ 1.5 ma/cm ² 2.35 V @ 9.4 ma/cm ² 2.18 V @ 30 ma/cm ²
Vco (Cutoff)	2.0	2.0	2.0	2.5V	2.0
Voltage Delay	< 1.0 V for > 10 Sec $@1.4 \text{ ma/cm}^2$	$<$ 0.2 V for $>$ 10 Sec $@3.3$ ma/cm ²			
Current Rated Density Max (ma/cm ²) Short	1.4 30 to 35 160 to 170	3.3 20	0.63 3.90 78	0.4 1.0 60	15 100 150 to 160
Dynamic Resist	$.1$ to $.25$.5 to 2	.3 to .5	3 to 12	1.5 to 2.1

TABLE I LITHIUM SYSTEMS

possess a much better low temperature characteristics with operation defined to -55°C.

Typical cell characteristics for some of the more prominent couples are shown in Table I. One characteristic which must be considered in the utilization of lithium systems is lithium passivation which induces a voltage delay on application of load after a long period of open circuit storage. In fact, one drawback is that the reserve system may encounter a "salting out" of the electrolyte when storerd at low temperature over a long period of time.

2.4.4 Applications

The lithium systems, possessing the high energy density coupled with long life, have great potential in the fields of implanted medical devices, hearing aids, watches, memory protection for computers in case of power failure, etc., also in the field of surveillance, security and communications with great promise for the missile and aerospace applications. Primary support for the development of the lithium systems has been by the military and DOD.

2.5 THERMAL BATTERIES

2.5.1 Background

Thermal batteries have been produced since 1946. Until recently, however, their extent of usage was relatively minute. But new developments in thermal cell now allows the thermal battery to compete in short term power applications once held solely by other types of batteries.

2.5.2 Design

Thermal batteries are composed of chemicals which are essentially passive until activated by a heat source. The thermal cell is an electrolytic mixture of anhydrous salt that conducts current when molten. Electric current is produced by the chemical action of oxidizing a metallic anode and reducing a cathode in the presence of an electrolyte. This entire arrangement is passive until application of heat normally generated by a pyrotechnic device or electric match. Heat paper or heat pellets (made from iron potassium perchlorate) are ignited by the heat source; this in turn melts the electrolyte in the adjacent cells and initiates electrochemical activity. Figure 2 shows the various generations of thermal cells. (5)

FIGURE 2f HEAT PELLET - DEB PELLET CELL

FIGURE 2 THERMAL BATTERY CELL CONFIGURATIONS

Development of the heat pellet — Depolariyer — Electrolyte — Binder (DEP) pellet has been the major leap in the state of the art. In this design, the cathode and electrolyte are formed into a single homogeneous cell instead of separate entities as with past cell designs. This DEP pellet, linked with a new heat source of iron rich Fe-KCLO $_A$, also produced in pellet form, integrate into a highly stable dynamically, longer life, low cost, and easily assembled thermal cell. Intercell connection becomes a advantageous by-product of the heat pellet — DEP pellet cell because the heat pellet itself becomes a conductor after combustion. Finally, the heat pellet also burns slower so as to retain its form longer, and serves as a heat reservoir to aid in the extension of battery life. (6) Figure 2 (f) depicts the simplicity of the heat pellet $-$ DEB pellet thermal cell.

2.5.3 Characteristics

From its very name, the characteristics of the thermal battery are highly dependent on temperature — both ambient and internal. Due to the chemistry of the battery, internal heat must be balanced or controlled to give optimum performance over the designed operating temperature range. The heat pellet — DEP pellet cell design aids in this balancing of heat because the pellet construction retains its shape and acts as a heat reservoir. Figure 3 shows a distribution of battery life versus ambient temperature. The peak of this life curve can be shifted to accommodate the specific temperature design conditions. Figure 4 from the Catalyst Research Corporation gives current capacity versus life for various sized heat pellet — DEP thermal batteries application. (7)

2.5.4 Applications

Past usage of thermal batteries have been mainly concentrated in the military field. Missile electronics, time fuses, aircraft ejection systems and spacecraft experiments are all perfectly adaptable to the main characteristic of the thermal battery-reliable, high electric power for short perious of time. But this source of reliable, cheap electric power has not been (until recently) considered for commercial application. Thermal batteries possess a 10 year plus storage life by its very nature; chemical activity is passive until activation. Storage life together with an increased active life of numerous minutes, makes the thermal battery much more attractive to the commercial field. Emergency transmitters, signaling devices, and medical equipment that require a reliable source of energy with a minimum of maintenance are just a few immediate application. But let's look into the future: Suppose one is traveling in a year 2000 $+$ electric car and a power shortage or - using the 1970's term "brown out" $-$ occurs in the area. No electricity is available to charge your already depleted car battery. How does one get to his or hers destination? A couple of sequencially activated thermal batteries running for 20 to 30 minutes at a time could easily increase your travel radius by 100 miles.

This low priced, easily produced, extremely long storage life, reliable, concentrated energy source called the thermal battery could play an important role in our nations quest for energy, energy conservation, and energy management.

2.6 NICKEL-CADMIUM

2.6. Background

The nickel-cadmium (Ni-Cd) couple has provided the principal battery utilized in rechargeable applications throughout the space effort. There has been more development and testing conducted on the Ni-Cd couple than any other battery in the missile and space industries. On each battery, matching of cells is extremely important to performance. Thus testing is conducted to insure that the capacity of the cells in a battery are matched to within $\pm 3.0\%$ with the end-of-charge voltage to be with ± 0.004 volts when charged at 24°C and within \pm 0.008 volts when charged at 0°C. Extensive testing has been conducted in the areas of storage life, depth-ofdischarge, cycle life, and reconditioning by means of thousands of simulated low earth and synchronous orbit conditions plus years of flight data. Even the general public is familiar with the conventional Ni-Cd batteries — calculators, electric shavers, toothbrushes, etc.

2.6.2 Design

The Ni-Cd couple is a wet alkaline couples. Present cells are normally of prismatic sealed construction with a nickel oxide positive and cadmium negative plate. There is a wide variety of separator materials used but the most prominent are polypropylene, cellophane, and asbestos. The carbonate content of the electrodes must be controlled to a minimum to reduce the possible carbonation of the electrolyte since this formation of K_2CO_3 reduces the conductivity of the electrolyte. The negative plates are teflonated to maximize electrolytic quantity added to the cell. Cell cases are usually deep drdawn stainless containers with a liner to prevent the cell pack shorts to the case. Covers are then welded to the case to form a hermetic cell. All cells are then packaged together with tension bolts and machined end plate frames for the purpose of conducting heat to the base.

2.6.3 Characteristics

The Ni-Cd couples is basically a long wet life rechargeable system, capable of providing years of wet life and thousands of cycles. The most prominent advantages of the NiCd battery is the data available from extensive investigation of the capability to recondition the cells in order to extend their cycle life. Method and control circuits have been developed to recondition the battery on an overall battery and an individual cell basis. Reconditioning on an individual cell basis has been shown to be effective for batteries having over 20 thousand cycles with capacities after reconditioning greater than 90% of the original capacity. (10) The general characteristics of the Ni-Cd couple are given in Table II. The actual chemical reactions at the electrodes are not clearly defined. However, a typical response of the half cell and full cell equations for the Ni-Cd couples are as shown. (11)

$$
Cd + 20H- \leftarrow Cd(OH)2 + 2e- 2Ni00H + 2H2O + 2e-
$$

$$
\leftarrow 2ni(OH)2 + 2OH-
$$

Charge 2Ni00H + Cd + 2H₂0 \pm 2Ni(0H)₂ + Cd(0H)₂ **Discharge**

TABLE II Ni-CAD CHARACTERISTICS (9)

2-6.4 Applications

The Ni-Cd battery has provided the main power source for **the** rechargeable space applications. The advent of the cordless commercial equipment has alerted the public to the **Ni-Cd** battery in many pieces of hand held electric **equipment.**

2.7 METAL-HYDROGEN

2-7.1 Background

With the definition of space missions moving into the low earth synchronous and go-synchronous orbits together with increasing deep space probe missions, the development of a rechargeable power source having an increased cycle-life, a deeper operating depth-of-discharge and a higher energy density efficiency is greatly needed to answer this challenge. The metal-hydrogen system came under intensive research and development in the early 1970's with cells development in 1972 to 1973.

2.7.2 Design (12)

The metal-hydrogen system imposes many new battery design criteria. This system is a high pressure system requiring a pressure vessel rather than a conventional cell case. The basic system consists of a catalytic gas anode (negative platinum electrode) coupled with either a nickel or silver cathode (positive electrode) and a non-woven nylon or polypropylene separator with teflon spaces in potassium hydroxide electrolyte. Hydrogen is displaced from the water, at the anode, during the charge cycle by electrolysis. The displaced hydrogen is consumed by oxidation at the anode producing electrical power during discharge. The cell is assembled in a discharged state then precharged with He to approximately 50 psia.

Cell capacity is limited to cathode size while maximum pressure limited both by cathode size and free volume. The positive cathodes are installed in the cell pack in a back-toback arrangement with the negative anode on each side enclosed by spacers from the next cell group of the electrode stack. The two half cell and full cell reactions of the couple including overcharge and overdischarge are noted in the following equations:

2.7.3 Characteristics

The metal-hydrogen cells have been shown to provide weight and volume energy efficiencies slightly better than the Ni-Cd couple with the major advantage being the increased operating depth of discharge. The cells are very tolerant to both overcharge and overdischarge conditions. The cell pressure is a direct measure of the state of charge of the cell.

2.7.4 Applications

At present the couple is in the development state. Flight evaluation tests are currently in progress with these types of batteries on board a space vehicle.

2.8 OTHER REFERENCES:

Design

Other batteriesd currently in the R&D stage include (but are not limited to)

- (1) Nickel Iron
- (2) Nickel Zinc
- (3) Hi Temp Iron Sulfide

3.0 SUMMARY

Several battery types out of the multitudinous number under R&D, lab testing, and production have been discussed. It is impossible to cover all types. The availability matrix presented in Figure 5. Summarizes the research initiated in the authors business. Much additional research is required to fill out and complete this matrix. With respect to implementing an electric vehicle, it appears that only limited activity, as far as production, will take place in the near future.

Status Battery Type	Available In	Development	Laboratory No Studies, Research	Longer Actively Being Researched
$Leaf - Acid$	X			
Advanced $Leaf - Acid$		X		
$Zinc - Air$				X
Nickel - Iron	X			
Nickel - Zinc	X			
Lithium Iron Sulfide			x	
Silver - Zinc	X			
Lithium Systems		X		
Thermal Batteries	X			
Nickel - Cadmium	X			
Metal Hydrogen		X		

FIGURE 5 AVAILABILITY MATRIX

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