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Extended Abstracts

of

BATTERY—ELECTRONICS DIVISIONS

Subject:

Materials for Batteries and Fuel Cells

Papers are scheduled as follows:

May 3, A.M.	No.	1-3
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PACEMAKER BATTERY SYSTEMS

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Over 500,000 pacemakers have been implanted as this device has become the treatment of choice for a variety of heart conduction disorders. The battery system that has been most extensively utilized as a power source is the mercury-zinc system. With increasing demands for longevity, hermeticity, high reliability and high energy density a number of alternate systems have been developed for this application.

Table I compares the properties of various pacemaker battery systems. The delivered/projected energy density values must be compared in the context of the battery design and the extent of testing. The values in Table I are for both production batteries and prototype cells. The rate of discharge is another important parameter effecting the delivered energy density. As the longevity requirements increase to the five to ten year time frame, time dependent phenomena such as self discharge and the stability of construction materials become more critical. These properties will be discussed for the pacemaker batteries based upon the systems shown in Table I.

TABLE I.   PACEMAKER BATTERY SYSTEMS

System	E^o (Volts)	Energy Density (wh/cc)	
		Theoretical	Delivered or Projected
Zn/HgO	1.35	2.5	0.55
Li/I$_2$-Polyvinyl.	2.80	1.7	0.8
Li/PbI$_2$-PbS	1.90	1.4	0.5
Li/Ag$_2$CrO$_4$	3.30	2.1	0.7
Li/SOCl$_2$	3.60	2.3	0.9
Na/Br$_2$	3.62	2.0	1.3

NICKEL-ZINC BATTERIES, AN OVERVIEW

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The nickel-zinc battery couple is of current interest because of desirable energy storage capabilities both with respect to weight and volume and relatively low cost. Over the past few years developments in zinc electrode, separator, and nickel electrode technology have contributed to the further realization of these capabilities. This paper reviews many of these developments.

The zinc electrode offers an attractive electrode potential and equivalent weight, but it also has the shortcomings of dendrite formation, shape change, and hydrogen liberation. A number of different electrode additives have been used to decrease the hydrogen evolution rate at the zinc electrode, as evidenced by the number of recent patents in this area. Some of these additives have been claimed to help retard zinc dendrite growth. The results of studies on the mechanism for zinc electrode shape change have been reported by several research groups, and some of these findings have been reduced to practice.

The separator system for nickel-zinc batteries must be adapted to the behavior of the zinc electrode in the battery electrolyte. Batteries with free electrolyte employ separators similar to those used in silver-zinc batteries. One separator system that shows promise in these applications is the PPO impregnated inorganic separator. Nickel-zinc batteries using this separator system are currently under evaluation for electric vehicle applications. Batteries incorporating a gelled electrolyte, such as in "D" size cells, can employ a more porous type separator.

The nickel electrode in nickel-zinc batteries can be of the sintered plaque, pressed plate, or pocket plate type. The electrochemical impregnation process, which was recently developed and refined, yields sintered plaque type electrodes with optimum loading levels, high strength, and minimal swelling both during electrode impregnation and battery cycling. Swelling of positive electrodes is recognized as a cause of performance changes and failure. The pressed plate nickel electrode affords an inexpensive nickel-zinc battery with good energy levels, but these electrodes can have severe swelling problems. The pocket plate type electrodes have poorer energy levels, but this can be improved. Swelling can also be severe in the pocket plate nickel electrode.

Pressed plate nickel electrodes are used in nickel-zinc "jelly-roll" configuration cells recently introduced in Japan. The use of a chemically oxidized active nickel component for this type cell has also been investigated. Prismatic configuration nickel-zinc cells incorporating pressed nickel electrodes have also been reported.

One enduring problem in nickel-zinc technology is determining the optimum method for charging these cells and terminating charging. The nickel electrode has descreased charging efficiency as it approaches full capacity, and requires overcharging to attain full capacity. The zinc electrode excess capacity is depleted during this overcharge, and battery capacity begins to fall off. A periodic maintenance cycle is then required both to restore available capacity, and to retard permanent loss of capacity and cycle life due to shape change and dendrite formation when the zinc electrodes become highly polarized. An auxilliary electrode could be one solution to this problem, but the variations in electrolyte level between the fully discharged and fully charged states coupled with the hydrogen gassing from the zinc electrode adversely effect the operation of an auxilliary electrode.

The progress that has been made in solving many of the difficulties associated with nickel-zinc cells is probably best shown by the performance now obtained from these cells. A delivered capacity at the C/5 rate greater than 65% of original capacity has been obtained after 230 deep discharge cycles without any maintenance other than adjusting the electrolyte level.

ZINC-AIR BUTTON CELLS

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The authors review the fundamentals of metal-air batteries as a prelude to their examination of state-of the-art zinc-air button cell technology. Gould's button cell design combines a conventional slurry zinc anode with a novel cathode structure which extracts oxygen (one of the cell's reactants) directly from the ambient air. This "air cathode" eliminates any need to contain active cathodic material within the cell. Accordingly, zinc-air cells contain more anodic material, giving them greater capacity than conventional alternatives. Several air cathode implementations are plausible; Gould's approach derives from fuel cell developments and uses a thin catalyzed conducting screen backed with a hydrophobic membrane.

Zinc-air button cells are ideally suited for the majority of ear-worn and eyeglass hearing aids. These devices have traditionally used one of two button cell systems: mercuric-oxide or silver-oxide.

Typical hearing aid current requirements range from a low of .3mA to a high of .5mA. Hearing aid design voltages conform to available battery systems: high gain aids, used by persons with severe hearing loss, often require the higher voltage of the silver system (1.5 volts., approximate); however, most hearing aids are designed to use mercuric oxide cells, with on-load voltage levels between 1.2 and 1.3 volts.

Gould's zinc-air button cells accommodate the full range of hearing aid current drains, at voltage levels between 1.2 and 1.3 volts; moreover, since they have the same external shape, size and polarity as do conventional ("mercury" and "silver") button cells, zinc-air button cells are perfect substitutes in most hearing aid applications. Gould has tested more than 10,000 prototype, zinc-air, ANSI 15 size button cells during 1975. Gould also evaluated comparable mercuric-oxide and silver-oxide button cells under identical programs, which included tests for discharge performance, leakage resistance, capacity retention and internal resistance.

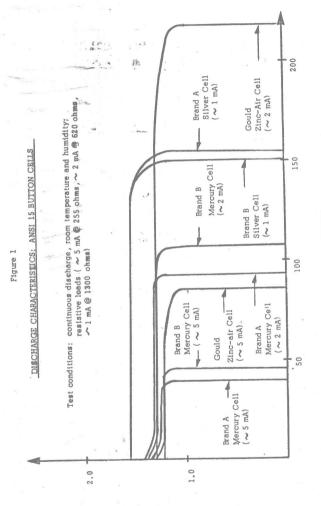The authors present comparative discharge data from recent tests.

Table 1 shows the delivered capacity of the three systems under various discharge conditions. Figure 1 presents several voltage vs. time characteristics which indicate zinc-air's performance relative to mercury and silver. In all cases, the zinc-air button cells deliver roughly twice the operating life; moreover, the zinc-air system maintains its capacity advantage over a wide range of ambient temperature.

The authors point out that the zinc-air system cannot substitute as well for mercury or silver systems in every button cell application. For better or worse, all electrochemical systems have their unique performance characteristics, which determine their relative suitability to a given application. Consider electronic watches, for example. Zinc-air button cells would perform poorly under the 60mA drains at 1.2 volts which LED watch displays presently require. On the other hand, they would perform admirably in electronic watches with mechanical or liquid crystal displays. The authors explain this performance dichotomy and go on to nominate several future applications for the zinc air button cell, including pocket calculators, and paging equipment.

ANSI 15 Button Cell Capacity
(based upon discharge duration to a .9 volt cutoff)

discharge condition	mercuric-oxide	silver-oxide	zinc-air
Approximately 5 milliamp continuously	185	152	399
Approximately 2 milliamp continuously	185	181	404
Approximately 1 milliamp 8 hours per day	187	191	347

Table 1

Figure 1

DISCHARGE CHARACTERISTICS: ANSI 15 BUTTON CELLS

Test conditions: continuous discharge, room temperature and humidity;
resistive loads (~ 5 mA @ 255 ohms, ~ 2 mA @ 620 ohms,
~ 1 mA @ 1300 ohms)

THE EFFECT OF DESICCANTS ON THE STABILITY OF AS-PLATED LITHIUM
TOWARD PROPYLENE CARBONATE BASED ELECTROLYTES

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A key hurdle to surmount in the implementation of a secondary
lithium battery is the development of a well-behaved Li electrode.
Though much work has focused on improving the compatibility of Li with
aprotic organic solvents, high efficiencies and cycle lives have yet
to be achieved.

Propylene carbonate (PC) is one solvent known to be generally
stable towards Li (1). Accordingly, we have employed it to probe the
effects of desiccants on Li-solvent reactions. Our premise is that
solvent impurities may promote heterogeneous reactions on the Li
surface, effectively isolating electrodeposited Li from subsequent
anodic dissolution. By removing these impurities, or at the very
least, by reducing their concentrations, the cycling efficiency of Li
in PC should be improved. To this end molecular sieves, silica gel,
and acidic, basic and neutral alumina were scrutinized in terms of
their ability to improve cycling efficiencies.

The chronopotentiometric plating and stripping efficiencies of Li,
and the isolation rate of Li at a Ni working electrode were found to
be the experimental techniques most sensitive to electrolye impurities.
Indeed, cyclic voltammograms of test solutions at either glassy C or
Pt working electrodes could not distinguish a "clean" electrolyte from
a "contaminated" one.

All experiments were conducted under an argon atmosphere in a
Vacuum/Atmospheres Co. dry box. The individual cell comprised a Ni
working electrode, a Li reference electrode, and a counter electrode
composed of Li ribbon pressed into expanded Ni screen. Details
regarding electrode dimensions and configuration are reported else-
where (2).

The electrolyte was treated with desiccants as follows: 50 cm^2
of a 1M solution of $LiClO_4$ or $LiAsF_6$ in PC was allowed to slowly
percolate through a column containing approximately 20 gm of desiccant.
The first 10% through a column was discarded, the remainder being
collected and stored in a tightly stoppered flask.

In a given cycle, Li was plated and stripped galvanostatically.
Each plating consisted of a 5 mA/cm^2 current for 100 sec, yielding
0.5 coul/cm^2 of Li plated on the Ni working electrode. After a 100
sec plate, the polarity of the working electrode was reversed and the

Li stripped at 5 mA/cm^2. A 50 sec pause between cycles was incorpo-
rated into the experimental routine. It was found that this pause
afforded a smoother efficiency decay rate as well as more reproducible
efficiency values from one experiment to another. Efficiency is
defined as the ratio of charge stripped to charge plated and is
expressed as a percentage.

Twenty successive plating and stripping cycles were recorded for
each desiccant and for untreated electrolyte. Base line efficiencies
for untreated electrolyte ranged from 60% on the first cycle to 40% on
the twentieth. These values are similar to those reported previously
(2). Molecular sieves afforded a slight improvement during the early
cycles (65-67%), though the efficiency dropped to 40% on the twentieth
cycle. Electrolyte treated with neutral activated alumina manifested
the highest cycling efficiencies -- from 82% on the first cycle to 60%
on the twentieth. Silica gel, acidic alumina, and basic alumina gave
efficiency values intermediate to those observed for the untreated
electrolyte and electrolyte treated with neutral alumina. Thus, these
desiccants in general and neutral alumina in particular improve the
cycling efficiencies of PC-based electrolyte.

We attribute this improvement to the ability of activated alumina
to adsorb organic impurities, as well as water. With the exception of
hydrocarbons, virtually every other organic functionality adsorbs on
alumina in preference to esters such as PC (3). Indeed, activated
neutral alumina suspended in acetonitrile or methylene chloride has
been found to increase the stability of electrogenerated organic
intermediates by scavenging potential nucleophiles (4).

ACKNOWLEDGEMENT

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