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SURVEY OF NEW DEVELOPMENTS IN SMALL BATTERIES

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SURVEY OF NEW DEVELOPMENTS IN SMALL BATTERIES

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SURVEY OF NEW DEVELOPMENTS IN SMALL BATTERIES

Introduction

The standard lead acid, alkaline, and Leclanché batteries were found in many cases to be inadequate for the requirements of modern warfare. Research during the war led to the development of several new types of cells and many modifications of the old types. Some of the new batteries were used considerably during the past war, while others are still in the developmental stage.

A comparison of the relative merits of the various batteries is not possible from a survey of the literature as no standard procedure has been used in testing them. In the following summary, the general characteristics, advantages, and disadvantages only will be given. Quantitative analyses of the performances will be found in the references listed at the end of the report.

(1) Perchloric Acid Cell (1,2,3,4)

This cell was developed by the U.S. Bureau of Standards for low temperature operation. The electrolyte is perchloric acid and the electrodes are lead and lead dioxide. These batteries will operate satisfactorily at temperatures down to -60°C. The electrochemical reaction is very efficient and therefore perchloric acid cells can be made smaller and lighter than storage cells of equivalent capacity.

The electromotive force of the cell varies with the concentration of perchloric acid and lead perchlorate in the solution. As the freezing point also varies with these concentrations, a compromise is necessary to obtain cells adapted to any particular purpose. For a temperature of -60°C., 41% perchloric acid is used and the emf is about 1.90 volts per cell.

Even at normal temperatures the discharge characteristics compare favourably with those of the ordinary dry cell. The voltage curve is flatter and higher flash currents are obtained with the perchloric acid cell.

The cell can be made in the charged unfilled condition. The electrolyte is added when required for service. The output of the battery is immediately available when it has been filled. It can be stored for considerable periods without loss in efficiency.

It is possible to use iron, cadmium, and aluminium for the negative electrode but these metals do not appear to give such a desirable electrochemical action as lead, although they offer advantages from the weight standpoint.

The perchloric acid cell in its present form has some limitations. It is rather difficult to fill with electrolyte and the acid is dangerous to handle. Other acids, such as fluoboric and fluosilicic may be used but the cell performance is not quite so good. No positive grid material other than the precious metals has been found which will resist attack in contact with perchloric acid for more than a few days.

(2) Methylamine Hydrochloride Cell [5]

The ordinary ammonium chloride type of dry cell is inoperative at temperatures of -20°C. The methylamine hydrochloride cell was developed by the U.S. Bureau of Standards for low temperature operation.

The electrolyte consists of 47% methylamine hydrochloride, 3% zinc chloride, and 50% water. African manganese ore is used as the depolarizing material. Ammonium chloride added to the electrolyte causes a stabilization of voltage, amperage, and capacity. The cells are constructed similarly to ordinary dry cells.

These cells have a voltage about the same as the ammonium chloride dry cell. At ordinary temperatures they have a slightly higher capacity but a lower flash current than ordinary cells. At -30°C. the capacity is approximately 10% of that at ordinary temperatures.

(3) Calcium Chloride-Ammonium Chloride Cell [5]

This cell, also developed by the U.S. Bureau of Standards, has a calcium chloride-ammonium chloride-water electrolyte. Only a few tests have been made but this cell appears to be superior to the methylamine hydroxide at a temperature of -30°C. and is still operative at -40°C.

(4) Lithium Chloride Cell [6]

The Burgess Battery Company has developed a dry cell capable of operating at -40°C. which has lithium chloride in the electrolyte. These cells are constructed similarly to ordinary dry cells and have approximately the same capacity at normal temperatures. At -40°C. the capacity is from 10 to 20% that at 21°C.

The electrolyte consists of 12% $ZnCl_2$, 15% LiCl, 8% NH_4Cl, and 65% water. The depolarizer is battery manganese hydrate and the conductive material is Shawinigan black.

(5) Silver Oxide-Zinc-Alkali Cell [7,8]

This cell, developed at the U.S. Naval Research Laboratory and U.S. Bureau of Standards, has a silver oxide positive, zinc negative, and potassium hydroxide electrolyte. They are designed for one shot application because the silver oxide is soluble in the electrolyte.

These cells have about twice the capacity of lead acid cells. They have a very flat voltage curve when discharged at a high current rate. The characteristics of the cell can be changed to some extent by modification of the components.

The limitation of this cell is that it must be filled with electrolyte shortly before being used and that all the current must be drawn at one time. Only a small amount of experimental work has been done on this cell and it has not had any specific application.

(6) Silver Chloride-Magnesium-Water Activated Battery [9]

The positive electrode consists of thin silver foil coated with electrolytically formed silver chloride. The negative electrode is commercially pure magnesium foil. Dry absorbent paper is placed between the electrodes and the cell can be kept indefinitely in this condition. The battery can be activated by the addition of common or salt water.

This cell has a very steady voltage on discharge. The output is 1.5 volts for most of the life of the cell. A high current may be obtained at a useful voltage but batteries have been built which operate successfully at currents as low as 7 ma, and for continuous service as long as 48 hours. The capacities are considerably greater than for dry batteries of equivalent size and weight.

These batteries must be activated at temperatures at which water is liquid but they may be operated at much lower temperatures. At -40°C. the voltage is somewhat reduced but the life is not greatly affected. The shelf life is indefinitely long when the cell is protected against excessive humidity.

The Burgess Battery Company has had these batteries in production for several years and they have been very successful in operation.

(7) Ruben Cell [10,11]

The Ruben cell was developed in the United States and was in production during the war. P.R. Mallory & Company, North Tarrytown, N.Y., are the manufacturers.

The positive electrode is a layer of mercuric oxide in the bottom of a steel container. The negative is crimped zinc ribbon and the insulation is cellulose paper. The electrolyte is potassium hydroxide which is impregnated in the paper insulation before assembly.

These batteries have a performance much superior to that of ordinary dry cells. The capacity is approximately eight times that of the ordinary dry cell per unit volume and four times per unit weight.

(8) German Batteries [12, 13]

The main German advance in battery design was the development of the sintered plate. This was used in the "Durac" nickel-cadmium-alkaline batteries. The sintered plate has a porosity of about 75% and this gives a large active surface.

The advantages claimed for this battery are:

(1) Practically indestructable

(2) Low internal resistance and therefore a high discharge rate can be obtained.

(3) Good low temperature performance.

(4) Efficiency comparable to lead-acid battery.

(5) Lighter than ordinary alkaline batteries.

(6) They can be completely discharged without damage to the plates.

These batteries were under test at the National Research Council and a report on them has been issued (ERB-172).

Another interesting type of battery is the Schmid cell which has carbon and zinc electrodes and an electrolyte called Galvanol. The cell can be recharged by refilling with Galvanol and replacing the zinc amalgam electrode, if necessary. When not in use the electrolyte must be separated from the electrodes. This cell has a flat voltage characteristic, averaging about 1.2 volts, and has low internal resistance.

(9) **Miscellaneous** (14,15,16,17,18,19,20,21)

Besides the development of new types of batteries, attempts were made to improve the low temperature performances of the standard types.

The Willard Storage Battery Company developed a lead-acid battery for one shot applications. This was used instead of dry cells and it operated successfully down to $-40^{\circ}F$.

Lead acid storage batteries are in general unsuitable for low temperature operation. However, in some applications it may be possible to provide heat externally or to decrease the cooling down rate by use of insulated battery boxes.

It is possible to keep dry cells at a temperature suitable for operation by passing alternating current through the cell. This method can also be used to bring cold batteries up to operating temperatures.

Considerable improvement has been made in the design of aircraft storage batteries. The weight is decreased by reducing the life expectancy down to a reasonable point for aircraft use. The supporting grids are made lighter by using 12% antimonial lead instead of 8%. The active material is in a very porous state and this increases the output currents as well as reducing the weight. Organic materials such as wood-dust, lignin, and hemp are added which improve the low temperature performance but have no effect at normal temperatures.

Some improvements in the low temperature characteristics of dry cells have been made by the introduction of new components. The Germans had a dry cell which operated down to -45°C. but only gave 50 to 60% of normal output at ordinary temperatures. This was accomplished by the addition of an anti-freezant such as glycol to their magnesium chloride batteries.

The Dow Chemical Company has been experimenting with a new type of battery using magnesium and graphite for the electrodes and chromic acid electrolyte. Theoretically, these batteries should be very efficient but considerable difficulty has been experienced in developing a practical cell.

U.S. Battery Research [22]

The United States has planned a broad post-war battery research program. A thorough investigation is to be conducted of the following:

Storage Batteries:

Airplane Batteries:

- Operating characteristics on constant potential charging systems.
- Effects of high and low temperatures.
- Separator materials and substitute for microporous rubber.
- Vent plugs to prevent spillage
- Automatic life cycling tests.
- Vibration tests.
- Materials for containers.
- Sealing materials resistant to plastic flow.
- Methods of heating batteries.

Propulsion Batteries:

High rate discharges.
Maximum capacity.
Comparison with foreign types.
Life cycling test.
Separator materials.
Gasing and spray elimination.

Small Types in Plastic Cases:

Operating characteristics.
Low temperature performance.
Charged and dry condition.
One shot applications.

Alkaline Storage Batteries:

The Edison type.
The Jungner type.
German sintered plate type.
American-made Nickel Cadmium type.

Storage Batteries for One Shot Applications:

Charged and dry.
Charged and filled.
Dunked batteries for meteorological applications.

Primary Batteries:

The Perchloric Acid Battery,
- Methods of plating lead dioxide.
- Substitutes for perchloric acid.
- Operating characteristics.
- Concentration of electrolyte:
  - In relation to load
  - In relation to temperature
- Performance at extreme low temperatures.
- Storage of batteries in dry condition.
- Methods of filling the cells.
- Plastic containers.
- Applications to meteorological work.
- Batteries for large power output.
- Batteries for low temperature applications.

The Silver Peroxide Battery,
Development of small form.
Problem of shelf life.
Batteries for large power uses.
Methods of filling the cells.
Highly active zinc negative plates.

Silver Chloride Batteries:
Water activated batteries.
Batteries for large power uses.
Smaller batteries for meteorological purposes.

Dry Cells:

Ordinary types,
Operating characteristics.
Standard tests and specifications.

Low Temperature types,
National Bureau of Standards type
Ray-O-Vac Company type.
Burgess Battery Company type.
Japanese type (Calcium Chloride).

Constant Voltage Cells:
Bureau of Standards type.
Low Temperature characteristics.

Conclusions

The U.S. program appears to cover all phases of battery research. Therefore, before starting a Canadian research program, it would be advisable to consult with American experts to determine which phase of the battery investigation could be most fruitfully undertaken in Canada.

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