LEAD INDUSTRIES ASSOCIATION

292 MADISON AVENUE
NEW YORK 17, N. Y.

August 2, 1960

SUBJECT: STORAGE BATTERIES

To Members of the Lead Industries Association:

We believe you will be interested in the attached copy of a paper delivered before the annual meeting of the Association of American Battery Manufacturers at Los Angeles on June 2, 1960. It was prepared and presented by the late Clifton G. Grimes, vice president, research, of the Electric Storage Battery Company and undoubtedly one of the best informed men in the country on the subject.

Additional copies are available as long as our limited supply lasts.

Very truly yours,

Robert L. Ziegfeld

Secretary

RLZ:JRM

Att.

THE CHALLENGE BY NEW BATTERY SYSTEMS

C. G. Grimes
The Carl F. Norberg Research Center
The Electric Storage Battery Company
Yardley, Pennsylvania

It is quite appropriate on this centennial of the first practical lead-acid storage battery to review the field and evaluate the potential threat posed by the more prominent competitive systems.

Over the years the lead-acid battery has been the mainstay and the work-horse in the field of secondary batteries. The relative simplicity of the electrochemical reaction, high cell voltage, absence of criticality in physical configuration, and a generous supply in nature of rather inexpensive basic materials are all factors which have contributed to the commanding position of lead-acid batteries. Lacking this fortunate combination of good technical and economic features, other systems were more or less relegated to a position of secondary importance, while industrial development emphasized the lead acid work. And contrary to the remark so often heard to the effect that the battery in your automobile today is no different than those used some forty years ago, the facts are quite different. There has been a great improvement in the battery during this period--improvement in its electrochemical performance, in the energy-density ratio, in packaging, and in life. Most of this improvement has been the result of years of development wherein progress has been achieved by incremental improvements as opposed to any profound advance which could be attributed to research. The latter has been very much neglected. In general, it might be said that research in lead-acid couples has become a reality only in the current postwar period. One seldom hears any reference to the electrochemical efficiency of the lead-acid battery. This is quite understandable when, after a hundred years of development, the efficiency is about one-half of what it could, and should be. Because of the rapidly growing appreciation of the value of research, even to those items of long standing acceptance, I fully anticipate that the advance in the technology of the lead-acid battery will be greater during the coming decade than during the past half century.

During the past two decades the generation of electrical energy in this country has had a phenomenal growth--from 130 billion KWH in 1940 to an estimated 600 billion in 1960. An increase of 360%. This growth is also reflected in the portable or packaged electrical energy sources. At the same time, there has been a rapidly growing demand for portable power units, or batteries, for specialized uses. In this myriad of new uses, the criteria by which batteries formerly were evaluated have been pretty well upset. In most cases a single characteristic is of

---

Presented at the meeting of the Association of American Battery Manufacturers, Inc., Los Angeles, California, June 2, 1960.

LIA19278

primary and vital importance to the successful application of the battery, other factors being made quite secondary considerations. For example, perhaps in a specialty application the energy-weight ratio may be all-important; in another, it may be cycle life, or shelf life, or energy-volume ratio, or cost. This situation has aroused new and intensified interest in the development of new battery systems to meet these specialized requirements.

Nearly all of these "new" battery systems are not new, but merely a new look at an old item. The nickel-cadmium and nickel-iron cell constructions were patented before the end of the 19th century. The mercury cell owes its origin to the Aron cell where it was first proposed as a storage battery in 1866. The use of silver oxide as a positive active material was proposed by Jungner in 1899, and the cell was first patented by Morrison in 1910. Certain types of primary cells also have applications which are part of the traditional marketing area of lead-acid batteries. The modern fuel cell is a direct descendent of Groves' well known gas battery which he described first in 1839, and later as a battery of 50 cells in 1842. Rechargeable alkaline cells in dry cell configuration, can be traced to the work of LeClanche in the 1850's. Another new form of portable electrical energy of concern to us is thermoelectricity, discovered by Seebeck in 1821.

In giving the "new" battery systems a dusting off it is apparent that the challenge to the lead-acid battery comes, not from a new chemistry, but from the application of modern technology to old and well known systems. Advances in science and engineering have made possible the fabrication of battery systems characterized by high energy-weight ratios, long shelf life, long cycle life, resistance to extra-environmental conditions, etc. They have also made available in many instances quantities of some elements and compounds at acceptable costs--materials which formerly were considered price prohibitive. Some of the new specialized applications will be best satisfied by the new battery systems. Some of them can be satisfied most economically and efficiently by lead-acid batteries.

The electrochemical systems most prominently considered today for storage battery use are lead-acid, nickel-iron, nickel-cadmium, silver-zinc, silver-cadmium, and fuel cells. The latter is, electrochemically, a battery. Back in 1839 it was known as a gas battery, quite a fitting and adequate description. Today it has been glamorized by a new name, which in my opinion is inappropriate. But nevertheless, it has great potential and one must not disregard this fact simply because of its misnomer.

In considering the choice of a battery system to best fulfill requirements of an application, many factors other than capacity must be weighed. Usually it is a compromise of many characteristics, among which are weight, volume, availability, rechargeability, cycle life, stand life, cost and maintenance. In Table I are listed values for

100 ampere-hour size batteries at the 10 hour rate for some of these battery systems. It is interesting to note that the lead-acid cell has one characteristic which sets it apart from those systems with which it is compared; that is, its high cell voltage. This factor offsets the higher density of the lead, and gives in fact a better energy-weight ratio than is found in the other "work type" batteries--nickel-cadmium and nickel-iron. It is also observed from Table I that the silver systems offer very great weight and volume advantages over the lead-acid. However, this simple comparison is but the first approximation as to choice of battery system for a particular application. Extended tables of the performance and economic factors for each system, under various conditions of load and temperature would be necessary to permit logical selection of the optimum system for a specific application. Nevertheless, it is apparent that where weight and size are critical factors, and cycle life or cost are of lesser importance, the silver-zinc and silver-cadmium systems are to be preferred to lead-acid.

Other factors which affect the choice of a system are shown in Table II. These factors include ease of recharge, life and costs. When we consider life and costs we find that the industrial type lead-acid battery is better than the other systems on the basis of cost per unit energy output over the life of the battery. Automotive type lead-acid batteries will have a lower initial cost than any of the systems, but because of its better cycle life, the industrial type is the more economical.

It is unnecessary to detail the advantages and disadvantages of the lead-acid battery. You are all familiar with its characteristics, and know quite thoroughly what it will do, and likewise its shortcomings. Considering the lead-acid battery as a standard, what comparative features of the so-called new systems have given rise to the renewed and intensified interest in these batteries? The nickel-cadmium system is, of course, no stranger and has maintained a relatively strong competitive position for many years. It has several attractive features, among which are long cycle life, good charge acceptance, sealability, and the ability to withstand abuse. While these desirable characteristics are offset to a great extent by its cost and low energy-weight and volume ratios, nonetheless in certain applications its advantages are such as to make it the logical choice. No practical system today can match the energy-weight and volume ratios of the silver-zinc battery. It is also characterized by excellent high rate capability and it is susceptible to ready operation in the sealed condition. High cost and short cycle life, however, preclude its widespread use except in those very special applications, chiefly military usage, wherein weight and volume are of overriding importance. The silver-cadmium cell is in general similar to the silver-zinc. It is superior to the latter in cycle life, but because of a lower cell voltage the energy-weight ratio is less.

The positions which the leading types of batteries have established in the market are shown in Table III. Primary cells have been included in the table in order to indicate the extent of the packaged power field covered by this general type of cell. The dividing line which differentiates between primary and secondary batteries is indeed a broad, grey area. Recent developments in primary batteries have produced successful rechargeable cells, or secondary batteries. Likewise, certain types of activated silver-zinc batteries may be considered as primaries, while sealed secondary batteries have been produced in the past few years which are marketed in the primary battery field.

If we are to consider any of the rival systems as possible replacements for all or even a significant part of the lead-acid production, because of any superior electrochemical performance, then let us consider the availability of materials. Shown in Table IV are the figures on national and world production of metals used in batteries in 1959. From these figures may be deduced some interesting conclusions. If it is assumed, for example, that but 30% of the lead used in lead-acid batteries enters into the electrochemical reaction in the cells,--the remainder being utilized for grids, posts, connectors, and "inactive" active materials,--the amount of lead used annually in the United States for the electrochemically active component of lead-acid batteries would be 30% of 380,700, or 114,200 tons. Taking into account the difference in densities between lead and cadmium, the Faraday capacities, and the fact that cadmium is used only in the negative plates, it is determined that 31,000 tons of cadmium would be required annually for batteries to replace the lead-acid type. This requirement for batteries alone represents about three times the world's annual production, or more than seven times the annual output in the United States. Similar considerations apply to nickel and silver. Battery usage is so widespread today that any system to be widely used must utilize only those materials which are plentiful.

So far, we have considered the challenge to the lead-acid battery posed by only electrochemical systems which are generally considered as storage batteries. There is also a challenge from other systems which, although not considered as storage batteries, are capable of fulfilling many of the same requirements for portable packaged power. These include nuclear batteries, thermoelectric cells, air or gas depolarized cells, small rechargeable alkaline cells in dry cell configuration, and the gas battery or fuel cell.

Nuclear batteries offer a great potential but the development of high rate, high energy-density, inexpensive batteries must await the development of new knowledge. For the foreseeable future, the nuclear battery will have application as a high-potential source, but will be seriously limited in rate performance, watts per pound, and cost. Thermoelectric cells, used for the conversion of heat energy to electrical energy, are merely a new approach to an old problem. The technical art in this field is still undeveloped and currently the systems suffer from low efficiencies, low energy-density figure, and cost. When fully developed, its applications will be chiefly in stationary generating equipment where, because of efficiency limitations imposed by the thermal cycle, it will meet stiff competition.

Remarkable progress has been m in the past ten years in the development of a practical fuel cell. of the reported fuel cell work done to date involves the use of hy , or mixtures of hydrogen and hydrocarbon as the fuel, and oxyge he oxidizer. While most of the interest in fuel cells is focused on its use as a power generating source, it has considerable potential, when utilizing carbonaceous fuels, as a chemical reactor producing both power and a useful by-product. Likewise the fuel cell electrode system is readily adaptable to use in chemical processing. Other features of the fuel cell make it very attractive to certain military applications, ranging from submarine propulsion to auxiliary power units in space satellites, and silent power sources for ground use.

In considering the impact of a practical fuel cell on the lead-acid battery market one must keep in mind the fact that a fuel cell is in fact an electrochemical battery wherein the "active materials" are stored externally to the cell and are capable of being fed continuously thereto. In other words, it is a battery capable of continuous discharge for extended periods of time. Consider therefore that the fuel cell consists of two major components--first, the "active materials" or fuel and oxidant, and second, the assembly of catalytic electrodes, fuel and oxidant handling systems, and product disposal system, electrical connections, electrolyte, and container. This second component I will term the "reactor." Hence, regardless of the watt-hour capacity of the unit there is a definite fixed weight and volume attributable to the reactor. This in turn is directly related to rate and voltage. The fuel cell is therefore at a decided disadvantage, weight and volume-wise, when applied to uses wherein the demand for continuous power supply is of relatively short duration. A comparison of the energy-densities versus duration of continuous discharge for storage batteries, fuel cells, and solar converters is shown in Figure I. From this figure it is evident that the theoretical hydrogen-oxygen fuel cell employing fuel storage in the solid state to reduce weight will have a lower watt-hour per pound rating than will a sealed silver-zinc battery when the duration of continuous power demand is less than six hours. Compared to the lead-acid battery the cross-over point is slightly in excess of one hour. For the solar converter in 100% light the values are 10 hours and 1.5 hours respectively.

There are many possible types of fuel cells, varying in complexity as well as efficiencies. And just as in the case of batteries, no one type will best fulfill all applications. The more complex types will in general be best suited to fixed installations while the simpler ones will have more use in portable units. At the present state of the art, it is extremely difficult to predict the economic factors. Yet, to gain widespread use the fuel cell must be economically competitive with other systems and, because of the great increase in efficiency possible in such a system, I am confident that eventually it will be not only cost competitive but will result in significant economic advantages.

There has been a great amount of publicity relative to the fuel cell--publicity which has aroused widespread interest and excitement, and has resulted in many very extravagant claims. I think that perhaps the underlying reason for all this may be attributed to the glamour attached to the name "Fuel Cell." Unfortunately, few of the claims can be substantiated by factual data on actual performance. To evaluate the possible challenge to the lead-acid battery posed by the fuel cell one must keep in mind the two points which I have already mentioned--viz., that a fuel cell is just another battery which, first, is capable of long sustained discharge periods; and second, for short periods of discharge it is at a decided weight and volume disadvantage compared to the conventional type secondary batteries. Consequently, I believe that the fuel cell will in general create its own markets as an extension of battery application rather than as a replacement.

I don't mean to imply that the fuel cell to which I have just referred is just around the corner. Such a cell is many years away, and a tremendous amount of work in research and development has yet to be done before such a system is developed to the point where it may fulfill the role I have predicted. However, in view of today's technological climate and the confidence characteristic of science and engineering, the fact that such a cell is theoretically feasible constitutes sufficient incentive to insure eventual success.

In 1859 Gaston Planté wrote, "The secondary electromotive force obtained with lead plates in water, acidulated with sulfuric acid, was greater and persisted longer than that of other combinations." A hundred years of battery development work, on which has been built a giant industry, has failed to upset that statement. I believe that for many years to come the lead-acid battery will continue to maintain its position in the storage battery field.

TABLE I Energy Densities of Common Battery Systems
100 AH Size

Battery Type	Voltage Per Cell: Open Circuit	Voltage Per Cell: Av. Voltage	* Energy Density for 12 V Battery: No. of Cells	whr/lb	whr/in^3
LEAD-ACID					
Aviation	2.1	1.9	6	13.1	1.0
Ironclad	2.1	1.9	6	13.1	1.35
Automotive	2.1	1.9	6	15.0	1.3
NICKEL-CADMIUM					
Pocket	1.28-1.30	1.2	10	11.0	0.6
Sintered	1.28-1.30	1.2	10	11.5	0.88
NICKEL-IRON					
Tube Type	1.5	1.2	10	10.6	.92
SILVER-ZINC	1.86 On higher plateau 1.58 On lower plateau	1.55	8	85-100	3.0
SILVER-CADMIUM	1.[illegible]0 On higher plateau 1.12 On lower plateau	1.06	11	50-75	2.5
O_2-H_2 FUEL CELL (Dry Chem. Fuel Storage)		0.7	16	≈120	

*Based on Room Temperature Discharges at the 10 hour rate

LIA19284

C. G. Grimes

The Challenge by
New Battery Systems

TABLE II Comparison of Battery Systems
100 AH Batteries - 12 V

Battery Type		Est. Life	Est. Initial Cost	Cost Year	Cost Cycle
LEAD-ACID	Constant Potential recharge or stepped current recharge in 5-10 hours				
Automotive		300 cycles 3 years	$ 40.	$ 13.	13 ¢
Industrial		5-10 years 1600 cycles	$ 70.	$ 9.	4.3 ¢
NICKEL-CADMIUM	Recharge at Constant Potential 7-8 hours				
Pocket		10-20 years 2000 cycles	$ 150.	$ 6.	7.5 ¢
Sintered	Vented cells can be recharged in 2 hours. Sealed cells can be recharged in 10 hours. Require no water.	10-20 years 3000 cycles	$ 300.	$ 20.	10 ¢
NICKEL-IRON	Charge at Constant Potential in 6-7 hours				
Tubular		15-20 years 2000 cycles	$ 130.	$ 7.5	6.5 ¢
SILVER-ZINC	Recharge at Constant Potential in 4-20 hours	1 year 200 cycles	$ 800.	$800.	400 ¢
SILVER-CADMIUM	Recharge at Constant Potential in 4-20 hours	2-3 years 500 cycles	$1000.	$400.	200 ¢

TABLE III Estimated Battery Sales in the United States - 1959

LEAD-ACID	NICKEL-CADMIUM NICKEL-IRON	SILVER-ZINC	PRIMARY CELLS
$625,000,000	$20,000,000	$18,000,000	$150,000,000
Including more than 30,000,000 automotive batteries valued at approximately $400,000,000.	Including a large number of hermetically sealed cells of the button type.	Mostly for military purposes.	Comprising about 1-1/2 billion units mostly of the LeClanche type and about 300,000 hearing aid batteries (HgO/Zn) valued at $30,000,000.

TABLE IV 1959 Production Figures for Battery Metals (In Short Tons)

	LEAD	NICKEL	CADMIUM	SILVER	ZINC
USA Production	239,400	11,600	4,300	800	417,000
World Production	2,420,200	309,000	10,000	7,900	3,071,000
USA Use	1,091,100	112,700	7,000	4,900	933,800
USA Use for Storage Batteries	380,700	500	100	120	25,000*
Percentage of Total Use	34.9	0.4	1.4	2.5	2.7
Average Price ($ per lb)	0.122	0.74	1.40	13.30	0.115

*Including dry cell batteries.

LIA19287

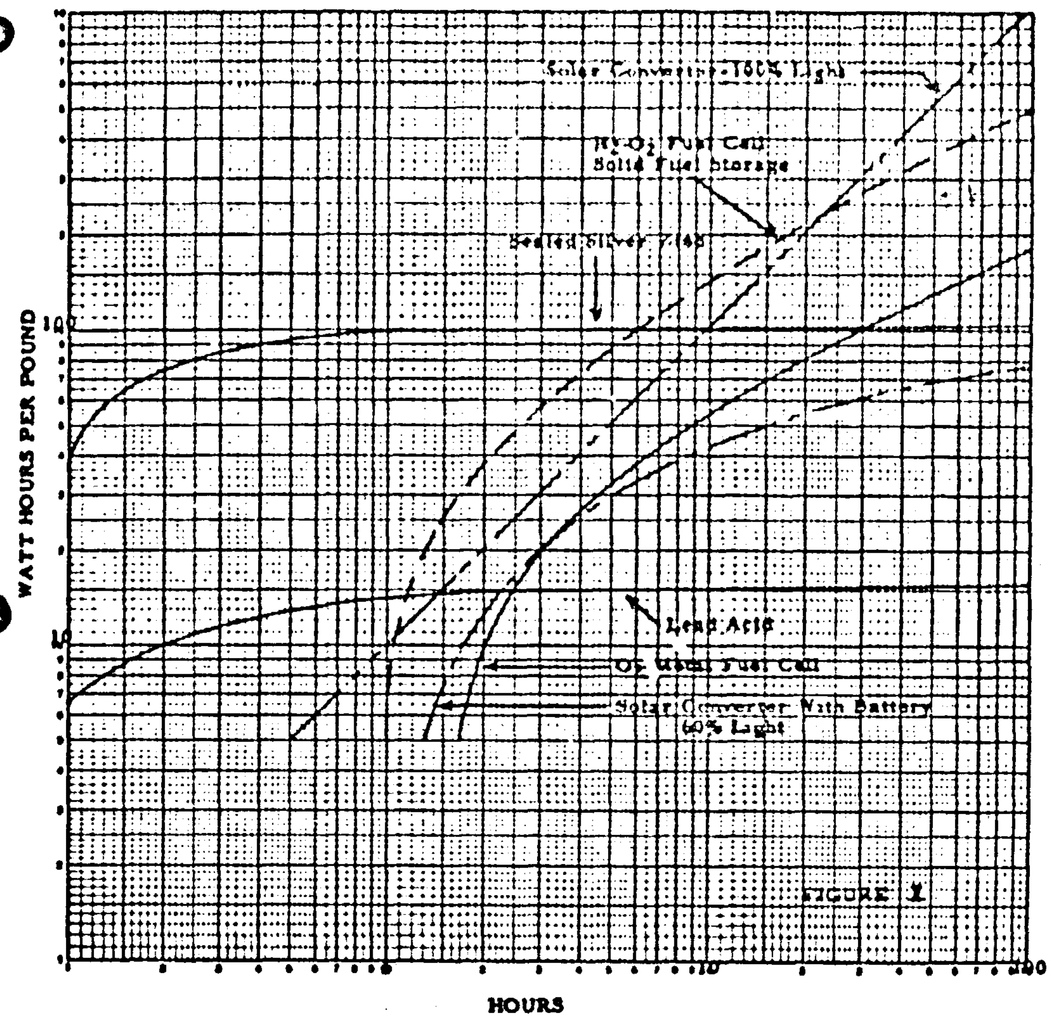

FIGURE 1