POWER SOURCES

11

Edited by

L. J. PEARCE

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RESEARCH AND DEVELOPMENT IN NON-MECHANICAL ELECTRICAL POWER SOURCES

Proceedings of the 15th International Power Sources Symposium held at Brighton, September 1986

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FOREWORD

Power Sources 11 is an edited record of the papers presented at the 15th Power Sources Symposium held at the Metropole Hotel, Brighton from 8th September to the 11th September 1986. Nearly 350 delegates from 27 nations attended the Symposium. For the first time in these symposia a poster session was staged. An edited record of the posters is included in this book.

An informal discussion chaired by the Editor and supported by keynote speakers (John Broadhead, Geoffrey Cooper, David Rand and Philip Reasbeck) set out to try and determine what directions research and particularly applied research programmes could or should be following in order to meet the likely demands of users one or two decades hence. The open discussion ranged over the disparate views of representatives from users, manufacturers and research institutions, one Australian speaker even resorting to the use of a 'far-seeing crystal ball' to aid projections. The only point which clearly emerged from the debate was that finding the 'winning way' to meet market needs for more energetic, more powerful, cheaper and more reliable power sources will remain as elusive as it is now. Hence these needs will only be met by broad-fronted, strong, research and development programmes.

Ray Goodyear is now retiring from the Symposium Committee after many years of valuable service. I would like to express my thanks to him and to all the other members of the Committee and the professional officers for their help in producing and bringing the 15th Symposium to a successful conclusion.

Finally, and most importantly, my thanks go to the authors of the papers and also of the posters whose efforts before and during the Symposium created for it such a sound and effective basis.

Admiralty Research Establishment
Poole
February 1987

L.J.P.

THE FRANK M. BOOTH AWARD

The Frank M. Booth award, established in 1970, is named after the founder of the Symposia. It takes the form of an engraved silver medallion and is presented in recognition of outstanding contributions to the advancement of Power Sources both technically and in furthering the effectiveness of the Symposia.

Previous recipients of the award have been:

Dr M. Barak Dr P. Reasbeck Mr A. L. Taylor	1960/70
Mrs Jeanne Burbank	1970
Dr J. F. Laurent	1972
Dr M. I. Gillibrand	1974
Mr D. H. Collins	1976
Prof. H. R. Thirsk	1978
Dr P. Ruetschi	1980
Mr M. J. H. Lemmon	1982

The 1986 award was made to Dr J. P. Gabano of SAFT (France) and to Professor F. L. Tye of Middlesex Polytechnic, formerly of the Ever Ready Co., to mark their distinguished work over many years in the field of primary batteries. Both have made many contributions in the form of papers since the 4th Symposium. Besides his acknowledged expertise in Leclanché and related battery fields, Frank Tye also served for a number of years on this Symposium's organising committee: Jean Paul Gabano is of course, well known for his work on lithium systems.

Dr. J. P. Gabano and Professor F. L. Tye.

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THE IMPACT OF GRID COMPOSITION ON THE PERFORMANCE ATTRIBUTES OF LEAD-ACID BATTERIES

Richard T. Johnson and John R. Pierson

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ABSTRACT

The emergence of a market for 'Maintenance Free' automotive batteries over the last ten years has resulted in a variety of approaches to the reduction of water loss and the enhancement of battery performance. Using non-antimony grid alloying elements to obtain ultimate protection from water loss has had the effect of sacrificing several benefits attributable to the presence of antimony in the positive grid and active material. As a result, the ability of the electrochemical system to survive in an increasingly hostile vehicle environment is compromised to gain protection from a relatively insignificant failure mode.

INTRODUCTION

The trend of internal combustion vehicles toward lighter weight, greater space utilisation and improved fuel efficiency, when combined with stringent emission requirements, has increased starting battery electrical capacity needs while creating simultaneously a deterioration in the battery operating environment. Recent changes in vehicle option content toward greater quantities of electrically powered accessories, combined with key-off loads of up to 60 mA are producing greater depths of discharge for the battery. Presently available electronic fuel, ignition and suspension management, electrically heated rear windows and windshields, and antilock braking systems, along with high volume heater/air-conditioner fans and radiator cooling fans for transverse mounted engines have forced vehicle electrical system designers to fit alternators capable of outputs in excess of 100 A. Future use of electrically powered steering, brakes, navigation aids and possibly coolant pumps will result in further increases in alternator capacity and battery depth of discharge. Vehicle size reduction combined with emission and fuel efficiency requirements in the US have also brought about smaller, hotter engine compartments resulting in higher battery operating temperatures. It is within this context that the Maintenance Free or any battery must exist and be evaluated.

Maintenance Free batteries were introduced into the US original equipment market over a decade ago with the intent of reducing the battery service required of the vehicle operator. This was a small part of an overall vehicle maintenance reduction goal and consisted of reducing water electrolysis rates and diminishing self-discharge rates. Additional motivation for some battery manufacturers was streamlining grid and plate making processes to increase production efficiency and reduce cost. In either case, manufacturers usually replaced antimony, the traditional grid alloying element of choice, with calcium. Some manufacturers used lead-cadmium-antimony and lead-tin-strontium alloys for limited periods.

The effects of non-antimonial positive grid alloys on battery performance and life characteristics are significant, and range from improvements in low temperature discharge power to reductions in service life. Historical information and recent experience with the use of non-antimony grid alloys points to a variety of differences in operational characteristics between batteries containing non-antimony grids and those with antimony alloy grids. These differences also hold true between 'non-antimony' batteries and the more recently introduced hybrid batteries, wherein the positive grids contain a lead-antimony alloy and the negative grids use a non-antimonial alloy, typically lead-calcium or lead-tin-calcium.

BATTERY RELIABILITY AND FAILURE MODES

Depth of discharge, discharge frequency and current density, recharge current and voltage, and operating temperature have been postulated as the most significant environmental factors affecting the wearout or life of the active material. The classic degradation mechanisms centre around the active materials and current carrying grid members. According to a number of literature sources (Simon and Caulder, 1975; Dawson *et al.*, 1979; Pavlov and Bashtavelova, 1986), the positive active material tends to change structure with repeated charge/discharge cycling from an agglomerate network or skeleton covered by small crystallites to a coralloid or crystalline form retaining little network character. At some point the crystals become either electrochemically inactive or detached from the agglomerate and are electrically isolated from the remaining portion of the skeletal structure or are swept away by gas or liquid convection. The negative material (Simon *et al.*, 1974) requires organic lignin expander and $BaSO_4$ to alter the discharge product morphology and prevent the growth and combining of individual crystals into a dense, low surface area structure having low capacity. Both active materials can form large $PbSO_4$ crystals and show reduced capacity (Bode, 1977) under a number of conditions such as operating at elevated temperature, operating continuously at low states of charge and standing in a discharged condition.

Positive grid corrosion and grid growth are also life limiting degradation phenomena. Literature abounds on these subjects (Bullock, 1979; Bullock and Tiedemann, 1980; Bullock *et al.*, 1983; Devitt and Myers, 1981; Kelly *et al.*, 1985; Mahato and Strebe, 1985; Simon, 1967; Valeriote, 1981; Valeriote *et al.*, 1984; and others). Oxidation of the grid metal to PbO or PbO_2 within the pasted plate has been shown to be a function of temperature, electrode potential, electrolyte concentration, grid composition and grid microstructure. Growth or elongation of grid wires has also been found to be dependent upon the same parameters, but in addition, it is dependent upon grid geometry and the creep properties of the grid alloy. Elevated tin concentration in the Pb-Sn-Ca positive grid, usually used to improve recharge capability, has been shown to increase the grid growth rate, as has the fine-grained wrought structure used in some expanded metal grids (Willhite *et al.*, 1980; Valeriote, 1981; Devitt and Myers, 1981).

Failure Mode Field Studies

A study (Hoover, 19[illegible]) of battery failures in the continental USA was presented to the Battery Council International which separated 'standard' and 'maintenance free' batteries into failure mode groupings. Although some of the 'maintenance free' batteries used low ($\leqslant 3$ weight %) antimony grids, overall conclusions can be drawn based on the identification provided by construction. First, average life of the 'maintenance free' (MF) batteries was less than the 36·7 months achieved by the standard batteries. The data showed a range of average lives depending upon the specific MF battery construction: 33·4 months—inaccessible, envelope separators, cast grids; 31·9 months—inaccessible, envelope separator, expanded grids; and 28·2 months—inaccessible, leaf separator, cast grids. Investigation into specific failure modes indicated that MF batteries had significantly higher percentages in the 'open circuit' and 'short circuit' modes. The category 'worn out', which contained low level (water loss) failures, while comprising 30·3% of the standard batteries evaluated, also showed the greatest average time to failure—50·4 months. No information was provided on water addition, but estimates of the frequency of battery maintenance are generally low for accessible electrolyte designs, particularly with the advent of self-service gasoline fuelling stations in the US.

After removing 23·5% of the 2215 batteries in the Hoover study from the sample because they were serviceable or physically broken or damaged, the most significant failure mode was poor plate condition, i.e. overcharge, paste adhesion and shedding, sulphation, and grid corrosion. Over 41% of the remaining standard batteries and 37% of the MF batteries fell into this category at average times to failure of 38·9 months and 27·5 months respectively. The 'worn out' category resulted in percentages of 30·3% at 50·4 months for standard batteries and 13·2% at 43·1 months for MF batteries. The next two most common reasons for failure were open circuits and short circuits, both reported to be 14% for standard batteries and 25% for MF batteries and having a relatively narrow range of 27 to 30 months to failure. Loose plates, broken straps, broken intercell connections, loose terminals and cell-to-terminal breaks made up the specific modes for open circuit failures. Shorting failures were classified as plate to strap shorts, plate to plate shorts, mossing shorts, separator shorts and vibration shorts. Within this group was the primary mode of failure for the sealed, enveloped, expanded grid products i.e. plate to strap shorts. Overall, it is felt the survey supports a hypothesis of failure mode shift brought about by 'maintenance free' material and construction changes.

A field reliability study conducted by Johnson Controls, Inc., during the period 1978 through 1982 also gave evidence of failure mode shift. The study placed over 70 000 batteries into service in four southern cities of the USA (Phoenix, Arizona; Las Vegas, Nevada; Dallas, Texas; and Altanta, Georgia) and covered three design variations; non-antimony grid batteries with filled-polyethylene envelope separators; low antimony (2·75% Sb) grid batteries of conventional leaf, 50% glass fibre/50% cellulose fibre separator construction; and hybrid (2·75% Sb positive, non-antimony negative) grid batteries of leaf, 100% glass fibre separator construction with added separator overlap on top, bottom and sides. All battery grids were book-mold, gravity cast and all batteries permitted electrolyte access. Since the programme was carried out in the replacement market, the vehicles were typical of the late-1970's vintage and prior. Few non-domestic and front wheel drive vehicles were included and, as a result, battery operating temperatures were lower than would be expected from a sample of more current vehicles. Part of the programme consisted of

TABLE I SOUTHERN US FIELD STUDY. BATTERY RETURN RATE AS PERCENTAGE OF SHIPMENTS FOR SELECTED FAILURE MODES. BATTERY AGE 0–30 MONTHS

Reason for return or failure mode	Battery return rate as per cent of shipments		
	Low Antimony	Hybrid	Non Antimony
Grid corrosion	0·94	0·43	10·56
Overcharge	0·61	0·56	0·21
Low level	0·44	0·15	0·04
Discharged/undercharged	0·89	1·64	0·90
Separator related	6·70	0·78	0·85
Other	11·1	11·4	11·4
Serviceable			
Damaged			
Mechanical defect			
Total returns	20	15	24

surveying vehicles and batteries for a one week period in Phoenix, Arizona as they were brought in for service. The average battery electrolyte temperature was 49°C when the maximum daily ambient temperature was in the order of 39 to 41°C. The maximum recorded electrolyte temperature was in excess of 70°C.

The data (Table I) showed positive grid corrosion to be a failure mode at a level of 0·43% of shipments for the hybrid batteries, 0·94% for the antimony batteries and 10·56% for the non-antimony batteries. Corrosion of the non-antimony positive grids proceeded intergranularly (Fig. 1 a) and antimony grids, uniformly (Fig. 1 b). Overcharge was present as a failure mode in 0·61% of antimony battery shipments, 0·56% of hybrid battery shipments and 0·21% of the non-antimony battery shipments. Low level (water loss) failure rates were 0·44% for antimony batteries, 0·15% for hybrids and 0·04% for non-antimony batteries. Although the data followed the expected trend, no quantitative conclusions can be drawn from the water loss failure rates because of electrolyte accessibility. Batteries found to be discharged or undercharged made up 0·89%, 1·64% and 0·90% of shipments for antimony, hybrid and non-antimony batteries respectively. The data also indicated that separator related failures of the hybrid and non-antimony batteries were comparable in rate at 0·78% and 0·85% of shipments, compared to 6·7% for the antimony batteries.

Perspective on the magnitude of all of these percentages can be obtained from the total rates of return after two and one-half years, which were approximately 20%, 15% and 24% for antimony, hybrid and non-antimony batteries respectively. All three groups exhibited the same ~11% return rate for all other reasons for return, including serviceable, physically damaged, or mechanically defective. Percentage returns as a function of time in service (Fig. 2) display similar rates of return for hybrid and non-antimony through the first 5–8 months whereas subsequently the grid corrosion of the non-antimony batteries accelerated their rate of return beyond that of the hybrid. The return rate of the non-antimonial product exceeded the return rate of the low antimony product at the 22 month point.

WEAROUT FAILURE MODES

The following is a list of typical modes of battery wearout other than mechanical design and manufacturing related failures:

- Undercharged/discharged
- Overcharged
- Positive paste shedding
- Grid corrosion
- Grid growth shorts
- Mossing shorts
- Separator shorts
- Discharged negative material
- Loss of negative capacity
- Polarization on recharge
- Water loss