

Metal-air Batteries

Developments in primary and secondary cells

Every two years since 1958 the Joint Services Electrical Power Sources Committee has sponsored a symposium in Brighton, devoted to research, design, development, production and use of electrical power sources (other than rotating machinery). The sponsoring committee includes representatives from the Ministry of Defence, Department of Trade and Industry, Government Communications Centre, Post Office, Atomic Energy Authority, N.R.D.C. and British Rail, and amongst other things, co-ordinates research and development on sources of electrical power in Government establishments, universities, and the industry. Of this year's record attendance — nearly 500 delegates — the majority were from abroad, with sizeable contingents from East Europe and Japan.

In our previous reports of these symposia, developments in well-known sources of electrical energy have been featured — lead-acid, alkaline (e.g. nickel-cadmium) and metal-halide secondary batteries, Leclanché and other primary sources, as well as fuel cells, solar cells and thermoelectric sources. Little was reported on the subject of metal-air cells, especially in rechargeable form, so this time we attempt to redress the balance.

Although the first zinc-air primary cell was demonstrated nearly a century ago, it is only recently that high-current-density air electrodes have become available as a result of fuel cell development. The cell can be thought of as derived from the Leclanché cell which it will be recalled, uses manganese dioxide as oxidizer at the cathode. It was in 1878, in fact, that L. Maïche replaced the manganese dioxide with pulverized catalyzed carbon to form the first air-depolarized cell. Zinc-air cells also resemble alkaline cells, which use potassium hydroxide as electrolyte, again with the mercuric oxide or manganese dioxide replaced by an air-breathing cathode.

Early air-depolarized cells could be discharged at high rates and had energy densities of over 200Wh/kg, but suffered from both low storage life and low active life due to water evaporation from the electrolyte. Life could be increased by adding water or electrolyte to the cells before, and during, use but there was still the disadvantage of the high cost of air electrodes, mainly due to the expense of catalysts used. A mechanically rechargeable cell was consequently developed, recharged by replacing anodes and electrolyte, but costs were still

relatively high and there were other problems with this system.

By the end of the 1960s cells were developed using low-cost catalysts in the air cathodes and the feasibility of making sealed cells had been demonstrated. And by 1972 sufficient progress had been made, especially in active life, to make commercial production feasible.

Thus the stage was set for the production of high energy and power density throw-away cells ideally suited to small motorized equipment (tape recorders, toys, shavers) and to communications equipment, pocket paging, and hearing aids. Applied to the portable transistor radio, the low internal resistance of the cell allows operation to a lower terminal voltage than with conventional cells.

Work on producing commercial cells is under way at Crompton Parkinson Ltd and at Energy Conversion Ltd. The Metair cells made by Energy Conversion are now in production in the R1 or N size. These have a capacity of 1.3Ah with a current rating of 150mA, at which rating energy density is 260Wh/kg. Discharge time at a current of 55mA is around 25h for comparison, the equivalent mercury-zinc cell would have a discharge time of around 6 hours. Production of further sizes is planned — R6 or AA size with a nominal capacity of 4Ah at 350mA, R14 or C size with a nominal capacity of 10Ah at 750mA and R20 or D size with a nominal capacity of 22Ah at 1.6A.

An important factor in zinc-air battery design is the need to ensure sufficient air access to the cathode areas. (A current of 100mA requires an air supply of 1.75cm³/min.) In these cells therefore the cathode is outermost with the anode inside, in contrast to the common Leclanché cell arrangement. The air-breathing cathode is made from a catalyzed nickel mesh with an hydrophobic layer of p.t.f.e. around the outside. Apertures in the cathode allow hydrogen evolved due to self-discharge at the anode to pass. (This self-discharge is kept to a minimum by amalgamation of the zinc with 2% by weight of mercury.)

The zinc anode is made from compacting electrolytic zinc with a high surface area to form a hollow porous cylinder, the amount of zinc determining cell capacity. The anode is wrapped with separator/electrolyte (KOH) material, effectively insulating it from the cathode. A porous paper membrane, to distribute the air over the cathode surface, and an air reservoir lie between the cathode and

plastics case. The advantage of this arrangement is that additional air can be provided to the cathode when high current pulses are demanded. The cell is protected by a plastics container and laminate film to minimize the diffusion of oxygen, water vapour and carbon dioxide into the cell, whose effects reduce storage life. Results of storage tests carried out at 20 and 40°C were 95 and 87% retained capacity respectively after 6 months storage. Active life — the time during which a useful discharge can be obtained after removing the cell from its container — has been dramatically increased for low-rate cells over the past two or three years, and at 0.6mA the cells would operate continuously for 12 weeks.

Metal-air secondary systems

The promise of the metal-air secondary system is electrical power at a competitive cost to, and at a higher energy density than, lead-acid batteries. A paper enticingly called 'A zinc-air battery for electric vehicle applications' turned out to be a negative report on the possibility of using the zinc-air system as a rechargeable battery. The target, based on experience with a lead-acid powered vehicle, was a peak battery power of 45kW (for a vehicle of 2,500kg total weight and payload) to give a traffic compatibility comparable with a 950-kg payload petrol or diesel-engined delivery vehicle (i.e. an acceleration of between 20 and 35s to 70km/h) with a battery weight of 25% of total. This implied an energy density of 110Wh/kg and a peak power density of 75W/kg (65kWh and 45kW peak from a 600kg battery).

The problem in air electrodes in metal-air secondary systems is that they must be capable of cathodic conversion of oxygen in the air during discharge while allowing anodic evolution of oxygen during recharging.

The first disappointment in this paper came in getting the required air electrode performance (a current density of 4kA/m² at 30kN/m² air pressure or 5kA/m² at 50kN/m²) together with the required resistance to damage under anodic-cathodic cycling conditions. The author, D.S. Adams of Joseph Lucas Ltd, felt this to be incompatible with the prevention of shorting in the zinc electrode. During discharge zinc dissolves into the electrolyte and is not deposited back on the electrode in the same shape it had before discharge. Zinc dendrites form

leading to internal short-circuiting. Other problems — water loss in the air and battery heating — as well as battery cost seem to put this one out of court. (Battery cost was estimated at £20 to £25 per kW of peak power plus £1 to £2 per kWh, 1970 prices.) These problems led to the conclusion that further investment in this source for this application was not justified.

Against this pessimism is to be balanced the optimism in a paper by S. Hattori and colleagues at Yuasa Battery Co., Japan. Their new cell design is claimed to avoid cell short-circuiting in zinc electrodes.

A third (nickel) electrode for charging is placed outside the air cathode and the discharge anode and on the anode side. During charge the electrolyte with zinc ions is circulated between cathode and adjacent electrode and the charge current flows from the third electrode. Almost all the zinc is deposited on the air-electrode side and even with charging at 4kAh/m² short circuits have not occurred.

Oxygen evolved during charge does not come into contact with the air electrode, avoiding deterioration. As the additional electrode is not used during discharge and the electrolyte circulates along both sides of the zinc anode all the zinc is cleared away so the zinc deposit is similar every cycle. There are still problems to be investigated despite this hopeful possibility for cell construction, like additives to minimize the quantity of electrolyte required for charge and discharge, materials for the anode, and electrolyte circulation systems. An energy density of 80Wh/kg might be hoped for in a fully engineered battery but, to quote Dr Adams' reaction, they would be "very hard pressed" to reach this level with current electrode performance.

Air electrodes developed for fuel cells allow cathodic conversion of oxygen but anodic transfer and stresses due to oxygen bubble formation limit lifetime. Unfortunately the solution of introducing a third electrode between the metal and air electrodes, to act as counter-electrode to the metal electrode for oxygen evolution during charging, results in an increase in weight and volume which is not what is wanted in lightweight applications.

An air electrode capable of combining the anodic and cathodic function without its life being limited by corrosion is under investigation at Siemens in Germany for application to an iron-air cell. It consists basically of two layers, one a hydrophilic porous nickel sheet next to the electrolyte (KOH) and the other a hydrophobic carbon layer (with filler, binder and silver) next to the gas phase. The hydrophobic layer is similar to the single layer oxygen electrode used in fuel cells, also has an additional layer of sintered p.t.f.e. on the gas side. The hydrophilic layer forms a gas-stop layer during reduction, or discharge, and evolves oxygen during charge with the help of a catalyst. Although both materials must be resistant to corrosion, the materials on the gas side do not have to meet this requirement,

which extends the range of materials to choose from. The gas-side layer is evidently protected from oxygen bubble stresses.

The most recent work reported at Brighton has achieved an increase in carbon activation by "gas treatment", eliminating the need for the additional silver catalyst. Unfortunately, the corrosion current increases dramatically for air and CO₂ treatment, and NH₃ treatment, which does not alter the corrosion current appreciably, only increases electrode potential by 50mV — still some way off the silver-coated potential. A limited coating of silver (200g/m²) improves this by a further 50mV. Work has shown that current densities of 150A/m² can be achieved — that needed for a peak output of 27.5kW (8.5kW continuous) estimated for a car of 1000kg and 2m/s² acceleration — with an iron-air battery using small-area electrodes.

Tests are being made now with larger electrodes (100cm²) making contact with the nickel layer rather than the carbon and using half as much silver (an economically "feasible" quantity), but so far poor connection between carbon and nickel layers has prevented meaningful results being obtained.

The widespread use of porous electrodes of course is to increase efficiency by increasing surface area, which can be thousands of times greater than the superficial area. A way of getting even greater surface area is to use a fluidized "bed" of small particles, by circulating electrolyte with a pump. Improved operating characteristics should be obtained as well because the diffusion rate of reaction products is increased with this fluid flow.

Particle agglomeration

A problem with such electrodes has turned out to be agglomeration of the particles during charging. Gillibrand, Gray and Gudger (Electric Power Storage Ltd) have developed an optical technique for observing this phenomenon and constructed an experimental perspex cell containing KOH and ZnO as electrolyte and a quantity of copper-coated glass particles 200μ in diameter. A fascinating film showed that a short time after applying a constant current, the particles became attached to the feed electrode and agglomerated; a little later zinc was seen to be deposited onto the particles. At higher fluid velocities, particles still stick together, though not to the feeder wire. Reversing the current separated the particles.

The zinc deposit was shown not to be responsible for this when the experiment was repeated without the ZnO in the electrolyte. Other electrolytes were tried, but this agglomeration occurred in both alkaline and acidic cases (but not in the case of a neutral solution of potassium sulphate). Spheres coated with a non-metal (carbon) showed no sign of this phenomenon at first, but when zincate was added to the electrolyte, agglomeration

again occurred, suggesting that a metal-to-metal bond was responsible. No agglomeration was found with nickel or cobalt-coated particles.

The theory put forward for this is that of a very weak cold weld, formed at roughly the potentials at which the element would only be stable in the unoxidized state. Particles which were partially oxidized would weld together after a short delay, when presumably the oxide had been electrochemically reduced to metal. Two anomalies to this theory are the failure of nickel and cobalt to agglomerate — the authors suggest that the surfaces may not be completely oxide-free — and the absence of agglomeration with potassium sulphate.

It might be feasible to break up collections of spheres outside the cell, but sadly the investigation is not being continued.

The next three symposia will be held on 16-18 September 1974, 22-24 September 1976 and 26-28 September 1978 and the first of these, at least, will be in Brighton.

New Battery for Pacemakers

The life of primary batteries is inconveniently short for many applications — an acute embarrassment occurring in the particular case of implanted pacemakers, where there is the need to frequently replace the battery surgically.

In this situation perhaps the most appropriate energy source is a radio activated element, with a long half-life. Plutonium 238 having a half-life of 90 years is used in a new French design. This half-life means an almost constant (down to 92.6%) output for 10 years and it is estimated that about a third of pacemaker patients could use it. (This new source becomes cheaper than conventional electrochemical ones after about 5 years or 2 re-implants, the cost of implanting being three times that for pacemakers using ordinary sources.) The other advantage of this isotope is that it gives out only α radiation in its pure state, which is absorbed by the capsule. Gamma or neutron radiation due to impurities like Pu236 or lighter elements, is reduced to a weak level by refining and by the cladding of several millimetres thickness. (Dose rate at the hotter points of the source is 2.5mrem*/h, being lowered by the surrounding tissue so that in a year the spinal cord receives less than 5 rem.)

Bismuth telluride is the thermoelectric element, the number of thermocouples being chosen to give an on-load voltage of at least 0.5V (the minimum necessary to operate d.c. converters) at the end of 10 years. The generator, called Gipsie, is not designed to have the best possible efficiency: safety, reliability and ageing are the most important factors. In fact, with an output of 0.3mW and an input of about 90mW, efficiency is 0.3%.

* The rem (roentgen equivalent man) is a measure of biological effect, being the product of dose in rad and r.b.e., the relative biological efficiency.