Solar cars and better batteries

When an odd assortment of 23 solar-powered vehicles glided out of Darwin last November on the inaugural World Solar Challenge — a demanding transcontinental race to Adelaide — the electric car moved one step closer to practicality. (Whether it will be 100% solar-powered, or a lesser percentage, depends on which crystal ball you gaze into.)

The clear winner, the General Motors *Sunraycer*, outshone the others with a dust-swirling average speed of 67 km per hour for the 3004-km journey. While the energy for the trip may have been free, the high-tech machine itself cost millions of dollars in advanced developments. It used high-efficiency gallium arsenide solar cells, a small powerful motor incorporating high-strength neodymium–iron magnets, lightweight construction, and an innovative aerodynamic design that earned it the name 'flying cockroach'.

Batteries for *Sunraycer* were expensive silver–zinc types, which possess high storage capacity and light weight. Good on you, General Motors!

But let's not forget the other competitors in the race, 11 of which made it to Adelaide at speeds ranging from 45 km per hour (an 8-day trip) to a sedate 11 km per hour (that's a gruelling 32 days on the road). It may come as something of a surprise to learn that half of the entrants used the familiar lead–acid battery, the origins of which go back more than 100 years.

It doesn't surprise Dr David Rand, an electrochemist at the CSIRO Division of Mineral Products, and official scrutineer of batteries for the World Solar Challenge. (For a description of what that entailed, see the box on page 12.) He is leading a research team looking into ways of improving the performance of lead–acid batteries, and he sees good prospects for squeezing considerably more ampere-hours from — and multiplying the cycle life of — that heavy block that sits almost forgotten under your car's bonnet.

Indeed, the failure of the much-promised 'alternative' batteries to enter the market has led to a widespread renaissance in lead–acid usage. It's hard to beat lead–acid for inexpensive reliable performance, and manufacturers of batteries and producers of lead are now supporting research and development to try to keep that advantage.

The energy output of present lead–acid batteries is less than half that theoretically attainable, so there's ample scope for improvement. Dr Rand's research, directed towards that end, is in fact partly sponsored by the battery and lead industries (about 60% of the world's lead production ends up in batteries).

New applications and new types are appearing. We now find lead–acid batteries providing back-up power for computers, driving portable tools, levelling the load of electric utilities, storing wind- or solar-generated electricity in remote homesteads,

An unlikely-looking assortment of solar-powered vehicles.

Scrutineering solar racers' batteries

Scientists from the CSIRO Division of Mineral Products played a key role in last year's World Solar Challenge — a race for solar-powered vehicles from Darwin to Adelaide along the Stuart Highway.

Race regulations stipulated that only energy from solar panels (maximum size 4 × 2 × 2 m) could propel the unlikely looking racing cars. Drivers set out at 8 a.m. each day, and pulled to the roadside, wherever they were, at 5 p.m. Solar-derived electricity could be stored in batteries, but everybody's solar panels had to be covered from 7 p.m. until 6 a.m.

To maintain keen competition, the organisers decided to allow replacement, in the event of malfunction or accident, of the whole or part of each vehicle's battery pack with healthy fully charged equivalents. This presented them with the major problem of how to formulate an effective and universal penalty for battery replacement.

Without it, competitors could gain strategic advantages during periods of overcast skies or head winds, and on hill climbs or the final stages of a day's racing. Such action would have boosted vehicle performance by, in effect, injecting fossil-fuel energy. The problem was exacerbated by allowing competitors to use different battery technologies.

The development of a simple, fair, and easily enforced battery-replacement regulation taking all factors into account was a tricky task. Nevertheless, Dr David Rand devised a regulation that effectively neutralised all the perceived opportunities for gamesmanship. The regulation demanded that vehicles be held by the roadside for a set period in the event of battery failure.

Dr Rand, assisted by his colleagues Mr Warren Baldsing and Mr John Hamilton, conducted pre-race scrutineering of the vehicles' battery packs and calculated the respective time penalties based on battery energy density and the number of whole (or part) replacements. To determine the performance of exotic batteries they used the Division of Mineral Products' battery-testing facility.

The CSIRO team followed the vehicles down the track and were on hand to adjudicate in times of crisis. There was only one instance of complete battery failure. The main problem for the racers was maintaining adequate charge during the unexpected bad weather on days 3 to 5.

As the diagram shows, *Sunraycer*'s superior performance put it ahead of the dark clouds, rain, and hail that afflicted the others, and that forced nine teams to retire.

Spirit of Biel might have come second if it hadn't lost 4 hours in an unfortunate right-of-way accident involving an Alice Springs motorist (for which the Swiss received an infringement notice) on day 5.

The table shows the final race positions, together with the type of battery each used.

How they finished

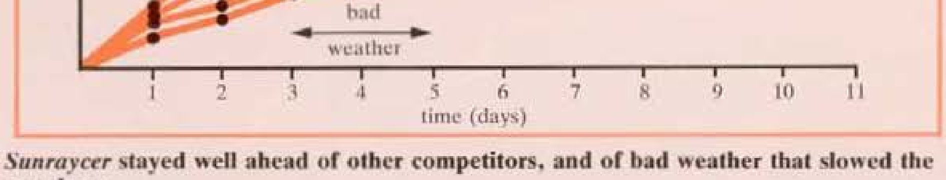
position	team	car	preliminary speed test (km per h)	battery type	time h	time min	average speed (km per h) for 3004 km
1	General Motors	*Sunraycer*	113	silver–zinc	44	54	66·92
2	Ford Motor Company	*Model S*	80	silver–zinc	67	32	44·63
3	Ingenieurschule Biel	*Spirit of Biel*	71	silver–zinc	69	58	42·94
4	Australian Geographic Team Marsupial		85	silver–zinc	81	26	36·90
5	Darwin I.T.	*Desert Rose*	35	silver–zinc	95	27	31·48
6	Chisholm I.T.	*Desert Cat*	67	lead–acid	98	12	30·60
7	Solar Resource Syndicate		42	lead–acid	117	05	25·64
8	Crowder College	*Star*	52	silver–zinc	-	-	-
9	Massachusetts I.T.	*Solectra IV*	-	silver–zinc	-	-	-
10	Sonderborg Teknikum	*Chariot of the Sun*	31	lead–acid	150	35	19·95
11	F. Castino and D.E. Lajovic	*Alarus*	-	lead–acid	146	27	20·51
12	Hoxan Corporation	*Phoebus II*	49	silver–zinc	153	31	19·57
13	Morphett Vale H.S.	*Photon Flyer*	29	lead–acid	189	04	15·89
14	Semiconductor Energy Laboratory	*Southern Cross*	-	lead–acid	279	21	10·75

The remaining 9 vehicles retired from race

The World Solar Challenge was a 3004-km race from Darwin to Adelaide. Five days after the winner finished, placings of cars that had not yet reached Adelaide were determined according to the distance travelled.

Control, selection, and performance of batteries in the 'World Solar Challenge'. D.A.J. Rand, W.G.A. Balsing, and J.A. Hamilton. *Electric Vehicle Development*, 1988, **7** (in press).

How the field stretched out



***Sunraycer* stayed well ahead of other competitors, and of bad weather that slowed the rest down.**

and of course, helping solar-powered vehicles along.

This article will look at some of the recent advances in lead–acid battery performance, in particular those that are likely to bring closer the day when electric cars, with solar panels on their roofs, take their place on the showroom floor. By the way, it may provide a few pointers to those who fancy entering the 1990 World Solar Challenge. We'll also look at some newly emerging uses for lead–acid batteries.

Miraculous workings

If you were to undertake a post-mortem on that (miserable) thing that finally failed to start your car, you would find two series of plates (positives and negatives), in various states of integrity, immersed in sulfuric acid. When a battery is fully charged, the positive plates comprise lead dioxide, and the negative plates spongy lead (no wonder they're heavy). As the battery discharges, both sets of plates convert to lead sulfate, a process that reverses upon charging.

That seems pretty simple, but the wonder is that it works at all, since lead sulfate is an insulator! Despite a century of chemical investigation, we still have many mysteries left to plumb, as we shall see.

Battery-makers jealously guard their formulas, and add a wide variety of secret ingredients to the traditional 'bubble and squeak' recipe. The basic process involves coating a paste of active materials onto a lead alloy casting (this is the skeleton your battery autopsy reveals, and it acts as a grid to collect electrical current). The all-important paste is largely 'grey oxide', a mixture of about three parts lead monoxide (PbO) and one part fine lead powder, mixed with sulfuric acid and water.

The trick is to form a plate that — although the active materials have good porosity so that acid can reach much of the mass and undergo electrochemical reaction — retains adequate rigidity and cohesion to withstand bumps and jolts in service.

In addition, the plate material, as the battery charges and discharges, undergoes changes in volume as it shifts back and forth from one chemical form to another. Maintaining the integrity of the positive plates, (particularly during deep discharge) is difficult, and softening and shedding of the positive plates is a major cause of battery failure.

Another effect is an increasing reluctance for the lead dioxide material to reduce to lead sulfate. In sum, the electrical conductivity of the plates suffers a progressive decline and the battery loses power — your car engine won't turn over.

Realising this, battery-makers continue to search for better 'glues' that will keep the positive plate intact. Ironically, though, many of them take for granted the basic 'curing' stage that is intended to bond the paste materials together, Dr Rand finds. Curing involves heating the plates in ovens (typically in a high-humidity atmosphere at 60°C for a day or more). Research by CSIRO has confirmed that curing involves complex and critical chemical transformations, but it's invariably the least-controlled stage of manufacturing.

The winner, *Sunraycer* (the 'flying cockroach').

Battery scrutineers for the event, the CSIRO team, 'mind' the World Solar Cup. Left to right, Mr Warren Baldsing, Dr David Rand, and Mr John Hamilton.

Large temperature differences often exist between racks of plates within a curing oven, and Dr Rand's investigations have shown that these can cause wide variation in plate composition. This results in a performance mismatch between the cells comprising a battery, and hence shortened battery life.

When it's closely controlled, curing can create preferred types of chemical species, crystal shapes, and degrees of porosity. It involves the reaction of polycrystalline forms of lead oxide and lead with sulfuric acid, water, and oxygen: this creates long interlocking crystals of certain lead sulfates. The original crystal shape tends to be retained throughout the life of the battery.

For starter batteries, it's best if you buy a battery that has been cured at around 50°C. At this temperature, crystals of tri-basic lead sulfate ($3PbO.PbSO_4.H_2O$) tend to form; these are smaller than other sorts, and so they have enhanced surface area and, consequently, greater electrical capacity.

But for use in electric cars (traction batteries), where deep-discharge is the norm, the cycle life increases if larger crystals of tetra-basic lead sulfate ($4PbO.PbSO_4$) are formed. Curing temperatures above 80°C are conducive to this result.

The difference in performance due to crystal type is not just academic; CSIRO research has found that different curing processes can alter the cycle life of an electric vehicle's battery pack by a factor of seven.

Dr Rand and his colleagues Dr Roderick Hill and Dr Ron Woods obtained cured plates from five Australian battery companies. They formed these plates into identical batteries and tested their cycle lives under simulated electric-vehicle use.

To find out why the batteries' performances differed so markedly, the researchers developed a special X-ray diffraction technique that could distinguish the various crystalline phases of the plates, at both the beginning and the end of battery life. They also used a scanning electron microscope and a neutron diffraction instrument.

They found that a key factor governing battery life was the ratio of *alpha* lead dioxide (α–PbO_2) to *beta* lead dioxide (β–PbO_2) in the cured plates after these had been 'formed'.

'Formation' is the last step in the manufacturing process, and essentially involves charging the cured plates so that their constituents change into lead dioxide (positive plates) and spongy lead (negative plates). Plates with tetra-basic lead sulfate as the major cured component mostly yield α–PbO_2 after formation into positive plates, whereas plates formed mainly from tri-basic lead sulfate tend to give β–PbO_2.

Increasing the operating temperature of some traction batteries to scalding point improves their electrical capacity.

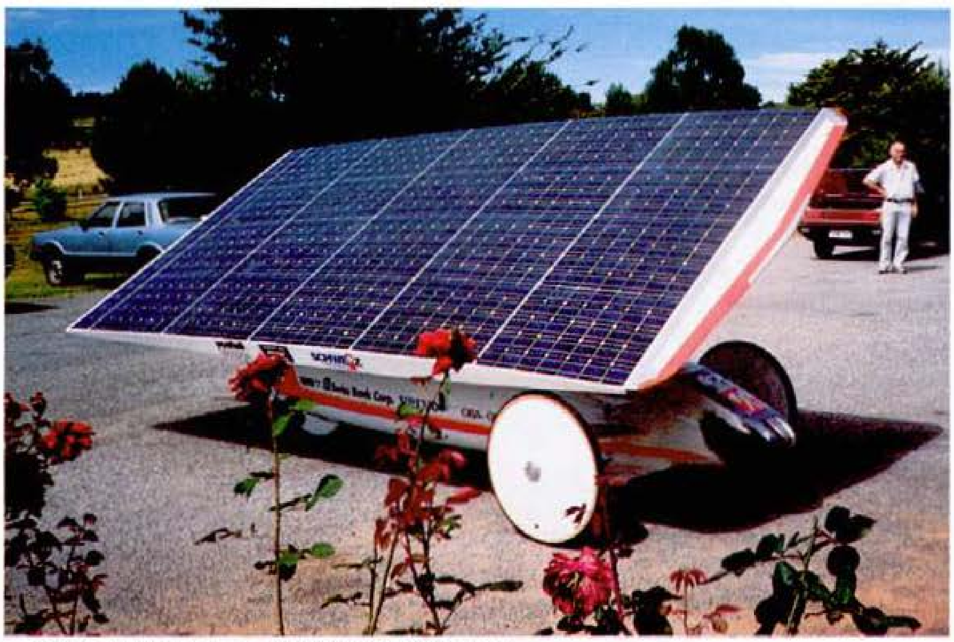
The graph demonstrates the importance of getting the right mixture of crystal types at the start of a battery's life. As you can see, to obtain the longest service life under deep-discharge conditions, you need a ratio of α–PbO_2 : β–PbO_2 close to 0·8.

One of the long-unsolved mysteries of lead–acid batteries was why this initial specification carries through to affect the life of the battery, for the simple chemical fact is that, during the first discharge, α–PbO_2 forms lead sulfate, which upon recharging forms β–PbO_2. Within the first few cycles the α:β ratio rapidly falls to about 0·1–0·2 and stays there for the rest of the battery's life!

Recent CSIRO research has provided the answer. Electron micrographs reveal that, regardless of the conversion from *alpha* to *beta* crystal forms, the interlocking needle-like structure of *alpha* persists, giving the plate material strength and rigidity.

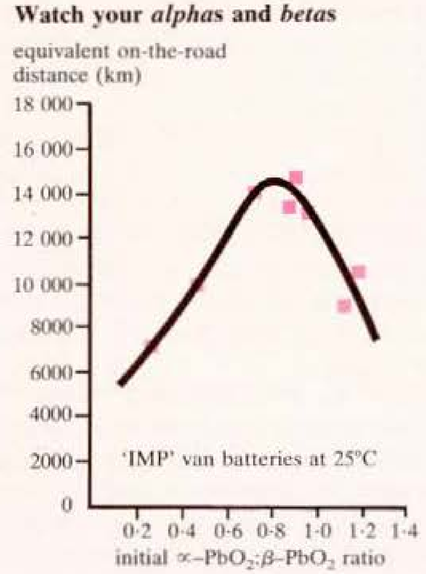
Production managers in battery factories have now acknowledged that they need to closely specify the crystal phases of the positive plates, and so many Australian and overseas battery companies have heeded the message of the CSIRO research and make use of X-ray diffraction equipment.

Ford's *Model S* came second...



...and the Swiss *Spirit of Biel* was placed third.

Watch your *alphas* and *betas*



Some like it hot

Another avenue for boosting traction battery performance comes from an unexpected direction — heat treatment.

Battery lore has it that elevated temperatures are detrimental to performance and life. Indeed, this is especially true where batteries are prone to corrosion of the positive grid. Nevertheless, the CSIRO scientists have found that the lore can be turned

Laboratory tests simulating electric van usage showed that, for optimum service life, the batteries' plates should start life with an *alpha:beta* ratio of lead dioxide crystals close to 0·8.

on its head when batteries are built with thick dense plates.

In this situation, they discover that carefully increasing the operating temperature to 60°C (scalding hot!) improves the batteries' capacity to store electrical energy by about half. And it can extend, by up to five times, the distance a set of batteries can propel a vehicle before they need replacing.

These results depend on a battery's rate of discharge, but they suggest that developing a safe and reliable regulator of battery temperature could be a good way of significantly improving, at a single stroke, the performance of an electric vehicle.

The researchers undertook this particular investigation after failing to find any published data on how temperature influences the performance of batteries operated under conditions typical of such vehicles.

At the Division they used computer-controlled test equipment to subject batteries to charge and discharge behaviour that mimicked the standard driving profile set down by the Australian Electric Vehicle Association. They controlled the batteries' temperature by using water baths, which they could set anywhere between 25°C and 70°C.

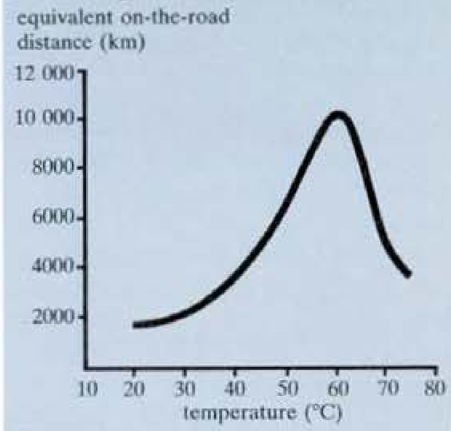
They found a large variation in how well individual batteries, even from the same manufacturer, responded to higher temperatures. Nevertheless, on average, batteries showed about a 2% increase in capacity for each 1° rise in temperature (up to at least 50°C).

As for service life, the graph shows how much longer the batteries lasted at 60°C. A battery that could withstand about 100 charge and discharge cycles at 25°C could see out close to 300 cycles at the higher temperature. Together with the increased capacity per cycle, this means that, with judicious heating, a set of batteries could drive a 'Battronic' electric van (average current 112 amps) about five times further than normal before they 'died' (that is, their storage capacity became unacceptable).

Under less severe discharge conditions, such as those imposed by an 'IMP' electric van (a more advanced design using an average current of 46 amps), operation at 60°C improved the service distance by a factor of about two.

Note that at 40°C performance shows only a marginal improvement, so hot days don't help much at all. Clearly, an automatic precise regulator of battery temperature would be very desirable. However, this would not be simple or cheap, since it would also need to incorporate ways of

How temperature affects battery life



The service life of a set of lead–acid batteries, expressed as the distance it could propel a 'Battronic' electric van, proved five times greater at 60°C than at 25°C.

preventing undue evaporation of the hot acid.

But perhaps such a device isn't necessary. A surprising finding to emerge from the tests was that high temperatures can rejuvenate an ailing battery. After reaching the end of its useful life at 25°C, a battery could be run at 50°C for almost as long as a fresh battery!

The finding that may make a battery-temperature regulator unnecessary is that a single high-temperature cycle may be enough to extend a battery's life considerably. However, more experiments are needed to quantify the effect.

Why does elevated temperature improve performance? It seems that the way the plate materials are utilised is improved by operation at 50°C. Different parts of the active plate materials are reworked by cycling at different temperatures — in effect, part of the material utilised at one temperature is 'rested' during operation at the other. Elevated temperature also seems to slow down the rate at which the positive-plate material softens and falls off.

Other investigations are planned to establish whether temperature cycling during a battery's manufacture may confer lasting benefits on its performance in the outside world.

As a footnote, Dr Rand warns people against trying to improve their normal batteries by heating them. Hot acid is dangerously corrosive, and hydrogen evolved from batteries is explosive.

Take out; put back

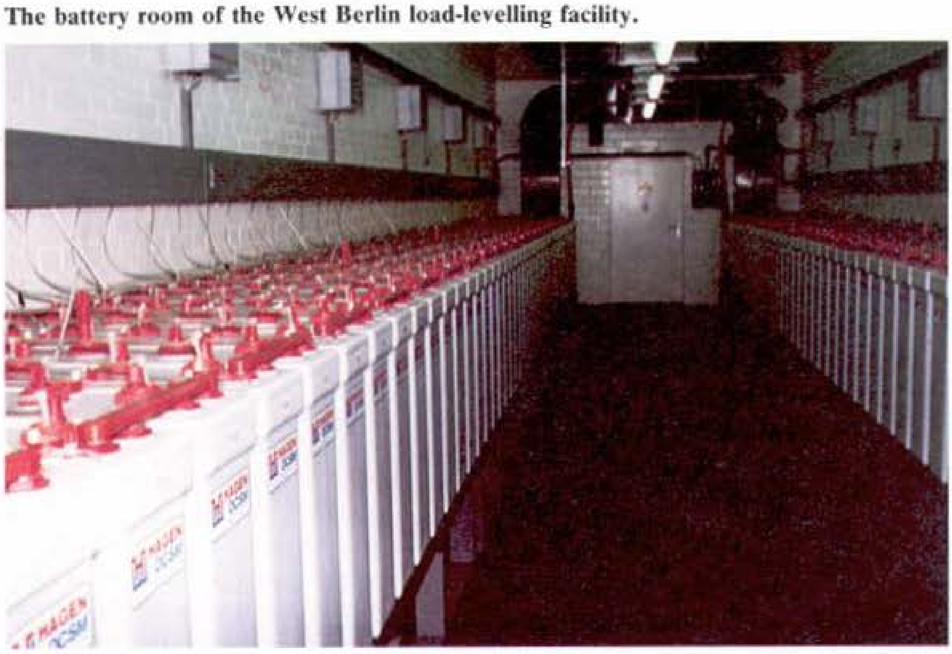
Most modern electric vehicles are equipped with regenerative braking — a facility whereby a vehicle's kinetic energy can be recovered and returned to the batteries when the driver is slowing down or going down hill. Instead of wasting the energy in the brakes, the vehicle's motor is operated in reverse, as a generator.

Obviously, a battery will be able to propel a vehicle further under such circumstances — a 15% extension of range is typical. But even neglecting this consideration, CSIRO tests have shown that the very act of using regenerative braking extends the batteries' performance.

Under typical electric vehicle conditions, it appears that regenerative braking by itself increases cycle life by about 15% and brings about an additional 15% improvement in the equivalent number of kilometres the vehicle can travel.

In another modern design feature, electric vehicles now employ solid-state switches to control their speed. Instead of exerting a continuous current drain, these devices turn the full battery current rapidly on and off. The speed of the vehicle then

The battery room of the West Berlin load-levelling facility.



Batteries in the power-supply grid

Imagine 250 000 car batteries strung together, and you get some idea of the storage capacity of the world's largest battery, which, at time of writing, was due to begin operating at Chino, California, in June this year.

The $US13 million demonstration facility, with a peak power output of 10 MW and a storage capacity of 40 MWh, is intended for load-levelling within the electricity grid of the Southern California Edison Company. It will supply power to satisfy peak demands, and soak up cheaper off-peak power at other times.

In many ways it's like pumped hydroelectric schemes, with similar advantages, but it isn't burdened with their stringent environmental and topographic requirements. You can site one in the middle of a metropolitan load centre (it's clean and quiet) and construct it in short order — less than 2 years. You can change its capacity to meet new requirements by adding (or taking away) batteries.

Electrical supply engineers like such facilities because they're fast-acting, making it easy to provide continuous and stable supply. A battery can be called on instantaneously to step in for a failed generator.

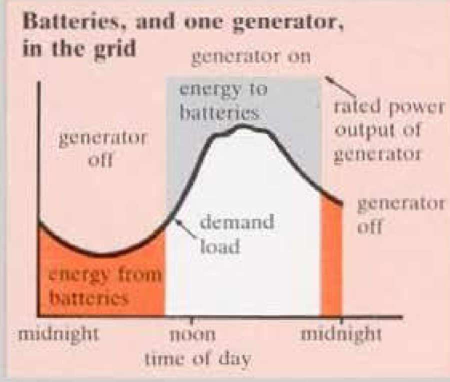
The maintenance-free batteries used at Chino had specifications calling for a life of 8 years and 2000 cycles of 80% discharge. Altogether, they required 2500 tonnes of lead. According to the American-based Electric Power Research Institute, 1 million tonnes of lead could be in use for load-levelling in that country by the year 2000.

As it happens, lead–acid batteries were used to store surplus electricity early this century, when electrical power was distributed as direct current. They disappeared when the 'new-fangled' AC took over. Now, with efficient solid-state converters, batteries are back. Efficiency of conversion from AC to DC and back to AC is about 75–80%.

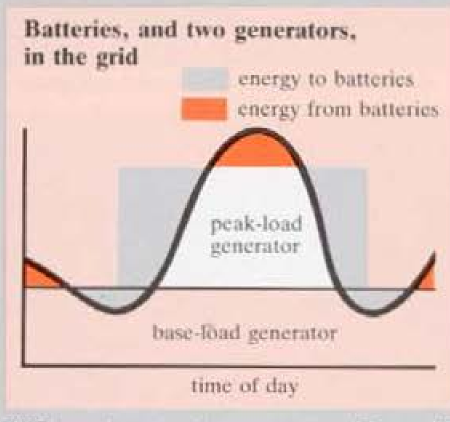
In Japan, a 1-MW load-levelling battery began service in September 1986 and is still operating well. Battery life seems to be about 3000 cycles.

In West Berlin, an 8·5-MW facility has been working since January 1987. Isolated from the East German grid, the West Berlin supply needs a lot of 'spinning reserve' (emergency back-up power) to cope with demand fluctuations and 'forced outages' of generators. This the battery system provides without fuss, and four more similar installations are planned.

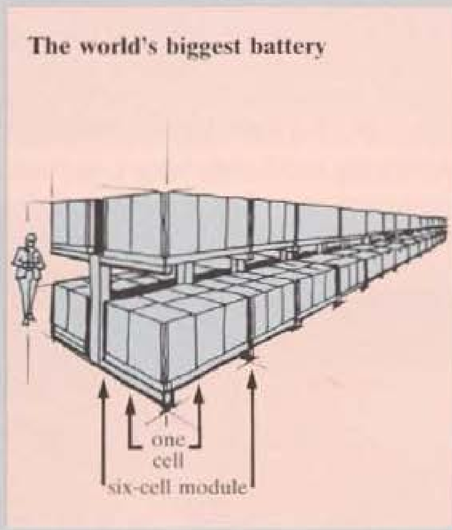
What a battery system can do for electricity suppliers it can also do for those consumers who are charged for their peak kW demand per month (most factories are in this boat). An emerging trend, in North America particularly, is for factories to install their own load-levelling batteries on the 'customer-side of the meter' (CSOM). A recent 600-kWh unit installed in Milwaukee, U.S.A., saves its owners $US5400 a month in power-supply charges.



How an isolated electricity grid, with a single generator, would use a set of batteries to improve efficiency. The batteries are charged during times of peak demand.



With two (or more) generators, grids would use batteries to help supply the peak load. A similar load-levelling scheme could be employed on the 'customer side of the meter' by industrial consumers so as to reduce their bill for peak load drawn.



The recently installed load-levelling battery at Chino, California, is the biggest in the world. Its 8256 cells can provide 10 MW for 4 hours.

On the local scene, the Australian Lead Development Association has commenced a study, initially in collaboration with the CSIRO Division of Construction and Engineering, of the Australian potential for load-levelling batteries.

Australia has a large number of small isolated grids, often with a single diesel generating set that has to meet a widely fluctuating load.

Dr Pratish Bandopadhayay and Mr John Mahoney, of the Division, conducted a survey of medium to large electricity suppliers in remote regions. Given the respondents' typical operating circumstances, the CSIRO researchers calculate that battery storage would need to cost no more than about $300 per installed kilowatt to just save the grid operator money (given a cost of diesel of 50 cents per litre).

Currently, they are likely to cost three times that figure. However, the costing of the battery system does not include other, uncosted, benefits such as improving supply stability and reserve capacity.

Battery systems considered here, with a single generator, would operate quite differently from the installations overseas. The battery would be charged during peak periods, and the battery would supply power during off-peak times, when the generator would be put on stand-by.

Why? It's to do with two factors: a single generator has (necessarily) a generating capacity in excess of peak demand, and its operating efficiency is best at high output and poor at low. Load-levelling would mean that the generator's efficiency at peak period would be impaired, and the extra fuel consumption incurred would outweigh some improved efficiency at off-peak times.

But charging the batteries at peak period is within the generator's capabilities, and allows the generator to be switched off at off-peak times when its efficiency would be low.

Of course, with two or three generators, or CSOM use, batteries would take on the task of load-levelling. The CSOM function appears to be the most economic application, with a system saving money even if it cost as much as $1200 per kW to install, according to the researchers.

One day soon, you may switch on an appliance and be unaware that the current it draws comes from a battery.

Batteries for isolated homesteads

If, like some 12 000 rural properties right now, yours can't get connected to mains power, you will have to generate your own electricity. You'll need a diesel generator and, to improve its efficiency and achieve continuous availability of power, a set of batteries.

But what sort of batteries, and how many? What is the optimum storage capacity for a given average load? The picture is complicated when you add a wind generator or an array of solar cells to the equation.

Commercial suppliers of remote-area power-supply systems (RAPS) rely on experience and educated guesses, but in the absence of adequate information they tend to adopt a conservative approach and usually make the battery bigger and more expensive than it need be.

Nevertheless, the battery is still the weakest component in any RAPS system, according to Dr Rand, and a trouble-free service life of more than 3 years is rare. Most batteries dislike being left in a discharged state for days at a time, as RAPS batteries tend to be. (Why go to the trouble of starting up the noisy generator when there's still some charge left in the batteries?)

Clearly, we need a long-life battery specially designed for RAPS use. For this reason, the battery-maker Pacific Dunlop is working with the CSIRO Division of Mineral Products to design a purpose-built RAPS battery.

As the first stage in the process, the scientists are putting the full range of currently available batteries, and some prototypes, through life-cycle testing to see which type performs best. With funding from NERDDC, testing is in progress right now, and already a number of batteries, principally the maintenance-free types, have failed.

The simulated duty cycles under which the batteries are being tested were developed in conjunction with Dr Ronald Zmood of the Electrical Engineering Department of the Royal Melbourne Institute of Technology and Mr Brian England of Powerstore Pty Ltd, a RAPS-system supplier.

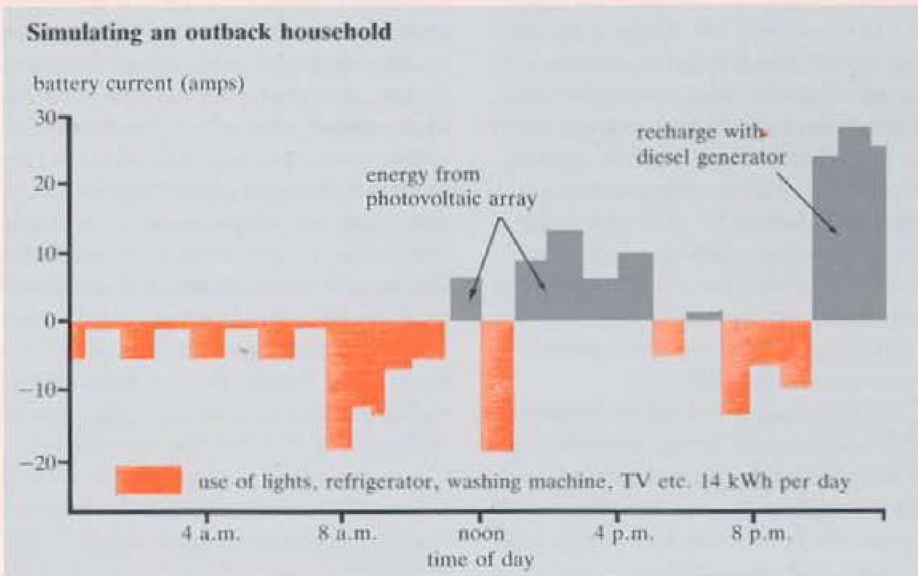
The duty cycles simulate the activity of two typical families — one with refrigeration (14 kWh per day) and one without (9 kWh per day). Both obtain renewable energy from a photovoltaic array, which is slightly under-sized, so that topping up with a diesel generator is required (daily, or every week). At present, more than 30 batteries comprising 14 types are under test using one of the specified schedules.

Solar cells have been chosen instead of a wind generator because their supply of energy is more regular and predictable. The CSIRO scientists assumed, for simplicity in testing, an unvarying daily energy supply.

It's still too early to draw clear conclusions about which batteries are best for RAPS use, except to say that maintenance-free types don't appear suitable.

Development of lead/acid batteries for domestic remote-area power supplies. D.A.J. Rand and W.G.A. Baldsing. *Journal of Power Sources*,1988, **23** (in press).

The CSIRO researchers adopted this representative profile of current flow in and out of a RAPS battery for their lab tests. It simulates how an isolated household would consume electricity. It's a punishing schedule for batteries, as they are recharged daily from 80% discharge.



depends on the average number of short current pulses that the batteries are called on to deliver per second.

Battery scientists have long debated whether pulsed or continuous current was kinder on the battery pack. Does the short rest the pack experiences between pulses make up for the heavier current drain when the switch is demanding full power?

The CSIRO scientists have done tests to examine the matter, and the simple answer is — it doesn't make much difference at all one way or the other.

Antimony antinomy

Among the lead–acid brigade in the World Solar Challenge, six teams opted to use 'maintenance-free' types — that is, batteries that don't require periodic topping up with distilled water. Because topping up is a fiddly job that is often neglected, use of maintenance-free batteries is increasing rapidly.

Two teams favoured a maintenance-free battery recently developed in Australia — the Pacific Dunlop 'Pulsar' — even though it is designed for starting cars rather than propelling them.

Because of novel construction, current in the Pulsar is collected along the whole vertical length of each plate — significantly decreasing resistance losses and increasing power output. Its manufacturers claim a 50% weight reduction compared with conventionally constructed batteries.

These factors might have contributed to the good performance of the Chisholm Institute of Technology's *Desert Cat*: this sleek vehicle was the first of the lead–acid types to finish (in sixth place).

Another maintenance-free battery, the Gates recombinant-electrolyte cell, proved popular, with three of the competitors using it. Perhaps they were influenced by recently published CSIRO studies showing that these batteries can give good cycle life under deep-discharge conditions — remarkable for a maintenance-free design.

Under conditions equivalent to urban use of an 'IMP' van, the Gates 'Cyclon'

Exchanging the battery pack of an electric van.

gave an exceptional performance, producing more than 1400 cycles — enough to drive the van some 180 000 km! No other battery CSIRO has tested has come close to it, suggesting that the Cyclon technology, if it can be scaled up (it uses a unique 'Swiss roll' construction to give a single 2-V cell), has enormous potential for electric cars.

However, part of the price of long life is a reduced energy density — the Cyclon battery was heavier, per ampere-hour, than those of other entrants. The other problem is that it uses a pure lead grid to achieve its maintenance-free property.

This raises the problem of the 'antimony-free effect' that most battery-manufacturers are struggling with. Maintenance-free batteries, which rely on an absence of antimony to avoid water loss, are liable to fail under the deep-discharge conditions imposed by an electric car.

For years, batteries have been made using lead–antimony alloys for the grids. Some 3–6% antimony improves the grids' hardness, corrosion-resistance, and strength. The problem with antimony is that it promotes 'gassing' — the electrolytic decomposition of water into hydrogen and oxygen.

The battery-maker's answer has been to use calcium instead of antimony. Calcium's more favourable electrochemistry means less opportunity for gassing. In 1986, lead–calcium batteries were fitted in 94% of the new cars sold in the United States.

Although mechanically robust, and good for starter-motor cranking, lead–calcium batteries still fall short in giving adequate service life under deep-discharge conditions. Without antimony present, increasing numbers of lead sulfate crystals obstinately refuse to revert to lead dioxide upon recharging. So the positive plates become insulated with irreversible lead sulfate, shed material, and lose capacity. The 'antimony-free effect' has struck.

The same problem afflicts both the original 'maintenance-free' types and those truly free of maintenance, the recent completely sealed variety (of which the Cyclon is a prime example). The demand for these new 'immobilised electrolyte' or 'recombination' types is increasing at a great pace. Totally free of maintenance, and of any acid leak or spray, they can be discharged and charged in any position.

You can now find them in portable equipment such as video cameras, television sets, compact-disc players, and toys. They are being used for stand-by power in computer systems, emergency lighting set-ups, and medical monitoring instruments.

Completely sealed batteries have now entered the car-starting market, and some are appearing in fork lifts, golf carts, and wheel-chairs.

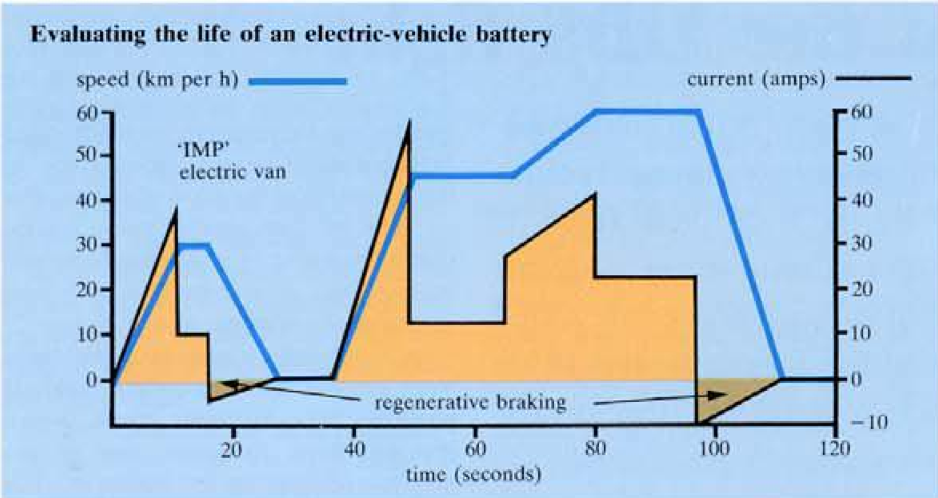
Unlike the electrolyte in normal 'flooded' types, the sulfuric acid within an 'immobilised electrolyte' cell is not free to move. It is held in either a wad of glass fibres or a gel. In addition, the positive plates contain a smaller amount of active material than the negative plates (a 'positive-limited' design).

As a result, the positive plates become fully charged first. Further charging then liberates oxygen from water at the positive plates, which diffuses through the bound electrolyte to the negative plates where it reacts with sulfuric acid to form lead sulfate and — can you guess? — water.

The lead sulfate so formed ensures that the negative plates never become fully charged and that no hydrogen is evolved. Rather, water continually undergoes a transformation from liquid to oxygen and back again.

But this neat solution does have a drawback: it's better for a battery to have a deficiency of active material on its negative plates ('negative-limited') than on its positive ('positive-limited'). In this way, the positive plates are subjected to a reduced depth of discharge and given protection from material instability prob-

Battery life was automatically tested in a thermostatically controlled water-bath.



The profile reflects the current an 'IMP' electric van would typically demand of a battery when covering a standard 1-km stretch of city roads. The CSIRO researchers counted how many times the battery could do this, between rechargings, before failing.

lems created by volume changes during charge–discharge cycling.

Alas for completely sealed batteries, tests by CSIRO have confirmed the advantage of the negative-limited design. The service lives of negative-limited experimental cells far exceeded those of positive-limited ones when all the other factors were the same.

Hints and hopes

So our longed-for maintenance-free battery suitable for electric-vehicle use still eludes us. Somehow we need to overcome the 'antimony-free effect'.

In an effort to do so, Dr Rand and his colleagues have been asking: what's so special about antimony? Recent investigations, sponsored by AM&S Metals Pty Ltd, have given no clear answer, but a few hints have emerged.

In particular, Dr Hill has found that the compound $PbSb_2O_6$ forms as a result of grid corrosion, and by virtue of its molecular structure helps to keep the grid together. It has a graphite-like structure that may, through slippage of layers, help reduce mechanical stresses created during charge and discharge. This slippage holds back the formation of large cracks that may cause plate material to fall off.

Another hint comes from the observation that $PbSb_2O_6$ resembles the structure of α–PbO_2, but not that of β–PbO_2. Thus, the presence of antimony in this form may encourage the formation of α–PbO_2, a species that, as we have seen, plays an important part in conferring mechanical strength to positive plates and extending their cycle life.

Mysteries there are, but events like the World Solar Challenge give extra incentive for scientists to solve them.

Andrew Bell

More about the topic

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Prospects for zinc–bromine

The energy crisis of the 1970s brought about a surge of interest in alternative rechargeable batteries, and the zinc–bromine system is still one of the most promising.

In this battery, zinc is deposited at the negative electrode and bromine liberated at the positive. Since zinc and bromine react rapidly, it is necessary to limit the concentration of bromine dissolved in the aqueous electrolyte.

One way of doing this is to lock up bromine in a compound such as one of the quaternary ammonium bromides. This results in a distinct liquid polybromide phase within the electrolyte, and it can be separated off and stored outside the cell. The advantage here is that self-discharge is minimised, and it leaves the aqueous phase low in bromine, necessary for high efficiency.

The polybromide phase is pumped through the cell when power is needed. Such a circulating electrolyte system means that these batteries are best suited to large applications, such as electric vehicles, remote-area power supplies, and load-levelling.

Several prototype zinc–bromine battery systems of this kind, with dozens of cells and tens of kilowatt-hours capacity, have been tested overseas. Two Australian firms, Sherwood Overseas Ltd and ZBB Ltd, both Perth-based, are also actively involved in developing this style of battery.

All these prototypes use lots of plastic. The frames are plastic and the electrodes are plastic-bonded carbon, so the batteries should be cheap when made in large quantities. The chemicals in the electrolytes shouldn't be expensive either.

The system thus promises to be competitive with lead–acid, and would display about twice the energy density. Cycle life has been demonstrated at some hundreds of cycles under deep discharge, with a few reports of units having been cycled more than 1500 times.

At the CSIRO Division of Mineral Products, Dr Keith Cathro and his colleagues have evaluated the performance of several possible zinc–bromine systems, using small single cells. They encountered problems with bromine diffusing too rapidly through separators, with the polybromide phase solidifying, and with short electrode life. However, they did find ways of largely overcoming these difficulties, and Dr Cathro believes that a commercial battery may be no more than a decade away.

No new rechargeable battery has come into widespread use since the nickel–cadmium type about 80 years ago. Perhaps zinc–bromine will be it.

Performance of porous plastic separators in zinc/bromine cells. K.J. Cathro, D.C. Constable, and P.M. Hoobin. *Journal of Power Sources*, 1988, **22**, 29–57.