Submarine battery technology — an aid to electric vehicle battery design?

Norman E. Bagshaw

59 Clement Road, Marple Bridge, Stockport SK6 5AG (UK)

Abstract

Submarine cell technology is reviewed, in order to examine its potential application in electric vehicle batteries. Characteristics covered include mechanical construction, electrical energy densities at various rates, improvements in high-rate performance by increased conductivity, methods of decreasing electrolyte stratification, reducing charge time, use of special alloys to reduce hydrogen evolution and improve charge retention, and heat management during charge and discharge.

Introduction

The largest electric vehicles (EVs) in everyday use are submarines. The early types of electric submarines were hybrids, using a battery for underwater propulsion and some form of engine, e.g. petrol, on the surface. From these early crude types, the modern conventional submarine has been developed which is all-electric, using a battery for propulsion when submerged and a diesel generator on the surface, for both propulsion and battery recharging.

The early submarines used elementary battery technology. For example, in 1901 the first UK submarine [1] — the Holland I — used a 60 cell battery of a Planté type. The positive plates were of the rosette or 'Manchester' type and the negative plates consisted of a lead framework with pastilles of lead chloride reduced to spongy lead. The capacity at the 4 h rate was 1920 A h and the energy density was 8.7 W h/kg.

Modern diesel-electric submarines need high amounts of stored energy and batteries of hundreds of cells, each weighing 500 to 700 kg, are not uncommon. For example, the Oberon class of UK submarine is installed with 448 cells, each weighing 515 kg. The German TR1700 U-boat is equipped with 960 cells, with a total weight of about 500 t.

The special requirements of submarine cells has resulted in some novel developments. With the current renewed interest in electric road vehicles it is an opportune time to examine the characteristics of submarine cells, to see if the technology is applicable. This paper therefore summarizes the requirements of conventional submarine cells and presents some of their design and performance characteristics, with the modern EV in mind.

Submarine cell requirements

Energy and energy density

Submarines are very large electric vehicles and therefore require large amounts of energy. Their batteries are normally rated at the 5 h rate and, for example, the energy required at this rate for a 2000 t submarine is over 7000 kW h. In order to keep the voltage to a reasonable level, this means that large cells of high capacity (8000-9000 A h) are required. Cells of this size might also be used in load-levelling applications but cells of much lower capacity are normally required for EVs.

Since submarines require ballast for submergence, the mass of the battery can be used to advantage. The gravimetry energy density is therefore less important than the volumetric energy density in the submarine application. This is in contrast to the requirements of EV batteries.

Discharge rates

Although submarine cells are rated at the 5 h rate, they have to perform over a very wide range of discharge rates. It is obviously important that the maximum submerged speed is as high as possible and the submarine cell must therefore have a good high-rate performance (high power density), usually measured at the 1 h rate or thereabouts. Because of its size, particular attention has to be paid to conductivity in a submarine cell to achieve a good high-rate performance at an acceptable voltage. EVs also need a good high-rate performance for acceleration in traffic and for climbing steep hills.

However, unlike EV batteries, submarine cells must also have a good low-rate performance (60 to 100 h rates), corresponding to a slow quiet get-away speed or simply to the 'hotel load' when waiting on the bottom of the sea.

Mechanical stability

Some attention has to be paid to the materials of construction. Because of the large size of a submarine cell, strong container materials are required for the cells to be self-supporting. In addition, the design must impart shock-resistant properties to the cell because of the possibility of depth charge attack. In the case of EVs, shock resistance is useful only in the event of an accident, but mechanical vibration resistance is, of course, important.

Electrolyte stratification

Lead/acid cells containing free electrolyte always have a tendency to suffer from electrolyte stratification. This is accentuated in the case of a submarine cell because of its extra height. The problem is also aggrevated when, because of operational requirements, the cells can only be given partial charges with no equalizing charge for a considerable period of time. Although the height of EV cells is much lower, stratification can be a problem if a vehicle is subjected to a regime of opportunity charging, with long intervals between full equalizing charges.

Heat management

In a large submarine cell there is always a potential problem of unacceptable increase in temperature because of heat evolved both on charge and during high-rate discharges. Some method of cell cooling is often needed. Although cells in EV batteries are smaller, their intensive use may also result in high temperatures and heat-management methods may have to be considered.

Gas evolution

In the confined space of a submarine, it is obviously important that, when submerged, hydrogen evolution is kept to a minimum. Special attention must therefore be paid to purity of materials and grid-alloy constituents, to reduce hydrogen evolved during discharge or on open circuit. In the case of EVs, this particular problem does not exist. However, low gas evolution is associated with better charge retention and lower maintenance (topping up), which are useful characteristics for EV batteries.

Durability

The submarine cell has to fulfil what is essentially a cycling duty, although the discharge rate and depth can vary enormously during operation, as can the extent and rate of recharge. The life of a cell is normally measured in years of operation and cells are expected to achieve at least five years. It is difficult to translate this into cycles because of the variability in operation, but a life of 600 cycles is a good approximation.

Design and characteristics of submarine cells

Construction

The dimensions of some common types of diesel-electric submarine cells are given in Table 1. Several of the cells are similar in size with a height of between 1000 and 1100 mm (excluding the terminals, etc.). However, the cells in many German designs, e.g., 209-class, are taller, although the total volume of the cell is about the same as in UK and French types. The cells for the popular Russian-designed Whiskey-, Romeo- and Foxtrot-classes are somewhat larger in volume.

Both flat plate and tubular plate constructions are used, the latter predominating in German designs. In the case of flat plate cells, double separators are used with a glass mat next to the positive plate, to support the active material. Western European cells use fibreglass reinforced resin containers, which are self-supporting.

The large cells used in submarines (with capacities of 8400 to 11 000 A h) may also be useful in peak-lopping or load-levelling installations, but are too big for EVs.

TABLE 1

Typical dimensions of submarine cells

Class	Country	Width (mm)	Length (mm)	Height (mm)
Whiskey	Russian Federation	365	656	1013
Romeo	Russian Federation	365	656	1013
Foxtrot	Russian Federation	365	656	1013
Guppy I	USA	361	451	1079
Daphne	France	360	450	1066
Agosta	France	360	450	1066
Sauro	Italy	379	620	980
Oberon	UK	360	449	1081
Upholder	UK	360	449	1157
205	Germany	310	379	922
209	Germany	290	450	1336

116

Shock resistance

The mechanical construction of a submarine cell must cater for good shock resistance. The most vulnerable components are the plates which must be given maximum protection. In some designs, shock absorbers are incorporated between the bottom of the plates and the bottom wall of the container. Similar shock absorbers can also be used in the top of the cell.

An alternative design is to suspend the plate groups from the high-strength fibreglass cover. The cover has a rubber undersole and the fibreglass container has a rubber lining with a lip which overlaps the top edge. If the cell suffers a mechanical shock, the shock wave is transmitted up the container wall, through the rubber-rubber seal between container and cover and finally to the plates themselves. By this time, the shock has been considerably attenuated.

Obviously, EV batteries are normally subjected to much lower values of mechanical shock and vibration, but similar design principles can be applied if necessary.

Electrical characteristics

Typical performance figures for a modern submarine cell are shown in Table 2 for a cell of weight 520 kg and volume 174.7 l.

The low rate performance (60 to 100 h) is essentially controlled by the volume and density of the electrolyte. At these rates, there is excess positive and negative active material which is still available and the capacity can be increased simply by increasing the volume of acid in the cell. The requirement for a good low-rate performance complicates the design considerations. In the case of the EV, this complication does not exist and the volume of acid should be tailored to the discharge rates involved. However, the use of electrolyte with higher density increases the performance at other rates, e.g., 5 h. Acid with a relative density of 1.29 to 1.3 has been used for many years in submarine cells and is now being applied to EV batteries to increase their performance.

The high rate performance (1-1.5 h) of any cell is limited by the conductivity of the components. This is accentuated in the case of a large submarine cell. The end of charge voltage and the mean voltage during discharge of a submarine cell are somewhat lower, particularly at high rates, than the corresponding figures for a traction or EV cell. Typical values are given in Table 3.

A submarine cell is designed to have a good volumetric energy density over a wide range of discharge rates (1-100 h) and the figures in Table 2 demonstrate this. For example, at discharge rates of approximately 1, 3 and 5 h, the volumetric energy

TABLE 2

Typical performance figures for submarine cells

Discharge rate (A)	Capacity (A h)	Energy density	
		(W h/kg)	(W h/l)
6080	6500	21.4	63.6
2700	8300	29.7	88.4
1760	9200	33.8	101
970	9950	37.5	112
525	10650	40.8	121
190	12130	47.1	140

TABLE 3

Typical discharge voltages of submarine cells

Discharge rate (h)	Mean voltage (V)	End voltage (V)
1	1.71	1.46
3	1.86	1.61
5	1.91	1.67
10	1.96	1.73
20	1.99	1.77
60	2.02	1.80

densities are 64, 88 and 101 W h/l, respectively. The corresponding gravimetric energy densities of 21, 30 and 34 W h/kg are also quite good. However, several factors militate against good gravimetric values: (i) the extra weight of nonactive components for strength, (ii) the extra weight of top lead for conductivity, and (iii) the extra weight of electrolyte for a good low rate.

In an EV battery, where the size of the cells is smaller, there is not such a stringent mechanical requirement and there is no low-rate requirement. The gravimetric energy density should therefore be improved. The technology developed in submarine cells is useful for EV batteries. Examples are the high density acid used in submarine cells since the late 1960s and the methods for improving conductivity used in submarine technology since the 1970s, both of which are now being considered for EV batteries.

Conductivity

In a submarine cell, the voltage drop from top to bottom of the plates is considerable. It was shown many years ago [2] that the length of a conventional plate should be limited to less than 1000 mm. The extra capacity obtained from longer plates could not be extracted at a useful voltage. In general, submarine cells have a height of less than 1100 mm and the length of the plates is 800-900 mm. However, with the advent of the German 209-class and subsequent German designs, the shape of the hull necessitated a much taller cell (1.34 m and later designs even higher) and the conductivity problem had to be solved. Two solutions were offered: the 'Etagenzelle' or 'double-decker' cell [3, 4] in which effectively there were two elements above one another in one container, connected in parallel by means of lead-coated copper frames, and the use of a lead-coated expanded copper grid [5] for the negative plate with a conventional tubular positive plate. Both these solutions increased the conductivity to the bottom of the cell, decreasing the voltage drop and enabling the use of the active material near to the bottom of the plates. Figure 1 shows the effect of copper-negative grids in tall submarine cells. The 1 h discharge rate to an end voltage of 1.46 V is increased from 50 to 63 min. The use of copper-negative grids together with conventional positive flat plates in cells of this height results in a discharge time of less than 50 min. This is because the discharge is limited by the conductivity in the positive plates which consists of two elements: the conductivity of the grid itself and also the conductivity within each pellet of active material.

Whilst cells used in EVs and industrial trucks are much smaller, the copper-grid technology can usefully be applied to obtain extra performance at higher discharge

118

1.90

1.80

1.70

1.60

1.50

1.40

VOLTAGE (V)

COPPER GRID

LEAD GRID

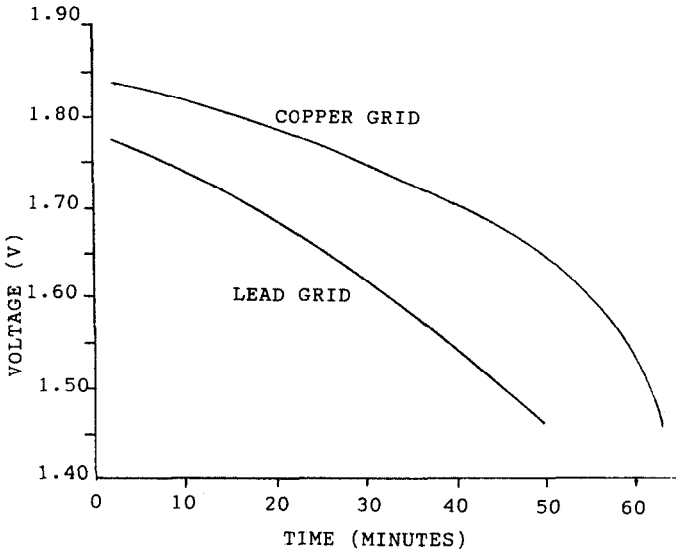0   10   20   30   40   50   60

TIME (MINUTES)

Fig. 1. Effect of copper-negative grids on performance of a submarine cell.

rates. The technology is well established in submarine cells and is now beginning to be applied to traction batteries.

It should be noted that one of the effects of the high-conductivity grids is that the discharge curve has a different shape. After the end-of-discharge voltage has been reached, the voltage falls off much more rapidly than in conventional cells. It is therefore essential to have a voltage scanning device on a submarine battery of several hundred cells, to measure the voltages of individual cells and thus to prevent overdischarge and reversal of the weaker cells. Although there are smaller numbers of cells in EV batteries, a voltage scanner would also be desirable in this case.

In submarine cells, copper inserts are used in the top straps or bars of both positive and negative plate groups (where it is protected by a thick layer of lead) and in negative grids. However, copper cannot be used in positive grids because, even if it is protected by a lead coating, corrosion eventually results in the leaching of copper into the electrolyte with subsequent plating on the surfaces of the negative active material. The resulting local cells on the negative plate result in excessive gassing and loss of capacity. An alternative high-conductivity metal which can be considered for positive grids is aluminium. Aluminium inserts have already been considered for the top walls of submarine plates. Tubular positive plates could conceivably be constructed by extrusion sheathing aluminium rods with lead by the method of Electrosource in the USA, and then fabricating a tubular spine. However, the problem is to maintain intimate contact between the lead sheath and the underlying aluminium metal. The tenacious film of aluminium oxide on the surface results in a high-resistance film between the two metals. One way of overcoming this problem is to coextrude or codraw a lead cylinder containing an insert of aluminium. As the duplex system is worked and a reduction in cross section takes place, the oxide film on the aluminium surface will be broken up and intimate contact established between the lead and aluminium. A possible alternative way of improving conductivity is by use of lead–aluminium alloys, produced by rapid solidification techniques. One method is by laser treatment [6]. If alloys can be developed with sufficient aluminium content, the

conductivity will be improved. The alloys would, of course, have to have sufficient corrosion resistance.

Electrolyte stratification

Submarine cells are always prone to acid stratification. The acid mixing due to gassing during an equalizing charge will overcome stratification but in operational periods, when only partial charging is applied, the problem can become severe.

A method of acid agitation by means of a simple air pump is therefore used. This is shown diagrammatically in Fig. 2. It consists of two concentric plastic tubes. Air is fed from a central supply system to the inner tube at a low pressure. When the air escapes from the end of the inner tube, part way down the cell, it rises to the top of the cell via the outer tube and draws up the denser acid to the top, thus ensuring mixing and absence of stratification.

Acid agitation also increases the efficiency of charging, in the case of a submarine cell reducing the charge time by about 1 h. This can be important in EV batteries where there is a need to reduce the amount of overcharge normally given to traction batteries. Stevenson [7] has recently claimed that agitation techniques can decrease the overcharge necessary and improve the electrical efficiency of battery use by 10%.

As might be expected, the movement of electrolyte in the cell can also assist diffusion during discharge and, especially at high rates, the discharge time can be increased. This may be important for EV batteries, although the extra energy obtained must be discounted by that consumed in the agitation process. Sunu [8] has claimed that electrolyte agitation can increase capacity by about 4% at discharge rates of 1 to 5 h.

Hydrogen evolution

The hydrogen evolved during discharge or on open circuit arises mainly from local cells on the negative plate between the spongy lead and antimony. There are two possible sources of antimony: in the negative grid itself, and from the positive grid, leached out by corrosion and plated on the negative active material. Special attention has therefore to be paid to grid alloys.

The source of antimony in the negative grid can be completely eliminated by the use of an antimony-free alloy and, for example a binary lead–calcium alloy has been
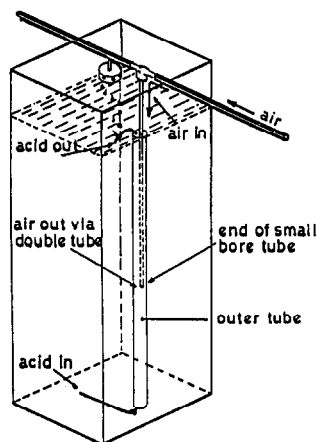

Fig. 2. Electrolyte agitation system.

used in negative grids of all UK submarine cells since the 1970s. Antimony-free alloys cannot be used in positive grids because of their poor creep resistance (resistance to plate growth) and their tendency to cause premature loss of capacity on cycling (antimony-free effect). Over the years, the possibility of using low-antimony alloys in positive grids has been extensively examined. For example, good properties were reported from a lead–2wt.% antimony–2wt.% cadmium alloy [9, 10]. The grain-refining action of selenium was also recognized and, since the 1950s, a lead–3wt.% antimony–1.5wt.% tin–0.05wt.% selenium alloy has been used in positive grids of UK submarine cells [11].

The hybrid arrangement of an antimony-free negative grid and an antimony-containing positive grid is quite effective and can be followed in traction cells and other cells intended for cycling. The principle of grain-refinement of low-antimony alloys by selenium has also now been used in low-maintenance automotive batteries. Such alloys could also be used in EV batteries to give better charge retention and maintenance characteristics.

Cell cooling

Various types of cell cooling have been applied. One method is to pass cooling water through a lead-coated copper coil immersed in the electrolyte. The obvious danger of this is the penetration of the lead coating by acid, which would result both in flooding of the cell with water and copper contamination. It is therefore usual to connect the coil to the negative plate, thus holding it at a potential which prevents the anodic corrosion of the lead coating.

The two methods of cooling in common use in Western Europe are shown diagrammatically in Fig. 3. Both these remove heat via the terminals. The external water cooling system consists of copper cooling plates, containing water ducts, which are clamped to each set of cell terminals. In the internal cooling method, there are
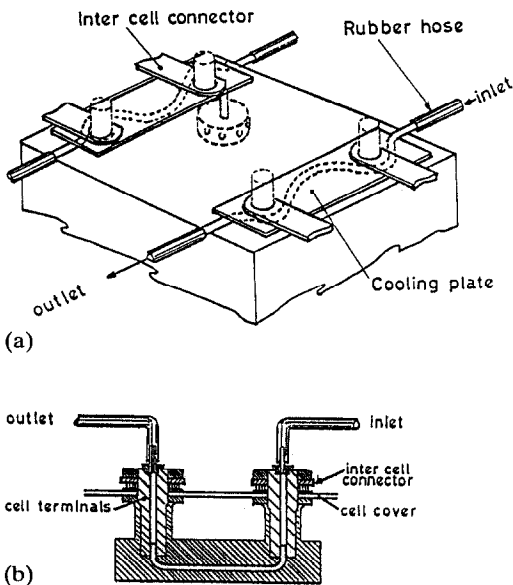

(a)

(b)

Fig. 3. Cell cooling arrangements (a) external and (b) internal.

channels in the copper inserts in the terminals and group bars, through which water can be passed. The internal system is more efficient than the external method and requires less than one-third the water rate to give the same degree of cooling.

The charge reaction in a lead/acid cell is slightly exothermic, giving an increase in temperature. Further, and more significant, increases in temperature are caused by the heat generated on passing the current through the resistive components in the cell. It is therefore advisable to have the cooling system operational during charging. Although the discharge reaction is slightly endothermic, the resulting small temperature decrease is normally completely swamped by the heat from the resistive effect and significant increases in temperature can occur. Since the heat generated is proportional to the square of the current flowing, the greatest rises in temperature occur during high-rate discharges and the cooling system should be used.

Although the cells in EV batteries are smaller than submarine cells, similar cooling systems could be used to good effect. In lead/acid cells, high temperatures can not only harm components but also shorten the life of a cell and cooling should therefore be considered.

Acid circulation?

Since one of the most critical parameters of both submarines and EVs is range and this is controlled by the capacity available, methods of increasing capacity are under continuous review. Once the principle of a water cooling system has been accepted, it is tempting to examine the possibility of circulating acid through the cells. It has been shown in specially constructed laboratory cells [12], that the capacity of a lead/acid cell is usually limited by the availability of acid and significant increases in performance can be obtained by passing acid through the plates. Whilst these experiments were on special cells, it would be interesting to see how much the capacity of a normally constructed cell could be increased by passing through excess acid (which would also act as a coolant). The design of such a system would need considerable ingenuity but it would be no more complicated than the circulation systems of the more exotic batteries which are under consideration for EV propulsion.

Conclusions

1. The particular requirements of submarine cells have resulted in the application of various design principles which are now well established and can be extended to other types of battery, particularly those used in EVs.

2. The use of lead-coated copper negative grids and tubular positive grids gives a significant increase in performance at high-discharge rates.

3. Further increases in high-rate performance could be achieved by incorporating aluminium in the positive grid.

4. Using a low-antimony alloy positive grid and a lead–calcium alloy negative grid reduces hydrogen evolution on open circuit, increases charge retention and decreases maintenance requirements.

5. The use of air agitation reduces electrolyte stratification, decreases charge time and can increase discharge performance.

6. The use of a cooling system is necessary in a large cell during charging and high-rate discharging. The system could be applied to EV batteries.

7. The circulation of excess electrolyte through the cells, in order to increase discharge capacity, could be considered for both submarine and EV batteries.

References

1 N. E. Bagshaw, *Batteries on Ships*, Research Studies Press, Chichester, 1982, pp. 92–93.
2 K. J. Euler and L. Horn, *Arch. Elektrotechnik*, *50* (1965) 85.
3 J. Brinkmann, *Ger. Patent 2 132 690* (1972).
4 H. Lawrenz, *Marine-Rundschau*, *9* (1980) 533.
5 H. Steig, *Ger. Patent 2 404 642* (1975).
6 M. M. Kim, *Proc. 5th Int. Lead/Acid Battery Seminar (ILZRO)*, *Apr. 17–19, 1991, Vienna, VA*, p. 41.
7 J. M. Stevenson and J. I. Dyson, *Proc. ERA Conf.*, *Apr. 7–8, 1992, London, ERA report 92-003*.
8 W. G. Sunu and B. W. Burrows, in J. Thompson (ed.), *Power Sources 8*, Academic Press, New York/London, 1981, p. 601.
9 W. C. M. Couch, *Br. Patent 613 208* (1948).
10 N. E. Bagshaw, *Proc. 3rd Int. Conf. on Lead, Sept. 1968, Venice*, Pergamon, Oxford/Elmsford, 1969, p. 209.
11 H. Waterhouse and R. Willows, *Br. Patent 622 512* (1949).
12 J. Bohmann, U. Hullmeine, E. Voss and A. Winsel, *Final Report, ILZRO Project LE-277*, 1982.