High rate partial-state-of-charge operation of VRLA batteries

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Abstract

The world market for 12 V SLI batteries currently stands at around US$ 12 billion. The lack of a serious challenge from other battery types has allowed lead–acid products to serve this market exclusively, with minimal demand for product improvement through research and development, and a sharp competition has, over time, cut sales prices to commodity levels. The electrochemical storage of energy in automobiles now faces the possibility of a major change, in the form of the proposed 36/42 V electrical systems for vehicles that remain primarily powered by internal combustion engines, and of the hybrid electric vehicle. The duty cycle for these two applications sees the battery held at a partial-state-of-charge (PSoC) for most of its life and required to supply, and to accept, charge at unprecedented rates. The remarkable advances achieved with VRLA battery technology for electric vehicles during the past 8–10 years will be of only passing value in overcoming the challenges posed by high rate PSoC service in 36/42 V and HEV duty. This is because the failure modes seen in PSoC are quite different from those faced in EV (deep cycle) use. The replacement of the 12 V SLI will not take place rapidly. However, if the applications which take its place are to be satisfied by a lead–acid product (probably VRLA), rather than by a battery of a different chemistry, a program of development as successful as that mounted for deep cycle duty will be required. The present phase of the Advanced Lead–Acid Battery Consortium (ALABC) R&D program has begun to shed light on those aspects of the function of a VRLA battery which currently limit its life in high rate PSoC duty. The program is also pursuing the several technologies which show promise of overcoming those limits, including multiple tab plate design, mass transport facilitation and minor component (both beneficial and detrimental impurity) management.

This paper presents a brief review of the changes which are taking place in lead–acid battery technology in response to the challenges of the new duty cycle.
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1. Introduction

The development of the valve-regulated lead–acid battery from its flooded precursor over the past 30 odd years has involved considerable technological effort—in managing the oxygen cycle, in grid alloy and separator design, and in optimization of charge strategies. At the start of the 21st century a new challenge is in view which is likely to prompt a further wave of development of the system.

Over the next few years the familiar 12 V electrical system will, progressively, be supplanted by other electrical systems. A part of the automotive market will be taken over by hybrid electric vehicles (HEVs) and the rate at which this shift is occurring has caught many pundits by surprise. Since the tentative introduction of HEVs to the market place in late 1999 total sales have already passed the 100,000 mark. All of these vehicles employ nickel metal hydride batteries because when they were designed it was understood that

lead–acid products were unable to cope with the required duty cycle for an adequate life.

The remainder of the market could retain a conventional internal combustion engine (i.c.e.) architecture, but with a higher voltage electrical system (36 V battery, 42 V alternator) to provide the higher power levels currently being sought by automotive design engineers. The time required for this change to be completed is unclear but the first product with a 36 V battery was launched, in Japan, in October 2001.

2. The challenge of high rate partial-state-of-charge operation

The batteries to be used in both hybrid electric vehicles and 36/42 V systems (the two are closely related, indeed overlap in some schemes) will be required to operate in a manner which is quite unlike the duty performed by 12 V SLI units at present. The new batteries will need to supply significant amounts of capacity for onboard electrical functions and will need to accommodate charge returned via

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Table 1
Typical range of state-of-charge, rates of discharge and recharge and failure modes

Duty	SLI	Deep cycle	High rate PSoC
Examples	12 V	EV	HEV/36–42 V
Range of SoC (%)	85–90	20–100	50–70, 70–90
Maximum normal discharge[a] (C)	10	4	15
Maximum normal charge[a] (C)	0.5	0.5	8
Failure modes	Corrosion, shedding	PCL 1, PCL 2	Negative plate under—charge, sulfation

[a] In multiples of the 1 h rate.

"regenerative braking" as part of the scheme to save fuel (and brake pads). This requirement dictates that the battery will operate continuously at a partial-state-of-charge (PSoC) and be able to accept charge at extremely high rates. Table 1 serves to emphasize how the duty cycle required in future automobiles will be quite different from anything that the battery has had to cope with in the past.

It goes without saying that a battery can only be acceptable in any particular application if it is capable of delivering an adequate period of life-in-service. As shown in Table 1 the life limiting processes (failure modes) for the SLI battery

(first 6 V and then 12 V) are well understood, and the battery has been developed sufficiently for the product to have been acceptable for the better part of a century.

When attention focussed on electric vehicles at the beginning of the 1990s it was clear that the VRLA battery could not deliver the desired life. However within a decade the industry, supported by the extensive research program mounted by the Advanced Lead–Acid Battery Consortium (ALABC), had made the necessary R&D investment to achieve a 10-fold increase in deep cycle life. The VRLA battery was then able to resist the challenge from alternative chemistries (nickel/metal hydride, lithium ion, etc.), and to become the battery of choice for electric vehicles.

The present challenge for the lead–acid community as it faces a change to the market which promises to be much more far-reaching than was the introduction of electric vehicles, is that, once again, the standard product is incapable of delivering an acceptable life. Table 1 shows that the duty required of the battery in the high rate partial-state-of-charge role demanded by HEVs and 36/42 V systems is quite different from that required in the conventional SLI or deep cycle modes. Lacking a construction which is purpose-designed for high rate PSoC operation, batteries typically lose 50% of capacity by the time they have run the equivalent of around 20,000 miles as shown in Fig. 1 [1].
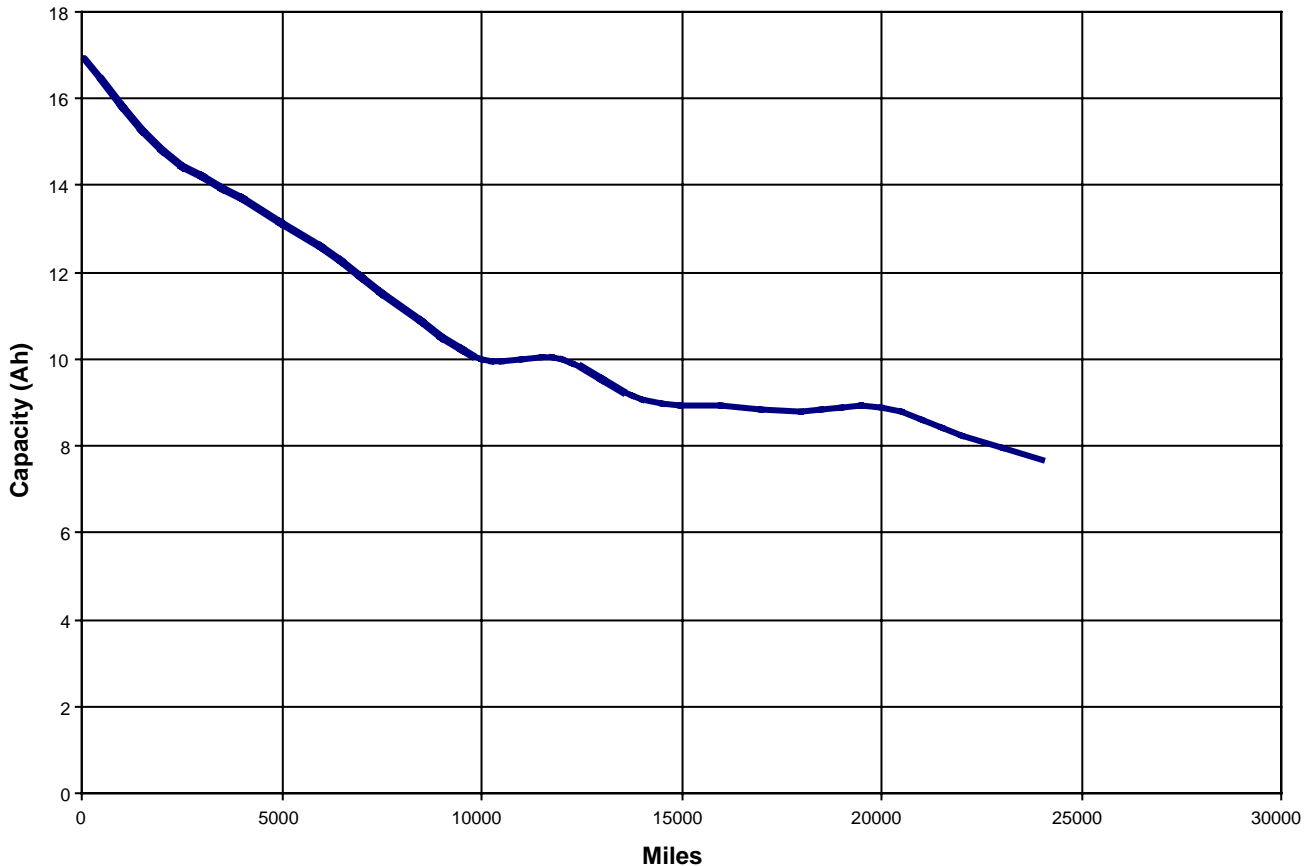

Fig. 1. Evolution of capacity of standard VRLA battery in HEV duty.

Table 2
Reactions taking place during discharge and recharge of a VRLA cell

Reactions occurring during discharge	Reactions occurring during charge
$PbO_2 + 3H^+ + HSO_4^- + 2e^-$ $\rightarrow PbSO_4 + 2H_2O$ (1)	$PbSO_4 + 2H_2O \rightarrow PbO_2$ $+ 3H^+ + HSO_4^- + 2e^-$ (3)
$Pb + HSO_4^- \rightarrow PbSO_4 + H^+$ $+ 2e^-$ (2)	$PbSO_4 + H^+ + 2e^- \rightarrow Pb$ $+ HSO_4^-$ (4)
	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ (5)
	$Pb + 2H_2O \rightarrow PbO_2$ $+ 4H^+ + 4e^-$ (6)
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $+$ heat (7)
	$2H^+ + 2e^- \rightarrow H_2$ (8)

This loss of capacity is accompanied by a rapid build-up of sulfate on the negative plate, especially towards the bottom. Since the battery is not brought to a full state of charge in PSoC duty there is no routine method available to remove sulfate [2]. The accumulation is progressive and the loss of capacity mentioned above is the result [3].

This failure mode arises from a charging inefficiency of the negative plate. Normally the charge efficiency of the negative plate is high until charging is almost complete, so that operation in a partial-state-of-charge ought to be a favorable mode. However it appears that at high rates of recharge (see the unique charge rates mentioned in Table 1), even from a partial-state-of-charge, the charge efficiency is diminished.

In order to understand the processes involved in the accumulation of sulfate on the negative plate during high rate partial-state-of-charge operation it is helpful to consider, once again, the reactions which are thermodynamically favorable in the VRLA cell during discharge and recharge. These are shown in Table 2.

During discharge of course there is only one reaction available at each electrode and the consequence of an increase in rate of discharge is that the reaction becomes limited by diffusion of species in solution [4] and the discharge voltage decreases. During recharge the situation is quite different. Reactions 3 and 4 in Table 2 represent the intended reversal of the discharge reactions. There are, however, four other reactions (labeled 5–8) which are allowable when the cell is on charge and these are thermodynamically preferred over the main charge reactions. Fortunately these so-called 'secondary' reactions proceed only slowly in normal charge regimes and it is possible to bring reactions 3 and 4 to completion [5].

At rates around $1C_1$, the two gas-producing reactions (5 and 8) proceed only slowly until the later stages of the charging process provided that the active materials do not contain catalytic contaminants. While the rate of oxygen-production (reaction 5) remains low the scope for recombination at the negative (reaction 7) should also be limited. Finally, corrosion of the positive grid (reaction 6) remains slow while the corrosion product layer is passive.

The accumulation of sulfate on the negative plate when the VRLA cell is operated at the extraordinarily high rates of recharge shown in Table 1 implies that the recharge reactions are then no longer proceeding more effectively than the secondary reactions, even at intermediate states of charge. This is likely to be because the charge reactions are more adversely affected by diffusion limitations at high rates than are the secondary reactions. The diffusion of HSO_4^- away from the reaction site is likely to be slower than the diffusion of the protons involved in the secondary reactions. As the rate of the charge reactions becomes constrained by limited mass transfer the charging potential must rise, and this will increase the rates of secondary reactions.

Two factors will focus the effects of this process on the negative plate rather than the positive. First the surface area of the negative active mass is generally substantially less than that of the positive plate. Thus, in order to maintain the same charge current through the two electrodes the diffusion process is required to 'reach further into the electrolyte' in order to supply reactants to the solid surface of the negative plate than it does for the positive. At low or medium rates this poses no difficulty, but as the rate of recharge increases the diffusion limitation will become critical at the negative plate first.

The second factor which aggravates the charging problem at the negative plate is that a portion of the oxygen generated at the positive is recombined at the negative and this process depresses the potential of the plate, making it more difficult to charge. As a result, the positive plate may successfully recover its charge while the negative does not. Further, since the high rate PSoC duty does not involve the battery being returned to full charge on a regular basis, there is no opportunity for the capacity loss at the negative plate to be restored.

Fortunately several possible remedies suggest themselves as described below. In order to overcome the processes which give rise to the accumulation of sulfate on the negative plate in high rate PSoC duty it is necessary to discourage the secondary reactions, particularly reactions 7 and 8 which occur at the negative plate, and to encourage the charge reactions.

3. Discouraging the secondary reactions during high rate recharge

3.1. Trace element control

Small amounts of trace elements can cause major changes in the over-potentials at the two electrodes and alter the rates at which the gassing reactions proceed. A thorough study undertaken by CSIRO in Australia, has shown that elements not required by the fundamental stoichiometry of the cell reaction can influence gas evolution either singly or in combination, when subtle synergistic effects can occur. Early indications are that, for example, zinc has a strong ability to suppress hydrogen gassing at the negative plate and a combination of antimony and iron can suppress the oxygen gassing effect of some transition metals at the positive [6].
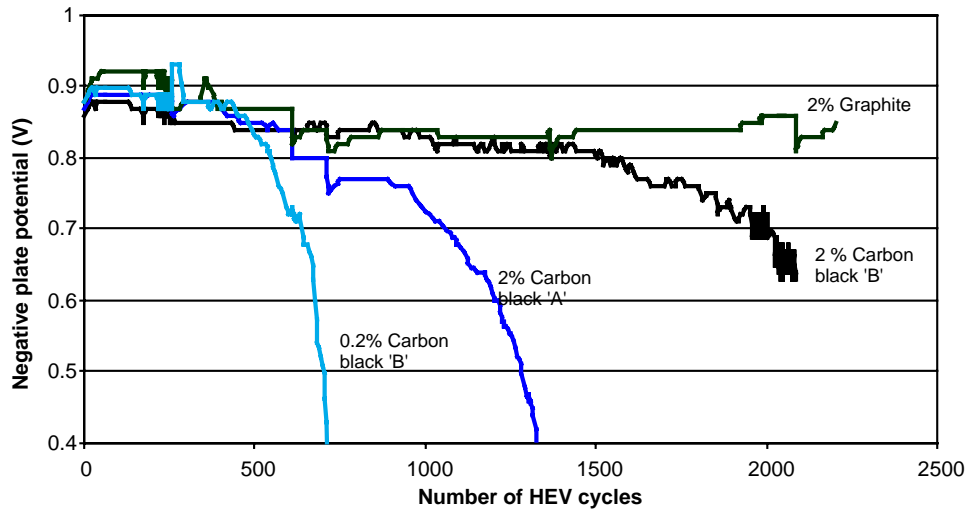
Fig. 2. End of discharge potential (vs. Hg/Hg$_2$SO$_4$ electrode) of prototype cells during simulated HEV duty. Curves marked CB1 represent cells containing 0.2 w/o carbon black in the negative plate. Curves marked 10CB represent cells containing 2 w/o carbon black in the negative plate. The curve marked 10GR represents a cell containing 2 w/o graphite in the negative plate.

3.2. Separator design

As has been pointed out elsewhere [7], the separator exercises a crucial function in VRLA cells. The transfer of some oxygen generated at the positive plate (reaction 5) through the separator for reduction at the negative (reaction 7) is a key component of VRLA strategy. Too much oxygen recombination at the negative plate, however, depresses potential at the plate and makes it very difficult to complete the charging process. Provision of a separator with the appropriate microstructure can constrain the rate of oxygen arrival at the negative plate and thus restrict the suppression of the negative plate potential caused by reaction 7.

3.3. Carbon inventory

The surface area difference between the two plates manifests itself as a difference in the surface area available to supply electrons to the reaction site. Without an electronically conducting surface neither reaction 3 nor reaction 4 can proceed. If the amount of electronically conducting surface available in the negative plate can be extended, however, then the unequal dependence on diffusion in the two plates could be overcome.

Interestingly, as shown in Fig. 2, an increase in the quantity of carbon in the negative active mass can extend the life of a cell in HEV duty to a significant extent [3]. Moreover, these early results, again from CSIRO in Australia, show that the form of carbon used is of critical importance. Graphite particles, evidently with a plate-like form well suited to inter-particle contact, perform far better than carbon black employed in the same weight fraction. Meissner [8] has shown that needle-shaped conducting particles are far more effective in increasing the conductivity of a resistive medium than equi-axed powders, by a factor of up to

1000, depending on aspect ratio. The case of plate-shaped particles does not seem to have been analyzed but, by analogy with the case of needle-shaped materials, it would seem that any departure from the spherical shape would be beneficial, so that the result shown in Fig. 2 is not unexpected.

4. Grid design for high rate operation

The uneven accumulation of sulfate with high rate PSoC cycling can be alleviated by suitable design of the battery grid. It has been pointed out that the performance of lead–acid batteries can be adversely affected by a non-uniform distribution of current over the plates as a result of ohmic losses [9]. Such effects become more pronounced the higher is the rate (of charge and/or discharge) and the larger the plate [10]. During high rate discharge the tops of the plates will tend to be worked harder and to produce more sulfate than the lower regions. On recharge an equivalent uneven current distribution would remove more sulfate from the top than from the bottom, apparently making good the original state of charge across the plate. However, in the case illustrated for high rate partial-state-of-charge in Table 1, the maximum charge rate is significantly higher than the discharge rate. Thus the unevenness of removal of sulfate from the plate (more from the top than the bottom) will be greater than the unevenness of sulfate deposition. The result will be an accumulation of sulfate in the lower half of the plate, which is never removed if there is no conditioning procedure in place.

It has been pointed out [11] that the addition of a second current take-off (tab), at the bottom of the plate, will bring considerable benefit in terms of improved performance of VRLA cells used in high rate PSoC duty such as in HEVs. The current passing through each tab is half that which
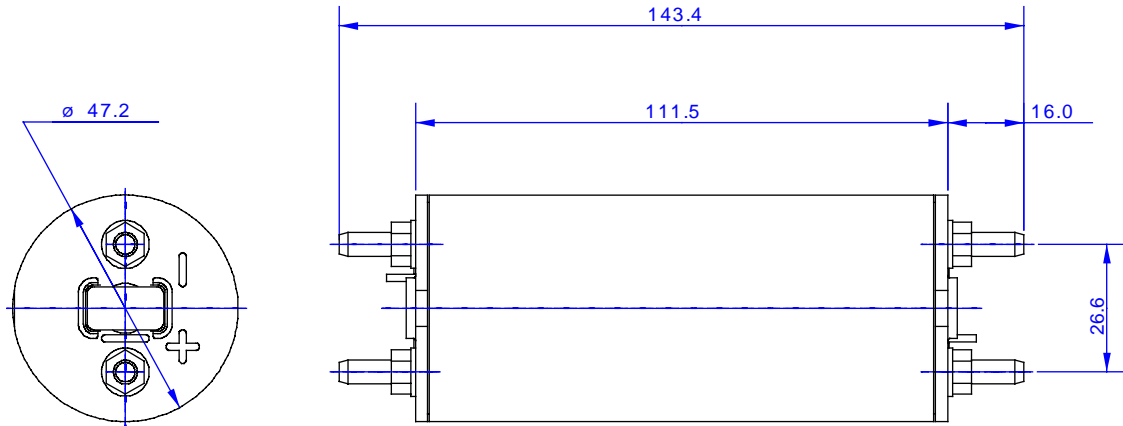
Fig. 3. Spiral wound cell with 'twin tabs'.

Fig. 4. 36 V battery of twin tab spiral wound cells on test.

would pass through a single take-off and the extra connection also acts as an additional heat-sink, maintaining lower plate temperatures.

This concept has been applied effectively to the spiral wound design of VRLA in a project funded jointly by the UK government and the ALABC to develop HEV batteries [12]. The design of the cell used in this demonstration is shown in Fig. 3, where the positive and negative connections can be seen projecting from both ends of the unit. The performance of this cell has been compared with that of the conventional, single tab, cell from which it was derived. Each design was deployed in an 18 cell, 36 V battery (Fig. 4 shows the twin tab variant) and subjected to an arduous HEV cycle typical of a vehicle driven around a steep hill circuit [12]. As shown in
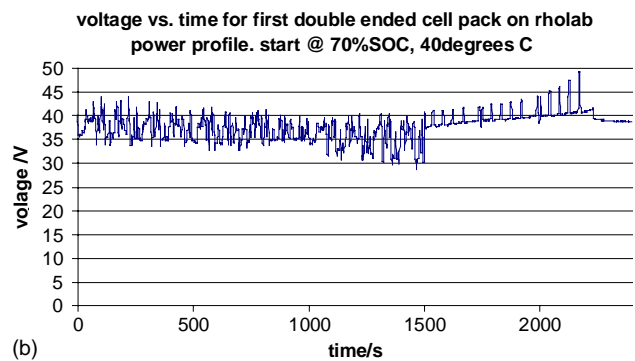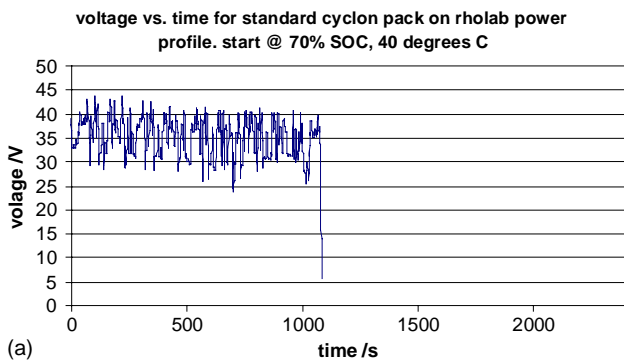

Fig. 5. HEV battery test sequence derived by running a Honda 'Insight' round the 'Hill Route' at the Millbrook test track in the UK. (a) The failure of the conventional battery to achieve one complete cycle. (b) The complete cycle as completed 65 times in succession by the twin tab battery.

the left-hand side of Fig. 5, the battery of conventional cells was unable to complete this cycle even once. By contrast the battery comprising 18 of the twin tab cells was able to reel off 65 of these heavy duty cycles (one such is shown on the right-hand side of Fig. 5) without failure.

This remarkable result bodes well for the contribution that purpose-designed VRLA batteries could make in the growing HEV automotive sector. Further benefit may accrue from the use of a battery management scheme being development as another component of the same project. The approach being taken is to manage each 2 V unit separately (their physical separation assists thermal management) and to add one extra cell to each set of 18 cells. This will allow charge to be moved around the pack in order to provide a systematic conditioning process as and when necessary.

Provided that the remarkable benefits associated with the twin tab design in high rate PSoC duty can be attributed to a reduction in ohmic losses [9,10], then it can be anticipated that a similar performance improvement would be achieved simply by reducing the cell height by a factor of two. Such an alternative approach might be expected to simplify manufacture, facilitate filling the cell with electrolyte and reduce the extent of acid stratification.

Another approach to reducing the ohmic losses would be to adjust the design of the grid wires (especially the vertical wires), but this would bring no benefits to the electrolyte filling nor to the stratification issue.

5. Concluding remarks

In both 36 V and HEV batteries longer series strings of cells will be used than has been necessary in 12 V batteries. These cells will have to be matched better than in the past and assembled in such a way that they will not tend to become unbalanced.

The establishment of a good mathematical model for the VRLA battery operating in the high rate PSoC regime will be a valuable asset in predicting the behavior of the battery in the new mode and helping with detailed design adjust-

ments. Well-developed computational fluid dynamics procedures [13] show good promise of being able to cope with this problem. In assembling a sound model of the processes taking place in high rate PSoC operation it will be important to establish experimentally how the high rate charging current is splitting between the main charging reaction and the secondary (parasitic) reactions.

It remains to be seen whether the benefits that can be gleaned from the several design adjustments outlined above, when employed together, will prove to be sufficient to provide a satisfactory life for the VRLA battery in a HEV environment. If they do, then the rewards, in terms of reduced battery costs for such vehicles, will be enormous.

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