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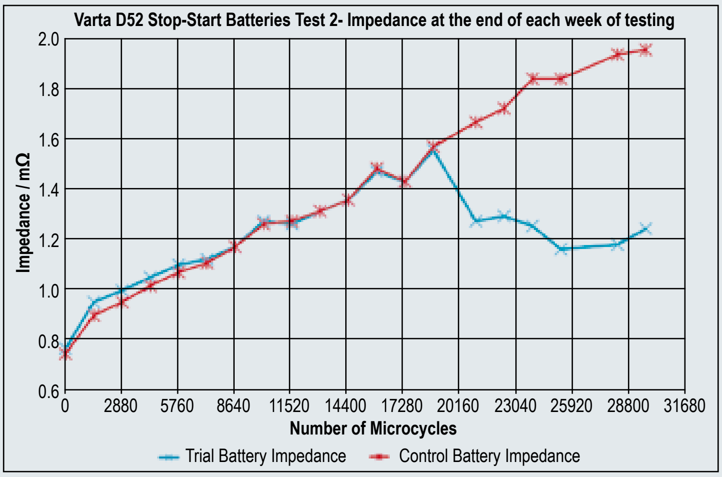
Letter to the Editor

I have great respect for lead-acid batteries and was surprised to find that they were performing badly in accelerated micro-hybrid tests. Ostwald Ripening is involved, of course, but I didn't think the battery was at fault at all: it was being abused. To me the real issue was ***inadequate charging!***

Accordingly, we tested two top-of-the line European VRLA batteries (complete with the latest carbon additives and four-nines lead) on a micro-hybrid test based on the Japanese SBA SO 101 protocol but with added 8-hour rest periods. We were shocked to see the impedance of the batteries rising linearly throughout the test, diminishing the battery performance as it aged. In an earlier test, similar batteries had died an early death at 30,000 micro cycles. Therefore, at about 19,000 microcycles we introduced our proposed solution: a periodic 100% automatic recharge of the experimental battery. The recharge frequency was intended to simulate, approximately, a monthly recharge in a real car.



As the graph shows, the impedance on the charged battery dropped immediately by about one third. The impedance of the control had continued to rise so it was now about twice that of the recharged battery; this after a single recharge! Subsequent recharges did not lower the impedance of the test battery much more although they did keep the impedance from rising again.

These results are exactly what one would expect with lead-acid batteries. The large initial improvement in impedance proves that "new sulfate" is easily dissolved while the lack of further large improvements shows that "old sulfate", subject to Ostwald ripening, is very hard to dissolve. Clearly, if our charging protocol had been used from the beginning of the test, as it would on a real car, the battery would never have a buildup in impedance at all. It would then have a better performance and, quite possibly, twice the life. Not bad for a bit of software, huh?

We filed a provisional US patent on the protocol which can be **seen below**. However, on reflection, we have decided to offer it **freely to any company that chooses to use it.** Volvo and Mercedes did this on safety patents years ago so this could be our contribution to a cleaner environment. Just let us know if it works well on real cars in the real world!

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Provisional Patent Application

Improved Battery And Control Systems For Batteries Maintained In A Partial State Of Charge Condition

Field of the Invention

[0001] The present invention relates to methods, systems and devices for improvements to batteries used in micro-hybrid vehicles and other uses where the battery is maintained in a partial state of charge.

Background

[0002] Cars and other fuel/engine powered vehicles dissipate kinetic energy in their brakes in the form of heat every time they come to a stop, thereby wasting energy, and thus lowering the fuel efficiency. By contrast, full-hybrid electric cars, such as the Toyota Prius, use their electric motors as generators to slow down the vehicle (also called “regenerative braking”) while generating electricity which is stored in their large main batteries, thereby saving much of the energy. This is partly why full-hybrid vehicles are so efficient in fuel usage, particularly in city driving. The high cost of the full-hybrid battery, however, is a major drawback.

[0003] A more recent fuel saving evolution for cars and similar vehicles is a compromise solution called a “micro-hybrid”, also referred to as “stop-start systems, which uses an internal combustion engine which is automatically shut down and restarted to reduce the amount of time the engine spends idling, thereby reducing fuel consumption and emissions. The micro-hybrid uses smaller batteries than in the full-hybrid vehicles, and operates as follows: During a deceleration, where the driver releases the acceleration pedal, for example as the vehicle approaches a red traffic light, the engine is shut down automatically and the vehicle generator is engaged with the wheels to decelerate the vehicle as in the case of the full-hybrid vehicle described above. The electrical energy thus produced is directed to charge a 12 volt lead-acid battery, typically a modified 12 volt battery as compared to batteries of conventional vehicles, although the battery voltage could be any suitable value. This recharge rate for the battery may be moderately high, usually about 100 amps DC or more or less as determined by a controller for the particular system. While the engine is off, the electrical load in the vehicle used by accessories is supplied by the battery for the duration of the stop phase.

[0004] Later, during the restart phase, for example when the car accelerates from the stopped position when the red traffic light turns green, the accelerator is pressed and the same 12 volt battery starts the engine automatically with a high electrical discharge rate for a few seconds. Now the vehicle can drive forward on engine power, as normal, to the next traffic light where the cycle begins again.

[0005] During each of these stop-start cycles, called “micro-cycles”, the car recovers a portion of the energy that would have been wasted during the stop and idle phases if the engine continued to run. It is believed that over time, this system can save 3 to 5 percent of the total amount of fuel used by the vehicle while also reducing carbon emissions. The amount saved is dependent on the duty cycle of the vehicle, e.g., the amount of stop-start driving taking place. In steady cruise mode, for example, no energy is saved because there are no micro-cycle stops. The controller in such vehicles includes a computer or microprocessor that optimizes the actions described above.

[0006] The Micro-hybrid system is less expensive to manufacture than a full-hybrid system and is becoming a standard for many new cars worldwide. Any defects or problems with micro hybrid vehicles will therefore affect many people adversely for many years to come. Conversely, improvements described in the present invention can make the low-cost micro hybrid vehicle even more energy efficient than the full hybrid vehicle in many applications larger due to a lighter overall weight, thereby contributing substantially to the reduction of greenhouse gases. Currently, there are problems with the batteries used in micro-hybrid vehicles. Some of these problems are discussed below.

Problems

[0007] Although highly advantageous, micro-hybrid systems have problems related to the batteries used in them. These are mainly battery failure problems believed to be due to the use of relatively small 12 volt lead acid batteries ranging from about 60 amp hours (Ah) in smaller cars to 100Ah in larger cars. Forcing so much energy rapidly into a relatively small battery requires the battery to have an improved characteristic called Dynamic Charge Acceptance (DCA). This is measure of the capability of the battery to receive a high charge current with reasonable efficiency. Modified conventional 12 volt starter batteries are presently used, but are failing early when used in a micro hybrid system due to a steady and irreversible decline.

[0008] A substantial development effort has been carried out by the battery manufacturers to correct this shortened life problem. One major development is the use of carbon additives in the negative active material (NAM) of the batteries. However, while carbon improves the DCA to a degree, the decline in DCA performance is believed to continue unchanged according to our laboratory tests. Beneficial though these developments have been, they have masked the reality that the main culprit for the battery failure is not so much an inadequate battery as an inadequate charging system. In short, it is believed that micro-hybrid batteries are not being charged properly.

[0009] Test protocols have been published that are designed to measure the performance of micro-hybrid batteries. One early test is the Japanese SBA SO 101 protocol. Batteries claiming to use the latest technology were tested in our laboratories with this protocol but survived only 30,000 stop-start micro-cycles before failure. This corresponds roughly to two years in service. As described further below with reference to Fig. 4, such batteries suffer a continuous decline in performance rather than a sudden failure, indicating a faulty process rather than a faulty product. This conclusion was reinforced when the batteries were dismantled for inspection: their plates appeared to be in excellent physical condition with no sign of corrosion or mechanical defects. Chemical analysis confirmed, however, that the batteries had failed due to a cumulative buildup of lead sulfate on the negative plates.

[0010] This failure mode is similar to that of a lead acid battery left on a shelf for a long period of time in warm conditions, which is not recharged. Typically, if a lead acid battery is not fully recharged periodically, the battery capacity degrades. During the normal discharge cycle of a lead acid battery, lead sulfate crystals grow on the NAM decreasing the design capacity of the battery. Other processes such as Ostwald ripening discussed below makes this process worse. Recharging the battery regularly to a full capacity dissolves the lead sulfate crystals. By not returning the battery to a full state of charge, the lead sulfate crystals are not dissolved and continue to grow, becoming large and insoluble, and ultimately lead to the shortened life of the battery which cannot be recharged. Moreover, while the lead sulfate crystals are growing, they diminish the design capacity of the battery, such that it can hold less and less total charge, thereby degrading the battery. In the case of batteries used for micro-hybrid vehicles, it is believed that such batteries had not died because they were made badly, but because the application was unsuitable for their chemistry. The following is a list of some of the complicated problems that the present micro-hybrid systems have created that end in battery failures.

[0011] 1. Partial State of Charge. Unlike conventional SLI batteries (starting, lighting, ignition batteries), which have been successfully used on engine powered vehicles for decades, a micro-hybrid vehicle battery must have “spare capacity” available inside waiting to store the electrical energy produced by the generator during vehicle deceleration. Therefore the battery cannot be kept fully charged at all times. The industry’s chosen means of achieving spare capacity has been to keep the battery permanently in a partial state of charge (PSOC), normally 60%, or more or less, of the battery capacity. This concept would be satisfactory for a solid state capacitor but lead acid batteries are electro-chemical devices and have very different characteristics. As discussed above, by not returning the battery to a full state of charge, lead sulfate crystals continue to grow on the NAM and ultimately lead to the shortened life of the battery. Accordingly, preventing this irreversible sulfation on the NAM is desirable.

[0012] In historical terms, PSOC is believed to be an unusual protocol for operating lead acid batteries which are traditionally either kept in a fully charged condition, like standby batteries, or are given regular equalization charges (a forced overcharge bringing all cells of the battery to similar levels) as is done with fork truck batteries. So on one hand PSOC is essential to make the micro-hybrid system work, but on the other hand PSOC is believed to be a fundamentally unsuitable condition for lead acid batteries in which to remain indefinitely. As described below, an advantage of the present invention is to resolve this conflict by creating a charging protocol that keeps the battery at a PSOC for a substantial period of time, but then recharges it fully. After this full charge, the battery is allowed by the controller to fall back to its designed PSOC.

[0013] 2. Ostwald Ripening. This is believed to be a damaging chemical process in lead acid batteries contributing to the failure of micro-hybrid batteries. As noted above, the battery is deliberately maintained in a PSOC state, e.g., 60% PSOC (meaning 60% of a full state of charge). For example, the battery is deliberately allowed to discharge to a 60% PSOC by the vehicle’s electronic control system by switching off the generator. It is then made to stay in that condition more or less indefinitely. Not restoring the battery to a full state of charge results in the growth of lead sulfate crystals on the NAM, which are very fine and reactive early in the battery life. With the Ostwald Ripening effect, the lead sulfate crystals will tend to grow larger and harder as time progresses. Eventually, these crystals will not be able to participate in the charging reaction. The longer the stand periods, the worse this effect becomes. Likewise, high temperatures will accelerate it according to the Arrhenius rule. Ostwald Ripening cannot easily be corrected. Again, preventing this irreversible sulfation on the NAM in the first place is desirable.

[0014] 3. Limited recharge voltage. The system controller of a micro-hybrid maintains a PSOC by deliberately preventing the battery from recharging fully and does so by limiting the battery recharge voltage. This is a problem. In a micro-hybrid system the PSOC must be maintained at 60% PSOC, e.g., so the recharge voltage is limited to about 14 volts (2.33 volts per cell) which is not enough to keep the battery fully charged. This low voltage, however, does limit electrolysis in the battery. Higher voltages will create electrolysis and produce oxygen and hydrogen gases in the cells, losing water in the process.

[0015] It is believed that methods to equalize the cells of the battery automatically and periodically in a micro-hybrid vehicle by using higher battery voltages are not used since this will lead to water loss and shorten the battery life. The present invention therefore proposes, in one form, to use catalysts in the cells so that during any overcharge period the oxygen and hydrogen gas is recombined into water.

[0016] 4. Unrealistic battery test method. Prior art test procedures for micro-hybrids focused mainly on the number of micro-cycles completed in the test and did not specify any stand or rest periods. This is unrealistic because private cars spend far more time standing than driving so it fails to replicate the conditions causing the issues due the growth of lead sulfate crystals, such as from Ostwald Ripening, which take place largely during long stand periods. Lightly used micro-hybrid vehicles will therefore tend to be more vulnerable to loss of capacity due to Ostwald Ripening than predicted by the tests. Newer more realistic tests have now been established by the international standards authorities. These tests include longer stand periods between the micro-cycles plus cooling for the batteries. Stand periods will make the problems worse while cooling will make them better. Neither will solve the problem.

[0017] 5. Impure negative active material. It is known, mainly due to research in the area of stationary Valve Regulated Lead Acid batteries (“VRLA”), see. e, g., U.S. Patent 6,285,167, that traces of metallic impurities in the negative active material (NAM) can cause self-discharge in VRLA lead acid batteries. These batteries are often used in expensive automobiles. This self-discharge has been shown to occur even during ideal charging conditions where the batteries were kept fully charged at all times. Self-discharge due to impurities can be cured by the use of Microcat® catalysts made by Philadelphia Scientific LLC.

[0018] A partial alternative to a catalyst is to use highly purified lead. As a result, most micro-hybrid batteries are now constructed with 99.99% pure lead in their NAM. This “four-nines” lead has a lower self-discharge rate than the commercial grade of oxides but is more expensive. As a result of this and other changes micro-hybrid batteries are now very expensive, typically twice as expensive as a conventional starter battery which, often lasts twice as long in service. So, despite the extra cost, the Ostwald Ripening effect is still not eliminated, only reduced. In contrast, the present invention aims to eliminate it.

[0019] 6. Carbon additives. The latest batteries designed for micro-hybrid vehicles have been modified with additional carbon in their NAM to reduce electrical resistance and even to act marginally as a capacitor for free electrons, thereby improving the Dynamic Charge Acceptance (DCA) of the battery. While carbon does provide moderate improvements the charge capacity of carbon is very small compared with lead so carbon is used only as an additive in micro-hybrid batteries. Ironically, some carbons contain metallic impurities so its addition to the NAM is not without risk. Catalysts will compensate for this source of impurity also.

[0020] In summary, the failures of micro-hybrid batteries were previously incorrectly believed to be due to inadequate battery designs. Accordingly, improvements are needed to obtain the full benefits of micro-hybrid vehicles.

Summary

[0021] The present invention provides methods and devices for improvements to batteries used in micro-hybrid vehicles. In one aspect, the present invention recognizes that current problems of micro-hybrid batteries may be due to the inadequate charging system leading to the buildup of lead sulfate on the negative plates. It further provides solutions for these problems. Thus in one form, the present invention provides methods, systems, and devices for periodic recharging of a micro-hybrid lead acid battery to a fully charged condition. An advantage of this is that it can be done a very low cost. In another form, the present invention provides catalysts in the battery cells for recombining oxygen and hydrogen gasses produced during the recharging process.

Brief Description of the Drawings.

[0022] The following detailed description will be better understood when read in conjunction with the figures appended hereto. For the purpose of illustrating the invention, there is shown in the drawings a preferred embodiment. It is understood, however, that this invention is not limited to this embodiment or the precise arrangements shown.

[0023] Figure 1 is schematic view of a micro-hybrid vehicle, such as a car;

[0024] Fig 2A is a schematic view of one cell of a six cell EFB battery;

[0025] Fig 2B is a schematic view of one cell of a six cell Semi-flooded EFB battery;

[0026] Fig 2C is a schematic view of one cell of a six cell VRLA battery;

[0027] Figure 3 is a graph showing the test results for a discharge/charging cycle (a micro-cycle) of a battery used in a micro-hybrid vehicle, from “The Flooded type UltraBattery for Micro-HEV Applications”, Jun Furukawa, PhD, presented at LABAT’2014 Pre-Conference SEMINAR on Batteries for Hybrid and Start-Stop Applications, 9 June 2014, Flamingo Grand Hotel, Albena, Bulgaria; and.

[0028] Fig. 4 is a graph showing the impedance as a function of the number of stop-start micro-cycles for a VRLA battery to which a full recharge in accordance with the present invention was applied, as compared to a control battery without a full recharge.

Description of the Invention

[0029] New and improved devices, batteries, micro-hybrid vehicles, and methods therefore are now described. The present invention provides devices and methods for improving micro-hybrid systems to make them last longer, perform better, and less expensive to manufacture.

[0030] With reference to Figure 1, a schematic illustration of a representative preferred micro-hybrid vehicle 10 is shown. The vehicle 10 has a body/frame 12, wheels 14 on which the vehicle is propelled over a surface, and an internal combustion engine 16, such as a gasoline engine, operatively connected to at least one of the wheels 14, here the rear wheels 14a as shown, via known mechanical means that may normally include a transmission (not shown) drive shaft, differential, axles, etc.. In the illustrated embodiment of Fig. 1, the engine 16 is operatively connected to an electrical generator 18 by means such as shaft 20 and clutch 22. The generator is also operatively, e.g., mechanically, connected to the wheels 14a by a second clutch 24, second shaft 26, differential 28 and axle 30. The vehicle 10 further includes a battery 32, e.g., a 12 volt lead acid battery modified for use with a micro-hybrid vehicle and a controller 34 which controls the system as described below. It is appreciated that the above description of the vehicle 10 is for illustrative purposes only for describing the invention as other known constructions of vehicles and drive trains are known in the art.

[0031] The battery 32 is a lead acid battery preferably having multiple cells, six cells for a typical 12 Volt battery, and preferably constructed for micro-hybrid use. Various types of batteries may be used, such as flooded batteries of the EFB type (Enhanced Flooded Battery), semi-flooded batteries, and valve regulated lead acid (“VRLA”) batteries, all of which are further described below. However, with reference to Fig. 2A, a basic battery construction is presently described with reference to the EFB flooded battery shown.

[0032] Fig. 2A shows a single cell 40 of a battery having six cells. The cell 40 has a housing 42 for containing therein a liquid electrolyte 44 having an electrolyte level 46. A negative electrode 48, such as multiple negative plates, and positive electrode 50, such as multiple positive plates, is fully immersed in the electrolyte 44. Positive and negative terminals 52 and 54, respectively, electrically connect the positive and negative electrodes of the battery to the vehicle electrical system as is known in the art. A head space 56 within the housing in which gasses can collect sits above the electrolyte level 46, and a vent 58 allows the gasses to freely vent to atmosphere. This construction is similar to a typical lead acid flooded battery with the exception that is has been modified for use in a micro-hybrid vehicle. For example, it has extra carbon added to the very pure NAM and has low-resistance radial grids (plate supports).

[0033] The vehicle 10 relies on the internal combustion engine 16 for power as does a conventional vehicle. During deceleration, and when regenerative braking takes place, the engine 16 is shut down automatically, preferably by the controller 34, the clutch 22 disengages the generator 18 from the engine, and the vehicle generator 18, still operatively engaged with the wheels 14a through the clutch 24 continues to rotate due to the rotation of the wheels, the deceleration braking force being provided by the generator 18 as it produces electricity. Put another way, the generator applies the braking force to the shaft 26 as it generates electrical energy. The energy thus produced is supplied to the battery 32. This recharge rate is moderately high and can range from about 50 to 100 amps or more depending on the type and size of the battery. In principle, it could be any substantial value. With the engine turned off, the electrical load in the vehicle used by accessories is supplied by the battery 32 for the duration of the stop phase.

[0034] During the restart phase, the accelerator (not shown) is pressed and the same battery 32 starts the engine 16 automatically with a high electrical discharge rate from the battery 16 for a few seconds. The clutch 22 and clutch 24 are engaged so that the engine can drive the vehicle forward. The vehicle 10 drives on conventional engine power, as normal, to the next traffic light where the stop-start cycle begins again. Such vehicles may have a starter for the engine or use the generator 18 for starting the engine.

[0035] A simplified example of a stop-start micro-cycle which includes the discharging (restart phase) and charging (stopping phase) of a battery used in a micro-hybrid vehicle is illustrated with further reference to the graph of Fig. 3. At D1, the vehicle is at rest for 59 seconds, such as stopped at a light, with the engine 16 off. Here, the battery 32 discharges about 45 amps for the 59 seconds which is a typical electrical load for accessories in the vehicle, such as the radio, lights, etc. At D2, with the depressing of the accelerator to get the vehicle moving, a higher rate of electrical discharge is drawn to power the starter as necessary to start the engine. Here 300 amps for 1 second is drawn to start the engine.

[0036] The battery 32 can be charged from the generator 18 due to the regenerative braking process when braking, or by the engine, or other source, as shown at C1. The charging current is 14 volts which gives an initial charging current of 100A from the generator, tapering at C2 to a lower level as the battery takes the charge. This is on the right hand side of the graph. The duration of the 100A charge depends on how well the battery accepts the charge. The initial constant 100A portion at C1 indicates that the Charge Acceptance is high so the current is limited by the charging circuit, e.g., the voltage as controlled by the controller 34. The tapering portion C2 indicates that the battery is no longer capable of taking the full 100A without the voltage rising above the 14 volt limit as the electrical resistance of the battery increases due to the additional charge in the battery. As noted, the state of charge (“SOC”) of the battery is determined by the voltage limit when charging. Here, the charging voltage is maintained at a voltage lower than that necessary to fully recharge the battery 34, which is insufficient to return the battery to a full state of charge, thereby maintaining the battery 32 in a PSOC. The cycle (or micro-cycle) then is repeated.

[0037] If the battery 32 is in a full state of charge or a higher state of charge than desired, for whatever reason, the battery will be allowed to discharge until it reaches a desired or predetermined PSOC, a reasonably fixed number or within a desired range. Then the battery will be charged, e.g., via regenerative braking, in accordance with the cycle discussed above. The actual SOC number or range used for the PSOC will be determined by the charge acceptance of the actual battery in the actual circumstances. It is not set directly by the controls but by the selected charging voltage which is usually 14.0V and which normally brings the battery into a PSOC of about 60%.

[0038] Generally, there is no need to remove excess charge when the SOC is above the PSOC. Using a charge voltage of 14 V, for example, the charge cannot fully recharge the battery unless the engine were to be run continuously for many hours. A charge at 14 volts is not enough to recharge the battery in any reasonable period of time. A higher voltage is needed for that. Thus, a battery that may start off at or somehow arrive at a state of charge higher than the desired PSOC will, with the charging voltage of 14 volts, ultimately discharge towards the desired PSOC range. It may be an option, however, to not provide charge from regenerative braking or other source until the battery SOC falls to the PSOC.

[0039] The discharging/charging cycle discussed above repeats itself. In real life, however, maintaining the battery in a PSOC, particularly where there is significant stand time when the vehicle is not in use, the sulfation process as discussed above within the battery cells will ultimately degrade and ruin the battery. As now discussed in more detail, the present invention removes the sulfation and thereby extends the life of the battery.

[0040] As noted previously, the failures of micro-hybrid batteries are believed to be blamed improperly on inadequate battery design whereas the blame is believed to rest with the development of sulfation. In broad terms, the present invention provides for periodic recharging of a micro-hybrid lead acid battery to a higher state of charge to remove the sulfation. This is will correct most of the problems of such a battery and will do so at a low cost, making it a preferred solution to the problems at hand.

[0041] In one form, the invention provides a method for removing the lead sulfate crystals by periodically charging the battery to a state of charge higher than the PSOC normally maintained for the battery in the vehicle. One means of carrying out this method is to arrange for the battery 24 to be automatically equalization charged periodically, preferably to a full charge, but to some other intermediate state higher than the normal PSOC if not. A full charge, called an equalization charge, might be done, for example, once a month, once a week, or some other fixed period of time, or based on an algorithm that would take into account, for example, the environmental temperature, the type of driving the system has to support such as highway versus city driving, the number and duration of the rest periods and other factors that affect the outcome.

[0042] Such a flexible automatic, semi-automatic, or manual equalization of the battery 32 will virtually eliminate all the sulfates in the negative plates 48 on a regular basis and remove the fundamental failure mode of present micro-hybrid systems, e.g., Ostwald Ripening, almost in its entirety. In one preferably automatic form, this system could be programmed to balance the benefit of the equalizing charge with the need to maximize the recovered braking energy. The system could be self-learning and self-optimizing, adjusting to conditions automatically. This charging protocol is capable of maximizing the energy efficiency of the vehicle while increasing the life of the battery and reducing its cost.

[0043] For a typical 12 volt battery, this may involve charging the battery at a voltage higher than the voltage used to recharge the battery during the 13 ACTIVE 31803604v5 03/16/2016 normal cycle in which the PSOC is maintained. For example, a charging voltage of 14V is used to maintain the PSOC. For equalization charging of a typical six cell 12 volt battery, a charging voltage greater than 14 volts should be used, a charging voltage in a range of about 2.4 to 2.5 volts per cell being preferred. This equalization charging process and the control of the voltage therefore can be controlled preferably by the controller 34 programmed for this additional use.

[0044] The equalization charge at the higher voltage is preferably provided until the battery cells are fully charged. There are various known means for monitoring the batter for determining when the full charge state is reached, such as monitoring voltage across the battery during the charging process. As a battery is charged, the voltage across the battery rises towards the charging voltage (the voltage set for the charger). As the battery reaches the full state of charge, the battery voltage reaches the charging voltage. The battery is fully charged when the change in voltage with respect to time (dV/dT) across the battery during the charging process becomes substantially zero. At this point it may be preferable add additional charge to ensure that all cells are equally charged, such as by continuing to charge by adding 2-4% additional current beyond what was added during the charging process.

[0045] Another embodiment of the present invention is the addition of catalysts 60 in the battery cells 40 capable of recombining oxygen and hydrogen gasses to water. Such catalysts will consume excess oxygen in the cells and recombine it with the normally available hydrogen to form water. Catalyst are of added benefit where equalization charging will cause electrolysis and loss of water from the electrolyte 44 in the battery cells. This is a great benefit especially for sealed VRLA batteries where a 10% water loss implies end of life. Catalysts will also work on flooded cells such as the EFB (Enhanced Flooded Battery) used widely for the lower priced cars. Importantly, where catalysts are used the battery cells can be substantially overcharged without losing water. Catalysts will also reduce the manufacturing cost of the battery by allowing the use of cheaper lead oxide for NAM production.

[0046] It is preferable to use oxidation catalysts in the battery cells of the battery 24. These catalysts will consume all free oxygen in the cells and recombine it with the always available hydrogen to form water — a major benefit for a sealed battery. Thus, the battery can be overcharged and equalized without consuming any significant amount of water, and without losing service life. Preferable catalysts include, among others, those described in U.S. patents 6,285,167, and 7,326,489, and PCT publication WO1999041798 A1, all of which are hereby incorporated by reference herein, and which are appended hereto. A preferable catalyst material is potassium hydroxide.

[0047] A catalyst can remove oxygen produced by overcharging. It therefore allows a charge voltage to be set much higher than the usual 14 volts on a 12 volt battery. This higher voltage, say 14.5V, or even higher, allows the battery 32 to receive a higher charge current and thereby store a greater amount of energy produced by the generator 18. All this can be accomplished without water loss. A compromise is also possible. If the lead used for the electrodes were pure enough, and the amount of liquid electrolyte in the battery large enough, the charging protocol might be practical without the use of catalysts.

[0048] Another benefit is that, because the charging current can be raised or lowered by adjusting the charge voltage, the present invention potentially allows even the PSOC level to be raised, for example, from 60% of capacity to 80% of capacity or any other value for that matter. This is possible because the NAM is largely free of hard sulfates and has a high Dynamic Charge Acceptance (DCA) which does not decline. It also has more capacity for engine starting and for auxiliary loads such as fans, radios etc., which is equivalent to having a larger battery for the same purchase price. Alternately, the battery may be made smaller to reduce vehicle weight which then reduces fuel costs and is an advantage for the car manufacturers. Another subtle advantage is that only half the amount of energy is needed to recharge from 80% to 100% than from 60% to 100%.

[0049] Yet another benefit is that the PSOC level can be chosen to be higher, lower or even continuously adjustable as the vehicle's sensors determine the need. For example, on long, fast drives, the micro-hybrid system is not in use and there are no micro-cycles. However, when the vehicle brakes from speed on a highway, it will regenerate a lot of energy so the PSOC could be automatically adjusted down to 50% or even less, to provide "space" for the charge. On the other hand, in city driving, such as a taxi operation, the number of micro cycles will be many and frequent. Here the PSOC could be adjusted upwards to 70% or 80% or more. The vehicle computer can easily do this automatically.

[0050] Currently Preferred Battery Types. Although any suitable battery type may be used in micro-hybrids, there are several presently preferred battery types which are further discussed herein. These include the two main presently preferred types: EFB (Enhanced Flooded Battery) and the VRLA (Valve Regulated Lead Acid) battery. The VRLA is used more for expensive cars and the EFB for the lower priced cars. A third battery design called the semi-flooded EFB battery is also discussed below.

[0051] The EFB battery cell shown in Figure 2A represents a flooded, vented battery and is basically similar to an old fashioned, non-antimony battery but with extra carbon added to the very pure NAM and with low-resistance radial grids. The negative plates 48 are submerged in the sulfuric acid electrolyte 44 and safe from oxygen in the cell headspace 56. In an EFB, there are no pressure relief valves and the cell vents freely to atmosphere through a vent 58. Any overcharge will simply electrolyze the water in the electrolyte 44 and shorten the operating life of the battery. A catalyst 60 in an EFB battery cell 40 will recombine the oxy-hydrogen gases produced by charging and thereby increase the life of the battery. An EFB battery costs less to make than a VRLA and it has, for the same size, about 15% more Ah capacity owing to the extra electrolyte 44 in the cells. EFB batteries are very likely to be subject to acid stratification with dense acid of the electrolyte falling to the bottom of the cell. Fully charging the battery periodically will eliminate that issue.

[0052] A Semi-flooded battery cell 90 as illustrated in Fig 2B is of the type disclosed in US patent 6274263 which is hereby incorporated herein by reference. This is a flooded cell like the EFB battery but with a VRLA pressure relief vent plug 92 and catalyst 60. However, the electrolyte level 46 is deliberately lowered to expose the top portion 96 of the plates 48, 50 above the electrolyte level, preferably about one quarter of an inch being exposed. This allows the oxygen cycle, necessary for a VRLA, to take place on the exposed lead surface 96 of the negative plates 48 without the extra cost of glass mats as used with traditional VRLA batteries. It also yields a 15% higher reserve capacity, like the EFB battery due to having more available acid than a VRLA with glass mats.

[0053] The VRLA (valve regulated lead acid) battery cell 100 shown in Fig 2C has AGM (Absorbed Glass Mat) separators 102 and a pressure relief vent 92 with catalyst 60. The plates 48, 50 are similar to the EFB plates but even more dependent on pure lead in the NAM. Their capacity is about 15% lower than an EFB in the same size compartment because there is less electrolyte 44 in the VRLA. The glass mats 102 may reduce stratification in the short term but may still have problems in the long term but there is no published data on this effect. The VRLA battery is substantially more expensive to build than the EFB.

[0054] It can be seen from the above discussion that the Micro-hybrid system, which helps conserve energy, but which presently has serious and fundamental problems of self-discharge and sulfation due to the necessity of being kept in an unstable partial state of charge, can benefit greatly and be improved substantially by the addition of catalysts to the cells in conjunction with specific modifications to the charging protocols.

[0055] De-Stratification of the Electrolyte. Another advantage of the present invention is that an equalization charge will “gas” the liquid electrolyte in flooded batteries such as the EFB battery or the Semi-flooded battery, thereby mixing the electrolyte with the gas bubbles and eliminating any damaging acid stratification that may otherwise occur.

[0056] Effect On Overall Energy Efficiency Of The Vehicle. It may appear that when the battery 32 is fully recharged by the generator 18, that the process will entail a waste of energy due to the recharge energy used. In practice, however, a substantial portion of that energy will be given back to the system by not having to charge the battery as it settles back down to its designed PSOC. In addition, because the DCA of a charged battery is always high due to the recharging process, more energy can be captured at other times by a healthy battery than one with a declining DCA.

[0057] Auxiliary Charging. In a further embodiment, auxiliary charging can be used for the equalization charging, e.g., recharge the battery to a full state of charge without using any fuel from the vehicle if the energy is delivered from sources other than the generator 18. For example, a small plug-in charger in a garage would be practical and effective, especially if it were subject and thus controlled by the controller 34. Essentially, this would reduce fuel usage by using electricity from the grid to equalize the battery.

[0058] Another example of an auxiliary source in sunny climates would be the use of a solar panel. For example, a small solar panel on the roof of the vehicle that would recharge the battery automatically with no action needed on the part of the driver. Since most cars are in a state of rest during the day, often in parking lots, this might substantially reduce the energy used to equalize the battery via the generator 18. A recharge of 10Ah (amp hours) per day for a 60Ah battery is substantial indeed. As before, it would be under the control of the controller 34 and only take place when needed.

[0059] Test Data. Fig. 4 shows the results of a test involving two identical 12 volt, six cell VRLA batteries, incorporating the latest stop-start battery technology, including having carbon in the negative plates. The batteries underwent a life test using stop-start micro-cycles (each micro-cycle includes a charge and discharge phase). Each micro-cycle had the same profile, a discharge of 300 amps for one second followed by a recharge to the PSOC charge voltage of 14 volts similar to that seen in Fig 3.

[0060] The two batteries were maintained in a partial state of charge during the normal micro-cycle operation by maintaining the charging voltage at 14V, or 2.33 Vpc (volts per cell). For the equalization charge, when applied, a charge voltage of 14.4V, or 2.4 Vpc was applied for a set time period of 8 hours. The Control battery graph line is 70 (no equalization applied) and the Experimental battery graph line is 72 (equalization applied).

[0061] In earlier tests conducted, the batteries failed at 30,000 micro-cycles so the Control battery on this test was nearing end-of-life conditions at point 74. End of life is basically the failure of the battery to start an engine. The batteries behaved almost identically on the initial part of the test as seen.

[0062] However, at about 19,000 micro-cycles, at point 76, the Experimental battery was treated to the charging protocol of the invention described above: it was recharged fully with an equalization charge at a voltage of 14.4 volts for 8 hours during the rest period and put back on test. There was no special charging termination action, such as terminating the charge when dV/dT=0 (measured change in battery voltage with respect to time equals 0), taken during this test, simply a termination after charging for 8 hours. The result was a major reduction in battery impedance as shown. The impedance of the Control battery continued to rise so the difference in impedance between the two batteries at 21,000 micro-cycles was in the order of 30% as seen by line 78. As the cycling continued to 24,000 micro-cycles the impedance of the Experimental battery was approaching half that of the Control battery. To put it another way, the impedance of the Experimental battery at over 20,000 micro-cycles was about the same as it was back at 10,000 micro-cycles.

[0063] Two later batches of micro-cycles at 80 and 82 with equalization charging were run but showed little further reduction in impedance. Here it is believed that the old lead sulfate created earlier in the test, caused by Ostwald ripening, could not be dissolved in the short recharge time available.

[0064] The graph indicates that if the charging protocol had been deployed from the beginning of the test, there would have been no substantial rise in impedance during the entire test thereby improving the Dynamic Charge acceptance and engine-starting capability of the battery during its entire life. Without the equalization charge, as shown by the Control battery, the battery condition deteriorates continuously with use. In the test the equalization charge was provided for a set time of hours. A set time period for an equalization charge is an option and can be determined based on various factors. This option is in addition to other options for determining when to stop the equalization charge, such as the option of applying the equalization charge until the change in voltage with respect to time (dV/dT) is substantially zero and then adding some small amount of additional charging time such as 2 to 4% as discussed above.

[0065] The present invention is a means of improving present micro-hybrid systems to make the batteries last longer, perform better, recover more regeneration energy, and cost less to manufacture, using mainly a combination of two actions which are based on fundamentals of lead acid battery design and operation. Starting with present production micro-hybrid batteries, including the improvements like carbon, two new and original actions are proposed which work together to form a substantially improved system.

[0066] The present invention is also applicable to uses other than micro-hybrid vehicles where a lead acid battery is maintained in a partial state of charge and sulfation is a problem.

[0067] It is appreciated that described above are novel methods, systems and devices. It is also understood that this invention is not limited to automotive batteries, but can be used with any lead acid battery used in a PSOC application. It is also understood that the invention is not limited to the embodiments and illustrations described above, and includes the full scope provided by the claims appended hereto.

Claims:

1. In a method for operating a lead-acid battery used with a micro-hybrid vehicle whereby the battery includes at least one cell maintained in a predetermined partial state of charge (the “predetermined partial state of charge” referred to hereinafter as the “PSOC”) so as to be capable of accepting electrical charge from regenerative braking, said cell including a positive electrode and a negative electrode and an electrolyte in contact with said positive and negative electrodes, wherein maintaining said PSOC includes use of a predetermined charging voltage which is sufficient to charge the cell to said PSOC but which is insufficient to charge fully the cell, and in which there is formed sulfation on the negative electrode when the cell is maintained in said PSOC which, if not removed, reduces the capacity of the cell to hold charge, the improvement comprising removing at least a portion of the sulfation by charging the cell to a state of charge higher than said PSOC using a charging voltage which is higher than that used for maintaining said PSOC, which cell is returned to said PSOC after having reached said higher state of charge above said PSOC.

2. A method according to claim 1 wherein said step of removing at least a portion of the sulfation by charging the cell to said higher state of charge comprises charging said cell to a full state of charge.

3. The method according to claim 1 or 2 wherein said battery includes six cells.

4. A method according to any one of claims 1 to 3 wherein said charging voltage used to obtain a full state of charge in said cell is high enough to induce in said electrolyte electrolysis, which produces hydrogen and oxygen gasses.

5. A method according to claim 4 further comprising catalytically converting at least a portion of the oxygen gas and a portion of the hydrogen gas to water which is retained in said cell.

6. A method according to any one of claims 1 through 5 wherein the step of charging the cell to said higher state of charge and then returning to the PSOC is repeated after predetermined time intervals.

7. A method according to any one of claims 1 through 6 wherein the step of returning the cell to said PSOC after being charged to said higher state of charge includes limiting charging of the cell until the PSOC is reached.

8. A method according to any one of claims 1 through 7 wherein said desired PSOC comprises a range of states of charges which are less than a full state of charge.

9. A method according to any one of claims 1 through 8 wherein said desired PSOC is within a range of about 60% to 95% of a full state of charge for said cell.

10. A method according to any one of claims 1 through 9 wherein the step of charging the cell to said higher state of charge and then returning to the PSOC is repeated after predetermined time intervals based on the driving conditions of the vehicle.

11. A method according to any one of claims 1 through 10 wherein the step of charging the cell to said higher state of charge is carried out during use of said vehicle sufficiently long to allow the full state of charge to be obtained.

12. A method according to claim 9 wherein said desired PSOC is within a range of about 60% to 80% of a full state of charge for said cell .

13. A method according to any one of claims 1 through 12 wherein the charging voltage used for charging said cell to said higher state of charge is at least about 200 mV to 500 mV in excess of the value of an open-circuit voltage of said cell.

14. A method according to any one of claims 1 through 13 wherein, when charging the cell to said higher state of charge, the cell is charged at least until the voltage of the cell stops increasing.

15. A method according to any one of claims 1 through 14 wherein the charge voltage for obtaining a full state of charge is no less than about 200mV to about 500mV in excess of the value of the open-circuit voltage of the cell.

16. A method according to any one of claims 1 through 15 wherein said cell is a valve regulated lead acid cell.

17. A method according to any one of claims 1 through 15 wherein said cell is a flooded vented cell.

18. A method according to claim 7 wherein said limiting step includes preventing any recharge from the regenerative braking.

19. A method according to any one of claims 1 to 18 wherein the open-circuit voltage of the cell when fully charged is about 2.15 volts and the charge voltage for said higher state of charge is no less than about 200mV to about 500mV higher than the open circuit voltage.

20. A method according to anyone of claims 1 through 19 wherein during charging of the cell to said higher state of charge there is produced at the positive and negative electrodes respectively oxygen gas and hydrogen gas, the improvement further comprising catalytically converting at least a portion of the hydrogen and oxygen gas to water which is returned to the electrolyte.

21. A method according to claim 20 wherein said step of catalytically converting includes a catalyst material which is a metal of the platinum group of metals.

22. A method according to claim 21 wherein said metal is palladium.

23. A method according to any one of claims 1 to 22 wherein said cell comprises a flooded cell having a sealed housing; a liquid electrolyte within said sealed housing in contact with said positive and negative electrodes, a gas space within said housing in which said oxygen and hydrogen gas collects, a portion of said negative electrode being exposed in said gas space to thereby expose a portion of the lead active material of the negative electrode to said gas space; a pressure relief valve in communication with said gas space to allow gas to escape said sealed housing while preventing oxygen from outside the housing to contact said negative electrode; and a catalyst for converting at least a portion of the oxygen gas and a portion of the hydrogen gas to water.

24. A method according to any one of claims 1 through 23 wherein said steps of maintaining said partial state of charge, removing the sulfation by charging the cell to a higher state of charge, and returning said cell to said PSOC after having reached said higher state of charge is carried out by use of a controller.

25. A method according to any one of claims 1 through 24, wherein said step of charging the cell to said higher state of charge is carried out with an uninterrupted flow of current.

26. A method according to any one of claims 1 through 24, wherein the means for charging the cell to said higher state of charge is carried out with an intermittent flow of current.

27. A method according to claim 10 where said predetermined time intervals for repeating said step of charging can change with each new step of charging the cell to said higher state of charge.

28. A method according to any one of claims 1 through 27 wherein the step of charging the cell to said higher state of charge is carried out by a charger external to said vehicle while the vehicle is at rest.

29. A method according to any one of claims 1 through 28 wherein the step of charging the cell to said higher state of charge is carried out by use of a solar panel.

30. In a method for operating a lead-acid battery which includes at least one cell maintained in a partial state of charge ("PSOC") so as to be capable of accepting electrical charge, said cell including a positive electrode and a negative electrode, and an electrolyte containing sulfuric acid in contact with said positive and negative electrodes, wherein maintaining said PSOC includes use of a predetermined charging voltage which is sufficient to charge the cell to a said PSOC but which is insufficient to charge fully the cell, and in which there is formed lead sulfate on the negative electrode when the cell is maintained in said PSOC which, if not removed, reduces the capacity of the cell to hold charge, the improvement comprising removing at least a portion of the lead sulfate by charging the cell to a state of charge higher than said PSOC using a charging voltage which is higher than that used for maintaining said PSOC, which cell is returned to said PSOC after having reached said higher state of charge.

31. A system for maintaining charge in a battery which is deliberately maintained in a partial state of charge (PSOC), said system comprising;

    a lead acid battery having at least one cell maintained in said PSOC so as to be capable of accepting electrical charge, said cell including a positive electrode and a negative electrode and an electrolyte containing sulfuric acid in contact with said positive and negative electrodes;

    a generator for generating electrical current, said generator being in electrical communication with said cell to provide a charging current thereto;

    a controller in communication with said cell so as to receive information for determining the charge status of said cell, and operatively connected to said generator for controlling the charging current directed to said cell, wherein said controller is configured to control the charging current to maintain the desired PSOC and, at intervals sufficient for removing at least a portion of lead sulfate that has formed on the negative electrode, charging the cell to a state of charge higher than said PSOC by providing a charging voltage which is higher than that used for maintaining said partial state of charge and then, after having reached said higher state of charge, returning to the lower charging current to maintain the desired PSOC.

32. A micro-hybrid vehicle, comprising:

    a combustion engine;

    vehicle wheels operatively connected to said engine; and

    the system as set forth in claim 31, wherein said generator is operatively connected to at least one of said wheels so as to generate electricity by braking said vehicle.

33. A micro-hybrid vehicle in accordance with claim 32 wherein said controller is further configured to start and stop the engine.

34. The micro hybrid vehicle of any one of claims 1 to 22 and 24 to 33 wherein said battery is a flooded battery, an EFB, a sealed battery, a VRLA battery, or a semi-flooded battery.

35. A method according to any one of claims 1 to 29 wherein said step of returning said cell to said PSOC after having reached said higher state of charge above said PSOC includes returning to said predetermined charging voltage which is sufficient to charge the cell to said PSOC.

36. A method for operating a battery maintained in a partial state of charge to remove sulfation that develops within said battery; comprising:

    (a) providing a lead acid battery having at least one cell, said cell including a positive electrode and a negative electrode and an electrolyte in contact with said positive and negative electrodes;

    (b) maintaining said cell in said predetermined partial state of charge so as to be capable of accepting electrical charge, wherein said maintaining step includes use of a predetermined charging voltage which is sufficient to charge the cell to said partial state of charge but which is insufficient to charge fully the cell;

    (c) charging the cell to a state of charge higher than said predetermined partial state of charge using a charging voltage which is higher than that used for maintaining said predetermined partial state of charge; and

    (d) returning said cell to said predetermined partial state of charge after having reached said higher state of charge above said PSOC; said returning step including returning to said predetermined charging voltage which is sufficient to charge the cell to said partial state of charge.

37. The method of claim 36 wherein said steps (b), (c), and (d) are repeated.

38. The method of any one of claims 36 and 37 wherein step (c) is carried out at least until the cell is charged fully.

39. The method of any one of claims 37 to 38 wherein the cycle time between each step (c) can vary.

40. The method of any one of claims 36 to 39 further comprising the step of (e) catalyzing at least a portion of any hydrogen and oxygen gasses within said cell by use of a catalyst.

41. The method of any one of claims 36 to 40 wherein said step (b) through (d) are controlled by a controller.

42. The method of any one of claims 36 to 41 wherein multiple micro-cycles are carried out during step (b) prior to the step (c), each micro-cycle including a discharge phase and a charging phase of the battery.

43. A method for operating a battery maintained substantially in a predetermined partial state of charge to remove sulfation that develops within said battery; comprising:

    (a) providing said lead acid battery having at least one cell, said cell including a positive electrode and a negative electrode and an electrolyte in contact with said positive and negative electrodes;

    (b) electrically discharging said cell to power a load electrically connected to said battery;

    (c) electrically charging said cell while maintaining said predetermined partial state of charge, said cell being maintained in said predetermined partial state of charge by limiting the charging voltage sufficiently to charge the cell to said predetermined partial state of charge but which charging voltage is insufficient to charge fully the cell;

    (d) repeating steps (b) and (c), each combination of steps (b) and (c) completing a micro-cycle;

    (e) after a plurality of micro-cycles, charging the cell to a state of charge higher than said predetermined partial state of charge using a charging voltage which is higher than that used in step (c); and

    (f) after step (e), returning said cell to said predetermined partial state of charge.

44. The method of claim 43 wherein step (f) comprises returning to steps (b) and (c).

45. The method of claim 43 or 44 wherein steps (b) through (f) are repeated.