



A Modified Lead-Acid Negative Electrode for High-Rate Partial-State-of-Charge Applications

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A simplified profile imitating the micro-hybrid driving mode is performed on the lead acid batteries to evaluate the effect of the modified negative electrode design with half carbon paste as part of negative plate under high rate partial-state-of-charge operation (HRPSoC). In this work, we report that the half side carbon paste replacing half of the spongy lead negative paste in negative plate has significantly improved the cyclability of lead-acid batteries under high rate partial-state-of-charge operation. This is mainly attributed to the high specific surface area and conductivity of the carbon black. In addition it minimises the formation of irreversible lead sulfate at the negative plate. Thus, half carbon black on negative plate in lead acid battery eventually improves the performance characteristics of lead-acid cells under HRPSoC cycling.

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Carbon based materials have been gradually entering a prominent place in energy storage and conversion. This material has long been incorporated into the electrodes of energy-storage devices as electro-conductive additives, supports for active materials, electron transfer catalysts, intercalation host and substrates for current leads, agents for the control of heat transfer, porosity, surface-area and capacitance.¹ Lead-carbon battery which has been recently introduced in energy storage application manifested itself to a great extent in improving specific energy of lead-acid battery (hereafter to be referred as LAB). A storage device suitable for a particular application must meet all its requirements.^{2,3} Various parameters influence the performance of lead-acid battery.⁴⁻⁹

The major negative aspect of LAB is the low specific energy and sulfation of negative electrodes under HRPSoC operation. Several publications established the effect of carbon addition to the negative plates of lead-acid batteries operated under HRPSoC conditions.¹⁰⁻¹⁵ In order to improve the specific energy and cyclability of LAB in PSOC application, carbon foams were investigated as potential substitutes instead of lead current collectors.¹⁶ Recently CSIRO and FURUKAWA developed a split-electrode (ultra battery) using electrodes of lead and carbon.^{17,18} Axion International developed a carbon based negative electrode for LAB.¹⁹

Interestingly, earlier studies have reported the cell potential and cycle life of the carbon/lead electrode and have not carried out characterization of the active material. In this study a single negative electrode consists of half spongy lead and half carbon without any split design was assembled. The charge storage mechanism on half carbon/lead electrode is a combination of electrical double layer, “hydrogen” pseudo capacitance on the carbon active material and conventional lead to lead sulfate on the lead active material. With the replacement of a half side carbon paste instead of spongy lead there is a decrease in the mass of the electrode which improves the specific energy of LAB.

We report herein the preliminary results of the lead-acid cells constructed with conventional spongy lead negative electrode, half carbon and half lead with single tab and dual tab (hereafter to be referred as NPHC ST and DT) negative electrode. The positive electrode was conventional lead dioxide (PbO₂) electrode. The potential of individual electrodes were quoted against cadmium reference electrode.²⁰

Experimental

Conventional lead-acid cell of 3.0 Ah capacity with leady oxide negative plate alone was also prepared (Fig. 1a) and compared with present investigation. The dimensions of the positive and negative plates made from Pb-Ca were of 55 mmX 50 mmX 2.5 mm and

55 mmX 50 mmX 1.5 mm, respectively. The modified negative electrode studied in this paper consists of vertical half side of lead alloy grid pasted with leady oxide and other half side pasted with carbon black (CB) as shown in Figs. 1b and 1c. The negative lead paste was prepared by conventional method and the carbon paste was prepared by addition of a binder. The aforesaid pastes were applied on the electrode without any split design. In addition to single tab, dual tabs were provided on lead grid to study the electron transfer path. The cells were filled with 45 mL of 1.25 sp.gr sulphuric acid (H₂SO₄).

The cell performance was evaluated under simulated HRPSoC conditions, using a simplified profile imitating micro-hybrid driving mode. The first step in this cycling profile was to discharge at $I = 1$ C A rate to 50% State of Charge (SoC) (Where C is the capacity after 1 h discharge determined from the Peukert equation). The cells were then subjected to cycling according to the following schedule: charge at 2 C rate for 60 s, rest for 10 s, discharge at 2 C rate for 60 s, rest for 10 s. The test was stopped when the end voltage reaches 1.83 V or when the upper voltage limit of 2.83 V was reached. The above-described cycling steps comprise of one cycle-set of the test. After this cycle set, the cell was fully re-charged (to 100% SoC) and their C₂₀ capacity was measured then followed to second cycle-set.¹³ The charge-discharge tests were carried out using Bitrode life cycle tester. Electrochemical impedance measurements were carried out with an AUTOLAB PGSTAT 30 instrument. After cycle test, Negative Active Mass (NAM) was removed from the grid and subjected to X-ray diffraction (XRD) and Scanning Electron Microscopic (SEM) analysis.

Results and Discussion

Presence of leady oxide (LO) and additives.— The specific energy of the cell is determined by total mass of its components. In this present study we are focusing on weight reduction of negative active mass. Fig. 2a shows that electrode made up of a large portion of the leady oxide. On the other hand, in NPHC cell 50% wt of leady oxide was replaced with 20% wt of carbon black material as represented in Fig. 2b. The results derived from these cells will be useful for illustrating the benefits of the half carbon negative plate cell performance in HRPSoC cycling. Addition of carbon black in NPHC cells will improve the charge acceptance, reduce the weight of cell and increase the active mass utilization which in turn increase the specific energy and prevent the irreversible lead sulfate in NAM during HRPSoC cycling. Generally the major limitation to reaction rate in lead acid battery is the transport of ions and electrons. If the migration pathways of ions and electrons are long, or difficult due to the conductivity of the materials, it takes a larger driving force to transport charge and more useful energy is converted to thermal energy instead of electric energy. For this reason, most efforts toward increasing specific energy are aimed at finding high-conductivity materials, increasing contact at

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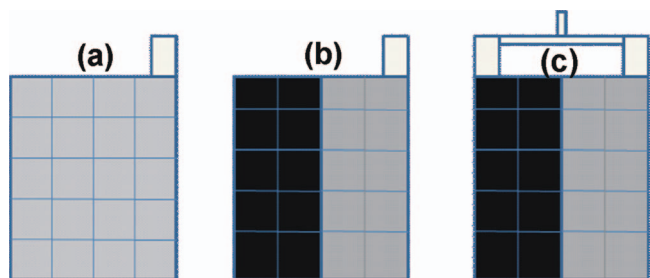


Figure 1. (Color online) Schematic illustration of the negative electrode design: (a) Blank; (b) NPHC ST; (c) NPHC DT.

interfaces and cell design to provide short conduction paths for ions and electrons.

Initial capacity of the test cells.— The initial capacity of the cells was determined at 20-h discharge rate. Each cell was subjected to 15 subsequent capacity cycle tests at room temperature. For NPHC cells, the initial capacity was low due to the reduction of the active material replaced with carbon. These cells are found to attain their stabilized capacity at 15th cycle. The utilization of negative active material was at a normal level initially but increased through the several cycles to reach the nearby capacity of the blank cell as shown in Fig. 3. If this performance were to be translated into a full size battery it would provide a higher specific energy compare with conventional batteries. Improving the performance of the negative electrode is of almost importance in lead–acid battery which is to be used as an electrical energy storage device for HEV applications.

Cycle life of cells in HRPSoC condition.— Charge /discharge current for HRPSoC regime was determined from the blank cell and this value was applied to both tabs of NPHC cells. The half carbon paste stores energy using a non-faradaic double layer formation and also due to faradaic pseudo capacitive process such as intercalation reaction of hydrogen. The spongy lead stores energy using a conventional faradaic process of lead to lead sulfate. The carbon black (CB) incorporated in the skeleton structure of grid surface improve high rate charge acceptance due to the non faradaic double layer process which in turn improves the charge acceptance of carbon particles and Pb crystals. An increased amount of charge can be stored on the half side carbon paste which in turn catalyzes the reactivity of lead (Pb) electrode reaction on the other half.

The higher cell voltage of NPHC ST and NPHC DT was mainly attributed to the polarization of the half carbon negative electrode (Fig. 4). During the discharge process of a NPHC cell, fast electron transfer initially takes place at carbon surface because of the double layer capacitance of half carbon paste which in turn reduces the impact of high current density over spongy lead and slows down sulfation of the negative plate. Apart from double layer capacitance, pseudo capacitance due to intercalation of hydrogen and lead ions in due course of the reaction on carbon and faradaic reactions on lead electrode were attributed to charge transfer reaction in the longer time region. The large surface area of the half carbon paste allows the negative electrode redox reaction to take place efficiently in the HRPSoC conditions.

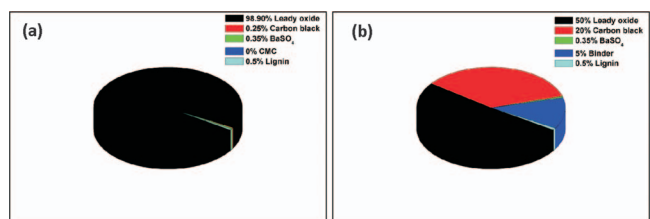


Figure 2. (Color online) Composition of negative electrode (a) Blank, (b) NPHC.

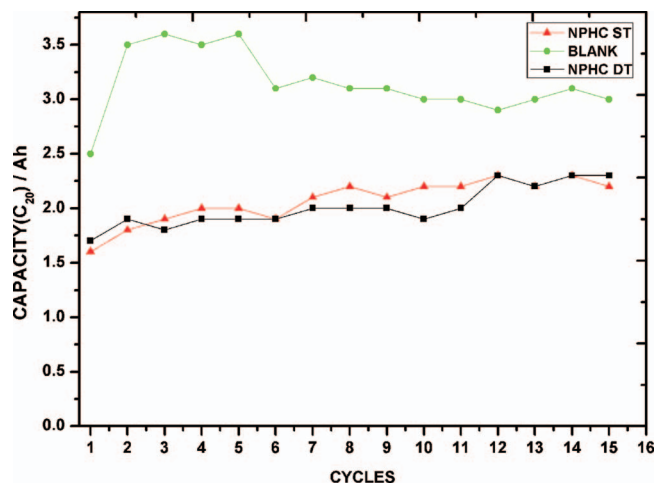


Figure 3. (Color online) Initial capacity of the cells at C/20 rate.

The result shows that carbon black makes easier to charge the accumulated lead sulfate. On the other hand, in the charging process of a NPHC DT cell, the electron flow conceded via both tab and the carbon side tab is more effective compared to lead side tab. The reason for less effective on the lead side tab may be due to lead sulfate which accomplish in the surface. Further, the horizontal rib of the grid was playing a key role in the charge process. Carbon paste is highly conducting and easily allows the electron flow of its surface to lead grid. The horizontal ribs present in the grid rapidly transfer the electron flow to the other half side (lead sulfate side) so that the process of reduction is efficiently carried out to convert back into spongy lead. The dual tab grid design provides excellent current collecting capabilities of the negative plate. The electron flow to the active sites in the negative-plate material was carried via the grid members since the electrical resistance of the grid metal is much smaller compared to that of the discharged material.²¹ The NPHC electrodes demonstrate an enhanced resiliency and an excellent electronic conductivity, which is the prime important factor for the battery to be used in HEV applications. The elevated electrical conductivity of CB and superior tab designs are influencing for improved performance.

Cell capacity (C/20) after each HRPSoC cycle set.— The behavior of the cell capacity after each cycle set shows in Fig. 5. After first HRPSoC cycle set the capacity of the blank cell has dramatically decreased. This is due to irreversible lead sulfate formed over the

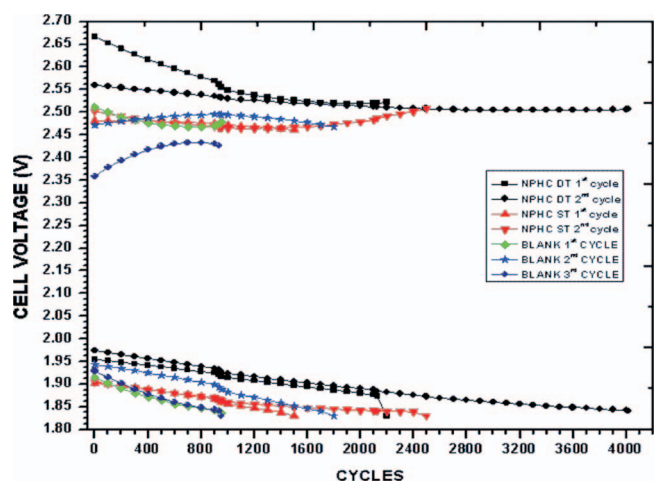


Figure 4. (Color online) Cycle and Charge/discharge cell voltage for blank and NPHC DT and NPHC ST cells on HRPSoC cycling.

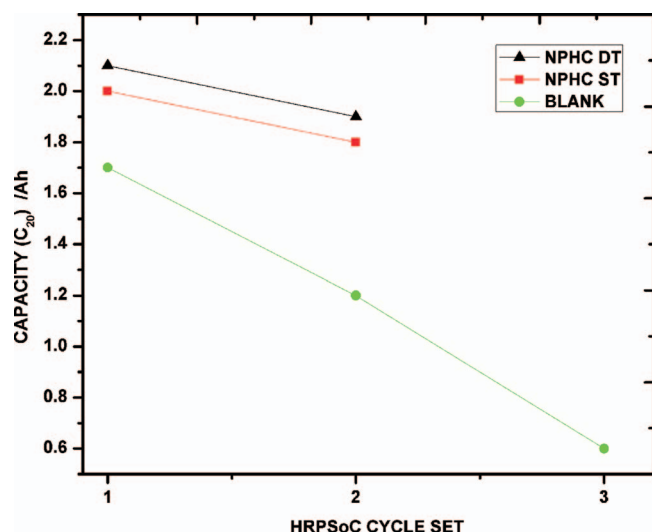


Figure 5. (Color online) Cell capacity after each HRPSoc cycle set.

negative electrode surface as shown in Fig. 6a. The discharge capacity of the NPHC cells after subsequent HRPSoc cycle sets shows a relatively small decrease in cell discharge capacity as compared to the initial capacity values. The results are shown in Fig. 5. The NPHC DT cell after completion of two HRPSoc cycle sets (that is after 6600 micro cycle) retained an 85% of initial capacity at C_{20} rate. In the case of blank (after 2750 micro cycle), retained only 40% of initial capacity at C_{20} rate. These data show that the performance of NPHC cell is substantially better than blank cell. This is well evidenced that NPHC cell has not affected by irreversible lead sulfate in the HRPSoc regime which is well established in SEM images Figs. 7b–7c.

Discharged state active mass.— Fig. 6a. Shows that there are much more large crystals of lead sulfate at the surface and inner layers of

reference negative plate (blank cell) whereas in Figs. 6b and 6c. NPHC ST and DT shows only small amounts of lead sulfate formed on the surface of the plates during end of discharge of 2nd HRPSoc cycle. The above fact is well supported with XRD pattern shown in Fig. 6d. In the remaining non-oxidized part of the negative plate, the carbon plays the role of current-conducting path. It conducts the electric current from the plate grid to each point of the half carbon paste then to inactive lead sulfate even when the plate is being discharged. This, in turn, leads to the formation of a tiny number of small crystals rather than a large number of big crystals.

Fig. 6d. shows the XRD pattern of discharged negative active material at the end of 2nd HRPSoc cycle. This analytical technique gives chemical composition and phases present on the electrode surfaces. Lead sulfate (PbSO_4) diffraction peaks are observed in all XRD patterns. The PbSO_4 peaks for NPHC DT and ST sample exhibits less intensity in relation to the blank. Further the XRD spectrum of standard negative plates (blank) superimposed on the corresponding XRD spectrum of modified negative plates emerges out that the lead sulfate peaks are more intense on the reference plates and there is an increase of the pure lead lines in the NPHC ST and DT plates as evidenced in the spectra. This is an indication that blank plate is sulphated more in HRPSoc application.

Charged state active mass.— SEM images of blank, NPHC ST and NPHC DT after charging are shown in Figs. 7a–7c. It can be seen that there are two phases namely PbSO_4 and Pb crystals in half side carbon paste added electrodes (Fig. 7b and 7c). The former are perfect crystals and the latter has a spongy structure. During charge, the major part of the discharged lead sulfate crystal has been converted to spongy lead. This is due to the formation of a conductive network between half carbon and spongy lead in the electrode which suppresses the accumulation of non-conductive lead sulfate. On the other hand, it is seen from Fig. 7a. The surface of the negative reference electrode (Blank) is completely covered with large crystals of lead sulfate. It is very clear that charging unable to convert the entire lead sulfate back to spongy lead when LAB is operated under PSoc condition.²¹ This sulfate gradually accumulates over a period of time

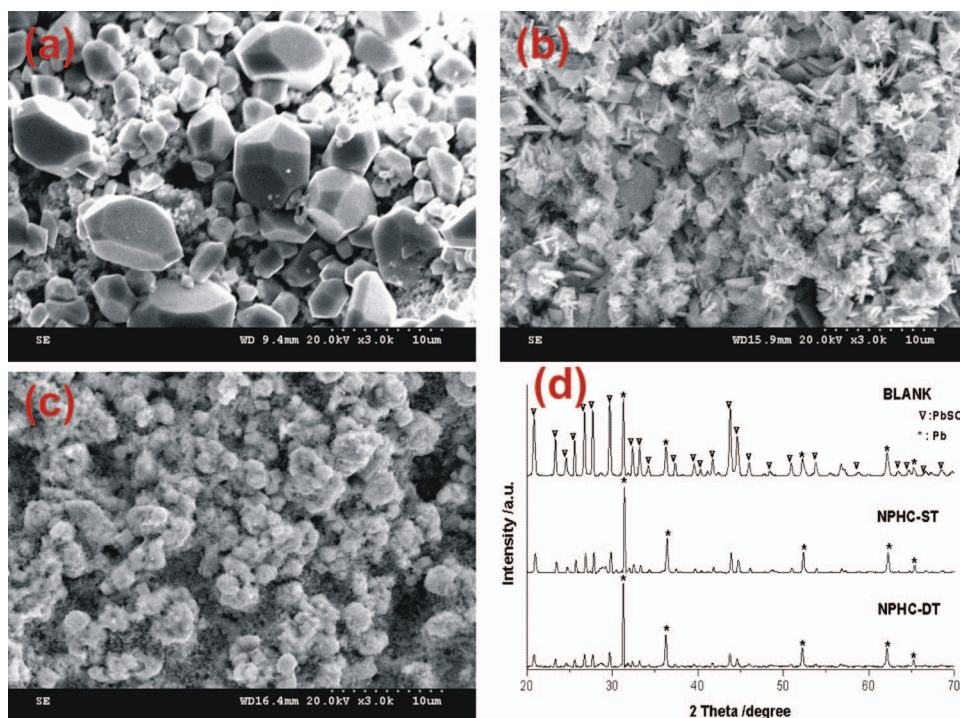


Figure 6. (Color online) SEM images of negative active material at the end of 2ndHRPSoc cycle (Discharged state): (a) Blank; (b) NPHC ST; (c) NPHC DT; (d) XRD patterns of negative active material at the end of 2ndHRPSoc cycle (Discharged state).

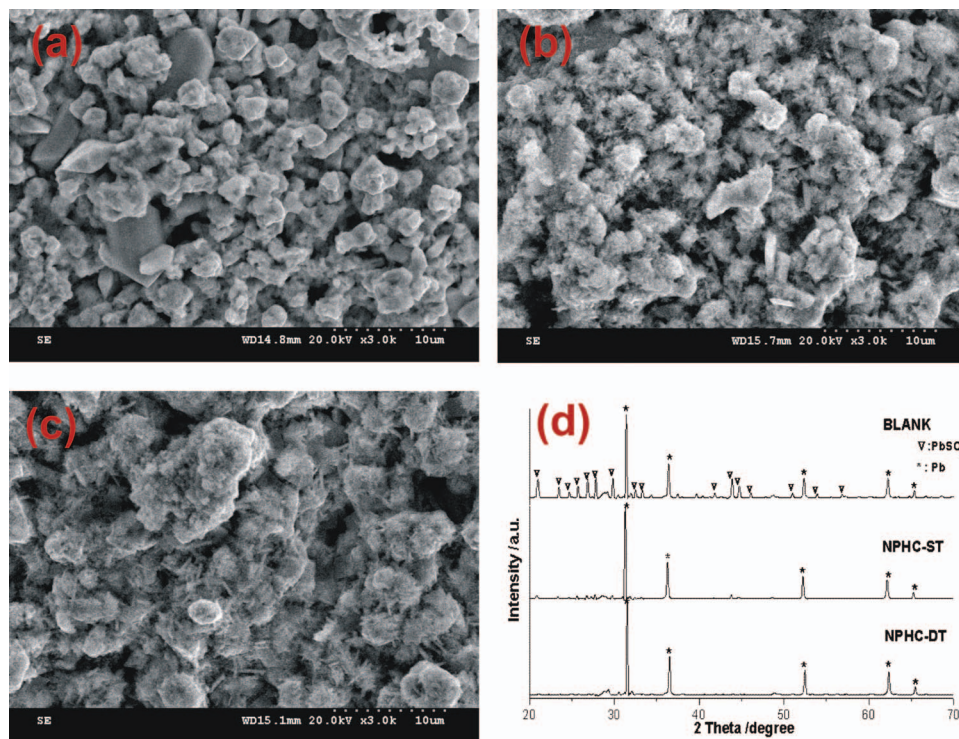


Figure 7. (Color online) SEM images of recharged negative active material: (a) Blank; (b) NPHC ST; (c) NPHC DT; (d) XRD patterns of the recharged negative active material.

and clogs the pores of the plates where the battery will not accept any charge. By adopting the novel negative plate design discussed in this paper we can reduce the accumulation of lead sulfate which will extend the cycle life of the lead-acid battery under HRPSoC condition.

Fig. 7d. shows the XRD pattern of the recharged NAM. The presence of irreversible lead sulfate on the surface of the blank cell suggests that certain amount of lead sulfate has not been converted back to spongy lead during charge. But in the case of NPHC cells even a

small amount of lead sulfate formed during HRPSoC cycling are converted back to spongy lead thus showing the improved reversibility of the NPHC cells.

Internal resistance measurement.— The study on the internal resistance of the cells indicates that there is a steep raise in internal resistance for the blank cell when the cell is in discharge mode. This is illustrated in Fig. 8. In the case of NPHC plates, the raise in internal resistance is less as compared with blank cell. This data also

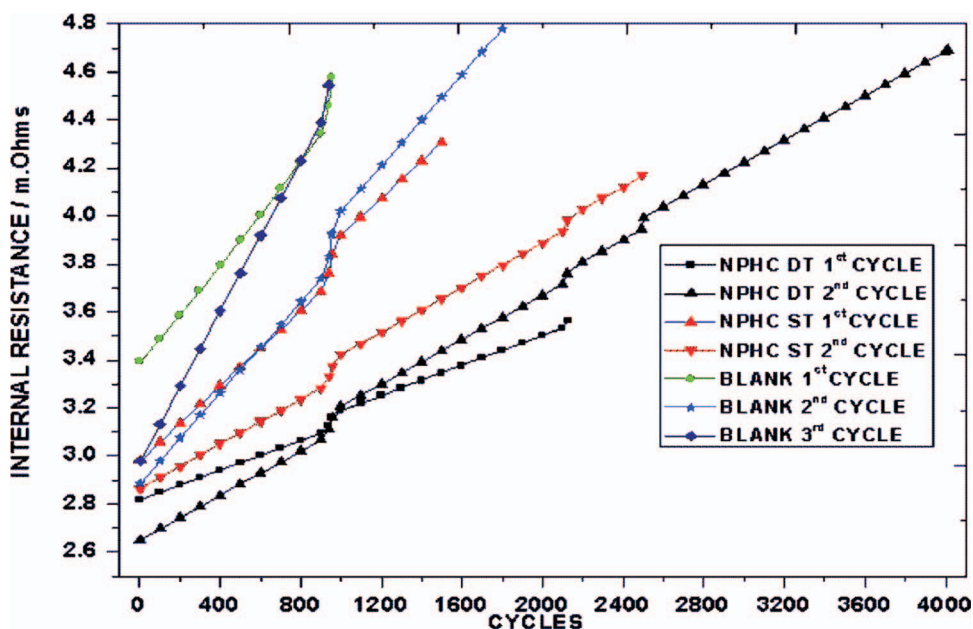


Figure 8. (Color online) Internal resistance in Blank; NPHC ST; NPHC DT cells in respective HRPSoC cycle.

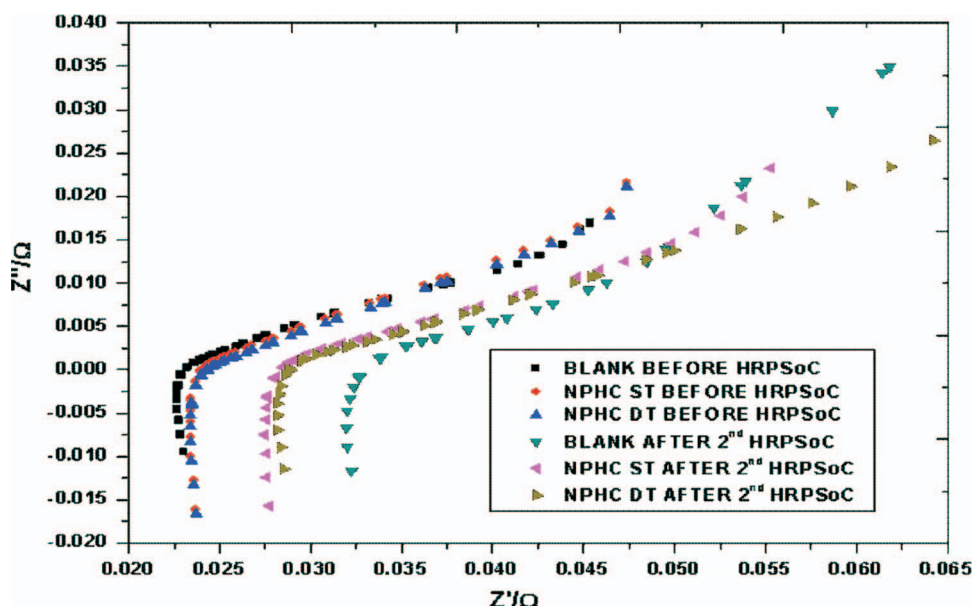


Figure 9. (Color online) Electrochemical impedance spectra for Blank, NPHC ST and NPHC DT cells before and after the HRPSoC cycle (Fully charged state).

supports the higher conducting nature of NPHC plates. Thus modified negative electrode resists irreversible lead sulfation as compared to a conventional lead acid-cell.

Impedance measurement.— Figure 9 shows the impedance measurements for the cells carried out with an AC amplitude of 5 mV and in the frequency range of 100 mHz to 100 kHz. Blank cell has significantly higher solution resistance (R_s) value than the other two. The results thus reflect that the overall resistance is decreased through half carbon paste introduction. Further the data clearly exhibits that the impedance values associated with the cells under HRPSoC are comparatively lower than those before HRPSoC cycle. This may be due to the high effective surface area, conductivity and the meso, micro and macro porosity of the carbon material which arise during the charge discharge reaction in the sulphuric acid electrolyte. The high frequency intercept on the Z' axis represents the sum of the resistances arising from the electrolyte, the intrinsic resistance of the active material and the contact resistance between the active material and the current collector.

A study on current component in the conventional lead acid negative, NPHC ST and NPHC DT cells during HRPSoC.— Special experimental arrangements were made to measure the current component on electrodes. Voltage changes of the NPHC cells were measured in the charge/discharge processes. The charge–discharge behavior processes that occur within one micro-cycle of 60 s discharge and 60 s charge of the HRPSoC cycling of carbon side (C) and spongy lead side (Pb) measured by some special arrangements provided in the grid frame to the both paste top as shown in Figs. 10b to 10c. The individual half sides and electrode potential (NEG) measured with cadmium reference electrode. This measurement carried out by using Bitrode battery lifecycle tester with typical cell voltage modules. Data sampling time was fixed between 10 seconds interval. This type of measurement only gives the precise performance of the potential within the NPHC cells. The changes in negative electrode potentials measured 10s interval during HRPSoC regime are presented in Fig. 11a to 11i.

To the best of our knowledge, throughout the experiment the carbon and spongy lead side individual potential of the negative electrode was measured for the first time.

Operational negative plate potential difference in cells.— *Blank cell.*— The measured potential of blank cell behavior summarized

in Fig. 11a to 11c. In blank cell negative plate potential drops very quickly (potential shifted to positive value) in discharging mode in comparison with NPHC cells. This effect is related that at high discharge current, the lead-ion concentration on the electrode surface is high, and the precipitation reaction $\text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4$ takes place quickly. During this operation, the solid lead sulfate is usually amorphous and has a high surface area. The number and the location of this lead sulfate depend on the reaction speed which is linked to the discharge current value. Fig. 11a to 11c shows that the negative electrode potential value changes almost linearly increasing then fully shifted to its end potential during all micro-cycle discharge. During discharge process, dissolution mechanism involves electron transfer; this phenomenon takes place only at the conductive sites and this is strongly dependent on the effective surface area of the negative active mass. In this case the surface of the electrode is fully covered by irreversible lead sulfate. These PbSO_4 act as an insulator and affect the potential or rechargeability of the negative plate. Furthermore this lead sulfate cannot be converted efficiently back to spongy lead after fully charged state. This is well documented in SEM and XRD results as summarized in Fig. (6a and 6d, 7a and 7d). The same type of behavior was not observed in Fig. 11e to 11g up to 30 s this is mainly attributed due to the presence of carbon paste presented in half of the negative electrode and share the discharge current.

NPHC ST cell.—It has been observed that combining carbon paste would significantly reduce the stress on the spongy lead paste in HRPSoC applications in which the batteries are subject to high current pulses in both charge and discharge. During charging, deposition process receives the electrons via grid member because the electrical resistance of the grid is smaller than the discharged product of lead

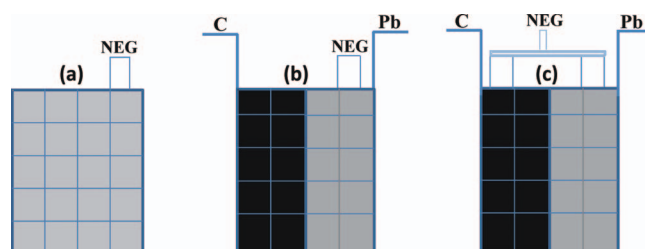


Figure 10. (Color online) Schematic illustration of the negative electrode design with special arrangements: (a) Blank; (b) NPHC ST; (c) NPHC DT.

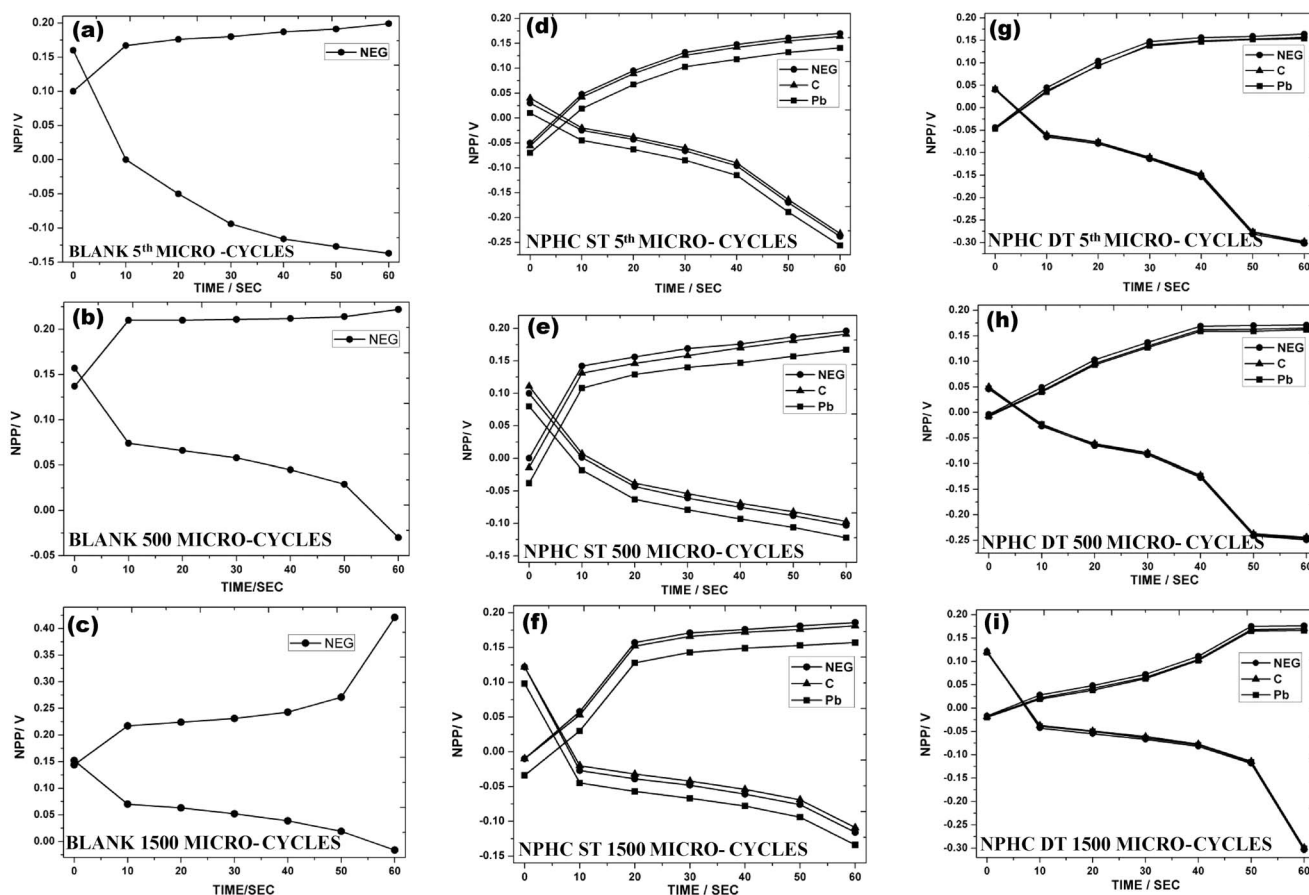


Figure 11. Operational potential difference in negative plate (a-c) Blank cell, (d-f) NPHC ST and (g-i) NPHC DT cells during respective HRPSoc cycles.

sulfate. In NPHC cells carbon paste has more conductive compare to another half side discharged product of lead sulfate which is entirely insulator. In addition carbon paste receives electrons very rapidly compared with another vertical half of conventional paste. In NPHC cells, the PbSO_4 starts to covert back to Pb was found to be much easier compare with blank cell.

In blank cell (1500 cycle) the conversion of PbSO_4 to Pb was very slow as shown in Fig. 11c. The cadmium potential is not shifted to negative value and it is strongly remains in the positive value. The time taken for the potential to reach the fully charging point depends upon the structure of the lead sulfate developed in the previous discharge stages. In NPHC ST cell, the effectiveness of carbon paste is not completely realized during the HRPSoc cycling. This is due to carbon and spongy lead sides are not connected directly through the tap or lug of the grid. The individual behaviors are only observed in both sides. In addition at high rate discharge, carbon paste acts as a buffer up to only 20 seconds after that the potential shifted to more positive value. During high rate charge the spongy lead side is easily charged due to current density phenomenon and that active material may not abundantly suffered from previous high rate discharge (i.e. Carbon act as a buffer and share the current) consequently more spongy lead being there in the active mass and it enhances the conducting nature.

NPHC DT cell.—From the Fig. 11d to 11i shows that the effect of carbon paste in the negative plates form a conducting path on inactive lead sulfate via the grid member because the carbon paste easily charge via non-faradaic reaction then it allows the electrons flow rapidly through the grid member thus leading to the improvement of the rechargeability or reduction or conversion of the lead sulfate to spongy lead. The NPHC cells were found to improve the reduction or conversion of PbSO_4 and slight polarization observed at the end of HRPSoc charge regime. This is due to presence of carbon paste.

In addition current drawn at spongy lead is reduced and the carbon paste supplies majority of transient current. This type of behavior reduces the stress of the battery and degradation of the active mass is reduced. This is summarized in SEM and XRD results as shown in Fig. 6c to 6d and 7c to 7d. In discharge mode the NPHC DT negative electrode remains steady up to 30–40 s and then shifted to more positive value. The voltage shows a slow raise initially up to 40s then increases progressively. This is because the carbon paste was more stable up to this period and shares the current. This indicates that the spongy lead side can be protected being discharged. A similar behavior is also observed in the all micro-cycles. This is due to carbon act as a buffer to share the discharge current within the electrode. There is also another important findings from this study. In NPHC DT design the carbon and lead side tabs are directly integrated together so there is not much individual potential difference as observed with NPHC ST cell. Carbon paste will contribute to increasing the electrochemically active surface and mixed potential observed in this type of cell.

Here we recognize the advantage of the carbon paste as a buffer unit to assist the spongy lead surface during high rate discharges and to avoid the formation of hard irreversible sulphation and degradation of the active mass.

Conclusions

An attractive approach to reduce the problem of sulfation in lead-acid battery is to use a modified negative plate as envisaged in this paper with a half carbon and spongy lead paste in the negative electrode. Since lead acid battery is one of the most promising energy storage cell even today, once lead acid battery with NPHC enter a

degree of maturity, the use of half negative electrode materials containing carbon improve both specific energy and cycle life. This will be characterized with high power of discharge and long service life without any grid design modification. Further development of this electrochemical system with the different surface area carbons with varied conductivity and in-depth focus on other electrochemical properties such as self discharge, diffusion will lead to the ultimate ever sought goal in lead-acid battery.

Acknowledgments

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