

Recovery of discarded sulfated lead-acid batteries by inverse charge

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ABSTRACT

The aim of this research is to recover discarded sulfated lead-acid batteries in order to save the energy. In this work, the effect of inverse charge on the reactivation of sulfated active materials has been investigated. At first, the battery is deeply discharged and the electrolyte of battery is replaced with a new sulfuric acid solution of 1.28 g/cm³. Then, the battery is inversely charged with constant current method (2 A for the battery with the nominal capacity of 40 A h) for 24 h. At the final stage, the inversely charged battery is directly charged for 48 h. Through these processes, a discarded battery can recover its capacity to more than 80% of a similar fresh and non-sulfated battery. Inverse oxidation and reduction of battery's active materials can transform inactive sulfates into active sulfates. Discharge and cycle-life behaviors of the recovered batteries were investigated and compared with similar healthy battery. The morphology and structure of plates was studied by scanning electron microscopy (SEM) before and after inverse charge.

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1. Introduction

Lead-acid batteries have been used as a practical power source for over 100 years because of their high performance, low cost, and safety. Great progress has been made since the advent of the first lead-acid battery. More and more applications of lead-acid batteries will eventuate as the performance is further improved [1]. One of the important consumers of lead-acid batteries is automotive industry. The standard lead-acid battery starts more than 600 million passenger vehicles globally and also powers golf carts, forklifts and other modes of transportation (at 2006). The purpose of using batteries in a car is a triple-role. First, it provides power to start the vehicle (S). To do this it must provide very high current for a short time as much as 300 A for 30 s. One in good condition will provide enough current to run the starter for much longer time. The 2nd and 3rd purposes are lighting (L) and ignition (I). Therefore, a car lead-acid battery is called SLI battery. It can be mentioned that a car battery filters out voltage spikes. The car's electrical system can have very high voltage spikes; for instance when the starter stops, a minus 200 V spike can occur. Large positive spikes can also occur. The battery does a good job as a filter because it acts like a large capacitor to absorb these spikes. A battery can provide the above mentioned purposes only when it has not been discarded.

Lead is a heavy metal toxic to humans, animals, plants and micro-organisms at low exposure levels due to its bio-accumulating properties. The estimated concentration of lead in municipal waste

is 1050 mg/kg (dry weight basis). A lead concentration greater than 150 mg/kg means the compost cannot be used on home lawns and gardens, and is restricted for use in agriculture and forestry. The lead-acid batteries are an important source for lead contaminations in the world. Each year 500,000 to 1 million used lead-acid batteries (ULAB) are discarded. From healthy points, the ULABs must be collected from all end-users. From economical point, all the ULABs should be used to recover the major parts including lead and plastic parts. It is averagely used 80% of the total discarded lead-acid batteries for recovering of lead and plastic parts for recycling. There are a better way to prevent toxic contaminations of ULABs and to save the money and energy. If the sulfation of plates cases to discard an ULAB, it can be recovered to a usable battery without recovering to its parts (lead, plastics and electrolyte). At this paper, it will be shown that a discarded ULAB can be directly recovered to a reusable battery. The presented method can be very interest from healthy and economy points.

Through an investigation into discarded batteries, one can divide them into five main types including scrapping of positive grids, scrapping of negative grids, scrapping of separator, scrapping of negative paste and scrapping of positive paste. In the following text, all scrapping processes for negative and positive plates will be investigated.

1.1. Scrapping processes for positive plates

There are many types of scrapped positive plates such as collapsed plates, oxidized plates, hard plates, cured plates and sulfated and colorless plates. Safe positive plates are chocolate

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brown. Collapse of active materials on surface positive plates happens due to the usual wear and tear of the battery. Batteries being used for many times collapse in the course of charge and discharge as a result of contraction and expansion. Dissociation of plates is seen as the main reason for the deposit of brown sludge in the floor case of battery but unusual collapse that separates part of active material comes into existence due to incorrect usage of the battery. This collapse may take place as a result of battery being slack in its place.

Oxidation of plate or skeleton decreases plan of section and plan of contact, and enfeebles plate, and this plate is consequently interrupted with the smallest pressure. This state happens as a result of the continuation of excessive charging of battery.

Curving process in positive plates takes place due to excessive discharge or putting battery in discharge state for a long time. This situation causes excessive expansion of sulfation and consequently produces curl plates. Moreover, excessive charge can also produce curvature plates.

When positive plate is excessively sulfated and active materials are hard at the time of scratching, plates may be recovered on usual state through a recharge process with low current during a long period of time. Unless, sulfates are produced on the all surfaces of electrode and all areas will be completely covered (fully sulfated). When charged with high current or charged excessively, as a result of the expansion of products in the plate, the external surface of the grid of these plates cracks.

Colorless positive plates are made by vaporizing the water of battery and reducing the level of electrolyte. When exposed to the air, the lead sulfate section of positive plates turns white, and such plates couldn't be recovered to the initial state. Even by adding some electrolyte, white lead sulfate will be produced on the positive plate of battery when it is hold in discharged state for a long time.

Among the above mentioned scrapping processes for positive plates of lead-acid batteries, full sulfation and formation of colorless lead sulfate are more common than the others.

1.2. Scrapping processes for negative plates

There are many scrapping mechanisms for negative paste in lead-acid batteries including the formation of sandy paste, sulfating of pastes and swelling of plates. In usual condition, negative plates are grey and become shining metallic when scratched. When the active material of a negative plate is in sandy form or is soft and pasty when contacting, it is told that the negative plate is destroyed. Such situation can happen because of short circuit connection of the battery, high specific gravity of the electrolyte or high temperature of the electrolyte.

On the other hand, colorlessness and whiteness of negative plates is often as a result of the formation of lead sulfate which happens due to the incomplete charge of battery or the low level of electrolyte level. If we apply a current to the battery so that it is excessively discharged, more expansion in active material of the plate happens and more lead sulfate is produced. Extensive expansion of active material causes the plate to swell. Thus active material in these plates becomes weak, mainly collapsed and unusable.

1.3. Scrapping of lead-acid batteries

When any of the scrapping mechanisms in any parts of the battery happens, the lead-acid battery is scrapped and discarded. In total, the main reason for scrapping of batteries is seen to be lead sulfate formation. When a lead-acid battery discharges or remains inactive, lead sulfate forms on the plates of the battery. Over a short period of time, this sulfate gradually accumulates and crys-

tallizes, and clogs the porous plates to the point where the battery will not accept or hold any charge. This process, known as sulfation, happens in all lead-acid batteries in every application, e.g. material handling, standby power, mining, trucking, automotive and marine industries. This process is the main cause of battery scrapping. Sulfation occurs when a battery is discharged. The deeper the battery is discharged, the more serious is the sulfation. The sulfation material is an insulating film, which covers the plates. A battery relies on clean plates and strong electrolyte to both receive charging current and offer strong discharge current. A sulfated battery can do neither. lead-acid batteries are usually discarded because of short life span. Ninety percent of the sulfated batteries lose their capacity and are scrapped. Lead sulfate is formed due to chemical reaction between the lead plates and the sulfuric acid during the normal discharge of a lead-acid battery. While recharging, lead sulfate is dissolved back into the electrolyte but a small fraction adheres to the battery plates and subsequently hardens the lead sulfate on the battery plates. This hard sulfate can not be dissolved back into the electrolyte through ordinary battery charging. This is a slow aging process and starts in any new battery; as a result of which a gradual loss of useful electrolyte and plate material is observed. This causes the battery plates to get coated with hard crystalline sulfates and the specific gravity of the electrolyte to drop; flow of the current is restricted because of insulating layer of sulfates and the outcome is a battery which normally can not be charged with a battery charger and thus is declared as a "dead" or "scrapped" battery.

The lead sulfate containing large crystals formed on the plates can not be transformed back into active material (Pb in negative pole and PbO₂ in positive pole) in charge stage. Lead sulfate has very weak electrical conductivity and high density. The deposits of lead sulfate cover both electrodes and make them inactive so that the effective capacity of cell is limited to lower than 10% of the nominal capacity. As the discharge process continues the internal resistance of cell increases. Increase in resistance is due to the formation of PbSO₄ and decrease in special conductivity of electrolyte happens due to consumption of sulfuric acid. Irreversible lead sulfate increases in each cycle and after some cycles, the electrodes are completely sulfated and discarded.

As mentioned above, sulfation is the most dangerous process for the health of the lead-acid batteries and makes them scrapped. The sulfation process is one of the major failure mechanisms for lead-acid batteries and scrap recovery processes for the sulfated plates will be of great interest in economical and commercial view. The sulfated lead-acid batteries are discarded if not recoverable; a process which is harmful to the environment. Therefore, there is a general need in the art for an improved method of recovering lead-acid batteries.

To the best of our knowledge, there are not any reports on the recovery of sulfated lead-acid battery recorded except only two patents about the recovery of incomplete sulfated lead-acid battery [2,3]. Palanisamy et al. recorded a patent [2] about an apparatus and a method for automatic recovery of sulfated lead-acid batteries relying on monitoring battery voltage, current and internal resistance during battery charging. Only some of the sulfated lead-acid batteries which have been incompletely and locally sulfated can be recovered by this method. In this report, the internal resistance was considered as a critical measurable parameter for the selection of charging current amount. Through this method, those batteries in which internal resistances are not lower than a critical limited can be recovered. The designed apparatus will automatically reject the sulfated batteries at lower internal resistances. Nevertheless, most of the discarded sulfated lead-acid batteries are fully sulfated and then this method can be applied to them. Therefore, recovery of the sulfated lead-acid batteries requires an improved method to tackle this problem in the lead-acid battery world.

In this work, the fully inversed charging before the main charging of sulfated lead-acid batteries was used to recover discarded industrial lead-acid batteries. To recover the lead-acid battery, the lead sulfate is converted back to active material by inverse charging before the main stage of charging happens. All locally and fully sulfated lead-acid batteries are recoverable in this method.

2. Experimental details

2.1. Materials

All materials and reagents used in these experiments were of industrial grade and produced in Iranian companies. All lead-acid batteries 40 A h used in this study were produced by Aranniru Battery manufacturing company (AMICO Industrial Group, Iran).

2.2. Instrumentals

Charge and discharge of batteries were done by a charge and discharge machine equipped with a computer to record data and apply a constant current. This machine is produced by Jin Fan Power Company (China). All measurements of voltage were done by digital multi meter HIOKI 3280 (Japan). To measure the acid, industrial glassy fluid mercury densitometer (France) and laboratory glassy densitometer (Simax) were used. A scanning electron microscopy from Philips Co. (XL30) was used for characterization of the prepared lead dioxide electrode. Energy-dispersive X-ray analyses (EDX) were performed by Philips 30 XL.

2.3. Procedure

Discarded batteries (40 batteries) used in this study were of vented-type and had the nominal capacity of 40 A h and the nominal voltage of 12 V. They were sampled among discarded and sulfated batteries accumulated in Aran Niru Company.

One sulfated negative plate was initially coupled with one sulfated positive plate to form a single unit lead-acid cell with the nominal voltage of 2 V. The constructed single unit cells were used to investigate the efficiency of different inverse charge methods including constant voltage, constant current and pulsed current methods. For this purpose, three sulfated batteries were broken and fully sulfated plates were extracted. Sample sulfated plates were washed with distilled water and utilized to assemble the sin-

gle unit cells. The assembled single unit cells were filled with sulfuric acid of 1.28 g/cm^3 . Each cell was charged by constant voltage of 2.67 V for 24 h and their available discharge capacity (initial capacity; C_i) was determined by constant current method. Based on the inverse charge method (constant voltage, constant current and pulsed current method), the discharged single unit cells were divided into three groups (each group including three batteries). Inversed charge was performed for 24 h and then the direct re-charge was applied for 48 h by constant voltage of 2.67 V. The new available capacity (C_f) for each cell was determined by the same constant current (similar to the initial capacity). The efficient inverse charge method was selected with respect to the ratio of C_f/C_i and simplicity of the method.

At final stage after selection of effective method for inverse charge based on single unit cells, further studies were conducted on discarded sulfated batteries (with the nominal voltage of 12 V and the nominal capacity of 40 A h including five negative plates and five positive plates in each cell). In this method, the electrolyte of the batteries was removed and filled and decanted by pure water. Finally, the batteries were filled by sulfuric acid of 1.28 g/cm^3 . The batteries were fully charged with the constant voltage of 16 V for 24 h. The initial discharge capacities (C_i) were measured at the constant current of 2 A (0.05% of the nominal capacity). The discharged batteries were inversely charged with the low constant current (3 A for batteries with nominal capacity of 40 A h) for 24 h. The inversely charged batteries were directly charged with the constant current of 3 A for 48 h. The batteries, after having been fully charged, were re-examined for the discharge capacities through the application of the constant current of 2 A until reaching to 10.5 V (cut off voltage).

In practical usages, the recovery of a sulfated battery can be performed only through inverse charge and direct full charge stages (lower 72 h).

3. Results and discussion

All sulfated and discarded batteries were selected among many discarded batteries from Aranniru battery manufacturing company through random sampling. To assure that discarded batteries are fully sulfated, several were broken and fully sulfated plates were selected. Fig. 1 shows the image of selected positive and negative plates. As it is seen from Fig. 1, most parts of the plates are covered with crystalline lead sulfates.

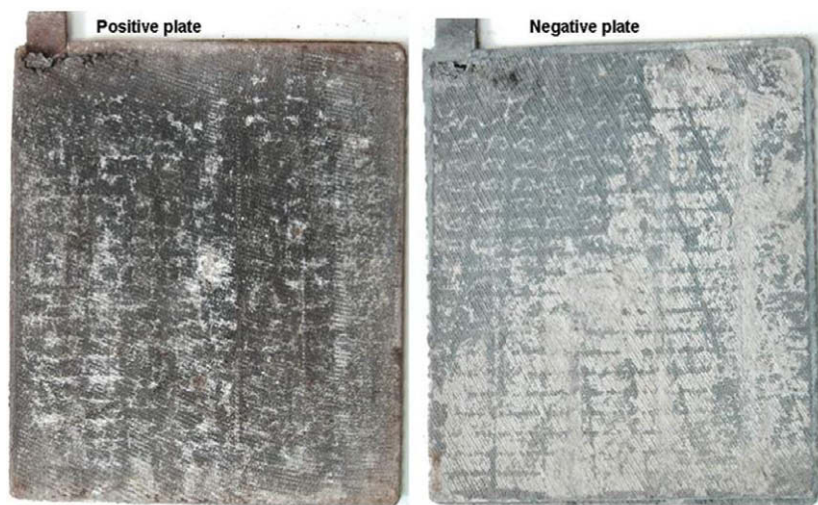


Fig. 1. Sample image of the selected positive and negative sulfated plates.

3.1. Investigation into inverse charge methods

Before conducting recovery experiments on discarded batteries, some inverse charge methods were studied to select a high performance and efficient method. Therefore, constant voltage, constant current and pulsed current methods at different amounts of controlled voltages, controlled currents and controlled pulse times were used to inversely charge the sulfated plates in single unit cells. At each experiment step, the recovery performance (R.P) was calculated from the following equation:

$$R.P\% = (C_f/C_n) \times 100$$

where C_f is the final discharge capacity (A h) after inverse charge and C_n is the nominal capacity (A h) of the battery.

In constant current method, several different constant currents at the range of 0–3 A were used for inverse charging. The results for discharge capacities show that the current of 0.75 A for each single unit cell is the best. At this current, the average recovery performance was 85%. The recovery efficiency increases with an increase in the ratio of C_f/C_i .

In constant voltage method, several different voltages at the range of 2.2–2.8 V were used for inverse charging. The results for discharge capacities show that the voltage of 2.67 V for each single unit cell is the best (the average recovery performance was 80%).

As it is well known, the current or voltage of charge should be controlled at the range in which the rate of nucleation and crystal growth for active material is suitable [4]. This concept can be used to explain the effect of current or voltage amounts of inverse charge.

In pulsed current method, the current of inverse charge was applied as shown in Fig. 2. At this stage, the amounts of “on” (the time during which the pulse of current is on) and “off” (the time during which the pulse of current is off) were varied at the range of 0–10 s while the pulse height was constant (0.75 A, the optimum amount for constant current method). At the optimum conditions, the “on” and “off” durations were 1 s and 3 s, respectively. By applying pulse program for synthesis and charge we intended to regulate the rates of nucleation and crystal growth for active material. At optimum pulse conditions, the time elapsed for nucleation and crystal growth to obtain the maximum discharge capacity is satisfactory. The average recovery performance in optimum pulse program was 90%.

The results obtained from these three methods show that, for inverse charging, the pulsed current method is more effective than constant voltage and constant current methods. Nevertheless, because of simplicity and lower price of constant current charging equipments, the constant current method will be perfect. Therefore, for further investigation in this study, the constant current method was selected.

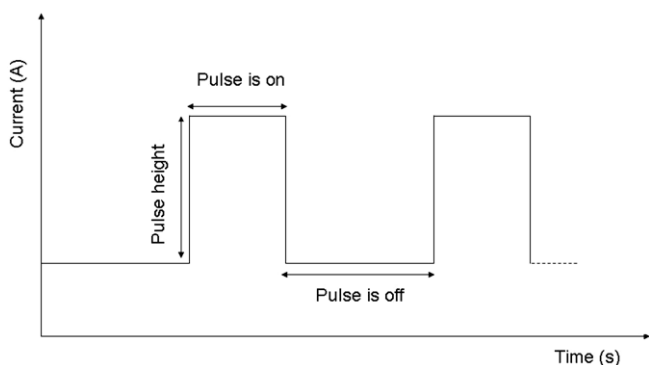


Fig. 2. Scheme of the applied pulsed current program for inverse charge; the on and off durations are 1 s and 3 s, respectively.

3.2. The recovery process of discarded batteries

The selected batteries (with the nominal voltage of 12 V and the nominal capacity of 40 A h) were fully charged and then discharged to determine initial available capacity (C_i). All of the selected batteries have an initial capacity lower than 25% of the nominal capacity of 40 A h. Discharged batteries were inversely charged with the constant current of 3 A for 24 h and then directly charged with the constant voltage of 16 V for 48 h. Charged batteries were discharged with the constant current of 2 A to determine new available capacities (recovered capacity; C_f).

Fig. 3 compares the discharge behavior of a fully sulfated lead-acid battery before and after inverse charging process. For the sample shown in Fig. 3, C_i and C_f can be calculated from the discharge data.

As it is seen from Fig. 3, during the discharge process, the battery can deliver much more energy after inverse charging is applied.

Experiments similar to those of Fig. 3 were repeated for several batteries and summary of results obtained for five batteries as samples are shown at Table 1. As it is obvious from Table 1, inverse charging, which yields the recovery performance of more than 80%, is a powerful method to recover the missing capacity for sulfated lead-acid batteries.

3.3. Scanning electron microscopic studies

The morphology of negative and positive paste at different statements was studied by scanning electron microscopy (SEM). In each SEM image, the nature and type of the observed crystals and other particles were determined by Dispersive X-ray analysis (EDX analyzer).

3.3.1. Investigation into positive electrode

Fig. 4 shows the morphology of a positive electrode paste before and after inverse charge, and also after discharge of the inversely charged electrode. As it is seen from Fig. 4a, before inverse charge, there are many large crystalline lead sulfates available on the surface of the fully charged positive electrode. As it is well known, the large crystals of lead sulfate can not regularly converted into lead dioxide in charge process. The inverse charge should be convert

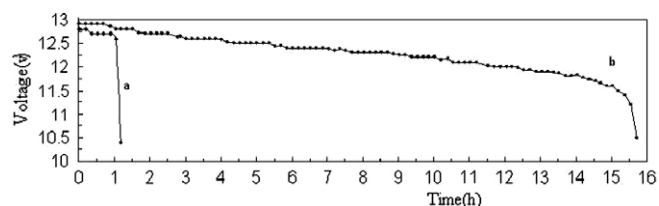


Fig. 3. Time-voltage behavior of a fully sulfated lead-acid battery during discharge process with the constant current of 2 A before inverse charge (curve a) and after inverse charge (curve b).

Table 1

Discharge capacities for several recovered batteries before and after inverse charge.

Discharge capacity (A h)		C_f/C_i	Recovery performance (%)
Before inverse charge (C_i)	After inverse charge (C_f)		
13	38	2.9	95
10	33	3.3	82
2	32	16	80
4	35	8.8	88
7	37	5.3	92

the large crystalline PbSO_4 into spongy lead (Pb) so that the yield lead will firstly converted into lead sulfate with small crystals and then into lead dioxide at directly charge step. Fig. 4b shows that the inverse charge converts the crystalline PbSO_4 into uniform spongy lead (Pb). For more clarification, the SEM image of Fig. 4a with high magnification is shown in Fig. 5. Fig. 5 shows that there are much more large crystals of lead sulfate in the inner layers of positive paste. It is expected that the large lead sulfate crystals can not be converted into lead dioxide so that the positive electrode be able to deliver very low energy at discharge stage.

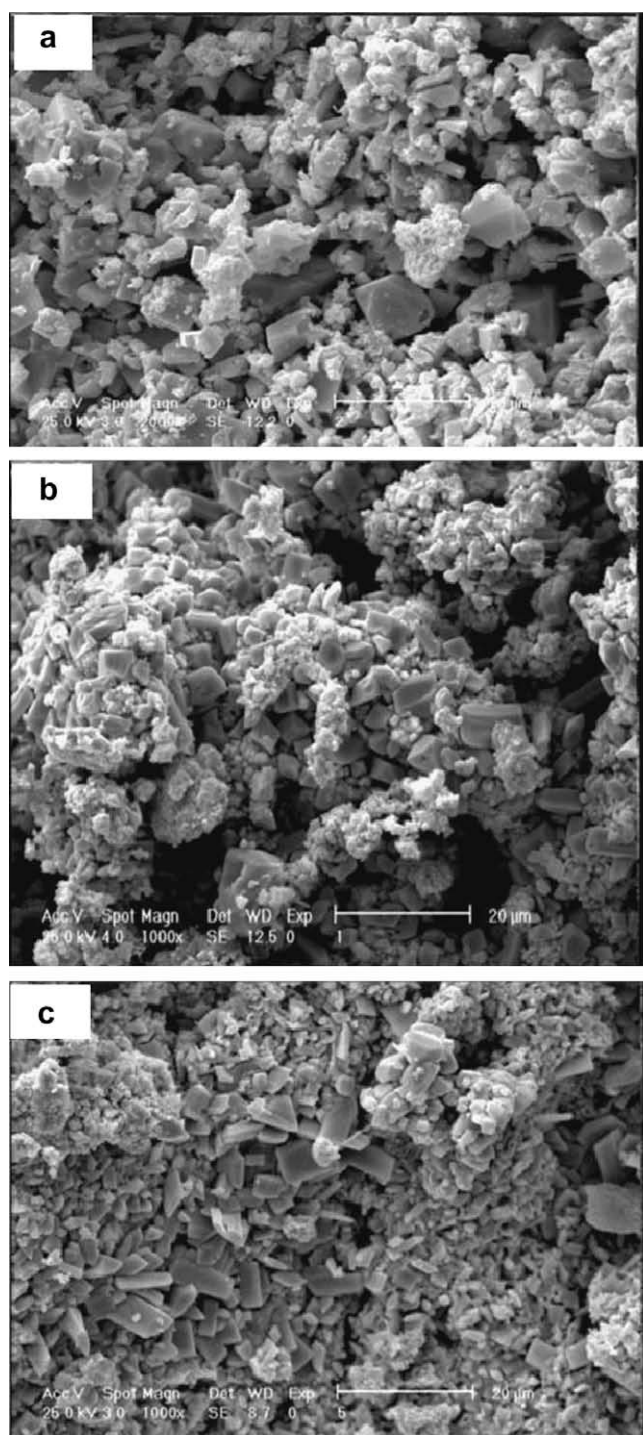


Fig. 4. SEM images of positive electrode (cathode) before inverse charge (a), after inverse charge (b) and after the processes of inverse charge, direct recharge and discharge (c).

Fig. 4b shows the positive electrode after inverse charge and direct recharge. As it is seen from Fig. 4b, major parts of crystalline lead sulfate are converted to lead dioxide crystals. As it is expected, this positive electrode is able to successfully take part in the discharge reactions so that the battery including these positive electrodes will deliver high discharge capacity (see Table 1).

To make sure of the formation of large crystals of lead sulfate at the next discharge processes, the surface of inversely charged and then discharged positive electrodes was studied by SEM (Fig. 4c). As it is seen from Fig. 4c, during discharge process, lead dioxide is converted to uniform small crystals of lead sulfate which can be transformed to lead dioxide at next charge process.

Inverse charge can convert large crystalline lead sulfates to active material. When the active materials (Pb in anode and PbO_2 in cathode) are converted to inactive large crystalline lead sulfate on paste during discharge or storing of the discharged batteries for a long period, this crystalline lead sulfate can not be converted into active materials through direct charge. During inverse charge process, large crystalline lead sulfate accumulated on the anode of the battery is converted to lead dioxide (PbO_2) and the part deposited on the cathode of the battery is converted to lead (Pb). Through direct charging at next stage, the obtained lead dioxide can be converted to spongy lead much easier than crystalline lead sulfate and also, the obtained lead (Pb) converted to lead dioxide. The SEM images in Fig. 4 shows the morphology of negative and positive pastes after inverse charge and direct charge processes. It can be seen in Fig. 4a that lead dioxide crystals are formed during charge process. Fig. 4b shows the presence of spongy lead. Dispersive X-ray analysis showed that there is some lead sulfate remaining in both positive and negative electrodes.

3.3.2. Investigation into negative electrode

It is expected that the amount of crystalline lead sulfate available on the negative plates be more than that on positive electrodes. Fig. 6 shows the surface of paste on the negative electrode before and after inverse charge and after discharge of the recovered electrode. As it is seen from Fig. 6a, the surface and also the inner layers of the negative paste of the fully sulfated electrode is completely covered with large crystals of lead sulfate. As it was also shown in Fig. 3a, the fully sulfated electrodes can not deliver considerable energy at discharge stage. The morphology of the fully sulfated negative plate after inverse charge is seen in Fig. 6b. As it is seen from Fig. 6b, the major part of crystalline lead sulfates has been converted to spongy lead so it is expected that it can deliver high discharge capacity as Fig. 3b shows this ability.

The surface of inversely charged and discharged negative plate is shown in Fig. 6c. Fig. 6c shows that formed spongy lead was

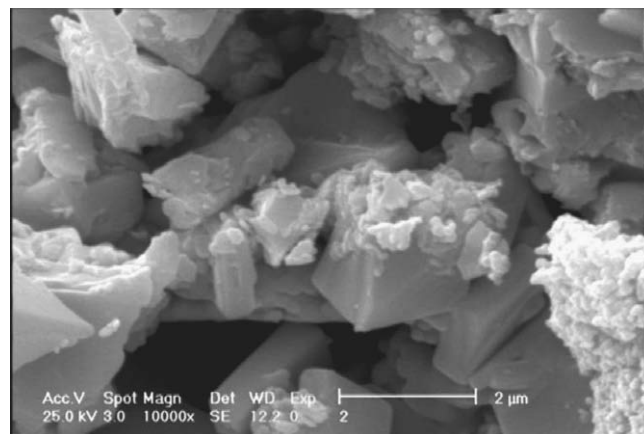


Fig. 5. SEM image of positive plate with high magnification before inverse charge.

transformed into uniform lead sulfate with small crystals so that they can take part in next charge–discharge processes.

3.4. Cycle-life test

The recovered battery was used for cycle-life test. During of 40 cycles of charge and discharge processes, the cycle-life behaviors of the recovered battery and a freshly assembled similar battery were

compared. The obtained results showed that the recovered batteries have cycle endurance 80% of the freshly battery or more. Therefore, it can be said that not only the presented recovery method has good efficiency for recovery of missed discharge capacity but also it can make high endurance for the recovered batteries in charge–discharge cycles. The cycle-life test shows that the recovered batteries can be reused for a long time.

3.5. Energy and cost

At experimental procedure, a 12 V–40 A h sulfated ULAB was inversely charged for 24 h (step 1) and then, directly charged for 48 h (step 2). The steps of 1 and 2 consume 144 A h electrical energy in an unfortunate state (maximum energy). The proposed energy is equal or lower than that the formation step need in battery production process. It should be mentioned that, when a discarded ULAB was conventionally recovered into lead and other initial parts, more amounts of the energy will be used. On the other hand, the recovered lead will consume energy and cost until converted into a new lead-acid battery.

To investigate the presented method from energy and cost points, it can be compared with a conventional recovering methods that the ULAB was recovered into lead, plastic and electrolyte parts for recycling of them as separately. At conventional recycling methods, a discarded ULAB is separately recovered to its parts. The recovering of a lead-acid battery into its parts is a complex, time consuming and polluter industry that need to high cost and energy. The current method directly recovers the discarded ULABs into the reusable batteries. The proposed method not only has very lower pollution level than the conventional recovering of a ULAB into its parts but also, it is a more perfect method with respect to energy and cost consuming. The recovered batteries by the suggested method can be reused for a long period of service.

4. Conclusions

Results obtained from the current industrial research shows the ability of inverse charge as a simple, cheap and high performance method for the recovery of discarded sulfated lead-acid batteries. Application of this method to fully sulfated batteries can recover them for over 80% of their nominal capacity. The recovered batteries can be reused for long time. At industrial applications, one sulfated battery can be inversely charged for 24 h and then directly recharged for 48 h. By only these two processes, a discarded battery can be recovered and taken back to service cycle. Because of the simplicity and reliability of this method at each battery factory, battery service and repairing place, the presented method can be of very interest in economical and commercial views.

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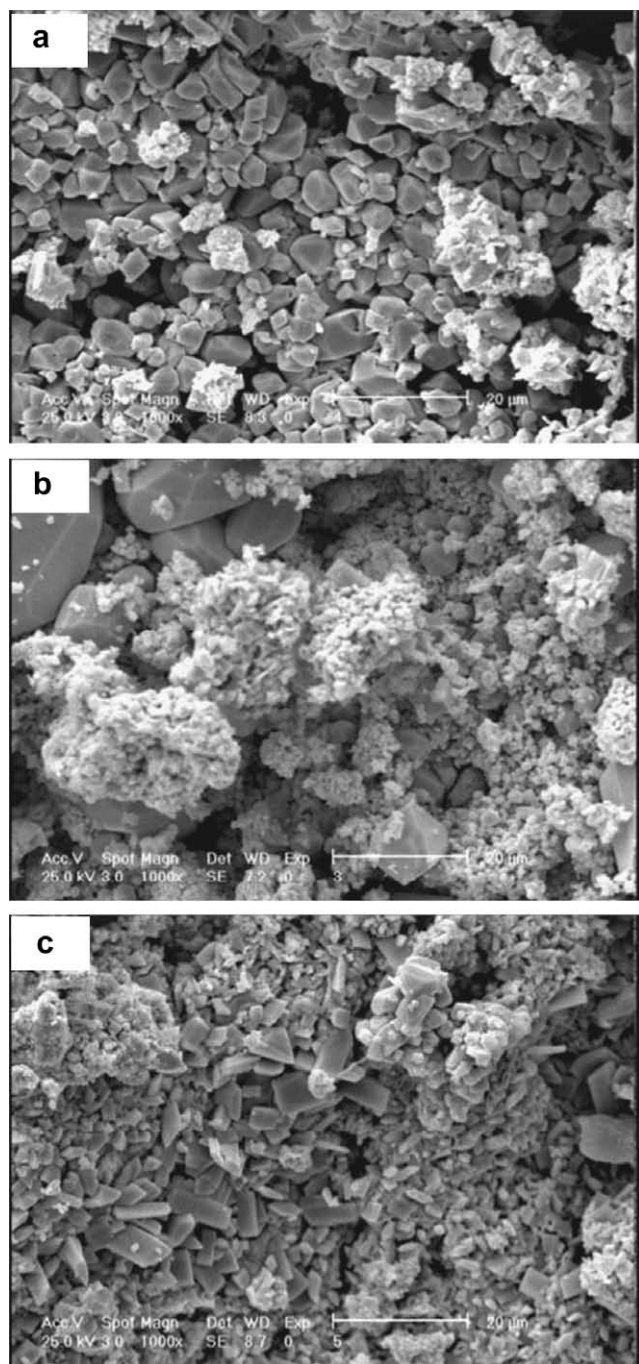


Fig. 6. SEM images of negative electrode (anode) before inverse charge (a), after inverse charge (b) and after the processes of inverse charge, direct recharge and discharge (c).