Recovery of discarded sulfated lead-acid batteries

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ABSTRACT

The aim of this research is to recover discarded sulfated lead-acid batteries. In this work, the effect of two methods (inverse charge and chemical charge) on the reactivation of sulfated active materials was investigated. At the inverse charge, the battery is deeply discharged and the electrolyte of battery is replaced with a new sulfuric acid solution of $1.28\,g\,cm^{-3}$. Then, the battery is inversely charged with constant current method (2 A for the battery with the nominal capacity of 40 Ah) 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.

At the chemical charge method, there are some effective parameters that including ammonium persulfate $[(NH_4)_2S_2O_8]$ concentration, recovery temperature and recovery time. The effect of all parameters was optimized by one at a time method. The sulfated battery is deeply discharged and then, its electrolyte was replaced by a 40% ammonium persulfate solution (as oxidant) at temperature of 50 °C. By adding of oxidant solution, the chemical charging of positive and negative plates was performed for optimum time of 1 h. The chemically charged batteries were charged with constant voltage method (2.66 V for the battery with nominal voltage and nominal capacity of 2 V and 10 Ah, respectively) for 24 h. By performing of these processes, a discarded battery can recovers its capacity to more than 84% of the similar fresh and non-sulfated battery. Discharge and cyclelife 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 recovery.

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1. Introduction

Lead-acid technology currently remains the most reliable, safe and affordable power source. None of the new developed battery types (e.g. Li-ion and Ni-MH batteries) has so far reached the commercial success of the lead-acid battery. Lead-acid batteries have many applications such as starting-lighting-ignition (SLI) in vehicles, tractions, telecommunications, children tools etc. There are increasing concerns for research in the improving of discharge capacity [1–4], cyclelife [2–4] and charge/discharge efficiency [5,6].

There are some reports about using persulfate salts to enhance battery formation and charge. Several attempts have been made to improve the conductivity of the positive paste through use of persulfate treatments. For example, Reid and Falls [7] used persulfate salts to improve lead-acid battery performance. This patent discloses treating battery plates, before they are formed, with a persulfate by incorporating the persulfate into the paste or through use of a pickling step. The reference specifically describes use of ammonium persulfate added in solid form to the lead oxide in preparation of the paste, or added as an aqueous solution of any strength up to a saturated solution.

Barnes et al. [8] dipped grid in ammonium persulfate, sodium persulfate, or a sodium perborate solution before paste operation to improve electrode performance. Belgian Patent No. 723,018 [9] relates to another attempt to improve the efficiency of the charge of the positive plates by adding potassium persulfate to the mixture of lead oxide and water to prepare the active material. Particularly, this reference discloses forming a pasty mixture of lead oxide (PbO) and potassium persulfate by mixing the two substances with water until the lead dioxide (formed by the reaction of the lead oxide and persulfate) is uniformly dispersed throughout the resultant mixture.

Another attempt to improve the efficiency of charge of the positive plates through persulfate treatments is shown in Spanish Patent No. 8,801,559 [10], which discloses the pre-treating of each positive plate, before the formation of the battery which persulfate solution. The reference suggests that the persulfate ion oxidizes the active materials of the plate ($PbSO_4$ and PbO) to conductive PbO_2, reducing the total charge time by up to 50%.

Matthew et al. [11] used potassium persulfate for negative and positive pastes of lead-acid batteries to improve battery performance.

Kao et al. [12], used ammonium persulfate in positive paste to improve its performance.

In a previous work, we used ammonium persulfate to improve discharge capacity, charge performance and cyclelife of positive

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paste of bipolar lead-acid batteries [13]. In this reference, chemical oxidation was carried out by both mixing and dipping methods using an optimized amount of ammonium persulfate as a suitable oxidizing agent.

Battery failure is a major problem in using of lead-acid batteries. Full sulfation is most important reason for failure of lead-acid batteries. There some reports about reduction of sulfation in lead-acid batteries [14–16]. Nevertheless, there is not any report for the complete preventing the sulfation in the lead-acid batteries.

Through an investigation into discarded lead-acid 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.

There are many types of scrapped positive plates such as collapsed plates, oxidized plates, hard plates, cured plates and sulfated and colorless 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 could not 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.

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. 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.

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 crystallizes, 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 cannot 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 cannot 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 cannot be transformed back into active material (Pb in negative pole and PO_2 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 $PbSO_4$ 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 [17,18]. Palanisamy et al. recorded a patent [17] 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 reference, 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 the reported method cannot 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, we selected many discarded lead-acid batteries which they were discarded because of sulfation. We used two different methods (inverse charge and chemical oxidation) to recover fully sulfated lead-acid batteries. In the inverse charge method, 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.

In the chemical oxidation method, chemical oxidation of sulfated negative and positive paste of discarded industrial lead-acid batteries was performed by ammonium persulfate solution 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 chemical oxidation before the main stage of charging happens. At both chemical oxidation and inverse charge methods, all locally and fully sulfated lead-acid batteries are recoverable.

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 Ah used in this study were produced by Aran Niru Battery manufacturing company (AMICO Industrial Group, Iran). Ammonium persulfate used in this studying was produced from Chinese companies.

2.2. Instrumentals

2.2.1. Inverse charge

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.

2.2.2. Chemical oxidation

Chemical oxidation of discarded batteries was performed in ammonium persulfate solution. Electrical Charging of chemically recovered batteries was done by electricity power machine that apply a constant voltage. All measurements of voltage were done by digital multi meter DT-830D. To measure the acid, industrial glassy fluid mercury densitometer (made by china) was used. A scanning electron microscopy from Philips Co. (XL30) was used for studying of morphology structure of negative and positive paste at different statements.

2.3. Procedure

2.3.1. Inverse charge

Discarded batteries (40 batteries) used in this study were of vented-type and had the nominal capacity of 40 Ah and the nominal voltage of 12 V. They were sampled among discarded and sulfated batteries accumulated in Aran Niru Company. In this study, all selected batteries were test for their failure reason. All selected batteries were discarded only because of plate sulfation.

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 single 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 recharge 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 Ah including 5 negative plates and 5 positive plates in each cell). In this method, the electrolyte of the batteries was removed and filled and decantated 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 20 h discharge rate (2 A per rated capacity of 40 Ah). The discharged batteries were inversely charged with the low constant current (3 A for batteries with nominal capacity of 40 Ah) 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 2 A (20 h discharge rate) 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).

2.3.2. Chemical charge

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 effect of different concentration of oxidant solution, temperature of oxidant solution and recovery time of inactive sulfates in chemical charge method. 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 chemical oxidation method, the discharged single unit cells were divided into three groups (optimizes of oxidant concentration, oxidation temperature and oxidation time).

Firstly, to investigation effect of ammonium persulfate concentration in recovery inactive sulfates, 9 different concentration of ammonium persulfate were carried out at the same condition of temperature (50 °C) and time (1 h) from 0 to 55% to optimize the concentration of ammonium persulfate. Negative and positive plates discharged single unit cells were placed on the ammonium persulfate solution of 0, 10, 15, 20, 25, 30, 40, 50, and 55% at 50 °C for 1 h. Chemical oxidized batteries were washed by pure water. Then, the batteries were filled by sulfuric acid of 1.28 g cm^{-3}. The batteries were charged for 24 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 initial capacity). The efficient chemical charge method was selected with respect to the ratio of C_f/C_i and simplicity of the method.

At next stage after optimization of concentration of ammonium persulfate solution, studies were performed on temperature of ammonium persulfate solution. It was performed 6 recoveries temperature at 25, 40, 50, 60, 70, and 80 °C for investigation effect of recovery temperature on restoring inactive lead sulfates. Negative and positive plates discharged single unit cells were placed on 40% of ammonium persulfate solution at different temperatures for 1 h. The recovered batteries were washed by pure water. Then, the batteries were filled by sulfuric acid of 1.28 g cm^{-3}. Charge of batteries was performed for 24 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 initial capacity). The efficient chemical oxidation method was selected with respect to the ratio of C_f/C_i and simplicity of the method.

At final stage, studies were performed on recovery time. To investigation the effect of reaction time on recovery of inactive lead sulfates, 5 recoveries were carried out at the same condition of concentration (40% ammonium persulfate) and temperature (50 °C). Negative and positive plates discharged single unit cells were placed on 40% of ammonium persulfate solution at 50 °C for 0.5, 1, 2, 3, and 4 h. Then, batteries were washed by pure water and

were filled by sulfuric acid of 1.28 g cm^{-3}. Charge of batteries was performed for 24 h by constant voltage of 2.67 V. The new available capacity (C_f) for each cell was determined by the same constant current. The efficient chemical charge method was selected with respect to the ratio of C_f/C_i and simplicity of the method.

In practical usages, the recovery of a sulfated battery can be performed only through chemical charge and charge stages (lower 26 h).

3. Results and discussion

3.1. Inverse charge

All sulfated and discarded batteries with identical histories were selected among many discarded batteries from Aran Niru battery manufacturing company. 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.

3.1.1. Investigation of 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:

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

where, C_f is the final discharge capacity (Ah) after inverse charge and C_n is the nominal capacity (Ah) 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 [19]. This concept can be used to explain the effect of current or voltage amounts of inverse charge.

In pulsed current method, 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 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.
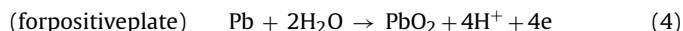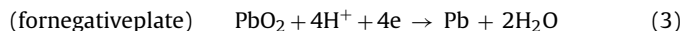
In the inverse charge process, the following reaction (Eq. (1)) is performed on the negative plate:

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e \tag{1}$$
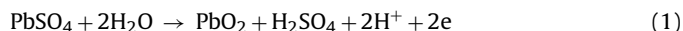
At this equation, irreversible lead sulfate oxidized to reversible lead dioxide. On the positive plate, inverse charge reaction as following (Eq. (2)):

$$PbSO_4 + 2H^+ + 2e \rightarrow Pb + H_2SO_4 \tag{2}$$
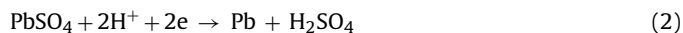
At next step, direct charge reconverts the produced reversible species as following:

$$(\text{for negative plate}) \quad PbO_2 + 4H^+ + 4e \rightarrow Pb + 2H_2O \tag{3}$$

$$(\text{for positive plate}) \quad Pb + 2H_2O \rightarrow PbO_2 + 4H^+ + 4e \tag{4}$$

3.1.2. The recovery process of discarded batteries

The selected batteries (with the nominal voltage of 12 V and the nominal capacity of 40 Ah) 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 Ah. 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
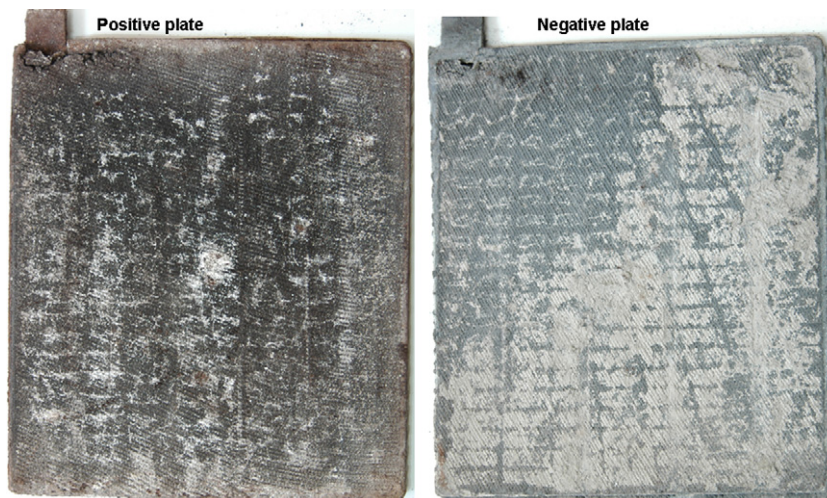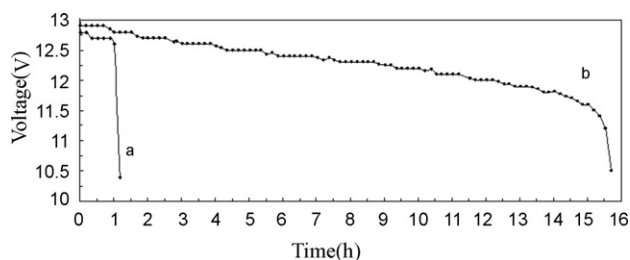

Fig. 1. Sample image of the selected positive and negative sulfated plates.

Fig. 2. Time–voltage behavior of a fully sulfated lead-acid battery during discharge process with the constant 20 h discharge rate before inverse charge (a) after inverse charge (b).

Table 1
Discharge capacities for several recovered batteries before and after inverse charge.

No.	Discharge capacity (Ah)		C_f/C_i	Recovery performance (%)
	Before inverse charge (C_i)	After inverse charge (C_f)		
1	13	38	2.9	95
2	10	33	3.3	82
3	2	32	16	80
4	4	35	8.8	88
5	7	37	5.3	92

with the constant current of 0.05 RC to determine new available capacities (recovered capacity; C_f).

Fig. 2 compares the discharge behavior of a fully sulfated lead-acid battery before and after inverse charging process. For the sample shown in Fig. 2, C_i and C_f can be calculated from the discharge data.

As it is seen from Fig. 2, during the discharge process, the battery can deliver much more energy after inverse charging is applied. Experiments similar to those of Fig. 2 were repeated for several batteries and summary of results obtained for 5 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.

3.1.3. 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) and XRD (X-ray diffraction).

3.1.3.1. Investigation of positive electrodes. Fig. 3 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. 3a, before inverse charge, there are many large crystalline lead sulfates available on the surface of the fully charged positive electrode.

Fig. 3b shows the positive electrode after inverse charge. As it is seen from Fig. 3b, major parts of crystalline lead sulfate are converted to spongy lead. The obtained spongy lead can be converted into lead sulfate and then to lead dioxide in direct charge process. 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 non-formation of large non-electroactive crystals of lead sulfate at the next discharge processes, the surface of inversely charged and then discharged positive electrodes was studied by SEM (Fig. 3c). As it is seen from Fig. 3c, during discharge process, lead dioxide is converted to uniform small crystals of lead
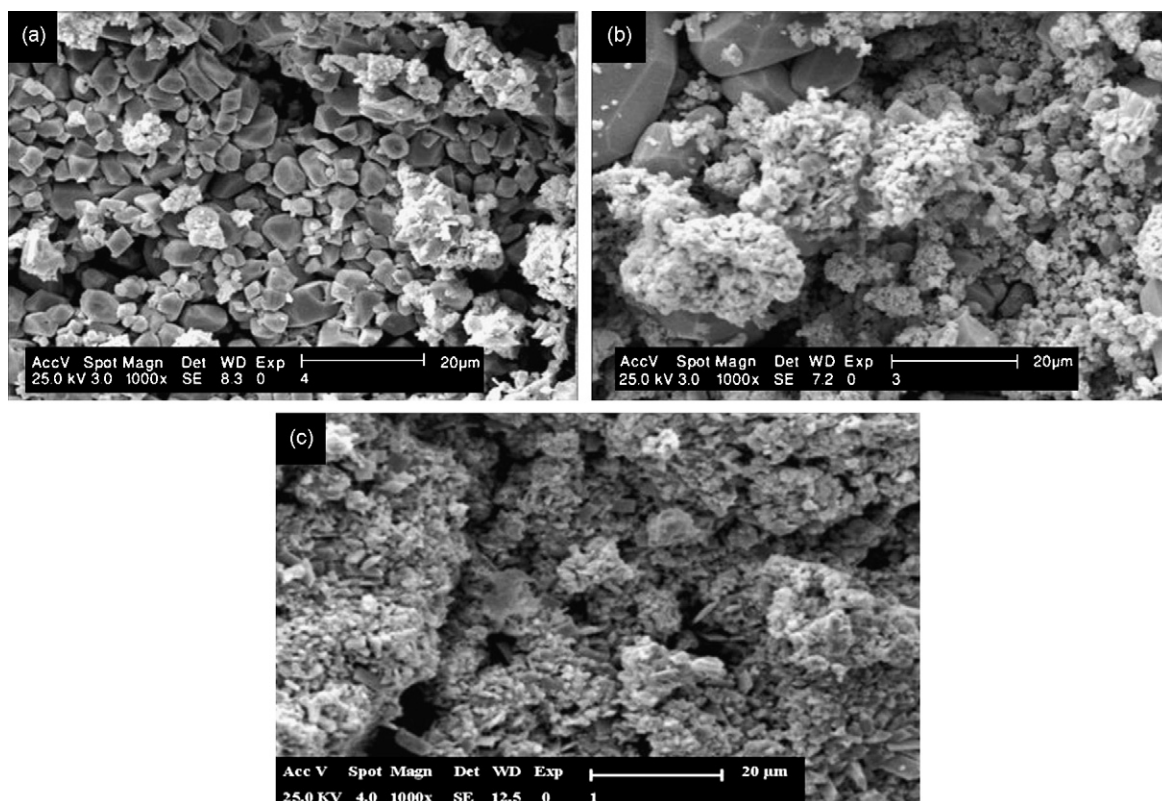
Fig. 3. SEM images of positive electrode (cathode) before inverse charge (a), after inverse charge (b) and after the processes of inverse charge and discharge (c). All SEM images are in magnification of 1000×.
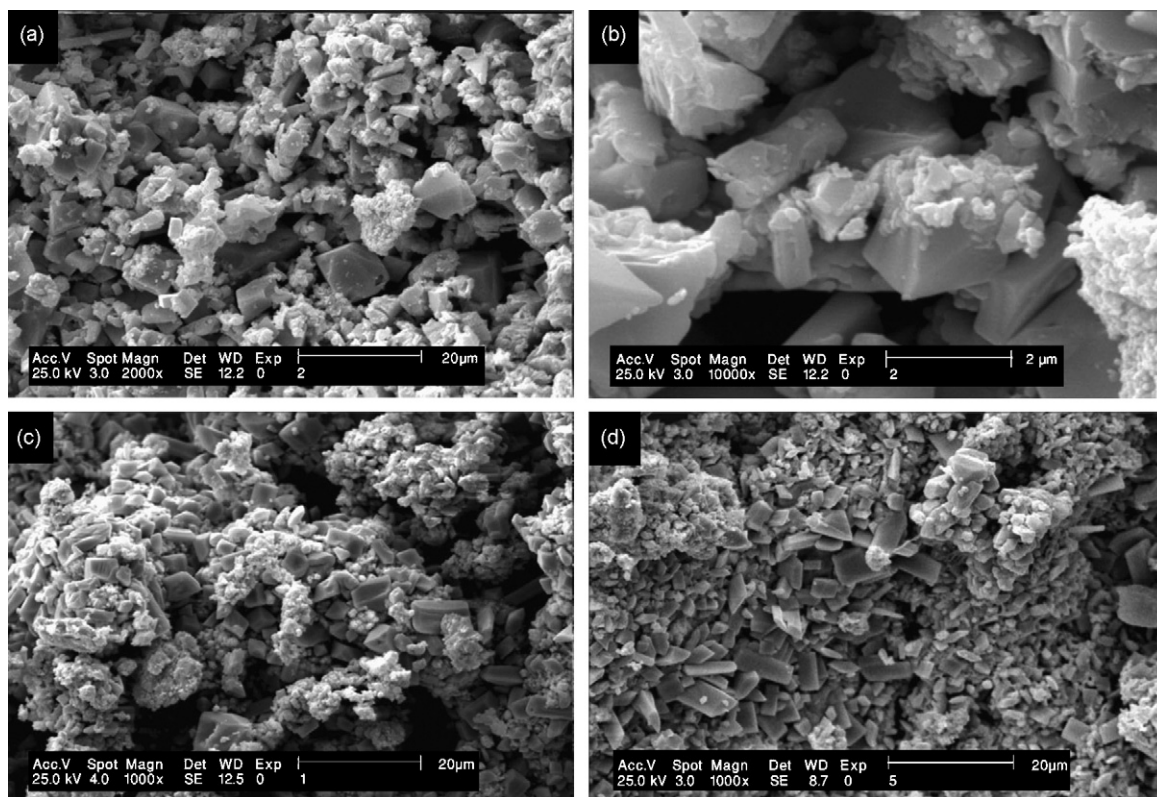
Fig. 4. SEM images of negative electrode (anode) before inverse charge (a), SEM image of positive plate with high magnification before inverse charge (b), after inverse charge (c) and after the processes of inverse charge and discharge (d). All SEM images are in magnification of 1000×.

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 cannot be converted into active materials through direct charge. During inverse charge process, large crystalline lead sulfate accumulated on the cathode of the battery is converted to spongy lead (Pb) and the part deposited on the anode of the battery is converted to lead dioxide (PbO_2). 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 spongy lead (Pb) (on positive paste) converted to lead dioxide.

3.1.3.2. Investigation of negative electrodes. Fig. 4 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. 4a, 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. For more clarification, the SEM image of Fig. 4a with high magnification is shown in Fig. 4b. Fig. 4b shows that there are much more large crystals of lead sulfate in the inner layers of

negative paste. It is expected that the large lead sulfate crystals cannot be converted into spongy lead so that the negative electrode be able to deliver very low energy at discharge stage. As it was also previously shown in Fig. 2a, the fully sulfated electrodes cannot deliver considerable energy at discharge stage.

The morphology of the fully sulfated negative plate after inverse charge is seen in Fig. 4c. As it is seen from Fig. 4c, the major part of crystalline lead sulfates has been converted to uniform crystals of lead dioxide so, it is expected that it can deliver high discharge capacity as it was previously shown in Fig. 2b.

The surface of recovered negative plates after discharge process plate is shown in Fig. 4d. Fig. 4d shows that the spongy lead was transformed into uniform lead sulfate with small crystals so that they can take part in next charge–discharge processes.

Each sample was characterized by XRD to determine the paste components. XRD analysis results were summarized at Table 2. Table 2 shows that sulfated negative and positive plates have lead sulfate as a major component of paste. After inverse charge, the major part of irreversible lead sulfate converts to spongy lead and lead dioxide on the positive and negative pastes, respectively.

3.1.3.3. Cyclelife test. The recovered battery was used for cyclelife test. During of 40 cycles of charge and is charge processes, the cyclelife behaviors of the recovered battery and a freshly assembled

Table 2
XRD analysis for the negative and positive pastes before and after recovery.

Sample	Component (%wt)						
	Pb	PbO	$PbO \cdot 4H_2O$	α-PbO_2	β-PbO_2	$PbSO_4$	$Pb_4O_3SO_4 \cdot H_2O$
Negative plate before recovery	24.46	3.5	–	–	5.15	45.51	21.38
Negative plate after recovery	–	4.22	2.24	3.8	79.04	5.20	5.50
Positive plate before recovery	–	4.34	3.87	5.13	20.62	42.17	23.87
Positive plate after recovery	67.67	8.98	4.28	–	10.55	4.15	4.37
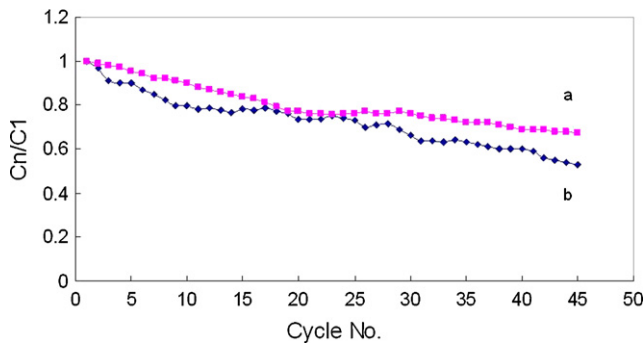
Fig. 5. Variation of discharge capacity during 45 cycles for a freshly prepared battery (a) and recovered battery by inverse charge method (b). At each cycle, discharge capacity was determined by 20 h discharge rate.

Fig. 7. Effect of oxidation temperature on the recovery of discarded sulfated battery in the chemical charge process. The ratio of discharge capacity after recover/discharge capacity before recovery was concerned as optimizing signal.

similar battery were compared (Fig. 5). As it is obvious in Fig. 5, the recovered batteries have cycle endurance 75% 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 cyclelife test shows that the recovered batteries can be reused for a long time.
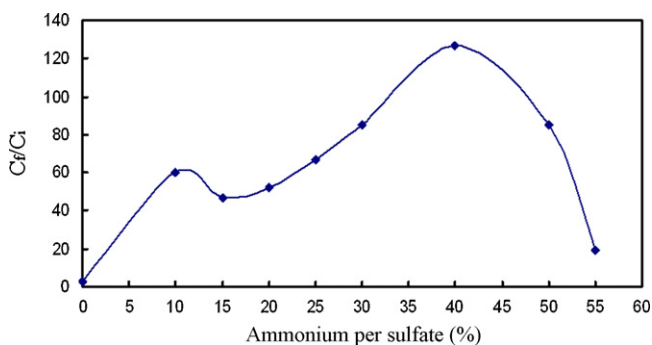
3.2. Chemical charge

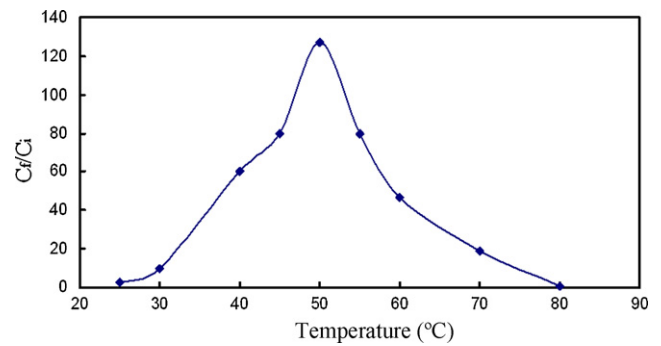#### 3.2.1. Optimization of the different effective parameters

In order to optimization of ammonium persulfate solution concentration, several different ammonium persulfate concentrations of 0, 10, 15, 20, 25, 30, 40, 50, and 55% were used for chemical charge. Fig. 6 shows the effect of ammonium persulfate solution concentration on recovery of large crystals of lead sulfate. As it has been shown in Fig. 6, at this concentration, rates of growth and nucleation are suitable for forming of active materials. The obtained results for discharge capacities show that concentration of 40% for each single unit cell is the best. At this concentration, the average recovery performance was 84%. The recovery efficiency is increased when the ratio of C_f/C_i increases. At this concentration, large crystalline lead sulfates convert to active material.

At optimization of recovery temperature, several different temperatures of 25, 40, 50, 60, 70, and 80 °C were used for chemical charge. Fig. 7 shows effect of recovery temperature on recovery of inactive sulfates in chemical charge process. Obtained results for discharge capacities show that the temperature of 50 °C for each single unit cell is the best.

At optimization of recovery time in chemical charge, several different times for recovery of inactive sulfates by ammonium persulfate solution for 0.5, 1, 2, 3, and 4 h were used for chemical
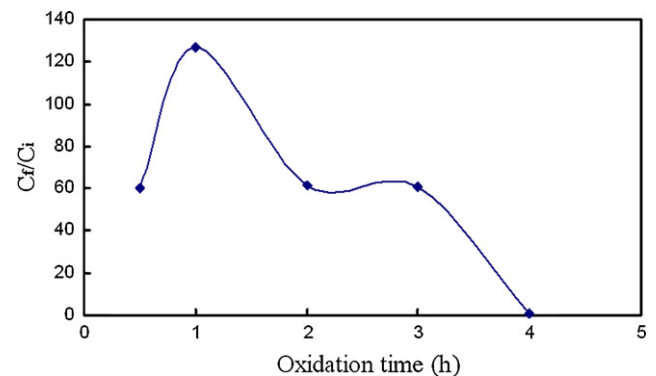
charging. The effect of recovery time on restoring inactive sulfates in chemical charge process has been show in Fig. 8. As it is seen at Fig. 8, time of 1 h for single unit cell is the best. The time of 1 h, is suitable for nucleation and crystal growth to obtain the maximum discharge capacity. At higher chemical oxidation times, more lead dioxide will be formed on the negative plates so that, at charge step, they cannot fully converted to spongy lead consequently, as a final result, the battery discharge capacity will be reduced.

The obtained results from optimizing of oxidant concentration, recovery temperature and recovery time show that the oxidant solution concentration of 40%, the temperature of 50 °C and the time of 1 h is the most effective for chemical charging. Therefore, these values were selected for further investigation at this study.

3.2.2. The recovery of the discarded batteries

New formed batteries (with nominal voltage of 2 V and nominal capacity of 10 Ah) were fully charged and then discharged to determine initial available capacity (C_i). Discharged batteries were placed on 40% of ammonium persulfate solution at 50 °C for 1 h then, they charged by constant voltage of 2.66 V for 24 h. The charged batteries were discharged with the constant current of 0.05 RC to determinate new available capacities (recovered capacity; C_f).

Fig. 9 compares the discharge behavior of a fully sulfated lead-acid battery before and after chemical charge process. For the sample shown in Fig. 9, C_i and C_f can be calculated from the discharge data. As it is seen from Fig. 9, during the discharge process, the battery can deliver much more energy after chemical charge. The chemical oxidation yields the recovery performance of more than 84% is a powerful method to recover the missing capacity for sulfated lead-acid batteries.


Fig. 6. Effect of ammonium persulfate solution concentration (%wt) on the recovery of sulfated lead-acid batteries. The ratio of discharge capacity after recover/discharge capacity before recovery was concerned as optimizing signal.

Fig. 8. Effect of oxidation time on the recovery of discarded sulfated battery in the chemical charge process. The ratio of discharge capacity after recover/discharge capacity before recovery was concerned as optimizing signal.
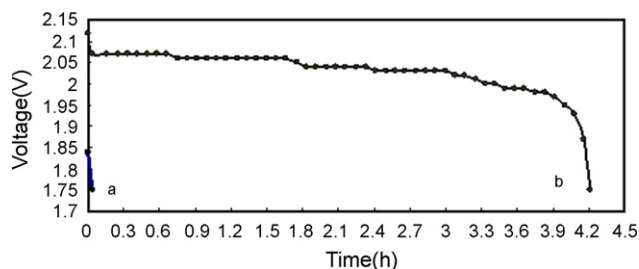
Fig. 9. Time–voltage behavior of a fully sulfated lead-acid battery during discharge process by 2 h discharge rate before chemical charge (a) and after chemical charge (b).

In the chemical charge process, ammonium persulfate ($(NH_4)_2S_2O_8$) oxidizes irreversible lead sulfate to reversible lead dioxide on the negative and positive plates as following (Eq. (5)):

$$PbSO_4 + (NH_4)_2S_2O_8 + 2H_2O \rightarrow (NH_4)_2SO_4 + PbO_2 + 2H_2SO_4 \quad (5)$$
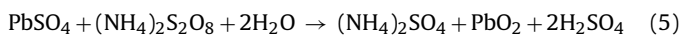
It should be mentioned that ammonium persulfate as sulfuric acid is hazardous to handle so operating persons should be take care. During chemical oxidation, some ammonia gas is also may emitted from recover reactions as following:

$$(NH_4)_2SO_4 \rightarrow NH_3 + H_2SO_4 \quad (6)$$

At next step, electrochemical charge reconverts the produced reversible lead dioxide to metallic lead in negative paste as following:

$$(for\ negative\ plate) \quad PbO_2 + 4H^+ + 4e \rightarrow Pb + 2H_2O \quad (7)$$
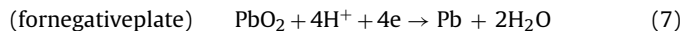
On the positive plate, electrochemical charge completes only the lead dioxide formation.

3.2.3. Scanning electron microscopic studies

The morphology of negative and positive paste at different statements was studied by scanning electron microscopy. In each SEM image, the nature and type of the observed crystals were determined.
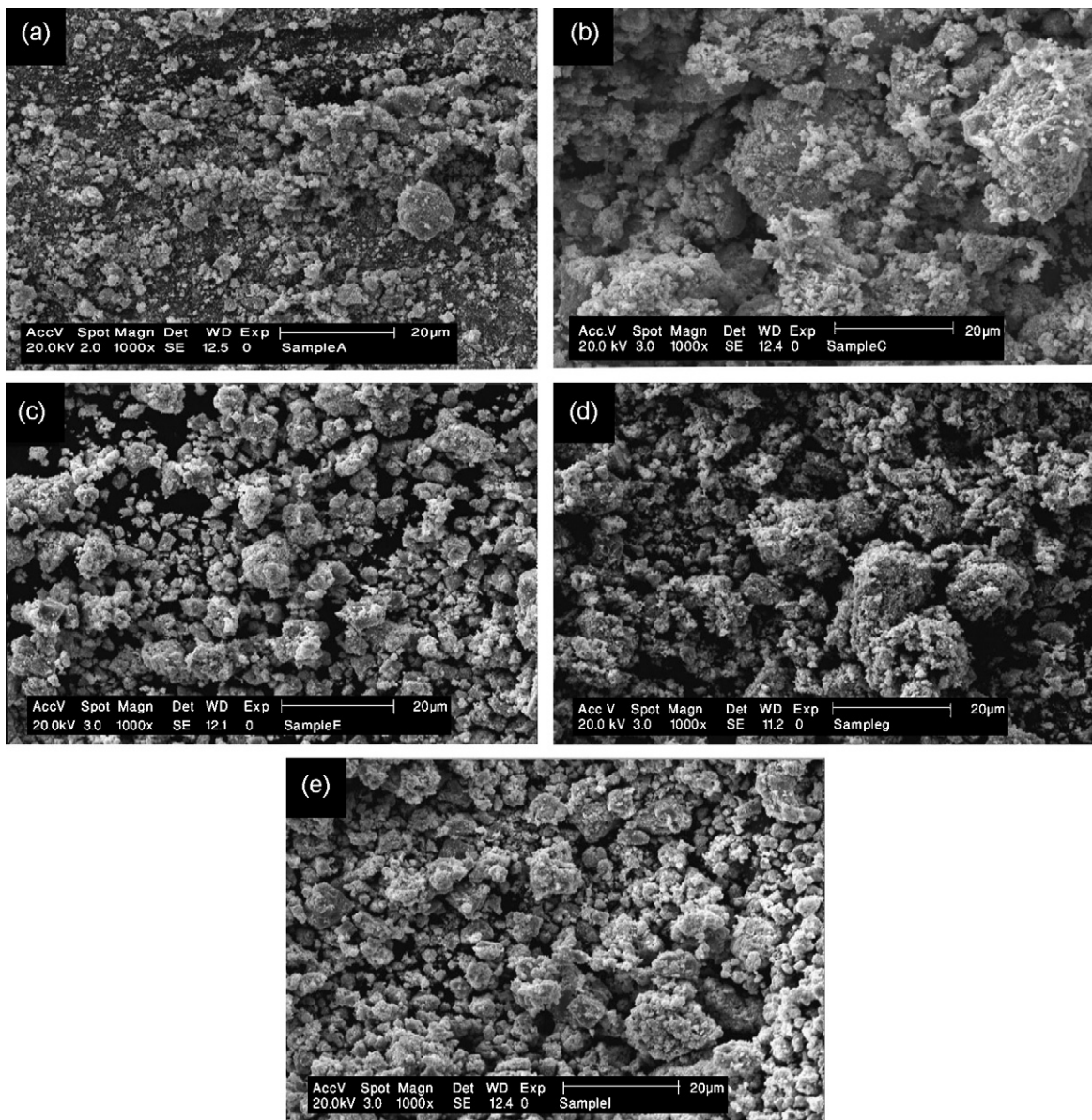
Fig. 10. SEM images of positive electrode (cathode) before chemical charge without discharge (a), after discharge without chemical charge (b), after chemical charge (c), after chemical charge and discharge (d), and after 10 cycles of charge and discharge (e). All SEM images are in magnification of 1000×.
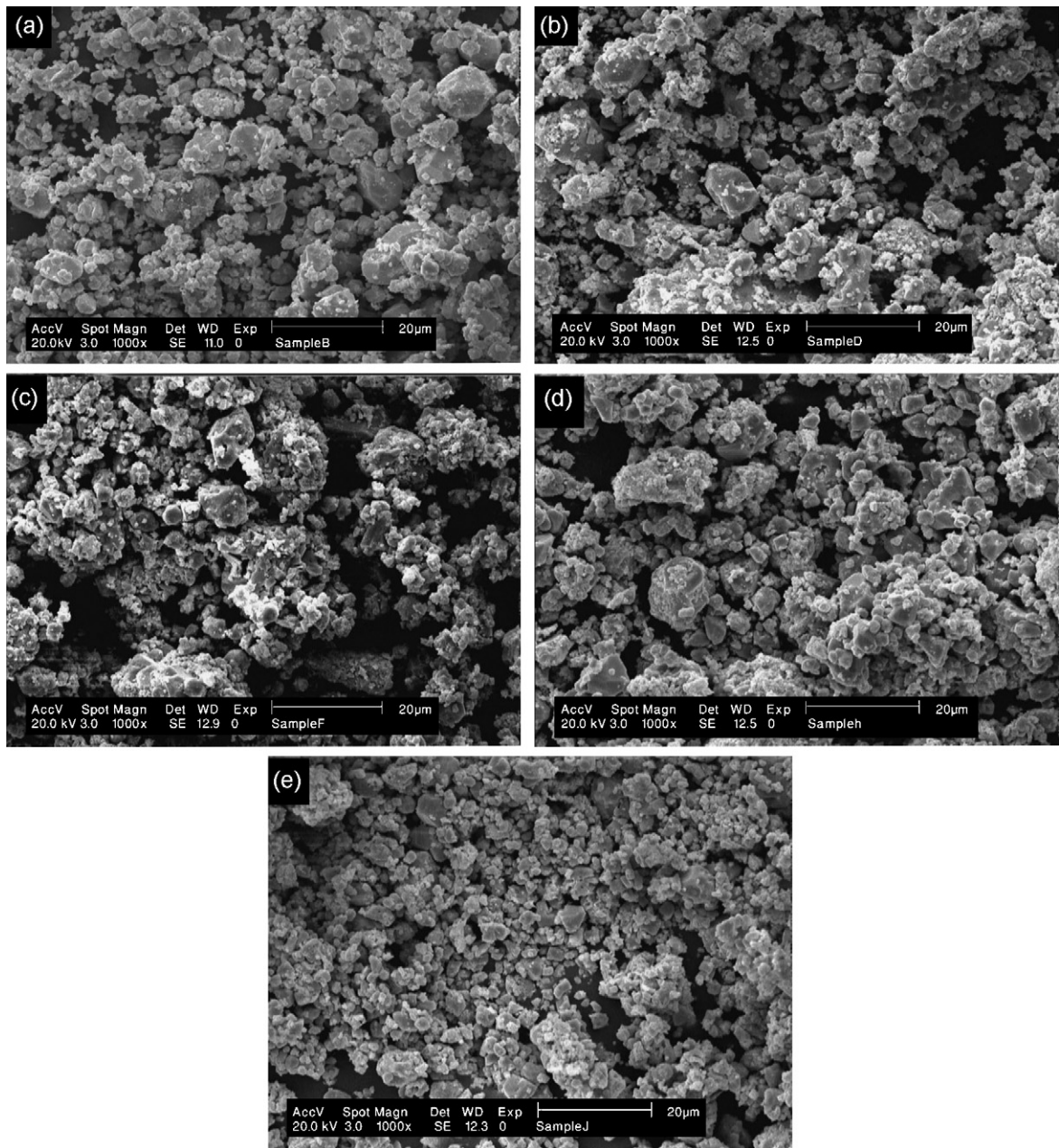
Fig. 11. SEM images of negative electrode (anode) before chemical oxidation without discharge (a), after discharge without chemical charge (b), after chemical charge (c), chemical charge and discharge (d), after 10 cycles of charge and discharge (e). All SEM images are in magnification of 1000×.

3.2.3.1. Investigation of positive electrode. Fig. 10 shows the morphology of a positive electrode paste after electrochemically charge without discharge, after electrochemically charge and discharge, after chemical charge, after chemical charge and also after 10 cycles of charge and discharge. As it is seen from Fig. 10, before chemical charge, there are many large crystalline lead sulfates available on the surface of the fully charged positive electrode. Fig. 10a shows that there are much more large crystals of lead sulfate in the inner layers of positive paste. Fig. 10b shows SEM image of positive paste after discharge process for determining of initial capacity (C_i). As it can be seen from Fig. 10b, during of discharge process, lead dioxide of cathode was transformed to insolvable and irregular lead sulfate crystals. These lead sulfate crystals cannot be convert to lead dioxide in the cathode during of next charge process. Fig. 10c shows the positive electrode after chemical charge. As seen from Fig. 10c,

major part of crystalline lead sulfate was converted to lead dioxide crystals.

Fig. 10d shows SEM image of positive paste after chemical charge and discharge. As it is seen from Fig. 10d, during of discharge process, lead dioxide is converted to uniform small crystals of lead sulfate which can be transformed to lead dioxide at next charge process.

Chemical oxidation 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 the paste during discharge or storing of the discharged batteries for a long period, this crystalline lead sulfate cannot be converted into active materials through direct charge. During chemical oxidation process, large crystalline lead sulfate on the anode of the battery is converted to lead dioxide (PbO_2) and also, on cathode of the battery

convert to lead dioxide (PbO$_2$). By the charging process at next stage, the obtained lead dioxide of the negative plates can be converted to the spongy lead very easier than crystalline lead sulfate.

Fig. 10e shows SEM image of positive paste after 10 cycles charge and discharge of chemically oxidation electrode. As it can be seen from Fig. 10e, during of successive discharge and recharge processes, lead dioxide converted to uniform small crystals of lead sulfate at discharge step and, they transform to lead dioxide at the next charge process.

3.2.3.2. Investigation of negative electrode. Fig. 11 shows the surface of paste on the negative electrode at different states. As it is seen from Fig. 11a, 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.

During the normal discharge of a lead-acid battery, lead sulfate forms on the plates of battery. When recharged, the lead sulfates are converted to the soft spongy lead. When this material fails to release from the battery's plates, it begins to harden and crystallize and then sulfated. Sulfation is the prime cause of a battery loosing the capacity to be successfully recharged. It cannot be reconverted during subsequent recharging. This creation of hard crystals the longer sulfation occurs, the larger and harder the lead sulfate crystals become. The morphology of the sulfated negative plate after fully discharged is seen in Fig. 11b. With comparison of Fig. 11b and a, it is seen that only a few amount of crystalline lead sulfate was transformed to active material. Nevertheless, the experimental results of discharge tests showed that the low amount oxidation of paste can help to recovering of the discarded battery.

The morphology of the fully sulfated negative plate after chemical oxidation is seen in Fig. 11c. As it is seen from Fig. 11c, 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 it was previously shown in Fig. 9b.

The surface of chemically charged and discharged negative plate is shown in Fig. 11d. Fig. 11d shows that formed spongy lead was transformed into uniform lead sulfate with small crystals so that they can take part in next charge–discharge process. These sulfates transform to spongy lead at recharge process.

Fig. 11e shows SEM image of negative paste after 10 cycles charge and discharge of chemically oxidation electrode. As it can be seen from Fig. 11e, during discharge process, soft lead sulfate crystals are formed in the pores and on the surfaces of the negative plates inside the battery. To recharge the battery, it is necessary to convert the lead sulfate material which attaches to the discharged areas of the plates back to active plate material. During of discharge spongy lead converted to uniform small crystals of lead sulfate that they transform to lead dioxide at recharge process. These sulfates transform to spongy lead at recharge process.

3.2.3.3. Cyclelife test. The recovered battery was used for cyclelife test. During of 45 cycles of charge and discharge processes, the cyclelife behaviors of the recovered battery and a freshly assembled similar battery were compared. The obtained results showed that the recovered batteries by chemical charge method have cycle endurance 70% of the freshly battery or more. The cyclelife test shows that the recovered batteries can be reused for a long time.

4. Comparison of efficiency of inverse charge and chemical charge

For the purpose of comparison of efficiency of inverse charge and chemical charge methods, two sulfated discarded 12 V–40 Ah batteries with identical histories were separately recovered by inverse charge and chemical charge and then, the recovery performance of two the recovered batteries was investigated along with 10 cycles
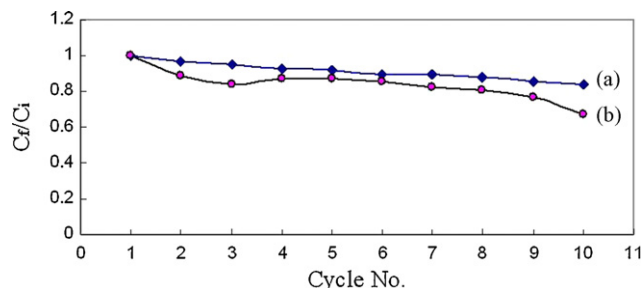

Fig. 12. Comparison behavior of the recovered battery by inverse charge with behavior of the recovered battery by chemical charge during of 10 cycles of charge and discharge processes; changes of relative capacity of the recovered battery by inverse charge (a), changes of relative capacity of the recovered battery by chemical charge (b). At each cycle, discharge capacity was determined by 20 h discharge rate.

of charge and discharge. The obtained results from these two methods are shown in Fig. 12. As seen from Fig. 12, during of 10 cycles of charge and discharge processes, efficiency of the recovered battery by inverse charge is better than efficiency of the recovered battery by chemical charge. The results of this test for 2 other pairs of discarded batteries were similar.

At inverse charge method, with applying lower current to sulfated plates, the major part of the inactive lead sulfates can be converted to active materials but at chemical charge with optimized oxidation time, only inactive sulfates of the outer layers of paste can be recovered to the lead dioxide. Therefore the recovered battery by chemical charge becomes involved of more capacity loss with respect to the recovered battery by inverse charge.

By attention to recovery percent in chemical charge (84%) and inverse charge (80%), from the view of recovery of inactive sulfates and recovery of discharge capacity, it is obvious that chemical charge method is more efficient than inverse charge. But by attention to Fig. 12, it is determined that, from the view point of capacity loss in cyclelife, inverse charge is better than chemical charge method. Of course, this numeral difference is not high and performance of two mentioned methods is almost the same specially, at higher cycles.

5. Conclusions

Results obtained from the current industrial research shows the ability of inverse charge and chemical charge, cheap and high performance methods for the recovery of discarded sulfated lead-acid batteries. Application of these methods 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, with inverse charge, one sulfated battery can be inversely charged for 24 h and then directly recharged for 48 h. And at chemical charge method, one sulfated battery can be chemically charged by oxidant solution of ammonium persulfate for 1 h and then charged for 24 h. By these two methods, a discarded battery can be recovered and taken back to service cycle. Because of the simplicity and reliability of these methods at each battery factory, battery service and repairing place, the presented methods can be of very interest in economical and commercial views. As a final result, it can be concluded that the both electrochemically inverse charging and chemically charging methods can be successfully applied in industrial applications for the recovery of the sulfated discarded lead-acid batteries.

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