

# Lead–acid bipolar battery assembled with primary chemically formed positive pasted electrode

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## Abstract

Primary chemically formed lead dioxide (PbO<sub>2</sub>) was used as positive electrode in preparation of lead–acid bipolar batteries. Chemical oxidation was carried out by both mixing and dipping methods using an optimized amount of ammonium persulfate as a suitable oxidizing agent. X-ray diffraction studies showed that the weight ratio of β-PbO<sub>2</sub> to α-PbO<sub>2</sub> is more for mixing method before electrochemical forming. The electrochemical impedance spectroscopy (EIS) was used to investigate charge transfer resistance of the lead dioxide obtained by mixing and dipping methods before and after electrochemical forming. Four types of bipolar lead–acid batteries were produced with: (1) lead substrate and conventional electroforming; (2) carbon doped polyethylene substrate with conventional electroforming; (3) carbon doped polyethylene substrate with chemical forming after curing and drying steps in oxidant bath, followed by electrochemical forming, and (4) carbon doped polyethylene substrate with primary chemical oxidation in mixing step, followed by conventional electroforming. The capacity and cycle-life tests of the prepared bipolar batteries were performed by a home-made battery tester and using the pulsed current method. The prepared batteries showed low weight, high capacity, high energy density and high power density. The first capacities of bipolar batteries of type 1–4 were found to be 152, 150, 180 and 198 mAh g<sup>-1</sup>, respectively. The experimental results showed that the prepared 6 V bipolar batteries of type 1–4 have power density (per cell unit) of 59.7, 57.4, 78.46 and 83.30 mW g<sup>-1</sup> (W kg<sup>-1</sup>), respectively.

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**Keywords:** Chemical forming; PbO<sub>2</sub>; Bipolar lead–acid battery; Conductive polyethylene; Curing; Discharge capacity; Power density

## 1. Introduction

The increasing concern for the environmental and the pollution problems caused by the vehicles, especially in large cities, have led to a worldwide interest for the development of efficient electrical and hybrid vehicles. The battery, as an autonomous energy system, is a key element in the operation of the electrical vehicles, due to its great influence on the final cost, range and performance of the vehicle. The characteristics of the batteries available in the market today impose hard restrictions to the performance of the electrical vehicles.

The lead–acid battery has been a successful article of commerce for over a century. Practical lead–acid batteries began

with the research and inventions of Raymond Gaston Planté in 1860, although batteries containing sulfuric acid or lead components were discussed earlier [1]. The advantages of lead–acid batteries include: low cost of manufacture, simplicity of design, reliability and relative safety when compared to other electrochemical systems. Relatively good specific power has enabled the widespread use of lead–acid batteries for starting, lighting and ignition of engine (SLI) purposes for vehicular (e.g., automotive, marine and aviation) applications. The lead–acid system has also found widespread use as traction batteries in golf carts and boats. However, the use of lead–acid batteries for electric cars as an alternative to fossil fuels has been limited by the need for better specific energy and deep discharge cycle lifetime. The bipolar lead–acid batteries have shown increasing promise in overcoming these limitations.

The on-going competition of more fuel economic cars has led to the introduction of the first hybrid electric vehicles (HEV), such as Toyota (Prius) and Honda (Insight). These high fuel

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economic cars make use of a high power battery, which stores the energy during braking and delivers the power for acceleration. The batteries of HEVs do not need to be charged separately, as they are charged during driving.

High power lead–acid batteries have traditionally been linked to automotive applications, mainly for vehicle starting, even at low temperatures [2,3]. However, novel industrial and automotive applications, such as 42 V and hybrid vehicles, demand an improved battery performance in terms of high power capability and cyclability. Although, use of advanced battery technologies, such as nickel/metal hydride or lithium-ion batteries, can provide such a performance, the high cost is a quite restrictive factor for most of their industrial and automotive applications. Nickel/metal hydride (NIMH) batteries as high power batteries have a very high specific power value of at least  $500 \text{ W kg}^{-1}$  and can be used in automotive applications and especially in hybrid electric vehicles (HEVs). However, the price of these batteries puts a serious limitation towards the large-scale introduction of the HEVs. This relatively high price is due to the complex production technology, low production volumes of high power NIMH batteries and the relatively high price of the basic materials like Ni. In order to lower the price of power packs, alternatives are investigated. An interesting alternative is the bipolar lead–acid battery which in principle can be produced at low cost, and possess high specific power values. Application of true bipolar electrodes in lead–acid batteries causes to increase the battery power up to  $35\text{--}65 \text{ Wh kg}^{-1}$  [4].

A battery with bipolar electrodes is known to be advantageous over the conventional monopolar electrodes in terms of power output. In a conventional battery, electrical current is generated by active materials travel to a current collector and through an outer circuit to reach the next cell. In bipolar battery, active materials of opposite polarities are placed on two surfaces of a bipolar substrate. Current can thus flow through the substrate to the next cell. Consequently, because of a much shorter electrical path, power loss due to ohmic drop in the circuit is minimized. The volume of the battery is reduced due to elimination of outer circuit materials such as straps, posts and tabs. Thus, there is an increasing interest in the use of bipolar systems in the construction of batteries [5–9].

In a typical bipolar lead–acid battery design, each electrode includes an electrically conductive and electrolyte impervious sheet or plate which serves as a partition between the battery cells. The positive active material (PAM) adhered to the positive side and negative active material (NAM) is adhered to the opposite negative side. The bipolar electrodes are stacked parallel to and on top of each other with the positive side of each electrode facing the negative side of the adjacent electrode. The current is collected perpendicular to the plane of the thin plates at the endplates terminating at both ends of the stack of bipolar plates. This arrangement allows for the possibility of batteries with lower internal resistance and, thus, higher specific power. With the bipolar battery design it is possible to choose lightweight conductive materials to construct bipolar electrodes that do not corrode under continuous deep discharge cycling. Despite the apparent advantages of bipolar lead–acid batteries,

the substantial effort to develop these batteries has yet to yield a commercially viable product.

In a bipolar lead–acid battery, the role of the substrate is paramount. The substrate serves as an intercell connection and as a support to active materials. It provides seals between and isolates electrolyte in individual cells. It must retain its electrical conductivity in the corrosive lead–acid environment and break communication of electrolyte in adjacent cells through the service life of the battery. Furthermore, it may not participate in or provide alternative routes to the battery reactions. To satisfy these requirements, the substrate must be electrically conductive, insoluble in sulfuric acid, stable in the potential window of the battery, possess high oxygen and hydrogen overpotentials, be inert to battery reaction, impervious to the electrolyte, having good adhesion to the battery active materials, and easy to process and seal to the battery case.

A practical bipolar plate should offer: the structural integrity to support the active material yet is lightweight, resistance to the various corrosion mechanisms occurring on both the positive and negative sides of the bipolar electrode during cycling, and the ability to be inexpensively manufactured. Corrosion may render the surface of the bipolar plate being perforated thus causing an electrical short between two adjacent cells and battery failure. Various substrates including stainless steel, lead, silver and carbon-polymer composite foils have been used in the construction of bipolar electrodes [7,10–15]. The aggravating disadvantages in the use of plastics as carriers for electroactive materials include low conductivity and lack of adherence to the electroactive layers. Usually, the electroactive materials are deposited onto the surface of a conductive carrier (metal or conductive polymer). A significant improvement of the originally poor adherence of the polymer foil to the electroactive layers can be achieved by mechanical (surface roughening) or chemical (etching) pretreatments [11–13].

The use of plastics with conductive fillers, like graphite and/or soot incorporated into the polymer, demands an intermediate layer between the carbon-filled polymer and the active material to prevent the formation of hydrogen gas by anodic corrosion, which is enhanced in the presence of carbon in any modification. The use of intrinsically conductive polymers like polypropylene and polyethylene as carrier materials requires special precautions and manufacturing processes because most of these polymers are insoluble and brittle. Thus, further treatment is hardly practicable. The advantage of intrinsically conductive polymers compared with filled plastics is that an intermediate layer between the carrier and the zinc is unnecessary. The achievable resistance of both plastics with conductive fillers and intrinsic conductive polymers are not comparable to that of metal carriers. However, the achievable resistance is sufficient for thin foils in bipolar arrangements.

Other promising method to form thin electrodes include: (a) a metallic layer, serving as a current collector, is deposited onto one side of a thin, porous polymer foil such as polyethylene or polypropylene [11] and (b) the electroactive material is electrolytically or mechanically deposited onto the surface of a metallized plastic [12].

The flexibility of the polymer has a positive influence on the volume change of electroactive materials because the plastic provides flexible ‘mechanical struts’. The plastic acts as a binder and, therefore, prevents an increase in the internal resistance due to contact problems.

In a lead–acid battery, lead dioxide as cathode has a very important role in performance of battery. There are many reports about improving energy storage capacity and cyclability of lead dioxide [16–24]. Major of previous reports were concerned to improving of lead dioxide performance in conventional lead–acid batteries.

In previous studies, we employed bipolar electrodes in construction of rechargeable batteries based on polyaniline [5,25]. In this work, bipolar lead–acid batteries were constructed by use of conventional negative paste and improved positive paste on two different bipolar substrates of tin–lead alloy and conductive polyethylene (carbon coped polyethylene). Use of conductive polyethylene as a bipolar electrode substrate caused to decrease battery weight considerably. A chemical preoxidation step by ammonium persulfate was found to improve the energy storage capacity and performance of positive paste in bipolar lead–acid batteries.

## 2. Experimental

### 2.1. Material and reagents

Battery lead oxide powder (Pb 27 wt% and PbO 73 wt%) was obtained from Behin Avar Co. (Tehran, Iran). Sulfuric acid, lead nitrate and Glycerol were provided from Loba Chem Co. (India). Palladium (II) chloride was obtained from Merck. Rashel salt, tin chloride, hydrochloric acid, copper sulfate and carbon black were provided from Iranian companies in industrial grade. Doped polyethylene was obtained from Zipperling Co. Humic acid (3,4,5-trihydroxybenzoic acid), 1,2-acid ( $\alpha$ -hydroxy- $\beta$ -naphthalene carboxylic acid) and barium sulfate with industrial grade were used as additive to negative paste. Distilled water was used in all experiments.

### 2.2. Instrumental

pH measurements were performed by a Metrohm 691 pH meter. All battery voltage readings were carried out by a Sa-Iran digital multimeter 8503 (Iran). X-ray diffraction (XRD) studies were performed by Decker D8 instrument. The ac Impedance measurements were made as function of frequency using electroanalytical instrument (A273, EG&G, USA). All charge, discharge and cycle-life tests of batteries were carried out with a home-made multi-channel battery tester.

### 2.3. Methods

#### 2.3.1. Paste preparation

Negative paste was prepared in conventional manner with the formulation shown in Table 1. Required amounts of battery leady oxide (PbO 73%, Pb 27%), carbon black, barium sulfate, 1,2-acid and humic acid were mixed in a small paste mixer for

Table 1

Shows the conventional formulations of negative and positive paste for the batteries

No.	Compound	wt%
1	Battery lead oxide powder	99.27
2	Carbon black	0.15
3	CMC	0.1
4	Humic acid	0.1
5	1,2-acid	0.1
6	Barium sulfate	0.2
7	Cellulose fiber	0.08

15 min. 200 ml water (for 5 kg battery leady oxide) was added to above mixture and mixed for 15 min. Then, 375 ml sulfuric acid ( $1.25 \text{ g cm}^{-3}$ ) was slowly added. Polyamide fibers was suspended in 175 ml water and added to paste in suspension form. Paste was mixed for a time period so that paste density became  $4.34 \text{ g cm}^{-3}$ . Water cooling system of mixer held the paste temperature lower than  $60^\circ\text{C}$ . The negative paste was used for all types of the batteries.

Positive paste was prepared in conventional manner as following for batteries types of 1, 2 and 3.

Leady oxide (a mixture containing PbO 73 wt% and Pb 27 wt%) and carbon black were mixed in a small paste mixer for 15 min. 200 ml water (for 5 kg battery leady oxide) was added to above mixture and mixed for 15 min. Then, 375 ml sulfuric acid ( $1.25 \text{ g cm}^{-3}$ ) was slowly added. Polyamide fibers was suspended in 175 ml water and added to paste in suspension form. Paste was mixed for a time period so that paste density became  $4.25 \text{ g cm}^{-3}$ . Water cooling system of mixer held the paste temperature lower than  $60^\circ\text{C}$ . The positive paste was used for three types of the batteries (types of 1, 2 and 3).

#### 2.3.2. Battery assembling

In all four battery types assembled in this study, special care was conducted to do curing of both the positive and the negative electrodes under the same conditions.

**2.3.2.1. Battery type 1.** A tin–lead alloy sheet was cast as a foil with a thickness of 4 mm and then machined for use as terminating anode, terminating cathode and bipolar electrodes, as shown in Fig. 1. After preparation of electrodes, the machined sides of terminating anode and terminating cathode electrodes were pasted by negative and positive paste, respectively. One machined side of each bipolar electrode was pasted the negative paste and the other machined side was with the positive paste.

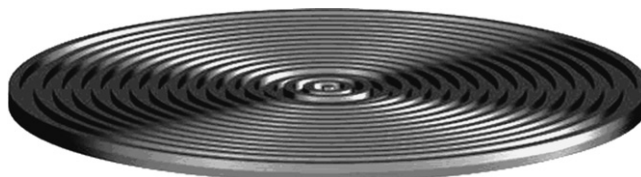


Fig. 1. The structure of bipolar electrode substrate for battery type 1. Thickness is 4 mm and total diameter is 50 mm. At terminating electrodes only, one side was machined and at bipolar electrodes, two sides were machined corresponding as this figure.

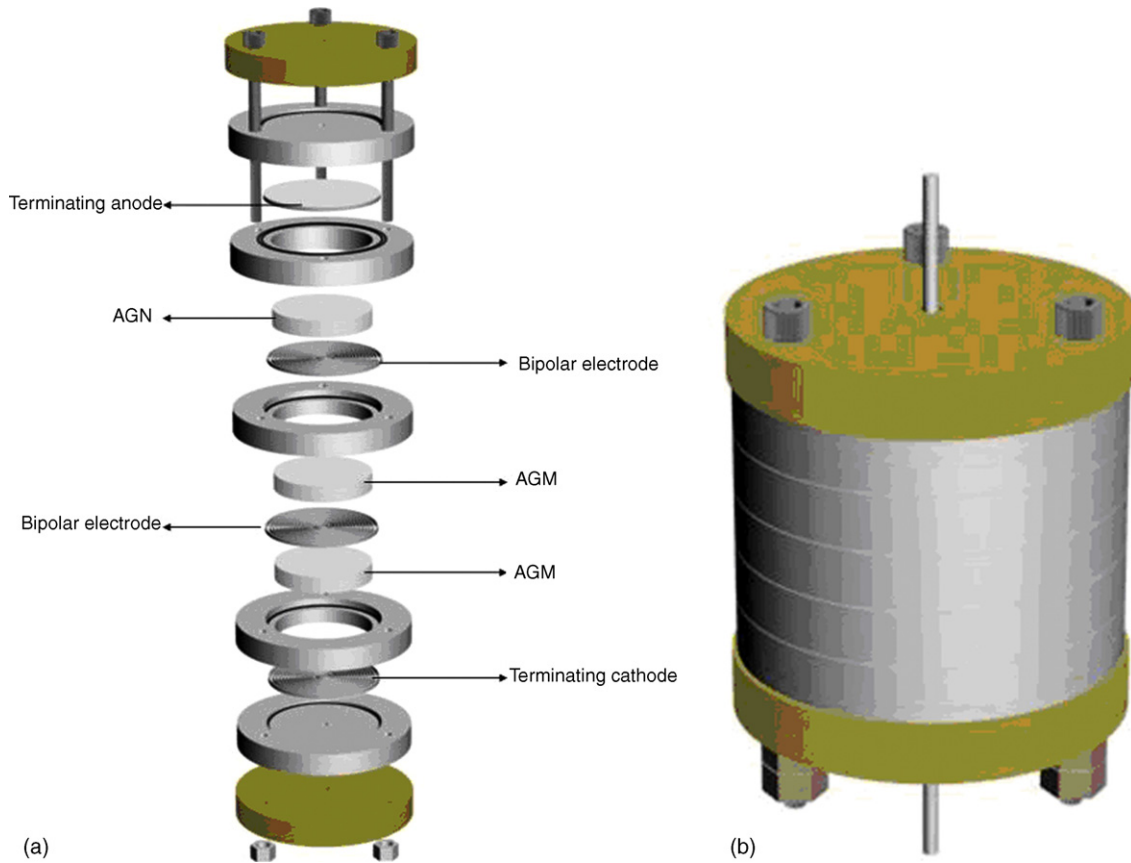


Fig. 2. (a) Scheme for all components of battery type 1; (b) scheme of the assembled battery type 1. Terminating electrodes and bipolar electrode was made from tin–lead alloy.

The pasted electrodes (terminating and bipolar electrodes) were cured in a relative humidity of 95% at 55 °C for 12 h. The cured plates were dried at temperature of 70 °C for 8 h. The dried plates (electrodes) were used in the assembling of bipolar lead–acid batteries as terminating and bipolar electrodes. The design and construction of battery type 1 is shown in Fig. 2. Absorbent glass mat (AGM) separator was used to isolate anodes from cathodes. After assembling, sulfuric acid solution (1.25 g cm<sup>-3</sup>) was slowly injected into separator during at least 15 min until fully filling of the sub-cells. After 1 h (this time was given for pouring of electrolyte into pastes), some electrolyte was again injected to each sub-cell to make sure that fully saturating of AGM. Finally, the batteries were formed by pulsed current method during 24 h.

**2.3.2.2. Battery type 2.** In type 2, conductive polyethylene (carbon doped polyethylene; CDPE) was used instead of tin–lead alloy. CDPE electrodes were prepared as following:

CDPE foils were machined as shown in Fig. 3. The machined CDPE electrodes were then coated by silver electroless, and then coated by lead electroplating process. Lead electroplating was carried out by use of a solution containing 0.1 M lead (II) nitrate and 0.2 M glycerol at constant current of 0.1 A cm<sup>-2</sup>. All electrodes assembled in a specialized vessel for simultaneous electroplating. The electroplated electrodes were pasted, cured and dried (as mentioned in Section 2.3.2). The dried electrodes were assembled as shown in Fig. 4. After assembling, other

steps (acid filling and formation) were carried out as done for the battery type 1.

**2.3.2.3. Battery type 3.** The CDPE terminating and bipolar electrodes were machined similar to the battery type 2. The electrodes were coated by silver electrodeless and then by lead electroplating (with a thickness of about 200 μm). The positive terminating electrode and one side of the bipolar electrodes were

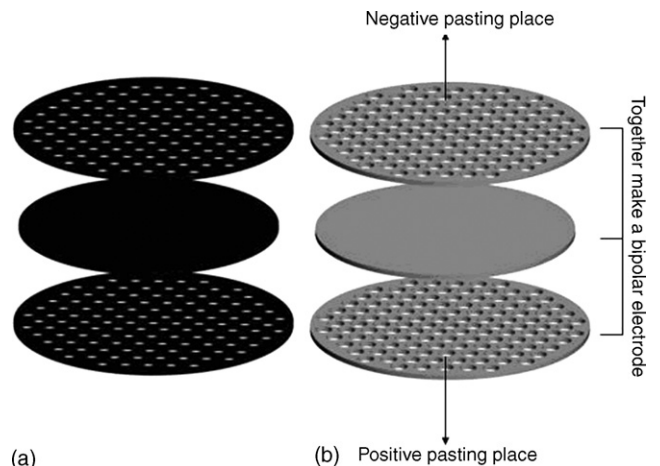


Fig. 3. Scheme of machined CDPE electrodes: (a) before electroless and electroplating; (b) after electroless and electroplating.

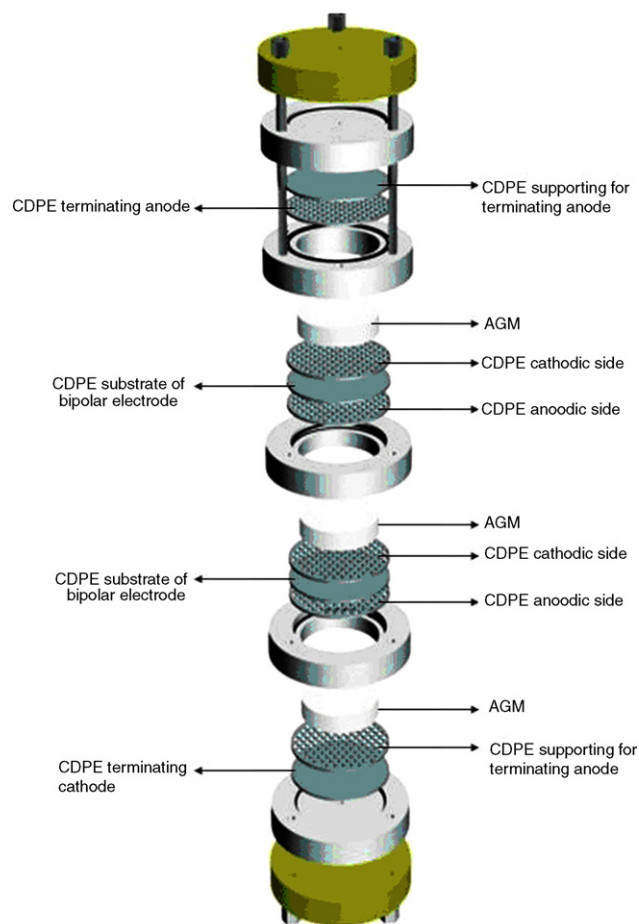


Fig. 4. Scheme for all components of battery type 2. Terminating electrodes and bipolar electrode was made from CDPE.

pasted by the positive paste. Then the electrodes were cured and dried without negative pasting on other sides. The dried electrodes were dipped in oxidant bath containing ammonium persulfate (15% wt) as oxidant at a temperature of 60 °C. Oxidation of outer layer of dried paste on the electrodes was started immediately after dipping. The rate of chemical oxidation of lead (II) oxide to lead dioxide was increased at first 15 min, and then the oxidation rate was decreased. The reaction time was completed after 1 h. After chemical pre-treatment, the oxidized electrodes were washed with distilled water and dried at 60 °C for 12 h. Then, the negative terminating electrode and the other side of bipolar electrodes were pasted with the negative paste. The pasted electrodes were cured and dried again. The obtained electrodes were assembled in a battery as shown in Fig. 4. After assembling, all electrodes were electrochemically formed in the battery container as discussed for batteries types 1 and 2.

**2.3.2.4. Battery type 4.** In this battery, the positive paste used was different from other types, while the negative paste was similar to the others. The positive paste of this battery was prepared as following:

750 g ammonium persulfate (oxidant) was dissolved in 780 ml de-ionized water containing enough amount of the fiber. The oxidant solution was slowly added to paste mixer contain-

ing 5 kg leady oxide at a high rotating rate during 30 min. Water cooling was used for temperature control ( $\theta < 60\text{ }^{\circ}\text{C}$ ). The paste was mixed for a period of time so that the density of paste became  $4.25\text{ g cm}^{-3}$ . The obtained positive paste was pasted on positive terminating electrode and only one side of bipolar electrodes. The same negative paste as other battery types was used for this battery. Other steps of battery preparation are exactly the same as battery type 2.

### 2.3.3. Electrochemical impedance spectroscopic studies

In this study, the positive electrodes of batteries types of 3 and 4, before and after electrochemical formation, and positive electrodes of battery types of 1 and 2, only after electrochemical formation, were used as working electrode in a triple electrodes cell for the electrochemical impedance spectroscopic studies. Sulfuric acid solution ( $1.28\text{ g cm}^{-3}$ ) was used as an electrolyte, as used in the bipolar lead–acid batteries. In each sample, the frequency was scanned from 1000 Hz to 0.1 Hz.

## 3. Results and discussion

### 3.1. Optimization of concentration of ammonium persulfate

In the dipping method, four parameters including ammonium persulfate concentration, weight ratio of oxidant solution to dried paste, initial temperature of oxidant bath and time of chemical forming were optimized by one at a time method. The observed maximum discharge capacity and reasonable economic cost were considered for the selection of the optimum values for these parameters.

The effect of ammonium persulfate concentration on final discharge capacity of the battery type 3 was shown in Fig. 5. As it is seen from Fig. 5, the maximum discharge capacity for battery type 3 after electrochemical formation was obtained in the presence of 20 wt% ammonium persulfate. The use of higher concentration of ammonium persulfate resulted in increased degree of chemical forming of the positive electrodes, while it does not have any considerable effect on the final discharge capacity (after electrochemical forming).

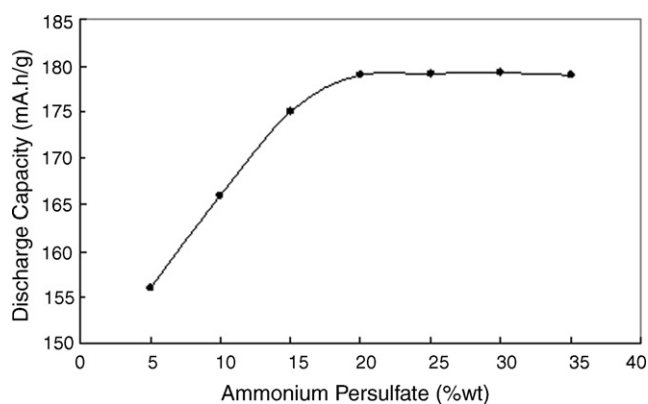


Fig. 5. The effect of ammonium persulfate concentration on final discharge capacity of bipolar battery type 3. Electrochemical formation was carried out at constant current of  $30\text{ mA g}^{-1}$  during the time of 8 h and the discharge was performed by a constant current of  $30\text{ mA g}^{-1}$ .

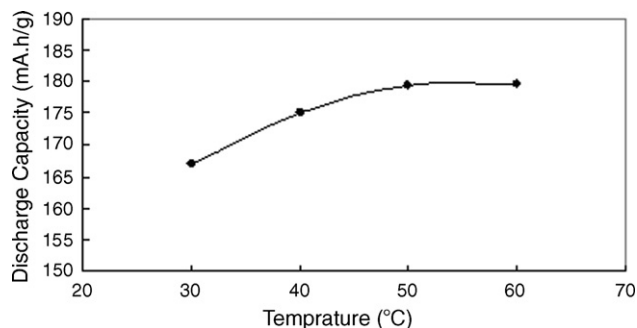


Fig. 6. The effect of initial temperature of oxidant bath on final discharge capacity of battery type 3. Electrochemical formation was carried out at a constant current of  $30 \text{ mA g}^{-1}$  during the time of 8 h and the discharge was performed by a constant current of  $30 \text{ mA g}^{-1}$ .

Fig. 6 shows the effect of initial temperature of ammonium persulfate bath on the final discharge capacity of the battery type 3. At initial temperature lower than  $30^\circ\text{C}$ , the rate of chemical oxidation of lead oxide (or lead sulfate) to lead dioxide by ammonium persulfate was very slow. Thus, the use of lower temperature was not acceptable. On the other hand, the use of initial temperatures higher than  $60^\circ\text{C}$  resulted in a fast and non-controllable reaction so that the bath solution started to boil and spoiled out. Meanwhile, an initial temperature of  $50^\circ\text{C}$  was found to be the most reasonable temperature that can be used for chemical oxidation of positive paste by ammonium persulfate in the dipping method.

The effect of dipping time on final discharge capacity of battery type 3 was shown in Fig. 7. As it is seen from Fig. 7, dipping time of 1 h showed the maximum final discharge capacity.

Fig. 8 shows the effect of weight ratio of oxidant solution to dried paste on final discharge capacity. As seen, a weight ratio of 2 is enough for obtaining maximum discharge capacity.

In the mixing method, positive pastes were prepared at different weight ratios of ammonium persulfate to initial leady oxide. The discharge capacities of the batteries prepared by these pastes are shown in Fig. 9. As it is seen from Fig. 9, the discharge capacity is increased from 150 to  $198 \text{ mAh g}^{-1}$  as the concentration of ammonium persulfate increases from 0 to 15 wt%. The use of  $>15 \text{ wt\%}$  ammonium persulfate resulted in an increase in degree of chemical forming (chemical oxidation), while it

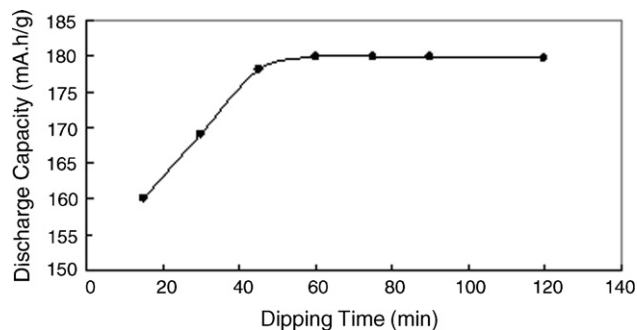


Fig. 7. The effect of dipping time of dried electrodes in oxidant bath on final discharge capacity of battery type 3. Electrochemical formation was carried out at a constant current of  $30 \text{ mA g}^{-1}$  during the time of 8 h and the discharge was performed by a constant current of  $30 \text{ mA g}^{-1}$ .

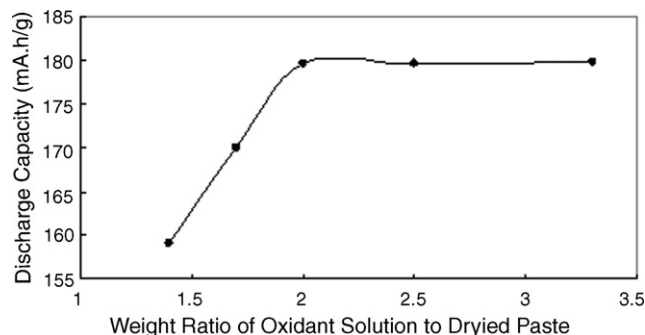


Fig. 8. The effect of weight ratio of oxidant solution to dried paste of dipped electrodes on final discharge capacity of battery type 3. Electrochemical formation was carried out at a constant current of  $30 \text{ mA g}^{-1}$  during the time of 8 h and the discharge was performed by a constant current of  $30 \text{ mA g}^{-1}$ .

caused minor increase in final discharge capacity (after electrochemical charge). Meanwhile, the use of more than 15 wt% ammonium persulfate is not also economically reasonable. It should be mentioned that, at an ammonium persulfate concentration higher than 20 wt%, the chemical reaction of ammonium persulfate with leady oxide is very fast, exothermic and dangerous.

### 3.2. Electrochemical impedance spectroscopic studies

Salkind and co-workers reported that ac-impedance spectroscopic study is a convenient way to confirm the battery results [26], as this method provides complementary information about the kinetics and thermodynamics of electrochemical processes. In this work, we used the electrochemical impedance spectroscopy for the determination of charge transfer resistance in lead dioxide pastes on six types of positive electrodes. The obtained Nyquist plots for lead dioxide of the positive electrodes of battery type 3 and 4 before electrochemical forming are shown in Fig. 10. As it is seen from Fig. 10, for these samples, Warburg impedance (line with slope of  $45^\circ$ ) is not observed. Therefore, the electrochemical reaction is only kinetic controlled process and, because of enough porosity of the positive pastes, evidences for a diffusion controlled processes does not observed. At the kinetic controlled zone of Nyquist plot, semicircle diameter is a

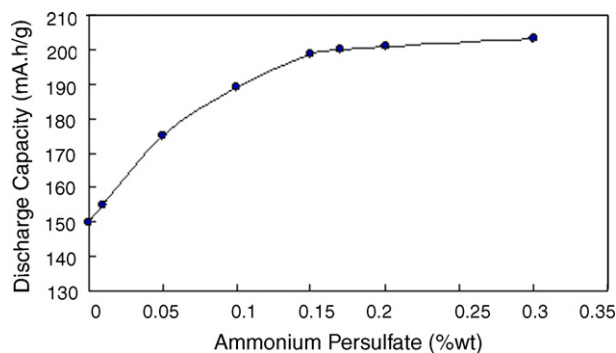


Fig. 9. Effect of ammonium persulfate amount on discharge capacity of lead-acid bipolar battery. Electrochemical formation was carried out at a constant current of  $30 \text{ mA g}^{-1}$  during the time of 8 h and the discharge was performed by a constant current of  $30 \text{ mA g}^{-1}$ .

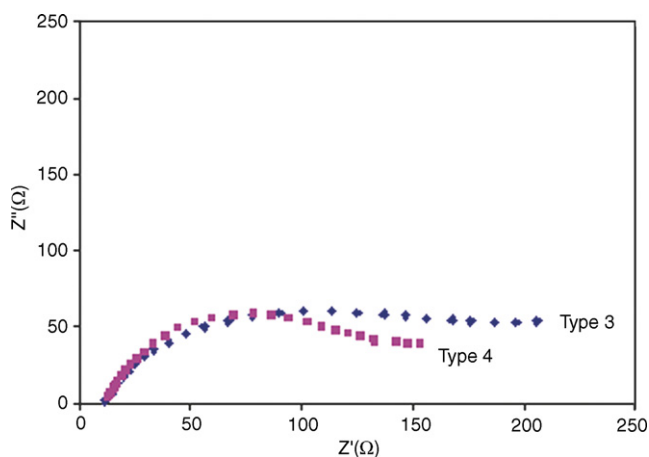


Fig. 10. Nyquist plot of positive pasted electrodes of battery type 4 (after chemical forming by mixing method) and battery type 3 (after chemical forming by dipping method) before electrochemical forming.

measure of charge transfer resistance. Accordingly, it is revealed that the charge transfer resistance for positive paste of battery type 4 (mixing method) is lower than that of battery type 3 (dipping method), as expected by regarding of discharge capacities of these batteries.

Fig. 11 shows the Nyquist plots of positive pasted electrodes of batteries types of 1, 2, 3 and 4, after electrochemical formation. As it is obvious in Fig. 11, the charge transfer resistances for positive paste of batteries varied in the order type 4 < type 3 < type 2 and type 1.

### 3.3. X-ray diffraction studies

X-ray diffraction (XRD) spectroscopy was used for the determination of  $\beta$ -PbO<sub>2</sub> and  $\alpha$ -PbO<sub>2</sub> on the plates obtained by

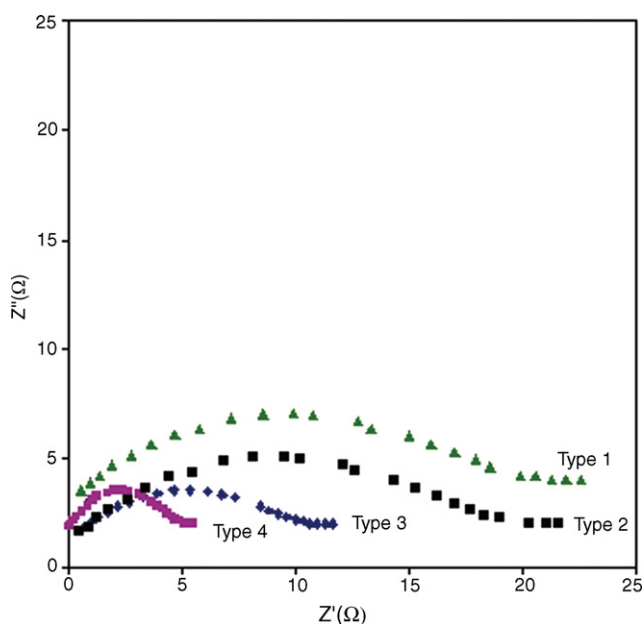


Fig. 11. Nyquist plot of positive pasted electrodes for batteries type 1–type 4 after electrochemical forming.

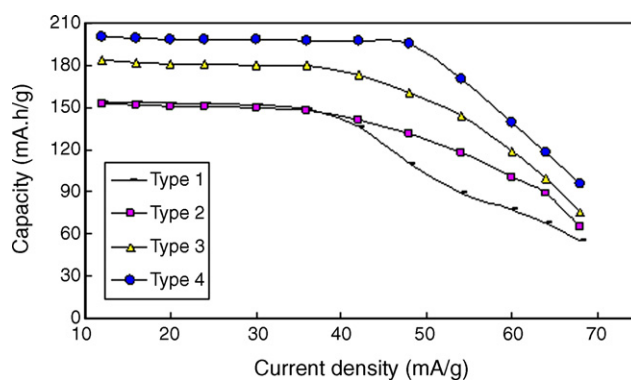


Fig. 12. Effect of discharge current density on battery capacity (for whole cell) for four types of prepared batteries. Electrochemical formation was carried out at a constant current of 30 mA g<sup>-1</sup>.

chemical oxidation in both the mixing and the dipping methods before electrochemical forming. The  $\beta$ -PbO<sub>2</sub> form was clearly identified from its most intense lines (1 1 0, at 25.4° 2 $\theta$ ) and (1 0 1, at 32.05° 2 $\theta$ ) and the  $\alpha$ -PbO<sub>2</sub> form from its (1 1 1, at 28.5° 2 $\theta$ ). The relative intensities of the characteristic diffraction lines for different phase in the paste and in the active mass after formation for battery type 4 are summarized in Table 2. XRD analysis showed that cathodes types 3 (dipping method without electrochemical forming) and 4 (mixing method without electrochemical forming) have  $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> weight ratio of 0.7 and 1.9, respectively. The presence of more  $\beta$ -lead dioxide in cathode type 4 shows the increased ability of chemical preoxidation (chemical forming) by the mixing method.

### 3.4. Optimum discharge current for operation of batteries

From each positive electrode type, a 6 V bipolar battery (two bipolar electrodes in each battery) was prepared and fully charged. Each battery was discharged under different current densities. The discharge capacity of each battery for any discharge current density was calculated. The obtained results are shown in Fig. 12. As it is seen from Fig. 12, batteries 1–4 can deliver the maximum capacity at discharge current densities of 30, 30, 36 and 42 mA g<sup>-1</sup>, respectively. At high discharge current, the outer layer of electroactive material can only share in discharge reaction. Consequently, the discharge capacities decrease. Because of regular structure and proper orientation of lead dioxide particles, battery type 3 and 4 can deliver higher discharge current than type 1 and 2. Electrochemical impedance spectroscopic studies of lead dioxide of four types of the batteries in full charged state confirmed this idea (Section 3.2).

Table 2  
XRD characteristic peaks for the positive paste electrode of battery type 4

Angle (° 2 $\theta$ )	<i>d</i> value (Å°)	Intensity (count)
25.4	3.49570	572
28.5	3.12363	552
32.05	2.79015	605

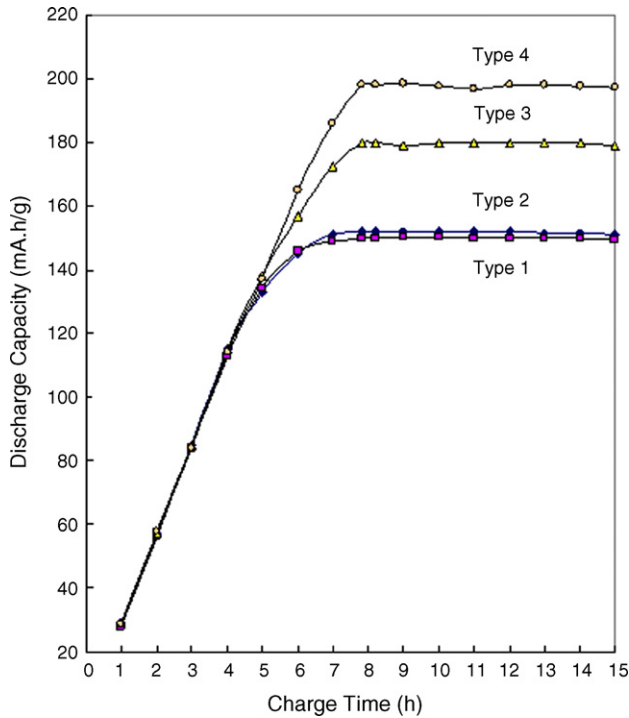


Fig. 13. Effect of time period of charge of batteries (at a constant current of  $30 \text{ mA g}^{-1}$ ) on the discharge capacities of four types of lead–acid bipolar batteries.

### 3.5. Determination of battery full charge time

All types of the batteries charged at different times and then, discharged to a cut off voltage of 5.1 V. The obtained results of discharge capacities for different charge time were shown in Fig. 13. As it is seen from Fig. 13, time necessary for full charge

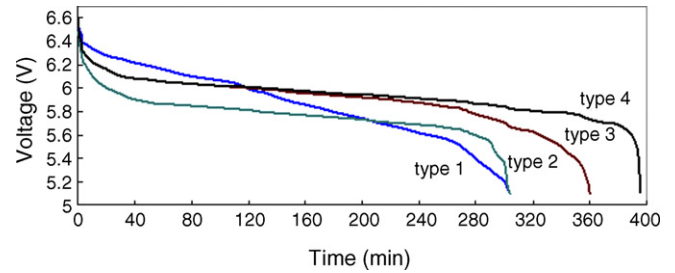


Fig. 14. Discharge curves for the four types of bipolar batteries at discharge current density of  $30 \text{ mA g}^{-1}$  with respect to the initial weight of leady oxide powder in cathodic side of one bipolar electrode. Electrochemical formation was carried out at a constant current of  $30 \text{ mA g}^{-1}$  during the time of 8 h.

of the battery types 1 and 2 is 7 h and for the battery type 3 and 4 is about 7.5 h.

The discharge capacity of battery type 4 is 30% higher than battery type 2 and capacity of the battery type 3 is 18% higher than battery type 2. While, optimum time for fully charge of the battery types 4 and 3 are only 7% greater than that of the battery type 2. It should be noted that in the course of battery cycling, the  $\text{PbO}_2$  structure obtained during formation changes depends on the particular conditions of cycling process.

### 3.6. Figures of merit

For the determination of discharge capacities and their easy comparison, the optimum discharge current of battery type 1 ( $30 \text{ mA g}^{-1}$ ) was used for the study of all batteries. All batteries were charged at constant current of  $30 \text{ mA g}^{-1}$  during 8 h. The time-voltage behaviors of all four types of batteries at capacity test are shown in Fig. 14. As it is seen, the batteries types 3 and 4 have more capacities than the two others.

Table 3  
Summary of output results of four types of the bipolar lead–acid batteries

Battery type	Discharge capacity ( $\text{mAh g}^{-1}$ )	MPV (V)	Energy density ( $\text{mWh g}^{-1}$ )	Power density ( $\text{mW g}^{-1}$ )	Power density per cell unit ( $\text{mW g}^{-1}$ )
1	150	5.890	895.3	179.1	59.70
2	152	5.781	867.0	172.2	57.43
3	180	5.940	1069.2	235.4	78.46
4	198	5.944	1176.9	249.9	83.30

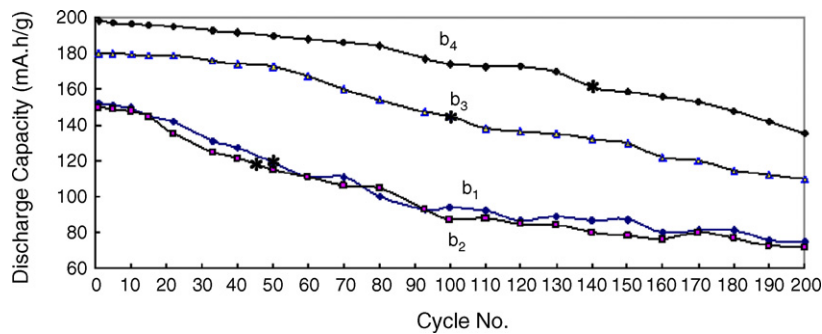


Fig. 15. Variation of discharge capacities of four types of batteries at discharge current densities of  $30 \text{ mA g}^{-1}$  with respect to initial weight of leady oxide powder used for each cathode.  $b_1$  = battery type 1,  $b_2$  = battery type 2,  $b_3$  = battery type 3,  $b_4$  = battery type 4. The end-of-life of different battery types based on the 80% of their rated capacity are marked in stars (\*) on the corresponding graphs.



Based on the results shown in Fig. 14, discharge capacities, mid point voltage (MPV), energy density and power density were calculated and summarized in Table 3.

One sample from each type of the batteries was charged by a constant current of  $30 \text{ mA g}^{-1}$  during a time period of 8 h and, discharged by  $30 \text{ mA g}^{-1}$  for 200 cycles. The discharge capacity for each cycle was calculated and the results are shown in Fig. 15. As it is seen from Fig. 15, the discharge capacities decrease with increasing cycle number. In addition, because of regular structure and proper orientation of lead dioxide particles, the capacity drop for battery type 4 is less than those for other battery types. It is interesting to note that based on data given in Fig. 15, the end-of-life of different battery types decrease in the order type 4 (140 cycles) > type 3 (100 cycles) > type 2 (50 cycles) > type 1 (45 cycles).

#### 4. Conclusions

The chemical preoxidation of leady oxide in positive paste of lead–acid batteries by ammonium presulfate can be carried out in paste mixing step or after curing of pasted positive electrodes (cathodes). The experimental results showed that the use of chemical oxidation in mixing step has more efficiency. The use of chemical formation technique for cathode of lead–acid batteries causes to increase the ratio of  $\beta$ -lead dioxide/ $\alpha$ -lead dioxide, capacity, energy density, power density and cycle-life of batteries. The use of chemical forming in lead–acid batteries can also be accepted from economical point of view. The practical characteristics of the proposed battery such as low weight, high capacity, high energy density and high power density (Table 3) have been significantly improved over traditional lead–acid batteries [27,28]. However, like other reported bipolar lead–acid batteries [29–32], the proposed battery more or less suffers from relatively complicated assembling as well as limited capacity.

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