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The effect of using nanostructures of synthesized lead oxide by mechanical milling on lead-acid battery performance using Taguchi method

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In this research, the effect of anode surface electrode coating on acidic lead batteries was investigated using nano-structured lead oxide synthesized by mechanical milling process. Investigations indicates that according to the different conditions of synthesis by mechanical milling, morphology, structural porosity, particle size, and electromagnetic properties are changed. Therefore, in this research, the effect of different parameters of mechanical milling process, such as milling time and ball-to-powder ratio, were optimized to obtain longer drain times of battery. For this purpose, the battery plates were coated using different levels of lead oxide nanostructures and the time spent on discharge of the batteries was measured and the results were analyzed by statistical software. The results show that the coating of battery plates with lead oxide nanostructures will increase the battery discharge time. So that the battery discharge time built using an optimal sample is better than normal battery life. Due to the high volume of nanostructures produced in the mechanical milling method, as well as the simplicity and cost-effectiveness of this method, the results of the research justify its use for industrial and large-scale applications.

Keywords: Lead-acid battery; Lead oxide nanostructure; Ball milling process; Design of experiment, Taguchi method.

INTRODUCTION

Lead acid batteries with a long history of more than 150 years have played an important role in human development and industrial development [1]. The batteries have potential benefits [2], including low construction cost, good performance, recoverability [2-6], their safety and economic for high power and voltage [7], easy design and relatively good special energy [8], which this has led them to have the largest share of sales compared to other rechargeable batteries [9]. Industry growth, rising energy prices and environmental problems caused by fossil fuels in recent years have led to a lot of research into the dev and improvement of these batteries and its use in motor and hybrid vehicles. In addition, the use of these batteries for the storage of electric energy generated by renewable sources, such as geothermal energy, wind energy, solar energy, etc., has been developed [4], which is why improving their performance seems more necessary than before.

The high lead weight used in these batteries limits their use in electric and hybrid cars requiring lightweight batteries with high specific energy [2, 7]. In hybrid electric vehicles, the high-rate battery partial state of charge acts continuously. In this working style, the active material of battery can't be used sufficiently and the $PbSO_4$ release product can't effectively be recycled to its original form, resulting in a growing $PbSO^4$ nonreversible accumulation on negative plate surface. This weakens the charge acceptance and reduces battery life [3, 5-7]. These negative screen failures severely limit the more sophisticated use of lead acid batteries for use in electrical vehicles [1].

Most commonly encountered with lead acid batteries are strongly dependent on negative electrodes [3]. The sulphating, the formation of almost insoluble lead sulfate crystals, is the most common inherent phenomenon associated with aging of lead acid batteries. During recharging, these crystals are restored to a low degree, which negatively affects the efficiency and longevity of the cell [3]. Due to the surface-to-high volume ratio and characteristics of very good electrical capacity of carbon material [5], studies show that the use of carbon materials such as carbon black, carbon nano-tubes, activated carbon, graphite [5, 10] and carbon nano-particles [10] on negative plates of lead acid batteries can improve battery life. Of course, the addition of carbon materials to lead acid batteries reduces the capacity of the battery, and the sedimentation phenomenon can dramatically reduce carbon offsets, which is another challenge [1].

Another way to prevent and reduce of sulphating is to use nano-structured materials on negative electrode, which the results of the research show it

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will improve the performance of the electrode [3]. In recent years nano-structured materials have been considered because these materials are different form polycrystalline materials due to the size of their crystals. The results show that nano-crystals have remarkable electrochemical performance, high specific capacity and good cyclic behavior [11]. By making active materials in the nanostructure, the surface-to-volume ratio increases and in turn increases the capacity and stability of the batteries [10]. Following this method, Heng et al. used nano-lead and nano-carbon to make negative plates, and they were able to achieve more capacity and performance than conventional batteries [2]. Ghasemi and colleagues synthesized nano-particles of lead dioxide by sono-chemical electro-deposition method and used them in cathode of lead acid batteries, and they found more discharge of battery capacity [12]. Alsandra et al. using electro-deposition method in the form of polycarbonate synthesized the nanostructure of lead and lead dioxide. Their results indicate that the use of these nanostructures in the anode and cathode of acidic lead batteries, improve drain (discharge) capacity and battery life considerably [2].

In industrial production of lead acid batteries, lead oxide is used as the primary active material both in the cathode and anodes of the batteries [8]. The use of lead oxide in the manufacture of lead acid batteries effectively reduces baking time and process cost [11]. Karami and colleagues to improve the discharging capacity and life time of lead acid batteries synthesized and studied the lead oxide nanostructures by various methods of sono-chemical and pyrolysis of sol-gel [8, 13, 14]. Their results suggest that using these nanostructures on positive and negative plates will improve battery capacity, discharge capacity, and battery life. Due to the high cost of synthesizing nano-particles, the development and improvement of inexpensive methods with the ability to produce massive amounts of nano-particles is most necessary. As an alternative, mechanical milling is a promising method for the preparation of metal nano-particles, including lead oxide [15], which so far, it has not been used to synthesize this material. Unlike other methods, this method does not require organic solvents and expensive and advanced devices, and in comparison with these methods, there is no need for thermal decomposition. In our previous work, nano-structured lead oxide was synthesized by mechanical milling [15]. Research shows that the mechanical milling process not only changes the particles size and their morphology, but also increasing the porosity of the powder will change the electromagnetic properties as well as the hardness of the powder [15].

According to the preliminary studies and previous research results, the speed and time of the mechanical milling process have the greatest effect on the morphology and size of the powder structure and, hence, on the duration of battery discharge [15]. Therefore, in this study, the effect of nano-structured lead oxide was synthesized and the parameters mentioned in the negative plates on the battery discharge time were investigated.

EXPERIMENTAL

Electrode preparation

The materials used in the experiments and their manufacturing company are listed in Table (1). All materials were used without purification. The laboratory environment was always between 23 to 28°C. The raw materials were weighed in a clean, non-contaminated environment with a digital scale of 0.001 g.

Table 1. Materials used to coat (cover) the battery plates.

Row	Composition	Wt%	The manufacturer
1	Lead oxide	99.27	Merck
2	Carbon black	0.15	Merck
3	CMC	0.1	Merck
4	Humic acid	0.1	Merck
5	1.2 Acid	0.1	Merck
6	Barium sulfate	0.2	Merck
7	Polyacrylic fiber	0.08	Merck

In order to coat the battery plates, firstly, the materials mentioned in Table 1 are combined after each weighing and using the magnet, the produced mixture is stirred for 15 minutes at a speed of 200 rpm. Then 100 cc sulfuric acid 50% is slowly added to the mixture and stirring is continued for another 15 minutes. Considering the increase in the temperature of the mixture due to the exothermic chemical reactions, due to the low melting point of lead and the possibility of agglomeration of particles; using a water bath, the temperature of the mixture is always maintained at about 45 °C. Then, the purchased raw plates of the battery are immersed in a paste mixture such as obtained, and it takes 1 hour to coat (cover) the plates by using lead oxide powders. At the end, the plates are dried using an oven and a temperature of 80 °C for 12 hours. This process is repeated for each of the nanostructures, so that at the end of the 8 samples of the coated plates of the 8 samples of nano-structured lead oxide synthesized in the previous step and 1 sample coated plate is obtained with the purchased raw powder of lead oxide.

Taguchi design of experiment

In this research, Taguchi design of experiment (DOE) and Pareto Analysis of Variance (ANOVA) have been used as tools for understanding the effects and the contribution of selected synthesis parameters. The Taguchi DOE optimizes a given process by identifying the most important process parameter affecting a target property of a process. The Taguchi DOE belongs to the same class with the full factorial design. However, it requires far less experimental runs to optimize a given process. Hence, process cost and time are fully optimized [16].

In order to comprehend the role of synthesis parameters in the life time of battery samples, the L9 Taguchi orthogonal experimental method with two parameters and three levels as shown in Table 2 was used. The SEM images of nanostructures used to cover the battery plates are shown in Figure 1.

Build the battery and test its performance

The battery was made using the positive plate of commercial battery company (a product of Aranniru Company, Iran) and the negative raw plate after coating by the nanostructure, and was placed in acidic water purchased from Kimia Tehran Acid Company, Iran, and for 2 hours, using a transformer was placed in 12 V electricity. After charging different batteries, the voltage of each battery was measured by a digital voltmeter, which is about 3 volts. Generally, however, batteries manufactured from nano-structured coated plates show higher voltages compared to conventional batteries. In order to compare the amount of time required to discharge batteries to half the original capacity, the batteries are made using a 2.5-volt bulb in the circuit. The duration of the lamp staying until the battery voltage reaches half the initial value as a benchmark for comparing the battery discharge capacity and the effect of nanostructures on their performance was examined.

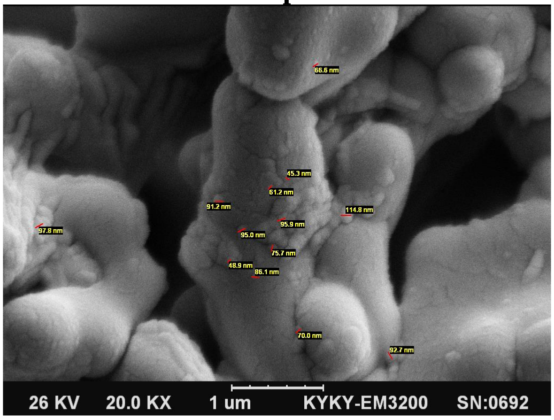
Table 2. Parameters and levels of Taguchi experimental method.

Sample	Time (hr)	Speed (rpm)	BPR	Size (nm)
0	0	0	0	1535.0
1	2	200	20	824.3
2	2	200	30	354.6
3	5	250	20	957.1
4	5	250	30	329.0
5	2	250	20	765.2
6	2	250	30	675.5
7	5	200	20	868.1
8	5	200	30	491.1

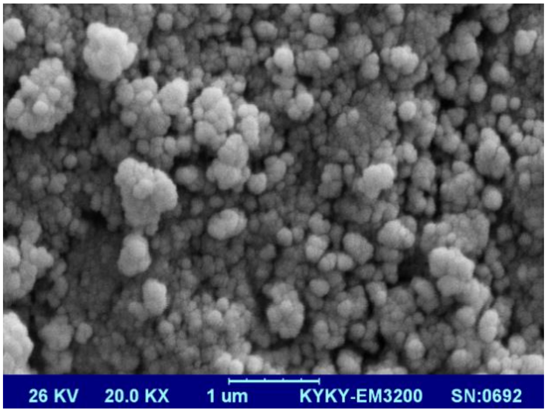
Table 3. The results of the discharge time, along with the specifications of each of the nanostructure of manufactured batteries based on it.

Sample	Time	Speed	Ratio	Size (nm)	Discharge Time (s)
0	0	0	0	1535.0	321
1	2	200	20	824.2	459
2	2	200	30	354.6	556
3	5	250	20	957.1	449
4	5	250	30	329.0	584
5	2	250	20	765.2	494
6	2	250	30	675.5	513
7	5	200	20	868.1	463
8	5	200	30	491.1	541

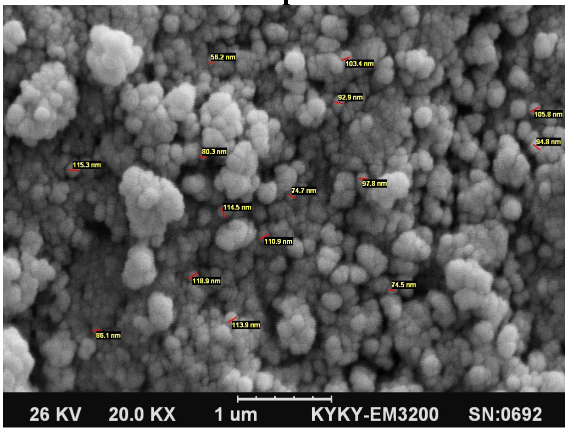
Sample 0



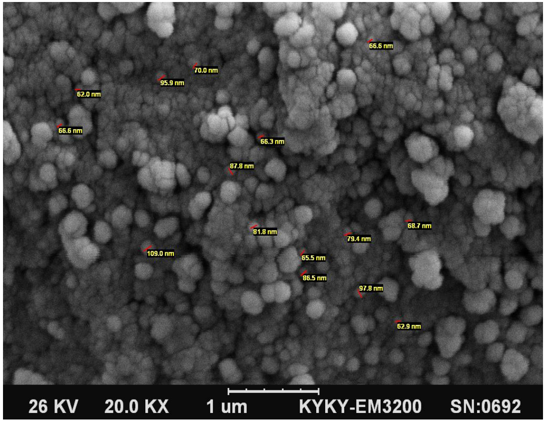
Sample 1



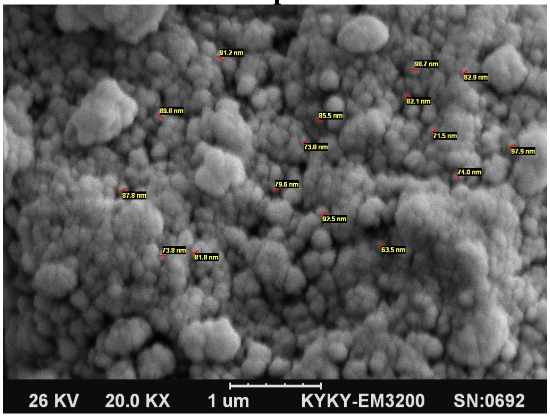
Sample 2



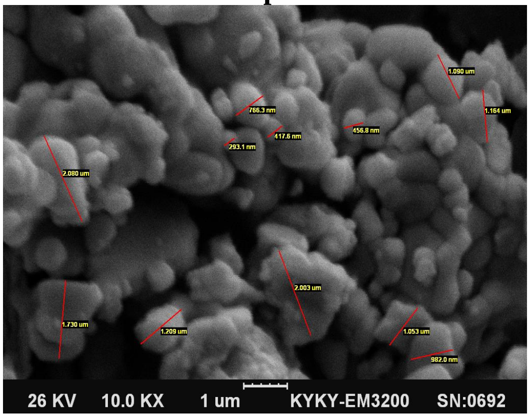
Sample 3



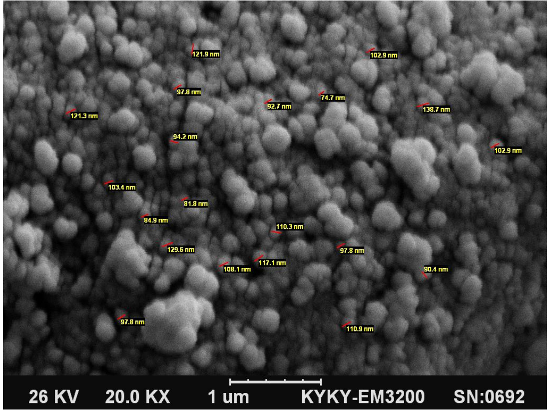
Sample 4



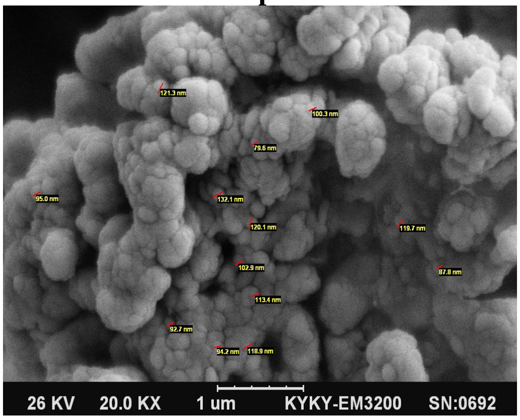
Sample 5



Sample 6



Sample 7



Sample 8

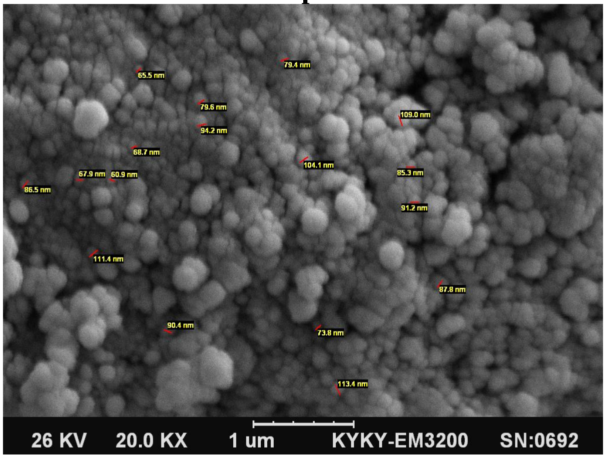


Fig. 1. SEM images of nanostructures used in Table 2.

RESULTS AND DISCUSSION

The specifications of nanostructures and the results of manufactured batteries discharge time with each of them are shown in Table 3.According to the SEM images of the raw sample and sample 3, the difference in size is not significant compared to the other samples, such as sample 4. However, just because of coating the surface of the battery plates using synthesized nano-powders has led to a relatively significant increase in the battery discharge time to half the original voltage. The reason for this phenomenon can be stated that due to the collision of the bullets with each other and the placement of powder particles between them, crystalline defects (including dislocations and atomic spaces) as well as the resulting porosity of the resulting powder increases severely leading increase in charge of the electrons in the plates, and thus the time for battery discharge increases. According to the results presented in Table 3, it is shown that the coating of battery plates by nanostructure increases the battery discharge time. So that the maximum discharge time for the optimal sample is sample number 4. The TEM image of the optimal sample is shown in Figure 2.

Figure 3 also shows the effect of nanostructure size on battery discharge time that is plotted by Matlab software. According to this figure, the discharge of the battery decreases with increasing nanostructure size. This is due to the specific morphology of the synthesized nanostructures. According to SEM images, with increasing powder particles, particles lose their regular geometric spherical shape, so that by increasing the size of the powder particles, the special volume of reduced particles is reduced due to electrical connections between particles, and this reduction in electrical connection can reduce battery discharge time [8].

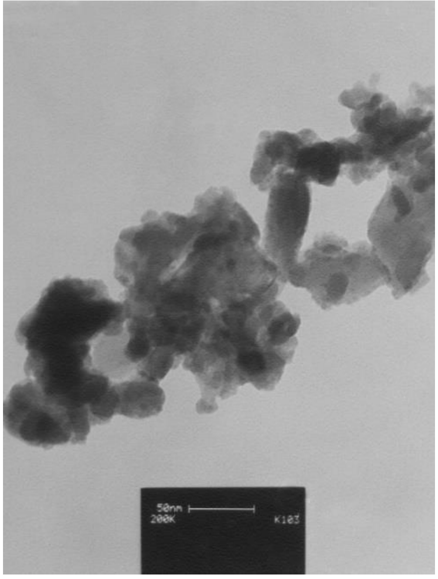


Fig. 2. TEM image of sample 4.

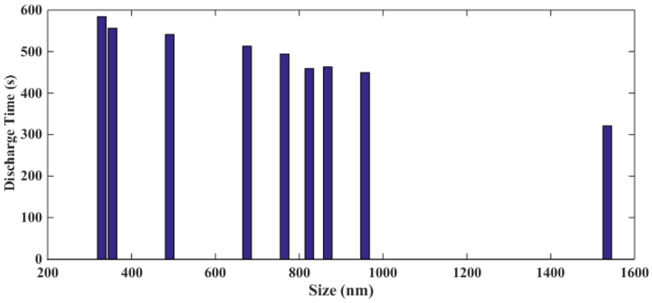


Fig. 3. The effect of powder size on battery discharge time

On the other hand, the nanostructure properties are influenced by the parameters affecting its synthesis conditions. For further evaluation, the effect of these parameters on the battery discharge time is shown in Figure 4.

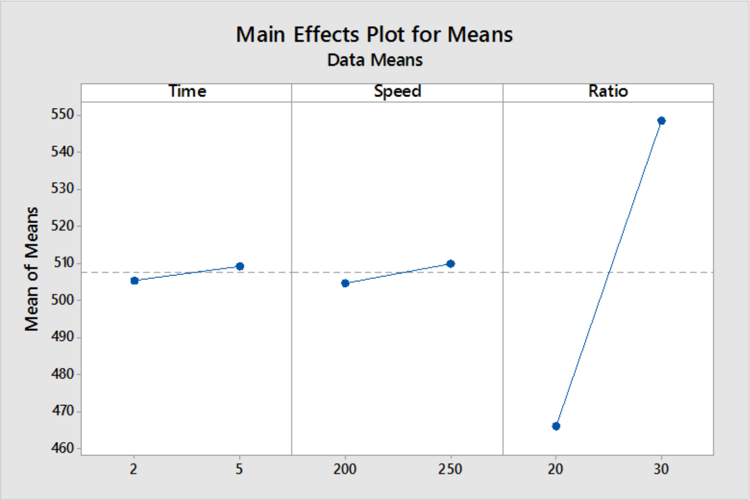


Fig. 4. Effect of milling time, milling speed and ball weight ratio on battery discharge time.

As shown in Figure 4, the increase of all three parameters of the time of the milling, the speed of the milling and the ball weight ratio to the powder (BPR) increases the battery discharge time. On the other hand, according to Figure 4, the BPR parameter has the most effect in increasing the battery discharge time. Increasing the BPR ratio, in addition to reducing the size of the nanostructure, increases the number of atomic spaces and the formation of porous structure, which, for the reasons stated above, increases the battery discharge time.

CONCLUSION

In this research, a simple and inexpensive method for the production and coating of a lead acid anode plate with the aid of a lead oxide nanostructure was presented. According to SEM images, by reducing the size of the powder particles, the spherical particles and the geometric shape are more regular, and they can be more effective in coating the battery plates. Reducing the size of the powder particles increases the special particle size and, as a result, increases the electrical connections between the particles leading increase in the battery discharge time. Due to the simplicity and cost-effectiveness of nano-powder synthesis and the effect of nano-powders on increasing the battery discharge time, the results of the study confirm the justification of powder synthesis in the proposed method in industrial and mass production applications for use in the battery industry.

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