

Synthesis and Characterization of Nano-Structured Lead and Lead Dioxide Electrodes for Advanced Lead-Acid Batteries- A Literature Survey

**A Project Report Submitted
As part of the requirements for the degree of**

MASTER OF SCIENCE

By

Hammad Ali

(Roll No. CY13M1013)

Under the supervision of

Dr. Surendra K. Martha



To the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY HYDERABAD
INDIA
MAY, 2015

Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of Dr. Surendra Kumar Martha

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Sonatha 06.05.2015
Signature of the Supervisor

Dr. SURENDRA K. MARTHA
Assistant Professor
Department of Chemistry
Indian Institute of Technology Hyderabad


Hamad
(Signature)

Hamad Ali
(- Student Name -)

CY13M1006
(Roll No)

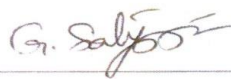
Approval Sheet

This thesis entitled "Synthesis and Characterization of Nano-Structured Lead and Lead Dioxide Electrodes for Advanced Lead-Acid Batteries- A Literature Survey" by Mr. Hammad Ali is approved for the degree of Master of Science from IIT Hyderabad.


D. S. Sharada 6/5/15

-Name and affiliation-


Examiner



-Name and affiliation-

Examiner

Dr. G. Satyanarayana
Associate Professor
Department of Chemistry
Indian Institute of Technology Hyderabad
Ordnance Factory Estate, Yeddumailaram


Surendra Kumar Martha
-Name and affiliation-

DR. SURENDRA K. MARTHA

Assistant Professor
Department of Chemistry
Indian Institute of Technology Hyderabad

6/5/2015

-Name and affiliation-

Co-Adviser

-Name and affiliation-

Chairman

Dedicated

...to my loving Parents

ACKNOWLEDGEMENTS

In the process of completion of my research work some people have supported me and guided me in the right direction. It is a great pleasure to acknowledge the assistance of those people who have taken an interest in my work and helped me during the project. Although I can never repay any one of them for the help and guidance that I received, these few words of gratitude which I have written today are a heartfelt tribute to my close associates for instilling in me confidence which made me able enough to submit my thesis.

I am heartily thankful to my supervisor Dr. Surendra Kumar Martha for his invaluable suggestions; timely advice, encouragement, and completely writing this thesis. My deepest regards for him for building up my confidence.

I am also thankful to Mr. V. Naresh and Mr. S. Krishna Kumar for their support, help and advices during my research and for their assistance in the laboratory experiments.

It gives me immense pleasure in acknowledging with sincere gratitude, the enthusiastic co-operation received from all my colleagues especially Sushant, Sourav, Kailash, Kuntul, Argha, Subhajit, Arif, Amreen, Dhvani, Topi, Kulsum, Puja and all other friends.

All that I have achieved so far in life would not have been possible without the guidance and support of my family members. I am indebted to my Parents (Mr. Sanaullah Khan and Mrs. Farhana Begum) and I offer my sincere regards and gratitude to them for being with me at all stages of my life. My parents have always given me the freedom to choose my own goals and have great faith in me. I love my Parents very much. I always try to make them happy and hope that I can live up to their expectations. I would like to thank to all my relatives who supported me a lot.

I am also very thankful to elder brother “Urooj Ahmed Khan”, without his support I cannot do anything in my whole life plume sincere thanks.

I am also very thankful to my grand-mother “Shamima Begum”, without her support I cannot do anything in my whole life plume sincere thanks.

Last, but not in that order, I thank The Lord Almighty Allah for giving me the strength, will, and wisdom to carry out the project work successfully and for everything You had given to me. . .

Abstract

Practical lead-acid batteries began with the research and inventions of Raymond Gaston Planté in France as early as 1859, and, even today, lead-acid battery remains the most successful battery system ever developed. Although lead-acid battery designs have been optimized in the past in several different ways, there are still certain new challenges facing lead-acid battery designers, such as grid corrosion at the positive electrode, water loss, self-discharge at the negative plate, sulfation at both the electrodes, poor charge acceptance of positive electrode, larger curing time and more significantly low energy density because of high atomic weight of lead. Novel material synthesis and electrode fabrication approach can play an important role for optimum performance of lead-acid batteries.

Nanoscale materials have attracted attention in recent times because of

1. Fast electron and ion transport compared to micron-sized particles, can increase the rate of charging and discharging. That means nanoparticles will enable us high C rate performance.
2. The volume changes caused during charge-discharge will be better accommodated by nano-materials compared to bulk materials due to faster stress relaxation and that prolongs the battery cycle life.
3. Enhancement of electron transport within the particle.
4. Increase in specific surface area of the active material greatly increases the mass specific amount of active material in contact with the electrolyte. This results in a higher flux of ion transport across the electrode/electrolyte interface and as a result, less impedance in the charge transfer reactions. Hence, the high surface area lead to enhanced electrochemical activity of the nanostructured Pb and PbO₂ electrode.
5. Besides nanomaterials can have ease of curing and electrochemical formation processes, good amount of active material utilization, hence good capacity (less sulfation) and cycle life of lead-acid batteries.
6. High surface area allows to fabricate batteries with small size and light weight. Hence high energy density batteries could be achieved.

This thesis summarizes literature survey of lead-acid batteries followed by new syntheses of approaches for syntheses of nano-structured lead and lead dioxide electrodes for advanced lead-acid batteries.

Contents

1.1.Introduction to lead-acid Battery

1.1a Overview of Lead-Acid Battery

1.1b. How Do Lead-Acid Batteries Work?

1.1c. Types of Lead-Acid Batteries.

1.1d. Preparation of Plates and Battery Assembly

1.1e. Formation and Testing of Lead-Acid Batteries

2.1. Current Research Work

2.1a. Selected-Control Synthesis of Nanostructured Lead Dioxide (PbO₂) Cathodes for Lead Acid Battery

2.1b. Synthesis of Nano Lead for Anodes of Lead-Acid Batteries

1.1. Introduction to lead-acid Battery

The project report provides basic information to lead-acid batteries containing background information, working principles, technologies, followed by literature survey of nanostructured electrode materials for advanced lead-acid batteries.

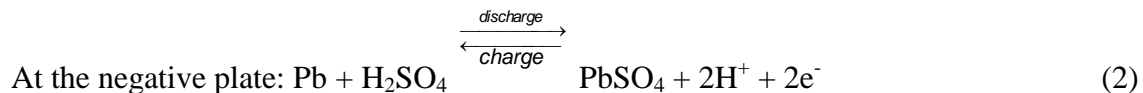
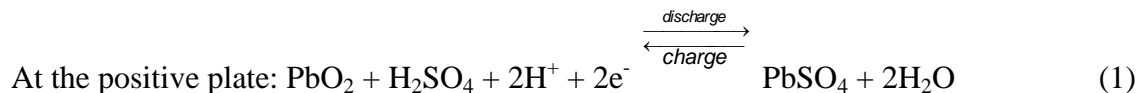
1.1a Overview of Lead-Acid Battery

One of the oldest types of recyclable battery is the lead-acid battery. The lead-acid battery was first invented by the French physicist Raymond Gaston Planté in the year 1859 [1]. The lead-acid battery was the first battery that could be recharged by passing a reverse current through it. Planté's first model consisted of two lead sheets separated by rubber strips and rolled into a spiral type. These batteries were used to power the lights in train carriages while stopped at a station [1].

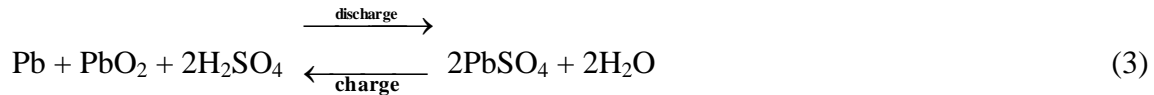
1.1b. How Do Lead-Acid Batteries Work?

Lead Acid batteries have changed little since the 1860's although improvements in materials and manufacturing methods continue to bring improvements in energy density, cycle life and reliability [2-6]. All lead acid batteries consist of flat lead plates immersed in a pool of electrolyte separated by a piece of separator which could be polyethylene, polypropylene or absorptive glass mat (AGM). Each cell is made up of a set of PbO_2 positive electrodes and Pb negative plates immersed in a dilute sulfuric acid (Generally 5 M) solution known as electrolyte, and each cell has a voltage of around 2.1 volts when fully charged. The six cells are connected together to produce a fully charged battery of about 12.6 volts. Regular water addition is required for most types of lead acid batteries although low-maintenance types come with excess electrolyte calculated to compensate for water loss during a normal lifetime [2-6].

The electrochemical reactions taking place at the positive and negative plates of a lead-acid cell are as follows.



Accordingly, the net charge-discharge processes in a lead-acid cell are represented by,

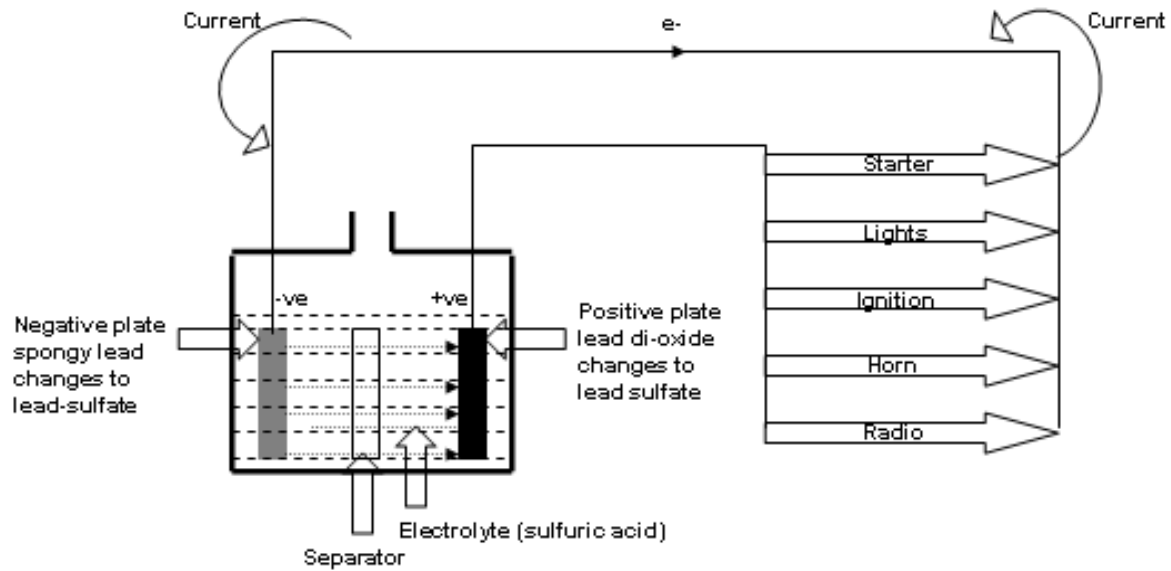


The net cell voltage is approximately 2.06 V which depends on acid concentration, [3-5] is the difference between the cathode voltage 1.7 V and anode voltage 0.36 V. In both the charge and discharge processes, solid conductors of electrons, namely, semiconducting lead dioxide (PbO₂) in the positive plate and metallic lead (Pb) in the negative plate reacts with sulfuric acid to form a non-conducting solid product of lead sulfate (PbSO₄). Both the discharge reactions are accompanied by an increase in volume of the solid phase [3-5, 7].

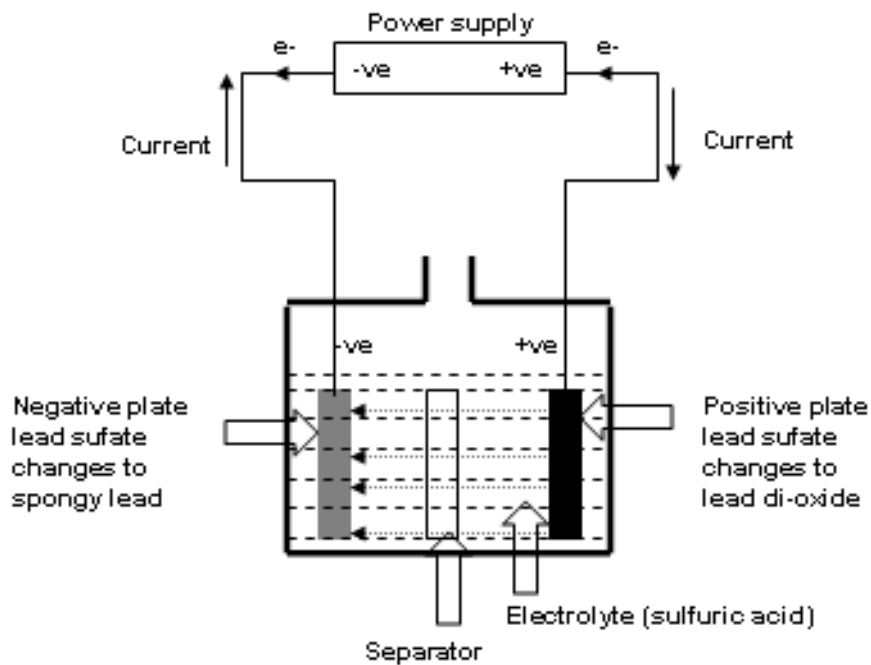
Electrochemical discharge and charge operations for a lead-acid battery are shown in Fig.1. During the discharge of a lead-acid cell, electrons flow from its negative plate to the positive plate as shown in Fig.1 (a). When the electrons flow from the negative plate to positive plate, they lose their energy. The loss in energy per unit charge is the voltage delivered by the cell. By convention, current flows in the direction opposite to the flow of electrons, and the product of voltage to the current is the power delivered by the cell. An opposite situation occurs during the charging process for the lead-acid cell as shown in Fig. 1 (b), where the power is delivered to the cell from an external d.c. source [3-5].

As the cell is discharged, sulfuric acid is consumed and water is formed. Consequently, both the electrolyte composition and density vary from about 40% by weight of H₂SO₄ (1.3 gm/cc) at full charge with an associated open-circuit voltage of 2.15V at 25°C to about 16% by weight of H₂SO₄ (1.10 gm/cc) when fully discharged with an open-circuit voltage of 1.98 V [3-5, 7].

There are secondary reactions occur at the electrode potential within the cell voltage. As the decomposition potential of water is 1.23 V, secondary reactions like hydrogen evolution and oxygen evolution always takes place within the cell according to:



(a) Battery discharging process



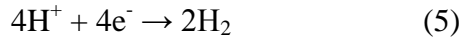
(b) Battery charging process

Fig.1.Electrochemical (a) discharge and (b) charge operations of a lead-acid battery.

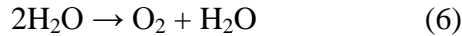
Oxygen evolution at the positive electrode:



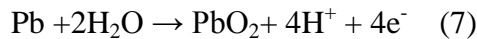
Hydrogen evolution at the negative electrode:



Overall water decomposition according to



At the potential of positive electrode lead is oxidized to PbO_2 and forms a protective layer according to



1.1c. Types of Lead-Acid Batteries

There are three types of lead-acid batteries in common use: (a) batteries with flooded or excess electrolyte, (b) low-maintenance lead-acid batteries with a large excess of electrolyte, and (c) batteries with immobilized electrolyte and a pressure-sensitive valve usually referred to as valve-regulated lead-acid (VRLA) batteries.

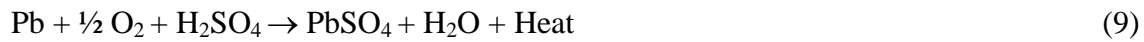
In the conventional ‘flooded’ lead-acid batteries, the electrolyte is filled to a level above the top of the plates and bus bars [3-7]. This has the disadvantage that the cells have to be vented to release the gases liberated during charging, namely oxygen at the positive plate and hydrogen at the negative. The consequence of this venting is that the batteries may be used only in the upright position, otherwise leakage of sulfuric acid takes place. Also, the released gases carry a very fine mist of sulfuric acid, which is highly corrosive. The flooded-electrolyte lead-acid battery requires checking of specific gravity of the electrolyte, periodic addition of water to maintain electrolyte above the top of the plates, and recharge soon after the battery discharge to mitigate hard sulfation that causes loss in battery capacity. The emission of acid fumes causes corrosion of metallic parts in the vicinity of the battery. The seepage of acid on the top cover of the battery leads to a leakage current resulting in increased self-discharge and ground-shunt hazards [8].

To overcome the aforesaid problems, VRLA batteries based on oxygen-recombination cycle have emerged [3-5]. These batteries offer the freedom of battery placement, cyclability without the addition of water or checking the electrolyte specific gravity, increased safety, and superior performance [3-5]. In the oxygen recombination cycle [3-5, 9-10], oxygen, which generates at the positive plate during charging, combines at the negative plate as shown below.

At the positive plate:



At the negative plate:



This shifts the potential of the negative plate to a more positive value and thus decreases the rate of hydrogen evolution to a much lower level, i.e. much less than the flooded design of the battery. A one-way pressure-relief valve is provided to ensure that even the small amounts of hydrogen produced do not generate a high pressure within the battery and hence the term ‘valve regulated’. Since the negative plate is simultaneously on charge, the PbSO_4 produced is immediately reduced electrochemically to lead through reaction (10), and the chemical balance of the cell is restored [3-5,7, 11-12].

In VRLA cells the electrolyte is completely immobilized in the separator and the active materials, and sufficient void space is left for oxygen to diffuse through the separator to the negative plate. They are more beneficial compare to flooded electrolyte cells as they can be used in orientation, no acid spillage, maintenance may not be required. There are two methods of immobilizing the electrolyte between the plates in VRLA cells, namely (a) by a gel, and (b) by absorbent-glass matrix. Lead-acid batteries with gelled electrolyte are called gelled-electrolyte VRLA batteries, while the batteries with electrolyte soaked in absorbent-glass matrix (AGM) are referred to as AGM-VRLA batteries [11-12].

In the gelled-electrolyte VRLA battery sulfuric acid is mixed with very finely divided, high surface-area silica (fumed silica). This forms a viscous solution, which develops in to a gel on

standing. Oxygen transfer occurs through the fissures in the gel that arise during the early stages of battery life as a result of partial drying out and shrinkage. [13-14].

AGM forms the separator in the AGM-VRLA battery. The separator is usually saturated with acid to about 90-95% of its absorption capacity. The remaining void volume is available for the passage of oxygen to the negative plate. The AGM separators must be in close contact with the plates to minimize internal resistance by allowing fast transfer of ions during both charge and discharge processes. [3-7, 15-17]

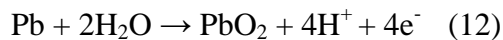
Even though VRLA designs are optimized in all directions still these batteries suffer from the following unwanted side reactions.

(a) Hydrogen evolution at the negative electrode and grid corrosion at the positive electrode together cause **water loss** [3-5].

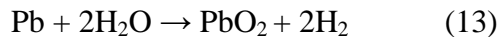
(i) Hydrogen evolution according to



(ii) Grid corrosion according to



In overall:

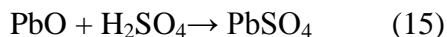


The water loss must be kept low as low as possible since it gradually increases the concentration of electrolyte and decrease its volume and thus influences the performance of the battery. Water loss cannot be compensated by adding of water. Water is the main cause for slight decrease of capacity that is observed from the very beginning in cycle test of VRLA batteries to keep grid corrosion and hydrogen evolution as low as possible.

(b) **Self-discharge** at the negative electrode according to

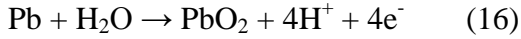


This is followed by reaction with H_2SO_4 forms lead sulfate which is the discharged product [18].



(c) **Grid Corrosion at the positive plate:**

Lead grids are used as current collectors for the positive electrode. Above the potential of positive electrode Pb^{4+} is stable and forms PbO_2 . Hence grid materials (Pb) at the positive electrode changed to PbO_2 according to



But Pb and PbO_2 cannot exist together because of thermodynamic reasons. So there exists an intermediate layer called PbO layer always exist between the grid and active material. This PbO layer is called corrosion layer as shown in Fig 2.

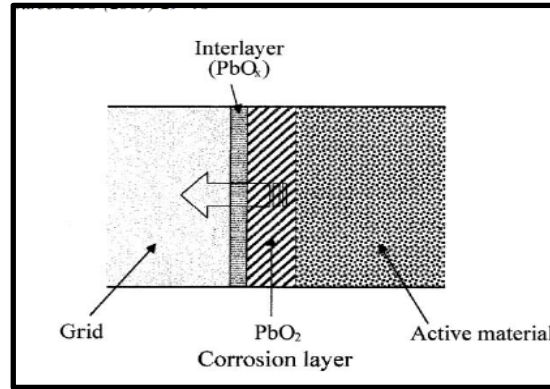
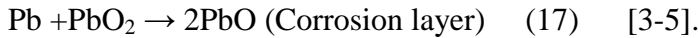


Fig.2. PbO corrosion layer at the positive electrode in a lead-acid battery.

1.1d. Preparation of Plates and Battery Assembly

Both positive and negative plates for the batteries are generally prepared using Pb–Ca–Sn–Al alloy grids. The batteries are assembled in ABS containers using 4.5 M H_2SO_4 as electrolyte. In brief, the positive plate pastes are prepared by mixing leady oxide (~85 wt. %), a binder such as sodium carboxy methyl cellulose, expanders such as Dynel fibres and aq. H_2SO_4 with de-ionized water. Similarly the negative plate paste is prepared by mixing leady oxide (85 wt. %), lignin, barium sulfate, Dynel fibres, carbon black, and aq. H_2SO_4 with de-ionized water. The paste densities for positive and negative plates are 4 and 4.4 gcm^{-3} , respectively. After pasting the active materials onto the grids, the plates are subjected to hydrothermal curing at ~ 95% humidity at 65°C for about 24 h. Subsequently, the plates are dried in the curing chamber at 65°C

for about 12 h. The lugs of the plates are cleaned by a buffing machine in order to prepare the plates for group-burning operation. Generally positive limited cells are assembled in VRLA designs [3-5, 7, 11-12, 15, 18-22].

1.1e. Formation and Testing of Lead-Acid Batteries

All the battery types are generally formed by charging them galvanostatically at C/20 or C/40 rate till 2.6 V/ cell followed by their discharge till 1.75 V/Cell. The charge/discharge is continued till the battery capacity is stabilized [18-22]. Subsequent to their formation charge-discharge, the batteries can be charged and discharged galvanostatically at various C rates and can be cycled in order to obtain cycle life. Impedance studies can be carryout in order to understand their resistances. The resistances measured from impedance studies can provide state of health of the battery. Cyclic voltammetry studies are generally conducted with respect to a reference electrode in order to understand the kinetics of electrode processes [18-22].

In summary, even though lead-acid battery is an oldest type battery, the technology development of lead-acid batteries has been continuing over the years to have best performance and cycle life. From the earliest open cell batteries, different advanced battery configurations such as VRLA designs are now available, which have been adopted in a wide range of applications. Although lead-acid battery designs have been optimized in the past in several different ways, there are still certain new challenges facing lead-acid battery designers, such as grid corrosion at the positive electrode, water loss, self-discharge at the negative plate, sulfation at both the electrodes, poor charge acceptance of positive electrode, larger curing time and more significantly low energy density because of high atomic weight of lead.

2.1. Current Research Work

This thesis summarizes a literature survey for a new synthesis of approach of nano-structured lead and lead dioxide electrodes for advanced lead-acid batteries” described below.

Nanoscale materials have attracted attention in recent times because of

1. Fast electron and ion transport compared to micron-sized particles, can increase the rate of charging and discharging [23]. That means nanoparticles will enable us high C rate performance.

2. The volume changes caused during charge-discharge will be better accommodated by nano-materials compared to bulk materials due to faster stress relaxation and that prolongs the battery cycle life [23].
3. Enhancement of electron transport within the particle [23].
4. Increase in specific surface area of the active material greatly increases the mass specific amount of active material in contact with the electrolyte. This results in a higher flux of ion transport across the electrode/electrolyte interface and as a result, less impedance in the charge transfers reaction. Hence the high surface area lead to enhanced electrochemical activity of the nanostructured Pb and PbO₂ electrode [7,11-12, 23].
5. Besides nanomaterials can have ease of curing and electrochemical formation processes, good amount of active material utilization, hence good capacity (less sulfation) and cycle life [7,11-12, 22].
6. High surface area allows to fabricate batteries with small size and light weight. Hence high energy density could be achieved [23].

2.1a. Selected-Control Synthesis of Nanostructured Lead Dioxide (PbO₂) Cathodes for Lead Acid Battery

The main drawbacks of the PbO₂ electrode in lead-acid cells are the low active material utilization, long-time of curing and electrochemical formation processes. Various attempts have been made to improve the utilization of PAM, among them the thin metal film technology was more successful [7, 11, 12, 22]. Also, several electrochemical methods have been developed recently to obtain PbO₂ with high activity [7, 11-12,22].

During the past last ten years, low dimensional nanostructured materials such as nano-sheets, nanotubes, and nano-rods have made a worldwide interest and because of in comparison of micro to nano fields they have changed properties in mechanics, optics and electromagnetism branches and vast uses in to making goods particularly like electrical contrivance etc [11]. Therefore, controllable formation or production or in situ of nano containing properties material with needed good structurally intended manner, shape, and sizes is extremely essential for both the materials science and technology [11,24].

In this work, we propose synthesis of nano-sized lead oxides (black-brown PbO_2) with rod like morphologies [25].

In a typical synthesis, cetyltrimethylammonium bromide (CTAB; 3 mmol) was added to 0.015 M $\text{Pb}(\text{OH})_3^-$ (70 mL) solution, which was formed by adjusting the pH of a lead nitrate solution with 1 M NaOH solution to pH 14. After the resulting solution was stirred for 30 min at 50 °C, which ensured the complete dissolution of CTAB, aqueous 1.5 M NaClO solution (1 mL) was added under constant stirring to the resulting clear solution to form a homogeneous solution. After the solution was maintained at 85 °C for 3 h, the resulting black-brown products (PbO_2 nano-rods) were collected, washed several times using absolute ethanol and distilled water, centrifuged, and dried under vacuum at room temperature for 5 h. For the preparation of the red Pb_3O_4 nanorods, the above homogeneous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 140 °C for 5 h [25]. It should be noted that both PbO_2 and Pb_3O_4 are the active materials for lead-acid batteries. The reaction scheme is presented in Scheme 1.

X-ray powder diffraction (XRD) patterns of the samples were collected by a Panalytical X-ray diffractometer with $\text{Cu K}\alpha$ radiation 1.54Å. The XRD patterns of the newly prepared PbO_2 nano-rods are shown in Figure 3. All the diffraction peaks in Figure 1 can be perfectly indexed to the tetragonal PbO_2 [space group: $4/mnm$] with lattice constants $a = 4.9525 \text{ \AA}$ and $c = 3.3863 \text{ \AA}$ (JCPDS 25-447), these results are consistent with those of PbO_2 bulk crystals. The XRD patterns indicate that the nanorods obtained via our current synthetic methods consist of pure phases.

Scheme 1

Preparation scheme of lead-dioxide (PbO₂) nano-rods

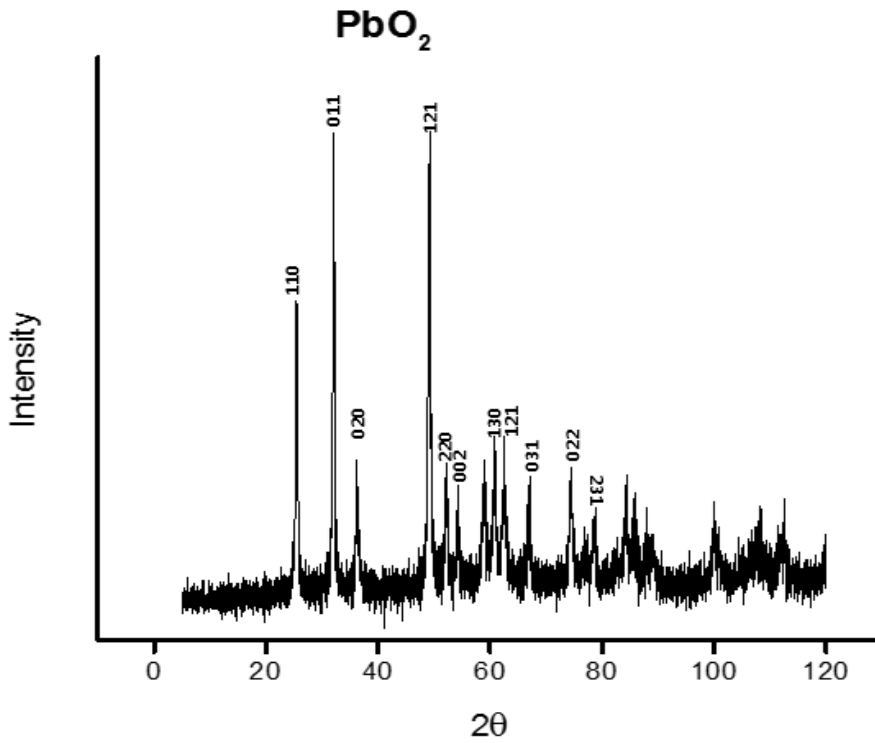
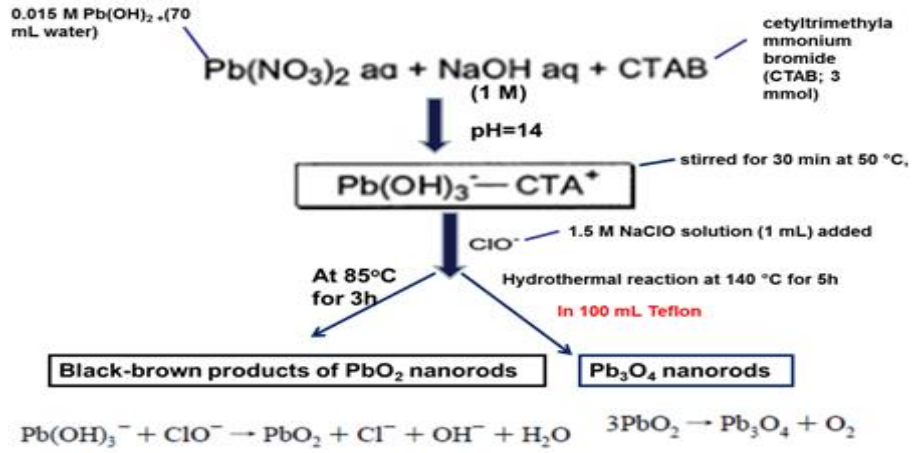


Fig.:3: XRD pattern for as synthesized PbO₂.

The morphology and microstructure of the prepared PbO_2 were further investigated with scanning electron microscopy (SEM). The SEM images in Fig 4a-c. From the SEM images it is very clear that as synthesized PbO_2 have rod like morphology having diameter about 50-100 nm and length about few microns.

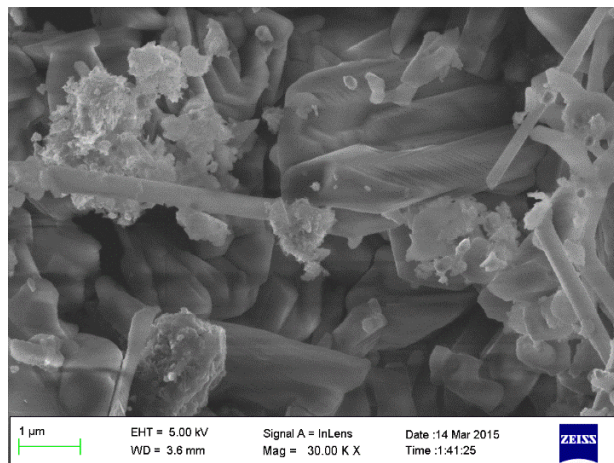
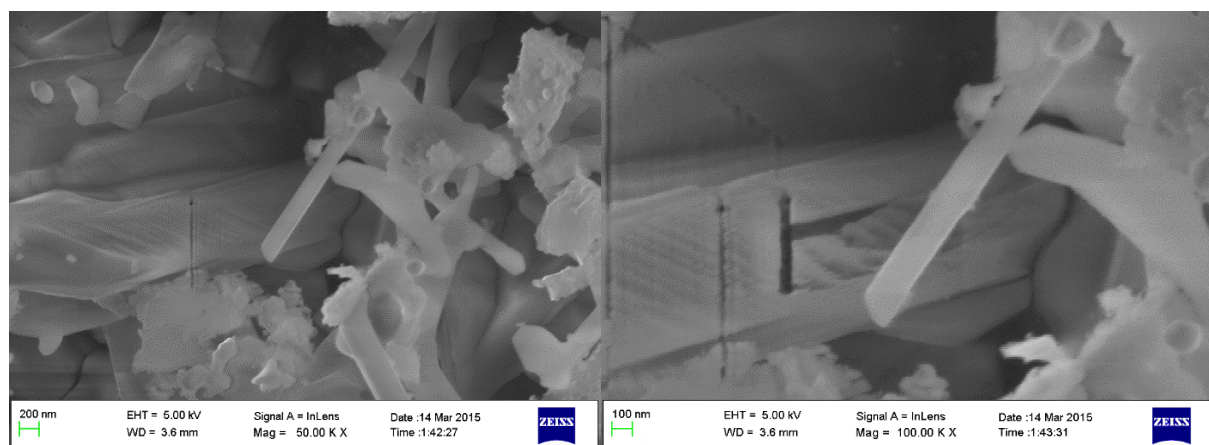


Fig 4(a)



(b)

(c)

Fig 4a-c- SEM images of PbO_2 Nano rods of various magnifications showing size and morphology.

2.1b. Synthesis of Nano Lead for Anodes of Lead-Acid Batteries

Metal nanoparticles can be synthesized using different physical and chemical methods, such as the metal evaporation, [26] the electrodeposition from solution, [27] the reduction of metal salts, [28] and the temperature or sonochemical decomposition of organometallic compounds [29].

Here we suggest synthesis of lead nanoparticles were synthesized by the thermal decomposition of lead stearate in octanol. The lead particle size can be controlled by both varying the concentration of lead stearate in octanol and changing the thermolysis time. Lead nanoparticles have an organic coat composed of decomposition products of lead stearate. This coat prevents the particles from oxidation in air and favours their dissolution in organic solvents. Here we use reactants like: $\text{Pb}(\text{NO}_3)_2$, sodium stearate, octanol, toluene, and isopropanol. Synthesis of Pb Stearate was performed by the precipitation from aqueous solutions [30]. A solution (20 mL) containing $\text{Pb}(\text{NO}_3)_2$ (4.278 g) was gradually poured with vigorous stirring to a solution (200 mL) containing Na Stearate (7.917 g) at $\sim 80^\circ\text{C}$. The precipitate of Pb Stearate was filtered off, washed with water, and dried in air at room temperature. Lead particles were separated from the solution using a centrifuge at 14000 rpm. SEM image of synthesized Pb nano particles presented in Fig. 5. The size of nano particles are in the range of 10s of nm having spherical morphology.

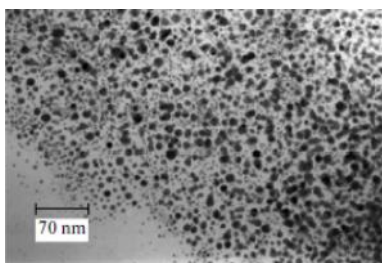


Fig.5. SEM image of synthesized nano lead particles.

In summary, the thesis summarizes brief review of lead-acid battery followed by methodologies to synthesize nano-structured lead and lead-dioxides by various synthetic routes. We expect the nano size particles could have ease of curing, and formation processes and good electrochemical performance. It is believed that the study will open up new possibility for lead-acid battery development.

References

1. G. Planté, C. R. Acad. Sci. Paris, **50**, 1860, 640.
2. P.T. Moseley and D. A. J. Rand, *J. Power Sources*, **78**, 2004, 2.
3. D. Berndt, *J. Power Source* **95**, 2001, 2.
4. D. Berndt, *J. Power Sources* **100**, 2001, 29.
5. D. Berndt, *J. Power Sources* **100**, 2001, 79.
6. M. Shimpo, H. Nakashima, S. Sasabe, Y. Kasia, *Yuasa Jiho*, **68**, 1990, 46.
7. P. Ruetschi, *J. Power Sources*, **127**, 2004, 33.
8. J. Leadbetter, L.G. Swan, *J. Power Sources*, **216**, 2012, 376-386.
9. Hariprakash B, Mane A U, Martha S K, Gaffoor S A, Shivashankar S A and Shukla A K
Electrochem.Solid-State Lett. **7A**, 2004, 66.
10. S.S Misra, T.M. Noveske, S.L. Mraz, A.j Williamson, *J. Power Source* **95**, 2001, 153.
11. D. Pavlov, *Lead-Acid Batteries: Science and Technology*, Elsevier, 2011.
12. R.D. Prengamam, *J. Power Source* **95**, 2001, 224.
13. P. Haring, H.Giess, *J. Power Source* **95**, 2001,153
14. E Meissener, *J. Power Source* **78**, 1999, 99-114.
15. D. Pavlov, P. Nikolov, T. Rogachev, *J. Power Sources* **196**, 2011, 5155-5167.
16. K. Takahashi, T. Sagawa, M. Tsubota, *GS News* **44**, 1985, 8.
17. L. Apateanu, A.F. Hollenkamp, M.J. Koop, *J. Power Sources* **46**, 1993, 239.
18. B. Hariprakash, S. K. Martha, A. Jaikumar, and A. K. Shukla, *J. Power Sources*,**137**,
2004,128-133.
19. S. K. Martha, B. Hariprakash, S. A. Gaffoor and A. K. Shukla, *J. Appl. Electrochem.*, **36**,
2006, 711.
20. S. K. Martha, B. Hariprakash, S. A. Gaffoor, D. C. Trivedi and A. K. Shukla, *J. Chem.
Sci.*, **118**, 2006, 93.
21. S. K. Martha, B. Hariprakash, S. A. Gaffoor, D.C. Trivedi, and A. K. Shukla,
Electrochem. Solid-State Lett., 8, 2005, A353.
22. S. K. Martha, B. Hariprakash, S. A. Gaffoor, S. Ambalavanan and A. K. Shukla, *J. Power
Sources*, **144**, 2005, 560.
23. S. K. Martha, B. Markovsky, J. Grinblat, Y. Gofer, O. Haik, E. Zinigrad, D. Aurbach, T.
Drezen, D. Wang, G. Denghenghi, I. Exnar, *J. Electrochem. Soc.*, **156**, 2009, A541.

24. Valve-Regulated Lead-Acid Batteries, edited by Patrick T. Moseley, Jürgen Garche, C.D. Parker, D.A.J. Rand, Elsevier, 2004.
25. M. Cao, C. Hu, G. Peng, Y. Qi, E. Wang, *J. Am. Chem. Soc.* **125**, 2003, 4982
26. K. J. Klabunde, D. Zhang, G. N. Glavee, C. M. Sorensen, G. C. Hadjipanayis, *Chem. Mater.*, **6**, 1994, 784.
27. C. A. Foss, G. L. Hornyak, J. A. Stockert, C. R. Martin, *J. Phys. Chem.*, **98**, 1994, 2963.
28. H. Bönemann, W. Brijoux, T. Jousen, *Angew. Chem., Int. Ed.*, **29**, 1990, 273.
29. J. S. Bradley, E. W. Hill, C. Klein, B. Chaudret, A. Duteil, *Chem. Mater.*, **5**, 1993, 254.
30. D. V. Akimov, O. S. Andrienko, N. B. Egorov, I. I. Zherin, and V. F. Usov, *Russian Chemical Bulletin, Int. Edn.*, **61**, 2012, 225-229.