# IZMIR KATIP CELEBI UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

# ELECTROCHEMICALLY MODIFIED CARBON FIBERS AS AN ACTIVE MASS ADDITIVE IN ENHANCED FLOODED LEAD ACID BATTERY

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**JUNE 2020** 

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PhD THESIS

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**JUNE 2020** 

# İZMİR KATİP ÇELEBİ ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

# ELEKTROKİMYASAL OLARAK MODİFİYE EDİLMİŞ KARBON FİBERLERİN GÜÇLENDİRİLMİŞ SULU KURŞUN ASİT AKÜLERDE AKTİF MALZEME KATKISI OLARAK KULLANILMASI

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To my family,

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## **ABBREVIATIONS**

CF	: Carbon Fiber
PAN	: Polyacrylonitrile
Zn	: Zinc
Sn	: Tin
Pb	: Lead
SEM	: Scanning Electron Microscope
XRD	: X-Ray Diffraction
DOD	: Depth of Discharge
PAN	: Polyacrylonitrile
NAM	: Negative Active Material
EAC	: Electrochamically Activated Carbon
Hg	: Mercury
Cu	: Copper
GPa	: Gigapascal
PbO <sub>2</sub>	: Lead Dioxide
$H_2SO_4$	: Sulphuric Acid
PbSO <sub>4</sub>	: Lead Sulfate
PbO	: Lead Oxide
CF/Zn	: Zinc Coated Carbon Fiber
CF/Sn	: Tin Coated Carbon Fiber
CF/Cu	: Copper Coated Carbon Fiber
CF/Pb	: Lead Coated Carbon Fiber
$Pb_3O_4$	: Lead Tetroxide
Hg <sub>2</sub> SO <sub>4</sub>	: Mercury Sulfate
BaSO <sub>4</sub>	: Barium Sulfate
SnSO <sub>4</sub>	: Tin Sulfate
CuSO <sub>4</sub>	: Copper Sulfate
ZnCl <sub>2</sub>	: Zinc Chloride
$Pb(NO_3)^2$	: Lead Nitrate
NaOH	: Sodium Hydroxide
NH4CI	: Ammonium Chloride
SEM	: Scanning Electrone Microscope
XRD	: X-ray difractometer
DoD	: Depth of Discharge
NAM	: Negative Active Material
PAM	: Positive Active Material
EAC	: Electrochemically Activated Carbon
CCA	: Cold Crank Amphere
Ah	: Amphere Hour
4BS	: Tetra Basic Lead Sulfate

3BS	: Tri Basic Lead Sulfate
1BS	: Mono Basic Lead Sulfate
Κ	: Kelvin
DIN	: German Instute for Standardization
JIS	: Japanese Internatioan Standarts
FCF	: Flexible Carbon Fiber
L <sub>C</sub>	: Crystallite Height
La	: Crystallite Width
FMEA	: Failure Modes and Effects Analysis
PP	: Polypropylene
DFMEA	: Design Failure Modes and Effects Analysis
RPN	: Risk Piority Number
C20	: 20 Hour Capacity Rate
DAD	: Diameter after Deposition
С	: Continuous
NC	: Non-continuous
Dev.	: Deviation
SI	: Stratification Index
HER	: Hydrogen Evolution Reaction
W/m.K	: Watt/meter.kelvin
g/cm <sup>3</sup>	: gram/cubic centimeter
GPa	: Gigapascal
μm	: Micrometer
Å	: Angstrom
V	: Voltage
$\Omega cm^{-1}$	: Ohm per Centimeter
mS/cm <sup>2</sup>	: Milisiemens per Centimeter
mΩ/10cm	: Miliohm per Ten Centimeter
ррт	: Parts per Million
A/dm <sup>2</sup>	: Amphere per Decimeter
wt %	: Weigth Percentage
Vol%	: Volume Percentage

## ELECTROCHEMICALLY MODIFIED CARBON FIBERS AS AN ACTIVE MASS ADDITIVE IN ENHANCED FLOODED LEAD ACID BATTERY

### ABSTRACT

The lead acid battery electrodes are produced by mixing lead oxide with  $H_2SO_4$  to yield a paste. Additionally, some carbon derivatives and some polymeric fibers are added into the mass, known as the active mass, to increase the efficiency and to improve the strength of the plates, respectively. For decades, various types of carbon derivatives have been studied by many researchers as an active additive material to improve the charge acceptance figures of the batteries. Carbon rich surface that constructs a conductive bridge in the active mass, also increases the electrochemical activity of the surface. Thus, carbon adding for active materials increases the cycle life of the lead acid batteries. However, adding carbon have some important disadvantages for maintenance free batteries as a result of the decrease in hydrogen over potential and the increase in water loss. The increment in water loss causes the increase in the acidity. Therefore, the corrosion rate of the active material increases, and battery life is shortened. Some studies showed that using electrochemically activated carbon together with individual metallic zinc and tin in the active material increased the hydrogen evolution and collaboration of carbon with Zn and Sn increased the cycle life of the lead-acid batteries. In contrast to the previous efforts, the purpose of this study is to use the carbon fiber (CF), electrodeposited Zn, Sn and Pb on carbon fiber (CF/Zn, CF/Sn, CF/Pb) increased conductivity of CF instead of polymeric nonconductive fibers that are used in previous applications. It is aimed to overcome the drawbacks such as the decrease in hydrogen overpotential, the increase in water and short cycle life by using carbon, Zn, Sn, and Pb structures together in the hierarchical structures. The electrochemically modified CF surfaces with Zn, Sn, and Pb examined with SEM and XRD analysis. Negative Electrodes of Batteries are prepared with active material doping Non-conductive polymeric fibers, Carbon fiber (CF), Zn electrodeposited Carbon Fiber (CF/Zn), Sn electrodeposited Carbon fiber (CF/Sn), Pb electrodeposited Carbon fiber (CF/Pb) components added into negative material and 2V battery cells produced. 2V cells tested according to 50% depth of discharge (DoD) to check the performance improvement and water consumption tests applied to analyze the water loss performance of cells. The maximum cycle performance was recorded in the sample CF and CF/Zn added cells. Other cells have less water loss and reduction in gassing caused acid stratification during charge-discharge cycle. For this reason, these cells had less cycle.

Keywords: Carbon Fiber, Electrodeposition, Lead acid battery, zinc,tin,lead

# ELEKTROKİMYASAL OLARAK MODİFİYE EDİLMİŞ KARBON FİBERLERİN GELİŞTİRİLMİŞ SULU KURŞUN ASİT AKÜLERDE AKTİF MALZEME KATKISI OLARAK KULLANILMASI

## ÖZET

Kurşun asit akü elektrotlar, kurşun oksidin  $H_2SO_4$  ile karıştırılmasıyla elde edilir. İlaveten, bazı karbon türevleri ve bazı polimer fiberler, aktif malzeme etkinliğini arttırmak ve plakaların mukavemetinin arttırılması için pastaya eklenir. Onlarca yıldır, birçok araştırmacı tarafından akülerin şarj olma kabiliyetini arttırmak için çeşitli karbon türevleri aktif katkı malzemesi olarak çalışılmıştır. Karbon bakımından zengin yüzeyler aktif malzemede iletken bir köprü oluştururken aynı zamanda yüzeyin elektrokimyasal etkinliğini de arttırır. Bu nedenle, aktif malzeme içine karbon ilavesi, kurşun asit akülerin kullanım ömrünü arttırır. Ancak, karbon ilavesi hidrojen çıkışı potansiyelini düşürmesi ve su kaybını arttırması nedeniyle bakım gerektirmeyen aküler için bazı dezavantajlara sahiptir. Su kaybındaki artış asitliğin artmasına neden olur. Bu nedenle, aktif malzemenin korozyon hızı artar ve akü ömrü kısalır. Bazı calısmalar, elektrokimyasal olarak aktif karbonun, aktif malzeme icine ilave edilen metalik çinko ve kalayın karbon ile kullanılmasının hidrojen gaz çıkışını azaltarak kurşun asit akülerin ömrünü arttırdığını göstermiştir. Önceki çalışmaların aksine, bu çalışmanın amacı daha önceki uygulamalarda kullanılan iletken olmayan fiberlerin yerine, yüzeyleri elektrokimyasal olarak metalik Zn, Sn, Pb kaplanmış karbon fiberlerin (CF/Zn, CF/Sn, CF/Pb) kullanılmasıdır. Karbonun Zn, Sn ve Pb hiyerarşik olarak birlikte kullanılması ile hidrojen çıkış potansiyelinin artması, su kaybının artması ve akü ömrünün kısalması gibi dezavantajların üstesinden gelinmesi hedeflenmiştir. Elektrokimyasal olarak yüzeyleri Zn, Sn ve Pb ile modifiye edilmiş karbon fiberlerin incelemeleri SEM ve XRD yöntemleri ile analiz edilecektir. Negatif akü elektrot aktif malzemesi içine iletken olmayan polimer fiberler, karbon fiber (CF), Zn elektrodepozitleme vapilmis karbon fiber (CF/Zn), Sn elektrodepozitleme vapilmis karbon fiber (CF/Sn), Pb elektrodepositleme yapılmış karbon fiber (CF/Pb) ilaveleri ile hazırlandı ve 2V hücreler üretildi. 2V hücreler 50% derin deşarj (DoD) ile test edilerek performans iyileşmeleri test edildi ve hücrelerin su kaybı performansları da su tüketim testi uygulanarak analizler gerçekleştirildi. En yüksek çevrim sayısı CF ve CF/Zn ilaveli hücrelerde elde edilmiştir. Diğer hücreler daha düşük su kaybı sonuçlarına sahiptir ve bu düşük gazlaşma çevrimdeki şarj deşarj sırasında asit stratificasyonuna neden olur. Bu nedenle bu hücrelerin çevrim testleri daha düşük gelmiştir.

Anahtar kelimeler : Karbon fiber, elektrodepozitleme, kurşun asit akü, kalay, çinko

### **1. INTRODUCTION**

Lead acid batteries convert the chemical energy contained in its active materials into electrical energy by means of an electrochemical reaction. Lead acid batteries are batteries composed of lead (Pb) negative electrode,  $(PbO_2)$  positive electrode and  $(H_2SO_4)$  as electrolyte. The Pb metals oxidized into Pb ion in the 2-oxidation state (abbreviated Pb (II) or Pb<sup>2+</sup>) during discharge reaction. Thus, The Pb (II) formed precipitates as PbSO<sub>4</sub> at the negative electrode by combining with sulfate ions from the electrolyte solution (1.1):

$$Pb + H_2SO_4 \xleftarrow{\text{Discharge/Charge}} PbSO_4 + 2H^+ + 2e^-$$
 (1.1)

The positive electrode proceeds by the reduction of  $PbO_2$  with Pb in the +4 oxidation state, Pb(IV) or  $Pb^{2+}$ to Pb(II), which precipitates as  $PbSO_4$  at the positive electrode (1.2) [1].

$$PbO_2 + 2e^- + H_2SO_4 + 2H^+ \xleftarrow{Discharge/Charge}{PbSO_4 + 2H_2O}$$
 (1.2)

The products of positive and negative electrodes are  $PbSO_4$  at the discharge steps.  $PbSO_4$  is reduced to form Pb at the negative and  $PbSO_4$  is oxidized to  $PbO_2$  at the positive electrode during charging reactions. Lead acid battery electrodes both positive and negative are manufactured in the discharged state, that is, as Pb (II). Lead oxide is mixed with  $H_2SO_4$  as a basic paste preparing method Various additives may be added, such as plastic fibers to strengthen the electrode plate and carbon black to increase conductivity of paste. Thus, the charge ability of the batteries is increased, and batteries can discharge more effectively [1].

The limited charge acceptance of the negative plate is the major problem for lead acid batteries in hybrid electrical vehicles. Lead sulfate accumulates first at the surface of the negative plate. On further cycling more  $PbSO_4$  is accumulated on the surface, forming an insulating layer there. The capacity decreases and cannot be restored under regular charge conditions. During charge lead sulfate is dissolved. The lead ions diffuse to the electronically conductive spots where they are reduced to metallic Pb. The most common solution of the problem has been adding carbon derivatives to the negative plate [1,2]. Carbon derivatives generally with a higher surface area and double layer capacitance, increases the charge acceptance substantially and eliminates sulfation.

Nowadays the need for new generation lead-acid batteries which can be utilized in hybrid electric vehicles and modern energy storage systems brought forward the next active component - carbon. The researchers are supposed to develop theories which allows the battery producers to get even more out of the battery. Carbon exists in various forms, all of them light and with special properties. During the last decades new carbon materials have been introduced as: carbon and graphite fibers, cloths, micro and nanofibers, nanotubes, aerogels, graphene's lead-acid battery [2]. When thePbSO<sub>4</sub> crystals in the negative active materials (NAM) increase significantly after the discharge of the battery, the added carbon derivatives increase the electrical conductivity.

When the hybrid electric vehicles were launched on the market, lead acid batteries began to take their place in these vehicles. However, it was figured out that the negative plates of these batteries were insufficient due to the high current requirements in hybrid vehicles [3]. Carbon derivatives incorporated into the negative pastes with the aim of increasing the electrochemically active surface of the negative active material.

The addition of various carbon derivatives such as carbon black and activated carbon to negative active materials enhances the charge acceptance of negative plates during high-rate cycling. Optimized paste recipe containing the three ingredients mentioned above guarantees that the negative plate will perform well at low temperatures [3]. Negative active materials with carbon black concentrations between 0.2% and 2.0% drastically decrease sulfation of the negative mass and increase cycle life of the lead acid batteries [4].

Carbon additives show much higher Faradaic current, compared to the bare Pb surface, which further increases with cycling. Carbon plays a key role in enhancing the electrochemical activity at the Pb-interface with the  $H_2SO_4$  electrolyte and that conditioning of the interface is taking place with cycling [5].

A different carbon polymorph, graphite, has been studied by some researchers for the active mass with titanium dioxide to improve the cycle life of the negative lead acid battery electrodes in the partial state of charge regime. The experimental results have been attributed to hindrance crystal growth of lead sulfate deposited in the electrode pores and increase the cycle life performance of the batteries [2].

The carbon additives decrease the hydrogen evolution potential. Hence, it is essential to increase the rate of hydrogen evolution during the charge steps. Decomposition of water can cause increase the acid density and shorten the battery life. To minimize, or even eliminate the water loss, researchers improved the performance of lead acid cell by using electrochemical active carbon and Zn in negative mass. Zn deposition on the carbon surface reduced the hydrogen evolution of the cell. Zn(II) additives can also improve the low-temperature and high-rate capacities of the cell with Electrochemically Activated Carbon (EAC) in negative mass, which ascribes to the formation of Zn on lead and carbon surface that constructs a conductive bridge among the active mass. The cell with 0.6 wt% EAC exhibits 84% reversible capacity after 2100 cycles and the control cell with no EAC and Zn(II) exhibits less than 80% reversible capacity after 1350 cycles [6].

Another effect of Zn in active material have performed and patented by George W. Mao in 1978. Adding Zn compounds such as zinc sulfate to the battery in amounts sufficient to decrease the float current that would otherwise occur during voltage regulated overcharge and increase the battery life [7]. Some Researchers successfully fabricated ZnO on carbon fiber by electrochemical method. The carbon fiber used here was used both as a base and as a heat source. They used zinc acetate dihydrate as a coating solution. With this study, the researchers provided new information to the research literature on zinc oxide coating and provided sample data for other oxide coating studies. Although Carbon fiber coatings studies are in the research media, materials do not use as an additive in lead acid battery mass from this aspect previous study will be different and innovative [8]. To improve the battery endurance performance tin added into active material by Shiomi Masaki et. al. and method were patented. Adding of optimal Sn oxide increases number of endurance cycles with improving the sulfation of lead during discharge step in cycle test[9]. Mehdi Shafiei et al. Electrochemically Coated Sn on the carbon fibre surface to produce commercial graphitic anodes for rechargeable Li-ion cells [10].

The correlation between plate capacity and the ratio between conductive and nonconductive particles in active material during discharge at different rates. Plates containing non-conductive particles such as polypropylene fibers and that additives decrease the utilization of the active material during charge and discharge steps. Hence, selection of the type and amount of additives to the positive paste should be made in view of the discharge rate. Batteries operating at low discharge currents should have positive plates containing additives that improve the electrical conductivity of active material.

In the present study, electrochemically modified conductive carbon fiber additives will be employed instead of non-conductive polymer fibers to improve the active material conductivity and increase the battery cycle life. Most of the researchers investigated the zinc and tin compound powders' beneficial effect on lead-acid battery performance [6;9;11]. Carbon additives decrease the hydrogen evolution potential and cause the water loss, incorporating zinc with carbon additives can suppress the water loss [6] and addition of tin element into the active material increases the endurance cycle life of the lead-acid battery. Therefore, the carbon fiber surface will be coated by zinc, tin and lead to improving both the wettability and conductivity of carbon surfaces. Hence, active material conductivity will be increased by carbon and coated Zn, Sn and Pb on the fiber surface can help to decrease the water loss amount.

### 2. THEORETICAL BACKGROUND

## 2.1 Lead Acid Battery

When the lead–acid battery performs, electrochemical processes take part in both electrodes. According to the reactions, one mol Pb produces two electrons flowing to a positive electrode. Hence, lead sulfate is occurrs at both plates. The reaction that takes part in negative electrode is oxidation of lead and reduction of lead dioxide during discharge [12]. Lead (Pb), lead oxide (PbO<sub>2</sub>), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) are the negative electrode, positive electrode, and electrolyte of lead acid batteries, respectively [1]. The positive electrode proceeds by the reduction of PbO<sub>2</sub> with Pb in the +4 oxidation state, Pb(IV) or Pb<sup>4+</sup>, to Pb(II), which precipitates as PbSO<sub>4</sub> at the positive electrode:

At positive electrode,

$$PbO_2 + 2e^- + H_2SO_4 + 2H^+ \xleftarrow{Discharge/Charge}{PbSO_4 + 2H_2O E^0} = +1.690 (2.1)$$

The Pb(II) so formed precipitates as  $PbSO_4$  at the negative electrode by combining with sulfate ions from the electrolyte solution:

At negative electrode,

$$Pb + H_2SO_4 \xleftarrow{\text{Discharge/Charge}} PbSO_4 + 2H^+ + 2e^- \qquad E^0 = -0.358 \quad (2.2)$$

where  $E^0$  is the standard electrode potential for each reaction, i.e, the electrode is in a standard state.

The overall reaction is:

$$PbO_2 + Pb + 2H_2SO_4 \xleftarrow{\text{Discharge/Charge}} PbSO_4 + 2H_2O \quad V^0 = +2.048 \quad (2.3)$$

where  $V^0$ , is the standard cell voltage. According to the above electrochemical reactions, the electrons generated at the negative electrode flow the positive electrode

through the conductor. It causes loss of electric energy from cell to an external consumer. Unlike this, the charge process occurs when there is an external power source. The electrons produced at positive electrode flow from positive electrode to negative electrode so that lead sulfate is reduced to lead. Thanks to this reverse process, battery re-charged with electric energy. The electric energy that is lost per unit charge is the cell voltage. It is presumed that electric current and electron flows are the opposite way as shown in Fig.2.1.



Figure 2.1 A schematic representation for lead-acid battery working principle [13].

As seen  $HSO^{4-}$  ions relocate to the negative electrode to react with the lead to form  $H^{4+}$  ions and lead sulfate (PbSO<sub>4</sub>) which is an extremely non-conductive component. When both plates are discharged, the plate surface with lead sulfate and water is occurred. Lead sulfate is formed on plates progressively in equal quantities. Discharge process also leads to decrease in electrolyte concentration, which helps the determining the degree of discharge or controlling the state of charge of the cell.

When reverse process, charging, is occurred the high amount of lead sulfate is converted to lead and lead dioxide. In the case of high current of electricity flows hydrogen and oxygen gases release at negative and positive electrode, respectively. These gases that are in stoichiometry result in lack of water from the electrolyte [12].

The potential for each  $Pb/PbO_2$  cell is nominally about 2.0 V. They are generally charged to less than 2.4 V per cell to minimize gas formation as shown in Fig. 2.2. The plates are connected in series within the battery case to boost the voltage. Fig.2.3 shows the common battery voltages are 12 V (six cells), but batteries with higher or lower voltages can be found.

A higher-voltage battery be made by connecting carefully matched, multiple batteries in series [1].



Figure 2.2 Discharge and charge voltage for a lead acid battery [1].



Figure 2.3 Cross section of a lead acid battery [1].

The battery negative electrode is one of the electrodes, which provides requirement capacity (Ah) and cold cranking ampere (CCA). It consists of negative lead grid and negative active mass that includes metallic lead and additives, such as carbon, lignosulfonate, etc.

The main purpose of the paste preparation process for positive  $(PbO_2)$  and negative (Pb) battery plates is to produce particles of exact shape and composition. These particles are the basic structural elements of the paste, after spreading to the grids, curing the plates and formation, yield lead-acid cell plates [3]. After preparing lead-

acid battery plates, wet plates passes through flash oven for 5-10 seconds to collect plates without sticking. The next stage of the manufacturing process is curing. The active material that forms the skeletal structure formed during the curing of the plates gives crystal structure [14].

During the curing process, the paste particles are bonded together to form a continuous force the porous mass (skeleton) which is tightly connected to the grid in turn (Fig.2.4).



Figure 2.4 Basic process of plate curing [3].

The following basic operations are performed during plate curing:

(i) The skeleton of the cured paste (hard porous mass) is constructed. Small crystals of pastes dissolve and grow larger ones. Water contained in thin liquid films the particles evaporate as a result of the bonding of 3BS or 4BS crystals and PbO particles.

ii) When curing is carried out at temperatures higher than 80°C, 3BS structures is formed to 4BS crystals.

iii) The free lead is oxidized, remaining in the leady oxide, during the process of paste preparation.

iv) The grid alloy surface is oxidized and the paste and grid surface bonding process is performed at curing step.

The cured plates of both positive and negative cannot create electromotive forces when the pasted plates are assembled into cells. The purpose of the formation is to convert the cured plates into electrochemically active porous materials:  $PbO_2$  in the positive plates and Pb in the negative electrodes. After curing is completed, the charging step of the plates is started [3].

The bonding between the grid and the active material begins in the curing process and continues throughout the formation. This attachment is an important factor affecting battery performance. In addition, the formation allows the crystal structure on the plate to change. There are three important parameters in the formation process that enables the exchange of crystals in the active material;

- 1. current density,
- 2. concentration of sulfuric acid, and
- 3. electrolyte temperature [14].

Electrochemical reactions during the formation of positive plates are represented by the following equations.  $E_h$  represents the equilibrium potential for the reaction at 298.15 K.

$$PbO_{2} + SO_{4}^{-2} + 4H^{+} + 2e^{-} = PbSO_{4} + 2H_{2}O$$
$$E_{h} = 1.685 - 0.118 \,pH + 0.029 \,lna_{SO_{4}^{2-}}$$
(2.3)

$$PbO_2 + HSO_4^{-2} + 3H^+ + 2e^- = PbSO_4 + 2H_2O$$

$$E_h = 1.628 - 0.88 \, pH + 0.029 \, lna_{HSO_4} \tag{2.4}$$

$$2PbO_{2} + SO_{4}^{-2} + 4e^{-} + 6H^{+} = PbO. PbSO_{4} + 3H_{2}O$$
$$E_{h} = 1.468 - 0.88 pH + 0.015 lna_{SO_{4}^{2-}}$$
(2.5)

$$4PbO_{2} + SO_{4}^{-2} + 8e^{-} + 10H^{+} = 3PbO.PbSO_{4}.H_{2}O + 4H_{2}O$$
$$E_{h} = 1.325 - 0.074 pH + 0.007 lna_{SO_{4}^{2-}}$$
(2.6)

$$3PbO_2 + 4e^- + 4H^+ = Pb_3O_4 + 2H_2O$$
  $E_h = 1.122 - 0.059 \, pH$  (2.7)

$$PbO_2 + 2e^- + 2H^+ = PbO + 2H_2O$$
  $E_h = 1.122 - 0.059 \, pH$  (2.8)

$$O_2 + 4H^+ + 4e^- = 2H_2O$$
  $E_h = 1.128 - 0.059 \, pH + 0.015 \, lnPbO_2$  (2.9)

All equilibrium potentials are referred to a standard hydrogen electrode. The  $Hg/Hg_2SO_4$  electrode which is 0.620 V more positive than the standard hydrogen electrode, is used in lead acid battery investigations. Electrochemical reactions progressing during the formation of positive plates are represented by the following equations (2.3 to 2.7). The higher the PbO Content in each compound, the more negative the oxidation potential to PbO<sub>2</sub>. Thus, upon oxidation of a mixture of PbSO<sub>4</sub>,

1BS, 3BS and  $Pb_3O_4$  in the cured paste, first PbO and then basic lead sulphates are oxidized in equation (2.7 to 2.9). The development of potential plateaus for different paste phases in the potential-time curve depends on the kinetics of redox reactions. For purely kinetic reasons, some phases in the paste may not be manifested by a plateau in the potential curves [3].

#### 2.1.1 Components of lead acid battery electrode

#### 2.1.1.1 Additives:

Additives are substances that improve some of the properties of the final product or facilitate and accelerate the technological process of its manufacture. The content of additives in the product's formulation is from 0.02 to 2.0% of the total weight balance of the initial materials [3].

During the lead acid battery discharge process, metallic Pb in the negative electrode and lead dioxide (PbO<sub>2</sub>)in the positive turn into lead sulphate (PbSO<sub>4</sub>) by electrochemical conversion. This lead sulfate formed in the positive and negative electrodes is semi conductive and its conductivity is 50  $\Omega$ cm<sup>-1</sup>.

It is very important that the positive electrode does not become inactive during these conversions. The formation of lead sulphate formed in the positive electrode that continues to discharge begins and HSO<sup>4–</sup> and H<sup>+</sup> ions pass through the pores. At this stage, lead dioxides in the positive electrode are electrically isolated.



Figure 2.5 Diagram of porous lead dioxide paste with diffusion [15].

Porous additives increase the supply of HSO<sup>4–</sup> and provide local reservoirs of this ion within the pores. Fig. 2.5 illustrates ion conduction through the pores to the inside of the active mass [15].

#### **2.1.1.2 Lead oxide** (PbO)

The lead compound has two polymorphic forms: tetragonal ( $\beta$  – PbO) and orthorhombic ( $\alpha$  – PbO). The solubility of these forms in water at 25°C is 0.0504 g L<sup>-1</sup> for  $\alpha$  – PbO and 0.1065 g L<sup>-1</sup> for  $\beta$  – PbO. Lead oxide forms lead hydroxides are 3PbO. H<sub>2</sub> and 5PbO. H<sub>2</sub>O. Pb(OH)<sub>2</sub> is a hydrated form of lead oxide that is a compound of amphoteric nature and dissociates to HPbO<sup>2–</sup> and Pb(OH)<sup>–</sup> ions. In the battery industry, lead oxide is obtained by partial thermal oxidation of lead and is called 'leady oxide', as it contains between 73% and 85% PbO, the remaining part being non-oxidized lead. Tet – PbO is the basic form of leady oxide, but orthorhombic PbO is also present, up to 5-6%. The pastes preparing with Leady oxide is pasted to electrodes of lead acid batteries [3].

#### 2.1.1.3 Lignosulfonate

Lignosulfonate is a kind of wood flour that is added to the expander formulation. Lignosulfonates disintegrated slowly during battery paste preparation if the negative plates lose capacity. During battery charge and discharge operation this wood flour decomposes gradually producing lignin [3]. The lignin types are strongly adsorbed on the lead surface, and during lead dissolution on battery operations, the Pb<sup>2+</sup> ions migrate through the adsorbed layer. The adsorption of the expander affects the anodic oxidation of Pb, the cathodic reduction of lead sulfate, the morphology of lead sulfate, and both the porosity and the surface area of the negative-plate material [16].

#### 2.1.1.4 Barium sulfate

 $BaSO_4$  performs as a nucleation surface that allows the nucleation of  $PbSO_4$  crystals. It ensures that the formed lead sulfate crystals form homogeneous in the porous structure in the active material [3]. Barium sulfate acts as a nucleus in  $PbSO_4$ formation. For this reason, small particle size barium sulfate additives are added to the active material, allowing  $PbSO_4$  nucleation [17]. This function of  $BaSO_4$  is a result of the isomorphism between  $PbSO_4$  and  $BaSO_4$  crystals [3].

#### 2.1.1.5 Carbon additives

Carbon additives are added in the paste mainly to increase the electric conductivity of the lead active material at the end of discharge when the content of  $PbSO_4$  crystals in NAM increases substantially. When the hybrid electric vehicles were launched on the market, lead acid batteries began to take their place in these vehicles. However, it was figured out that the negative plates of these batteries were insufficient due to the high current requirements in hybrid vehicles [3]. The life-limiting mechanism of lead–acid batteries in this application involves progressive accumulation of lead sulfate (PbSO<sub>4</sub>) in negative plates. This failure mode is commonly called 'sulfation'. It has been reported that addition of highly conductive carbon to negative active material is effective in arresting sulfation. It enables easier charging of negative active material discharged with high conductivity carbon additions. On the other hand, PbSO<sub>4</sub> cannot prevent the growth of particles. Therefore, the contact paths between the carbon particles and PbSO<sub>4</sub> increase the conductive paths in the negative plates, thereby increasing the charging ability. Different additives added to the active material are used to prevent the PbSO<sub>4</sub> particles from growing gradually [17].

#### 2.1.1.6 Polymeric fibres

Polymer fibres improve the consistency of the paste and reduce the production waste during plate manufacture and increase the paste strength.

#### 2.1.2 Impurities

Impurities in the battery or active material cause some secondary reactions during the operation of the battery. In some cases, these secondary reactions do not have a negative effect, while in some cases they reduce battery life. These impurities should generally be less than 0.01% by weight [3].

#### 2.1.2.1 Silver in active material

Research has clearly shown that the silver contained in the active material does not affect the hydrogen evolution. However, when there was silver in the positive active material, some increase in oxygen evolution was determined. As the silver level was increased, there was a corresponding increase in the number of DIN cycles, which could be achieved. It is understood that silver has a positive effect when it is between 50 and 100 ppm in the active material. This positive effect of silver may be due to the increase of conductivity of the active material. Silver can facilitate recharging of the battery by allowing the active material to conduct current even in the case of deep discharge [18].

#### 2.1.2.2 Bismuth in active material

Previously studies demonstrate that 500 ppm bismuth was mixed into the  $PbO_2$  previously produced. It was determined that the cells added to Bismuth gave a higher initial capacity and the post-cycle capacities of the cells increased. On the other hand, cells prepared using lead produced from oxide containing 0.05% bismuth were tested according to the Japan industry standard (JIS) or the IES protocol. According to the test results, the number of cycles of bismuth containing batteries is 18-32% higher than that produced with pure oxide. Cells produced with non-bismuth pure oxide were determined to act due to  $PbSO_4$  increase during the cycle. It showed that the 32% improvement in the number of cycles was due to the improvement of the negative charge after the addition of bismuth [18].

#### 2.1.2.3 Zinc in active material and electrolyte

Zinc is a beneficial element in reducing the float current of lead batteries. zinc was the only element other than bismuth, which was effective in reducing both the positive and negative gassing currents [18].

Thus, Adding zinc suppressed the hydrogen evolution of the cell in the presence of the carbon additives in negative mass is significantly reduced by 58-73% adding Zn(II) additives [6].

#### 2.1.2.4 Additions of tin sulfate

Many methods have long been studied to enhance the specific energy of lead-acid batteries. One of these proposed methods is to add tin in the active material to enhance the discharge properties of the lead-acid battery. However, this approach is disadvantageous in that the tin thus added is eluted from the positive active material with the electrolyte and then deposited on the negative plate to lower the hydrogen overvoltage of the negative plate and hence cause much water loss. Tin has been added to the positive active material as  $SnO_2$ , or as  $SnO^{2-}$  coated glass and carbon fibers

have shown that such additions improve formation efficiency and plate performance by improving the conductivity of the active material and providing improved utilization at high rates [9].

### 2.2 Carbon Fiber

Thomas Edison made the first carbon fibers in 1879. He carbonized the cotton yarn to produce a filament for a bulb and It was not entirely successful. Edison eventually replaced the fiber by a tungsten wire. Large-scale production of carbon fibers had to wait until the late 1950's, when cloth and felt from carbonized rayon were commercialized. These materials are still produced now [19].

Carbon fiber is defined as a fiber containing at least 92 wt % carbon, while the fiber containing at least 99 wt % carbon is usually called a graphite fiber. In recent years, the carbon fiber industry has been growing steadily to meet the demand from different industries such as aerospace (aircraft and space systems), military, turbine blades, construction (non-structural and structural systems), light weight cylinders and pressure vessels, offshore tethers and drilling risers, medical, automobile, sporting goods, etc. [20].

#### 2.2.1 Structures and properties

The structure of the carbon fiber is in the form of layers of carbon atoms arranged in a regular hexagonal atomic pattern, as shown in Figure 2.6. This sequence is similar to that of graphite consisting of graphene layers. Layer planes in carbon fiber can be turbostratic, graphitic or hybrid depending on production processes and precursors.



Figure 2.6 Crystal directions and structures of crystals [20].

In graphitic crystals, layer planes are arranged regularly and parallel to each other. Atoms in a plane are covalently bonded through the sp2 bond, while the interaction between the layers is relatively weak Van der Waals forces.

The d-spacing (d002) in the two graphene layers is approximately 0.335 nm. The elastic constant of this single graphite crystal is 1.060 GPA and 36.5 GPA for C11 and C33, respectively. On the other hand, the shearing of C44 is as low as 4.5 GPa.

However, the structural unit of many carbon fibers consists of a turbostrate layer pile. In a turbostratic structure, parallel graphene layers are arranged irregularly or randomly folded, bent or divided. Studies have shown that the presence of irregular stacking and Sp3 binding can increase the d-range to 0.344 nm. Johnson and Watt investigated the crystal structures after PAN carbon fibers had been heat treated at 2500°C. In this review, they reported that turbostrate crystals had crystalline height (Lc) and 6-12 nm crystalline width (La) in at least 12 layer planes [19]. On the other hand, the sheets of carbon atoms are randomly folded, leading to a wrinkled structure in turbostratic FCF. Therefore, it is possible to produce graphene oxides from FCF by modified Hummers' method and hence create defects in the FCF surface that are shown in figure 2.7.



Figure 2.7 Structures for a single flexible carbon fiber (FCF) from its array [21].

#### **2.2.2 PAN based carbon fibers**

Production of PAN based carbon fiber requires the polymerization of PAN or PAN copolymer, followed by fiber spinning and drawing before stabilization in air (~200 - 300°C) and carbonization in an inert environment (1000 - 1700°C) [21].

Carbon fibers have the highest tensile strength and a wide range of tensile modulus and can be easily produced with different processes. During the copolymerization of the PAN, by adding a small amount of additives such as methyl acrylate or vinyl acetate, it decreases the glass transition temperature from 120°C to 100°C and improves the tensile properties.

The production process of PAN-based carbon fibers can be divided into the following five steps:

- 1. Spinning the PAN co-polymer to form a fiber
- 2. Stretching
- 3. Oxidation and stabilization at 220°C under tension
- 4. Carbonization in inert atmosphere up to 1600°C
- 5. Graphitization up to 3000°C [19].

#### 2.2.3 Pitch based carbon fibers

Natural Pitch may contain higher than 80% carbon which is synthesized during production of synthetic polymers by using destructive distillation of petroleum and coal. The composition of a step depends on the source tar and processing conditions.

The pitch created from coal is generally more aromatic than oil pitch. Pitch as a precursor has the advantage of lower material cost, higher char yield, and higher degree of orientation compared with PAN. Structures determined in graphitic structure have higher elastic modulus, high thermal properties and electrical conductivity compared to structures in pitch-based carbon fibers [20].

#### 2.2.4 Thermal and electrical properties

The thermal conductivity of PAN and pitch based carbon fibers is directly dependent on the vacancies concentration in the atomic structures, interstitial atmos, impurities and crystal orientations. These properties vary depending on the temperature of the carbonization process. The point defects in its increases with concentration of imperfections and the crystalline perfection as the carbonization temperature increases, thereby increasing the thermal conductivity. It is formed by combinations of phonones and electrons of thermal conductivity of carbon fibers. It is known that the electron additive at room temperature is ~ 0.40-0.66 W / m / K, this evidence is ~ 10% of the reported thermal conductivity of commercial PAN based carbon fibers such as IM7 (5.4 W / m / K) and provides evidence that the thermal conduction in carbon fibers is actually a having a phono domination process [22].

### **2.3 Electrochemical Deposition**

Metal electrodeposition is the method to coat metals to metallic or other conductive surfaces by the electrochemical process. Electrodeposition is used both for protecting materials from corrosion and natural influences and for decorative purposes. Construction metals are used because of their mechanical properties and machinability at a low price, but some materials are not resistant to corrosion [23]. In this situation, surfaces are coated by corrosion-resistant material. On the other hand, some materials used for decorative purposes are coated with better visual impact material. The most common coating metals are zinc, tin, chromium, copper, nickel, depending on the reason for the coating.

Some of the purposes of electroplating are;

- I) Appearance,
- II) Protection
- III) Special surface properties
- IV) Engineering or mechanical properties.

The components of an electroplating process are the substrate (cathode) to be plated, a second electrode completes the circuit is named as an anode. Negative electrodes and positive electrodes are immersed in the electrolyte and the external circuit, consisting of a source of direct current (dc), means of conveying this current to the plating tank, and associated instruments such as ammeters, voltmeters, and means of regulating the voltage and current at their appropriate values. During electrolysis metal is deposited on to the work and metal from the bar dissolves (2.10 and 2.11) Faraday's laws of electrolysis govern the amount of metal deposited [23].

cathode 
$$M_{z+(aq)} + ze \rightarrow M(s)$$
 (2.10)

anode 
$$M(s) \rightarrow Mz + (aq) + ze$$
 (2.11)

Determination of the concentration of free metal ions  $A^{z+}$  and consequently the redox potential  $E_{eq}$  of the reaction  $A^{z+} + ze \rightarrow A_{crystal}$ , which is given by Nerst equation (2.12):

$$E_{eq}(A) = E_{A^{z+}}^{0} + \left(\frac{RT}{zF}\right) \cdot \ln a A^{z+}$$
 (2.12)

Where  $E_{A^{z+}}^{0}$  is the standard redox potential for A, R = 8.314 J /mol.K is the gas constant, T the absolute temperature, z the number of electrons Exchanged, F = 96845 A.s / moils the Faraday constant, and  $a^{z+}$  is the activity of the ion  $A^{z+}$ . A metal can be electrodeposited from such solution when the potential applied to the substrate electrode  $E_{appl}$  is more negative than  $E_{eq}(A)$ ; the driving force for film formation is the deviation from equilibrium (2.13), and is called overpotential:

$$\eta = E_{appl} - E_{eq}(A) \tag{2.13}$$

In most practical electrodeposition processes however, a metal A is reduced from  $A^{z+}$  on a foreign substrate S, and an equilibrium for this system cannot be defined strictly unless the system is left to spontaneously achieve its own equilibrium. In some cases, this equilibrium can quickly reach high reactive metal surfaces as an example, while equilibrium is disabled in metal deposition on the other silicon. Thus, the over potential for nucleation can be defined for this condition. This over potential begins to deposition, these quartz crystals are determined with the microbalance. The potential corresponding to the measured deposit amount may be more negative (~ 200 mV) than A's redox potential, depending on the atomic details of the nucleation process [24].

#### **2.3.1 Surface treatment**

Surface preparation for proper coating includes substrate surface cleaning and pretreatment. This is the most important step to adhere the coatings, surfaces must be free from oily soils, corrosion products.

Different solvents or aqueous chemicals, or mechanical cleaning are used for cleaning surfaces. Cleaning method depends on the substrate, size and shape of the object.

To improve the coating adhesion, pretreatment is applied after cleaning. Acids are used to remove loosely adhering contaminants [25].

The carbon fibers have poor wet and adsorption ability with most resins because the carbon fiber surface is non-polar and compound of highly crystallized graphitic basal planes with inert structures and sized by polymeric materials. To improve the wettability of carbon fibers several techniques for surface treatment on carbon fibers have been applied, including plasma, electrochemical oxidation, wet chemical and thermal treatment [26, 27]. In oxidation treatment, effectiveness of treatment depends on the temperature, treatment time and oxidative medium [27]. The sizing materials (generally, 0.5–1.5 wt. %, sizing is usually applied to the fibers to produce a layer approximately 0.03  $\mu$ m thick on a 7 $\mu$ m fiber). Formic acid, acetone and ethanol is used to remove polymeric sizing material from CF surface to improve the CF surface wettability on the coating process [26].

## 2.4 Metal Electrodeposition

### 2.4.1 Zinc electrodeposition

Commercial zinc plating is carried out in several different systems: cyanide baths, alkaline non-cyanide baths, and acid chloride baths. In the 1970s, most commercial zinc coatings were made in conventional cyanide baths, but the passing of environmental control laws around the world led to continuous development and widespread use of other processes. Nowadays, bright acid zinc plating (acid chloride bath) is possibly the fastest growing system in the field. Approximately half of the existing baths in developed countries use this technology, and most new plants specify it [28].

### 2.4.1.1 Cyanide zinc baths

Cyanide zinc plating was applied for a long time to many workhorses in the industry. Cyanide baths are prepared from zinc cyanide (or zinc oxide sodium cyanide), and sodium hydroxide, or from proprietary concentrates. Sodium polysulfide or tetrasulfide, commonly marketed as zinc purifier, is generally required in standard, midcyanide, and especially low-cyanide baths [28].

#### 2.4.1.2 Alkaline noncyanide baths

Cyanide was replaced by complexing or chelating agents such as sodium gluconate, triethanolamine, or polymeric amines. Cyanide was replaced by complexing or chelating agents such as sodium gluconate, triethanolamine or polymeric amines [28].

The resulting baths presented problems with both waste treatment and iron deposition. The second generation of organic additives eliminated the chelating agents, but there were other drawbacks. The special additives and brightening agents are specified as the properties of an alkaline non-cyanide system. The zinc deposit may have 0.3 to 0.5 wt % C contaminations, which come off from additives [29].

Many of the existing processes have overcome these problems by using a completely new family of organic products. Platers are available with low chemical alkali noncyanide zinc (low metal bath) or high chemical alkali non-cyanide (high metal bath) options. In addition, potassium-based baths have been introduced which offer faster coating speeds and higher yields [28].

#### 2.4.1.3 Chloride zinc baths

Generally used acidic zinc chloride baths are divided into two types; they are based on ammonium chloride and potassium chloride. Ammonium based baths have been developed before potassium based baths. Ammonium based baths can work with higher current densities during coating. Both ammonium and potassium baths may contain high amounts of wetting agents between 4 and 6 to dissolve the brightening additives. It also facilitates the use of ammonium systems, which are easier to control. However, it acts as a complex agent in waste streams containing ammonium ions, nickel and copper wastewater and should be disposed of in many places by expensive chlorination. This was the main reason for the development of potassium chloride bath.

The chemical composition, amount of zinc, total chloride, pH and boric acid amount of coating baths should be checked and maintained at appropriate intervals. High zinc content and low current density cause zinc deposition on the surface. High chloride causes the polishers to separate and reduces bath conductivity. High pH values cause precipitate formation and anodic polarization in the bath. On the other hand, low pH decreases the quality of the coating [29].

#### 2.4.2 Tin electrodeposition

Tin coating can be carried out in alkaline or acidic baths. Alkaline electrolytes usually contain a metal stannate and applicable hydroxide to obtain coating. The current equipment used for the coating is the same as that used in other coatings. A rectifier for converting alternating current to direct current or a pulse-plating rectifier, which allows more precise control of electrical parameters, can be used. Tin anodes must be properly polarized in alkaline solutions to dissolve with the tin in the Sn +4 state. Once established, the anode film continues to provide the tin as Sn +4. The anode parts are coated in the bath for 1 minute by applying a higher current density than normally used. Another method is to apply the current while slowly lowering the coating to the bathroom.

Many acidic electrolytes are available for tin plating applications. Two of these are tin sulfates and tin fluoborate solutions are general systems that can adapt to any application. To produce tin, electrolytes such as halogen (a chloride-fluoride-based system) and Ferrostan (a special sulfate-based system) have been developed for high-speed cold-rolled steel strip tin coating. Acid electrolytes differ from alkali electrolytes in many ways. Tin salt dissolved in a water solution of the applicable acid does not form a soft, sticky residue on a cathode. Therefore, a refining additive such as gelatin or peptone, should be used. Generally, these materials are not directly soluble in a water solution, and a wetting agent type material such as p-naphthol is also required.

Tin sulfate electrolyte is the most widely used solution for tin plating. The amount of coating depends on the optimum amount of metal in the solution concentration. A fixed bath is operated at a cathode current density of 1 to 2  $A/dm^2$  (10 to 20  $A/ft^2$ ). With appropriate electrolyte agitation, current densities of up to 10  $A/dm^2$  (100  $A/ft^2$ ) are possible. High current density will cause burnt deposits [29].

#### 2.4.3 Lead electrodeposition

Lead coating is carried out to protect metals from corrosive environments such as dilute sulfuric acid; the lining of brine refrigerating tanks, chemical apparatus, and metal gas shells; and barrel plating of nuts and bolts, storage battery parts, and equipment used in the viscose industry [29]. Lead coatings and alloy (5 - 10% tin) protect the steel substrate, especially in industrial areas with SnO<sub>x</sub> atmosphere. At the
time of initial exposure, pitting on the lead surface occurs; however, the pits heal spontaneously, and then the lead surface is protected by the formation of insoluble lead sulfate. Very little protection is provided by these coatings in contact with soil.

Lead is electrodeposited in such baths as nitrate, acetate, fluorosilicate, and fluoroborate solution. The use of a copper or nickel strike before plating improves the corrosion resistance of the coating [30].

## 2.5 FMEA and Risk Assessment

Failure Modes and Effects Analysis (FMEA) is widely used in various industries and it is a practical way to evaluate possible reliability troubles in the early hours at the progress cycle. It is very important to identify the root causes and mitigation methods [31]. FMEA can be applied to recognize probable failure modes, conclude their effect on the process of the product, and categorize actions to diminish the failures.

The potential failure mode; is defined so that the process can potentially fail to meet the process requirements and / or design objective. Potential failure modes should be defined in physical or technical terms, not as a symptom unnoticed by the customer. Typical failure modes can be: Bent, Cracked, surface too rough, deformed, too deep hole, open position, etc.

Potential effects of failure; are defined as the effects of failure mode on customers. For the end user, impacts should always be initiated in terms of product or system performance as follows: Inoperable, unstable leaks, etc. And for the next process, the effect should be started in terms of process performance, such as: cannot fasten.

The potential cause of failure; is defined as how the failure can be defined as something that can be corrected or controlled [32].

Risk Assessment; is to define the goal of the risk assessment. Each of the below topics require clear definitions and a corresponding scale to rank the possible impact.

Severity: if a failure were to occur, what effect would that failure have on the product quality and on the patient (if any)? Effects are the results of failure, where each individual effect is given a Severity ranking in Table 2.1. Probability of occurrence: how likely is it for a failure to occur? Causes are selected from the design inputs or

past failures and placed in the Cause column when applicable to a specific failure mode in Table 2.2.

Detectability: what mechanisms are in place (if any) to detect a failure if it were to occur [31]? Actions are determined to improve the controls if they are insufficient to the Risks determined in Table 2.3.

EFFECT	CRITERIA: SEVERITY OF EFFECT	Ranking
Hazardous- without warning	May endanger machine or assembly operator. Very high severity ranking when a potential failure mode affects safe vechile operation and/or involves noncompliance with government rgulation. Failure will occur without warning.	10
Hazardous - with warning	May endanger machine or assembly operator. Very high severity ranking when a potential failure mode affects safe vehicle operation and/or involves noncompliance with government rgulation. Failure will occur without warning.	9
Very High	Major disruption to production line. 100% of product may have to be scrapped Vehicle/item inoperable, loss of primary function. Customer very dissatisfied.	8
High	Minor disruption to production line. 100% of product may have to be sorted and a portion (less than 100%) scrapped. Vehicle operable, but at a reduced level of performance. Customer dissatisfied.	7
Moderate	Minor disruption to production line. A portion (less than 100%) of the product may have to be scrapped (no sorting). Vehicle/item operable, but some Comfort/Convenience item(s) inoperable. Customers experience discomfort.	6
Low	Minor disruption to production line. 100% of the product may have to be reworked. Vehicle/item operable, but some Comfort/Convenience item(s) operable at reduced level of performance. Customer experiences some dissatisfaction.	5
Very Low	Minor disruption to production line. The product may have to be sorted and a portion (less than 100%) reworked. Fit & Finish/Squeak & Rattle item does not conform. Defect noticed by average customer.	4
Minor	Minor disruption to production line. The production may have to be sorted and a portion (less than 100%) reworked. Fit & Finish/Squek & Rattle item does not conform. Defect noticed by average customers.	3
Very Minor	Minor disruption to production line. The production may have to be sorted and a portion (less than 100%) reworked. Fit & Finish/Squek & Rattle item does not conform. Defect noticed by discriminating customers.	2
Low	No effect.	1

**Table 2.1** Severity ranking of FMEA [33].

Probabillity of Failure	Possible Failure Rates	Ppk	Ranking
Very High:	≥1 in 2	≥0.33	10
Failure almost inevitable	1 in 3	≥0.33	9
High: Generally associated with	1 in 8	≥0.51	8
processes similar to previous processes that have often failed.	1 in 20	≥0.67	7
Moderate: Generally associated	1 in 80	≥0.83	6
with process similar to previous	1 in 400	≥1.00	5
processes which have experienced occasional failures, but not in major proportions.	1 in 2000	≥1.17	4
Low: Isolated failures associiated with similar processes.	1 in 15000	≥1.33	3
Very Low: Only isolated failures associated with almost identical processes.	1 in 150000	≥1.50	2
Remote: Failure is unlikly. No failure ever associated with almost identical processes.	1 in 1500000	≥1.67	1

# Table 2.2 Occurancy ranking of FMEA [33].

# **Table 2.3** Detection ranking of FMEA [33].

Detection	CRITERIA: Likelihood the Existence of Defect will be Detected by Process Controls Before Next or Subsequent Process, or Before Part or Component Leaves the Manufacturing or Assembly Location.	Ranking
Almost Impossible	No known control available to detect cause/mechanism of failure or the failure mode	10
Very Remote	Very remote likelihood current control will detect cause/mechanism of failure or the failure mode	9
Remote	Remote likelihood current control will detect cause/mechanism of failure or the failure mode.	8
Very Low	Very low likelihood current control will detect cause/mechanism of failure or the failure mode.	7
Low	Low likelihood current control will detect cause/mechanism of failure or the failure mode.	6
Moderate	Moderate likelihood current control will detect cause/mechanism of failure or the failure mode.	5
Moderately High	Moderately likelihood current control will detect cause/mechanism of failure or the failure mode.	4
High	Highlikelihood current control will detect cause/mechanism of failure or the failure mode.	3
Very High	Very high likelihood current control will detect cause/mechanism of failure or the failure mode.	2
Almost Certain	Current control almost certain to detect cause/mechanism of failure or failure mode.	1

# **3. EXPERIMENTAL STUDIES**

#### 3.1 Materials and Methods

As mentioned in previous sections polypropylene (PP) fibers were commonly used in lead acid batteries so as to increase the paste strength. However, it is reported that, the charge acceptance levels of the PP fibers became limited todays automotive requirements [3]. With this motivation, in this study, pristine CF and CF plated with Zn, Sn, Pb, as alternative fillers against PP, were prepared as the additives of negative pastes in batteries. PP (INCI GS YUASA) and CF (AKSA-CA TYPE-42) were purchased and used without any further process. In order to grow Zn films on CF via electroplating, **ZnCl<sub>2</sub>** based electrolyte (Temeka LLC), zinc electrolyte (Temeka LLC) and carbon fiber electrode holder (self-design) were used with configuration depicted in Figure 3.1.a. Sequentially, Sn acidic bath (ES/TINUX) were used as illustrated in Figure 3.1.b.

Finally, In order to plate the lead over CF, a copper layer was deposited, to act as a buffer layer of Pb deposition, by using  $CuSO_4$  based electrolyte as shown in Figure 3.1.c. So, lead was plated in a non-cyanide  $Pb(NO_3)^2$  electrolyte given in Figure 3.1.d. The tests and analyzes required for the investigation of the coating properties and the effects on lead-acid batteries were initially evaluated with FMEA study.

## **3.2 Design FMEA and Risk Assessment of Study**

Failure mode studies were applied to determine the possible risks of metal deposition and anodizing processes. The FMEA study details indicating the causes and effects of the failures were given in Table 3.1. To prevent these causes, preventive activities were determined. Scores were made for each failure mode and the highest priorities were defined. Failure mechanisms of the lead acid battery which directly affects the customer as the final product are crucial for the automotive industry. Therefore, DFMEA scores are mostly considered with high ranks for battery performance. According to Design FMEA control results, solution pH measurement, temperature and coating current controls should be performed during the coating process. The conductivity of the fibers after coating will be determined as this will affect battery performance tests. Normally, fiber resistance is expected to decrease. In this case, resistance of the fibers should be measured to determine the changing in conductivities. Battery performance tests were determined to find out the effects of coatings on the CF surface using representative cells. Water consumption tests were performed to examine the effect of different metals coated on CF surface on battery water loss performance. Before determination of water loss and cycle performance of the battery, capacity tests were conducted to determine the cells initial characteristics. Another performance effect is tested with the 50% depth of discharge test in which the number of charge-discharge cycles upto a 50% decrease in capacity recorded. The effect of the improvement of the battery plates on the battery life should be determined by 50% DOD test.



Figure 3.1 Electrodeposition process setup for a) CF/Zn b) CF/Sn c) CF/Cu d) CF/Cu/Pb structures

<b>Table 3.1</b> Design FMEA study for Coating and Battery Performa
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					2	CURRENT CONTROL				
NO	ITEM FUNCTION	POTENTIAL FAILURE MODE	POTENTIAL EFFECT OF FAILURE	SEVERTY (G	POTENTIAL CAUSE MECHANISM OF FAILURE	OCCURENCY	PREVENTION	DETECTION	DETECTION	RPN
1	Carbon fiber surface treatment	Unremoved polymeric surface on CF	Low quality coating	4	Wrong treatment chemical	2	Chemical property check	* pH control for Chemical *Visual Control for CF (SEM)	4	32
				4	Wrong pickling chemical	2	Chemical property check	* pH control for Chemical *Visual Control for CF(SEM)	4	32
				4	Low Temperature	2	Temperature Control during operation	* Thermometer for Chemical *Visual Control for CF (SEM)	7	56
				4	Less chemical exposure time	2	Exposure time definition	Visual Control for CF (SEM)	7	56

					Y	CURRENT				
NO	ITEM FUNCTION	POTENTIAL FAILURE MODE	POTENTIAL EFFECT OF FAILURE	SEVERTY (G	POTENTIAL CAUSE MECHANISM OF FAILURE	OCCURENCY	PREVENTION	DETECTION	DETECTION	RPN
2	Zinc Coating	Wrong metal coating	Increase water loss of battery	6	Coating solution impurity	2	Element check	*XRD analysis	4	48
		Less Coating Thickness	Carbon surface come out during battery running	4	Low temperature	3	Temperature check	* Thermometer for Chemical *Visual Control for CF (SEM)	7	84
				4	Low coating current	2	Coating current check	* Multimeter Check *Visual Control for CF (SEM)	7	56
				4	Low coating time	2	Coating time optimization	*Visual Control for CF (SEM)	7	56
				4	Solution decomposition	2	Coating solution check.	* pH control for Chemical *Visual Control for CF(SEM)	5	40

				Υ	CURRENT	CONTROL	1			
NO	ITEM FUNCTION	POTENTIAL FAILURE MODE	POTENTIAL EFFECT OF FAILURE	SEVERTY (G	POTENTIAL CAUSE MECHANISM OF FAILURE	OCCURENC	PREVENTION	DETECTION	DETECTION	RPN
3	Tin Coating	Wrong metal coating	Increase water loss of battery	6	Coating solution impurity	2	Element check	*XRD analysis	4	48
		Less Coating Thickness	Carbon surface come out during battery running	4	Low temperature	3	Temperature Check	* Thermometer for Chemical *Visual Control for CF (SEM)	4	48
				4	Low coating current	2	Coating current check	* Multimeter Check *Visual Control for CF (SEM)	7	56
				4	Low coating time	2	Coating time optimization	*Visual Control for CF (SEM)	7	56
				4	Solution decomposition	2	Coating solution check.	* pH control for Chemical *Visual Control for CF(SEM)	5	40

							CURRENT	CONTROL		
NO	ITEM FUNCTION	POTENTIAL FAILURE MODE	POTENTIAL EFFECT OF FAILURE	SEVERTY (G)	POTENTIAL CAUSE MECHANISM OF FAILURE	OCCURENCY	PREVENTION	DETECTION	DETECTION	RPN
4	Copper Coating	Less Coating Thickness	Inhomogeneous Lead coating	4	Low temperature	3	Temperature Check	* Thermometer for Chemical *Visual Control for CF (SEM)	4	48
				4	Low coating current	2	Coating current check	* Multimeter Check *Visual Control for CF (SEM)	7	56
				4	Low coating time	2	Coating time optimization	*Visual Control for CF (SEM)	7	56
				4	Solution decomposition	2	Coating solution check.	* pH control for Chemical *Visual Control for CF(SEM)	5	40

						(E)	CURRENT	CONTROL	Z	
NO	ITEM FUNCTION	POTENTIAL FAILURE MODE	POTENTIAL EFFECT OF FAILURE	SEVERTY (0	POTENTIAL CAUSE MECHANISM OF FAILURE	OCCURENC	PREVENTION	DETECTION	DETECTIO	RPN
5	Lead Coating	Wrong metal coating	Increase water loss of battery	6	Coating solution impurity	2	Element check	* ICP from Chemical *XRD analysis	4	48
		Less Coating Thickness	Copper&CF surface come out during battery running	4	Low temperature	3	Temperature Check	* Thermometer for Chemical *Visual Control for CF (SEM)	4	48
				4	Low coating current	2	Coating current check	* Multimeter Check *Visual Control for CF (SEM)	7	56
				4	Low coating time	2	Coating time optimization	*Visual Control for CF (SEM)	7	56
				4	Solution decomposition	2	Coating solution check.	* pH control for Chemical *Visual Control for CF(SEM)	5	40

					Υ	CURRENT	CONTROL	Z		
NO	ITEM FUNCTION	POTENTIAL FAILURE MODE	POTENTIAL EFFECT OF FAILURE	SEVERTY (0	POTENTIAL CAUSE MECHANISM OF FAILURE	OCCURENC	PREVENTION	DETECTION	DETECTIO	RPN
6	Battery Performance	Low Capacity	Low battery life	6	Low electrical conductivity of fibers	3	CF Resistance check.	Multimeter Control	6	96
				6	Low electrical conductivity of plates	3	C20 > Theorical Capacity	50342-1:2015 EN C20 rate test	5	90
		High Water Loss	Low battery life	6	Impurity in electrolyte	2	W < 8g	50342-1:2015 EN Water Loss test	4	48
				6	Coated metals on CF	4	W < 8g	50342-1:2015 EN Water Loss test	4	96
		Low cycle life	Low charge efficiency	6	Low electrical conductivity of fibers	3	CF Resistance check.	Multimeter Control	6	96
				6	Low electrical conductivity of plates	3	Cycle > 80	50342-1:2015 EN 50%DOD test	6	96
			High battery internal resistance	6	Un proper contact Coated/anodized CF and Active Material	5	Cycle > 80	50342-1:2015 EN 50%DOD test	6	180
			High water loss	6	Coated metals on CF	3	Cycle > 80	50342-1:2015 EN 50%DOD test	4	72

### **3.3 CF Surface Treatment**

To create a highly conductive CF surface, desizing was applied to remove outer less conductive shell over the CF based on the similar procedures applied in literature. Jalel Kareem Ahmed et al. used Acetone and nitric acid for chemical pre-treatment [26]. Junfeng Ma et al. used acetone at room temperature for 72 h and then in nitric acid for 72h for cleaning CF sizing material. Although researchers applied pre-treatment to improve the quality of the composite process, the goal has been to increase the surface polarity by cleaning the polymeric surface on the fiber. With this process, they aimed to increase Van der Waals's bonding and hydrogen bonds [8]. Similarly, In this work, acetone and nitric acid were used to remove sizing material from the CF surface and then nitric acid used for etching CF surface to improve the surface adhesion. CF immersed in Acetone at 40°C for 2 hours, then the same CF dipped into nitric acid (~70%) at 40°C for 2h and the resulting surfaces physical aspects of the surfaces were inspected by scanning electron microscopy (SEM).

#### 3.4 Electrochemical Metal Deposition

In this study, Zn, Sn and Pb metal were deposited on the carbon fiber surface through simple two electrode electroplating processes as represented in Figure 3.1. The research is based on two main experimental steps, first, the preparation of modified carbon fiber steps includes electrochemical Zn, Sn and Pb coating on the CF steps and their structural and morphological characterization. The second is the evaluation of the battery performance step using modified CF as a battery component in 2V and application 50% DoD and water loss tests as given in Fig.3.2.

Process of preparing Zn, Sn and Pb coating on the surface of carbon fiber can be briefly described as follows: Zn and Sn electrode will be set as cathode and carbon fibers, set as anode. However, the situation for lead is slightly different, lead plating was done in two stages. The fiber surface was firstly coated with copper since lead cannot be coated directly on CF.



Figure 3.2 Flow chart illustration of experimental procedure.

## 3.4.1 Zn coating

Zn plate (99.9%) was set as an anode and desizing CF was set as a cathode in the two electrodes system. A commercial zinc bath containing 40 g L<sup>-1</sup> ZnCl<sub>2</sub>, 174 g L<sup>-1</sup> NH<sub>4</sub>Cl, 0.041 g L<sup>-1</sup> H<sub>5</sub>BO<sub>5</sub> and 1.0 ml brightener solution (pH<7), was used to deposits Zn film on CF under a DC current 2 A for 1 to 4 minutes at  $30 - 60^{\circ}$ .

#### 3.4.2 Sn coating

Sn plate (99.9%) and CF was set as an anode and cathode, respectively. Sn coating performed in  $30g SnSO_4$ , 100ml (98%)  $H_2SO_4$ , 30ml ES/TINUX, 0.5ml ES/TINUX 2 and 0.3ml ES/TINUX 3, operating at DC current 2.5 A at  $25^{\circ}C$  temperature. A pulse electrodeposition method, 15 s on and 10 s off, was used to provide continuous coating.

#### 3.4.3 Pb coating

In order to coat lead on the carbon fiber surface, the copper surface was initially coated to act as a buffer layer. Carbon fibers were subjected to copper electrocoating in electrolyte comprised of 1 M CuSO<sub>4</sub> and 0.5 M  $H_2SO_4$  using copper sheet anodes at 40°C. Electrodeposition current was 1 A for 2 min. Electrodeposition of Pb on CF/Cu surface was performed in a non-cyanide bath containing 0.1M Pb(NO<sub>3</sub>)<sup>2</sup> and 0.2M NaOH concentrations under currents from 0.01 to 0.05 A for 2 minutes.

# **3.5 Materials Characterization**

The surface morphology and crystallographic structure of Zn, Sn and Cu/Pb on CF surface were analyzed with scanning electron microscope (SEM) and x-ray diffractometer (XRD), respectively.

## **3.5.1 Scanning electron microscope (SEM)**

Scanning Electron Microscopy (SEM) is a test procedure that scans a sample with an electron beam to obtain an enlarged image for analysis. The method is also known as SEM analysis and SEM microscopy and is used very effectively in microanalysis and failure analysis of solid inorganic materials. Electron microscopy is performed at high magnification rates, produces high resolution images and accurately measures very small features and objects.

In the scope of this thesis, the microstructural observation of CF, coated CF surfaces (CF, CF/Zn, CF/Sn, CF/Pb) and active material crystals of battery electrodes after formation were carried out by using the Zeiss Sigma 300 VP instrument and Tescan Vega 3 UBS.

## 3.5.2 X-Ray diffraction (XRD)

X-ray spectrometry is one of the few techniques that can be applied to solid samples of various forms. Although most x-ray spectrometers are in laboratories, many are finding application in routine analyses for production and quality control and in specialized tasks. Growth in the capability and economy of microcomputer technology will enhance these applications. Many of these same principles, practices, and instrumentation developments are common to electron microscopy and electron microprobe analysis. Phase structures and the crystallinity of the samples were characterized via X-Ray diffractometer (Thermo Scientific ARL K-Alpha) Cu-K $\alpha$  irradiation ( $\lambda = 1.54$  Å) scanning between 20 of 10° and 70°. Analyses were performed by a scanning speed 0.1 and for 600 seconds.

#### **3.5.3 Electrical properties**

The main aim of the study is to use conductive modified fibers. In this reason, determination of CF, CF/Zn, CF/Sn and CF/Pb resistance is important to figure out the study beneficial effect. To determine this relationship, the resistance measurements of CF and surface modified fibers with 10 cm lengths were carried out using a multimeter (fluke 87-V).

# 3.6 Battery 2V Cell Preparation and Tests

Commercial lead acid batteries have 6 cells and each cell has a fully charged potential around 2.1 volts (Fig.3.3). The six cells are connected in series to produce a fully charged battery of around 12.6 volts. Therefore, in the thesis, battery performances were tested using one cell.



Figure 3.3 A comercial battery with lead plates and cell connections

#### 3.6.1 Electrode preparation

Positive and negative plates were prepared with ball-mill leady oxide using the Inci GS Yuasa paste formulas. The positive plates were prepared as in the serial production. Negative pastes were prepared using modified CF/Zn, CF/Sn, CF/Pb instead of non-conductive PP fibers as listed in Table 3.2. In addition to fibers, 0.7 - 1.0 wt.% barium sulphate, 0.15 - 0.18 wt.% lignosulphonate, 0.15 - 0.18 wt.% carbon and carbon dry mixed PbO prior to water and sulfuric acid. 10-12.5 wt.% of water was added over several minutes while mixing, followed by 5.5 - 7.5 wt.% of 1.4 specific gravity sulfuric acid (Merck grade) slowly dripped into the mixture. In the next step, the pastes were applied on the Ca-Sn lead grids. Curing was performed in an oven at 55°C temperature and higher humidity (70%) for 24 h. Then electrodes were dried at 60°C for 12 h.

	Paste1	Paste2	Paste3	Paste4	Paste5
Fiber type	PP	CF	CF/Zn	CF/Sn	CF/Pb
Amount % (wt)	0.11	0.11	0.11	0.11	0.11

Table 3.2 Fiber types and amounts for each paste.

## 3.6.2 2V cell preparation

A range of cureless plates were assembled into 2V cells as 4 positive plates surrounded by 4 negative plates. Positive active material (PAM) and Negative active material (NAM) utilizations were calculated as seen in Table 3.3.

The cured negative plates with CFs were produced as previously mentioned. The positive and negative plates were separated using Polypropylene separators.

Plate pices	Positive& Negative Grid (g)	Dry PAM (g)	Dry NAM (g)	PAM/ NAM	PAM Utilization (%)	NAM Utilization (%)	Capacity (Ah)
4/4	52	80	65	1.23	40	42	30

The cells were placed horizontally in a rigid plastic battery container with a rigid plastic lid compression plate on top (Fig. 3.4). After plates were placed into plastic container, acids were filled to each cells for charging. The cells were charged due to ampere hour according to design requirements as seen Table 3.4.



Figure 3.4 Images of cells after plates were placed in a rigid battery container.

#### 3.6.3 Capacity ability tests

2V cells prepared with different CF and modified CF negative electrodes were discharged with constant 1.5 A until reached the cut-off of 1.75 V. This test is also known as C/20 capacity to measure the low discharge rate performance.

After tests were finished, the cells were recharged for 24h at 2.67 V with a current limit of 0.25 A. Test was carried out in a water bath at  $25 \pm 2^{\circ}$ C Float currents were measured during the whole recharge [34].

	time	current	Ah	Ah%
Step No	min.	Amp.	_	
1	25	2.0	0.8	0.4%
2	35	5.7	3.3	1.7%
3	25	7.1	3.0	1.5%
4	395	10.0	65.8	34.1%
5	30	0.00	0.0	0.0%
6	960	7.5	120.0	62.2%

Table 3.4 Formation programs of batteries.

#### 3.6.4 50%DOD tests

Accelerated cycling is the most commonly used procedure and is the basis of most existing standards [35]. DOD tests are conducted according to TS EN 50342-1:2016 standards;

After capacity testing the cells are to be connected to a device whereby, they undergo a continuous series of cycles, each cycle comprising:

**Table 3.5** 50% DOD cycle test parameters [35].

Test Temperature	Charging voltage	Constant current	Charging ratio
40 ± 2 °C	15.6 V	In	1.08

- a. The battery shall be placed in a water bath and maintained at a temperature as state in Table 3.5.
- b. Discharge the battery for 2 h with a constant current of I = 5 In. Cut off criterion for this test is the voltage during the discharge. If it drops below 10,5 V the test shall be terminated.
- c. As first step recharge the battery for maximum 5 h with a constant voltage and a current limitation of 5 In. Record the recharged capacity Crch (Ah) during the charging.
- d. The voltage during discharge is above the limit or until the number of cycles of the requirement level is reached as defined in Table 3.6 [35].

Requirement Level	Number of Cycle
E1	80
E2	150
E3	230
E4	360

 Table 3.6 Endurance in cycle test - requirement levels[35].

#### 3.6.5 Water loss tests

Batteries used should necessarily be with low maintenance characteristics, a procedure for assessing the topping up the requirement of a distilled water has been included. It is recognized that the loss of water from the battery is a function of several factors like alloy composition, electrolyte volume, venting system, ambient temperature, the overcharge current and the charging system (with good voltage regulation). These are considered while designing the test procedure. Water Consumption test will be conducted according to TS EN 50342-1:2016 with the following steps;

- a. The battery, after being charged, shall be cleaned, dried, and weighed, in grams, with an accuracy of  $\pm 1$  g for batteries. The initial weight shall be recorded.
- b. The battery shall be placed in a water bath and maintained at a temperature of  $+60^{\circ}C \pm 2$ .
- c. The battery shall be charged at a constant voltage of 14,40 V  $\pm$  0,05 V (measured across the battery terminals) without adding water for 42 days as stated in the requirement.
- d. Immediately after this overcharge period, the battery shall be cleaned, dried and weighed under the same conditions.
- e. The weight loss is calculated [36].

#### **3.6.6 Battery stratification analysis**

A common failure mode during the 50% DoD cycling test is the acid stratification and generally the bottom side of plates active material are shedded because of the higher acid density. Sulfuric acid is consumed and water is produced on the positive plates during discharging of flooded batteries. Thus, low acid concentration is formed on both types of plates. High acid density acid accumulates the cell bottom and low-density acid accumulates top of the container [37; 3]. Dominik Schulte et. al. described the

'Stratification index' in order to quatity acid stratification and compare different batteries and battery designs. In their study, they the lower and upper acid densities were measured and the index was calculated with using the formula below (3.1) [38];

$$SI = \frac{\rho \text{ bottom part} - \rho \text{ top part}}{0.84 \text{ g cm}^{-3}} X \ 100\%$$
(3.1)

The value, With 0.84 g. cm<sup>-3</sup>, is a difference in the specific gravity between concentrated sulphuric acid and water. The index is zero if the electrolyte has the same density at the bottom and upper sides. If there is 100% concentrated acid at the bottom and pure water at the top. Stratification index (SI) will be in the range of 0% and about 35% [38]. Based on this approach, acid densities were measured form upper, middle and bottom side of the cell container using Anton Par DMA-35 portable desnity meter and the SI values of the cells were calculated after 50% DoD test. Different regions of the plate have different degree of sulfation due to the regional change of acid density in the battery acid. These sulfation amounts were determined from the upper, middle and lower part of the plate.

Sulfate analysis from plate; 10 g battery paste which is called sample was taken and put to moisture anaylzer in order to get rid of moisture of sample. After that, the sample was put into the beaker. 100 ml Na<sub>2</sub>CO<sub>3</sub> was added and stirred gently and the solution was boiled for 20 minutes. At the end of the boiling process, solution was taken to the volumetric flask (500ml) and adding some water. After this, the solution was filtered and it was re-heated. Concentrated HCl was added to neutralize the solution. While the solution was boiling, 40 ml BaCl<sub>2</sub> was added. After waiting for a while, the solution was filtered. Precipitate was taken into the crucible and kept in the oven at 600-700°C for 3 hours. Lastly, remain ash content on crucible was measured and the amount of BaSO<sub>4</sub> was calculated.

# 4. RESULTS AND DISCUSSION

# 4.1 Morphological Analysis

Prior to the electrodeposition process, the surfaces of the CFs were prepared by removing the less conductive polymeric coating on the surface. In figure 4.1 the SEM images of the sized and desized CFs were given. The images showed that there are significant changes on the surface of carbon fiber after desizing procedure. After acetone application fiber surface roughness increased. The studies of Jaleel Kareem Ahmed et. all showed that treatment with nitric acid created better modification on the CF surface and it was demonstrated that there was significant decrease in diameter [26]. Similar to their study, it was determined that fiber diameter was reduced by approximately  $2 - 3 \mu m$  with a nitric acid application.

#### 4.1.1 Microstructure and morphology analysis of fibers

SEM micrographs of the Zn electrodeposited on the fiber surfaces were presented in Fig. 4.2, 4.3, 4.4. In literature, it was stated that the most suitable coating temperature in acidic zinc baths was 35°C. In contrast, at temperatures of 21°C and below, it is mentioned that the bath crystallizes, and different additives are required [29]. For this reason, deposition process was conducted in the range of 35-50°C for optimization. Under a constant current regime (2A), deposition duration determined as 2 and 4 minutes.



**Figure 4.1** SEM images of bare CF in 12000 magnification a) without desizing, b)desized with Acetone  $40^{\circ}$ C for 2h b) desized with Acetone  $40^{\circ}$ C for 2h and then nitric acid at  $40^{\circ}$ C for 2 h.



**Figure 4.2** SEM images of electrodeposited Zn on CF surfaces at 35°C 2A 2 min. in several magnifications a) 2000X, b) 2500X.



**Figure 4.3** SEM images of electrodeposited Zn on CF surfaces at 35°C 2A 4 min. in several magnifications a) 500X, b) 5000X.



**Figure 4.4** SEM images of electrodeposited Zn on CF surfaces at 50°C 2A 2 min. in several magnifications a) 500X, b) 4000X.

Sample ID.	Current	Temp.	Time	DAD*	Coating quality**
	А	°C	min.	μm	
35CFZn22	2	35	2	7-14	NC
35CFZn24	2	35	4	6-27	NC
50CFZn22	2	50	2	12-17	С

Table 4.1 Coating parameters and evalution of the CF/Zn

\*DAD : Diameter after deposition, \*\*C : continuous, NC : non-continuous

Results also showed that the coating time and temperature would directly affected the coating quality. As shown in Fig. 4.2, 4.3, 4.4 within the same current (2A), higher deposition time 4 minutes cause to inhomogeneous coatings and diameter after deposition was changed from 6 to 27  $\mu$ m. Nevertheless, on further increasing the temperature from 35 to 50°C, Zn deposits were obtained homogenously. Uncoated CF surfaces were observed (Fig. 4.3 and 4.4) in lower coating temperature since the deposition energies could not be enough.

Continuous Zn coating could be formed in situ on the carbon fiber surfaces (Fig. 4.4) only when the temperature increased up to  $50^{\circ}$ C. At the end, the 50CFZn22 samples with continuous nature, were decided to be used for 2V cell assembly. Electrodeposited Sn on the CF surface's SEM images were shown in figure 4.5. The constant current was used 1A to 3A and different deposition times as 0.5, 1.0 and 2.0 minutes were applied at  $25^{\circ}$ C.



**Figure 4.5** SEM images of electrodeposited Sn on CF surfaces in 2000X magnifications a) 25CFSn12; 1A and 2.0 min., b) 25CFSn21; 2A and 1.0 min., c) 25CFSn205; 2.5A and 0.5 min.

The images after current applied 1A for 120 seconds showed that tin was not coated on the surface. Therefore, the current was applied from 1A to 2.5A. Coating times were set

as 60 s and 120 s. for the tin coating optimization, coating times were changed under DC current 2.5 A at  $25^{\circ}$ C temperature. Pulse electrodeposition method was used for continuous coating on CF. Ashutosh Sharma et. al. studied pulse electrodeposition of Sn on copper substrates and results showed that tin deposits were smooth and uniform at lower current densities (0.1-0.3 A/cm<sup>2</sup>). On the other hand, increasing current densities increase the porosity and roughness of coating [39]. In this study, the pulse electrodeposition was applied as 15 sec on and 10-sec dwell route so as to deposit films represented in in figure 4.6, 4.7 and 4.8.



**Figure 4.6** SEM images of electrodeposited Sn on CF surfaces at 25°C 2.5A 30s. in several magnifications a) 5000X, b) 15000X.



**Figure 4.7** SEM images of electrodeposited Sn on CF surfaces at 25°C 2.5A 15s x 3 in several magnifications a) 5000X, b) 15000X.



**Figure 4.8** SEM images of electrodeposited Sn on CF surfaces at 25°C 2.5A 15s x 4 in several magnifications a) 5000X, b) 15000X.



**Figure 4.9** SEM images of electrodeposited Sn on CF surfaces at 25°C 2.5A 15s x 5 in several magnifications a) 5000X, b) 15000X.

The SEM images of the CF/Sn were shown in Fig. 4.6.a and higher magnification SEM micrograph of the Sn-coated carbon fibers marked as 'b' are presented in Fig. 4.6 b. The Sn non-continuous coating on CF was determined at 30 second deposition time. At lower magnifications, uncoated fiber surfaces were observed, and thickness measurements showed that coating thickness varied within 6-8 µm at higher resolutions. When the other studies were examined, it was found that it was similiar to the tin coating images made on the carbon surface [40]. The pulse electrodeposition method was used to improve the non-continuous coating properties on the fiber surface. As it was seen in Figure 4.7, it

was determined that the coating was more homogeneous, smooth and continuous on the surface when 3 times dwell was applied. The diameter after deposition was determined as 7-9  $\mu$ m. When the repeated coating current application is increased, there was no significant change in coating morphology and thickness (Fig. 4.8 and 4.9). As it was clearly seen in Table 4.2, the change in diameter after deposition was not more than 1-2 microns depends on the dwell times of pulse electrodeposition.

Sample ID.	Current	Temp.	Desposition duration	Dwell Times	Dwell duration	DAD*	Coating Quality**
	А	°C	S		S	μm	
25CFSn2.5-30	2.5	25	30	0	10	6-8	NC
25CFSn2.5-15x3	2.5	25	15	3	10	7-9	С
25CFSn2.5-15x4	2.5	25	15	4	10	8-10	С
25CFSn2.5-15x5	2.5	25	15	5	10	8-10	С

Table 4.2 Coating parameters and evalution of the CF/Sn

\*DAD : Diameter after deposition, \*\*C: continuous, NC: non-continuous

The lead coating was formed on the fiber surface in two steps. In order to coat the lead on the fiber surface, copper was firstly coated. Copper is generally preferred as a substrate for coating applications since it increases the electrical conductivity, fills the gaps on the surface and is easy to coat. In some studies, in order to improve the battery performances, researchers used copper honeycomb electrodes. They coated copper on carbon surfaces before coating lead-tin alloy [41].

In the present study, the coating of lead firstly tried without substrate and coating could not be deposited. Therefore, the surfaces were coated with copper before the lead coating. The copper coating was applied at 1A and 40°C. It was previously expressed that higher bath temperature enhanced the electrical conductivity due to thermal acceleration of anion and cation ions in the electrolyte [42]. The deposition duration was set as 30, 60 and 120 seconds. SEM images as shown in figure 4.10, 4.11 and 4.12. In regard to images the efficient deposition duration was determined as 120 seconds. The CF surfaces had continuous copper deposition and these parameters were decided to use for copper coating before lead electrodeposition. Jiaqi Ni et. al. studied to plating copper on fiber surfaces in an acidic copper bath. Different coating currents between 1 and 5mS/cm<sup>2</sup> were conducted and the coating times were 5 minutes to 30 minutes. The results showed that increasing coating time leads to the homogenous coating at low current densities [42].



**Figure 4.10** SEM images of electrodeposited Cu on CF surfaces at 40°C 1.0A 30s in several magnifications a) 1000X, b) 2500X.



**Figure 4.11** SEM images of electrodeposited Cu on CF surfaces at 40°C 1.0A 60s in several magnifications a) 1500X, b) 5000X.

When the previous studies were examined, there were no lead coating studies on carbon fiber surfaces. It was determined that for the lead coating on carbon and derivatives surface firstly metal-coated as a substrate such as copper, nickel, vs. K. Ji et al. produce electrodeposited lead foam grids as a lead-acid battery electrode and copper was coated as a substrate. The lead was coated on a copper surface in a fluoborate solution [43].

In this study, the copper was coated through the parameters of 1A, 40°C and 120s, and lead plating was performed on their surfaces as it was shown in Figure 4.12. The research on electrodeposition of lead showed that the common electrolytes are acid and based

chloride, bromide, iodide, nitrate, and fluoborate. In acidic coating, lead solutions is mainly present as  $Pb^{+2}$  but lead halide complexes can also be formed [44]. For this reason, it was decided to use alkaline lead nitrate and sodium hydroxide bath, since halides are accelerating the corrosion of lead and reduce battery life.



**Figure 4.12** SEM images of electrodeposited Cu on CF surfaces at 40°C 1.0A 120s in several magnifications a) 2000X, b) 10000X.



**Figure 4.13** Electrodeposited Pb coated CF surfaces SEM images at 30°Cand 4 min. a) coating current 0.1 A 2800X, b) coating current 0.1 A 5000X

SEM images of the lead coating on CF/Cu surfaces were depicted in Fig. 4.13, 4.14 and 4.15. The electrodeposition was conducted with current between 0.1 to 0.3 A at 30°C for 4 minutes. The SEM images showed that increasing coating current affected coating quality. It was determined that the electrodeposited lead had good contact with the copper

substrate in 0.3 A coating current according to fig. 4.15 a. and b. The flaky structures were clearly seen in these images.



**Figure 4.14** Electrodeposited Pb coated CF surfaces SEM images at 30°C and 4 min. a) coating current 0.2 A 3200X, b) coating current 0.2 A 5000X



**Figure 4.15** Electrodeposited Pb coated CF surfaces SEM images 30°C and 4 min. a) coating current 0.3 A 2500X, b) coating current 0.3 A 5000X

The rough surface of the copper coating as shown in figure 4.12 made it difficult to get continuous coating of lead during the lead electrodeposition process [43]. If the coppers' non-continuous coated surfaces were exposed to the acidic electrolyte due to the insufficient coating of lead, then hydrogen evolution would be inhibited the electrochemical reactions of NAM during charge and discharge cycles. The diameter after deposition of copper and lead-coated carbon fiber was measured by using the best coating

results in given Fig. 4.10 and 4.13. Diameter after depositions were given in Table 4.3. Copper coated CF diameter was measured 12  $\mu$ m and Lead coated CF dia. was measured 20  $\mu$ m. In this case, CF diameter that was decreased from ~ 7  $\mu$ m to ~ 5  $\mu$ m after etching with nitric acid, increased up to 12  $\mu$ m with coating copper and ~ 20  $\mu$ m with lead coating. Increasing DAD means that copper coating thickness was around 7  $\mu$ m and lead coating thickness was around 8  $\mu$ m.

Sample ID.	Current	Temperature	Desposition duration	DAD*	Coating quality**
	А	°C	Min.	μm	
40CFCu1-2	1.0	40	2	10 - 12	NC
30CFPb0.3-4	0.3	30	4	12 - 20	NC

Table 4.3 Coating parameters and evalution of the CF/Cu and CF/Pb.

\*Diameter after deposition, \*\*C:continuous, NC:non-continuous

#### 4.1.2 Structural analysis of fibers

Crystalline structure and phases of the coated samples named CF/Zn, CF/Sn and CF/Pb were determined by examining the x-ray diffraction (XRD) patterns. XRD patterns of CF/Zn samples were given in figure 4.16. Zn metal on CF surfaces exhibit peaks at 2 $\Theta$  angles of 36.29, 38.99, 43.22, 54.32 and 70.63 corresponding to the (d<sub>002</sub>), (d<sub>100</sub>), (d<sub>101</sub>), (d<sub>102</sub>) and (d<sub>110</sub>)spaces, respectively (JCPDS file no. 01-087-0713). And it was clearly detected that amorphous carbon was located at around 26.5.



Figure 4.16 XRD analyses of the Zn Coated CF samples (CF/Zn).

Figure 4.17 showed the XRD patterns of CF/Sn samples. The XRD peaks were observed at 2 $\theta$  angles and spaces of 30.63 (d<sub>200</sub>), 32.01 (d<sub>101</sub>), 43.86 (d<sub>220</sub>), 44.89 (d<sub>211</sub>), 55.33 (d<sub>301</sub>), 62.52 (d<sub>112</sub>), 63.77 (d<sub>400</sub>), 64.57 (d<sub>321</sub>), 72.40 (d<sub>420</sub>) and 73.15 (d<sub>411</sub>) coincide with the JCPDS: 01-089-2761 which correspond to crystal structure of tin. And very small amorphous carbon peaks were determined at around 26.5.

This pattern showed that coating was completely continuous and highly crystalline over the carbon fiber. Similar to Sem images, Sn peaks in XRD analysis clearly supported the quality of Sn deposition.



Figure 4.17 XRD analyses of the Sn Coated CF samples (CF/Sn).

Copper and lead peaks were included in the XRD analysis taken after lead coating. Because copper coating was applied to CF surfaces before lead coating. XRD patterns of CF/Pb samples were given in figure 4.18.Lead metal peaks at 2 $\Theta$  angles of 31.70, 33.28, 35.74, 56.29, and 61.16 corresponding to the (d100), (d002), (d101), (d110) and (d110) spaces, respectively (JCPDS file no. 00-023-0345). Other metal copper peaks peaks were observed at 2 $\theta$  angles and spaces of 43.31 (d111), 50.44 (d200), 74.12 (d220) and 89.93 (d311) coincide with the JPDS values (PDF Card No: 01-089-2838) which correspond to crystal structure of copper. In convenience to the SEM results, it can be expressed that lead deposition was not continuous and including amorphous features.



Figure 4.18 XRD analyses of the Pb Coated CF samples (CF/Pb).

#### 4.1.3 Resistance measurement of electrodeposited fibers

Although carbon fibers, thanks to their graphitic structure, have a degree of conductivity, they are not highly conductive as metals. The main focus of this research is to create higher conductivity in the battery structure. With this motivation, CF and coated CF's electrical resistance was measured using a multimeter and 10 cm 12K fiber's electrical resistance were given in Table 4.4.

Sample ID.	Mean Resistance	Std. Dev.
	Ohm /10cm	±
CF without desizing	3.81	0.12
CF with desizing	3.75	0.08
50CFZn22	1.57	0.11
25CFSn2.5-15x3	2.11	0.16
30CFPb0.3-4	2.76	0.08

Table 4.4 Resistance measurement of desized and coated fibers.

There were no significant differences in without desizing CF and with desizing CF resistance measurements. However, it was determined that the coating did not adhere to the surface in the non-desing fiber coating. For this reason, the plastic coating on the fiber

surface was cleaned. Kang et al. Coated Cu and Ni metal on the carbon fiber surfaces. They examined the contribution of metal coatings to fiber resistance. As a result, they found that metal coating on the fiber surface increased the conductivity of the carbon fiber [45]. In the previous study, the resistivity of CF is found at  $3.75 \pm 0.08 \text{ m}\Omega/10$ cm. Without removing the polymeric coating from CF, the resistance was measured  $3.81 \pm 0.12$ m $\Omega$ /10cm. No differences between measurements showed that the tip of the multimeter probe was applied to the fibers with a certain pressure, it showed that the polymeric structure on the surface was deformed and there were no significant differences. Resistance measurements of Zn, Sn, and Pb coated fibers were changed in direct proportion with the metal conductivity given in the literature [46]. According to literature, when resistance values were put in order from lower to higher, Copper, Zinc, Tin and Lead respectively. Zinc coated CF resistance was measured as the highest conductivity with  $1.57 \pm 0.11 \text{ m}\Omega/10\text{cm}$ . When fiber surfaces were coated with tin resistance was determined as 2.11  $\pm$  0.16 m $\Omega$ /10cm. And although the metal with the highest conductivity among these metals was copper, CF/Pb resistance was measured  $2.76 \pm 0.08$ m $\Omega$ /10cm because of the lead coating on copper.

## 4.2 Battery Electrode Analysis

Electrodes produced with and without modified carbon fibers are cured after pasting to the Pb-Sn-Ca grid. Moistures and temperatures were monitored during curing and the figure was given in 4.19.



Figure 4.19 Curing temperature and humidity graph of Lead-Acid Battery plates.

The structure of the active material was important to the performances of a battery's capacity and cycle life. Hence, the morphology of the crystal structures in the plates was checked by SEM to investigate the effect of modified carbon fiber additives on plate structure. The crystal phase composition of the paste varies during operation depending on the amount of  $H_2SO_4$ , the additive of the expander and the curing [47]. Curing provides crystalline structure to the active material and during formation, the microcrystalline structures transform as a skeleton. Curing allows the plate to form the crystal structure and pore structure in the active material. Curing is generally performed in temperature and humidity controllable chambers so that temperature and humidity are independent of the seasons [14]. In this study, paste recipe, expander additive amounts and curings were used the same in all electrode production.

The paste for negative battery plates had 3BS, PbO and small amounts of Pb after curing. The basic lead sulfate is partially reduced to  $PbSO_4$  and Pb forms during formation [3]. In Fig.4.20, the SEM morphology of the negative active materials showed that a compact structure built by small lead sulfate particles. No larger lead sulfate crystals were observed, and the crystals were homogeneous throughout the plate. There were no significant differences in the plate crystal structures. It has been found that the adding of polymeric fiber, carbon fiber, and modified carbon fiber did not affect to the crystal structure after curing.

The same positive plates were used in preparation of the battery cells to eliminate the variations. The positive electrode crystal structures should also be in a 3BS structure form. Otherwise, the batteries losses the capacity and cycle life performances. The positive plate crystal morphology used in all cells were given in Figure 4.21. The paste for the positive plates consists of 3BS, PbO, and Pb plus small amounts of 1BS, or of 4BS, PbO and Pb. These compounds are oxidized to  $PbO_2$  during formation [3]. As it was shown in the figure, the positive plates consisted the 3BS structures which is between 3 and 5 µm length. It was enough crystal structure for good battery charging performance.



**Figure 4.20** Microstructure of NAM with adding 0.11% a)PP fiber, b) CF, c) Zn Coated CF, d) Sn Coated CF, e) Pb Coated CF.



Figure 4.21. Microstructure of Positive Electrode a) 5000X and b)10000X

# 4.3 Battery Performance Test Results

#### 4.3.1 Capacity ability

2V cells with 4 positive plates surrounded by 4 negative plates were conducted to discharge test. The discharge studies were carried out at the C/20 rate with 1.5 A until the cut-off of 1.75 V was reached. The discharge capacity trend of battery cells were presented in Fig. 4.22.



**Figure 4.22** The 20 h rate curve of cells manufactured by PP, CF, CF/Zn, CF/Sn, CF/Pb. As clearly indicated in the literature, the battery capacity is based on the  $PbSO_4/PbO_2$  conversion in the positive electrode. In order to achieve high capacity of the

negative plates, the discharge processes should involve not only the surface of the NAM but also layers from its volume [3]. Additives added to the negative active material can affect battery capacity. In a study with the addition of sodium sulphate to the negative active material, additions of 0.5 to 4% were found to cause a reduction in the discharge capacity of 20h [48]. But in this study, the discharge data for CF and coated CF added cells had no obvious differences. The capacity results changed between 37.2 and 38.2 as it was shown in Table 4.5. All cells voltage curves reached the end of voltage 1.75 V at a very similar time around 25h. According to this result, it was determined that there was no difference in battery discharge capacity when CF and coated CF's were used instead of PP.

#### 4.3.2 Water consumption

Water Consumption performance of 2V cells were assessed using a charge/discharge regime designed to accelerate the battery failure. Water loss is functioning of the lead acid battery is possible thanks to the high over-potentials of oxygen evolution at the lead dioxide electrode and hydrogen evolution at the lead electrode.

Impurities are introduced in the battery with the materials for its production, contaminants may proceed at lower over-potentials and leading to increased water loss [3]. Thus, water loss tests were performed, and the test results were given in Table 4.5.

Cell No.	Capacity (Ah)	Water Loss (g/Ah)
Cell 1- PP	38.2	4.49
Cell 2 - CF	38.1	5.47
Cell 3 – CF/Zn	38.8	5.35
Cell 3 – CF/Sn	38.2	4.26
Cell 3 – CF/Pb	37.2	4.43

**Table 4.5** Water Compsumptions of the Cells

When the water loss results were evaluated, the cells containing CF and CF/Zn were determined to be 5.47 and 5.35 g/Ah, respectively. It can be stated that the water loss of these cells were close to each other. The water loss of the PP fiber cells were observed 21% lower and was 4.49 g/Ah. Likewise, the water loss of CF/Sn and CF/Pb fiber doped cells is approximately 21% lower than CF. Water loss values were 4.26 and 4.43 g/Ah,
respectively. According to water loss test results, CF and CF/Zn added cells were lost approximately 21% more water. Water loss is related with reactions that could place on the negative plate are the following steps; i) reduction of PbSO<sub>4</sub> to Pb, ii) oxidation of Pb to PbSO<sub>4</sub> are the reaction that is mainly produced during the charge and discharge, and iii) reaction is related to Hydrogen Evolution Reaction (HER). When the hydrogen evolution occurs the cells charging efficiency is low since part of the energy is spent in reducing the protons to hydrogen. This process causes water loss increment and it leads to the consequent increase of the sulphuric acid density and, thus the increase of the positive plates passivation [37]. On the other hand, stratification is reduced by providing acid mixing with some gassing in the cell. The effect of this situation will be figured out in the PSoC cycle test, that was, in the continuous charge-discharge cycle.

#### 4.3.3 50% DOD tests

In order to know the behavior of the different Carbon Fibers during PSoC operation conditions, a 50% DoD cycling test was performed. It is known that an accelerated life test to figured out the behavior of the battery in the field after years usage. The negative plates are not charged efficiently when the cells are working in these PSoC [37]. For this reason, 50% DoD test was carried out by adding carbon fiber and coated carbon fibers to the negative active material in order to increase negative plate efficiency. Cycle numbers and end of voltages of each cell were given in Figure 4.23.



Figure 4.23 End of voltages of cells manufactured by PP, CF, CF/Zn, CF/Sn, CF/Pb.

The control PP added cell just reached up the 117 charge-discharge cycle. The highest cycle life was attained by the cell with a negative electrode containing CF, namely 176 cycles, and by that with Zn coated CF fiber, namely 164 cycles.

The number of cycles of CF/Sn and CF/Pb added cells were higher than the PP added cell. The number of cycles of cells reaching 1.75 V end of voltages were 140 and 146, respectively.

Teardown analysis was performed on the cells to explain different cycle numbers with different negative additives and stratification formations were examined. Acid densities were measured from the top, middle and bottom of the cell after the test was completed to investigate the causes of the failure as it is seen Table 4.6. Based on SI index approach, the SI values of the cells were calculated after 50% DoD test. In CF and CF/Zn added cells, the SI value is around 6%, indicating that the acids were mixed more since the SI values of other cells were between 14-17%.

The positive plates get increasingly passivated at acid concentrations higher than 1.280 g. cm<sup>-3</sup>. At higher H<sub>2</sub>SO<sub>4</sub> concentrations, HSO<sub>4</sub><sup>-</sup> ions are absorbed in the lead dioxide zones on positive plates and block the active sides which where the electrochemical reactions of PbO<sub>2</sub> reduction proceed. At these sites in the lead dioxide zones the discharge reaction proceeds yielding PbSO<sub>4</sub> instead of Pb(OH)<sub>2</sub> which blocks the discharge process and eventually reduces the capacity of the positive plates [3].

	Acid Density ( <b>g</b> . <b>cm</b> <sup>-3</sup> )				
	РР	CF	CF/Zn	CF/Sn	CF/Pb
Cycles	117	176	164	140	146
Тор	1.224	1.280	1.280	1.235	1.230
Middle	1.321	1.298	1.294	1.312	1.306
Bottom	1.362	1.334	1.331	1.358	1.345
SI	16.42	6.42	6.07	14.65	13.69

**Table 4.6** Acid densities from top, middle and bottom side of the container

However, it is more correct to analyze negative plate sulfate at 50% DoD test since the positive active material structure is shedding by corrosion due to acid density. Therefore,

the cells were cut and sulfation on the negative plates was examined after acid density measurement as seen in Table 4.7.

			PbSO <sub>4</sub> %		
	PP	CF	CF/Zn	CF/Sn	CF/Pb
Cycles	117	176	164	140	146
Тор	7.65	3.22	3.10	6.78	8.45
Middle	18.76	6.78	8.16	17.32	18.16
Bottom	17.65	9.12	12.22	18.40	16.34

**Table 4.7** The number of cycles performed by every fiber added and negative plates lead sulfate concentrations.

It is clear from the Table 4.7 data that the failure mode during this test was the amount of irreversible lead sulfate that was found in the negative plate. When Table 4.6 and 4.7 data are related, acid concentrations in the middle part of the cells with CF and CF/Zn added have approximately 1.290 g. cm<sup>-3</sup>. Therefore, when the sulfate amounts in this region are analyzed, it is calculated that the sulfation in the negative plate with CF and CF/Zn added cells is 6.78% and 8.16, respectively. The sulfation in the middle and bottom of other PP, CF/Sn and CF/Pb added cells was determined that were higher than 15%. As it can be understood from here, it can explain that the CF and CF/Zn doped cell gives a longer number of cycles than other cells.

## **5. CONCLUSIONS AND FUTURE PLANS**

In conclusion, carbon fibers and metal electrodeposited carbon fibers added into negative electrodes instead of polypropylene fibers to increase the battery performance and lead acid battery performances were tested with using standart test method afforded as titled in the thesis.

Within this scope, DFMEA and risk assessment studies were applied to determine the controls and battery tests. The polymeric coating on the carbon fiber surface was removed and fiber surfaces etched for suitable coating adhesion. Afterwards, Zn, Sn and Pb metals were coated on the carbon fiber surface with different coating applications and optimization. Continuous and discontinuous metal coatings formed on the carbon fiber surface were observed in the SEM analysis. Optimization parameters of coatings were determined according to the coating images.

All the structural data obtained from XRD analysis for the CF/Zn, CF/Sn and CF/Pb point out that; the XRD patterns of the coatings showed that Zn and Sn metals were continuously coated on CF surfaces since amorphous carbon peaks intensities were very low. However, copper and amorphous carbon peaks were observed on CF/Pb coated surfaces.

The best continuous coating parameters for zinc coating determined from SEM images were 2A coating current for 2 minutes at 50°C. Diameter after deposition was measured 12-17  $\mu$ m. Pulse coating method was used for the continuous coating of the tin. The parameters obtained for continuous coating were realized at 25°C in 2.5 amp current application. For the continuous coating, the current was applied 3 times for 15 seconds. For lead coating, firstly copper coating was applied to the fiber surface by applying 1.0 A at 40°C for 2 minutes. After the copper coating was carried out, lead coating was applied to the surfaces in lead nitrate solution with 0.3 A for 4 minutes at 30°C. The fibers were coated with suitable coating methods and battery negative electrodes were prepared with adding fibers. Batteries were produced by adding PP, CF, CF/Zn, CF/Sn and CF/Pb

fiber to their negative electrodes and taken into performance tests. As for the battery test, The capacity test results, which are the most basic performance indicator of the battery, did not change much with PP fiber, CF fiber and metal coated CF adding into the negative plate. All cells voltage curves reached the end of voltage 1.75 V at a very similar time around 25h. The capacity results changed between 37.2 and 38.2 Ah. The water consumption was conducted at 60oC with a 14.40 constant voltage for 42 days. After this overcharge period, the battery water loss were calculated. When the water loss was compared PP, CF/Sn and CF/Pb added cells had approximately 21% less consumption then CF and CF/Zn cells. In the 50% DoD test, the best cycle life 176 and 164 was determined, respectively, as linked as water consumption with CF and CF/Zn added cells. The control cell PP added cell just reached the 117 charge-discharge cycle. The cycle number of CF/Sn and CF/Pb cells were140 and 146.

According to these results, the battery cycle gave the best performance in CF and CF/Zn added cells. However, cell water losses were higher. Higher cycle life of cells was associated with acid stratification. Acid mixing occurred in CF and CF/Zn cells due to gassing. Thanks to this, the life of the cells has increased. Water losses results showed that gassing was suppressed in other PP, CF/Sn and CF/Pb added cells. However, this reduction in gassing caused acid stratification during the charge-discharge cycle. For this reason, these cells had less cycle.

As denoted in the title of the thesis; Carbon fiber surfaces were coated successfully in proper coating baths. These modified carbon fibers are added into battery electrodes as an active mass additive. According to test results improvements were observed for battery cycle performances. These results indicate that this study has some innovations for the battery performance. The research presented in this thesis seems to have raised question that it has answered. There is a new of research arising from this work which should be pursued. The use of Carbon fiber in the electrode increased the cycle life of the battery while increasing the water consumption. It was understood that this was slowed down by surface coating, but it was determined that it decreased in life performance, the study of the amounts of modified CF in the next study may provide this optimization. More efficient optimization experiments can be done by using Design of Experiment method while examining the effects of modified CF additions into the electrode

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# **CURRICULUM VITAE**

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#### **EDUCATION**

PhD	Department of Materials Science and Engineering	Izmir Katip Celebi University	2020
Postgraduate	Department of Metalurgical and Materials Engineering	Dokuz Eylul University	2012
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#### WORK EXPERIENCE

Title	Department	Company	Years
R&D Supervisor	R&D	İnci GS Yuasa Akü San. ve Tic. A.Ş	2017 - Today
R&D Specialist	R&D	İnci Akü San. Ve Tic. A.Ş	2013 - 2017

#### **PRESENTATIONS & CONFERENCES**

- **Turhan Alper**, Erol Mustafa (2019). Zinc/Carbon Fiber Structures as Lead Acid Battery Mass Additives. 3rd International Students Science Congress (oral presentation).
- Metin Yurddaşkal, Serdar Yıldırım, Sinan Yılmaz, **Alper Turhan**, Erdal Çelik, (2015), "Fabrication, chractarization and industrial application of ceramic added

flame retardant polymeric nanocompasite materials" IX. Ceramic Congress with International Participitation, 26-28 November 2015, Afyonkarahisar/Turkey.

- Alper TURHAN, Sinan YILMAZ, (2013)." The Influence of Additives on Mechanical Properties and Corrosion Behavior of Lead Alloy for Lead-Acid Battery", International Electrochemical Congress, Poster presentation, 4-8 September, Konya/Turkey.
- Alper TURHAN, Buğra KARAHAN, İskender İNCE, Aylin ALBAYRAK, Ahmet ÇAKIR, (2012) "Synergism Caused by a Blend of Nitrite Based Inhibitors and Vaccinium Myrtillus Plant Extract on Boiler Steel in De-aerated Weak Acid" (Keynote) European Corrosion Congress 09-13 September, İstanbul/Turkiye.
- Buğra KARAHAN, Alper TURHAN, İskender İNCE, Aylin ALBAYRAK, Ahmet ÇAKIR (2011) "Inhibition of EN 10204 Steel in H<sub>2</sub>SO<sub>4</sub> by a Mixture of Hypericum Perforatum Plant Extract and Nitrite Based Inorganic Inhibitors" European Corrosion Congress 04-08 September, Stockholm/İsveç.
- Buğra KARAHAN, Alper TURHAN, İskender İNCE, Ahmet ÇAKIR, (2010). "İnorganik ve Bitki Esaslı Doğal Koruyucular Arasındaki Sinercik Etki" Uluslararası Korozyon Sempozyumu 06-09 October, Eskişehir/Turkey.

### PROJECTS

- TEYDEB, 1501, Project No: 3190885, (2019). Sürekli Döküm Teknolojisine Uygun Korozyon Özellikleri Optimize Edilmiş Pozitif Elektrot Alaşımı Geliştirilmesi. Project Leader: **Alper Turhan**, Reearchers; Berna Enginar, Özgür Çalık, Hasan Hassümer, Hürkan Çatalkaya, İlayda M. Yırtıcı.
- TEYDEB, 1501, Project No: 3181419, (2019). Mikrohibrid Akü Uygulamalarına Yönelik Modifiye Edilmiş Karbon Fiber Katkılı Elektrotların Geliştirilmesi. (Devam). Project Advisor: Mustafa Erol, Project Leader: Alper Turhan, Reearchers: Berna Enginar, Özgür Çalık, Hasan Hassümer, Hürkan Çatalkaya, Osman Demirci.
- TÜBİTAK 2209-B, (2018). Elektrokimyasal Olarak Modifiye Edilmis Karbon Fiberlerin Akü Katkı Malzemesi Olarak Kullanılması. Academic Advisor; Mustafa Erol, Industrial Advisor; **Alper Turhan**, Project Students; Feyzan Coşkun, Şerife Bakacak.
- TEYDEB, 1501, Project No: 3180036, (2018) Otomotiv sektöründe kullanılan bataryalara yönelik otomatik test, analiz ve raporlama sistemi geliştirilmesi.

Project Leader; Osman Demirci, Researchers; **Alper Turhan**, Hürkan Çatalkaya, Hasan Hassümer, Nurullah Tuncer, Sinan Aktaş.

- TEYDEB, 1501, Project No: 3140756, (2015). Yeni Teknoloji Negatif Izgara Alaşımlarının Mekanik Özelliklerinin Arttırılması ve Korozyon Davranışlarının İncelenmesi. Project Leader: **Alper Turhan**, Researchers: Sinan Yılmaz, Sevtap Aksoy, Berna Yıldız, Özgür Çalık, Hasan Hassümer, Gökhan Abacı, Mert İnç.
- SAN-TEZ, 1600.STZ.12-2, (2012). Akümülatör Sisteminde Kullanılan Polipropilen Bileşenlerinin Yanmaya Karşı Dirençli Polimerik Nanokompozit Malzemelerden Üretilmesi, Geliştirilmesi ve Endüstriyel Uygulaması. Project Advisor: Erdal Çelik, Industrial Advisor; Sinan Yılmaz, Researchers; Metin Yurddaşkal, Serdar Yıldırım, Alper Turhan, Gökhan Abacı.
- TEYDEB, 1501, Project No:3120465, (2012). Pozitif kurşun ızgaralarda mekanik özelliklerin arttırılması ve korozyon direncinin iyileştirilmesi, Project Leader; Sinan Yılmaz, Researchers: **Alper Turhan**, Sevtap Aksoy, Berna Yıldız, Veli Vatansever, Hasan Hassümer.
- SAN-TEZ, 00528.STZ.2010-1, (2010). İnorganik korozyon koruyucularla doğal organik bileşik karışımlarının imalat çeliğinin korozyonu üzerindeki sinercik koruma etkisi ve çevre dostu koruyucu geliştirme, Project Advisor: Ahmet Çakır, Researchers: **Alper Turhan**, Buğra Karahan, Aylin Albayrak.

#### **AWARDS and SCHOLARSHIPS**

- 1. Productivity Project Awards, Industry Ministry, (2015) "Product Development Category" **Second price**, Kurşun Asit Akülerde Negatif Izgara Alaşım Optimizasyonu Projesi.
- 2. Dokuz Eylul University, Department of Metalurgical and Materials Engineering (2010), **Top student of the department.**