

DEVELOPMENT OF ASYMMETRIC POLYSULFONE MEMBRANE FOR
THE APPLICATION IN TROPICALIZED LEAD ACID BATTERY

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Dedicated to *ma* and *abah*,
you are the wind beneath my wings.

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ABSTRACT

The objectives of this research are to develop asymmetric polysulfone membrane for the application in lead acid battery and to investigate the effect of fabrication conditions on the performance of the membrane-assisted lead acid battery and its morphology. The function of the membrane is to prevent electrolyte losses by minimizing the rate of vaporized electrolyte disposed into the atmosphere. Lead acid batteries in tropical countries normally face the problem of water decomposition, caused by the combine factors of the charge-discharge process and the heat accumulation caused by hot tropical climate and heat generated from engine compartment. This causes unpleasant setbacks such as corrosion of parts inside the car bonnet and having to top up the electrolyte whenever it reduces. The membrane will be functioning as a water-retaining device when applied onto the battery vent holes by delaying the permeation of hydrogen, oxygen and traces of water vapor during charge-discharge processes. Effects of polymer concentration and casting shear rate were investigated in order to produce the most suitable membrane. The prepared membranes were tested on lead acid battery during charging process to evaluate their performance in retaining electrolyte as well as minimizing pressure build up. Results showed that decreasing polymer concentration in casting solution decreases compactness of the polymer matrixes in the membrane structure, therefore decreases pressure build-up in battery casing during charging process. Increasing shear rate resulted in a decrease of skin layer thickness and in turn, lowers the pressure build-up during battery charging process. Membrane with 13 wt/wt % Polysulfone (PSF) and 87 wt/wt % of N-N-dimethylformamide (DMF) and at shear rate of about 233.33 s^{-1} was found to be the most suitable membrane to be applied on the maintenance free battery. At room temperature, the electrolyte losses of a membrane-assisted lead acid battery is about 6.67 grams per hour, while for conventional battery is about 26.67 grams per hour. During charging process at temperature about 80°C , membrane assisted lead acid battery can save up to 40% of electrolyte losses compared to the conventional battery. Membrane characterization using Scanning Electron Microscopy (SEM) and Raman Spectroscopy were also carried out to investigate the structure of the membrane and to differentiate the components of the permeated electrolytes from both membrane-assisted and conventional batteries. Based on SEM images, it can be observed that the membrane cast at the shear rate of about 233.33s^{-1} has the most suitable skin layer thickness. The membrane is permeable enough to minimize the pressure build up inside the battery and sufficiently selective enough to minimize the electrolyte losses. In the Raman spectrometer analysis, it was proven that with the application of membrane, the intensities of hydrogen and oxygen gases in the permeated vaporized electrolyte had been suppressed to about 50-60% and 10-30% respectively. Therefore this research is considered as a revolutionary step in the establishing a new age of maintenance free battery with the application of membrane technology into lead acid battery.

ABSTRAK

Objektif penyelidikan ini adalah untuk membangun membran polisulfona asimetrik bagi aplikasi pada bateri asid plumbum dan mengkaji kesan keadaan pembikinan terhadap prestasi bateri asid plumbum berbantu membran serta morfologinya . Fungsi membran adalah untuk menghalang kehilangan elektrolit dengan meminimumkan kadar pembebasan elektrolit teruwap ke atmosfera. Bateri asid plumbum di negara tropikal sering mengalami masalah kehilangan air yang terurai disebabkan oleh gabungan faktor proses cas-nyahcas dan pengumpulan haba disebabkan oleh cuaca panas tropika serta haba terjana daripada bahagian enjin. Ini mengakibatkan kesan sampingan seperti karatan alatan bahagian enjin serta terpaksa menambah air suling apabila takat elektrolit berkurang. Membran ini akan berfungsi sebagai peralatan penahan air apabila digunakan pada lubang bateri dengan memperlahankan kebolehtelapan hidrogen, oksigen dan wap air ketika berlakunya proses cas-nyahcas. Kesan kepekatan polimer serta kadar tuangan telah dikaji bagi menghasilkan membran yang paling sesuai untuk tujuan ini. Membran yang terhasil diuji pada bateri asid plumbum ketika proses pengecasan bagi menilai prestasi membran menghalang kehilangan air serta mengurangkan peningkatan tekanan dalaman bateri. Keputusan bagi ujikaji menunjukkan pengurangan kepekatan polimer dalam larutan tuangan mengurangkan kepadatan matriks polimer dalam struktur membran, oleh itu menurunkan peningkatan tekanan dalaman bateri ketika proses pengecasan. Peningkatan kadar tuangan menyebabkan pengurangan ketebalan lapisan kulit membran dan ini mengakibatkan pengurangan peningkatan tekanan dalaman bateri. Membran dengan formulasi 13 berat/berat % polisulfona (PSF) dan 87 berat/berat % N-N-dimetilformamida (DMF) dan kadar tuangan sebanyak 233.33 s^{-1} didapati paling sesuai bagi aplikasi pada bateri bebas penyelenggaraan. Pada suhu bilik, kehilangan air bagi bateri berbantu membran adalah sebanyak 6.67 gram per jam manakala bagi bateri konvensional adalah sebanyak 26.67 gram per jam. Ketika proses pengecasan pada suhu 80°C pula, bateri berbantu membran mampu mengurangkan 40% daripada kehilangan air berbanding dengan bateri konvensional. Pencirian membran menggunakan kemikroskopan elektron imbasan (SEM) dan spektroskopi Raman juga telah dijalankan bagi mengkaji struktur membran serta membandingkan komponen elektrolit teruwap dari bateri berbantu membran dan konvensional. Berdasarkan imej SEM, didapati membran yang dituang pada kadar tuangan sebanyak 233.33 s^{-1} menghasilkan ketebalan lapisan kulit paling sesuai. Membran ini cukup telap untuk meminimumkan peningkatan tekanan dalaman bateri serta mempunyai kememilihan yang sesuai untuk mengurangkan kehilangan air. Analisis Raman pula telah membuktikan bahawa dengan aplikasi membran, keamatan gas hidrogen and oksigen dalam elektrolit teruwap telah dapat dikurangkan sebanyak 50-60% dan 10-30%. Oleh itu, penyelidikan ini dianggap sebagai langkah revolusi dalam pembangunan bateri bebas penyelenggaraan dengan penggunaan teknologi membran dalam bateri asid plumbum.

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NOMENCLATURE

A	-	Surface area of flat sheet membrane (m^2)
C	-	Concentration ($\text{cm}^3(\text{STP})/\text{cm}^3$)
D	-	Diffusion coefficient (cm^2/s)
I		Current (Ampere)
k	-	Mass transfer coefficient
l	-	Membrane thickness (cm)
l_r	-	Pore length (cm)
p	-	Pressure (cmHg)
p_o	-	Atmospheric pressure (cmHg)
\bar{p}	-	Mean pressure (cmHg)
Δp	-	Transmembrane pressure (bar)
P	-	Permeability coefficient ($\text{cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$)
P/l	-	Pressure-normalized flux or permeability ($\text{cm}^3(\text{STP})/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$)
Q	-	Volumetric flow rate (L/h)
S	-	Solubility coefficient ($\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{cmHg}$)
T	-	Temperature (K)
V	-	Permeation velocity of product
α	-	Selectivity (dimensionless)
$\dot{\gamma}$	-	Shear rate (s^{-1})
i	-	Component i
j	-	Component j
T	-	Total

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CHAPTER 1

INTRODUCTION

1.1 Lead Acid Battery

1.1.1 History of Lead Acid Battery Development

Practical lead acid batteries began with the research and inventions of Raymond Gaston Plante in 1860. In Plante's fabrication method, two long strips of lead foil and intermediate layers of coarse cloth were spirally wound and immersed in a solution of about 10% sulfuric acid. The early Plante cell had little capacity, since the amount of stored energy depended on the corrosion of one lead foil to lead dioxide to form the positive active material, and similarly the negative electrode was formed by roughening of the foil (on cycling) to form an extended surface. But since then, there had been so much improvement on the traditional Plante cell, on the aspect of its design, capacity, and even practicality, in order to suit so many applications related to the portable power source.

1.1.2 Lead Acid Battery: The General Chemistry

A lead acid battery is a device, which converts the chemical energy contained in its active materials directly into electric by means of an electrochemical oxidation-reduction (redox) reaction (Linden, 1995). This type of reaction involves the transfer of ions from one material to another through an electric circuit. A cell, the basic electrochemical unit, is a circuit where ions are transferred during charging and discharging state. Each cell must consists of three major components such as:

i) The anode or the negative electrode

The reducing or fuel electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

ii) The cathode or the positive electrode

The oxidizing electrode, which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

iii) The electrolyte

The ionic conductor that provides the medium for transfer of electrons, as ions, inside the cell between the cathode and anode. The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids or alkalis, to impart ionic conductivity. Some batteries use solid electrolytes, which are ionic conductors at the operating temperature of the cell.

Physically the anode and cathode are electronically isolated in the cell to prevent internal short-circuiting, but are surrounded by the electrolyte. In practical cell designs a separator material is used to separate the anode and the cathode electrodes mechanically. The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity. In some cases the electrolyte is immobilized for a non-spill design. Electrically conducting grid structures or materials may also be added to the electrodes to reduce internal resistance.

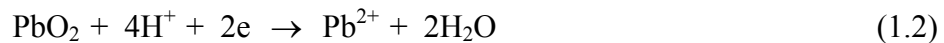
1.1.2.1 Operation of a Lead Acid Battery Cell During Discharge

The operation of a cell during discharge is shown schematically in Figure 1.1(a). When the cell is connected to an external load, electrons flow from the anode, which is oxidized, through the external load to the cathode, where the electrons are accepted and the cathode material is reduced. The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively. The discharge reaction can be written as below, whereas lead (Pb) as the anode material and lead oxide (PbO₂) as the cathode material. And finally we get the overall reaction for discharge as in Equation 1.3:

At negative electrode: anodic reaction (oxidation, loss of electrons)



At positive electrode: cathodic reaction (reduction, gain of electrons)



Overall reaction: (discharge)

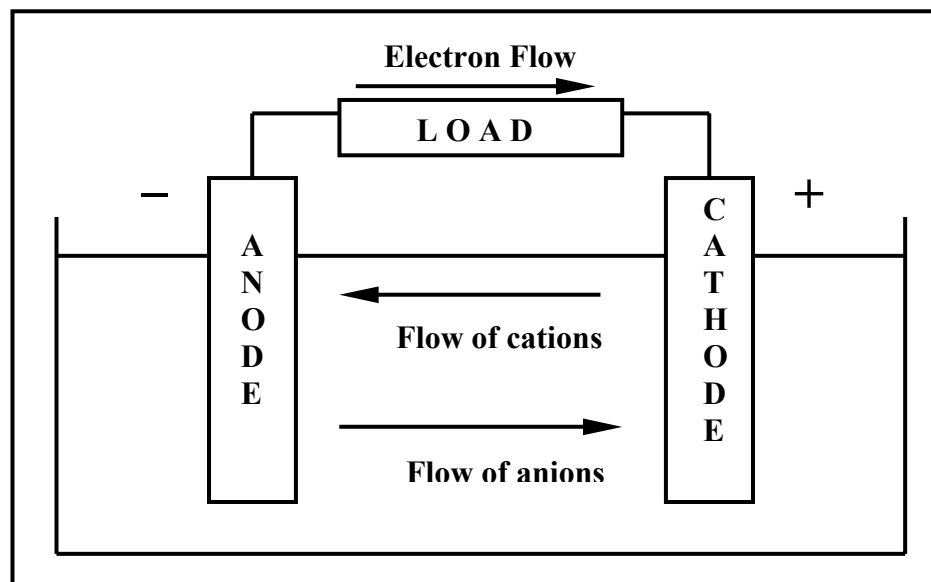
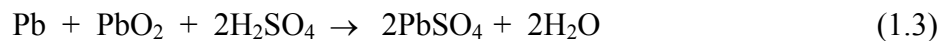


Figure 1.1(a) Cell operation during discharge state

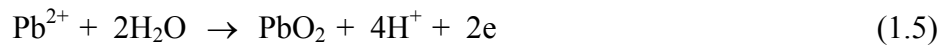
1.1.2.2 Operation of a Lead Acid Battery Cell During Charge/Recharging

During recharge of a rechargeable secondary battery such as lead acid battery, the current flow is reversed and oxidation takes place at the positive electrode and reduction at the negative electrode, as shown in Figure 1.1(b). As the anode is, by definition, the electrode at which oxidation occurs and the cathode the one where reduction takes place, the positive electrode is now the anode and the negative is the cathode.

At negative electrode: cathodic reaction (reduction, gain of electrons)



At positive electrode: anodic reaction (oxidation, loss of electrons)



Overall reaction: (charge/recharge)

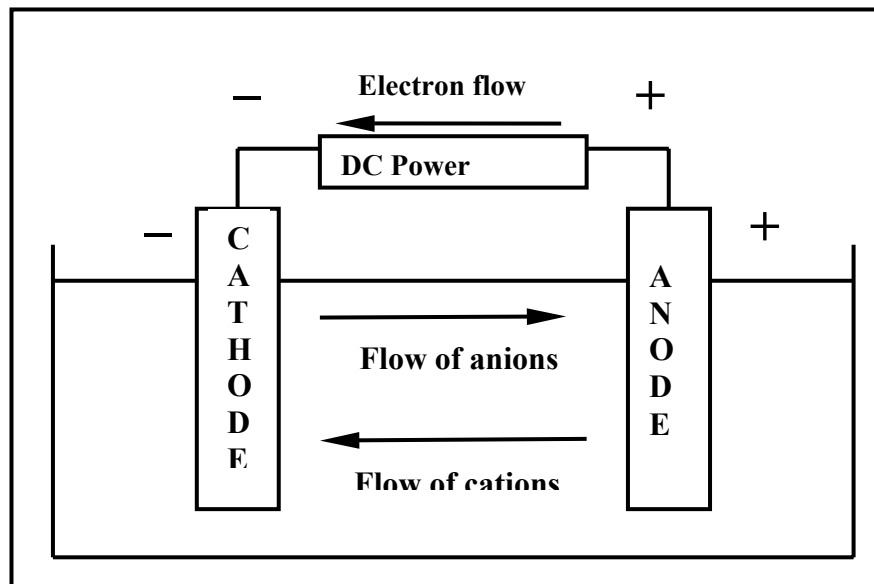
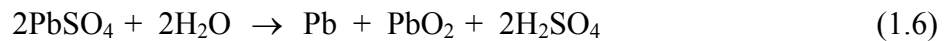


Figure 1.1 (b) Cell Operation During Charge/Recharge

Nevertheless there is another side reaction that occurs during charging of lead acid battery instead of the primary reduction-oxidation (redox) reaction as mentioned above. During the final stage of charging, whenever the cell nearly approaches full charge, or when most of the lead sulfate (PbSO_4) has been converted into lead (Pb) and lead oxide (PbO_2), the cell voltage will become greater than the gassing voltage. At this point and onwards, overcharge reactions occurs, and as a result, hydrogen and oxygen is produced at anode and cathode. The reaction, known as the gassing reaction is shown as below:

At negative electrode



At positive electrode



Overall reaction



This gassing reaction, however, is said by battery researchers to be the main factor to the water decomposition in lead acid batteries.

1.1.3 Types and Characteristics of Lead Acid Batteries

Lead acid batteries were designed in many configurations to suit many applications that require portable and dependable power source. As listed in Table 1.1, there are four main types of lead acid batteries and by far, the automotive starting, lighting and ignition (SLI) type is the most popular and the widest in use. The factor that causes its popularity is due to the blooming of the motor industry, which apparently translates to the demand of SLI batteries. In this research work, the emphasize has been given to SLI batteries since it is the most commercialized type and has the most advancement in its design and technology. Most significant of the

Table 1.1: Types, characteristics and applications of lead acid battery (Linden, 1995)

Type	Characteristics	Applications
Automotive Starting, lighting and ignition (SLI)	Popular, low cost secondary battery, moderate specific-energy, high rate, and low temperature performance;	Automotive SLI, golf carts, lawn mowers, tractors, aircraft, marine
Traction (motive power)	Designed for deep 6-9 hour discharge, cycling service	Industrial trucks, material handling, electric vehicles, special types for submarine power
Stationary	Designed for standby float service, long life, VRLA designs	Emergency power, utilities, telephone, UPS, load leveling, energy storage
Portable	Sealed, maintenance free, low cost good float capability, moderate cycle life	Portable tools, small applications and devices, and portable electronic equipment

advances are the use of the lighter weight plastic containers, the improvement of shelf life, the dry charge process and the maintenance free design (Linden, 1995).

1.1.3.1 Starting, Lighting and Ignition (SLI) Battery

The design of lead acid batteries is varied in order to maximize the desired type of performance. Tradeoffs exist for optimization among such parameters as power density, energy density, cycle life, “float-service life” and cost. A starting, lighting and ignition (SLI) battery whose main function is to start an internal combustion engine discharges briefly but at a high current. Once the engine is running, a generator or alternator system recharges the battery and then maintains it on float at full charge or slight overcharge. Other characteristics for starting, lighting and ignition (SLI) are tabulated in Table 1.2.

Table 1.2: Typical characteristics of a starting, lighting and ignition (SLI) battery

Characteristics and unit	SLI Figures
Chemistry	
Anode	Pb
Cathode	PbO ₂
Electrolyte	H ₂ SO ₄ (aqueous solution)
Cell voltage (typical), V:	
Nominal	2.0
Open circuit	2.1
Operating	2.0-1.8
End	1.75
Operating temperature, °C	-40 to 55
Energy density (at 20 °C)	
Wh/kg	35
Wh/L	70
Discharge profile (relative)	Flat
Power density	High
Self discharge rate (at 20 °C) % loss per month	20-30 (Sb-Pb)
Calendar life, years	3-6
Cycle life, cycles	200-700
Advantages	Low cost, ready availability, good high-rate, high and low temperature operation, good float service
Limitations	Relatively low cycle life, limited energy density, poor charge retention and storability, hydrogen evolution
Major cell types available	Prismatic cells: 30-200 Ah at 20h rate

1.2 The Malaysian Motor Trade Scenario

The Malaysian motor trade has started during mid 1960's where all motor vehicles found on the roads were imported. Since then, the Malaysian motor trade has not changed a lot where most of vehicles were imported from Europe and due to the colonial background, the majority of the motor vehicles were British origin. In the late 1960's, Japanese cars were slowly introduced to the Malaysian roads and began gaining popularity because of their low price and fuel consumption. At the same year also, the government of Malaysia approved the setting up of car assembly plants and within ten years almost every European, Japanese and Australian make was assembled in Malaysia by eight industrial groups producing more than fifty variants.

Under the scenario of economic success, Malaysia went through an economic boom in the 1970's and the early 1980's making it one of the fastest growing markets in Asia. Manufacturing goods is increasingly becoming an important feature of the country's economy, with so many companies inside and outside the country constructing their plants here, including the manufacture of Proton Saga automobile in 1984. Due to the low price and good dependability, Proton Saga and its variants have gained their popularity among the Malaysian people and the sales has boomed where more than 1 million Proton cars were sold throughout the nation.

1.3 Malaysian Battery Market

In keeping up with the development of motor vehicle trade in Malaysia, the sales of lead/acid batteries grew at almost the same pace. The first company to set up its lead/acid battery manufacturing plant in Malaysia was the Chloride Group, which was built in Kuala Lumpur in the year 1959. This is followed by the commissioning of a new lead/acid battery plant by Century Batteries. Many battery manufacturing companies have been setup since then, where lead acid battery demand seems to increase year by year due to growth in manufacturing and car population and also by lead acid battery life expectancy.

Battery and various other manufacturing industries were enjoying the emerging economic bloom during the '80s. Investments were pouring from inside and outside of the country due to the Malaysian economic and its stability. Today, there are about twelve major battery manufacturers of lead/acid batteries of many varieties such as starting, lighting and ignition battery (SLI), storage battery, stationery battery and others (Ibrahim, 1988). Famous foreign brand names such as Yuasa, Yokohama and Century are setting up their manufacturing plants here, seemingly that the market for these batteries are secured here. This phenomenon occurs also as a respond to the growth of lead acid battery industry that concentrates not only for domestic market but also for the export-based production (Wong, 1992). As presented in many review articles concerning lead acid battery industry, a very positive future is forecast for the battery manufacturing industry globally, as well as in Europe and Asia (Billard, 1992; da Silva, 1997; Hawkes, 1997).

As more and more companies are manufacturing their products here, the competition of becoming the best seller in the country has begun to be stiffer. Each company is working hard in producing new items that are not only relatively low in price, but offers better performance than other normal products. Normally the product that they are developing is the maintenance free battery, which needs no topping up of deionised water whenever the electrolyte level goes low.

1.4 Influence of Water Decomposition In Lead Acid Batteries

It is aforementioned that the main reason for the decomposition of water inside the lead acid battery is caused by electrolysis due to overcharging. However, water decomposition is not solely caused by this factor, as there are few other factors that cause water losses. Table 1.3 summarizes the estimation of other influences of water decomposition in lead acid battery.

- a) Through electrolysis due to overcharging

The electrolysis phenomenon occurs normally whenever the battery is charged. The basic electrode processes in the positive and negative electrodes

involve a dissolution-precipitation mechanism and not some sort of solid-state ion transport or film formation mechanism (Ruetschi, 1978). As the sulfuric acid in the electrolyte is consumed during discharge, producing water, the electrolyte can be considered an “active material” and in certain battery designs can be the limiting material.

As the cell approaches full charge and the majority of the PbSO_4 has been converted to Pb and PbO_2 , the cell voltage on charge becomes greater than the gassing voltage and the overcharge reactions begin, resulting in the production of hydrogen and oxygen (gassing) and the resultant loss of water (Linden, 1995).

b) Antimony content of the grids and cyclic durability

During the construction of lead acid batteries, specifically alloy production, antimony is added into the lead paste to harden it because pure lead is too soft (Linden, 1995). The objective of antimony addition into the lead paste is to make sure that the lead alloy stays attached to the grid. There is also another literature cited that explains antimony content in the alloy have a stabilizing effect on the active materials under cyclic stress (Kiehne, 1989).

It is understood that during charging, high over voltage slows down reactions at the electrodes substantially, as some single steps of the reaction are impeded effectively. Thus the system is in an unstable condition and any substance that facilitate these partial

Table 1.3: Losses of water in the lead acid battery (Kiehne, 1989)

Factors affecting water losses in lead acid battery	Estimated quantity of water losses per day (eg. Traction battery, one cycle per day, charging coefficient 1.10)
Electrolysis	
Due to overcharging	3.4 g
Due to self-discharge	0.06 g
Diffusion of water by gassing	0.07 g
Evaporation	0.01 g
Water in acid vapor	$< 2 \times 10^{-4}$ g
Diffusion of water by the gas by circulation pumps	< 0.1 g
Corrosion of the positive grid	< 0.2 g

reaction steps can in some cases accelerate the gassing process and therefore greatly influence the water decomposition process (Kiehne, 1989).

c) Through heat build up and evaporation

It is a well-known fact that the climate for Malaysia is hot and humid throughout the year. As the sequence, battery electrolyte will evaporate easily as the battery casing absorbs heat whenever the car is parked outdoor in the scorching sun. In addition to that, in certain car bonnets such as Proton cars, place their battery too close to the engine, and this will add up to the heat build up due to the hot climate. These two factors are considered to be the main reasons why batteries in tropical countries need to be topped with deionised water frequently. On average, the temperature measured inside the battery is between 60 to 80°C, and at this point, evaporation occurs.

1.5 Problem Statement

The lead acid battery especially in tropical countries has a critical water decomposition problem, which seems to be deteriorating its life cycle and performance. The combination factor of overcharging and hot weather contributed to the water losses in lead acid battery. This is causing the electrolyte level to decrease.

Whenever the electrolyte level goes down, the acid concentration becomes stronger and this leads to a corrosion problem where the strong acidity will attack the connector between grid and terminal and to a certain extent, the connector will break. Another subsequent to the water decomposition problem is the consumer has to top up the electrolyte level every time it goes lower than the minimum level. These are some of the problems faced in the flooded starting, lighting and ignition (SLI) batteries that seems need some review in its design to improve the performance.

Some manufacturers introduced the so-called “maintenance free” batteries that uses gelled electrolyte in their products. However, it is a disappointment that this immobilized electrolyte fails to operate in hot engine condition as reported in oriental cars, where the temperature inside the booth compartment can reach up to 60 °C to 80 °C. Therefore, it is thought that the application of gas separation membrane would be ideal in solving the water decomposition problem in lead acid batteries. The membrane, which acts as a selective barrier, retains electrolyte level by controlling or minimizing the rate of vaporized electrolyte disposed into the atmosphere. Hydrogen and oxygen gases formed during overcharging will be vented minimally as to balance the pressure build up inside the battery. The membrane skin layer thickness needs to be adjusted in order to suit the battery operating conditions.

1.6 Research objectives

Based on the aforementioned background and the problem statement, therefore the main objectives of this research are as follows:

- a) To develop gas separation membrane for the application on tropicalized lead acid battery.
- b) To investigate the effect of fabrication conditions on the performance of the membrane-assisted lead acid battery and its morphology.

1.7 Scopes of Study

In order to achieve the aforementioned objectives, the following scopes have been drawn:

- a) To develop the optimum casting solution and casting condition in fabricating the most suitable gas separation membrane for application on lead acid battery.
- b) To measure and analyze the performance of the membrane assisted lead acid battery during the lead acid battery charging process.
- c) To quantitatively measure the composition of vaporized electrolyte of both conventional and membrane assisted lead acid batteries using Raman Spectroscopy.
- d) To determine structure of asymmetric membranes by using scanning electron microscopy (SEM).