Effect of polysulfone concentration on the performance of membrane-assisted lead acid battery

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Abstract

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The application of lead acid battery in tropical countries normally faces the problem of water decomposition. This phenomenon is due to the factor of charge-discharge reaction in the battery and heat accumulation caused by hot tropical climate and heat generated from engine compartment. The objective of this study is to analyze the effect of polysulfone concentration on the performance of membrane-assisted lead-acid battery. Gas separation membranes, prepared through wet-dry phase inversion method and using various polysulfone concentrated formulations, were applied on the battery vent holes, for the purpose of preventing electrolyte from evaporating to the atmosphere. The best membrane, which retains the most electrolyte, will be chosen to be applied on the soon-to-be-developed "membrane-assisted maintenance-free battery". This maintenance-free battery will need no topping up of deionized water every time the electrolyte level goes low.

Key words : lead-acid battery, asymmetric membrane, gas separation, polysulfone

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Since 1980, there has been a rapid increase in the demand for, and manufacturing sector of, lead-acid battery (Ibrahim, 1988), (Wong, 1992), (Billard, 1992), (da Silva, 1997). Together with the developing motor vehicle manufacturing sector, the lead-acid battery industry has never been so competitive, with so many companies having been brought up in manufacturing lead-acid batteries. However, due to the regional tropical hot and humid climate, the performance of lead-acid batteries has been affected, whereby the electrolyte losses occur. This phenomenon occurs due to the overcharging of the battery and the high temperature condition in the engine compartment (60° to 80°C). During the charging period, O_2 gas will be dominantly produced on the positive electrode, while H_2 gas mildly produced on the negative electrode (Linden, 1995).

There have been previous works emphasizing water decomposition eradication including hydrogen-oxygen recombination system (Kiehne, 1989); immobilized electrolyte system (Dietz, 1992); suppression of hydrogen and oxygen reduction effect (M. Maja, 1988); application of additional volume (Armenta-Deu, 1998) and many others. Considering the fact that electrolyte losses will cause many unpleasent outcomes such as corrosion of car engine compartment parts and deterioration on the electrode connector, a revolutionary step in solving this problem was yet to emerge until the introduction of membrane separation technology onto the lead-acid battery. Knowing the special characteristics possessed by the membrane, such as high acidity condition durability, ability to retain water vapor from getting out of the battery casing due to its hydrophobicity and functions as an acid mist filter in protecting car engine compartment parts, membrane separation technology has been selected as the ultimate step in solving the electrolyte losses in lead-acid battery. Therefore the objective of this study was to investigate the effects of polysulfone concentration of gas separation membrane on the performance of lead-acid battery.

Experiment

Materials

The polymer that was used in the experiment is Polysulfone (Udel bisphenol A polysolfone (Udel P1700)) (purchased from Amoco Performance Products). It was selected as the membrane material because of its commercial availability, processing ease and favorable selectivity-permeability characteristics, and its mechanical and thermal properties. All the chemicals such as *N,N*-dimethylacetamide (DMAc), dimethylformamide (DMF), ethanol and tetrahydro-furan (THF) were laboratory grade and purchased from Aldrich Co.

Membrane preparation

Asymmetric polysulfone gas separation flat sheet membrane were prepared through a simple dry/wet phase inversion method. The flat sheet membrane was prepared by casting a dope solution on a glass plate by using a pneumatically controlled casting machine with appropriate shear rate. The asymmetric membrane was then quenched immediately and smoothly in an aqueous bath at room temperature and remained there for two whole days for solvent-nonsolvent exchange process to occur. After that, the membrane was immersed in an alcohol nonsolvent bath for a day and then dried at room tempearture for another day. The casting solution formulations are shown in Table 1.

Eight types of membranes with different formulations were prepared. GS1, GS2 and GS3 were prepared from ternary solution formulations, and GS4, GS5, GS6, GS7 and GS8 came from binary solution formulations. These membranes differ from the each other in their polymer concentration, with the descending order of polymer weight percentage in each casting solution (GS1>GS2>GS3 and GS4>GS5>GS6>GS7>GS8).

Gas permeation test

Gas permeation cell test is done to determine the membrane's permeability towards certain gases. This test is based on the principle of air

Table 1. Different casting solution formulations in weight percentage

Polymer/Solvent / Nonsolvent	GS 1	GS 2	GS 3	GS 4	GS 5	GS 6	GS 7	GS 8
Polysulfone (PSF)	22%	18.7%	15.2%	20 %	15 %	13.5 %	12.5%	11%
N,N-dimethylacetamide (DMAc)	31.8%	33.2%	34.6%	-	-	-	-	-
Dimethylformamide (DMF)	-	-	-	80 %	85 %	86.5%	87.5%	89%
Tetrahydrofuran (THF)	31.8%	33.2%	34.6%	-	-	-	-	-
Ethanol	14.4%	14.9%	15.6%	-	-	-	-	-
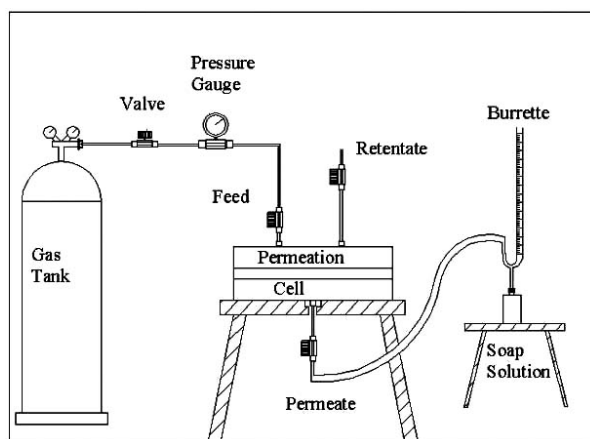
Figure 1. Schematic drawing of a gas permeation apparatus

bubble flow meter. During charging of a battery, the reaction in the electrode produces oxygen and hydrogen gases. By testing the membrane's permeability towards oxygen and hydrogen, it can be estimated how fast these gases can permeate in the lead-acid battery. A schematic drawing of a gas permeation testing rig is shown in Figure 1.

Lead-acid battery charging test

After membranes were fabricated, these membranes were then tested on a lead-acid battery to find out whether they are capable of maintaining electrolyte level inside the battery.

Preliminary screening membrane applied lead-acid battery test

Before putting the membrane up to the real test, a preliminary test was done to see which membrane formulation was suitable to be applied on the lead-acid battery. This was done to screen down the suitable membranes that are to be used in the real membrane applied lead-acid battery charging simulation test. Through this preliminary test, all the membranes fabricated in the earlier stage were applied on lead-acid battery capped with epoxy adhesive, and then the battery was charged using an alternator and charged on average at 12 to 15 ampere. The objective of this method was to scan roughly the best membrane formulation to be applied on the lead-acid battery.

Membrane applied lead-acid battery charging test

After the preliminary charging test was done, the best membrane formulation was be applied into a battery cap. The spiral end stainless steel battery cap which holds the membrane, was applied on the battery vent hole, and the battery then charged using an alternator. Gas permeating from the battery cap was measured using a soap bubble flow meter. To measure the water losses from the lead acid battery, the initial mass of the battery was measured before and after the charging test was done.

Scanning Electron Microscopy (SEM) analysis

Membrane structure and morphology were examined using scanning electron microscopy (SEM). Samples (cross-section) chosen from different batches of membrane were fractured cryogenically in liquid nitrogen to leave an undeformed structure, and mounted on sample stubs

with double-surface Scotch tape. The samples were then deposited with gold using a sputter coater (Biorad Polaron Divison). After that, the samples were imaged and photographed by employing a scanning electron microscope (Philips SEMEDAX; XL40; PW6822/10) with potential of 20 kV under magnifications ranging from 250x to 300x.

Results and Discussion

Effect of polysulfone concentration on the permeation of vaporized electrolyte

Each and every type of the cast membranes was tested for its permeation of pure hydrogen and oxygen gases. All membranes showed different standards of performance, with higher permeabilities for lower polymer concentrated membranes and vice versa. However, data for low polymer concentration membranes such as GS 6, GS 7 and GS 8 could not be obtained due to the rapidness of gas permeating from these membranes. Therefore, permeation rates of these membranes could not be calculated. However, it is can be assumed that these membranes had greater permeation rates compared to the higher polymer concentration membranes.

From Figure 2, for ternary system such as in GS 1, GS 2 and GS 3 (GS1 with highest polysulfone concentration and GS3 with the lowest polysulfone concentration), the polymer concentration for each of the formulations decreased and
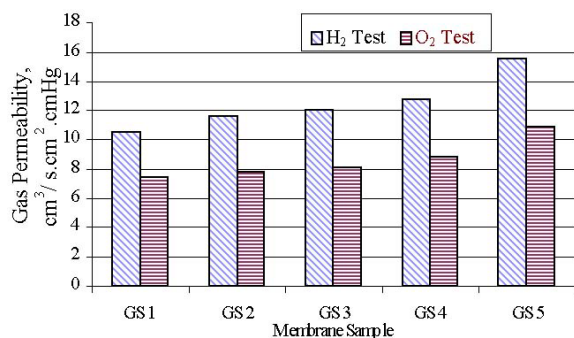
**Figure 2. Permeability rates for five different membranes**

it was found that the permeability for GS 3 was higher than that for GS 1. This phenomenon is because whenever the higher the polymer concentration in the casting solution, the thicker the membrane and the deeper the polymer matrixes. Therefore permeability will be lower every time the polymer concentration is increased. This also is the same for binary system such as found in GS 4 and GS 5. It seems that the polymer concentration for GS 5 is lower than that for GS 4, therefore permeability for GS 5 is higher than that for GS 4. The only difference between binary and ternary systems is the structure of the membrane, where binary system membranes have more uniform structure than do those of the ternary system.

From the observations made from the preliminary test as tabulated in Table 2, after a few hours of charging, the membrane that was applied on top of the battery cap had swollen. It was also observed that the battery casing became swollen and the level of electrolyte fluctuated. This was due to the pressure build-up inside the battery casing because the membrane pore size was too small for the vapor to diffuse through. The next step taken after finding out the battery casing became swollen was to stop the charging in case an explosion would occur.

By looking at the results of the membrane applied on battery test, membranes GS 1 to GS 5 were still too tight as the pressure built up inside the battery casing and caused the casing to swell. Meanwhile, the lower polymer concentration membranes such as in GS 6, GS 7 and GS 8 showed better permeability than the latter membranes. This was proved through the observation of battery electrolyte level and the compactness of the battery casing. However, GS 7 displayed poor electrolyte retaining characteristics as water droplets emerge on its surface. Meanwhile GS 8 membrane ruptured after the battery was charged for 1.5 hour. This indicates that the polymer matrixes in GS7 and GS 8 are not as strong and compact as those membranes which permeate gases easily. As for GS 6, it showed the best permeation of vaporized electrolyte and at the same time showed minimum pressure build up

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Table 2. Preliminary screening membrane applied lead acid battery test result

Membrane	Rate of electrolyte loss , %	Comment
GS 1	10	Battery casing severely swollen after 2 hours of charging
GS 2	10	Battery casing swollen severely after 2.5 hours of charging
GS 3	13	Battery casing severely swollen after 3.0 hours of charging
GS 4	13	Battery casing severely swollen after 3.25 hours of charging
GS 5	15	Battery casing swollen after 3.5 hours of charging
GS 6	15	Battery casing moderately swollen after 4 hours of charging
GS 7	20	Battery casing mildly swollen after 2 hours of charging, but water droplets emerge on the membrane surface
GS 8	25	Battery casing mildly swollen after 1.5 hours of charging, but the membrane sheet ruptured
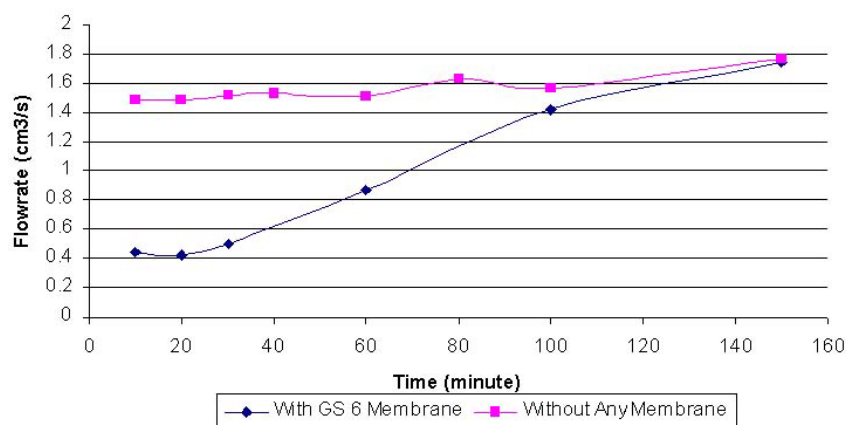
Figure 3. Flow rate of vapor permeating from lead acid battery during charging

inside the battery casing. It can be justified that GS 6 membrane has passed the preliminary test and practically can be used as an electrolyte-retaining device.

As can be seen in Figure 3, the flow rates of gas permeating from the battery during charging without application of membrane continuously increased. Meanwhile the battery with membrane application showed low permeation during the initial stages of charging. Somehow as charging proceeded, the permeation of vaporized electrolyte increased. Until reaching a certain point of charging, the flow rate of vaporized electrolyte became constant. This shows that electrolyte was being retained inside the battery casing and electrolyte losses could be eradicated by membrane application on lead-acid battery.

Effect of gas separation membrane application on the electrolyte losses rom lead acvid battery

As shown in Figure 4, the rate of electrolyte losses in a battery that used GS 6 membrane was much slower than the rate of a battery that did not use any membrane. As calculated, the average rate of electrolyte losses in a battery that uses GS 6 membrane is 8 gram per hour, while the rate of electrolyte losses in a battery that does not use any membrane is 24 gram per hour. In another way, when a membrane is applied to a battery vent hole, it can retain more electrolytes from getting vented to the atmosphere. This means that GS 6 membrane is suitable to be used as an
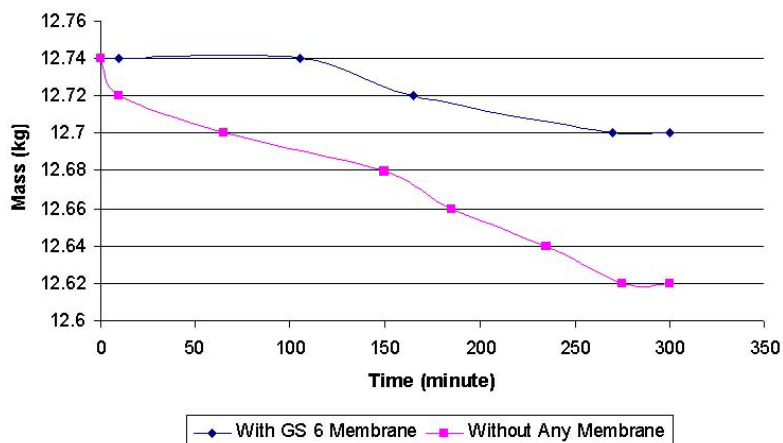
Figure 4. Electrolyte losses during battery charging
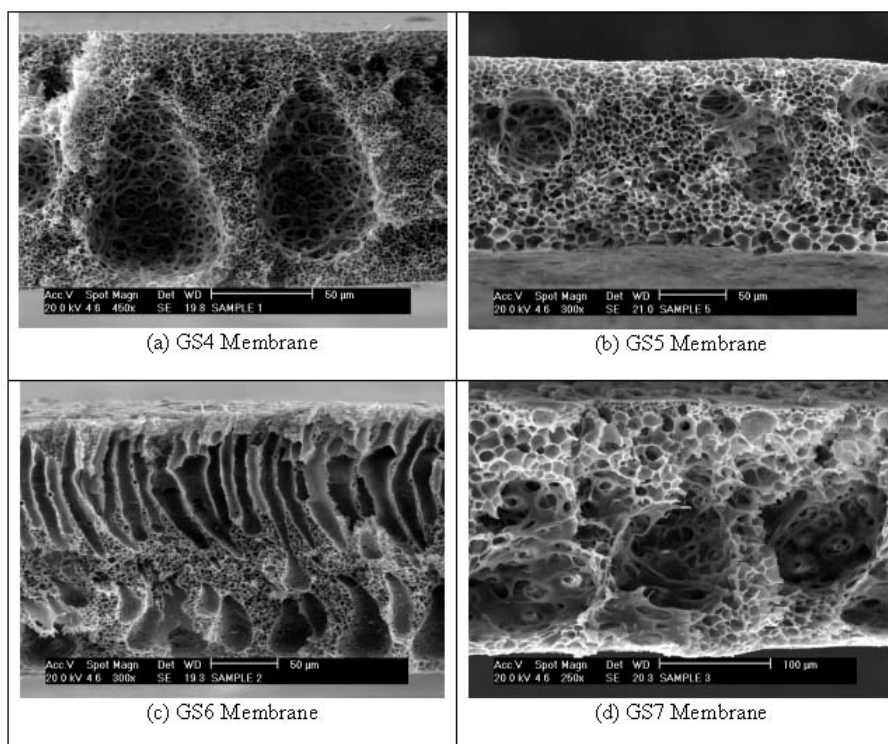

Figure 5. Scanning electron micrograph of the cross-section of the prepared asymmetric gas separation membrane (a) GS4 at 450 magnification; (b)GS5 at 300 magnification; (c) GS6 at 300 magnification; and (d) GS7 at 250 magnification

electrolyte-retaining device in lead acid battery.

As shown in SEM photographs of Figure 5, the prepared membranes show the typical asymmetric structure. As can be observed, there is a two-layer structure, which consists of a thin and dense selective skin; and a porous sublayer that supports the selective skin. A trend of average pore size can be detected in the images here,

where the lower the polymer concentration in the casting solution, the bigger is the average pore size, and vice versa (Koros and Flemming, 1983). The membrane with high polymer concentration, GS4, has the smallest average pore diameter and the smallest permeation rate, whereas GS7, with a lower polymer concentration, has a larger average pore diameter and a higher permeation rate. GS6, however, has the most suitable polymer concentration to be applied on lead-acid battery, where the permeability is essential in avoiding pressure build-up in the battery casing but good enough in maintaining electrolyte level of the battery.

Conclusion

This study suggests that asymmetric gas separation membrane can be used for the application on lead-acid battery in maintaining electrolyte level. The results prove that the membrane is practically useful in minimizing electrolyte losses. However, the most suitable or optimized formulation has yet to be found. Parameters in preparing a membrane need to be manipulated strategically in order to obtain a membrane that really serves the objective in fully maintaining electrolyte in lead-acid battery. Pore size of the membrane needs to be enlarged to facilitate a better venting of the gas coming out during charging and the thickness must be reduced to give a higher permeability. These two aspects need to be optimized, as membranes with too large pores will fail in retaining electrolyte.

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