

Influence of separator structure on the performance of valve-regulated batteries

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Abstract

Glass-microfibre separators used in valve-regulated lead/acid batteries have anisotropic structures with pores through the separator larger than those in the other two planes. The size of these pores depends on the fibre composition and certain processing treatments during manufacture. The resulting structure has a considerable influence on the wettability and acid distribution within a cell, which in turn affects the internal resistance, and the recharge and oxygen-recombination efficiencies. The effect of the contrasting structure of plates and separators is discussed. A better understanding of these structural influences will help to design separators with optimal wetting characteristics for particular battery applications.

Introduction

Absorbent glass-mat separators of the type widely used in valve-regulated lead/acid batteries have additional functions to those of the more conventional separator used in vented batteries. In the latter, the separator is essentially a permeable insulating diaphragm that allows ionic transport whilst preventing the conduction of electrons. It must be both acid and oxidation resistant and have a controlled and well-defined pore size. High quality separators of this type, such as those made from microporous polyethylene, can also be formed into envelopes to eliminate edge shorting. The designs with a thin back web have a low internal resistance whilst maintaining sufficient interelectrode space to accommodate the required amount of electrolyte.

In valve-regulated batteries, the separator has several other functions that play a critical role in the performance of the battery. It serves as an acid reservoir since the electrolyte is totally absorbed and must be distributed uniformly and quickly. Consequently, pore volume and acid absorbency is an important characteristic. To maintain electrical contact, and adequately support the active material, the separator must be compressible and resilient in both the wet and the dry condition. In addition, the structure must allow oxygen to flow through the separator when the pores are substantially filled with electrolyte.

All these requirements are influenced by a structure that differs substantially from that of the more conventional separator. For example, polyethylene separators made by extruding a polymer/silica/oil composition, with subsequent extraction of oil, are very durable membranes with small and tortuous pores that have little or no directional

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variations. By contrast, absorbent glass mats, made by wet laying glass microfibres, have high porosity and relatively large pores with considerable directional differences.

These features affect the distribution and mobility of liquid and gas within the plate/separator combination, and the resilience of the separator in both wet and dry conditions. It is important to understand these influences if the applications of valve-regulated batteries are to be extended.

Basic structure of glass-microfibre separators

Glass-microfibre separators are made by wet laying a mixture of fibres that range in diameter from 0.1 to 10 μm . Since small diameter fibres are more expensive, manufacturers choose a blend aimed at satisfying the duty requirements at the lowest cost. The fibres are dispersed and agitated, prior to feeding to the paper machine, which reduces the fibre length to about 1 to 2 mm and may cause some fibrillation.

Wet laying results in a fibre orientation that gives an anisotropic network of the type demonstrated in Fig. 1. The pores and channels through the separator (i.e., measured in a direction perpendicular to the plane of the separator, or z direction) are larger than the pores in the other two planes (x and y). Typically, the diameter of the pores in the z plane is 10 to 25 μm , and 2 to 4 μm in the x and y planes. For comparison, Fig. 2 is a scanning electron micrograph of an ENTEK microporous polyethylene separator that exhibits a uniform distribution of small pores averaging 0.1 μm in size.

The dispersion techniques vary with each manufacturer and enhance fibre entanglement to give a random distribution of fibres. The resulting pore size and the associated properties such as tensile strength and compressibility are influenced by the fibre composition and subsequent treatment. In addition, some manufacturers use chopped fibres to improve uniformity. A high proportion of small diameter fibres increases the surface area and reduces the pore size as indicated in Table 1.

The properties of four commercially-available glass-microfibre separators are listed in Table 2. The pore size is the maximum equivalent pore diameter measured by the bubble-flow technique [1] and varies from 14 to 45 μm . The specific surface area (determined by gas absorption) shows the expected trend, i.e., high surface area with the smallest pores. Figure 3 gives the pore-size distribution of sample 3, as obtained by low-pressure intrusion methods. It can be seen that about 90% of the pore volume consists of pores between 10 and 24 μm . These are mainly in the z plane. A small

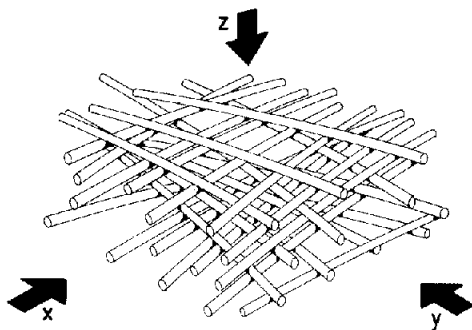


Fig. 1. Wet-laid fibrous structure.

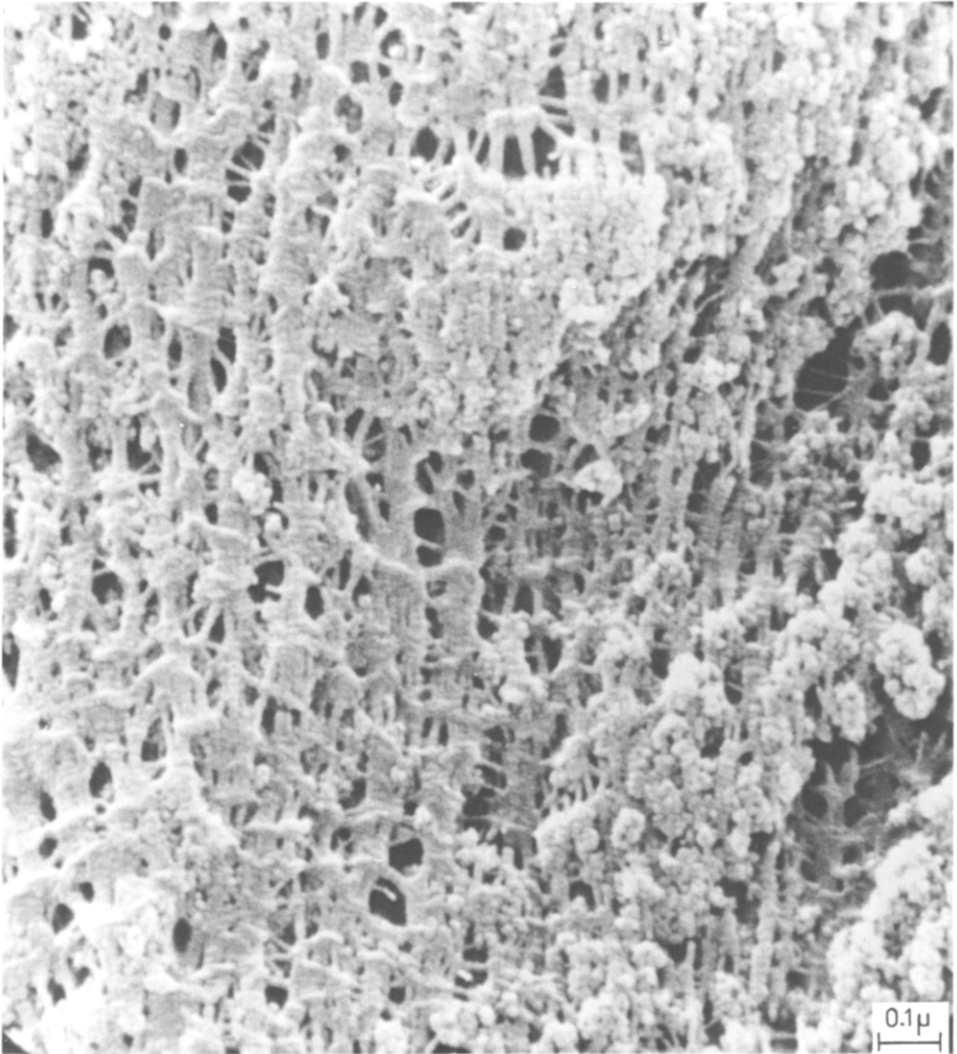


Fig. 2. Structure of ENTEK microporous polyethene separator.

percentage of pores are less than $10\ \mu\text{m}$ while about 5% of large pores are in the range 30 to $100\ \mu\text{m}$. It is believed these large pores are caused by edge effects, possibly the result of sample preparation, and are not truly representative of the structure.

Microscopic examination confirms that pores in the x and y planes are much smaller. Their size is best estimated by measuring the capillary rise (or wicking) of acid into the separator, Culpin and Hayman [2] showed that the capillary action of sulfuric acid in glass-microfibre separators follows the simplified form of the Washburn equation and that the rate of rise of acid is directly proportional to the size of the pore, viz.:

$$h^2 = \frac{\gamma r t \cos \theta}{K^2 2\eta} \quad (1)$$

TABLE 1
Influence of fibre diameter

Fibre diameter (μm)	0.1	0.5	1.0	2.0	5.0	10.0
Fibre length (m kg^{-1})	4.7×10^{10}	1.9×10^9	4.7×10^8	1.2×10^8	1.9×10^7	4.7×10^6
(m m^{-3})	1.1×10^{13}	4.5×10^{11}	1.1×10^{11}	2.8×10^{10}	4.5×10^9	1.1×10^9
Surface area ($\text{m}^2 \text{kg}^{-1}$)	14800	2960	1480	741	296	148
($\text{m}^2 \text{m}^{-3}$)	3.5×10^6	7.1×10^5	3.5×10^5	1.8×10^5	7.1×10^4	3.6×10^4
Pore size	→ increasing →					
Tensile strength	→ decreasing →					
Cost	→ decreasing →					

TABLE 2
Properties of glass-microfibre separators

Sample	1	2	3	4	
Surface area ($\text{m}^2 \text{g}^{-1}$)	0.5	0.9	1.2	2.6	
Maximum pore size (μm)	45	31	24	14	
Thickness					
mm at 10 KPa	dry	2.58	1.78	1.65	1.39
	wet	2.51	1.71	1.60	1.35
mm at 20 KPa	dry	2.03	1.49	1.47	1.27
	wet	1.99	1.47	1.44	1.26
mm at 30 KPa	dry	1.86	1.40	1.40	1.23
	wet	1.87	1.39	1.41	1.21
Grammage (g m^{-2})	280	240	240	180	
Wicking height (mm)					
1.300 sp. gr. acid					
1 min	42	39	37	33	
5 min	94	88	83	75	
1 h	195	205	210	220	
2 h	240	280	300	370	
10 h	360	410	455	550	
Tensile ($\text{g}/25 \text{ min}$)	1900	1870	1950	1600	

where h is the capillary rise, γ the gas/liquid interfacial tension, r the radius of pore, t the time, θ the solid/liquid contact angle, K the tortuosity factor, and η the viscosity.

The initial slope of the curve obtained when h^2 is plotted against t avoids the influence of gravitational effects and gives a measure of the maximum pore size in the vertical plane. The experimental data in Table 2 gives a mean pore diameter of 1.7 and 2.6 μm for samples 4 and 1, respectively. These measurements were made with uncompressed separator. The ratio of pore sizes in the two planes is 17:1 and 8:1 and is a measure of the relative anisotropy of the samples.

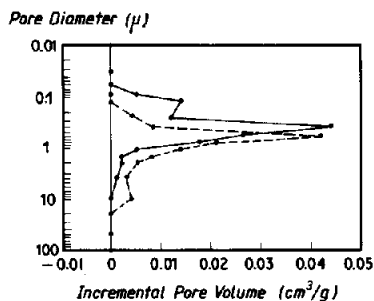
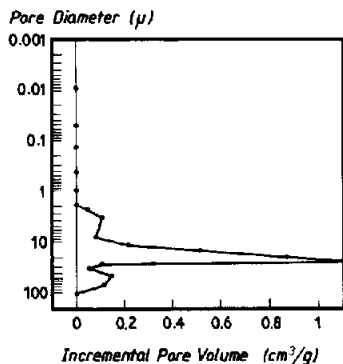


Fig. 3. Pore-size distribution of glass-microfibre separator.

Fig. 4. Pore-size distribution of battery plates: (---) positive plates; (—) negative plates.

Acid distribution effects

In addition to providing an estimate of the effective pore diameter in the vertical plane, the tests (Table 2) show that the maximum height after an extended period of wicking is inversely proportional to the pore size, i.e. the greatest height is with the smallest pore.

Similarly, electrolyte will distribute within a porous structure according to the capillary pressures and, consequently, small pores fill preferentially. Within a battery assembly, the pore structures of the separators and the closely contacting plates are different. The active material in both positive and negative plates has only minimal difference between dimensional planes. With new, fully formed plates, more than 80% of the porosity consists of pores that are smaller than $1 \mu\text{m}$, as Fig. 4 shows. This compares with 10 to $24 \mu\text{m}$ diameter pores in the z plane and $2 \mu\text{m}$ pores in the x and y planes of the separator.

The normal manufacturing process of absorbed electrolyte batteries is to add a measured amount of acid to each cell. Further reduction in saturation and gravity adjustment is achieved, if required, by charging above the gassing potential. In some processes, the cell is evacuated prior to filling so that the acid is distributed more quickly. In such an arrangement, unless there is sufficient acid to fill all pores in plates and separators, the plates will fill preferentially and the separator will be partially saturated. A further exception is, of course, when the plates are gassing and acid is forced out of the plates and then the latter is quickly absorbed into the separator until the latter is fully saturated.

Measurement of the rate of capillary rise of acid into a separator is a standard quality control and acceptance procedure. In addition to giving a measure of the maximum effective diameter of pores in the vertical plane, it is an indication of the absorption and distribution of acid in the fibrous network. Capillary-rise measurements on sample 3 (Table 2) at 15 and 25% compression gives pore sizes of 1.3 and $1.1 \mu\text{m}$ diameter in the vertical plane, compared with $2.1 \mu\text{m}$ when uncompressed. Within the compressed assembly of plates and separators, acid will distribute itself firstly in the plates and then preferentially in the smaller pores in the separator.

Gravitational effects may cause variations in saturation and acid strength in the vertical plane. When this occurs, the charging efficiencies vary in different parts of

the plates. This is more prevalent in cycling applications, particularly when charge time is short, and can progressively reduce the capacity. The use of separators with smaller pores and higher compressions within the assembly tends to immobilize the acid and reduce the problem to some extent. The problem can best be reduced by appropriate designs.

Nonuniform acid distribution can also result in the development of lead dendrites in the separator. Shorting through a separator is not an uncommon failure mode in lead/acid batteries. It can be caused either by physical transfer of particles of active material and corrosion product, or by dissolution of sulfated material in the electrolyte followed by deposition at a new location. The former is influenced by pore size, tortuosity and puncture resistance, and it is to be expected that fibrous separators consisting of relatively large, 'straight-through' pores are more prone to this problem. Nevertheless, with good quality plates (i.e., free of lumps and other defects) and with adequate care in assembly, this form of shorting is uncommon.

On the other hand, internal shorting due to lead dissolution and precipitation is more prevalent in designs that are excessively starved of acid or if the acid is not uniformly distributed. In these regions, the pH of the electrolyte can be high and lead dendrites can quickly develop, particularly when the battery is deeply discharged and at high temperatures. Buffering agents such as sodium sulfate reduce the problem to some extent, as does some adjustment of the pore size to improve the mobility of the electrolyte. The problem is reduced more effectively by optimizing the ratio of plate and separator pore volumes to ensure sufficient electrolyte.

Separator resistance

The resistance of a separator is that of the acid held within the pores, and a network of cylindrical parallel pores filled with electrolyte obeys Ohm's law. Polymeric separators have tortuous and some closed (or dead-end) pores that are essentially nonconductive. With wet-laid glass-fibre separators, there are no closed pores, although gas trapping can have a similar effect. The conductivity of these separators, when fully saturated, can be expressed by eqn. (2), viz.:

$$\frac{\bar{k}}{k} = \frac{V}{\tau^2} \quad (2)$$

where k is a specific conductivity of the electrolyte, \bar{k} the specific conductivity of the separator, V the volume fraction of pores, and τ the tortuosity factor (ratio of real length of pore to thickness of the separator).

With a volume porosity of about 90% in the compressed condition, the conductivity of the separator is:

$$\bar{k} = \frac{0.9k}{\tau^2} \quad (3)$$

With glass-microfibre separators, the tortuosity factor is approximately unity, and, consequently, their resistance approaches that of the electrolyte gap. For example, an absorbent glass-mat saturated in sulfuric acid has a resistance that is approximately 15% higher than the acid it displaces. Polymeric separators have a higher resistance due to their lower porosity and more tortuous structure, although a decrease of the thickness of the back web of polyethylene separators has enabled further reductions in recent years [3].

The resistance of porous materials increases as they become progressively de-saturated and can be very high at low saturations. Crouch and Reitz [4] showed that as the saturation decreases from 100 to 80%, the increase in resistance is small but below this level it increases considerably. At 60% saturation, the resistance is approximately double that of the fully saturated separator, as shown in Table 3, which also gives the resistance of other separators. In these situations, the high power capability of the battery is reduced, see Fig. 5. The same graph shows the effect on a 25 A discharge. In this case, the diffusion of acid is not limiting and the capacity is proportional to the amount of electrolyte in the separator.

In controlled-operating conditions, the rate of water loss due to inefficiencies in the gas-recombination reaction, transpiration of water through the container or overcharge abuse, is slow. For example, a typical 80 A h valve-regulated battery of the type widely used in Telecom and uninterruptable power supply (UPS) applications, floating at 2.27 V/cell at 25 °C has a gas-recombination efficiency of over 99% and loses about 40 cm³ of water per cell over a 10-year operating period. This is about 5% of the total filling volume, but since the electrolyte will distribute according to the capillary forces in the plates and separators, the saturation of the separator decreases by about 8% from the initial value. Over a normal lifetime service of 10 years, the resistance increase due to this loss is slight and does not affect the performance.

In certain duties, such as cycling applications where faster charging is required and without adequate controls, the water loss may be greater and the separator will desaturate preferentially. This increases the resistance and promotes the risk of the development of a runaway situation.

TABLE 3

Resistance of separators (in 1.280 sp. gr. acid at 25 °C)

Separator type	Resistance ($\Omega \text{ cm}^2$)
Absorbent glass-mat	0.05
Absorbent glass-mat (60% saturated)	0.11
Microporous polyethene (ENTEK)	0.07
Sintered PVC	0.15
Microporous rubber	0.17
Cellulosic	0.16

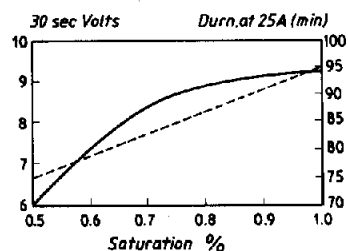


Fig. 5. Influence of separator saturation on performance: (—) CCA V/-18 °C; (---) 25 A min/25 °C.

Gas recombination

In normal charging modes, the higher inefficiency at the positive electrode results in oxygen being evolved at an early stage with the proportion of energy used to produce oxygen increasing as the charge proceeds [5]. In vented designs, evolved gases permeate between the plates and separators and enter the head space. In valve-regulated batteries, the compressed nature of the assembly hinders this path to some extent, but provides an alternative route through the separator to the negative plate. The reduction of oxygen on lead in the cathodic potential region is diffusion controlled [6] and dependent to a certain extent upon the degree of saturation of the separator.

As acid is added to the separator, it arranges itself spatially to minimize the surface energy. Because of the high air/liquid interfacial tension, the area of contact with the glass microfibre will be maximized with minimum surface area in contact with the gaseous phase. As the saturation increases, acid bridges across smaller pores and leaves the larger pores open and free to the passage of gas. At higher saturations, pores of increasing size are blocked successively. At around 90% saturation, the largest of the pores is bridged and the residual 10% (by volume) of gas is contained within isolated and discontinuous bubbles that play no effective part in the transfer of oxygen.

As a result of the above behaviour, the rate of oxygen transfer across the separator at low saturation (<60%) is similar to gaseous diffusion, whilst at saturation levels >90%, it is several orders of magnitude lower and approaches the rate of diffusion through a liquid. These low diffusion rates cannot sustain the recombination rates required for the successful operation of a valve-regulated battery. The fact that significant gas transport occurs, and effective recombination is achievable, in designs that are more than 90% saturated is explained by partial displacement of acid. In tightly-packed assemblies, the evolved oxygen creates a differential pressure across the separator which builds up until it exceeds the critical pressure needed to displace electrolyte from the larger pores and pass through the separator to the surface of the negative plate.

This behaviour is similar to that of gas-diffusion electrodes and Khomskaya *et al.* [7] found that when the rate of transport is limited by diffusion, only 5% of the evolved oxygen reaches the negative plate and is reduced. By pressure-assisting the transport, the reduction currents are increased by an order of magnitude.

Assuming the pores in the separator are cylindrical and with a contact angle for sulfuric acid on glass equal to zero, gas movement will take place when the pressure at the surface of the separator, p , is greater than the capillary pressure, viz.:

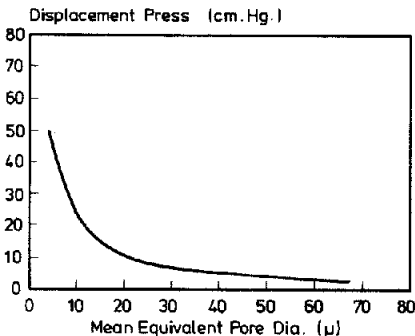


Fig. 6. Critical displacement pressure vs. mean pore diameter.

$$p > \frac{4\gamma}{d} \quad (4)$$

where γ is the surface tension and d is the mean pore diameter.

At a surface tension of $\gamma = 75 \text{ dyne cm}^{-1}$ ($75 \times 10^{-5} \text{ N cm}^{-1}$), the critical pressure required to displace electrolyte for different pore diameters is shown in Fig. 6. A capillary pressure of 9 cm Hg (1.8 psi) is necessary for gas to flow through a highly saturated separator with a mean equivalent pore size of 20 μm . For smaller pores, a higher pressure is required to displace acid with the increasing probability that the evolved gases will enter the head space and exhaust through the low-pressure valve.

Further comments

Valve-regulated lead/acid batteries have been in large-scale commercial use for over ten years, mainly in stand-by applications where they are continuously charged at low currents and discharged only infrequently. The rate of oxygen evolution is low and the reduction currents at the lead electrode are 0.1 to 0.2 mA cm^{-2} . This is equivalent to a charging current of $C/1000$.

Increasingly, there is a desire to use the benefits of valve-regulated batteries in other fields such as engine starting, defence, and duties where extended cycling and rapid charging are essential. These applications need a low resistance throughout service, minimal stratification, good charge acceptance and efficient gas recombination at high charging currents.

A significant feature of glass-microfibre separators is their anisotropic structure. The small pores in the x and y planes aid both the distribution and the retention of acids whilst the larger, nontortuous pores through the separator provide both a low resistance and direct routes for gas transport. Most valve-regulated batteries in use today have sufficient electrolyte to substantially saturate the separator (i.e., >90%) and also have a low internal resistance. Under these conditions, oxygen transport across the separator will be pressure assisted and, therefore, will be dependent on the pore size in the z plane. Wetting characteristics can be improved by maximizing the surface area through the use of densely-packed, small-diameter fibres, but this is undertaken at a higher cost and with the likelihood that recombination efficiencies will decrease.

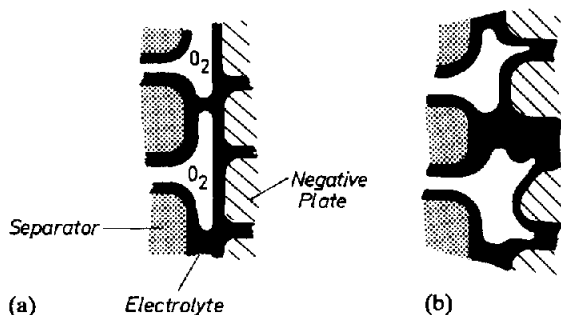


Fig. 7. (a) Electroreduction at negative surface only; (b) some penetration into the negative plate.

The contrasting structures of the plates and separators is also relevant to the functioning of the battery. The capillary pressures dictate that electrolyte fills plates preferentially. This appears to be the ideal situation since it can best support the electrochemical reaction and will leave the separator partially saturated so that movement of electrolyte can provide pathways for gas transport. On the other hand, if the overall saturation is too low or there is excessive loss of water, the separator will dry out preferentially and cause an increase in the internal resistance.

The relationship between separator and plate structure may also be important in other ways, as shown with sealed Ni/Cd batteries [9]. With a combination of large pores in the separator and fine pores in the electrode, there may be little penetration of gas into the negative plate after passing through the separator. Consequently, at high charging currents, only limited reduction occurs and unreacted oxygen moves up the interface into the head space and is exhausted (Fig. 7(a)). Separators with smaller pores hold gas at a somewhat higher pressure and thus increase the penetration (Fig. 7(b)) and minimize water loss at higher charging rates.

If the use of valve-regulated lead/acid batteries is to be extended into other main stream markets (such as automotive, motive power and electric vehicles), certain operating characteristics need to be improved. The structure of the separator affects its wettability and has a major influence on the internal resistance, high power performance, charging/recombination efficiency, and service life of the battery. The basic parameters of wetting can be used to design a separator structure with optimal wetting characteristics for particular battery applications.

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