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Separators for acidic and alkaline batteries*

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Separators are important components of batteries. For a comparison of their main properties an electrolyte-independent description is necessary and useful as this type of description also leads to very simple models on the interaction of the battery's electrodes. This paper provides such an electrolyte-independent description as well as some additional suggestions for improving the properties. Fleece, sintered and skeleton separators are discussed, together with their porous properties, and their influence on diaphragm and flow resistance, as well as bubble-point and gas flow resistance. The ability of separators to avoid the formation of metallic bridges, which penetrate the separator, is correlated to the inner specific surface area of the separator material.

Nomenclature

R_{dia}	diaphragm resistance per cm^2
l	effective pore length
σ	specific resistance of the electrolyte
n	number of pores per cm^2
n'	diffusion flux
r, r'	pore radius
u	tortuosity factor
d	separator thickness
f	fraction of pore area of 1 cm^2 separator dimensionless
p	porosity
R_{flw}	flow resistance for electrolyte
k	fitting parameter from a fluid-grading experiment
$v_{\max}$	maximum filling velocity
h	level of electrolyte inside separator in fluid-grading experiment
t	time
p_{k}	capillary force of electrolyte inside separator
h'	derivative of h with time
x, y	coordinate variables
D	diffusion constant
c	concentration
δ	indicates derivative
Δc	concentration difference between two sides of separator
d_{eff}	effective thickness
v	velocity
$\mathbf{k}$	permeability tensor
∇	gradient
P	pressure
B	constant
S	inner surface of a separator
k^*	fitting parameter
η	viscosity

1. Introduction

Generally, the task of a separator is to separate two active spaces while hindering the desired electrode reactions as little as possible and keeping the necessary losses and expenses to a minimum. In order to classify different separators their properties have to be compared. Therefore, a common description has to be used in terms of an electrolyte-independent parameter such as effective thickness. Some of the properties of a separator will be described in this article in an electrolyte-independent way. The separators will be divided into three groups depending on their method of manufacture [1]; these are fleece, sintered and skeleton separators.

2. Tasks and properties of separator

The main tasks of a separator are: electronic separation of both electrodes; minimal resistance of the electrolyte between the electrodes; minimal prohibition of diffusion of the reactive components of the electrolyte; minimal flow resistance to compensate for the electrolyte solvent transported by the ions in the electric field; mechanical and chemical resistance, especially against oxidation by oxygen and oxides; minimal ageing of the properties; no soluble substances in the separator which may influence the battery adversely; complete wetting during all operating conditions in the case of gas flow being unnecessary; prevention of transport of colloidal particles of the active substances to the counter electrode (self-discharge and dendrite formation). We will characterize a separator as a porous body in which physical effects such as osmosis, electro-osmosis, electrophoresis, electrodialysis and dendrite formation will be neglected. Diffusion, flow of electrolyte, and – if needed – gases induced by pressure, should be possible. For

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Table 1. Properties of some separators

Sample	*Thickness* (mm)		*Flow conductivity*[1] (ml cm^{-2} bar s)	*Bubble point* (bar/H_2)	*Type*	*Supplier*	*Material*
	Real	*Eff.*					
FS2140	0.20	3.03	0.6	0.26	Fleece	Freudenberg	PSU
FS2182	0.20	0.35	–	0.03	Fleece	Freudenberg	PVOH
FS2125	0.29	0.51	–	0.02	Fleece	Freudenberg	PP
V22087	0.28	0.40	–	0.02	Fleece	Freudenberg	PPS
Asbestos	0.70	1.35	0.38–3	0.50	Fleece	Siemens	Asbestos
PVC	0.54	1.98	11.28	0.15	Sint. sep.	Dr Jungfer	PVC
PVC	0.28	0.47	29.30	0.05	Sint. sep.	Varta	PVC
Uni Da	0.24	0.75	1.5–3.3	0.30	Sint. sep.	Uni Darmstadt	Nickeloxid
Mipor S	0.54	2.22	–	–	Sint. sep.	Varta	Rubber
Celgard	0.06	0.34	1–3	0.50	Membrane	Cellanese Corp.	
SM-11906	0.16	1.33	0.2–0.6	0.33	Skeleton?	Satorius	Polyamide
SM20006	0.13	0.26	0.4–0.6	0.60	Skeleton?	Sartorius	Polyamide
Grace	0.07	0.33	1–3	0.56		Grace	Polypropylene + TiO_2
Porvic M	0.4–1.1	2.80	8–3	0.5	Skeleton	Chloride	PVC

[1] Flow conductivity in reciprocal of flow resistance.

these latter effects the separator is treated like a slice of electrolyte possessing a wider thickness than the real separator.

The structure of the separator influences its properties considerably. The influence of porosity and pore diameter on diaphragm and flow resistance will be discussed on the basis of a simple model involving cylindrical pores of equal diameter.

3. Types of separators

Separators can be divided into fleece and matrix separators depending on their manufacture. The latter group can be subdivided into sintered and skeleton separators. Examples of different separators are listed in Table 1 together with their properties. The sintered separators will be discussed first.

3.1. *Sintered separators: the first matrix type and variation of porosity*

The manufacture of a sintered separator will be described through the example of a PVC separator. Such sintered PVC separators are, for instance, manufactured and used by VARTA Batterie AG. A thin layer of PVC powder is spread on a steel strip; this is then passed through a sinter furnace and sintered into a multi-pored body at a temperature of 200–300° C. The PVC powder is treated as an assembly of particles of equal diameter. In the absence of friction, and under slight vibration, this powder would form a dense sphere packing and exhibit a porosity of almost 26%, independent of the pellet diameter.

However, actual powder mixtures show a less theoretical behaviour between porosity and particle radius. The friction between the powder particles increases with decreasing particle radius and hinders some particles reaching their theoretical places. Therefore, some places are vacant and this increases the porosity with decreasing particle diameter.

The particle size distribution of the powder also influences the porosity. The wider the distribution, the smaller the porosity because the smaller particles fill the voids between the larger ones. Even sintering time influences the porosity. When the sintering time is extended, thermoplastic particles tend to lose their shape and fill the voids, thus again reducing the porosity.

In order to influence the porosity further, part of the separator material may be replaced by a filler material (in the following simply called filler) during manufacturing. According to the amount of filler added the mechanical stability decreases after leaching out, ultimately to the point of instability [2]. In order to avoid this, the soluble filler can be replaced by insoluble microporous substances. Despite increasing porosity the mechanical stability is almost constant in this case.

The theoretical influence of the filler content on the porosity is calculated for a closed sphere packing. Table 2 shows the results for a soluble as well as a

Table 2. Porosity of a sintered separator as a function of filler content, calculated for a dense sphere packing

Amount of filler (vol %)	*Porosity* (vol %)	
	Soluble filler	*Microporous filler (50% porosity)*
0	26	26
20	41	33
40	56	41
60	70	48
80	85	56
100	100	63

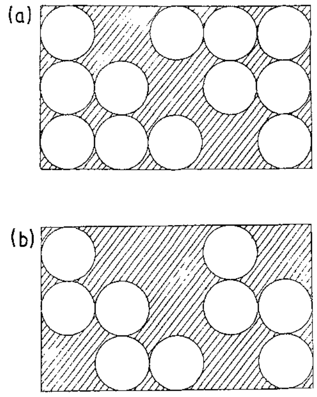

Fig. 1. Model of one single layer of a separator containing filler. (a) Model of one layer of a dense sphere packing containing 20% filler. (b) Model of one layer of a dense sphere packing containing 40% filler. Circles, separator particles; hedging, cavity.

microporous filler, the latter containing 50% porosity. It is apparent that the porosity can be manufactured to any desired value, the only limitation being the mechanical stability. In the case of a microporous filler with 50% porosity the porosity of the separator can be manufactured ranging from 26 to 63%.

3.1.1. Influence of porosity on diaphragm and flow resistance. The homogeneous pore model, all pores having the same radius r and length l, with n equal pores per cm^2, leads to the diaphragm resistance R_{dia}

$$R_{dia} = l\sigma/(n\pi r^2) \qquad (1)$$

In this equation σ represents the specific resistance of the electrolyte and l the effective pore length, which is the product of the separator thickness, d, and tortuosity, u.

When measuring the pore area of a defined sample sector it is found that the total area represents a fraction, f, of this sample sector. The porosity, p, is defined as the ratio of the total volume of pores and separator. The pore volume itself is given by the product of the effective pore length and the pore area. This yields other expressions for the diaphragm resistance

$$R_{dia} = \sigma ud/f \qquad (2)$$

$$R_{dia} = \sigma u^2/p \qquad (3)$$

An empirical equation describes the relation between tortuosity and porosity

$$u^2 \sim 1/p \qquad (4)$$

which yields

$$R_{dia} \sim 1/p^2 \qquad (5)$$

Analogous to the above, and using the Hagen–Poiseille law, gives the flow resistance R_{flw}

$$R_{flw} \sim 1/p^2 r^2 \qquad (6)$$

Equations 5 and 6 show that the diaphragm resistance is independent of and the flow resistance dependent on the pore radius.

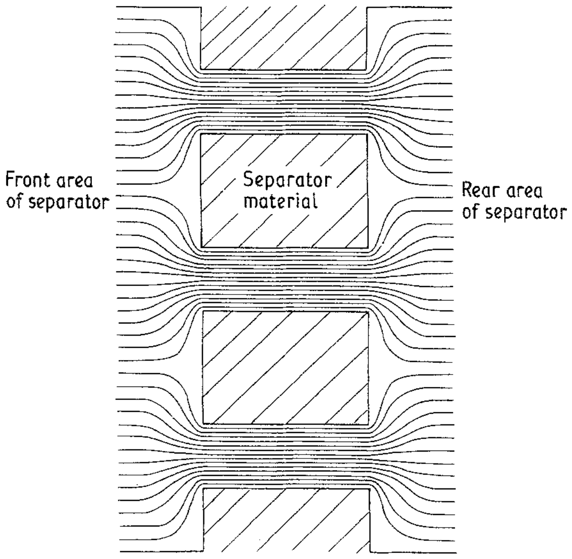

Fig. 2. Concept of the constriction resistance effect.

3.1.2. Real separators. These calculations do not take into account the influence of the so-called constriction resistance, which is located outside the separator on both sides. This additional resistance takes into account the fact that the current has to concentrate in a small area in front of a pore when entering it, i.e., not making use of the whole area, and this leads to a higher resistance (Fig. 2).

The calculation of constriction resistance starts [3] with the restriction resistance R of a region between a single cylindrical pore and a conducting medium of infinite dimension, which is defined by the following expression

$$R = 1.05\sigma/4r \qquad (7)$$

In Equation 7 r is the pore radius and σ the specific resistance of the electrolyte. The separator has many pores and, therefore, the current does not concentrate in front of a single pore. The value for R given by Equation 7 is too high and must be corrected. For this correction we use a second radius r', which divides the complete resistance – given by Equation 7 – into two parts. The first part is the restriction resistance of a pore with radius r', and the second part is the restriction resistance R_E between the pore with r' and the pore with r

$$R_E = 0.26\sigma(1/r - 1/r') \qquad (8)$$

n pores per unit area, with an area of f times the unit area, yields expressions for r and r'

$$r = \sqrt{f/n\pi} \quad \text{and} \quad r' = \sqrt{1/n\pi} \qquad (9)$$

Using the Expressions 9 we get

$$R_E = 0.26\sigma\sqrt{\pi/n}(1 - \sqrt{f})/\sqrt{f} \qquad (10)$$

The complete diaphragm resistance consists of three parts, the first being the electrolyte resistance in the pores (usually called diaphragm resistance), and the other two are the two constriction resistances

$$R_{dia} = \sigma[ud/f + 0.52\sqrt{\pi/n}(1/\sqrt{f} - 1)] \qquad (11)$$

The expression in brackets has the dimension of length and is called the effective thickness.

In separators with few pores per cm^2 the constriction resistance may reach a value comparable to the diaphragm resistance. It can be easily imagined that with a constant porosity the constriction resistance depends on the pore radius and is proportional to it. Consequently, a fine-pored separator of equal porosity and thickness has a smaller diaphragm resistance than a separator with coarser pores.

The constriction resistance can be determined in such a way that the diaphragm resistance is measured for an arrangement of one, two and so on, separators. The extrapolation of the resistance versus number of separators to zero results in twice the constriction resistance.

A constriction resistance occurs even inside the separator because the pore diameter changes continuously. In a measured diaphragm resistance the tortuosity factor includes this phenomenon. The tortuosity factor, therefore, includes the inner constriction resistance. For a more precise calculation of the porosity one cannot use the complete tortuosity factor and this results in additional terms. These terms were neglected because we only need the proportionality between porosity and resistance for our statements.

The pore size and its influence on the flow resistance is of great importance in battery manufacture. When a battery is filled with electrolyte the air inside the separator has to be replaced by the electrolyte. To achieve this, the electrolyte must enter and flow through the separator. The air inside the pores can only escape through empty ones, i.e. the velocity at which a separator can be filled completely with electrolyte has an upper limit. For a simple model, the maximum filling velocity can be calculated [4]

$$v_{\max} \leqslant 4k/d \tag{12}$$

In this equation d symbolizes the separator thickness and k an experimental factor. This factor is derived from a fluid-grading experiment which measures the fluid level, h, of the electrolyte inside a separator strip, which stands upright with its bottom line in the electrolyte. The relation between level h and time t defines k by fitting the experimental data to the following equation

$$h(t) = \sqrt{2kt} \tag{13}$$

This equation is the solution of a differential equation describing the wetting of the separator. An apostrophe above a letter indicates the derivative with time. The wetting force is given by the capillary force p_k. This force is in balance with the friction of the electrolyte in the pores – approximated by $(1/k)hh'$ – and the gravity force; the latter is very small compared to the capillary force and can, therefore, be neglected. This yields the differential equation:

$$p_k = (1/k)hh' \tag{14}$$

The root of Equation 14 gives the upper limit of filling velocity as described above.

3.2. *Skeleton separators: the second type of matrix separators*

The second type of matrix separators are the skeleton separators. Their basic structure is similar to that of sintered separators except that the porous volume of the sintered separator is now the separator material and vice versa. To manufacture such a separator a sintered separator formed of a soluble filler is made and its pore system is filled with an insoluble material. Afterwards, the filler is extracted. In this way a continuous structure is formed, the so-called skeleton. The porosity of such a separator is theoretically 74%, providing the filler has formed a dense sphere packing.

An alternative method of manufacture is to start with a filler-doped sintered separator which is sintered until all voids are filled with separator material, thus again forming a skeleton. In this case the porosity is less than 74%. This alternative is very difficult to realize due to decomposition of the separator material.

A third possibility – called phase inversion – starts with a homogeneous polymer solution containing a good solvent, a precipitant and sometimes a swelling agent for the polymer. During the evaporation of the solvent the homogeneous solution separates into two phases. The phase containing precipitant is then dispersed drop-wise into the polymer–solvent phase. Further evaporation of the solvent enriches the polymer on the surfaces of the drops, and there it is precipitated within the gap between them. In this way a skeleton-like structure is formed. During evaporation the drops burst and leave a large number of pores behind, thus building up a porous structure [5].

3.3. *Fleece separators: the second separator type*

The fleece separators consist of an irregular arrangement of single fibres of the separator material. These separators have a better mechanical stability than matrix ones because the fibres tangle firmly. The average pore radius of these separators is relatively large and, therefore, very often cannot be used if gas separation is required. Fleece separators are made of various fibres using a kind of scoop method. Examples of this type of separator are paper-like separators made of asbestos, cellulose or synthetic fibres.

4. Definition and measurement of important separator properties

To compare the individual separator's suitability for application in batteries, its most important properties should be measured, and their influence on the battery should be described using very simple models.

4.1. *Effective diaphragm thickness for diffusion across and electrolytic conduction through separator*

In the absence of specific absorptions of the electrolyte inside the separator, and a large enough pore diameter, it is possible to show that current transport and diffusion obey the same law.

Fick's law of one-dimensional diffusion describes the diffusional flux per sample section for a pore with uniform diameter. As in Equation 14 an apostrophe indicates the derivative with time. The concentration is represented by c, the diffusion coefficient by D, the time by t, the diffusion flux density by n' and the coordinates by x and y. The diffusion takes place inside the separator, but we want to describe it in the outer coordinate system. Therefore, we had to transform Fick's law. We imagine the separator to be divided parallel to the surface into several slices. If one wishes to reach a certain slice, one has to walk a distance y in the outer system. To reach the same slice inside the separator one has to walk the distance x, which is larger due to the tortuosity. Therefore we can write

$$x = yu \tag{15}$$

with u as a tortuosity factor. The original Fick's law is

$$n' = -D\frac{\delta c}{\delta x} \tag{16}$$

The separator's available inner cross-section for diffusion is reduced to the cross-section of the pores, and this is obtained by f as shown above. The transport is, therefore, reduced by the same factor. Changing from x to y gives us

$$n' = -Df\frac{\delta c}{\delta y}\Big/u \tag{17}$$

In the case of a steady state the diffusion flux through the separator is constant and is given by solution 18 of the differential Equation 17

$$n' = -Df\Delta c/(du) \tag{18}$$

In Equation 11 the effective thickness, d_{eff}, was defined as the term in brackets. Using this term, and neglecting the constriction resistance, we can write

$$n' = D\Delta c/d_{\mathrm{eff}} \tag{19}$$

Δc represents the concentration difference between the two sides of the separator and $\Delta c/n'$ represents the diffusion resistance, which is equal to d_{eff}/D. Diffusion and diaphragm resistance are both proportional to the same effective thickness. The additional constriction resistance also occurs in the case of diffusion. It is, therefore, sufficient to measure the effective thickness (which includes all additional constriction resistances), and to calculate the diffusion flux from it. This treatment of the diffusion problem neglects the influence of electrolyte flowing inside the pores, which runs parallel to the diffusion process.

4.2. *Diaphragm resistance*

Usually the diaphragm resistance is measured by means of an a.c. bridge or a related set-up. The diaphragm resistance is the real part of the measured impedance. Evaluation of the effective thickness is achieved, either by a comparative measurement on pure electrolyte, or by a calculation based on the known conductivity of the electrolyte and the surface of the layer.

Table 3. Different properties of separators and their electrolyte-independent description

Effect	*Electrolyte-independent description*
Electrolyte resistance	Effective thickness
Diffusion	Effective thickness
Flow resistance	Resistance per unit area and normalized viscosity
Bubble point	Pressure drop for normalized surface tension
Gas flow resistance	Resistance per unit area and normalized gas viscosity

4.3. *Flow resistance*

The flow resistance may also be described in terms of an effective thickness. This, however, needs a pore model with an associated pore structure, which is too complicated. It is much simpler to measure the flow resistance per cm^2 and to normalize to a viscosity of one, which is then also electrolyte independent, or to normalize with respect to the viscosity of water. The latter method gives more illustrative values.

The theoretical treatment [6] of the flow of an electrolyte inside a porous body shows that the velocity v is given by

$$v = -\boldsymbol{k}\nabla P \text{ (Darcy equation)} \tag{20}$$

$\boldsymbol{k}$ represents the permeability tensor and P the static pressure. The tensor itself is given as the quotient of a constant B and the viscosity. The constant itself depends on the inner surface, S, the porosity, p, and a fitting parameter, k^*.

$$B = \frac{p^3}{k^*(1 - p^2)S^2} \text{ (Carmen–Konzeny equation)} \tag{21}$$

From these equations a flow resistance R_{flw} per unit area results

$$R_{\mathrm{flw}} = d\eta(1 - p^2)S^2k^*/p^3 \tag{22}$$

with d as the separator thickness.

4.4. *Bubble point and gas flow resistance*

A certain gas overpressure will allow gas to pass through the wetted separator. This is called the bubble point, and is proportional to the surface tension of the electrolyte. These values may then be normalized to a surface tension of one, or to that of water. The characteristic value is only of interest in processes where the gases have a strong influence. Should the gas transport be of interest, the gas flow resistance should be measured per unit area and then normalized to a defined viscosity.

Table 3 lists the different properties of separators as described above, and their electrolyte-independent description.

5. Prevention of metallic bridges

One very important task of the separator is to prevent formation of metallic bridges between the electrodes of a galvanic cell. There is no work in the literature which shows a correlation between the porous properties of a separator and its ability to prevent bridge formation. When being recharged the negative electrode of a galvanic cell tends to shorten the distance between the electrodes. In doing so, the electrode metal penetrates into the pore system of the separator. The surface area of each metallic bridge inside the separator is determined by the shape of the separator pore. Therefore, the surface energy of the metal is the higher the larger the inner specific surface area of the separator. If we compare the specific surface of a bridge to that of the negative electrode itself, we can state our expectation as follows. A separator can avoid the formation of metallic bridges in a galvanic cell if the ratio of surface area to the volume of metal is larger inside the separator than on the negative electrode. In this case the formation energy for a metal particle is lower at the surface of the electrode and the separator can act, by means of energy, as a barrier to the formation of metallic bridges.

6. Suggestions for modifying separator properties

The main property usually expected of a separator is that it exhibits a diaphragm resistance as low as possible. As shown in quantitative terms, this resistance depends on the porosity and the thickness of the separator. Increasing the porosity or decreasing the thickness results in weakening the mechanical stability. To solve this problem several methods are available: using fibres as support material to increase the mechanical stability while reducing the thickness; using a homogeneous powder with finely graded particles for sintered separators, except in those cases where flow of electrolyte and gases through the separator is important; using soluble or microporous filling materials; strengthening the particle–particle boundaries for sintered separators by using capillary forces to deposit resins selectively in this area.

7. Discussion

The great advantage of describing separators by normalized or effective parameters is the comparison of different separators independent of the measuring process. This advantage becomes obvious if one searches for a separator for a specific purpose and needs to compare properties. Depending on the factory producing the separator, the parameters are measured by different methods and, in the worst case, the method is not described. In this case a comparison is impossible and the separator properties have to be measured. Another case is that the electrolyte needed for a specific task differs from the electrolyte used to measure the properties; then one needs the physical parameters of both electrolytes to calculate the correct separator properties.

A disadvantage of the medium-independent description is that the expansion of the separator material leads to a temperature dependency of the effective thickness, which depends also on the construction of the battery. However, electrolyte-dependent descriptions of separator properties experience the same problem.

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